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Fundamentals of Soil Science

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Editorial Committee

Dr. N.N. Goswami (Chairman)
Dr. R.K. Rattan
Dr. G. Dev
Dr. G. Narayanasamy
Dr. D.K. Das
Dr. S.K. Sanyal
Dr. D.K. Pal
Dr. D.L.N. Rao

Published on behalf of the Indian Society of Soil Science by:
Dr R.K. Rattan
Secretary, Indian Society of Soil Science
Ist Floor, National Societies Block
National Agricultural Science Centre Complex
Dev Prakash Sastri Marg, Pusa, New Delhi -110 012
Phone : 0091-11-25841991; Fax: 25841529
Email: isss1934@gmail.com; isss.secretary@gmail.com
Web page : www.isss-india.org

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Preface

First edition of the *Fundamentals of Soil Science* was enthusiastically received by the readers and it instantly became the knowledge-mascot of the Society. This book specifically serves the Post Graduate students of Soil Science as well as the Under Graduate students having elective in Soil Science, besides serving as the compendium book for the teachers. Going by the feed-back received from the different classes of readers and rapid generation of knowledge in the field, necessity was felt to undertake the revision of this book. Realizing the need for having a re-look at the contents of the book, Council of the Indian Society of Soil Science in its meeting held on 27 February 2006 constituted a Committee with the composition: Dr NN Goswami (Chairman), Dr G Dev, Dr G Narayanasamy, Dr DK Das, Dr SK Sanyal, Dr DK Pal, Dr DLN Rao and Dr RK Rattan (Member-secretary). This Committee, which transformed itself as the Editorial Committee, going by the sentiments expressed in the Council, undertook the job of bringing out the second edition as the revised and enlarged one by reorganizing some of the existing chapters and adding new chapter on Soil and Water Quality. Upholding the sentiments of Late Dr GS Sekhon, Chairman of the Editorial Committee of the First Edition, specific examples of benchmark soils of India have been included while undertaking the revision. Editorial Committee places on record the services rendered by Dr Sekhon and other members for having worked tirelessly in bringing out the first edition. Efforts made by the Scientists of the Indian Institute of Soil Science, Bhopal and National Bureau of Soil Survey and Land Use Planning, Nagpur, in generating data for the benchmark soils for inclusion in the book are sincerely acknowledged.

Chapter on Basic Chemical Principles in Soil Science has been excluded in the revised edition by incorporating the necessary principles in the respective chapters. Two Chapters on Water management have been merged into one and also the Soil Colloids and Ion Exchange in Soils have been merged into one chapter. Chapter on Soil and Water Quality has been added in this edition. Inclusion of new authors in the Chapters has made value-addition to the quality of the contents of the book. Editorial Committee places on record sincere thanks to all the authors for undertaking major revision of their chapters. I highly appreciate the untiring efforts undertaken by Dr RK Rattan, but for which it would not have been possible to get this Edition printed within the stipulated time-frame. Services rendered by the Secretariat of the Society are gratefully acknowledged.

It is a happy coincidence that when revision of this book was being undertaken, the Indian Council of Agricultural Research was also developing its model uniform course curriculum for different subjects of Agriculture including Soil Science. This edition has amalgamated the newly developed curriculum of Soil Science and also the syllabus of Agricultural Research Service of the ICAR. It is hoped that this enlarged edition will enhance the capabilities of Soil Science students in their pursuit of excellence.

New Delhi
Dated: 22 December 2009

N.N. Goswami
Chairman, Textbook Committee
Indian Society of Soil Science

Preface to the First Edition

This book "Fundamentals of Soil Science" is an outcome of a perception by the Indian Society of Soil Science of the need for a good textbook on soil science for undergraduate students of agriculture in India. The motivating thought in bringing out this publication was that while dealing with basic principles of soil science and management of soil as a natural resource, the text should essentially project Indian data and examples.

The Textbook Committee, constituted by the Council of the Indian Society of Soil Science, comprised Dr GS Sekhon (Chairman) with Dr JS Kanwar, Dr NN Goswami, Dr DK Das, Dr G Narayanasamy, Dr CL Acharya, Dr PK Chhonkar, Dr JL Sehgal, Dr SR Poonia, Dr JS Samra, and Dr BK Khosla as Members and Dr RK Rattan as Member-Secretary. This Committee identified the available teachers for contributing manuscripts of different chapters of the book. The Textbook Committee constituted an Editorial Committee for processing the manuscripts through various stages of printing. The Editorial Committee is grateful to Dr SK Sanyal and Dr DK Pal for their technical help. Dr BS Aggarwal, formerly of the National Institute of Science Communication (CSIR), needs particular thanks for his assistance in language editing, proof correction and preparation of subject index.

The Textbook Committee deeply appreciates the honorary efforts of all the contributors. It also thanks Dr JS Samra, Dr CL Acharya, Dr KS Gajbhiye, Dr VK Nayyar, Dr AK Singh and the Potash and Phosphate Institute of Canada for providing the colour photographs reprinted in this book. The Society Secretariat has done a yeoman service in coordinating this project.

I sincerely hope that teachers and students of Soil Science in agricultural universities and institutes would find this textbook useful in learning and teaching different aspects of Indian soils and their management. I would appreciate receiving comments and suggestions, if any, on any aspect of this publication; these would immensely help in improving the future editions of this book.

GS Sekhon
Chairman, Textbook Committee
Indian Society of Soil Science

New Delhi
Dated: 2nd May, 2002

List of Contributors

ACHARYA, C.L., Former Director (IISS, Bhopal), 28, Nagarcot Colony, Thakur Dwara, P.O. Maranda, Palampur-176 102, Himachal Pradesh

ADHYA, T.K., Director, Central Rice Research Institute, Cuttack-753 006, Orissa

AGRAWAL, R.P.*, Former Dean (CCS HAU, Hisar), House No. 244, Sector 22, Gurgaon-122 015, Haryana

ANAND SWARUP, Head, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi-110 012

ARORA, B.R.*, Former Head (Department of Soils, PAU Ludhiana),744-I, Bhai Randhir Singh Nagar, Ludhiana-141 002, Punjab

ARORA, C.L., Former Senior Soil Chemist (Department of Soils, PAU, Ludhiana), 101-C, Rajguru Nagar, Ludhiana-141 002, Punjab

AULAKH, M.S., Dean, College of Agriculture, Punjab Agricultural University, Ludhiana-141 004, Punjab

BAJWA, M.S., Former Director of Research (PAU, Ludhiana), House No. 2103, Sector 16, Mohali, Punjab

BARUAH, T.C., Professor, Department of Soil Science, Assam Agricultural University, Jorhat-785 013, Assam

BENBI, D.K., Professor, Department of Soils, Punjab Agricultural University, Ludhiana-141 004, Punjab

BHARDWAJ, K.K.R., Former Project Coordinator, Krishna Agrifarm, Village- Daringoma, P.O. Davhla, Teh.-Ghumarvin, Distt. Bilaspur-174 021, Himachal Pradesh

BHATTACHARYYA, TAPAS, Principal Scientist, National Bureau of Soil Survey and Land Use Planning, Amravati Road, Nagpur-440 010, Maharashtra

BIJAY-SINGH, ICAR National Professor, Department of Soils, Punjab Agricultural University, Ludhiana-141 004, Punjab

BISWAS, D.R., Senior Scientist, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi-110 012

BRAR, M.S., Former Senior Soil Chemist (Department of Soils, PAU, Ludhiana), 130-B, Rajguru Nagar, Ludhiana-141 002, Punjab

CHAMUAH, G.C.*, Former Head, NBSS & LUP, Regional Centre, Jorhat, Assam

CHHONKAR, P.K., Former Head (Division of SSAC, IARI, New Delhi), A-3, Shaman Apartments, Plot No. 9, Sector 23, Dwarka, New Delhi-110 075

CHOPRA, USHA KIRAN, Professor, Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi-110 012

DADHWAL, K.S., Head, Division of Soil Science and Agronomy, Central Soil and Water Conservation Research and Training Institute (CSWCRTI), 218, Kaulagarh Road, Dehradun-248 195, Uttarakhand

DAS, D.K., Former Head (Division of Agricultural Physics, IARI, New Delhi), A/D-115C, Shalimar Bagh, Delhi-110 088 (*Contributor:* Physical Properties of Soils)

DAS, D.K., Head, Department of Agricultural Chemistry and Soil Science, BCKV, Mohanpur-741 252, West Bengal (*Contributor:* Soil Pollution and its Control)

DATTA, S.C., Principal Scientist, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi-110 012

DATTA, S.P., Senior Scientist, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi-110 012

DEB, D.L., Former Project Director (NRL, IARI, New Delhi), I-1644, Chittaranjan Park, New Delhi-110 019

DHIR, R.P., Former Director (CAZRI, Jodhpur), 498, Defence Colony, Kamla Nehru Nagar, Jodhpur-342 009, Rajasthan

GAJRI, P.R.*, Former Senior Soil Physicist, Department of Soils, Physical Agricultural University, Ludhiana-141 004, Punjab

GHOSH, KUNAL, Senior Professor and Ex-Head, University of Calcutta, 4A Ratnabali, 7A Judges Court Road, Alipore, Kolkata-700 027, West Bengal

GOSWAMI, N.N., Former Vice Chancellor (CSAUAT, Kanpur), JD 20 D, Pitampura, Delhi-110 088

GUPTA, RAM K., Former Director of Research Services (JNKVV, Jabalpur), G-90 (FF), Pushkar Enclave, Paschim Vihar, New Delhi - 110 063

KANWAR, J.S., Deputy Director General (Emeritus), ICRISAT, 17 Krishi Nagar, ICRISAT Colony, Phase II, Hashmepet Road, Secundrabad-500 009, Andhra Pradesh

KAR, S., Former Head (Department of Agricultural and Food Engineering, IIT, Kharagpur), Plot 80, Hizli Co-operative Society, Prembazar, Dist West Midnapore, Kharagpur-721 306, West Bengal

KHANNA, S.S., Former Vice Chancellor (NDUAT, Faizabad), 323, Krishi Apartments, Bodella, D Block, Vikaspuri, New Delhi-110 018

MAJUMDAR, S.P., Head, Department of Soil Science, S.K.N. College of Agriculture, Jobner-303 329, Rajasthan

MANNA, M.C., Head, Division of Soil Biology, Indian Institute of Soil Science, Berasia Road, Bhopal-462 038, Madhya Pradesh

MOHANTY, S.K., Former Principal Scientist (Division of Soil Science and Microbiology, CRRI, Cuttack), Mothany Lane, 'Debashish', Rajendra Nagar, Cuttack -753 010, Orissa

NARAYANASAMY, G., Former Professor and Head (Division of SSAC, IARI, New Delhi), E 25 C, Mayapuri, New Delhi-110 064

NAYYAR, V.K., Former Head (Department of Soils, PAU, Ludhiana), 220-C, Bhai Randhir Singh Nagar, Ludhiana-141 004, Punjab

OSWAL, M.C., Former Head, Department of Soil Science, CCS Haryana Agricultural University, Hisar-125 004, Haryana

PAL, D.K., Head, Division of Soil Resource Studies, National Bureau of Soil Survey and Land Use Planning, Amravati Raod, Nagpur-440 010, Maharashtra

PANDA, N., Former Vice Chancellor (Sambalpur University), 62/63, First Floor, Opposite Unit–8, Boys High School, Bhubaneswar-751 003, Orissa

PAREEK, R.P., Former Professor, Department of Soil Science, G.B. Pant University of Agriculture and Technology, Pantnagar-263 145, Uttarakhand

PASRICHA, N.S., Former Director (PRII, Gurgaon), 219-C, Bhai Randhir Singh Nagar, Ludhiana-141 004, Punjab

POONIA, S.R., Former Dean (College of Agriculture, CCS HAU), House No. 296, Sector-15A, Hisar-125 001, Haryana

PRIHAR, S.S., Former Head (Deptt. of Soils, PAU Ludhiana), 136-D, Kitchlu Nagar, Ludhiana-141 004, Punjab

RAO, D.L.N., Project Coordinator, Indian Institute of Soil Science, Nabi Bagh, Berasia Road, Bhopal-462 038, Madhya Pradesh

RATTAN, R.K., Professor, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi-110 012

SAKAL, R., Former Director, Sugarcane Research Institute, Pusa-848 125, Samastipur,Bihar

SAMRA, J.S., Chief Executive Officer, National Rainfed Area Authority, NASC Complex, Dev Prakash Shastri Marg, New Delhi-110 012

SANYAL, S.K., Vice Chancellor, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741 252, West Bengal

SARKAR, A.K., Dean, Faculty of Agriculture, Birsa Agricultural Univeristy, Kanke, Ranchi-834 006, Jharkhand

SARKAR, DIPAK, Director, National Bureau of Soil Survey and Land Use Planning, Amravati Road, Nagpur-440 010, Maharashtra

SARMA, V.A.K., Principal Investigator, DST Project, National Bureau of Soil Survey and Land Use Planning, Regional Centre, Bangalore-560 024, Karnataka

SEHGAL, J.L.*, Former Director (NBSS &LUP Nagpur), EA-220, Maya Enclave, New Delhi-110 064

SEKHON, G.S.*, Former Director (PRII Gurgaon), 38, The Mall, Amritsar-143 001, Punjab

SHARMA, K.L., National Fellow, Central Research Institute for Dryland Agriculture (CRIDA), Santosh Nagar, P.O. Saidabad, Hyderabad-500 059, Andhra Pradesh

SHARMA, P.K., Director, Punjab Remote Sensing Centre, Ludhiana-141 004, Punjab

SHARMA, PRADEEP K., Dean (PG Studies), CSK Himachal Pradesh Krishi Vishwavidyalaya, Palampur-176 062, Himachal Pradesh

SHARMA, U.C., Former National Coordinator, NAIP, ICAR, New Delhi

SIDHU, P.S., Senior Agricultural Specialist, SASRD, The World Bank, 70 Lodi Estate, New Delhi-110 003

SINGH, ANIL KUMAR, Deputy Director General (NRM), Indian Council of Agricultural Research, Krishi Anusandhan Bhawan II, Pusa Campus, New Delhi-110 012

SINGH, MOHAN, Principal Scientist, Indian Institute of Pulses Reasearch, Kalyanpur, Kanpur-208024, Uttar Pradesh

SINGH, T.A., Former Head (Deptt. of Soil Science, GBPUAT, Pantnagar) 20-38/5, West Venkatapuram, Secundrabad-500 015, Andhra Pradesh

SUBBA RAO, A., Director, Indian Institute of Soil Science, Berasia Road, Bhopal-462 038, Madhya Pradesh

SUDHIR, K., University Head, University of Agricultural Sciences, Bangalore-560 065, Karnataka

TANDON, H.L.S., Director, Fertiliser Development and Consultation Organization, 204-204A, Bhanot Corner, 1-2, Pamposh Enclave, New Delhi-110 048

TIWARI, K.N., Former Director, PPIC–India Programme, 5/1074, Viram Khand, Gomati Nagar, Lucknow-226 010, Uttar Pradesh

TOMAR, V.S., Vice Chancellor, Rajmata Vijayaraje Scindhia Krishi Vishwavidyalaya, Gwalior, Madhya Pradesh

TRIPATHI, R.P., Former Professor (Department of Soil Science, G.B.P.U.A.T., Pantnagar), 133C, Bhrigu Marg, Chota Bahara, Allahabad-221 002, Uttar Pradesh

VELAYUTHAM, M., Former Director (NBSS&LUP, Nagpur), 2A-Gardenia Apartment, 275, Kilpauk Garden Road, Kilpauk, Chennai-600 010, Tamil Nadu

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* Deceased

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Chapter 1

Introduction

J.S. KANWAR

Soil and land, though related, are two different entities. Land is two-dimensional entity representing geographical area and landscape, while soil is a three-dimensional body with length, breadth and depth and is hidden below the land surface. It is largely hidden from the outside world until it is lost and goes out of the site. It is recognized by digging a pit and exposing its profile. The profile of a soil with well marked horizons called A, B and C, tells the history of its formation and bears the imprint of many physical, chemical and biological processes which have led it to the present form. The soil entity dictates much of what societies can do. Soils are formed by weathering processes of rocks which in the words of Hans Jenny can be depicted by the equation:

$$S = f(cl, r, p, o, t, \ldots.)$$

where, S = Soil, cl = Climate (rainfall, temperature, snow, etc.), r = Relief or topography, p = Parent material (rocks, minerals and geological formation), o = Organisms (plants and animals), and t = Time or age.

Some of these factors of soil formation are passive but the organisms (biosphere) and man are most active in the transformation of soils and in modifying its properties. These are the effects of human activities or the human-induced changes in the modern times, which are largely responsible for the existing diversities in soil properties. Human beings, through their negligence, ignorance or greed, can accelerate soil degradation and through scientific management, improve its quality. A soil scientist has to understand both the human-made and the natural soil processes and develop strategies for appropriate remedial action to meet the needs of the society or the current managers of the land.

'Soil Science' provides the eyes and ears to the society in translating what the idealistic dreamers envision as the utopian society into the reality of what nature will allow. Soil scientists must know soil, understand its potential and limitations to answer the following type of questions:

- What is the carrying capacity of a given soil?
- What is its productivity?
- How should we realize the potential of a soil and how should we remove its constraints?
- How can one prevent soil degradation and restore its productivity?

The relationship of soil, environment and society is intimate and depends on soil quality and its management. Those who develop the concepts, the science and the facts about this thin skin that interspaces the lithosphere and atmosphere and help manage it, often control the fate of societal visionaries. The laws of physics, chemistry and biology are inviolable and the manner in which a society utilizes them to manage the soil, determine the returns on investments in soil management and its use.

Soil is an interface of the organic and inorganic chemistry of the terrestrial world, combining nitrogen and carbon from the atmosphere with the various elements of mineral lithosphere via the organisms anchored in the soil, intercepting energy of the sun and moisture from the hydrosphere and atmosphere. The soil fractionates the hydrologic cycle in the terrestrial area into runoff, percolation and evapotranspirational components. It is a source as well as a sink to adsorb, desorb, fix or release mineral elements and gases and grow plants and decompose crop residues incorporated into it. It is a living factory where millions of tiny organisms are ceaselessly working day and night, transforming the organic matter and participating in carbon and nitrogen cycles and many mineral elemental cycles. Without life, there is no soil and without soil, there is no life on the planet Earth. It is no wonder that the astronauts landing on the moon searched for evidence of soil, life and water there and brought with them soil samples to make detailed studies for an evidence of life.

To understand and rationalize the use and management of soil, the soil scientists, especially pedologists, have been developing methods of soil survey and classification of soils. A widely used system is the 'Soil Taxonomy' developed by the United States Department of Agriculture. Indian soil scientists, using the same system, have mapped and classified their soils. India is virtually a museum of soils of the world, as almost all the Soil Orders classified anywhere in the world, are found in India. The National Bureau of Soil Survey and Land Use Planning is a repository of soil information in the country. The Bureau has delineated 20 agro-ecological regions and 60 agro-ecological sub-regions by integrating the information on soils, physiography, climate and effective plant growing period. This is a valuable information for land use planning, soil management and use.

Ever since the dawn of civilization, man's interest in soil has been to produce food, fibre, fuel and timber, but in modern times besides the growing demands of society for these products of the soil, the use of land for industry, civic purposes, roads, airports, habitations, etc. is also increasing and the problems of soil degradation are assuming greater dimensions. Prime lands are going out of agricultural use and marginal lands are coming under the emerging needs of the society, including agriculture. Thus, the demand on soil scientist's expertise is becoming too wide and too difficult. He/She is expected to respond to man's ever increasing, constantly changing needs and respond to most challenging tasks. Thus, a shift in paradigm of soil science and information technology research and education has become necessary to meet the demands of the time and of the situation. Advances in science, such as biotechnology, space technology, computer sciences and modelling techniques have their impact on soil science and soil management technology and a major shift in education becomes inevitable. Since soil is a pivot of natural resources, its management has to be fully integrated with the eco-friendly techniques. It is no surprise that many research and educational organizations are making soil science as an integral part of natural resource education and research systems.

Soil and water are integral parts of the system for plant growth and no study of soil is complete without consideration of water regime and its interaction with the soil and plant as one system. It also draws heavily on knowledge of soil physics and water management. Likewise for understanding the dynamics of plant nutrients in the soil, knowledge of soil chemistry, soil fertility, soil biology, soil biochemistry and soil microbiology is essential.

The chemical and physical properties of soil, its mineral composition and stock of nutrient resources for plant growth and the changes therein call for a regular monitoring of the availability, rate of depletion and addition to the soil system. Ever since the dawn of civilization, man has been exploiting the native fertility of soil but with the advancement of science and compulsion of growing needs of agricultural products from the soil, the use of chemical fertilizers has emerged as the most important input for increasing productivity in agriculture. No country, whether developed or developing, can hope to produce more and more food from less and less land without resorting to the enhanced use of fertilizers. However, their imbalanced application or use without organic manures/ green manures and overmining of soil resources of nutrients is leading to declining yields and increasing deficiency of many nutrients. Moreover, poor management of irrigation, neglect of rainwater management and soil conservation practices is accelerating soil degradation, salinization, alkalinization and groundwater pollution and in nutshell, deterioration of soil quality. A soil scientist needs to have intimate knowledge of soil degrading processes and should develop strategies for integrated use of all the inputs such as plant nutrients, water, energy and crop management technology for optimizing productivity and minimizing environmental degradation.

India is home to 18% of the world's human population and 15% of the animal population, but owns only 2.0% of the world's geographical area, out of which 51% is the net cultivated area. This meagre resource has to support the ever-growing population, which has grown from 361 millions in 1951 to over 1000 millions in 2000, and is projected to become about 1400 millions in the next 25 years. The land to man ratio will be reduced to 0.10 ha by 2025 from the 0.14 ha in the year 2000. The scope for extending agriculture to new areas is extremely limited and the only option left for us to meet the challenge of growing needs of food, fibre, fuel and timber is through increase in productivity of the land already under the plough. But, this has to be done without detriment to environment.

The country receives on an average 1130 mm of rainfall every year but it is unequally distributed, both in time and space and most of it comes in a few months of the monsoon season. It is the erratic distribution of rainfall, which leads to frequent droughts and floods and makes Indian agriculture a gamble in monsoons. No doubt one-third of the cultivated area is irrigated but its productivity is hardly one-third of the potential attainable with the present day technology and inputs. This gap needs to be bridged. Two-thirds of the country's cultivated area is unirrigated and follows rainfed farming. These soils are not only thirsty but also hungry. Farmers' poverty makes the soils poor and they, in turn, make the farmers poorer. This is a vicious circle. Whether it is irrigated or unirrigated area, the future food security lies in increasing its productivity. Soil and water (irrigation as well as rain water) management and scientific knowledge-based precision farming offer great scope for realising the potential of these favourable as well as harsh environments. Diversification of agriculture, and alternative land use systems are the needs of the times. Increasing use efficiency of agricultural inputs, including water for improving the economy of the system along with prevention of degradation of environment, are important challenges of the day.

Soil is neither an inexhaustible store of plant nutrients nor a renewable natural resource, capable of withstanding onslaught of the exploitative agriculture and soil degrading processes. It is only through scientific management that its productivity, quality and sustainability can be maintained. Arresting the fall in organic matter is the most important weapon to fight soil degradation and to ensure sustenance of soil quality and agricultural productivity. Addition of nutrients such as N, P, K, Ca, S, Mg, Cu, Mn, Fe, Zn, B and Mo becomes essential from external sources to maintain input-output balance and to ensure their ready availability for meeting the needs of growing crops. Harnessing microorganisms for augmenting nutrient supply and availability will make integration of nutrient management system more economical and sustainable.

Long-term experiments under intensive cropping systems in different agro-ecological regions have provided ample evidence of rapid exhaustion of soil and nutrient deficiencies which are increasingly becoming limiting factors for crop production. Indian soils are mostly deficient in N and the application of nitrogenous fertilizers is essential for crop production in all soils, but the lower use-efficiency of nitrogenous fertilizers and high cost of fertilizers dictate the conjunctive use of nitrogenous fertilizers, organic manures and biological N fixing technology should be practised for improving their use-efficiency and economy. Soil organic matter is the key to N economy and soil quality. The world is becoming more and more conscious of depleting soil organic matter stock and its consequences for both crop production and environment quality.

Increasing industrialization, urbanization and negligent use of agricultural chemicals are multiplying the problems of pollution and deterioration of quality of groundwater. Soil, no doubt functions as a buffer and a sink for these pollutants, but it can do so only within certain limits and an understanding of these limitations is the key to soil health and environment improvement.

Water is the critical factor for crop production. But the cost involved in developing sources of surface irrigation, rapidly falling groundwater-table due to over-exploitation of underground water resources and increasing salinization and alkalization in irrigated areas are becoming the chronic problems of irrigated farming. Increasing water-use efficiency and prevention of soil degrading effect of poor water management should receive high priority for research and education in soil science.

Soil is a limited and non-renewable resource but a pivot for agriculture, food security, nutritional security, environmental safety and quality of life. A dynamic system of soil management requires a knowledge of all the sciences, bearing on the nature of problems that the soil scientists are called upon to handle and the technologies that can be put to use. Soil and society are undoubtedly two inseparable entities on this planet Earth. 'Soil scientist moves from the field to the laboratory to diagnose and develop a technology for solving the soil-related problems and gets back from the laboratory to the field to evaluate his strategy'; it is the secret to success. The chapters included in this textbook endeavour to address all these issues in a coherent manner.

Chapter 2

Weathering and Soil Formation

P.S. SIDHU, R.P. DHIR and T. BHATTACHARYYA

1. Introduction

Soil is a surface-covering on most of the earth's land area, an aggregation of unconsolidated mineral and organic particles produced by the combined action of wind, water and organic decay. Soils are formed from hard rocks, loose and unconsolidated transported inorganic materials and accumulated organic residues. Even the loose mineral materials from which soils are formed, are originally constituted by the weathering of rock masses to stones, gravels, sands, silts, clays and soluble salts. Organic soils are developed mostly from plant parts that have accumulated in stagnant waters where decomposition is slow due to lack of oxygen (anaerobic conditions).

2. Soil and Regolith

The unconsolidated material overlying the rocks is known as regolith (Figure 1). Its thickness may vary from a few centimetres on sloping hills of the Himalayas to tens of metres in the Indo-Gangetic alluvial plains. It might have accumulated *in situ* from the weathering of underlying rock (as in the Deccan plateau) or might have been transported from elsewhere by water (in alluvial plains and coastal areas), wind (in the Thar desert) or ice (in higher reaches of the Himalayas) and deposited on the bedrock or on other materials covering the bedrock. Thus, the composition of regolith can vary widely.

The characteristics of upper 1-2 metres of regolith are markedly different from those of the underlying materials. It generally has higher content of organic matter and has been subjected to more weathering than the lower portions. Consequently, it can be differentiated into characteristic layers called 'horizons'. This upper and biochemically weathered portion of the regolith is called 'soil'.

Soil formation comprises two different processes. The first is referred to as 'weathering' which changes the hard consolidated rock mass into unconsolidated loose materials. The second is referred to as 'soil formation' and covers changes occurring within the loose materials as time passes. In nature, the change from a solid rock mass to loose soil materials and other changes within the soil profile occur simultaneously. The term soil formation is used to mean both the formation of unconsolidated materials by the weathering processes, and the soil profile development which encompasses the changes involved in the development of horizons in a soil.

3. Weathering

Weathering refers to the chemical and physical disintegration and decomposition of the rocks, and the minerals contained in them. It is basically a combination of transformation and synthesis. As a result of weathering, the rocks are broken down physically into the smaller fragments and eventually into individual mineral grains. Simultaneously, the rock fragments and minerals undergo chemical changes to form new minerals by either minor modifica-

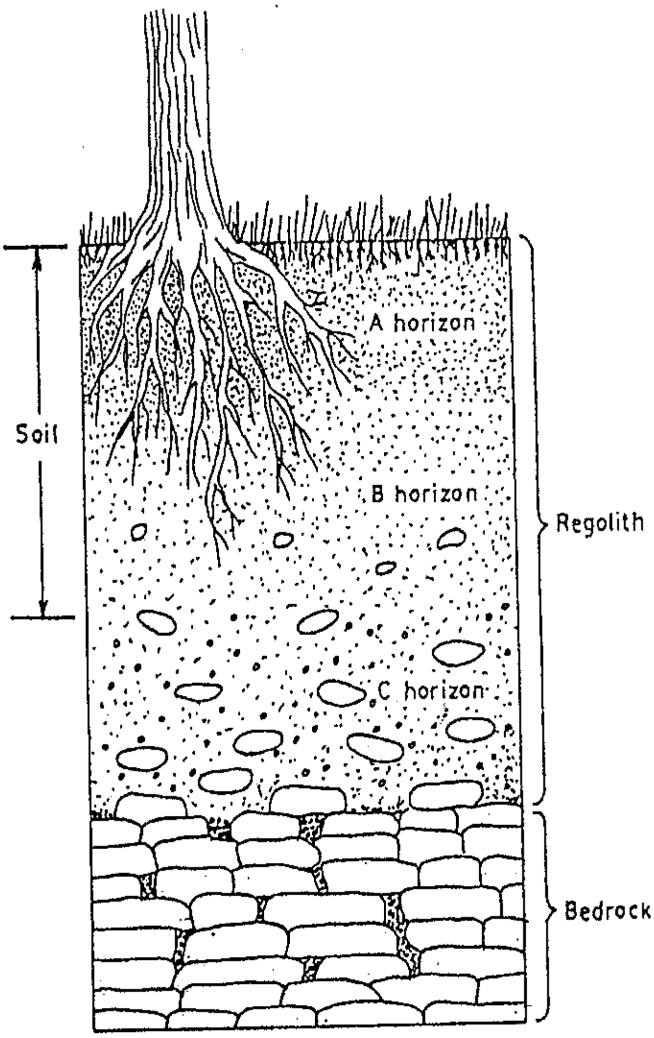

Figure 1. Regolith in relation to soil and bedrock

tions (simple transformations) or complete chemical and structural changes. The chemical changes are usually accompanied by a reduction in particle size and release of soluble constituents which may be lost through drainage water or may be recombined to form new (secondary) minerals. Weathering of the initial materials precedes soil formation in hard rocks and accompanies it in soft rocks and soil materials. It is a continuing reaction during soil development to the point where no more reactants are available. Thus, weathering results in mechanical (or physical) and chemical breakdown of rocks. The former is often designated as 'disintegration'. However, both these processes operate simultaneously. In drier (Thar desert) and/or cooler (upper Himalayas) climates, physical breakdown is more pronounced. In humid tropical climates, chemical breakdown predominates resulting in the formation of deep to very deep soils.

3.1. Physical Weathering

Physical weathering is a mechanical process, causing disintegration of consolidated massive rocks into smaller pieces. Under very cold or very hot and dry conditions, such as in the central Himalayas or the Thar desert, physical weathering is prominent and is operated through various agents, viz. temperature, water, ice, wind and living organisms. The role of these agents are discussed below.

3.1.1. Temperature

Rocks may be classified into two types, viz. monomineralic (made up of one mineral), and polymineralic (made up of more than one mineral). In nature, polymineralic rocks are common. As a result of diurnal temperature changes, the rocks get heated during the day and cooled during the night. Different minerals in the rocks have different coefficients of expansion and thus heating and cooling of rocks results in differential expansion and contraction of minerals. With every temperature change, therefore, differential stresses are set up which eventually produce cracks in rocks, thus facilitating their mechanical breakdown.

Because of slow heat conductance, the outer surface of a rock is often warmer or cooler than the inner parts which are more protected. With the passage of time, this differential heating and cooling produce, lateral stresses which may cause the surface layers to peel away from the underlying parent mass. This phenomenon is referred to as 'exfoliation'. Some rocks may have entrapped water also. Water expands by about 9% on freezing. The freezing of this entrapped water thus may exert a tremendous force on the rock surface, if space is not available to dissipate this pressure. The force exerted by the freezing of water is equivalent to about 1465 tonnes (mega grams) per square metre (Mg/m^2) or 150 tonnes/ft^2 — a pressure that widens the cracks in huge boulders and dislodges the mineral grains from smaller fragments. Role of temperature thus can be overwhelming in the physical weathering of rocks.

3.1.2. Water

The rainwater falls on the land and travels towards the low lying areas such as rivers, lakes and oceans, continuously detaching, and shifting, sorting and reworking the sediments that it carries. When loaded with sediments, flowing water has a tremendous cutting power, resulting in the formation of gorges, ravines and valleys. Of all the agents of physical weathering, the effect of water perhaps is more pronounced and widespread. The rounding of sand grains on ocean beaches in the Eastern and Western Ghats is indicative of the abrasion that accompanies the water movement.

3.1.3. Ice

The moving ice is an erosive detachment and transporting agency of tremendous capacity. Snow received at higher elevations or polar regions accumulates and starts moving in the form of glaciers. During their movement, glaciers cause great deal of cutting and crushing of the bedrocks. Although glaciers are not so extensive in the present day environments; in the recent geological past, they had transported and deposited parent materials over millions of hectares on this planet. At present, glaciers are active in upper parts of the Himalayas.

3.1.4. Wind

Wind, an important agent of transportation of suspended particles, also exerts an abrasive action. Generally, the effect of wind is more pronounced during arid climates. Dust storms of almost continental extent have occurred in the past. Particles from the bare land surface are picked up by the blowing winds, particularly during dry months. Poorly aggregated or single grained deposits are prone to wind erosion. As dust is transported and deposited, abrasion of one particle against the other occurs. Dust-ladden winds also act as an abrasive agent against such obstacles as rock outcrops and exposed rocks, which come in their way. The rounded rock remnants in the Aravalis are caused largely by wind action. Wind in combination with ocean waves causes mechanical disintegration along the sea coasts, as in the Eastern and the Western Ghats.

3.1.5. Plants and Animals

Some plants, like mosses and lichens, grow on the exposed rock. They accumulate dust, which further encourages plant growth, and a thin film of highly organic material is formed. Sometimes, roots of higher plants exert a prying effect on rocks (as the root girth increases with plant growth), which results in some disintegration. Burrowing by rodents, movement of animals, and human activities (cultivation, quarrying, land levelling, construction of roads, buildings, railway lines, etc.) also result in physical weathering. Such influences, however, are of relatively limited importance in producing parent material when compared to the drastic physical effects of water, ice, wind, and temperature changes.

3.2. Chemical Weathering

Physical disintegration is accompanied by chemical decomposition which produces changes in the nature and composition of rocks and minerals. Chemical weathering takes place mainly at the surface of rocks with the alteration or disappearance of some minerals and formation of (new) secondary minerals. The process of chemical weathering is controlled by various agents, viz. water, temperature, and different organisms. The presence of water facilitates chemical weathering. The rate of chemical reaction increases with increase in the amounts of dissolved carbon dioxide and other minerals in water, and with increase in temperature. Chemical weathering is minimal in the desert areas, due to scarcity of water and in the cold regions, due to low temperatures. Due to availability of sufficient water and the presence of favourable temperature, chemical weathering is well pronounced in the humid tropical climate. The presence of organic and inorganic acids, which are formed as a result of microbial breakdown of plant residues, also accelerates chemical weathering. These agents commonly act in a synergistic manner to convert primary minerals (e.g., feldspars, micas, amphiboles, etc.) into secondary minerals (e.g., kaolinite, vermiculite, hydrous oxides, etc.) with release of water soluble ions. The principal processes of chemical weathering are described below. For a clear understanding of individual processes, these have been described separately, but in nature they mostly occur simultaneously.

3.2.1. Solution

Water is a universal solvent. Its solubilizing action is enhanced when it contains dissolved carbon dioxide, organic and inorganic acids or salts in it. Most of the minerals are affected by the solubilizing action of water, though by varying degrees. Some minerals such as halite (NaCl) dissolve readily in water, whereas the solubility of some silicates such as quartz in water is very low. Solution helps in the continuous removal of weathered materials but the total removal by simple solubilizing action is very limited. In the arid climates, due to paucity of water, even water-soluble minerals remain in rocks and sediments, whereas these are completely washed away in the semi-arid and humid regions.

3.2.2. Hydration

Hydration means chemical combination of water molecules with a mineral to form a new mineral. Many anhydrous minerals undergo hydration when they come in contact with water. Hydration reactions occur primarily on the surface and edges of mineral grains, but may pervade the entire structure in simple salts. Some examples of hydration reactions are given in Equations (1) and (2):

$$\underset{\text{(Anhydrite)}}{CaSO_4} + \tfrac{1}{2}H_2O \rightarrow \underset{\text{(Hemihydrate)}}{CaSO_4.0.5H_2O} \quad ...(1)$$

$$\underset{\text{(Anhydrite)}}{CaSO_4} + 2H_2O \rightarrow \underset{\text{(Gypsum)}}{CaSO_4.2H_2O} \quad ...(2)$$

Hydration is always accompanied by an increase in volume. The characteristics of hydrated minerals are different from those of their anhydrated counterparts. The hydrated minerals are usually soft and are readily weatherable. The absorbed water provides a bridge or entry way for the hydronium (H_3O^+) ions or protons (H^+) to attack the structure. Slaking of certain rocks is mainly due to hydration of their mineral constituents. Under the hot desiccating conditions, dehydration (reverse of hydration) can also occur.

3.2.3. Hydrolysis

Hydrolysis is one of the most important processes in chemical weathering and results in complete disintegration or drastic modification (in structure and composition) of weatherable primary minerals. Hydrolysis involves the partial dissociation of water into H^+ and OH^- ions. The pure water undergoes very limited dissociation, but in the presence of dissolved carbon dioxide, minerals and organic acids in it, the concentration of H^+ ion increases, resulting in an accelerated hydrolytic action of water. Hydrolysis is a double decomposition process and a hydroxide of some kind is usually formed. Water thus acts like a weak acid on silicate minerals, as depicted in Equations (3) and (4):

$$H_2O \rightarrow H^+ + OH^- \quad ...(3)$$

$$\underset{\text{(Orthoclase)}}{KAlSi_3O_8} + H^+ \rightarrow HAlSi_3O_8 + K^+ \quad ...(4)$$

Another example of hydrolysis reaction is the replacement of interlayer potassium in micas by protons or hydronium ions to produce vermiculite:

$$\underset{\text{(Muscovite)}}{K(Si_3Al)Al_2O_{10}(OH)_2} + H^+ \rightarrow \underset{\text{(Vermiculite)}}{(K,H)(Si_3Al)Al_2O_{10}(OH)_2} + K^+ \quad ...(5)$$

The products of hydrolysis are wholly or partially removed by the percolating water, depending on the climatic conditions and permeability of the residual materials. They may also recombine with other constituents to form clays. In a way, hydrolysis reactions may be considered as the forerunners of clay formation.

3.2.4. *Oxidation*

Oxidation is an important chemical reaction occurring in well-aerated rock and soil materials where oxygen supply is high and biological demand is low. It is particularly important in rocks and minerals that contain iron and manganese — elements that are easily oxidized. In most of the primary minerals, iron is present in the ferrous (Fe^{2+}) form. On oxidation, it undergoes the following reaction [Equation (6)]:

$$Fe^{2+} - e^- \rightarrow Fe^{3+} \quad ...(6)$$

Oxidation of iron is a disintegrative weathering process in minerals containing ferrous as part of their crystal structure. Reduction in size and increase in electrical charge on oxidation of Fe^{2+} to Fe^{3+} create electrical and structural imbalances in these minerals. Rocks containing ferromagnesian silicates such as pyroxenes, hornblende, biotite, glauconite and chlorite, are susceptible to oxidation. In other cases, ferrous iron may be released from the mineral and is almost simultaneously oxidised to the ferric form. An example of this is hydration of the mineral olivine and the release of ferrous ions from it, which may be immediately oxidised to ferric form which has very low solubility. When ions such as Fe^{2+} are removed or are oxidised within the minerals, the rigidity of the mineral structure is weakened and the mechanical breakdown becomes easier. This provides a favourable environment for further chemical reactions. Similarly, minerals containing the manganous form of manganese and sulphide groups are also susceptible to oxidation.

3.2.5. *Reduction*

Reduction occurs where a material is water-saturated (such as below the water-table level), oxygen supply is low, and the biological oxygen demand is high. The net effect of these conditions is the reduction of a metal, say iron, to its highly mobile form, ferrous (Fe^{2+}) in this case. In this form, it may be removed from the system if there is a downward and/or outward movement of groundwater. If ferrous iron persists in the system, it tends to form sulphides and other ferrous compounds. These impart characteristic green and blue colours to many reduced soil materials. Under certain conditions, there could be formation of lepidocrocite (γ-FeOOH), resulting in the characteristic orange and yellow mottles.

3.2.6. *Carbonation*

Carbonic acid (H_2CO_3), although a weak acid of carbon dioxide, is very important in the chemical weathering of rocks and minerals as it makes minerals more soluble. The atmosphere contains only 0.03% carbon dioxide, but the rain water may contain as high as 0.45% carbon dioxide. The decomposition of organic matter and the respirations of roots and other soil organisms (macro and micro) liberates carbon dioxide in large amounts. The CO_2 concentration in soil is thus much higher (0.25%) than atmosphere. Carbonation tends to produce carbonates and bicarbonates as shown in Equations (7) and (8):

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad ...(7)$$

$$\underset{\text{(Calcite)}}{CaCO_3} + \underset{\text{(Carbonic acid)}}{H_2CO_3} \rightarrow \underset{\text{(Calcium bicarbonate)}}{Ca(HCO_3)_2} \quad ...(8)$$

The solubility of calcium bicarbonate is considerably higher than that of calcite.

3.2.7. *Integrated Weathering Processes*

Different types of chemical reactions described above occur simultaneously and are interdependent. For example, hydrolysis of a given primary mineral may release ferrous iron that is quickly oxidised to ferric form, which, in turn, is hydrated to give a hydrous oxide of iron. Hydrolysis also may release soluble cations, silicic acid, and aluminium or iron compounds. These substances can recombine to form secondary silicate minerals such as silicate clays.

3.3. *Factors Affecting Weathering*

Different minerals weather at different rates. Three major factors which affect weathering of rocks and minerals are: climatic conditions, physical and chemical characteristics of the rocks, and stability of minerals.

3.3.1. Climatic Conditions

The climatic conditions influence the rate and nature of weathering profoundly. Under arid conditions, the physical weathering predominates. The size of particles decreases with relatively little change in the chemical composition of a mineral. The original primary minerals are prominent, whereas the content of secondary minerals is low. Physical changes due to temperature fluctuations and wind action are accompanied by only limited chemical changes. Consequently, the soils of arid regions are remarkably like the parent materials from which they are formed. Similarly, in extremely cold climates, the rocks and minerals undergo mechanical disintegration with little modification in chemical composition. In humid regions, the forces of weathering are more varied. Vigorous chemical changes accompany physical disintegration. New minerals such as silicate clays and oxyhydroxides and oxides of iron and aluminium are predominant. Chemical alteration is accelerated and intensified by the action of organic acids formed by the decomposition of large quantities of organic matter produced by abundant plant growth.

In the humid tropical regions, as in southern and north-eastern India, the year-round high temperatures and the luxuriant plant growth provide optimum conditions for intensive weathering. In these regions, the primary silicate minerals succumb to weathering and only the highly-weathered silicate clays persist. Resistant products of chemical weathering, such as oxides of iron and aluminium, tend to dominate soils of the humid tropical regions.

3.3.2. Physical Characteristics

The physical characteristics that influence weathering include particle size, hardness, and nature and degree of cementation. Rocks comprising minerals with large crystals, disintegrate easily than those with fine crystals because of pronounced expansion and contraction due to changes in temperature. However, once the rocks get disintegrated into smaller fragments, the finer crystals undergo relatively rapid chemical changes than the larger ones because the fine-grained materials provide larger surface area for chemical attack.

Rate of weathering also depends on the hardness and cementation. For example, a dense quartzite or a sandstone cemented strongly by a slowly weatherable mineral can resist mechanical breakdown and presents only a small total surface area for chemical activity. On the other hand, porous rocks, such as volcanic ash, coarse limestone or sandstone, are readily broken down into smaller particles and are easily decomposed.

3.3.3. Chemical and Structural Characteristics

Chemical composition and structural characteristics of minerals also influence the ease of their removal or breakdown. Some minerals such as gypsum ($CaSO_4.2H_2O$) or calcite ($CaCO_3$) can be solubilized in water saturated with carbon dioxide and can be easily removed from the parent material. Some minerals such as ferromagnesian silicates like olivine and biotite, contain readily oxidizable iron (ferrous), and their component ions are not very tightly packed in the mineral crystal structures, and therefore can be easily weathered. In contrast, the relatively tightly packed nature of crystal units and lack of oxidizable iron in muscovite impart considerable resistance to weathering.

3.3.4. Stability of Minerals

Minerals can be arranged in the order of stability or weatherability. In view of the differences in surface area and consequent reactivity, it is desirable to separate mineral par-

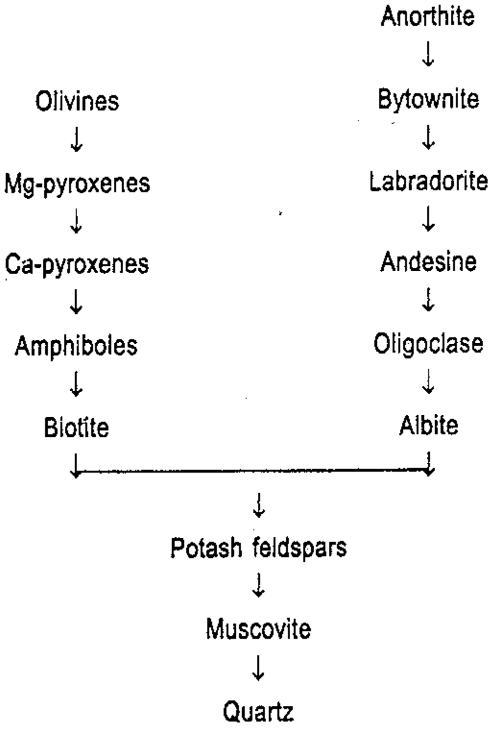

Figure 2. Stability sequence of different minerals

ticles into two classes when we discuss their weatherability: clay size and sand-silt size. The weatherability of the common primary minerals is illustrated by the 'stability series' (Figure 2) proposed by Goldich (1938). On the left hand or the 'basic' branch of this series, there is an increasing silica-tetrahedral linkage with increasing stability from top to bottom. The least stable mineral (olivine) has independent tetrahedron and the silicon tetrahedra are held together by forming bonds with easily hydrolyzable magnesium or oxidizable iron. On the other hand, in quartz, one of the most stable minerals, there is a three-dimensional network of silicon tetrahedra. All the oxygen atoms are shared with the adjacent tetrahedra. Also, there is a decrease in the content of easily hydrolyzable bases from the least to the most stable mineral. On the right hand or the feldspar branch, there is a decreasing distortion of the lattice from calcic to potassic feldspars. In anorthite, 50% of the silicon in tetrahedral sites is replaced by aluminium, whereas in potash feldspars, this replacement is only 25%. Divalent calcium (in anorthite) does not fit well into the framework structure of feldspars. On the other hand, the large monovalent potassium fits snugly in the feldspar structure. Thus, orthoclase (albite) is more stable than anorthite.

The minerals at the top of both series were formed during the early stages of cooling and crystallization of magma at high temperatures, whereas quartz was the last mineral to crystallize from cooling of magma. Thus, higher the temperature of crystallization of a mineral from the magma, the more unstable it is. Obviously, this higher instability is related to the greater disequilibrium with the environment in the pedosphere (lithosphere-atmosphere interface) as compared with temperature of formation of these minerals from magma.

Besides the stability of primary minerals, the persistence of clay-size minerals in soils is also important. The sequence of weathering is largely controlled by the intensity and capacity factors as a function of time. Weathering produces minerals which may be assigned with a particular index. This index known as 'weathering index' (WI) may help to array the clay-size minerals according to weathering sequence (Jackson *et al.*, 1964). Higher WI shows increase in the resistance to weathering (Table 1). During weathering of a primary mineral, each particle is considered as a closed system. The easily-weatherable minerals in order of increasing weathering indices are: gypsum<

Table 1. Weathering indices of some clay-size minerals in soils

Typical clay-size minerals	Weathering index
Gypsum	1
Calcite, dolomite, aragonite, apatite	2
Olivine-hornblende, pyroxenes, diopsides	3
Biotite, glauconite, nontronite	4
Albite, microcline	5
Quartz, cristobalite	6
10Å Mica, muscovite, sericite	7
Vermiculite, 2:1:1 minerals, where brucite layer is Fe/Mg	8
Montmorillonite, beidellite	9
Pedogenic chlorite (2:1:1 mineral)	9
Kaolinite, halloysite	10
Gibbsite, boehmite	11
Allophane	11
Hematite	12
Anatase	13

Source: Bear (1964)

calcite < olivine < biotite. Interestingly, the secondary chlorites (2:1:1 mineral) have more weathering stability (WI 8) than the ideal chlorite (WI 4). The other form of chlorite (2:1:1 mineral) with aluminous hydroxy-interlayering has been grouped under minerals showing weathering index of 9. The kaolinites are the most resistant phyllosilicate minerals (WI 10).

Gibbsite has for a longtime, been considered as index mineral showing advanced stage of weathering. Although gibbsite has been reported to be formed from kaolinite, this transformation appears improbable since it involves a desilication process which can happen only above pH 9 (Millot, 1970). Interestingly the soils showing the presence of gibbsite are all acidic and oxidic. Recent evidences show that gibbsite present in the Ultisols of the Shillong plateau are formed in an alkaline pedo-environment (Bhattacharyya *et al.*, 2000). The model understanding of the formation of gibbsite indicates two important points, viz., (i) gibbsite is present as a remnant of an earlier alkaline pedochemical environment, and (ii) its formation even in the presence of a considerable amount of 2:1 minerals discounts the hypothesis of an anti-gibbsite effect (Jackson, 1963; 1964). The presence of gibbsite in these soils should not, therefore, be considered as a conclusive proof of extreme weathering conditions of soils (Macias Vasquez, 1981; Jenkins, 1985; Lowe, 1986). This fact assumes importance since Jackson's weathering index assigns gibbsite as a mineral with very high weathering index (WI 11). Iron and titanium containing minerals have been found to be most resistant to weathering as may be judged by their weathering indices (WI 12 and 13, respectively, Table 1).

There are different ways to evaluate the weathering stage of a soil. The concept of molar ratio (viz., silica:sesquioxides; silica:iron oxides; silica:aluminium oxides; silica:bases) has been found to be effective. Other quantitative evaluation, namely 'weathering mean' (m) has been useful since it involves the knowledge of quantified value and the weathering index (WI) of each mineral (Table 1). The weathering mean (m) is given by

$$m = \frac{\Sigma(p * WI)}{\Sigma p}$$

where,

p = Percentage of the mineral, and

WI = Weathering index of that mineral.

Weathering mean is a sensitive measure of degree of weathering and it is more sensitive to minerals with weathering index 4 to 9 (Table 1). This mean value increases as a function of time and intensity of soil weathering. If p (% mineral) is plotted against the weathering index (WI), a distribution curve is obtained (Figure 3). This curve gradually moves to the right (in Figure 3) when the soil represents advanced stage of chemical weathering.

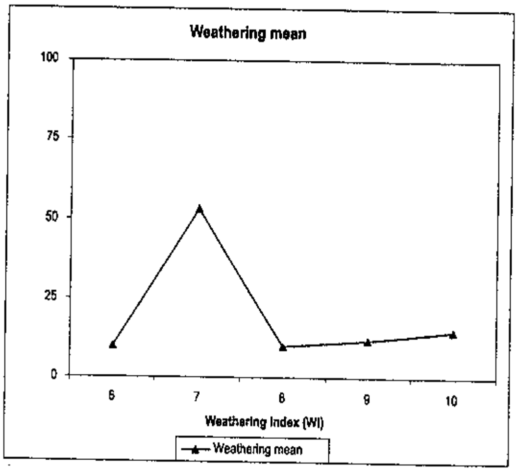

Figure 3. A schematic diagram of frequency curves of a soil showing 10 % quartz (WI 6), 50% mica (WI 7),10% vermiculite (WI 8), 12% montmorillonite (WI 9) and 15% kaolinite (WI 10) The minerals are in clay fractions (<2μm)

4. Soil Formation

At any specific location on the surface of earth, at least five factors act simultaneously to produce soil. These are:

- Parent material
- Climate
- Relief
- Biosphere, and
- Time or age.

These factors are not of equal significance in development of different soils. Although some of them may be more effective in determining the nature of soils under a particular set of conditions, all of them are inter-related and complement one another. Jenny (1941) expressed the relationship of these five factors to the soil properties by Equation (9):

$$S = f(cl, r, o, p, t, \ldots\ldots..) \qquad \ldots(9)$$

where,

S = Any soil property, e.g. organic matter content of surface horizons, pH, soil texture, etc.
f = Function of or dependent upon
cl = Climate
r = Relief or topography
o = Organisms (flora and fauna)
p = Parent material, and
t = Time or age.

Thus, any soil property is a function of the collective effects of all these five soil forming factors.

Joffe (1949) divided these factors of soil formation into two groups, viz. active and passive factors of soil formation. Passive factors represent the source of soil forming mass and conditions affecting it. These are: (i) parent material, (ii) relief, and (iii) time. Active factors represent the agents which supply energy that acts on the parent material for the development of soils. These factors are the driving forces that promote the processes causing changes in soil during the course of soil genesis. Climate and organisms are the active factors of soil formation. Soils are often defined in terms of these factors as 'dynamic natural bodies having properties derived from the combined effect of climate and biological activities, as modified by topography acting on parent material over a period of time'.

4.1. Parent Materials

The parent materials on which soils are developed can be divided into two broad groups, viz. sedentary (formed in place) and transported. The transported materials can be sub-divided according to the agencies of transportation and deposition as shown in Figure 4. Different types of parent materials are described in the following sections.

4.1.1. Residual Parent Materials

When the soils develop at a place from the underlying rocks, they are said to have been formed from the residual parent materials. Such materials develop *in situ* from the underlying rock. Typically, they have undergone prolonged and often intense weathering. In a warm, humid climate, as in some parts of eastern states, north-eastern states, Kerala, Tamil Nadu and Karnataka, the parent materials are likely to be thoroughly oxidized and well leached. Red and yellowish brown colours imparted by haematite (α-Fe_2O_3) and goethite (α-FeOOH) minerals, are characteristics of intense weathering in hot, humid climates. In cool and especially dry climates, weathering is less drastic and the oxidation and hydration of iron is hardly noticeable. On the other hand, such parent materials may contain high contents of calcium and magnesium due to limited leaching. Residual parent materials are encountered

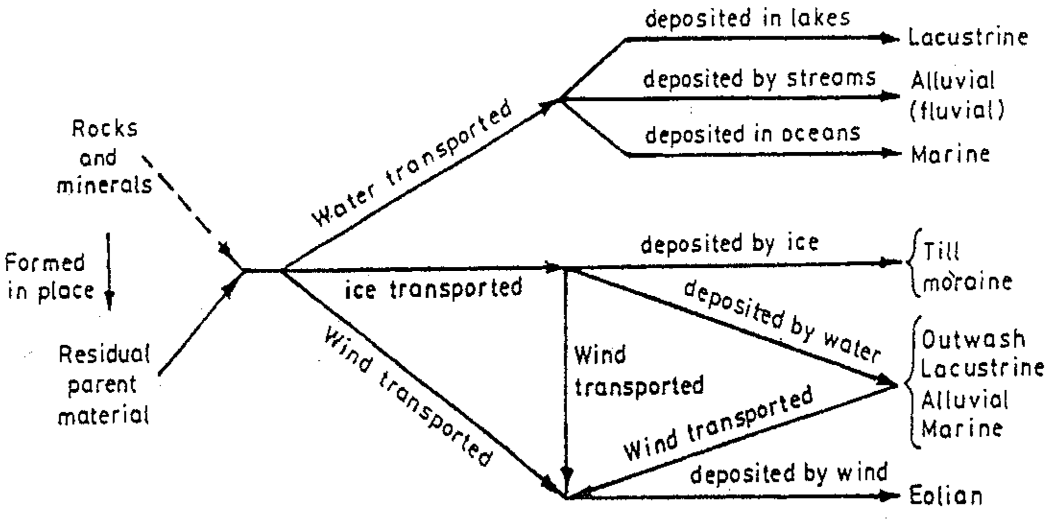

Figure 4. Different types of parent materials

mainly in the Deccan plateau and some parts of central India and are of relatively limited significance in the Aravalis and the Himalayan region.

4.1.2. Colluvial Parent Materials

Rocks or soil debris at the foot of a slope that have moved there due to gravity, are called colluvial materials. A colluvial material exists to some extent at the base of all slopes, but it is especially noticeable in the mountainous or hilly topography where rock slides, slips and avalanches are common. It is made up of fragments of rock detached from the higher parts and is carried down the slopes mostly by gravity. The 'frost action' has also much to do with the development of such deposits. A parent material developed from colluvial accumulation is usually coarse and stony, because physical rather than chemical weathering is dominant. Soils developed from the colluvial materials are not of significant agricultural importance generally, because of their small surface area, inaccessibility, and unfavourable physical and chemical characteristics. However, some useful timber, horticulture, plantation and grazing lands in mountainous regions have colluvial materials.

4.1.3.Parent Materials Transported by Water

Sediments that are deposited by the flowing water such as streams, rivers, etc. are called 'alluvial materials'. These deposits include floodplains, alluvial terraces, alluvial fans, and deltas. These are described in the following paragraphs.

Floodplains — During rainy seasons, streams and rivers overflow their banks and flood the surrounding area. The parts of a valley and alluvial plains, which are inundated during floods, are referred to as 'floodplains'. Sediments carried by the swollen streams are deposited during the flood, with the coarser materials being laid down near the river channel and the finer materials farther away. Such deposits are found to some extent along every stream. Depending on topography and lithology of the area, and gradient of the river or stream, the floodplains may be very narrow or wide. For example, at some places, the floodplain along the Brahmaputra and the Ganges are tens of kilometres wide. The soils derived from these sediments are generally rich in nutrients, but they may require drainage and protection from the overflow during the rainy seasons. The floodplain soils are young and highly stratified.

Alluvial Terraces — The sedimentary deposits that were laid down by the rivers but are not subject to flooding now are called 'alluvial terraces'. These terraces are generally located at a higher elevation than the floodplains and are separated by escarpments of different heights. Most of the Indo-Gangetic Plains are alluvial terraces.

Alluvial Fans — Sediments deposited by streams of flowing water when they enter plains from the hilly areas are known as 'alluvial fans'. Because of the presence of steep slopes, the flow velocity of streams in hilly and mountainous regions is high. When these streams leave a narrow valley in an upland area and suddenly descend a relatively flat and broader valley below, the sediments are deposited in the shape of a fan. Generally, these deposits are coarse textured, gravelly and stony, somewhat porous and well-drained. Alluvial fans occur in the transition zones between the lower Himalayas and the Indo-Gangetic alluvial plains.

Delta Deposits — Most of the coarser sediments suspended in the stream water are deposited as alluvial fans, alluvial terraces and floodplains. By the time these streams reach the oceans and seas, the flow velocity is considerably reduced and the finer particles are deposited near the mouth of the river as 'delta deposits'. These deposits are fine-textured and are subject to flooding, i.e. they are clayey and swampy in nature. Delta deposits of the Ganges are well known.

4.1.4. Marine Deposits

Marine deposits are formed by the deposition of sediments carried by streams into the bodies of static water. The stream-carried sediments are eventually deposited in oceans, lakes, seas, and gulfs. The coarser fragments are deposited near the shore and the finer particles away from the shore. These underwater sediments are built-up over long periods of time. In some areas, these marine deposits get raised above the sea level due to changes in the elevation of the earth's crust. These deposits are variable in texture. Some are sandy, others are clayey. Since the marine sediments have been subjected to soil-forming processes for relatively short periods of time, the properties of the soils that develop on them are predominantly determined by the nature of the marine parent materials. Although not of widespread occurrence, marine deposits are found in some coastal areas.

4.1.5. Lacustrine Deposits

The sediments deposited in fresh water lakes are known as 'lacustrine deposits'. Lakes are inland bodies of static water. As a result of deposition of sediments, these lakes that were once filled with water may become filled with mineral sediments. The source of these sediments is erosion of lake banks and/or particles suspended in streams which get discharged into the lakes. The lacustrine deposits are relatively rare. These may also be formed as a result of glacial activity. When an ice front comes to a standstill at a point where there is no ready escape for the water, ponding begins and ultimately very large lakes are formed. The deposits formed in these glacial lakes range from coarse delta materials and beach deposits near the shore, to larger areas of fine silt and clay deposited from the deeper and relatively still waters at the centre of the lake. Areas of inherently fertile soils have developed from these materials as the lakes dried.

4.1.6. Glacial Deposits

In polar regions, snow continues to accumulate and the pressure of its weight changes the snow to ice. After centuries of such a build-up, the ice starts moving in the form of glaciers. The glaciers transport materials embedded in them and also remove the rock protuberances which come in their way. Materials deposited by the glaciers are called glacial deposits. The materials deposited directly by the glacial ice are called glacial till. These are heterogeneous mixtures of the debris of wide diversity, which vary from rocks and boulders to clay. Glacial till is found mostly as irregular deposits called moraines, of which there are various kinds. Terminal moraines are hilly ridges that characterize the southernmost extensions of the various ice lobes in the northern hemisphere when the margin was stationary for long enough period to permit an accumulation of debris. Terminal moraines occupy little land area. Relatively thinner and more level deposits called ground moraine are by far the most widely distributed glacial deposits which are formed when the ice retreated to the north. An outstanding feature of glacial till is its variability. Consequently, the soils derived from such material are highly heterogeneous.

4.1.7. Glacial Outwash Sediments

As the glaciers melt, torrents of water gush constantly from the ice lobes of glaciers, especially during the summer. The vast loads of sediments carried by such streams are either dumped immediately or carried to other areas before deposition. An outwash plain is formed by streams flowing from the ice which are heavily loaded with glacial sediments. Since the sediment is sorted by the flowing water, sands and gravels are common. Outwash deposits are found in valleys and on plains where the glacial waters were able to flow away freely.

4.1.8. Aeolian Deposits

Sand dunes and depositions from the materials transported by wind are called 'aeolian deposits'. These occur in the Thar desert covering western parts of India and the adjoining areas. Except for places where they have been stabilized by vegetation, sand dunes are of limited agricultural value and may become menace to agriculture if they are moving. During the glacial period, conditions were ideal for wind erosion. The weather was cold and windy, and the vegetative cover in areas to the south of the glaciers in the North America was sparse or non-existent. During winters, winds picked up fine alluvial materials, deposited during previous summers by the ice-fed streams and moved them southward. Fine particles from glacial till and even the residual material were similarly transported. These wind-blown materials, comprised primarily silt or silt with some fine sand and clay, are called 'loess'. Aeolian deposits other than sand dunes and loess include volcanic ash. Soils derived from the volcanic ash occur in some parts of the USA, Japan and New Zealand. The volcanic soils are light and porous and are generally of lower agricultural value than the soils developed from the loess.

4.2. Parent Materials and Soil Formation

The parent materials influence soil formation by their different rates of weathering, the levels of nutrients they contain, and their particle size distribution. During the initial stages of soil development, the parent materials exert a greater influence in determining the properties of soil. Thus, in slightly weathered soils such as those in floodplains, the parent material is dominant in determining soil properties. Soil developed on weakly cemented sandstones are sandy. Soils developed on shales are shallow and fine-textured. Glacial till, loess or limestone deposits undergo very limited changes, except accumulation of organic matter, development of some structure and loss of soluble salts. Even moderately to well weathered soils may retain rocks in glacial moraines or preserve nature of clays in deltas or sands in river terraces.

The nature of parent material influences the soil characteristics to a great extent. For example, soil texture is highly influenced by the parent materials. In turn, soil texture influences the downward movement of water, and thereby affecting the translocation of fine soil particles and plant nutrients. Clay illuviation and the identification of Bt (textural B) horizon have been considered as the most important signatures of highly-weathered soils such as Alfisols and/or Ultisols unlike Oxisols (Soil Survey Staff, 1999). Ideally, the term laterite is equivalent to Oxisols in the USDA Soil Classification System (Buol and Eswaran, 2000). The primary requirement for the formation of an Oxisol is the development of an oxic horizon with low CEC, low ECEC (effective cation exchange capacity) and low amount of weatherable minerals (< 10%). The states of Kerala, and Maharashtra (in the Western Ghats) and the north-east region fulfill all the requirements conducive for the formation of Oxisols. Yet, these soils have not reached the stage of Oxisols (Bhattacharyya *et al.*, 1993; Krishnan *et al.*, 1996; Sen *et al.*, 1999; Velayutham and Bhattacharyya, 2000). Studies on these soils as well as a few selected Oxisols from abroad (Beinroth, 1982; Jones *et al.*, 1982; Fox, 1982; Macedo and Bryant, 1987; Buurman *et al.*, 1996; Muggler, 1998) indicate an adequate amount of weatherable minerals in these soils. This suggests that the transformation of Alfisols and Ultisols to Oxisols with time, as often envisaged in the model of soil genesis, is difficult to reconcile (Chandran *et al.*, 2005).

The chemical and mineralogical compositions of parent materials also influence weathering directly and can simultaneously affect the natural vegetation. For example, the presence of limestone in the parent material delays the development of acidity, a process that humid climates encourage. In addition, the leaves of trees growing on limestone deposits are relatively high in calcium and other base-forming metallic cations. As these high-base-content leaves are incorporated into the soil and are decomposed, they further delay the process of acidification.

The parent material also influences the quantity and the type of clay minerals present in the soil profile. The parent material itself may contain different types of clay minerals. The nature of parent material also influences the kind of clays that can be formed. The nature of the clay minerals present, in turn, markedly affects the kind of soil that develops. The quality of parent material in influencing formation of different type of soils has been illustrated by various case studies.

4.2.1. Formation of Ferruginous Red Soil (Alfisols)

Myth about the highly-weathered red ferruginous materials that were hitherto referred to as laterites on the basaltic Deccan plateau has been resolved in the light of quality of basalts as parent material. In soil science parlance, these weathered materials are of 60 million years. The persistence of these non-kaolinitic and/or non-oxidic red soils has been possible due to the presence of base-rich zeolites of amygdoloidal basalt. The quality of parent material thus helps in the persistence of these red soils in the humid tropical climate. It is also an evidence of the role of parent material in preventing the loss of soil productivity even in an intense leaching environment to preserve the natural soil resources in the Western Ghats (Bhattacharyya *et al.*, 1999).

4.2.2. Formation of Black Soils (Vertisols)

Although formation of smectitie minerals in soils has been a phenomenon of humid climate, the soils rich in these minerals are common in the semi-arid to arid climate. Since smectite minerals are ephemeral in high rainfall areas, the formation and persistence of black soils (Vertisols) which are rich in these minerals, are difficult to reconcile. The quality of basalts in the Western Ghats of Maharashtra permits the persistence of black soils even under very high rainfall (> 3,500 mm).

The amygdoloidal zeolites in the basalts provided sufficient bases to prevent the complete transformation of smectite minerals. The presence of smectites and zeolites made the formation of black soils possible in micodepressions even in a tropical humid climate (Bhattacharyya *et al.*, 1993).

4.2.3. Formation of Mollisols

In contrast to generally observed non-acidic and less-weathered Mollisols in temperate semi-arid and humid climate (Fenton, 1983; Fanning and Fanning,1989), acidic and fairly-weathered Mollisols on the Deccan basalt are observed in the hills of central (Satpura Range, Madhya Pradesh) and western India (Western Ghats, Maharashtra) under forest in the tropical humid climate condition. The presence of zeolites as a part of parent material inhibits the transformation of smectites. Retention of adequate amount of smectite and continuous supply of bases from zeolites make the formation of Mollisols possible. The formation and persistence of these Mollisols in association with acidic Alfisols under sparse forest in basaltic landscape of millions of years in central and western India demonstrate the primary importance of the quality of parent material rich in expanding clay minerals and bases on their formation. This unique example thus expands the basic knowledge on the formation of Mollisols even in the humid tropical part of the world (Bhattacharyya *et al.*, 2006).

4.3. Climate and Soil Formation

Climate is a dominant factor in soil formation, mainly because of the effects of precipitation and temperature. Some direct effects of climate on soil formation include:

(i) Retention or accumulation of lime (carbonates) at shallow depths in areas having low rainfall. It is because calcium carbonate and bicarbonate (from dissolving carbon dioxide, minerals, and lime) are not leached out due to limited amount of water moving through the soil. Such soils are usually alkaline.

(ii) Formation of acidic soils in the humid areas is due to intense weathering and pronounced leaching of basic cations (calcium, sodium, magnesium, and potassium).

(iii) Erosion of soils on sloping lands constantly removes developing soil layers.

(iv) Deposition of soil materials downslope buries the developing soils.

(v) Weathering, leaching and erosion are more intense and of longer duration in the warm and humid regions where the soil does not freeze. The reverse is true in cold climates, as in the central Himalayas.

Water plays a key role in the soil formation. A soil is said to be developed when it has detectable layers (horizons), such as of accumulated clays, organic colloids, carbonates, or soluble salts that have been moved downward by water. The extent of colloid movement and the depth of their deposition are determined partly by the amount and pattern of precipitation, which produce the leaching action.

Climate influences the formation of soils through its influence on different soil forming processes, namely clay illuviation, formation of $CaCO_3$ and development of soil sodicity. Vertisols (commonly referred to as black soils) are common in humid, sub-humid (moist), sub-humid (dry), semi-arid (moist), semi-arid (dry) and arid (hot) climates in India. The characteristic shrink-swell behaviour of these soils is governed by high amount of clay (< 2 µm) dominated by smectitic minerals formed from weathering rocks (mainly by basalts) during humid climate. Formation of Vertisols thus occurred in a much wetter climate and are still preserved in the non-leaching clay environment. These Vertisols show different types of properties due to the change in climate (from humid to semi-arid and arid) and bear signatures of more than one genetic episode. Consequently, they qualify for polygenetic soils (Pal *et al.*, 2001). A view of the polygenesis in Vertisols of a climo-sequence from humid to arid the evolution of soils is presented in Figure 5. This evolution sequence remains as an evidence of climatically-induced natural soil formation process (Pal *et al.*, 2003a;b).

Climate influences the soil formation indirectly also through its action on vegetation. Semi-arid climates support scattered shrubs and grasses. Arid climates supply only enough moisture for sparse, short grasses or shrubs, which may not be dense enough to protect the soil against wind and water erosions. Many arid soils show very limited profile development and contain low amounts of organic matter.

The soils formed under the year-round hot and humid climate are very deep, reddish in colour (due to the presence of oxidized iron as haematite), contain well-decomposed organic matter, and are low in essential elements because of intense leaching.

4.4. Biota and Soil Formation

The activities of living plants and animals, and the decomposition of their organic wastes and residues (the living environment, the biota) markedly influence the soil development. Differences in soils that have resulted primarily from the variability in vegetation are specially noticeable in the transition zone where trees and grasses meet. Under the humid forest vegetation, soils that develop may have many horizons, but are leached (washed, eluviated) in the surface layers, and have slowly decomposing organic-matter layers on the surface. In contrast, some grassland soils near the transition zone of forests have surface horizons rich in well-decomposed organic matter, frequently extending down to a depth of 30 cm or more into the mineral soil.

Burrowing animals— rodents, earthworms, ants, and termites— are very important in the soil formation, if present in large numbers. Soils that are habitat of many burrowing animals have fewer but deeper horizons because of the constant mixing within the profile, which nullifies the organic colloid and clay movements downward.

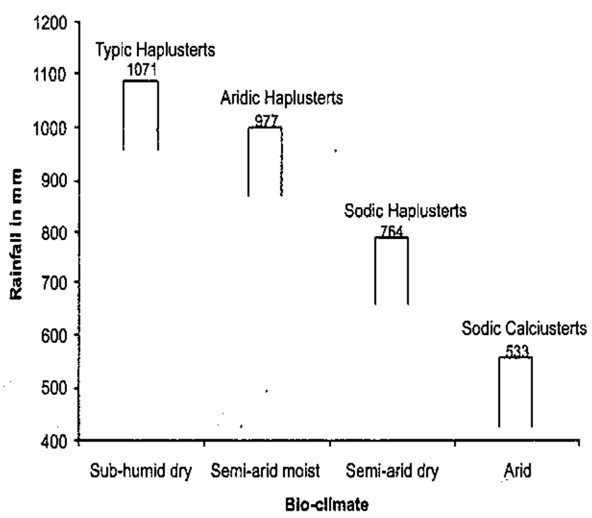

Figure 5. Pedogenic evolution of Vertisols in a climosequence

Microorganisms help the soil development by decomposing organic matter slowly and forming weak acids that dissolve minerals faster than water. Some of the first plants to grow on weathering rocks are crustlike lichens, which are beneficial (symbiotic) combination of algae and fungi.

4.5. Topography and Soil Formation

The configuration of land surface is known as 'topography' or relief. Topography influences soil formation primarily through its effects on modifying water and temperature relations. Soils within the same general climatic area developed from the similar parent materials and on steep hillisides typically have thin horizons because limited amount of water moves down through the profile as a result of rapid surface runoff and rapid erosion of surface. Similar materials on gently sloping hillisides have more water passing vertically through them than do materials on steeper slopes. The soils on gentle slopes generally are deeper, have more luxuriant vegetation, and the organic matter level is higher than in soils on similar materials on steep slopes.

The materials lying in landlocked depressions receive runoff waters from the surrounding higher areas. Such conditions favour better vegetation growth but exhibit slower decomposition of dead plants because of oxygen deficiency in the waterlogged (saturated) soils. This results in soils with a large amount of organic matter. If the area remains wet for many months of a year, organic (peat or muck) soils develop. If the accumulating waters dissolve salts from the surrounding soils, the depression may become a salt marsh with unique salt-tolerant plants, or it may develop toxic salt conditions where no plants can grow. When soils in a watershed are strongly acidic, iron may leach from them and get deposited in depressions to form the bog iron (limonite). Alkaline soils on the sloping topography in humid regions may result in lime leaching which gets eroded into depressions, leading to the formation of a marl.

In the northern hemisphere, soils on south- and west-facing slopes receive more direct rays of the sun and are, therefore, warmer and drier than north- and east-facing slopes. In the arid climates, these drier south- and west-facing slopes are often less productive than the soils on north- and east-facing slopes. The opposite slopes are affected in the southern hemisphere. In cold, wet areas, these warmer sites may be highly productive. Higher temperature on south- and west-slopes results in greater loss of water by evaporation; the net result in regions where water is limited, is formation of soils with thinner horizons and less vegetative cover than the soils on north and east slopes.

Topography has been reported to influence the soil properties and hence soil types. Interestingly, micro-topographic variations on a landscape have immense control over the soil formation. In the Western Ghats of Maharashtra, micro-topographic variations have influenced the formation of black soils even in the humid tropical climate with very high mean annual rainfall (Bhattacharyya *et al.*, 1993). Recent studies on soil formation in the micro-high (MH) and micro-low (ML) in two important food production zones of India, namely the Indo-Gangetic Plains (IGP) and the black soil region (BSR) have shown the formation of soils with different characteristics even within a short distance in the landscape. In the BSR, formation of sodic Vertisols in MH alongside non-sodic Vertisols in ML positions is a unique phenomenon. The different types of soil formation has been possible due to micro-topographic variations which modify distribution of water across the landscape and facilitate deeper penetration of rainwater in ML position (Vaidya and Pal, 2002). In the IGP, on the other hand, non-sodic and moderately sodic soils (Alfisols) in the MH and highly sodic soils (Alfisols) in the ML position are formed. The main soil-forming processes have been clay illuviation, deposition of calcium carbonate and concomitant development of sodicity. The ML positions are repeatedly flooded with surface water in IGP during the brief and high intensity showers. These soils are thus subject to cycles of wetting and drying, leading to (i) steady supply of alkalis (Ca and Na ions) by hydrolysis of feldspars, (ii) precipitation of $CaCO_3$ at high pH, and (iii) development of highly sodic soils throughout the depth. Such events of flooding and the associated effects are minimal in the MH position, resulting in the formation of non-sodic and/or moderately sodic soils (Pal *et al.*, 2003b).

4.6. Time and Soil Formation

The length of time required for a soil to develop the distinct layers called the 'genetic horizons' depends on many interrelated factors of climate, nature of parent material, organisms, and topography. Horizons tend to develop rapidly under the warm, humid and forested conditions when there is adequate water to move colloids. Acid sandy loams lying on the sloping topography appear to be the soils most conducive for a rapid soil profile development.

Under ideal conditions, a recognizable soil profile may develop within 200 years. Under less favourable circumstances, the time may be extended to several thousand years. Soil development proceeds at a rate determined by the combined effects of time and intensities of climate and biota (organisms), further modified by the effect of land relief (topography) on which the soil is situated and the kind of parent material from which it is developing.

Different surfaces of earth's lands have been exposed for different lengths of time. Some plateau soils have been exposed for hundreds of thousands of years. Glacial till surfaces are more recent but may still be a few hundred thousand years old. More recently, rivers have flooded and covered floodplains and valley bottoms with recent deposits; these land surfaces may be only a few years or decades old, and the soil development has just started.

The soil on different-aged surfaces have been forming for different lengths of time. Recent deposits have shown little soil development, whereas land surfaces exposed for thousands of years may have well-developed profiles that are quite different.

5. Interaction of Soil Forming Factors

The formation of soil is a diverse and complex process, with effects from the five major factors working in combination. For instance, soil with good drainage (topography or parent material) and mild temperature and high rainfall (climate) will probably support ample plant life (biota) because favourable drainage provides an aerated location for the plant roots. The plants, in turn, decompose, producing carbon dioxide (CO_2), which combines with water from rainfall to form carbonic acid (H^+ and HCO_3^-). The resulting acidity increases the solubility of parent materials; sodium, potassium, calcium and magnesium are dissolved and leached in the draining soil water, and the soil becomes more acidic. High rainfall also translocates some clays and organic colloids deeper into the B horizons.

The same climate (or clayey parent material) but different topography (a low lying valley or depression instead of a gentle slope) might produce a waterlogged soil (which has poor drainage). The poor drainage results in stagnant water and non-aerated soil, often with the resultant poor plant growth and decreased rates of organic matter decomposition. The accumulating drainage waters also lead to the accumulation of dissolved salts. The horizons of these soils, developed from common factors but with differing topography, will become very different.

The regions of high rainfall and good drainage typically develop acid soils having upper horizons (A) of organic matter accumulation, and removal of colloids from the upper horizons and their accumulation in the deeper horizons (B). The soluble materials move deeper or completely below the rooting depth. If the soils have been developing for a long time (dozens of centuries), they tend to have high clay content, well differentiated horizons, acidity in wet climates, and salt accumulation in some soils of arid regions. The wet and cool forest soils become strongly acidic, accumulate slowly decomposing organic matter on their top, and exhibit extensive colloid translocation. The wet and warm climates promote a faster organic matter decomposition. In the semi-arid areas, vegetation is sparse, and carbonates often accumulate at shallow depths to form whitish carbonate zones. Accumulation of soluble salts is also common.

A parent material may not be highly altered during its exposure to the factors of soil formation because of many other conditions that retard the development of a soil profile. Some of these conditions are:

(i) Low rainfall (slow weathering, washing of little soluble material from soil) as in the Thar desert

(ii) Low relative humidity (little growth of micro-organisms such as algae, fungi, and lichens) as in the Thar desert

(iii) High lime or carbonate content of parent material such as limestone (keeps soil material less mobile)

(iv) Parent material that are mostly quartz sands, with low amounts of silt and clay (slow weathering, few colloids to move)

(v) High clay content (poor aeration, slow water movement)

(vi) Resistant parent rock materials, such as quartzite (slow weathering)

(vii) Very steep slopes (erosion removes soil as fast as the upper horizon develops; low water intake reduces leaching)

(viii) High water table (slight leaching, low weathering rate)

(ix) Cold temperature (slowing of all chemical processes and microbial activity)

(x) Constant accumulations of soil material by deposition (continuous accretion of new material on which soil development must begin afresh) as in floodplains

(xi) Severe wind or water erosion of soil material (exposes new material to begin afresh to develop a profile)

(xii) Mixing by animals (burrowing) and humans (tillage, digging) minimizes the net downward colloid movement, and

(xiii) Presence of substances toxic to plants, such as excess salts, heavy metals, or high concentration of herbicides and pesticides.

Conditions opposite to the above favour more rapid rates of soil development. For example, under nearly level topography (not eroding) in an area of high rainfall and warm humid climate, easily weatherable and porous parent materials would rapidly develop into a well differentiated soil profile.

6. Pedogenic or Soil Forming Processes

Coming into being of a well-formed soil from regolith or newly deposited parent material is the outcome of several processes which are collectively called pedogenic or soil forming processes. Though physical and chemical weathering discussed earlier continues to operate even during pedogenesis, there are several other processes involving addition, leaching, redistribution, neo-synthesis or reorganisation which lead to the development of a soil with distinct profile. Example of addition is the build-up of humus or salts; that of redistribution is movement of clay or lime from the upper part of a soil profile to lower depths; that of leaching is the removal from entire soil profile of soluble salts; and that of neo-synthesis is formation of organo-mineral/clay-humus or free sesqui-oxides. The development of soil structure is a reorganisation phenomenon. Some of these processes such as redistribution of lime or build-up of humus take place at a faster rate and reach a near equilibrium state in a few hundred to few thousand years, others like laterisation require a few thousands to millions of years to reach maturity.

An examination of a soil pit or a fresh roadcut indicates distinctive horizontal layers. These layers will not be found if a similar cut were to be made in unconsolidated materials recently deposited by a volcanic eruption or flowing water during floods. Obviously, significant changes are made as soils develop from the relatively unconsolidated materials. A study of soil formation (genesis) gives an indication of as to how these changes occur and why they can lead to the formation of so many different kinds of soils. Soil genesis is brought about by a series of processes as mentioned above, the most significant of which are:

(a) Weathering and organic matter breakdown, by which some constituents are modified or dissolved and others are synthesized,

(b) Translocation of inorganic and organic materials up and down the soil profile, the materials being moved mainly by water but also by soil or organisms, and

(c) Accumulation of soil materials in layers (horizons) approximately parallel to the soil surface.

The role of these major processes can be seen by following the changes that take place as soils form from relatively uniform parent material. When plants begin to grow and their residues are deposited on the surface of the parent materials, soil formation has truly begun.

Table 2. Some important pedogenic processes

Structure development	Grouping of individual particles (clay, silt and sand) together with humus and free sesquioxides into aggregates or peds of fairly distinctive size and shape
Humification	Transformation of raw organic matter into humus
Translocation of lime	Removal in solution of lime from the upper part of the profile and its partial or total accumulation in the lower part. The process leads to the formation of a *kankar* or calcic horizon
Leaching	Removal in solution of a constituent from soil, e.g. soluble salts
Salinization	Accumulation of soluble salts in soil
Clay migration or lessivage	Removal of clay, particularly of fine clay in suspension from the upper part of soil profile and its accumulation in the lower part
Braunification/Rubification/ Ferruginisation	Release of iron from primary minerals and their dispersal as coatings on soil particles or as complexes with organic matter/clay or as discrete aggregates to impart a brown to red colour to the soil
✓ Laterization	Removal of silica from soil and accumulation of sesquioxides (goethite, gibbsite, etc.) with or without the formation of iron stone and concretions
Podzolization	Removal of iron and aluminium, often as complexes with humus, from the upper part and its deposition at some depth
Regur fomation	Formation of intensely dark colour complex of smectitic clay and humus. It is a dominant process in black cotton soils
Gleization	The reduction of iron under anaerobic (waterlogged) conditions with production of bluish to greenish grey colour with or without mottles or ferro-manganese concretions

Common soil forming processes are listed in Table 2. Several of these processes operate simultaneously though some may start acting sequentially. An example of the latter is translocation of clay within a profile which occurs after leaching of soluble salts. However, in the long-run, one or two of these processes dominate and lead to the development of a soil with a distinctive profile dictated by factors of soil formation described earlier.

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Sample Questions

Q. 1. Which phyllosilicate mineral is the most resistant? How does the stability of two different types of chlorites (ideal and secondary chlorite) vary? Explain with the help of weathering indices of these minerals.

Q. 2. Calculate weathering mean of a red soil with the following information. Also draw the frequency curves for all the three horizons.

Soil depth (cm)	Clay mineral (%)		
	Mica	Montmorillonite	Kaolinite
0-17	23	0	77
100-113	25	0	75
207-223	32	20	48

Q.3. What might be the reason for no report of Oxisols from India, judging by the properties of soils of advanced stage of weathering (such as Alfisols, Ultisols and Oxisols)?

Chapter 3

Soil Classification

J.L. SEHGAL

1. Introduction

Classification is the grouping of objects in some orderly and logical manner. It is based on the properties of objects for the purpose of their identification and study. They are termed as differentiating characteristics as they differentiate and serve to separate one class from the others; for instance, soils are classified as sandy, loamy or clayey soils on the basis of their characteristics. For classifying the individuals of a large and widely varying population, such as soils, it is useful to group individuals into classes, and further into higher classes. This kind of grouping is called a multi-categoric or hierarchical system of classification. The individual soils are grouped into classes of lower category (e.g., *soil series*), which are further grouped into classes of higher categories (e.g., *soil orders*). The lower categories are defined by a large number of differentiating characteristics and higher categories by a few differentiating characteristics. Within each class, there is a central core or nucleus to which the individual members are related in varying degrees. It is called the central concept or an idealized individual which typifies the class.

1.1. Purposes of Soil Classification

Like the flora and fauna, soils are classified in a systematic manner, to remember their properties and understand their relationships. The purpose of a classification is to:

- Organise knowledge leading to economy of thoughts
- Recognize properties of the objects
- Learn new relationships and principles in the population being classified
- Establish groups or subdivisions (classes) of the objects under study in a manner useful for practical and applied purposes in:
  - predicting their behaviour,
  - identifying their potential uses,
  - estimating their productivity, and
  - transferring agro-technology from research farms to cultivators' fields.

2. Evolution of Soil Classification Systems

2.1. Early Systems

The early systems of soil classification were quite simple and practical; their aim was utilitarian; for instance:

- *Economic Classification*: It is the grouping of soils based on their productivity for the purpose of taxation.
- *Physical Classification*: It is the grouping of soils based on their texture — a property of soil closely associated with soil productivity and management, for instance, loamy, sandy and clayey soils.
- *Chemical Classification*: Grouping of soils based on the composition of soil having a bearing on their chemical characteristics, e.g. acidic, alkaline, calcareous, gypsiferrous soils, etc.
- *Geological Classification*: Grouping of soils based on the nature of underlying par-

ent rock/parent material, e.g., basalt, limestone, sandstone, etc. or transported material like alluvium, aeolian material.

- *Physiographic Classification*: Grouping of soils based on the characteristics of landscape, for instance, levee, basin, terrace, mountain, valley, upland and lowland soils, etc.

Since the above systems were based on a single character, their utility was limited. Hence, the need for a more comprehensive system was felt.

2.2. Dokuchaiev's Genetic System

In the later part of the 19th century, Dokuchaiev, working in Central Russian Upland, observed that a rather uniform loess parent material extended for hundreds of kilometres with increasing temperature gradient from north to south and an increasing rainfall and moisture gradient from east to west. These differences in climatic conditions were associated with important vegetation patterns, varying from forest to steppe (prairie), which left their imprint on the parent material, producing distinct soil differences. Such observations led Dokuchaiev– the founder of the modern pedology– to establish the concept of soil as an independent natural body and develop a series of publications on soil genesis and classification. The Russian approach tends to emphasize on soil genesis, and hence is termed as *Genetic System* of soil classification.

Dokuchaiev (1900) divided soils into three categories; *Normal*, *Transitional* and *Abnormal*. These categories were later termed as *Zonal*, *Intrazonal* and *Azonal soils*, respectively.

Zonality Concept — The soils that have fully developed soil profiles, and are in equilibrium with the environmental conditions, such as climate and vegetation, are termed as *Zonal Soils*, for instance, Sierozem, Chestnut, Podzol and Laterites. The soils formed in regions, where time has been a limiting factor to produce fully-developed horizons are termed as *Azonal Soils*, for instance, Alluvial soils and Regosols. Still others, occurring within the zonal areas and having characteristics that are determined largely by the local conditions, like topography, parent material, etc. are termed as *Intrazonal Soils*, for instance, Calcimorphic and Hydromorphic Soils.

2.3. Marbut's Morpho-Genetic System

Although the Dokuchaiev's (Russian) approach was based on sound principles of soil genesis, it had an inherent weakness of laying undue emphasis on climate and vegetation rather than on the intrinsic properties of the soils. Marbut in the USA was greatly influenced by the Dokuchaiev's approach. He accepted the concept of the Russian *Soil Type*, but gave it the name of Great Soil Groups. Marbut (1927) was the first to advocate classification of soils on the basis of their intrinsic properties rather than on soil-forming factors, thus reducing emphasis on geology or parent rock. Marbut evolved his scheme in successive steps and published it in the *Atlas of American Agriculture*. It was based on the iron-alumina and lime contents. At the highest category level, he divided *Zonal Soils* into two classes: *Pedalfers* and *Pedocals*, the former showing accumulation of iron and aluminium oxides and the latter of calcium as calcium carbonate. The Pedalfers were presumed to occur in the areas of high rainfall having real surplus of water for leaching. The Pedocals were supposed to occur in areas of high evaporation having real deficit of water.

2.4. Baldwin and Associates Genetic System

The major limitation of Marbut's system was that it was based, in part, on assumptions concerning soil genesis. As such, many of the soil series, recognized in the USA, could not find a place in the system. Hence, the Morphogenetic System of Marbut (1935) was revised and elaborated by Baldwin *et al.* (1938) and Kellogg and Thorp (1949) (Table 1). The system marked the beginning of a comprehensive approach. The salient features of this system are:

- A return to the zonality concept of Russian School,
- The pedocal-pedalfer concept was de-emphasized, and

Table 1. Genetic system of soil classification

Order	Suborder	Great Soil Groups
Zonal soils	1. Soils of the cold zone	Tundra soils
	2. Light-colour soils of arid regions	Sierozem soils Brown soils Reddish Brown soils Desert soils Red Desert soils
	3. Dark-colour soils of the semi-arid subhumid, and humid grasslands	Chestnut soils Reddish Chestnut soils Chernozem soils Prairie or Brunizem soils Reddish Prairie soils
	4. Soils of the forest grassland transition	Degraded Chernozem soils Noncalcic Brown soils
	5. Light-colour podzolized soils of the timbered regions	Podzol soils Gray Wooded, or Gray Podzolic soils Brown Podzolic soils Soil-brun acide Gray-brown Podzolic soils Red-yellow Podzolic soils
	6. Lateritic soils of forested warm-temperate and tropical regions	Reddish-brown Lateritic soils Yellowish-brown Lateritic soils Laterite soils
Intra-zonal soils	1. Halomorphic (saline and alkali) soils of imperfectly drained arid regions and littoral deposits	Solonchak or Saline soils Solonetz soils (partly-leached Solonchak) Soloth soils
	2. Hydromorphic soils of marshes, swamps seep areas, and flats	Humic-gley soils Alpine Meadow soils Bog and Half-bog soils Low Humid-Gley soils Planosols Groundwater Podzol soils Groundwater Laterite soils
	3. Calcimorphic soils	Brown Forest soils Rendzina soils
Azonal soils	No suborder	Lithosols Alluvial soils Regosols

Source: Baldwin *et al.* (1938), as modified by Throp and Smith (1949)

- More emphasis was laid on soil as a three-dimensional body with its own characteristics.

A new category, viz. *Soil Family*, was introduced between Great Soil Group and Soil Series; but neither soil families nor the higher categories were defined in terms of soil properties.

Serious problems arose when some soil series did not fit in any of the existing Great Soil Groups. Therefore, as a stop-gap strategy, the system was revised in which three new Great

Soil Groups were introduced and three others were merged with the existing Great Soil Groups. The soils were grouped in three Orders, viz. *Zonal, Intrazonal* and *Azonal,* following the Russians zonality concept, as under:

Zonal Soils — The soils whose characteristics are determined primarily by the environment, especially climate and vegetation (Figure 1).

Intrazonal Soils — These soils occur within a zone, but reflect the influence of some local conditions, such as topography and/or parent material.

Azonal Soils — The soils that have poorly developed profiles because of time as a limiting factor, e.g. young soils without horizon differentiation.

The three orders were further subdivided into nine suborders on the basis of specific climatic and vegetative regions. Each suborder, in turn, was divided into Great Soil Groups, which are an expression of more specific conditions. The Great Soil Groups were further subdivided into numerous Soil Families, Series and Soil Types.

2.5. Limitations of the Genetic Systems

The major limitations of the Genetic Systems are:

(i) The two highest categories are defined in genetic terms and not on the basis of properties of the soils.

(ii) The concepts and definitions of the highest category, i.e. the Order, in terms of soil properties, are not clear.

(iii) The Great Soil Group concepts and definitions are based on environmental factors, rather than on the soil properties. Hence, their definitions are comparative and qualitative.

(iv) Many of the soils are defined in terms of properties that were obvious under virgin soil conditions and are destroyed during cultivation and hence the classification of such arable soils becomes ambiguous.

(v) There are tendencies to attempt definition of units in the lower categories in terms of too few properties thought to be important for one interpretation.

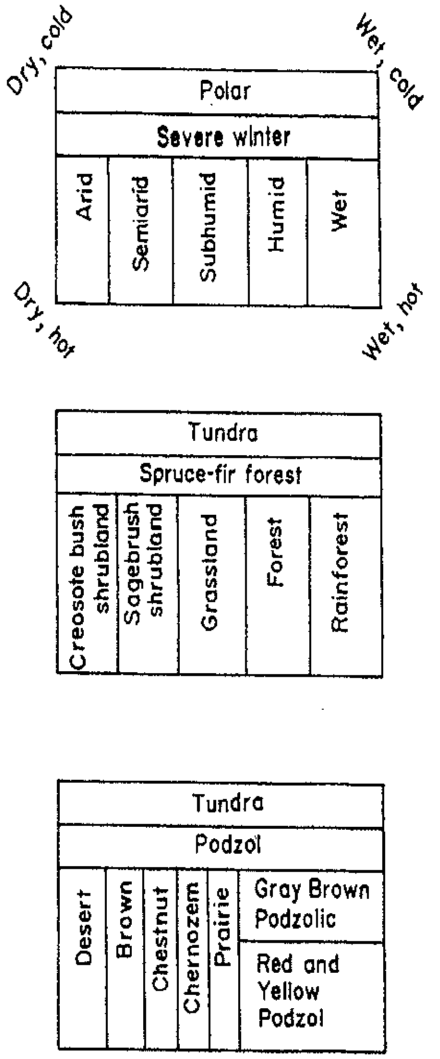


Figure 1. A schematic relationship of climate, vegetation and soils (top: climate types; middle: vegetation types; bottom: soil groups)
Source: Sehgal, 1996

(vi) The nomenclature in the highest categories laid too much emphasis on colour or vegetation rather than on the salient properties of the soils.

(vii) The nomenclature was evolved from several languages, and with the mixtures of nouns and adjectives; it was difficult to name the intergrades.

According to Kellogg (1963), most systems of soil classification, as used in 1950s, including that of the USA, had one or more serious limitations because most of these over-emphasized the virgin soils. The conclusion is that different schools of thought inevitably needed some compromise in their divergent opinions to meet the important need to classify arable soils (of which at least the upper horizons had been mixed); the alluvial soils (which have no well-developed soil horizons) did not find a suitable place in the system having a strong genetic bias. Hence, a desirable system should be based on combinations of soil characteristics known to be significant to genesis and behaviour, but not directly on the either. In other words, the classification must be one that can be interpreted in terms of genesis and behaviour, but the genesis and behaviour should be a step behind the classification itself.

2.6. Soil Taxonomy : A Comprehensive System

In order to overcome the shortcomings of the Genetic System, the US Soil Survey Staff, in cooperation with many other institutions, have been working since 1951 to arrive at a classification that narrows the differences in different view points. Each year, starting from 1953, an approximation was produced and tested. In 1960, a Comprehensive System of Soil Classification, popularly known as the "*7th Approximation*" (Soil Survey Staff, 1960), was published. The system was put into official use in the USA and was adopted in many other countries, including India, Iraq, Belgium, The Netherlands, etc. Ultimately in 1975, the system was brought out as Soil Taxonomy (Soil Survey Staff, 1975); its second edition appeared in 1999. The Soil Taxonomy was designed to serve the needs of soil survey.

2.6.1. *Salient Features*

The Comprehensive System is a morphogenetic system in which morphology of soil, that is an outcome of soil genesis, serves as a guide (Smith, 1963). It is based on the properties of soils as they exist today. Although one of its objectives is to group soils similar in genesis, the specific criteria used to place soils in different groups are those of soil properties. The system has an edge over the earlier systems in the following respects:

- Unlike the Genetic Systems, the Comprehensive System is based on measurable soil properties that exist today.
- It considers all such properties which affect soil genesis or are the outcome of soil genesis.
- The common definition of a class of taxonomic system is type or orthotype.
- The nomenclature, using coined words, is derived mainly from *Greek* and *Latin* languages. Although it appears difficult, once understood, it is the most logical nomenclature and helps in relating the place of taxon in the system and in making interpretations.
- A new category, viz. *Subgroup*, has been introduced to define the central concepts of Great Groups and their intergrades in order to express and recognise more clearly that soils are in continuum and show gradual change in many properties.
- Unlike the Genetic System, it is an orderly scheme without prejudices, but facilitates easy recognition of the objects.

2.6.2. *Diagnostic Horizons*

Diagnostic horizons are understood to reflect genetic horizons widely occurring in soils, which fairly well describe and define soil classes. Thus, a *diagnostic horizon* is defined as one, formed through pedogenic processes and having distinct properties or features that can be described in terms of measurable soil properties. In fact, a set of pedogenic processes operate in a soil for a significant period to leave their mark in the form of distinct horizons or features, which can be measured. The diagnostic horizons are largely used not only for identifying soils but also in classifying them at various categoric levels, especially Great Groups. A number of diagnostic horizons have been defined in Soil Taxonomy. Based on their locations in soil profiles, these horizons are of two types, viz. surface and subsurface.

The diagnostic surface horizons are called ***epipedons*** (Greek *epi*, over, upon and *pedon*, soil). The epipedons are simply the upper most soil horizons and include the upper part of the soil darkened by organic matter. They are not synonymous with A-horizon. Nine epipedons, viz. folistic, histic, melanic, mollic, anthropic, umbric, ochric, plaggen and grossarenic are recognised, but generally speaking, three of these, viz. *mollic, ochric* and *umbric*, are of importance in India.

The diagnostic subsurface horizons are called ***endopedons*** (Greek *endodermis*, subsurface or deep-seated and *pedon*, soil). The endopedon includes the lower part of the soil where soil materials accumulate. Nineteen endopedons, viz. argillic, natric, agric, spodic, sombric, cambic, kandic, oxic, sulphuric, salic, placic, albic, glossic, calcic, gypsic, duripan, fragipan, petrocalcic and petrogypsic are recognised. Of these, eight, viz. argillic, natric, cambic, kandic, oxic, salic, calcic and gypsic are commonly observed in India. The major features of the diagnostic epipedons and endopedons are briefly given as under:

2.6.3.Diganostic Surface Horizons (Epipedons)

The nine epipeons are described below:

Folistic Epipedon – A surface layer that is never saturated with water for more than 30 days (cumulative) in normal years (and is not artificially drained) and either consists of organic soil material (containing 75% or more, by volume, of *Sphagnum* fibres) or has a bulk density (moist) of less than 0.1 Mg/m^3 or is 15 cm or more thick; *or* is an Ap horizon (up to 25 cm) that has an organic carbon content (by weight) of 16% or more if the mineral fraction contains 60% or more clay or 8% or more with no clay. Most folistic epipedons comprise organic soil materials that remain saturated for less than 1 month.

Histic Epipedon – A thin organic horizon (if virgin) or horizon with very high organic matter content depending on clay content, that remains saturated with water for 30 days or more (cumulative) during some season of the year, unless artificially drained. It is thinner than 30 cm if drained, or 45 cm if not drained. Note the differences in Folistic and Histic epipedons, especially in terms of saturation with water.

Melanic Epipedon – A thick black horizon at or near, but within 30 cm of the soil surface and having andic soil properties. It contains 6% or more organic carbon as weighted average, and 4% or more organic carbon in all layers. The deep dark colour is due to the accummulation of organic matter resulting from root residues, supplied by graminace-eous vegetation, result in colour value (moist) and chroma of two or less throughout.

Mollic Epipedon – A thick, dark colour, soft mineral horizon with high (> 50%) base saturation and strong structure. It contains 1% or more organic matter (when mixed to a depth of 17.5 cm) with colour values darker than 3.0 (moist) and 5.0 (dry) and chroma less than 3.5 (moist). Soil structure cannot be massive and hard, very hard or extremely hard when dry. Base saturation is over 50% and the epipedon is not naturally dry in all parts for more than nine months in a year.

Anthropic Epipedon – A surface horizon, like the mollic, but formed under long continued system of farming that involves large additions of organic matter (compost). It contains 1500 mg or more of citric acid (1%) soluble P_2O_5 per kg soil, which distinguishes it from mollic and umbric epipedons.

Umbric Epipedon – A surface horizon like the mollic, but is low (< 50%) in base saturation (dominantly saturated with H^+) with high C : N ratio and is not naturally dry for more than three months in a year.

Ochric Epipedon – A surface horizon that is light in colour [colour values > 3.5 (moist) or > 5.5 (dry)]. It contains less than 1% organic matter, or is hard or very hard and massive when dry; or remains dry for more than three months in a year.

Plaggen Epipedon – A thick (> 50 cm) man-made surface horizon, produced by a long and continued manuring with sod. It can be easily identified by artefacts, such as bits of brick, pottery, etc. It also shows spade marks.

Grossarenic Epipedon – A sandy (loamy fine sand or coarser) horizon, 100 cm or more thick over an argillic horizon.

2.6.4. Diagnostic Subsurface Horizons (Endopedons)

The characteristics of 19 endopedons are discribed below:

Argillic Horizon – A silicate-clay-enriched horizon formed by illuviation of clay. The fine clay is carried downward by percolating water and is deposited as clay skins or cutans on ped faces and on the walls of pores. In general, a B-horizon that has at least 1.2-times as much clay content as some horizon above, or 3% more clay content if the eluvial (bleached) layer has < 15% clay, or 8% more clay if eluvial layer has > 40% clay. It should be at least 1/10 of all overlying horizons or more than 15 cm thick, whichever is thinner.

*Natric Horizon**– A high sodium-clay-enriched horizon with columnar or prismatic structure. The horizon meets all the requirements of an argillic but in addition, has 15% or more of the exchange complex saturated with Na^+, or has more exchangeable Mg^{2+} plus Na^+ than Ca^{2+} plus exchange acidity at pH 8.2.

Agric Horizon – An illuvial horizon of clay, silt and humus formed directly under the plough layer due to long and continued cultivation.

Spodic Horizon – A humus- and/or sesquioxides-enriched subsurface horizon with or without iron. There are many specific limits dealing with Al, Fe, organic matter and clay ratio, depending on whether the overlying horizon is virgin or cultivated. It is generally formed in cold humid regions. A spodic horizon must have 85% or more of spodic materials in a layer 2.5 cm or more thick that is not a part of any Ap-horizon. Such a horizon is rarely observed in India. The so-called Podsols, as reported to occur in the Himalayas, do not meet the requirements of spodic horizon as laid down in Soil Taxonomy.

Sombric Horizon – A free-draining horizon located not under an albic horizon; has colours (darkness) and base status like an umbric epipedon, and has been formed due to illuviation of humus and not of aluminium or sodium.

Cambic Horizon – A colour or structural B-horizon formed due to alteration by the physical movement or chemical weathering. The pedogenic processes have altered the material enough to form soil structure (if the texture is suitable, i.e. very fine sand, loamy very fine sand or finer) to liberate free iron oxides to form silicate clays, and to obliterate most evidences of the original rock structure in more than 50% of the volume. The alteration is not enough to completely destroy volcanic glass, allophane, glass, feldspars and micas. Similarly, illuviation of oxides, humus or clay should not be enough that will qualify it for *argillic* or *spodic* horizon. The horizon is extremely variable in mineralogy because of its pedogenic youthfulness, occurs under widely differing environment and may develop in the presence or absence of fluctuating groundwater.

Kandic Horizon – A subsurface horizon of low activity clays with or without clay-skins. It has CEC of < 16 cmol (p^+) kg^{-1} soil at pH 7, and effective CEC (ECEC) of < 12 cmol (p^+) kg^{-1} soil. It shows a clay content increase at its upper boundary of > 1.2 × clay within a vertical distance of < 15 cm, that is, abrupt or clear textural boundary. It shows no stratification.

Oxic Horizon – A horizon enriched with Fe- and Al-oxides with dominance of 1:1 type clay minerals and from where silica has leached. It is atleast 30 cm thick and is sandy loam or finer in texture. It has dominance of low charge clays (1:1) type, e.g. kaolinite with CEC of 16 or less cmol (p^+) kg^{-1} at pH 7 and apparent ECEC of 12 or less cmol (p^+) kg^{-1} clay. The increase in clay content is gradual than in Kandic horizon. It contains less than 10% weatherable minerals in the sand fraction.

Sulphuric Horizon – A mineral or organic soil horizon that has a pH of < 3.5, is toxic to plant roots, and has yellow mottles of jarosite.

Salic Horizon – A horizon with secondary accumulation of water soluble salts (NaCl, Na_2SO_4, etc.) at some depth in the soil profile. The horizon is atleast 15 cm thick with secondary soluble salt enrichment of over 2%, and the product of thickness and salt percentage is 60 or more. The salt content, in terms of electrical conductivity (EC) in a saturated paste should be 30 dS/m or more, and the product of EC (dS/m) and thickness (cm) is equal to 900 or more.

Albic Horizon – A bleached E-horizon of podzols and planosols. It has typical colour values of > 5 (dry) or > 4 (moist).

Glossic Horizon (Gr. *Glossa,* tongue) – Glossic horizon is a horizon which shows albic horizon characteristics gradually intruding into an argillic, a kandic or a natric horizon. It may be 5 cm or more thick and consists of an eluvial part which constitutes 15 to 85% (by volume) of the glossic horizon and an illuvial part (i.e. partially-altered or degraded argillic, kandic or natric horizon).

Calcic Horizon – A horizon with secondary Ca- and/or Mg-carbonate-enriched materials. It is 15 cm or more thick, has 15% or more of secondary accumulation of carbonates and contains at least 5% more carbonates than any underlying horizon.

Gypsic Horizon – Calcium and/or magnesium sulphate-enriched horizon. It is more than 15 cm thick, and contains at least 5% more calcium sulphate than the underlying horizon/layer.

Petrocalcic Horizon – An indurated calcic horizon that has hardness of 3 or more (Moh's scale) and whose one-half or more of dry fragments break down in acid, but not in water.

Petrogypsic Horizon – A strongly cemented gypsic horizon whose dry fragments do not slake in water.

Placic Horizon – A thin (2-10 mm thick), slowly-permeable, dark reddish brown to black colour iron or manganese pan that lies within 50 cm of the surface.

These are not the complete definitions, but are highly abbreviated versions. Many of these are still being discussed and revised. The basic meaning attached to each term (given above) remains the same.

2.6.5. Diagnostic Organic Materials

Different diagnostic organic materials are described below:

Fibric Soil Material (formerly peat) – The fibrous material in an unrubbed condition, constituting over 2/3 of the mass, and yields almost clear solution when extracted with sodium pyrophosphate.

Hemic Soil Material (formerly mucky peat or peaty muck) – The fibrous material in an unrubbed condition constituting 1/3 to 2/3 of the mass, in an intermediate stage of decomposition.

Sapric Soil Material (formerly muck) – The identifiable fibrous material in an unrubbed condition, constituting less than 1/3 of the mass; it produces sodium pyrophosphate extracts with colours lower in value and higher in chroma than 10YR 7/3.

Humilluvic Material – Illuvial humus that accumulates after prolonged cultivation of some acid organic soils.

Limnic Materials – Organic or inorganic materials deposited in water by the action of aquatic organisms, or derived from underwater and floating organisms. For instance, marl, diatomaceous earth, and sedimentary peat (coprogenous earth).

2.6.6. Diagnostic Characteristics for Both Mineral and Organic Soils

Aquic Conditions – Soils with aquic (Latin *aqua,* water) conditions are those that are continuously or periodically saturated with water and undergo reduction. For details, see under soil moisture regimes.

Cryoturbation (Frost Churning) – It is the mixing of soil matrix within a pedon that results in irregular or broken horizons, accumulation of organic matter over the permafrost table, silt capping on rock fragments and oriented rock fragments.

Densic Contact (L. *densus,* thick) – A thick contact between soil and densic material(s) below. It has no cracks.

Densic Materials – These are relatively unaltered materials that do not meet the requirements for any other named diagnostic horizons that have a non-cemented, rupture-resistance class. It has bulk density that does not allow root penetration, except through cracks. These are dense earthy materials, such as mine spoils, volcanic mud flows till. Being non-cemented, these differ from paralithic materials which are cemented.

Gelic Materials – These are mineral or organic soil materials that show evidence of cryoturbation (frost churning), which is manifested by irregular and broken horizons, accumulation of organic matter generally on top of the permafrost and silt-enriched layers. The structure is platy, blocky and/or granular.

2.6.7.Other Diagnostic Soil Characteristics

Several other layers or horizons and macrofeatures are recognized and named in Soil Taxonomy (Soil Survey Staff, 1999). These features are usually used as diagnostic criteria at a somewhat lower level in the classification system than the subsurface diagnostic horizon (endopedons) and epipedons.

Abrupt Textural Change – It refers to a boundary of a considerable increase in the clay content within a short vertical distance between a surface (ochric epipedon or albic horizon) and an underlying subsoil (argillic horizon). It can be established using the following criteria: If the surface material has < 20% clay, clay content doubles within 7.5 cm; if the surface (ochric epipedon) horizon has 20% or more clay, an absolute increase of at least 20% clay content is required within 7.5 cm.

Durinodes – These are weakly-cemented to indurated nodules, cemented by SiO_2.

Duripan – It is a subsurface horizon at least half cemented by SiO_2. The air-dry peds do not slake in water or HCl, but are destroyed by hot KOH after acid washing.

Fragipan – It is a subsoil layer(s) of high bulk density. It is brittle when moist, and very hard when dry. It does not soften on wetting, but can be broken in the hands. The air dry fragments slake in water.

Low Chroma Mottles – These are moist soil colours of two or less chroma; 4 or more value often represent gley conditions.

Permafrost – It is a layer where soil temperature is always < 0 °C. It may either be very hard or loose.

Plinthite (Greek, *Plinthose*, brick) – It is a humus-poor, sesquioxide-rich horizon, which hardens irreversibly to ironstone hardpans or aggregates with repeated wetting and drying. The red, indurating portions of the layer, are usually mottled with yellowish, greyish or white materials.

Soft Powdery Lime – It is authigenic lime translocated within the soil, normally present as coating on the ped surfaces.

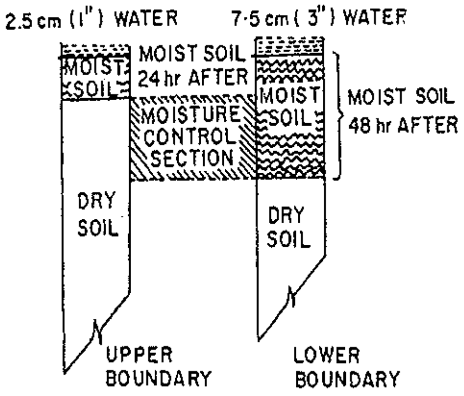
Tonguing – It is used when albic horizon material (of at least 5 cm deep and 5 mm wide) penetrates into an underlying argillic or natric horizon (*see* glossic horizon).

2.6.8.Diagnostic Contacts (to "Non–Soil" Material)

Lithic Contact – A boundary between soil and continuous coherent, underlying material that has hardness of > 3 on the Moh's scale and through which roots cannot penetrate.

Paralithic (Lithic-like) Contact – A boundary between soil and continuous non-coherent, underlying material that has hardness of > 3 on the Moh's scale. The roots can penetrate, at irregular and infrequent intervals, to 10 cm or more.

Petroferric Contact – A boundary between soil and an indurated layer of iron cemented material.



THE UPPER & LOWER BOUNDARIES OF THE SOIL MOISTURE CONTROL SECTION (SMCS)

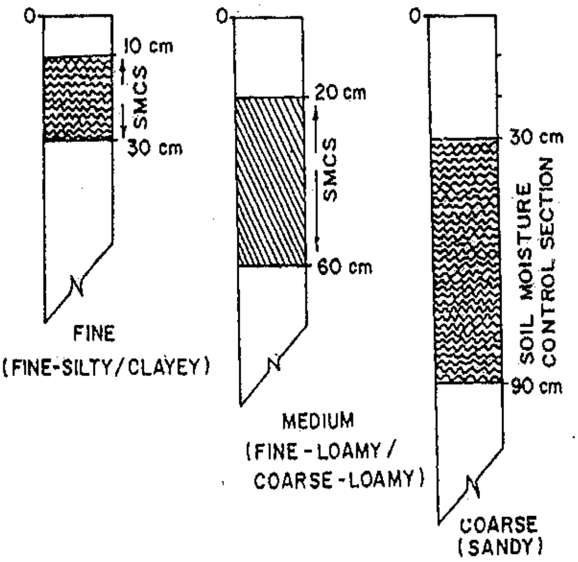


Figure 2. Soil moisture control section (SMCS) based on particle size class

Source: Sehgal (1996)

2.6.9. Soil Moisture and Temperature Regimes

Each soil has a specific environment under which it has developed. Soil moisture and temperature regimes control and guide soil utilization for plant growth. Since these can be measured, they are used in classifying soils at different categoric levels.

Soil Moisture Regimes (SMR) – Soil moisture regime (*SMR*) refers to the presence or absense of water in a soil at different times of a year. Soil is considered moist when it is at moisture tension of less than 1500 kPa (15-bar) and dry when the tension is 1500 kPa (15-bar) or more within the *Soil Moisture Control Section* (SMCS). The limits of SMCS are determined by the soil depth to which the soil at wilting point is moistened when 2.5 cm and 7.5 cm of water are added at the surface. In general, the upper and lower limits of SMCS in loamy soils are at 20 cm and 60 cm, respectively (Figure 2).

The availability of water to plants is also influenced by dissolved salts. Consequently, a soil is considered to be dry when it is at moisture tension of 1500 kPa (15-bar) or more, or when salt concentration reaches the level that limits moisture availability to plants. Under such conditions, the soil is considered to be physiologically dry.

The SMR is a partial function of climate, soil and landform. It is defined in terms of the number of days the SMCS remains moist with moisture tensions between 33 kPa (1/3-bar) and 1500 kPa (15-bar). The SMCS, considered important for moisture supply to crops, is defined as the depth limits of soil that regulate the moisture supply, and this depends on its texture. Besides controlling crop growth, SMR is important not only in understanding pedogenesis and nutrient availability, but also in the classification of soil at different categoric levels, such as Soil Family, Suborder and occasionally at Order level (as in Aridisols).

In nature, there exist three dominant soil moisture regimes:

(i) ***Saturated*** – Taxonomically characterized as AQUIC, which is a condition when soil pores are completely filled with water, resulting in anaerobic conditions. It is not conducive to normal crop growth.

(ii) ***Non-leaching*** – Taxonomically characterized as ARIDIC, where water moves into SMCS for a very short period in a year and gets completely withdrawn by high potential evapotranspirative (PET) demand.

(iii) ***Leaching*** – Taxonomically characterized as UDIC, where water moves into the soil almost throughout the year (if not frozen).

In between leaching and non-leaching environments, there exist two partially-leaching soil moisture regimes which, according to Soil Taxonomy, are termed as *Ustic* and *Xeric*. The former is indicative of summer monsoon rains (as in India) and the latter, of winter rains (as in the Mediterranean region). In these regimes, farmer can grow one crop a year (in summer or in winter).

A knowledge about the prevailing bioclimate, quantified by precipitation (P) and potential evapotranspiration (PET), and soilscape characteristics, in terms of available water capacity (AWC), are helpful in characterizing SMRs. The model runs as the SMCS starts moistening when P exceeds 0.5 PET and the supply of moisture to SMCS continues till P falls short of 0.5 PET. Thereafter, the water need is met from storage (if stored water is available) and continues till about 80% of the available stored moisture is exhausted by evapotranspiration. Thus, the number of days the SMCS remains moist is worked out from the total sum of:

a. moist period (PET < P or P > 0.5 PET);

b. humid period (P > PET);

c. period to evaporate more than 80% of stored available moisture after P falls short of PET (Figure 3).

As a thumb rule, any month with an average precipitation of more than 50 mm is considered to keep the SMCS partially moist.

The broad soil moisture regimes, viz. *aquic*, *udic*, *ustic*, *xeric*, *aridic*, *torric*, and their criteria are given in Table 2.

The Soil Moisture Regime Map of India (Sehgal, 1996) shows that India is dominantly

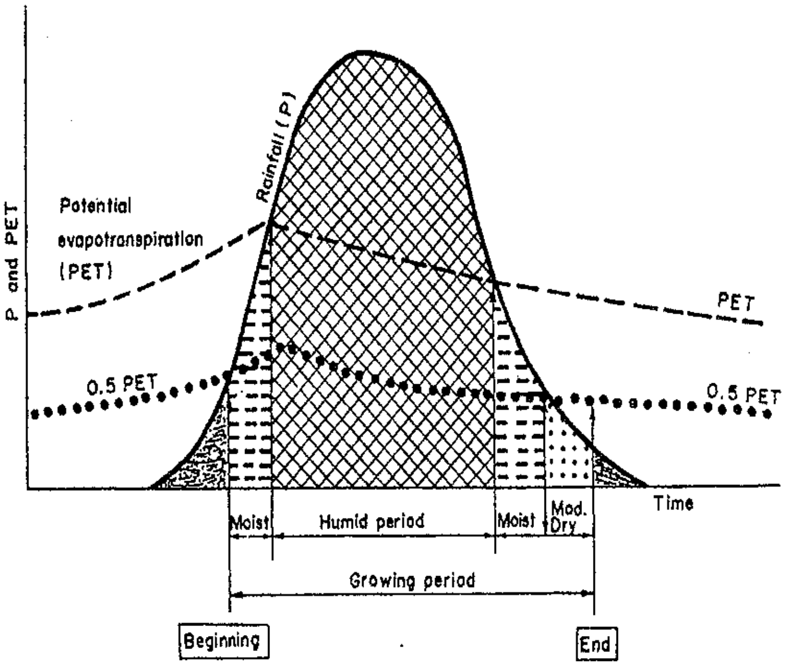


Figure 3. A model for estimation of moisture availability

Source: Sehgal (1996)

represented by *ustic* soil moisture regime covering almost three-fourth (72%), followed by *aridic* (16%) and *udic* (12%). It suggests potential need for additional irrigation water, in areas representing *aridic* and *ustic* SMRs for supporting one to two crops in a year which is most crucial for increasing agricultural production.

Soil Temperature Regimes (STR) – These are the ranges in temperature classes within which biological activity of different degrees prevails.

Table 2. Class criteria of different soil moisture regimes

Gleying/ Aquic	Moist soils throughout	Soils with limited moisture		Soils with negligible moisture
	Udic	Ustic	Xeric	Aridic
Saturated for some time in a a year. Reduced soils because of lack of dissolved oxygen Peraquic Moisture regime in a close, land locked depression with perennial streams	Not dry any part for as long as 90 cumulative days (to exclude from Ustic) Not dry in all parts for for as long as 45 consecutive days following summer solstice* (to exclude from Xeric)	If MAST > 22 °C or MSST and MWST differ by < 5 °C < 5 °C (tropical condition), then Dry in some or all parts of 90 cumulative days. But the SMCS is moist in some parts for 180 days (cumulative) or continuously moist in some parts for atleast 90 consecutive days. If MAST > 22 °C and MSST and MWST differ by > 5 °C. Dry in some or all parts for ≥ 90 (cumulative) days. But is not dry in all parts for > 6 months (the Aridic and Torric regimes). It is not dry in all parts for 45 consecutive days within 4 months following summer solstice it is not moist in all parts for 45 consecutive days or more in 4 months following winter solstice+(Xeric)	Associated with Mediterranean climate MAST < 22 °C, MSST, MWST differ by > 5 °C, the SMCS is: Dry in all parts for 45 or more consecutive days within 4 months following summer solstice in 6 or more years out of 10 years. Moist in all parts for ≥45 consecutive days following winter solstice	Dry throughout for more than 180 days (cumulative), the soil temperature is > 5 °C Never moist in some or all parts for as long as 90 consecutive days when the soil temperature is above 8 °C. No moisture in all parts for as long as 45 consecutive days during 4 months following the winter solstice (if MSST and MWST differ by > 5 °C and MAST is < 22 °C (i.e. to exclude from Xeric)

* from 22nd June onwards; + from 23rd December onwards

MAST = Mean Annual Soil Temperature

MSST = Mean Summer Soil Temperature

MWST = Mean Winter Soil Temperature

SMCS = Soil Moisture Control Section

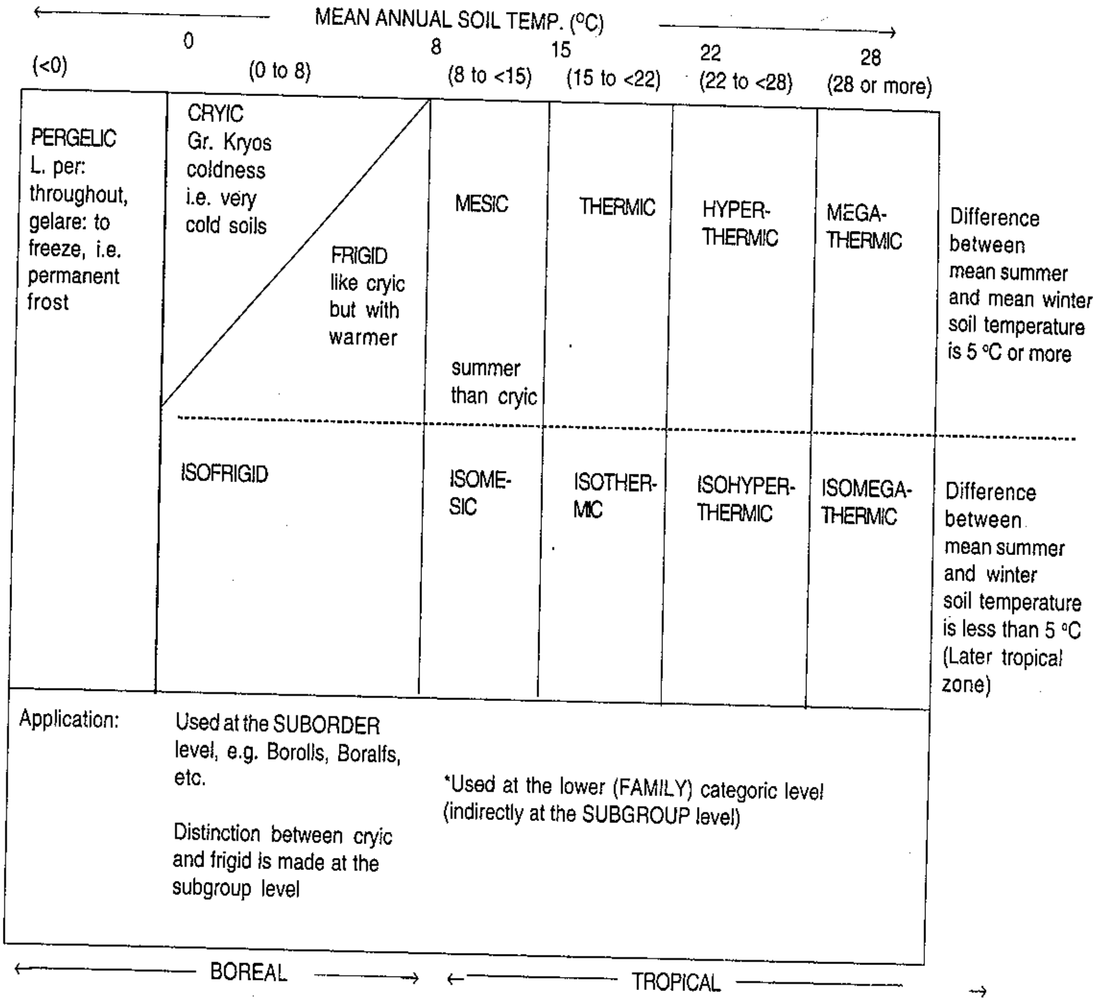


Figure 4. Class criteria of different soil temperature regimes
Source: Soil Survey Staff (1975)

There is no biotic activity at temperatures below freezing point (0 °C). Between 0 and 5 °C, root growth and seed germination of most plants are impossible; there is no respiration by plants and thus soil is called inactive. Like lower limit of soil temperature (around 5 °C) that acts as thermal pan to root growth and germination, there exists an upper limit of soil temperature (35 °C or more) above which root growth and germination of most of the mesophytic plants are severely restricted. Therefore, the temperature range from 5 to 35 °C is important in determining the degree of biological and chemical activities and physical processes going on in soils and hence are used in soil classification systems.

Soil temperature regimes play an important role in classifying soils at the Family and Suborder levels. The nomenclature of the different soil temperature regimes and the criteria used are given in a schematic diagram (Figure 4).

In all there are six soil temperature regimes, viz. *pergelic*, *cryic/frigid*, *mesic*, *thermic*, *hyperthermic* and *megathermic*. The prefix *iso* is used if the difference between the mean summer and mean winter temperature is less than 5 °C to separate tropical areas. Further the diagram shows that a Mean Annual Soil Temperature (MAST) of 8 °C is used as a limit to separate *frigid* (cold) soils from *mesic* (cool to warm) soils. Similarly, a MAST of 22 °C is used to separate *thermic* (warm to hot) from *hyperthermic* (hot) soils and a MAST of 28 °C (introduced for Indian Soils) is used as the limit to separate *hyperthermic* (hot) from *megathermic* (very hot) soils.

The MAST can be computed from the mean annual air temperature (MAAT) by adding:

- 3.5 °C to the mean air temperature for areas situated between 8° and 16° N latitude;
- 2 °C for areas situated between 16° and 26° N latitude and;

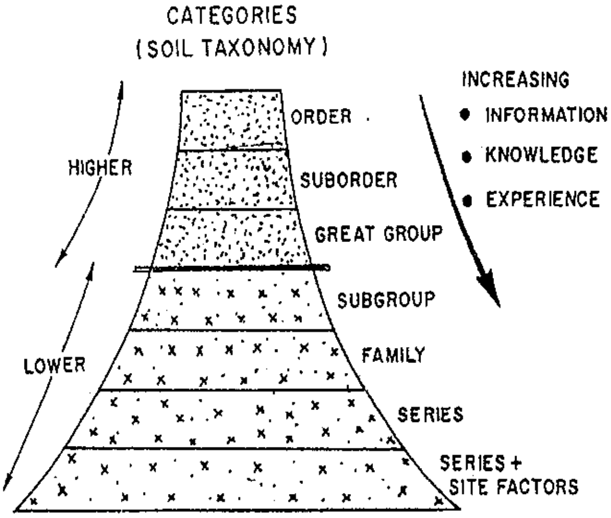


Figure 5. The hierarchy of Soil Taxonomy
Source: Sehgal (1996)

- 1.5 °C for areas situated between 26° and 33° N latitude.

Similarly, for areas situated above 33° N latitude, a temperature of 1°C is added to the MAAT for determining the mean annual soil temperature.

2.6.10. Definition of Soil Taxa

In the definitions of the taxa, differentiating characteristics selected are properties of the soils, including soil temperature and moisture regimes. The genesis of soil is neither directly deployed nor is in the forefront, except as a guide to relevance and weighing of soil properties. The definitions are quantitative and precise rather than comparative and are written in "operational" terms.

2.6.11. Nomenclature (Soil Taxonomy)

Most of the names used in the genetic system are biased in favour of colour (brown/ red soils) and vegetation (prairie/ forest soils) and show no similarity or relationship with each other. They also do not show the place of taxon in the system. In view of these limitations, the nomenclature used in Soil Taxonomy is altogether different and is based on coined words from Greek or Latin languages. The basic principles followed in coining the names, according to Heller (1963), are that the name should :

- be most easily remembered,
- suggest some properties of the object,
- suggest the place of a taxon in the system,
- be as short as possible,
- be as euphonic as possible, and
- fit readily in as many language as possible.

The names of the classification units are combinations of syllables. These names may sound strange at first, but, with experience, one can appreciate and use these with advantage. Each part of the name conveys a concept of soil character or genesis. For example Aridisol (L. *aridus* means dry; *solum*, soil) – the soils of dry places; Vertisol (L. *verto* means turn; *solum*, soil) – the soils which churn or invert.

Structure –The system has six categories of classification (Figure 5) from the highest to the lowest levels of generalization. These are grouped under two broad categories, viz. higher and lower.

Higher Categories

1. *Order* – The highest category in the system.
2. *Suborder* – Comparable to great soil groups of the genetic system
3. *Great Group* – A basic category, based on diagnostic subsurface horizons

Lower Categories

4. *Subgroup* – A new category designed to define the central concepts of Great Groups
5. *Family* – A practical category for making predictions for land use plans.
6. *Series* – The lowest and the most specific category.

The category **Subgroup** has been added to define the central concepts of Great Groups. The Subgroups are intergrades between two Great Groups (and extragrades transitional to a not-soil population) in order to emphasize the fact that soils are a continuum with gradual changes in morphology and soil properties. The category Soil *Type* has been dropped in favour of surface *Phase.*

The nature and kind of differentiating characteristics used in the six categories (mentioned above) are given in Table 3. These categories may be compared with those used for the classification of plants. Just as *Acacia nilotica* identifies a specific kind of plant, the *Ghabdan clay loam* or *Tigris silt loam* identifies a specific kind of soil. This similarity between the soil and plant classification schemes can be followed to the highest category, for instance *Phylum* for plant and *Order* for soil.

2.6.12. *Application of Differentiating Criteria*

The names of the Orders, the formative element in the Order name, used as an identifier at lower categoric levels, derivation or source of the formative element and the mnemonicon or memory device for each Order along with their approximate equivalents in the Genetic and FAO Systems are given in Table 4. The names (of the Orders) are coined words and have a common ending, 'sol' (L.

Table 3. Differentiating characteristics of different categories in soil taxonomy

Category (Number of Taxa)	Differentiating characteristics and description
Order (12)	There are 12 Orders "A VAGAMI HOUSE*" phrase suggested to facilitate naming of all the Orders. These are based largely on morphology, as produced by soil-forming processes, and indicated by the presence or absence of major diagnostic horizons.
Suborder (63)	There are 63 Suborders within 12 Orders. These emphasize genetic homogeneity, wetness, climatic environment, parent material and vegetational effects. The differentiate used vary, but most tend to emphasize wetness and moisture regime.
Great Group (240+ approximately)	There are 240 Great Groups within 63 Suborders of 12 Orders. The major emphasis is on the diagnostic horizons (except in Entisols which have no such horizon) and presence or absence of diagnostic layers, base status, soil temperature and moisture regimes.
Subgroup (1000+)	There are more than 1,000 Subgroups. The Typic is used to define the central concept of a great group; the others are used to indicate intergraded to great groups, suborders and orders, and the extragraded to 'not soil'.
Family	The soil properties that are most important for plant growth (like texture, mineralogical class (dominant of solum), soil temperature class (based on MAST at 50 cm depth) and pH are used to differentiate families. They meet the need for making practical prediction for land-use planning.
Series (Approximately 200+ in India; and 12,000 in the USA)	It is the lowest category in the system. The series is a collection of soil individuals, essentially uniform in differentiating characteristics (like colour, texture, structure, consistence, pH and EC) and in arrangement of horizons. It is the series which is most useful for making land-use plans of a small area. The series are named after the geographic name of the place where it was first recognized or where they have wide extent of distribution, e.g. Jodhan loam, Tigris silt loam. The textural name, along with the series name, suggest the surface phase.

*A-Aridisols, V-Vertisols, A-Alfisols, G-Gelisols, A-Andisols, M-Mollisols, I-Inceptisols, H-Histosols, O-Oxisols, U-Ultisols, S-Spodosols, E-Entisols.

Table 4. Formative elements of soil orders and their derivation

Name of Order	Formative element* in name of Order	Derivation of formative element	Mnemonicon or Memory Device	Soils equivalent in other systems
Entisol	ent	Nonsense syllable	Recent	Azonal, some low-humic Gley soils
Vertisol	ert	L.** *verto*, turn	Invert	Grumosols, Black Cotton soils (Regur)
Inceptisol	ept	L. *inceptum*, beginning	Inception	Ando, Sol Brun Acide, Forest and Humic Gley soils
Aridisol	id	L. *aridus*, dry	Arid	Desert, Reddish Desert, Sierozem Solonchak, some brown and reddish brown soils
Mollisol	oll	L. *mollis*, soft	Mollify	Chesnut, Chernozem, Brunizem (Prairie) Rendzinas, some Brown Forest and associated Solonetz
Spodosol	od	Gk. *spodos*, wood ash	Podzol; odd	Podzols, Brown Podzolic and Ground-water Podzols.
Alfisol	alf	Nonsense syllable	Pedalfer	Grey-brown Podzolic, Grey Wooded, and Non-calcic Brown soils, Degraded Chernozems, and associated Planosols
Ultisols	ult	L. *ultimus*, last	Ultimate	Red-yellow Podzolic, Grey wooded, and associated Planosols and Half-bog soils
Oxisol	ox	French *oxide*, oxide	Oxide	Laterite soils, Latosols
Histosol	ist	Gk. *histos*, tissue	Histology	Bog soils
Andisol	and	Jap. *and*,	Ando	Volcanic ash soils
Gelisol	el	Gk, *gel*, ice	Frost churning	FrozenTundra soils, showing cryoturbation

* The element (ent, ert, id, etc.) starts with the first vowel of the Order name and ends with the last consonant preceding the connecting vowel, e.g. oll, ist, etc.

** L stands for Latin and Gk. for Greek

Source: Soil Survey Staff (1975)

solum, soil) with the connecting vowel 'o' for Greek and 'i' for Latin and other roots. A formative element is abstracted from the name of each Order, e.g. *oll* from Mollisol; the element starts with the first vowel (o) and ends with the last consonant (l) preceding the connecting vowel (i). The formative element is used as an ending for the names of all Suborders, Great Groups, Subgroups and Families within an Order, such that with a little experience one can make several statements about soil properties simply by analysing the name of the soil.

Each Suborder name consists of two syllables. The first is suggestive of a property of the class (i.e. Suborder), and second, the name of the Order as reflected by the formative element (e.g. *oll* for Mollisol). For instance, the names: *Udoll, Xerert, Fluvent* are first unique to the Suborders and secondly, suggest the property of the Suborder (*ud* from udic*, *xer* from xeric*, *fluv* from fluviatile) and the name of the Order (*oll* from M*oll*isol, *ert* from V*ert*isol, and *ent* from *Ent*isol).

Likewise, the names of Great Groups are coined by prefixing one additional prefix (formative element) to the appropriate Suborder name, for instance, *Hapl*-udoll, *Calci*-xerert, and *Usti*-fluvent. If a Great Group is distinguished from others within the same Suborder by a particular diagnostic horizon or property, the name of that property is used as the root of a prefix to form the other Great Group(s), e.g. *Argiudoll, Haploxerert, Udifluvent*, etc. The Great Group names also suggest the Suborder and Order names to which each one belongs.

Subgroup names consist of the name of the appropriate Great Group modified by one more adjectives, e.g. *Typic Hapludoll, Typic Ustifluvent.* The adjective *Typic* is used to typify the central concept of the Great Group *(Hapludoll or Ustifluvent).*

The nomenclature, as it relates to the different categories in the classification system, is illustrated as follows:

M*oll*isol	Order
Ust*oll*	Suborder
Argiust*oll*	Great Group
Typic Argiust*oll*	Subgroup

The three letters *'oll'* identify each of the lower categories as being in the *Mollisol* Order. Likewise, the Suborder name Ustoll is included as part of the Great Group and Subgroup names. From the Subgroup name (*Typic Argiustoll*), the names of the Great Group (*Argiustoll*), Suborder (*Ustoll*) and Order (*Mollisol*), to which the soil belongs, can easily be known.

2.7. Salient Characteristic and Differentiating Properties of Different Soil Orders

In Soil Taxonomy, there are twelve Soil Orders, including the newly-proposed Andisols and Gelisols. They replace the Zonal, Intrazonal and Azonal Orders of the 1938 (revised in 1949) system and are roughly equivalent to the Great Groups of that classification with regard to the level of abstraction. The names of the Orders and their equivalent Great Groups in the 1949 (revised) system are shown in Table 4. These represent broadly the geographic areas that almost coincide with the bioclimatic boundaries (Figure 6).

2.7.1. Key to Soil Orders

Key to Soil Taxonomy – To avoid confusion, one must use the key schematically represented in Figure 6 to check differentiating characteristics for keying out soils. For instance, the presence of a mollic epipedon may not always suggest that the soil is a Mollisol, as some soils having a mollic epipedon may key out as another soil Order. Similarly, all soils having an argillic horizon may or may not qualify for Alfisols or Ultisols. Hence, the use of Key becomes imperative.

ENTISOLS (recent)

Concept

These are very recently developed mineral soils with no diagnostic horizon other than an ochric or anthropic epipedon. The main feature of Entisols is a slight degree of soil formation, because of either limiting time or exceedingly unfavourable conditions.

Entisols, by virtue of plant growth and root penetration, show some mineral weathering and surface accumulation of organic matter, but the original crystalline, metamorphic or sedimentary features of their parent materials are little altered by soil formation. Entisols are thus as variable as their parent materials, which range from recent alluvium, through sand dunes, to a variety of rocks. Their topographical setting is also variable. Some are found on young geomorphic surfaces, such as floodplains and on steep slopes where erosion removes soil material as it is formed. They are formed under a variety of climatic conditions.

Classification

Based on the fluvial nature, extreme texture and remnants of old artifacts, soil moisture and temperature regimes, Entisols have been subdivided into the following five Suborders showing 2 syllables; first is characteristic of suborder and the second, of order name:

- *Aquents* : Entisols developed under aquic or hydromorphic conditions
- *Fluvents* : Entisols showing fluvial nature
- *Psamments*: Entisols suggesting extreme sandy nature
- *Arrents*: Entisols showing fragments of diagnostic horizon within one metre
- *Orthents*: Other common well-drained non-fluviatile Entisols

It is beyond the scope of this chapter to discuss further about the suborders and their lower categories (Great Group, Family, etc.)

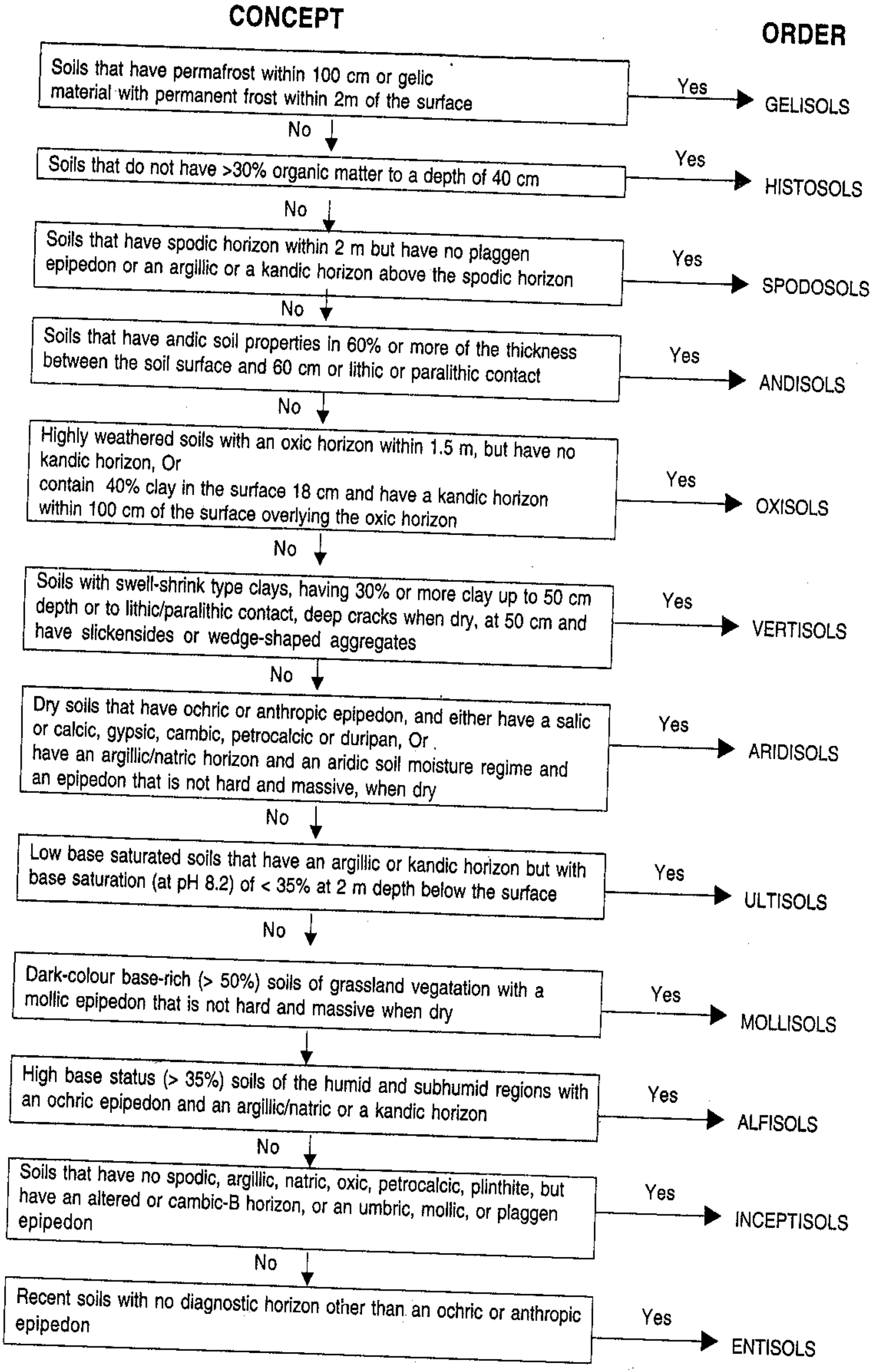


Figure 6. A flow diagram giving simplified key for classifying soils in different orders of Soil Taxonomy

Land Use

In the rocky humid or subhumid mountain regions of Himachal Pradesh, medium-textured Entisols (Orthents) are common. On sand dunes and sand-bars of Rajasthan, Haryana, central Punjab, extremely sandy Entisols (Psamments) are observed. The fluviatile Entisols (Fluvents) are observed in the recent flood plains.

Some of the Entisols on steep rocky slopes support trees along streams. Some Entisols are too stony, infertile or poorly drained for cultivation. However, large areas of Entisols in alluvial bottom lands are cultivated for a variety of grain and vegetable crops, and used for pasture; however, the inter-dunal areas are used for raising a single crop in a year on conserved moisture.

INCEPTISOLS

(L. *Inceptum*, meaning beginning)

Concept

The soils, representing early stage in soil formation, which is beyond that of Entisols (least developed) but still short of the degree of development, as observed in Alfisols, are Inceptisols. They may have some accumulation of clay in a subsurface horizon, but it is not sufficient enough to qualify for an argillic horizon, which is diagnostic for Alfisols and Ultisols. Similarly, they may have dark colour surface horizon which may be limiting in depth, organic matter content or base saturation to qualify for a mollic epipedon (Mollisols).

The Inceptisols are usually not dry and have one or more of the diagnostic horizons (cambic, umbric, or mollic with low base status). They have developed rather recently owing to the alteration of the parent material to develop soil structure, but without much leaching and accumulation of material in the subsoil.

These soils occur almost throughout the world. In India, these are observed all over, except in hot and arid regions.

Classification

In the past, most of these soils were classified as Brown Forest, Andisol and Sol Brun Acide. In India, these soils are observed extensively in many states. Based on the criteria of wetness, temperature and moisture regime, and the presence of diagnostic epipedon, viz. anthropic or plaggen, Inceptisols have been subdivided into six Suborders, viz.

- *Aquepts:* Inceptisol, that have aquic condition
- *Anthrepts*: Inceptisols that have a plaggen/anthropic epipedon
- *Cryepts*: Inceptisols that have cryic soil temperature regime
- *Ustepts*: Others that have an ustic soil moisture regime
- *Xerepts:* Inceptisols that have a xeric soil moisture regime
- *Udepts*: Others that have a udic soil moisture regime

Land Use

Many Inceptisols are agriculturally productive and provide excellent natural grazing grounds. They can be cultivated for improved pasture and for growing a variety of vegetable and grain crops. The Inceptisols, in general, are very productive. There are, however, Inceptisols whose productivity is limited because of imperfect drainage and/or sodicity. Most of the Inceptisols (e.g. Ustepts) of Punjab under assured irrigation conditions produce wheat yield as high as 4.5 tonnes/ha.

VERTISOLS (L. *Verto*, meaning invert)

Concept

The concept of Vertisols is derived from their morphological manifestations. These are uniform, thick (at least 50 cm) tropical black and other dark colour, cracking-clay mineral soils that have high content (> 30%) of clay. These soils swell on wetting and shrink on drying. The swell-shrink process induces the development of wide, deep cracks associated with gilgai microrelief or intersecting slickensides.

These soils are predominantly observed in India, NE Africa, Australia and Southern USA. In India, they are dominantly observed in Madhya Pradesh, Maharashthra, Gujarat, Andhra Pradesh, Tamil Nadu and Rajasthan.

Classification

Based primarily on the soil moisture and termperature regime, and the period the cracks remain closed or open (up to the surface in a year), the Vertisols have been subdivided into six Suborders, viz.

- *Aquerts*: Veritsols having aquic conditions within 50 cm
- *Cryerts*: Vertisols that have a cryic soil temperature regime
- *Xererts*: Vertisols having a thermic, mesic or frigid soil temperature regime and if not irrigated, have cracks that remain open for 60 or more consecutive days and closed for > 60 consecutive days in winter
- *Torrerts*: Other Vertisols under natural conditions, have cracks that remain closed for less than 60 consecutive days (when soil temperature is > 8 °C)
- *Usterts*: Vertisols, if not irrigated, have cracks that remain open for 90 or more cumulative days in a year.
- *Uderts*: Other Vertisols

Land Use

Because of their shrink-swell character and development of deep, wide cracks and slickensides, these soils pose many tillage problems during cultivation, or when used for building foundations, laying drainage and gas pipelines and installing irrigation networks. Tilting of trees, fences, poles and sinking of floors are typical characteristics observed wherever such soils occur.

Constraints

These soils offer excellent natural grazing, and, with irrigation, they can be cultivated for two crops in a year. Under rainfed conditions, these soils can support one crop of cotton, sorghum, pigeonpea, etc. in a year either during monsoon (*kharif*) period or on stored moisture in *rabi* (winter) season. Paddy is grown on Vertisols in lower topographic positions and where irrigation is available. These soils are basically very productive, provided, they are managed properly.

MOLLISOLS (L. *mollis* meaning soft)

Concept

These are soils of grassland (tall or short) vegetation under subhumid (semi-arid, moist) to humid environment. They have a dark colour, well developed, base-rich, well-structured (granular or crumb) surface horizon, that is rich in organic matter (mollic epipedon). The subsurface horizons, rich in illuviated clay (argillic or Bt), calcareous (calcic or Bk) or gypsiferous materials (gypsic or By) may be present, but are not definitive of the Order. Their characteristic features result from decomposition of organic material, especially fine roots of grassy vegetation, producing some stable dark compounds, and reworking of soil burrowing activity of diverse populations of soil invertebrates, especially earthworms.

Mollisols are predominantly observed in the central USA, from east to west across the heartland of Russia, and in the central South America. In India, such soils are dominantly observed in the 'Tarai' region of Uttar Pradesh and Uttrakhand and occasionally to commonly in the Himalayas (Kulu region) of Himachal Pradesh, northern Bihar and in Maharashtra and Madhya Pradesh in association with Vertisols (Bhattacharyya *et al.*, 2006)

Classification

Based largely on moisture and temperature regimes, Mollisols have been subdivided into the following seven Suborders :

- *Albolls:* Mollisols that have an albic (bleached) horizon over an argillic or natric horizon and which has chroma of 2 or less. They also show aquic conditions for some time in a year.
- *Aquolls*: Mollisols that have an aquic (wet) soil moisture regime
- *Rendolls:* Other Mollisols that have 40% or more of $CaCO_3$-content either within or below the mollic epipedon, have a udic soil moisture and/or a cryic soil temperature regime
- *Cryolls*: Mollisols that have a cryic soil temperature regime
- *Xerolls*: Others that have a xeric temperature regime
- *Ustolls*: Others that have an ustic temperature regime
- *Udolls*: Others that have an udic temperature regime

Land Use

The Mollisols are inherently the best agricultural soils of the world. In India, these soils produce optimum yields, both under irrigated and unirrigated conditions with minimum inputs. The soils in the drier regions are used mostly for grazing. In subhumid regions, they are widely cultivated for a variety of crops, such as wheat, maize, sorghum, etc. They can also produce a variety of vegetables. In the Tarai region (Uttar Pradesh and Uttrakhand) of India, because of summer monsoon rains, these are cultivated for maize and sorghum.

ARIDISOLS (L. *Aridus*, meaning dry)

Concept

These are mineral soils of dry places (arid and semi-arid) and of areas having high groundwater table. The soils remain dry for most part of the year, and salts accumulate at the surface and/or in the solum, resulting in the development of a salic, gypsic or calcic horizon.

The Aridisols widely occur in the arid climatic environment, especially in South Asia, north and north-east Africa, Australia, southwest part of south America, south-west and northern USA, South Africa and through east to west of Russia. In India, these soils occur in western and north-west India (Rajasthan, Gujarat, Haryana, etc.) in pockets.

Classification

These soils were formerly designated as Desert, Reddish Desert, Sierozem, Reddish Brown Solonetz and Solonchak. Aridisols have been classified into the seven Suborders, largely based on the presence of diagnostic subsurface horizons, viz. cambic, argillic, calcic, gypsic, salic, etc. and on soil temperature regime, viz. cryic.

- *Cryids*: Aridisols that have a cryic soil temperature regime
- *Salid*: Aridisols that have a salic horizon within 1 m of the soil surface
- *Durids*: Aridisols that have a duripan within 1 m of the soil surface
- *Gypsids*: Others that have a gypsic or petrogypsic horizon that starts within 1 m of the surface
- *Argids:* Aridisols with an average argillic (or natric) horizon that starts within 1 m of the soil surface
- *Calcids:* Aridisols that have a calcic or petrocalcic horizon that starts within 1 m of soil surface
- *Cambids*: Other common type of Aridisols

Land Use

These soils do not support a crop without irrigation. These are best left for sparse native grazing. However, if irrigated for cultivation, they pose the risk of salinization or developing sink-holes in gypsiferous landscapes. A network of such sink-holes formed due to slow dissolution of gypsum, leads to formation of big drainage channels underneath and the land sinks leaving behind uneven surfaces for cultivation and/or irrigation. However, in non-gypseferous landscapes of Haryana and Punjab (India), they are used for growing one crop (usually pearl millet) in a year by following water conservation practices during summer monsoon period and growing a crop on stored moisture. The Aridisols have limitations of xerophytic climatic conditions and brackish groundwater which comes to surface due to high evaporative demand, rendering the soils saline and unsuitable for plant growth, except for salt-loving vegetation.

ALFISOLS (from *Pedalfer* of Marbut)

Concept

Alfisols are base-rich, timbered, mineral soils of subhumid and humid regions. These are characterized by a light-colour surface horizon (ochric epipedon) over a clay-enriched argillic subsurface horizon that is rich in exchangeable cations with base saturation of more than 35%. Alfisols are less weathered than the Ultisols.

These soils are widely distributed in the USA, South America, Northern Europe, southeast and north-west Africa, Brazil and southeast Asia. In India, the Red Soils (Rhod-, Pale-, Hapl- ustalfs) are predominantly observed in different agro-ecological regions covering parts of the states of Andhra Pradesh, Assam, Bihar, Arunachal Pradesh, Himachal Pradesh, Maharashtra, Karnataka, Tamil Nadu, Orissa and Madhya Pradesh.

Classification

In the past, these soils were classified as Gray Brown Podzols, Planosols and some Half

Bog Soils. Based on soil moisture and temperature regimes, Alfisols have been subdivided into five Suborders, viz.:

- *Aqualfs*: Alfisols that have aquic conditions
- *Cryalfs*: Alfisols that have a cryic or isofrigid temeperature regime
- *Ustalfs*: Other Alfisols that have an ustic moisture regime
- *Xeralfs*: Other Alfisols that have a xeric moisture regime
- *Udalfs*: Other Alfisols that have a udic moisture regime

Land Use

Because of the high base saturation, favourable textures and location in semi-arid (moist) to humid regions, Alfisols are naturally fertile and productive. They are used for forestry, grazing, and once cleared, they are suitable for growing a variety of fruit, vegetable and grain crops. In India, they are used for growing crops, like wheat, maize, sorghum, rice and horticultural crops, especially mango, litchi, cashew and jackfruit. The sodium-rich Alfisols need ameliorative measures, such as application of gypsum (as an amendment).

SPODOSOLS

(Gr. *Spodos*, meaning wood-ash)

Concept

These are mineral soils with accumulation of sesquioxides and humus in the subsurface horizons. These develop under cool, humid climate and coarse-textured siliceous parent material which favours free leaching conditions. These are sparsely formed in hot humid tropical, and in warm humid regions, where the parent material is sandy (quartz-rich) and groundwater fluctuates. The diagnostic feature of these soils is an illuvial horizon, enriched with free sesquioxides (Bs) and humus (Bh) underlying a bleached, wood-ash-colour eluvial E-horizon.

These soils are largely distributed in north-west Europe, northern and north-east USA, and Canada. In India, Spodosols are seldom reported.

Classification

In the earlier systems of soil classifications, these soils were classified as Podzol, Brown Podzolic, and Hydromorphic Soils (groundwater Podzols) by recognizing the bleached, ash-colour eluvial, E-horizon.

In the Soil Taxonomy, emphasis has been laid on the subsoil diagnostic horizon, i.e. spodic B-horizon rather than the characteristic of the eluvial E-horizon. The Spodosols have been classified into the following four Suborders based on mixed criteria, such as soil moisture regime and humus content.

- *Aquods*: Spodosols that have aquic conditions as manifested by redoximorphic features
- *Cryods*: Spodosols that have a cryic soil temperature regime
- *Humods*: Other Spodosols having high (> 6%) organic carbon within the spodic horizon
- *Orthods*: Other common types of Spodosols

ULTISOLS (L. *Ultimum,* meaning last)

Concept

The Ultisols are comparable with Alfisols, except for having low (< 35%) base saturation on the exchange complex, which is due to their advanced stage of weathering. These are base-poor, timbered, mineral soils of humid regions developed under high rainfall and forest vegetation. They are characterized by a clay-enriched subsurface argillic or kandic horizon.

The soils are most extensive in the warm, humid and subtropical regions of the world. These are most predominant in south-east USA, South America, south-east Asia, central Africa and India. In India, they are observed in Kerala, Tamil Nadu, Orissa, Assam and some north-eastern states.

Classification

Based on the criteria of moisture regime and humus content, the Ultisols have been subdivided into the following five Suborders.

- *Aquults*: Ultisols having aquic conditions
- *Humults*: Ultisols having high organic carbon (12 kg/m^2 or more) within 1 m of the soil surface
- *Udults*: Soils having udic soil moisture regime

- *Ustults*: Other Ultisols having an ustic soil moisture regime
- *Xerults*: Other Ultisols that have a xeric moisture regime

Land Use

Because of the low-fertility and low-base status, these soils pose limitations for agricultural use. Generally, these soils are used for forestry, but may produce good agricultural and plantation crops, when they are adequately limed and fertilized. In the tropical regions, such soils are cultivated for pineapple, sugarcane, coffee, cocoa, coconut, rubber, etc. These are also cultivated for vegetables, but only upon adequate fertilization.

OXISOLS (Fr. *Oxide*, oxide)

Concept

These are strongly and deeply-weathered mineral soils of the humid tropics that are poor in fertility. These are characterized by a uniform profile having negligible amounts of weatherable minerals, and are dominated by the kaolinitic and sequioxidic-rich deep subsurface (oxic) horizon. In some cases, deeply-weathered mottled horizons (plinthite) may also develop. Most Oxisols have brick-red colour; but some are also yellow or grey in colour.

Oxisols are dominantly observed in the tropical world, on gently sloping very old landscapes in central Africa, north-east South America and south-east Asia. In tropical India, such soils are not reported yet. Their occurrence in other areas (desert savannas) is indicative of a climatic change.

Classification

In the past, these soils were classified as true Laterites, Latosols and Groundwater Laterites. Based on the considerations and the criteria of soil moisture regimes, the Oxisols have been subdivided into the following five Suborders:

- *Aquox:* Oxisols that have aquic features
- *Torrox:* Oxisols that have an aridic moisture regime
- *Ustox* : Oxisols that have an ustic or xeric moisture regime
- *Udox*: All other Oxisols and those having a udic moisture regime
- *Perox*: Other Oxisols that have a perudic moisture regime

Land Use

Oxisols are chemically-degraded soils and need careful management for agricultural use. These are mainly used for grazing and forestry; some are used for growing crops such as coffee, rubber, cocoa, sugarcane and tropical fruit crops (pineapple, coconut, jackfruit, etc.)

Shifting agriculture is a common practice adopted in such areas. This practice was satisfactory when the shifting cycle was of >20 years, but with the increasing population pressure and demand for food, the cycle has been reduced to 3 to 5 years, resulting in serious problems of soil erosion by water and nutrient depletion.

HISTOSOLS (Greek *histos,* meaning tissue)

Concept

The central concept of Histosols is that of soils formed on organic soil materials. As a thumb rule, a soil without permafrost is classified as a Histosol if half or more of the upper 80 cm is organic. A soil is also called as a Histosol, if the organic materials rest on rock. These are organic-rich soils with thick, peaty horizon (histic epipedon) that develop in lower topographic positions in a permanent water-saturated environment, where plant species (bog, swamp and marsh) are limited in diversity. The main process in their formation is the accumulation of peat, and that happens when organic matter produced by native vegetation is more than its decomposition in the soil. The rate of peat accumulation for woody peat is 0.5 to 1mm per year; however, the rate is much lower in swamps than herbaceous vegetation (marsh, grasses). The amount of organic matter required for a soil to qualify as Histosol depends on the clay content. The minimum amount of organic matter required is 20%, if the clay-content is nil (Figure 7).

The Histosols are of local importance and occur in some selected, nothern parts of Europe, northern USA, Canada and north-west Asia. In India, such soils are expected to occur in pockets of Kerala, Tripura and Andaman and Nicobar Islands.

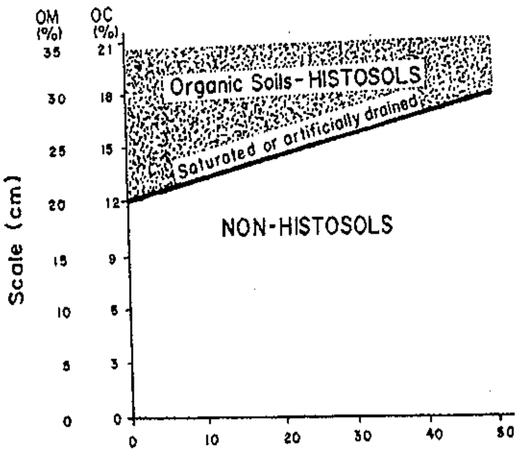


Figure 7. Distinction between Histosols and Mineral Soils based on organic matter content (Organic soils that are never saturated for more than a few days and containing 20% organic carbon are also included in Histosols)

Source: Sehgal (1996)

Classification

In the past, these soils were termed as Peat, Muck, and Bog soils. Based largely on the degree of decomposition of the humus, the Histosols have been subdivided into four suborders, viz. Hemists, Fibrists, Saprists, and Folists.

Land Use

Most of the Histosols, especially Fibrists, located in depressions and flat areas are best left under natural vegetation. The Folists are freely drained. They represent ustic, xeric or torric soil moisture regime and are used for growing vegetables. The Hemists show moderately decomposed organic matter and are used for natural vegetative cover and as woodland/ rangelands. For their management, it is necessary to drain these soils for plant growth and to facilitate operation of farm machinery. However, when drained, they oxidise and subside, making the drainage difficult.

ANDISOLS (from Japanese, black soil)

Concept

Andisols were first recognised in Japan and were named as Volcanic ash material. The central concept is of soils developed on volcanic ash. They are typically of dark colour, low bulk density soils that do not have an albic horizon, but must have andic properties [loose or friable colour mollic or umbric surface horizon overlying a brown cambic B-horizon and one or both of the following: low bulk density (< 0.9 Mg/m^3) or 60% or more vitric volcanic ash within 60 cm of the mineral soil surface].

The typical characteristic of these soils is the high content of allophane which gives them a very low bulk density and fluffiness, especially in the B-horizon. The low bulk density and high fertility of these soils make them easy to cultivate.

Normally, Andisols can be observed on all topographic positions and under all soil moisture and temperature regimes. However, these are identified on uplands with undulating topography in Indonesia. Since the Andisols are dominantly developed on volcanic ash, or materials derived from it, such as volcanic alluvium, volcanic loess, they are dominantly observed around the Ring of Fix in the Pacific, including Japan, New Zealand, Indonesia and Philippines. They are also observed in the 'Rift Valley' of Africa, especially Kenya, Western Coast of USA and South America. In India, such soils are expected in the Islands of Andaman and Nicobar where volcanic activity is observed often.

Classification

They are keyed out after Histosols in the Soil Taxonomy. The Andisols have been recently defined in *Soil Taxonomy* (Soil Survey Staff, 1999) in the form of a newly introduced soil Order, viz. Andisols. These soils were earlier grouped under the Order Inceptisols, Suborder Andepts.

Based generally on the soil moisture and temperatue regimes, the Andisols are divided into eight suborders, viz.:

- *Aquands*: Andisols that have either a histic epipedon or aquic conditions
- *Cryands*: Other Andisols that have a cryic soil temperature regime
- *Torrands*: Andisols that have an aridic moisture regime
- *Xerands*: Other Andisols that have a xeric moisture regime
- *Vitrands*: Other Andisols that have a duripan or a petrocalcic horizon

- *Ustands*: Andisols that have an ustic moisture regime
- *Udants*: Andisols that have a udic moisture regime
- *Vitrands*: Other Andisols that have a duripan or a petrocalcic horizon

Land Use

Andisols that occur on steep slopes, have the limitation of mechanized farming. However, Andisols in favourable climatic conditions, are thickly populated and intensively cultivated. It is advantageous to grow crops that show little response to the application of phosphorus, for instance sweet potatoes (*Ipomoea batata*). The major limitation in the use of Andisols is their high phosphorus fixation capacity, which renders P unavailable. Andisols are generally stable and resist water erosion because of high infiltration and permeability rates. When dry, they are susceptible to wind erosion.

GELISOLS

(from *gelic*, meaning frost churning)

The Order Gelisols is the most recently introduced one to accommodate soils with permafrost in the extreme northern hemisphere.

Concept

The Gelisols are conceptually the soils with gelic materials (mineral or organic soil materials that show evidence of cryoturbation, i.e. frost churning) underlain by permafrost. Diagnostic horizons may or may not be present in Gelisols as thawing and freezing play an important role in their evolution. Permafrost influences their pedogenesis by acting as a barrier to the downward movement of the soil solution. Cryoturbation (commonly known as frost churning or mixing) is an important process in Gelisols development.

Gelisols are dominantly observed in the areas of permafrost, which include northern USA, Canada, Greenland, Russia, Mongolia and other areas in the extreme northern hemisphere. In India, such soils have not been observed or reported so far. They may be observed in higher Himalayas with permafrost conditions (ice caps in extreme north of Jammu and Kashmir and Sikkim).

Classification

The Gelisols are subdivided in the following three suborders:

- *Histels*: Gelisols that have organic soil materials or are saturated with water for 30 or more days in a year.
- *Turbels*: Gelisols that show cryoturbation in the form of irregular, broken or distorted horizon boundaries.
- *Orthels*: Other common type of Gelisols.

Land Use

The Gelisols are not cultivated and left to support natural vegetation. The Orthels of anhydrous condition, support little or no vegetation.

2.8. Advantages and Applications

The recently-developed system is the most elaborate system marked by great care and precision with which the classification units have been defined. For the following three reasons, the students of soil science may find this system very useful.

- The primary basis for identifying different classes in the system is the properties of soils as they exist in the field.
- The nomenclature (with Latin and Greek origins) employed gives a definite connotation of the major soil characteristics.
- The system has an in-built mechanism to permit addition of new soil groups, suborder, or even new order without being disturbed, e.g. new Orders, viz. Gelisols, Andisols, have been included in the system recently.

Other advantages of this system are:

- It permits classification of soils rather than soil forming processes.
- It focuses attention on the soil rather than on the related sciences, such as geology and climatology.
- It permits the classification of soils of unknown genesis.
- It permits greater uniformity of classification as applied by different soil scientists located far apart from each other.

2.8.1. Applications

Soil Taxonomy is based on widely-accepted principles and criteria and is being used by many countries, including India. The system has emerged as the most logical soil classification scheme today.

The goal of a classification system is to help soil survey in correlating soils and making predictions by assessing their potential and constraints and in agro-technology transfer, using soil taxa as wheels.

3. Major Soils of India

India, situated between the latitudes of 08°04' and 37°06' N and longitudes of 68°07' to 97°25' E, has a geographical area of 329 Mha. Physiographically, it can be divided into the three broad regions, viz. Peninsula (a triangular Plateau in the Deccan and south of the Vindhyas), Extra-Peninsula (mountain region of the Himalayas), and the Indo-Gangetic Plain separating the two above-mentioned regions (Figure 8).

Geologically, a great part of the Peninsula is occupied by the Archean rocks comprising gneiss, schists and other rocks of diverse nature. Red soils (*Alfisols*) generally predominate in this region. Next in order of age are the *Cuddapah* and *Vindhyan* rocks, followed by the coal-bearing Gondwana formations supporting rocks of the Mesozoic and Tertiary groups. These are mainly distributed over the north-central and NE-central parts where red soils (Alfisols, Inceptisols and Entisols) have

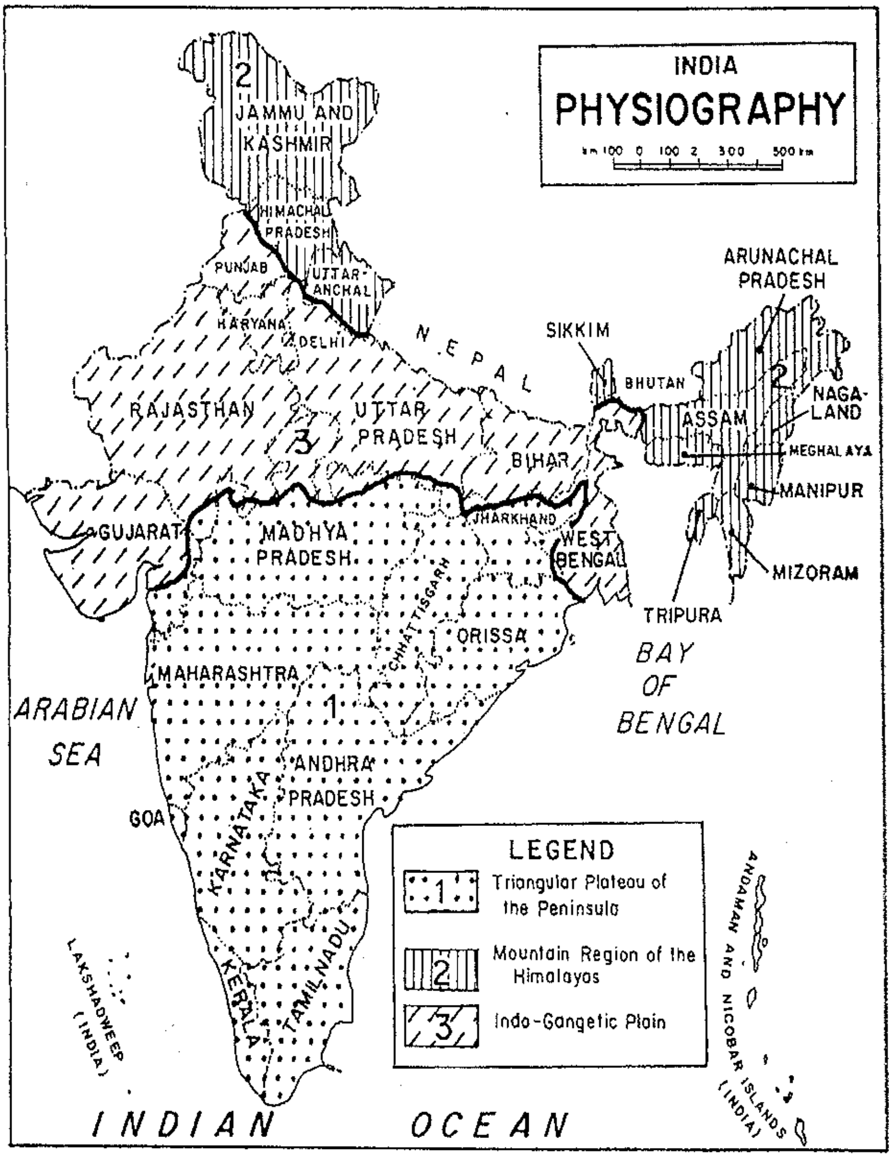


Figure 8. Physiography of India
Source: Sehgal (1996)

developed. The western and central parts are covered by lava flows of the Deccan trap where basaltic rocks predominate. Here, black cotton soils of different thickness (Vertisols, Inceptisols) predominate.

The extra-peninsula, on the other hand, shows the development of marine sediments of all ages, especially in north of the Himalayas. The major rock formations are Tertiary-old sedimentary (sandstone, limestone, etc.) and igneous (granites) (at places metamorphosed to gneisses and schists). Here, non-calcic brown soils (Inceptisols, Alfisols, Entisols, Mollisols) predominate.

The vast Indo-Gangetic and other plains of the Pleistocene origin are composed of alluvium of the great river systems flowing in this region. These are the alluvial soils. However, depending on the age of alluvia and degree of development, they can be classified in the Orders, Inceptisols, Entisols or Alfisols in Soil Taxonomy.

Climatically, India shows three distinct seasons, viz. cool and mainly dry winters from November to February, hot and mainly dry summers from March to June and monsoon rainy season from mid-June to September. Rainfall is received during June to September (from the south-west monsoon) and during December to February (from the north-eastern winds). The Western Ghats and the eastern Himalayan ranges receive the maximum rainfall because of their alignment across the summer monsoon winds. The Indo-Gangetic Plains receive moderate rainfall; Rajasthan receives little rainfall as the Aravallies lie along the path of moisture-bearing winds.

The other climatic element, viz. temperature, has particular significance for plant growth, especially in northern India during winter; high temperature promotes evapotranspiration during summer and causes crop-affecting aridity. Peak temperatures of 42 °C to 47 °C are observed during summers (May to June), which fall sharply with the onset of monsoon rains (in July to September). Sub-zero temperatures are observed during winters in the extreme northern regions where germination of seed becomes a problem.

The bio-climate is the climate prevailing a few metres above and below the soil surface where biological activity prevails. The different climatic elements of relevance to plant growth are expressed in the bioclimatic map (Figure 9). The soil temperature and moisture regimes as discussed earlier, play an important role in classifying soils and crop planning, as each plant species requires, specific soil temperature and moisture conditions for its optimal growth. India is dominantly represented by thermic and hyper-thermic temperatures and Ustic, Aridic and Udic moisture regimes.

India with a wide variety of landforms, geological formations and climatic conditions, exhibits a large variety of soils; the variety is so diverse that barring a few soil orders (Andisols, Spodosols,Oxisols), India represents all the major soils of the world.

The grouping of these soils can be achieved by using either of the two systems, viz. Genetic and Soil Taxonomy. Whereas the Genetic System is based on genetic factors and processes, the Soil Taxonomy is based on the properties of soils, which are the reflection of soil genesis and are measurable. The major soils of India, according to the Genetic approach, can be classified into a few soil groups, viz. alluvial, black, red, forest and desert soils. But, in terms of Soil Taxonomy, they key out in nine out of the twelve Soil Orders and a large number of great groups. Since the objective of this section is to apprise students of the major soils of India, it is considered desirable to do so in terms of a few soil groups as per the Genetic approach rather than explaining a large number of soil groups in terms of Soil Taxonomy. For instance, the Alluvial Soils (in Genetic System) can be keyed out in three or more soil orders, viz. Entisols, Inceptisols, Alfisols, or Ultisols, depending on the age and degree of development. Hence, the major soils of India are discussed in genetic terms giving their equivalents in Soil Taxonomy (Figure 10).

3.1. Alluvial Soils

The name alluvial is given to the soils that have developed in alluvium, irrespective of their place of occurrence and degree of development. They are one of the important groups of soils for agricultural production. They are extensively distributed in the states of Punjab, Haryana, Uttar Pradesh, Uttrakhand, Bihar,

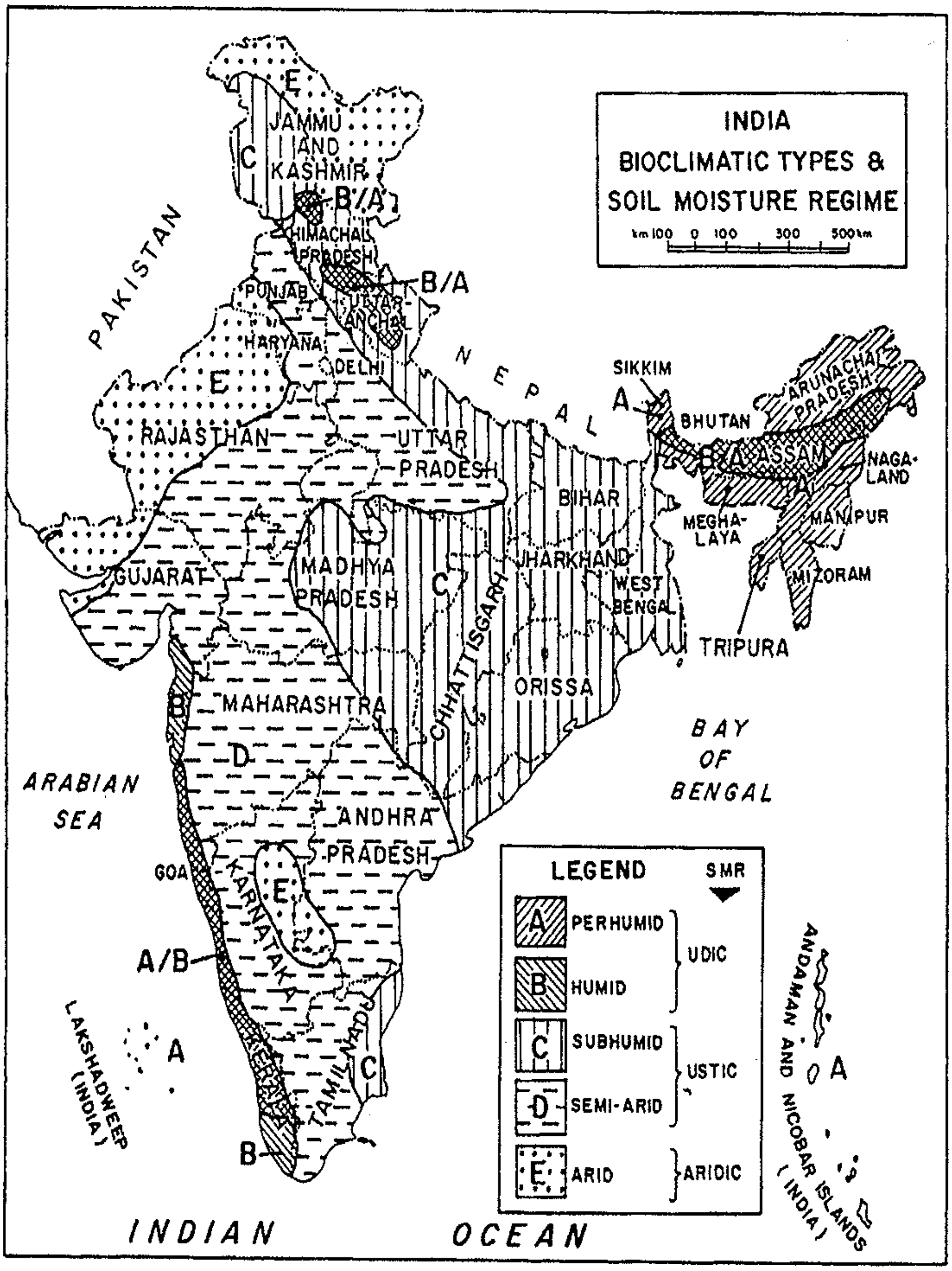


Figure 9. Bioclimates and approximate soil moisture regimes (SMR) of India

Source: Sehgal (1996)

West Bengal, Assam and coastal regions of India and occupy an estimated area of 75 Mha in the Indo-Gangetic Plains and Brahmaputra Valley alone.

The parent material of these soils (alluvium) is of recent origin and has been derived from the deposition of erosion products brought and laid down by various river systems; coastal alluvium is, however, laid down by the sea currents.

3.1.1. Salient Characteristics

The salient characteristics of alluvial soils are:

- The Alluvial soils, in general, are varible in texture, depending on the source of parent material and their place of deposition. They are coarser near the source and become finer in proximity to the sea (delta area).
- They are fluvial in nature (stratified) which is reflected in their texture and irregular distribution of organic matter with depth.

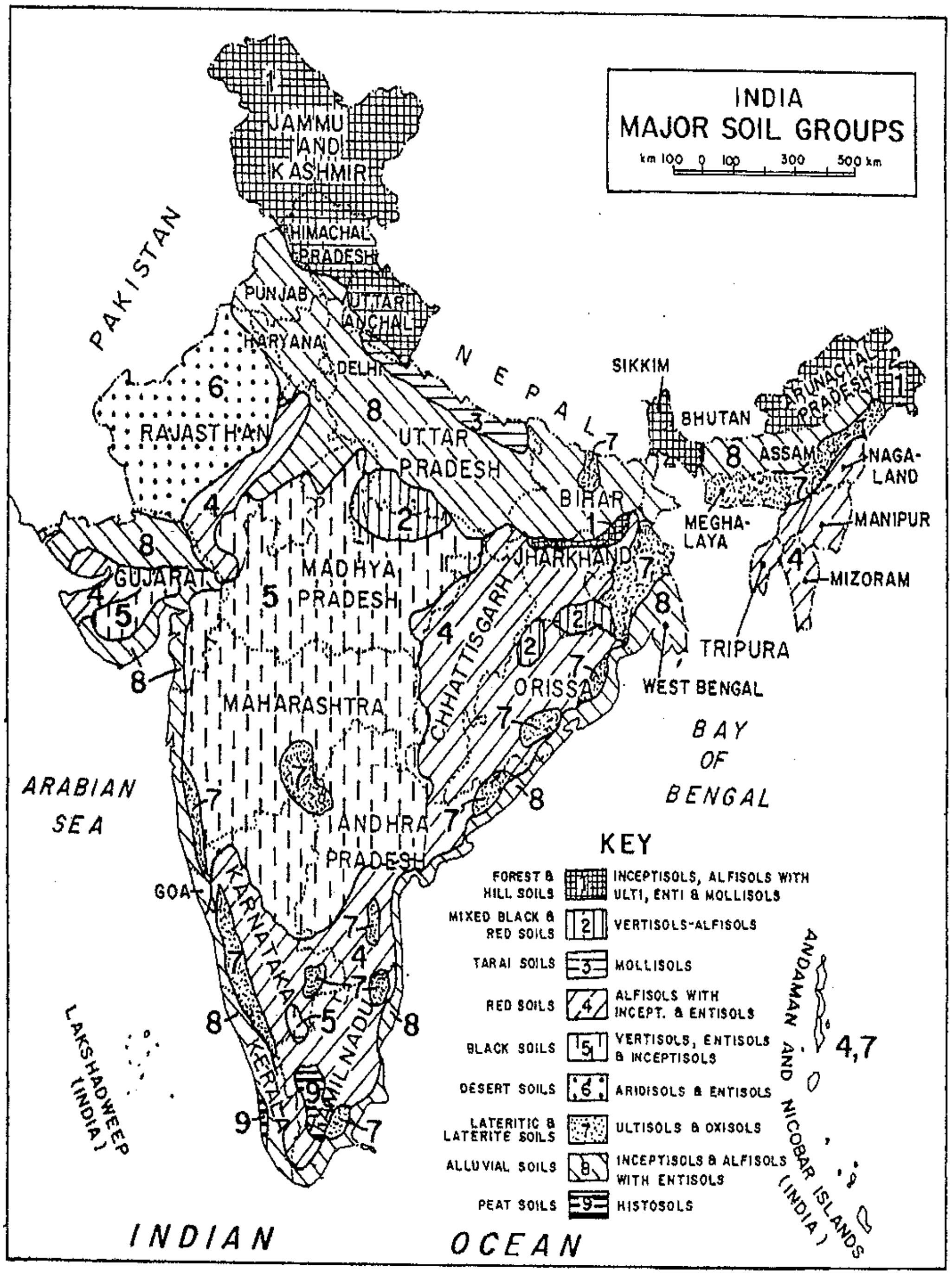


Figure 10. Major soils of India
Source: NBSS&LUP (1985)

- They are either alkaline (in aridic and/or ustic regime) or acidic (in udic regime).
- They exhibit different profile developments from least-developed A-C to well-developed A-B-C profile, depending on the prevailing climate and age of the alluvium.
- They are inherently rich in plant nutrients. In general, they are fairly sufficient in phosphorus and potassium, but are deficient in nitrogen and organic matter contents.

In the Genetic System, these soils are classified as 'Alluvial soils' belonging to the Order 'Azonal'. In terms of Soil Taxonomy, such soils may key out in any one of the following Orders:

(i) Entisols (with A-C profiles), and depending on their nature and morphology, they may fit in with Fluvents, Psamments, Arrents, Orthents or Aquents (at Suborder level).

(ii) Inceptisols (with A-(B)-C profiles) and further depending on their moisture and temperature regimes, as : Aquepts, Cryepts, Ustepts, Xerepts or Udepts.

(iii) Alfisols [with A-Bt-C profiles] and further as Aqualfs, Cryalfs, Ustalfs, Xeralfs or Udalfs as above.

(iv) Aridisols [with A-(B)-C profiles] and further as Cryids, Salids, Durids, Gypsids, Argids, Calcids or Cambids, depending largely on the kind of diagnostic horizon and temperature regime.

3.1.2. Land Use

The major constraints of some of these soils are stratification that restricts leaching and drainage, extreme sandy nature that promotes excessive leaching of water and plant nutrients, hydromorphic condition that promotes reduction and results in poor aeration for plant growth. These soils, if managed well, can be fruitfully used for most of the agricultural and vegetable crops. They can be rendered saline where evaporation exceeds rainfall (aridic zone).

3.2. Black (Cotton) Soils

The name black is given to soils that are very dark in colour and turn extremely hard on drying and sticky and plastic on wetting, and hence are very difficult to cultivate and manage. These soils are comparable with the Grumosols of the USA. In view of thier black colour, they are comparable with the Chernozems of Russia and Prairie soils of the USA, but differ in their physicochemical properties.

These soils are dominantly distributed in the central, western and southern states of India (Figure 10). According to a recent study, different members of black soils occupy an estimated area of 74 Mha.

Typical Black (Cotton) soils, with characteristic swell-shrink nature, have developed on basaltic material (rock or alluvium) under semi-arid to sub-humid climatic conditions. The natural vegetation of the area is tropical dry deciduous and tropical thorny forests with fairly dense growth of grasses. The weathering product of the parent rocks (basalt and other metamorphic, containing lime and soda-lime feldspars) are basic and rich in clay, which is dominantly of smectitic type with high co-efficient of expansion and contraction, and therefore set up a steady churning process in the pedon. Churning causes vertical mixing in deep soils and leads to the development of deep (> 50 cm) and wide (> 1 cm) cracks, gilgai micro-relief and/or closely intersecting slickensides.

3.2.1. Salient Characteristics

The salient characteristics of these soils are as follows:

- These are highly clayey with clay content ranging from 30% to 80%.
- Being calcareous, they have pH ranging from 7.8 to 8.7, which may go up to 9.5 under sodic conditions.
- Being rich in smectitic-clay minerals, they have high exchange capacity [30-60 cmol(p^+)kg^{-1} soil].
- These have high water and nutrient holding capacity. The moisture holding capacity, although is high (150-250 mm/m), large part is of it is not available for plant growth, because it is held tenaciously by the dominant smectitic clay. It also reduces permeability and hence poses drainage problem.
- These do not exhibit any eluviation and illuviation process, because of churning. Moreover, under calcareous conditions, the clay stays flocculated and doesn't move with percolating water.
- These have high bulk density (1.5-1.8 Mg/m^3) because of the swelling and shrinking nature of the soil.
- These are very dark in colour which may be due to clay-humus complexes and/or the presence of titaniferous magnetite mineral.
- These are highly sticky and plastic and thus pose many problems in both agricultural and non-agricultural sectors.

3.2.2. Classification

These soils, as per the Genetic system, are classified in the Orders: Intrazonal (Grumosols, '*regur*') and Azonal (Regosols, Alluvial soils). According to Soil Taxonomy, the deep, black soils are keyed out in the Order: Vertisols and Suborders Usterts, Torrerts based on the moisture regime. The shallow soils, however, key out in the Orders: Inceptisols and Entisols, depending on the degree of profile developement.

3.2.3. Land Use

The major contraints in their land use are: narrowing of workable moisture range, low infiltration rate and poor drainage, poor moisture and nutrient availability for plant growth, poor in some available plant nutrients, especially nitrogen, phosphorus, sulphur, their calcareous nature adversely affects the availability of micronutrients and due to their swell-shrink nature, these are unsuitable for laying foundations, construction of buildings, laying of pipelines and electric communication poles, etc.

The soils are inherently very fertile and, under rainfed conditions, they are used for growing cotton, sorghum, millet, soybean, pigeon pea, etc. Under irrigated conditions, they can be used for a variety of other crops, such as sugarcane, wheat and citrus plantations.

3.3. Red Soils

The name Red is given to soils rich in sesquioxides that have developed on rocks of Archean origin (granite, gneiss) and on welldrianed, stable and higher land forms under hot, semi-arid to humid subtropical climatic conditions. Under such conditions, the weathering is moderately intense and leads to enhanced decalcification. Some weathering products are leached out leaving behind the less mobile elements, like silica, iron and alumina. The iron and aluminium under oxidised conditions, form sesquioxides (Fe-oxides and Al-oxides), imparting red colour to these soils.

These soils are predominantly observed in the southern parts of the Indian Peninsula, comprising the states of Andhra Pradesh, Tamil Nadu, Karnataka, Maharashtra, Orissa and Goa and in N-E States. In Andhra Pradesh, the Red and the Black soils occur under similar bioclimatic conditions, but on different parent materials and landforms. The Red soils develop on igneous (acidic) rocks and occupy higher topographic positions, whereas the Black soils develop on basalt (basic) rock or on alluvium derived from basalt, and occupy lower positions on the landscape. The soils grade from shallow, gravelly and light-colour (of the uplands) to much fertile, deep, dark reddish brown in the plains and valleys.

3.3.1. Characteristics

The main characteristics of these soils are:

- These are red to yellowish in colour which is the result of coating of ferric oxides on soil ped sufaces, rather than to a very high proportion of iron. It is red when ferric oxide occurs as haematite or anhydrous FeO and yellow when it occurs in the hydrated form (called limonite). In general, they have hues of 7.5YR (or redder) in upper topographic positions and darker hues in the valleys.
- These soils are highly variable in texture, ranging from loamy sand to clayey; but in general they vary from loam to clay loam in texture.
- They are shallow and poor gravelly in the uplands to very deep, fertile in the plains and valleys.
- They are well to excessively drained, depending upon their topographic position and texture.
- They are, in general, neutral to acidic in nature, depending upon the content of iron oxides.
- The SiO_2/sesquioxide ratio (in clays) varies from 2.5 to 3.0; the amounts of iron and aluminium are generally high (30-40%).
- The cation exchange capacity and base saturation of these soils are relatively lower than those of the Black or Alluvial soils. Some Red soils, occurring in association with Lateritic soils, have low exchangeable bases [~20 cmol(p^+)kg^{-1} soil]. The CEC (clay) ranges from 25 to 40 cmol(p^+)kg^{-1} soil.
- These soils are generally deficient in nitrogen, phosphorus and potassium. They are also poor in organic matter and lime contents.
- These show common presence of kaolinite (1:1 type) clay mineral.

3.3.2. Classification

In the Genetic scheme, they qualify as Red loam, Reddish and Yellowish-brown soils. According to Soil Taxonomy they key out as: Alfisols and Ultisols (well developed soils with high and low base saturation, respectively), Entisols (very shallow and crusty soils), or as Inceptisols (moderately developed soils).

3.3.3. Land Use

The soils pose limitations of soil depth (on hills and hill slopes), poor water and nutrient holding capacity, surface crusting and hardening, excessive drainage and runoff, poor natural soil fertility (N, P, Ca, Zn, S). Under good management practices, these soils can be profitably used for a variety of agricultural, horticultural and plantation crops (depending on the moisture regime), such as millets, rice (both direct seeded and transplanted), groundnut, maize, soybean, pigeonpea, green gram, jute, tea, cashew, cocoa, grapes, banana, papaya, mango, etc.

3.4. Laterite and Lateritic Soils

The term 'Laterite' was originally used by Buchanan in 1807 for the highly ferruginous, vesicular and unstratified material observed in the Malabar Hills of south India. The laterites are typically formed in tropical climate experiencing alternate wet and dry seasons. With monsoon type of climatic conditions acting on the basic parent rock, the siliceous matter is leached almost completely during weathering and the sesquioxides are left behind. On drying, these are converted into irreversible iron oxide and aluminium oxide. The soils thus formed are rich in sesquioxides, devoid of bases and primary silicate minerals, hard or capable of hardening like bricks when exposed to drying after wetting. It is a compact to vesicular rock-like material composed of a mixture of hydrated oxides of iron and aluminium with small amounts of manganese oxides and titania. They are generally observed on hill-tops and Plateau landforms of Orissa, Kerala, Tamil Nadu, etc.

The Lateritic soils are formed under almost comparable climatic conditions as described in the preceding paragraph, but do not require alternate wet and dry conditions and the groundwater level may not be very near the surface. Such soils are widely distributed in the states of Maharashtra, Andhra, Karnataka, Tamil Nadu and North-East region, and occupy about 25 Mha of the total geographical area of India.

3.4.1. Characteristics

The Laterites have following characteristics:

- They have hues of 5 YR or redder with maximum intensity in the B-horizon.
- These are deeply-weathered soils with high clay-content.
- These soils lose bases (Ca, Mg, Na, K) and silica due to pronounced leaching with relative accumulation of sesquioxides and the soils are rendered acidic with silica: sesquioxides ratio of < 2.
- These are predominant in kaolin clay minerals.
- These are low in CEC (clay), which is <16 cmol(p^+) kg^{-1}, and base saturation (< 40%).

The Lateritic soils (Ultisols, Alfisols) remain dry for 4 to 5 months in a year, and have SiO_2/R_2O_3 and SiO_2/Al_2O_3 ratios of > 2. Kaolin is the dominant clay mineral with occasional presence of gibbsite. These are relatively high in base saturation (> 40%).

3.4.2. Classification

The true Laterites (Oxisols in Soil Taxonomy) are not yet observed in India. Most of the laterite soils key out in the order of Ultisols (Chandran *et al.*, 2005) and Suborders, Aquults, Udults, Ustults, depending upon the moisture regime.

3.4.3. Land Use

The major limitations posed by these soils are deficiency of P, K, Ca, Zn, B, etc. and high acidity and toxicity of aluminium and manganese. Liming of these soils is not practical because of non-availability of lime due to high cost of transportation. The experience of liming of temperate soils cannot be applicable in tropical area having low-activity clays. Evidences suggest that calcium is more important as a nutrient than for neutralization of acidity.

The Laterites of lower topographic positions are used for growing rice, banana, coconut and arecanut, and of higher topographic positions, for cocoa, cashew, tea, coffee, rubber, etc. Shifting agriculture is mainly practised in these areas, but the shifting cycle should be of 20 years or more.

3.5. Desert (Arid) Soils

The name Desert/arid is given to the soils supporting negligible vegetation, except xerophytic plants, unless irrigated. Such areas may be observed in cold or hot temperature regime. A large tract of hot arid region, with a growing period of < 60 days in a year is situated in the north-west India (Rajasthan, Gujarat, Haryana and Punjab). It covers an area of about 29 Mha, and poses desertic conditions of geologically recent origin. It differs from other deserts that are cold (in the extreme north, Leh and Ladakh) and tropical (in the south in Karnataka and Andhra Pradesh). The soils of hot arid belt are comparable with those of Alluvial soils, but have an aridic moisture regime. The aeolian action moves and carries the sandy material and deposits it in the direction of wind in the form of a thick mantle of sand at the surface. The sandy material, under arid climatic conditions, results in poor profile development.

3.5.1. Salient Characteristics

The salient characteristics of these soils are:

- These are sandy to loamy fine sand in texture with clay content varying from 3.5% to less than 10%.
- These are pale brown to yellowish brown in colour and are either single grained or have weak subangular blocky structure.
- These are generally poor in nutrient and water-holding capacity
- These are slightly to moderately alkaline in reaction (pH 7.8-9.2) because of their calcareous nature. The calcitic nodules in varying amounts (5-50%), are observed in dispersed form or as a layer; their depth of accumulation varies depending on the rainfall and topographic position.
- These are gypsiferrous in extreme arid areas (such as Bikaner, Jaisalmer) that may form a gypsic horizon. Such gypsiferrous soils need special attention to avoid formation of sink holes, if irrigated.
- These are poor in soil fertility status, especially N, P, K, S, Zn.

3.5.2. Classification

In the Genetic Scheme, the calcareous desertic soils are classified as Pedocal Sierozems or Calcareous Sierozems. The sandy soils of the Thar desert with 300-500 mm rainfall are classified as Grey Brown (Desert) and the more drier, as Desert soils. In general, these sandy soils can also be classified as Regosols within the Order Azonal.

According to Soil Taxonomy, these soils qualify for the Orders: Aridisols (Suborders: Cambids, Calcids, Salids) and Entisols (Suborders: Psamments — the sandy members and Orthents).

3.5.3. Land Use

The major constraint of these soils is less water which restricts their use for raising agricultural crops. However, the Psamments (sandy) member, situated in the interdunal valleys receiving additional rain water as runoff from the surrounding areas, are used for growing a crop (millet or pulse) during monsoon period. The Orthents are used for raising a crop on conserved moisture of monsoon rains. The Gypsids may best be used as pasture land to avoid dissolution of gypsum to form sink holes. If irrigated, all members (except gypsiferous) can be profitably used for growing two crops in a year.

3.6. Forest and Hill Soils

This name is implied for soils developed under any forest cover. In India, the total area under different forest species (tropical, deciduous, coniferous, tropical evergreen) is estimated to be 75 Mha and is observed dominantly in the states of Himachal Pradesh, Jammu and Kashmir, Uttar Pradesh, Uttrakhand, Bihar, Madhya Pradesh, Maharashtra, Kerala and North-East region. While the climatic conditions and altitude control the kind of forest species, the kind of forest and topography control the kind of soils and their degree of profile development. The major soils observed in different forest areas are: Brown Forest and Podsolic (in northern Himalayas) and Red and Lateritic (in the Deccan Plateau). The Himalayan soils have developed on sand-limestone, conglomerates, granite, gneisses and schists under cool/cold (sub) humid climate (acidic environment), and the Deccan Plateau soils are formed on igneous and metamorphic rocks (basalt, granite, gneisses) under (sub) tropical climatic conditions (slightly acidic, neutral or basic environments), and hence differ in their properties.

3.6.1. Podsolic Soils

The soils, found under coniferous vegetation in the presence of acid humus and low base status, show some characteristics associated with Podsols, but because of the unfavourable (non-siliceous) parent material and absence of breaking down of soil minerals in the unsaturated organic acids, the process of podsolization is restricted up to the mobilization of sesquioxides and hence the true podsols in northern Himalayas are not formed. The Podsolic soils have the following characteristics:

- These soils are moderately to strongly acidic in reaction (pH 4.5-6.0).
- These soils are high in organic matter content (3.0-3.5%) and, in general, low (< 50%) in base status.
- These soils are variable in exchange capacity [10-15 cmol(p^+)kg^{-1}]. The clay content varies from 20% to 30%.
- These soils are deficient in phosphorus since it gets precipitated as iron phosphate and aluminium phosphate.

The soils developed under pinus vegetation and cool (sub) humid conditions qualify largely for Alfisols, but those under (per) humid conditions, for Ultisols. The soils on slopes are Inceptisols.

These soils face a major problem of erosion by water. They are used for growing a variety of crops, especially rice, maize, soybean, etc. on terraces and tea and other fruit plants on slopes.

3.6.2. Brown Forest Soils

The other soils, developed on sedimentary rocks and/or alluvium under subhumid to humid climate and mixed vegetation are Non-Calcic Brown or Brown Forest soils. They, in general, possess the following characteristics:

- These are neutral to slightly acidic in reaction (pH 6.0-7.0); the calcareous members under subhumid conditions may have a pH around 8.2.
- These are moderate to high in organic matter content (2-3%) which decreases regularly with depth; they also show biological acitivity.
- These are moderate in cation exchange capacity [15-20 cmol(p^+)kg^{-1} soil] and the exchange complex is almost saturated with bases (70-90%).

The soils key out in the Orders: Inceptisols and Mollisols on stable landforms and as Entisol on eroded surfaces or steep slopes. The aspect and topography play an important role in their evolution and classification. While the north-facing slopes largely support Alfisols and Inceptisols, the south-facing slopes support Mollisols and Inceptisols.

The soils have great potential for growing agricultural crops such as rice, maize and fruit plants, such as apple, almond, pear, apricot, etc.

3.7. Salt Affected Soils

The soils, occurring in the arid and semi-arid regions, are Intrazonal as they are interspersed with the other Zonal dominant soils of the region. According to the estimates of the Central Soil Salinity Research Institute (CSSRI), Karnal, such soils occuppy 10 Mha, of which a major fraction (say 7 Mha) is sodic and occurs in the Indo-Gangetic Plain, followed by the Deccan (Peninsula) Plateau supporting Black soils; the rest (about 20%), in the arid and coastal regions, are saline.

The sodic soils of the Indo-Gangetic Plain, occupy relatively lower topographic positions where products of weathering accumulate during the monsoon rains by surface runoff; evaporates and the soil solution becomes concentrated resulting in increased sodium adsorption ratio (SAR) and hence, increased ESP and pH. The displaced calcium is precipitated at high pH and temperature, as calcium carbonate. The process, repeated over years, results in the formation of sodic soils (Pal *et al.*, 2003). The saline soils of the coastal region result from the rise of brackish underground water due to capillary action under excessive evaporation; the water evaporates leaving the salts at or near the surface depending upon the equilibrium established between leaching and capillary action. The salts precipitate as white efforescence and may qualify for a salic horiozn.

The soils are classified as Solanchaks (saline) and Solonetz (sodic). In terms of Soil Taxonomy, they fit in the Orders of Aridisols, Inceptisols, Alfisols and Vertisols, depending upon the profile development.

The sodic soils pose serious problems of high sodium on the exchange complex, poor physical conditions, especially soil structure and drainage, nutrient and water availability and micronutrient deficiency. Another problem is of receding groundwater in the central sectors and the south-west sectors of Punjab, Haryana and some parts of Rajasthan. The rise in groundwater causes salinization of soils and the farmers are obliged to switch over to growing rice and eucalyptus in areas whch till recently were used for raising cotton and citrus plantation.

Despite many limitations, the sodic soils, once ameliorated by applying gypsum , are used successfully for growing rice, followed by wheat. The amount of gypsum, required for their amelioration would depend on sodium on the exchange complex (ESP). In saline soils, having high and brackish groundwater, the objective is to reduce the soluble salts by leaching with fresh water and introduction of drainage network in order to bring the salts within the safe limit for growing crops. The presence of gypsum in such soils eliminates dispersion of clay during the amelioration process.

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Chapter 4

Soil Survey and Mapping

P.K. SHARMA and DIPAK SARKAR

1. Introduction

Soil science today embraces the knowledge about soils accumulated mostly during the past 60 to 90 years. Thousands of different kinds of soils exist in the world. Their properties differ from place to place because of the interaction of various soil forming factors and processes in their evolution. Soil scientists strive to recognize and understand the soils in nature. The soil in this chapter is a natural body comprised of solids (minerals and organic matter), liquid and gases that occur on the land surface, occupies space and is characterized by one or both of the following : horizons or layers that are distinguishable from the initial material as a result of additions, losses, translocation and transformation of energy and matter or the ability to support rooted plants in a natural environment.

The upper limit of soil is a boundary between soil and air, shallow water, live plants or plant materials that have not begun to decompose. Areas are not considered to have soil if the surface is permanently covered by water too deep (typically more than 2.5 m) for the growth of rooted plants. The lower boundary that separates soil from non-soil matter underneath is difficult to define.

Good cultivable lands are not only limited but differ also in their production potential. The soil variability within a village, district or state influences the use of soils for different purposes. In order to make optimum use of our limited soil resources, we need detailed information about their characteristics, kinds, and distribution on landscape. This information is collected through soil survey and mapping.

Soil surveys began in 1899. These surveys were simple at that time and were intended to answer practical agronomic questions about soil differences and limitations which were important for improving and expanding crop production. The soil surveys expanded in details and concept with advances in the scientific knowledge and demand for more useful information.

2. Objectives of Soil Survey

The broad general objectives of a soil survey could be grouped as fundamental and applied:

- Fundamentally, a soil survey helps in gathering information about the properties, genesis, classification and nomenclature of soils.
- The applied aspect in a soil survey includes interpretation of soil data for use in agriculture, forestry, recreational purposes, urban, industrial and pasture development, etc.

Both the fundamental as well as applied objectives are pursued with equal emphasis during a soil survey. Soil surveys are planned in such a way so as to provide information about soils to different users.

3. Uses of Soil Survey

Soil surveys are of great significance to any nation as they provide inventory of soil resources. Major uses of soil surveys are indicated below:

(i) They provide information for the development of land use plans for both arable and non-arable lands and for predicting the long-term effects of a particular land use on environment.

(ii) They help in predicting the adaptability of identified soils to various uses and also their behaviour and productivity under defined sets of management practices.

(iii) Soil resource inventory helps in recognising the areas having constraints like salinity, alkalinity, acidity, erosion, waterlogging, flooding, and also in taking suitable measures for their management.

(iv) Soil information generated through soil surveys is useful for land settlement, tax appraisal, locating and designing highways, airports and other engineering structures.

In short, soil surveys provide information about the soils of a country and form the basis for land use planning.

4. Characteristics of Soil Survey

Soil surveys are basically of two types:

(i) single purpose soil surveys, and

(ii) standard soil surveys.

4.1. Single Purpose Soil Surveys

These are designed for a specific objective with limited applications such as soil fertility appraisal, crop suitability, soil conservation, soil erosion assessment, irrigation suitability, land settlement, trafficability, revenue and taxation.

4.2. Standard Soil Surveys

These involve comprehensive data collection about soils and lands in such a manner that these could be used for a variety of purposes and encompass most of the single purpose soil surveys.

A standard soil survey involves a series of interlinked activities, some of which are mentioned below.

- Study of important characteristics of soils and the associated external land features such as landform, natural vegetation, and slope.
- Laboratory analyses of soils to support and supplement the field observations.
- Correlation and classification of soils according to the standard system of classification.
- Mapping of soils, that is drawing and fixing soil boundaries of different kinds of soils on a standard base map.
- Transfer of agrotechnology through soil taxa which serves as a wheel for such transfers.

5. Practical Difficulties Encountered in Soil Survey

A soil surveyor's task is difficult and he/she is encountered with several practical constraints, as mentioned below.

- The distribution of different soils may be so complex in a field or may occupy so small areas that their delineation on a map, at any practical scale, becomes difficult.
- It is difficult to follow the geographic boundaries of soils because of the vegetative cover and their hidden nature.
- Soil survey and mapping are expensive and many developing nations may not afford them unless they serve the practical needs.
- The inaccessibility of certain areas because of transportation problems may restrict the number of sampling points.

6. Base Maps

Irrespective of the type of soil surveys, a fundamental requirement of all mapping activities is a suitable base map. These base maps need to be complete in details of features and accurate in their location to enable the surveyor to delineate soil boundaries more correctly and conveniently. Depending on the intensity of mapping, following types of base maps are used for soil surveys in India and in many other countries.

6.1. Cadastral Maps

Cadastral maps on the scale of 1:2640 (24" = 1 mile) to 1:7920 (8" = 1 mile) or 1:15,840 (4" = 1 mile) in plain areas and 1:1200 (52.8" = 1 mile) in hilly areas are used for detailed mapping. Cadastral maps show field boundaries and field or revenue survey number; however, they lack topographical details (contours, elevations, etc.).

One advantage of using cadastral base is that the soil survey information or interpretations can be communicated to individual farmers by reference to the field survey number. The cadastral maps can be procured from the village revenue official (*Patwari*) or concerned district revenue officer (*Tehsildar*).

6.2. Topographical Maps

Topographical maps are published on the scale of 1:25,000, 1:50,000 and 1:250,000. These are used as base maps for various types of soil surveys in India. Earlier, the scale of these maps used to be four inch to a mile (1:253,440), one inch to a mile (1:63,360) or even two inch to a mile (1:31,680).

Topographical maps show physical features and contain topographical details also in the form of contours and elevations above the mean sea level for Survey of India benchmarks. These maps have reliable planimetric accuracy facilitating measurement of distances and easy preparation of soil map. In India, topographical maps are prepared and published by the Survey of India, Dehradun, and can be obtained from its head office at Hathibarkala, Dehradun or its regional offices.

6.3. Aerial Photographs

Aerial photographs are the pictures taken by camera fitted in an aircraft and flying over the terrain at a predetermined height, depending on the scale of aerial photography and focal length of camera. Aerial photographs give a bird's eye view of large areas. Typically, successive photographs contain 50 to 65% overlap which is essential for stereoscopic viewing and analysis of stereo pairs. The aerial photographs ranging in scale from 1:8000 to 1:60,000 are used in different types of soil surveys.

In soil surveys, we mostly use panchromatic black and white air photos taken with a black and white film. In these photographs, there are many shades of grey colour. The black and white air photos can indicate lot of information about land forms, vegetation, human interference as well as soils. Natural colour and infrared films are also used for aerial photography, especially for forest areas to discriminate forest types/species.

Relief can be perceived by stereoscopic study of aerial photographs. Relief features help in identifying various kinds of landforms which are related to different types of soils. Many landforms, e.g. terraces, flood plains, sand dunes, coastal plains, plateaus, palaeochannels, hills, valleys and mountains can be recognised on the photographs from their shapes, relative heights and slopes. Differences in tone or colour may also reflect soil differences.

When we look at an aerial photograph, we can see various objects of different sizes and shapes. Some of these objects may be readily identifiable while others may not be, depending on the interpreter's perception and experience. Individual objects like trees, houses, roads, foot paths, field boundaries, lakes, river courses, etc. are imaged clearly depending on the scale of photographs. These 'landmarks' serve as effective 'reference points' or 'local control points' that facilitate a soil surveyor in orientation and navigation during the field work and in demarcating soil boundaries of high 'local accuracy'. Base maps for publication can be prepared from the aerial photographs economically and in a reasonable time.

Both speed and accuracy of soil mapping are increased on using aerial photographs as the mapping base. However, field work cannot be eliminated, the soils must be examined to a depth of 1 to 2 metres or to the depth of solid rocks as the soils are hidden below the surface beyond the present reach of most remote sensors (cameras or scanners).

Aerial photographs have some limitations also in soil survey and mapping. Elevations are not shown on the photographs. Scale is not precisely uniform and the differences of scale between adjoining photographs create some difficulties in matching and transferring of soil boundaries. Distances and directions cannot be measured as accurately as on topographical maps. Nevertheless, the advantages of aerial photographs generally outweigh the limitations and make them a valuable tool for soil mapping.

6.4. Remote Sensing

Remote sensing is the science of obtaining information about objects or phenomenon in the environment through the use of sensing devices located at a distance without any physical contact between the object and the sensing device. Electromagnetic energy is the means by which information is transmitted from an object to the sensor. The interaction of electromagnetic waves with natural surfaces and atmosphere is highly dependent on the frequency of waves. Waves in different spectral bands (e.g. microwave, infrared and visible regions) tend to excite different interaction mechanisms such as electronic, molecular or conductive.

The Sun's energy commonly referred to as electromagnetic spectrum (EMS), is an electromagnetic radiation characterized by wavelength or frequency. When the radiation is incident on matter, it can be reflected, scattered, absorbed or transmitted. All the processes are strongly dependent on the wavelength of the incident radiation as well as the atomic and molecular structure of the material and its condition. The interaction between the radiation and the object of interest (e.g. soil, land, water, vegetation, crop, snow, building, etc.) conveys information on the nature of the object. This is possible by measuring electromagnetic radiations which are reflected/scattered or emitted by an object using sensing devices. Different objects behave differently and return different amount and kind of radiant energy, depending on the surface conditions, reflection coefficient, emittance, and roughness.

Earth orbiting satellites equipped with sensors, including cameras provide analogue (imagery) and digital data. Sensors used for remote sensing can be broadly classified as those operating in the Optical-Infrared (OIR) region and those operating in the Microwave region. These can be further sub-divided into 'passive' and 'active' sensors. The sensors which sense the reflected/scattered/emitted radiation from the Earth's surface are *passive sensors* and those which illuminate the targets with their own energy and then measure the scattered or reflected radiations from the targets are called *active sensors*. The active and passive sensors could be classified as imaging sensors and non-imaging sensors. Imaging sensors provide data which has one to one correspondence with several locations in a given area on the ground surface, whereas non-imaging sensors provide data which is the average value over a given area. In other words, an imaging sensor provides a picture, whereas a non-imaging sensor provides a numerical value. The non-photographic imaging sensors can perceive the part of EMS from ultraviolet (wavelength less than 0.38 micrometre) through microwave to the upper wavelength of 100 cm. Remote sensing technology makes use of visible (0.4-0.7 μm), infrared (0.7-3.0 μm), thermal infrared (3-5 μm and 8-14 μm) and microwave (0.1-3.0 cm) regions of EMS to collect information about various objects on the Earth's surface.

Satellite data from Indian and foreign satellites are being used for soil mapping by many national and state agencies in India. Before the launch of first Earth Resource Technology Satellite (ERST-1) in 1972 by the USA (later renamed as Landsat-1), aerial photographs were used as a remote sensing tool for soil mapping. India has well conceived the earth resource satellite programme. Till date (September, 2008), Indian Space Research Organization (ISRO) has launched fourteen Indian Remote Sensing Satellites (IRS) starting with IRS-1A in March 1988, followed by IRS-1B in August 1991, IRS-1E in September 1993 (Satellite could not be placed in orbit), IRS-P2 in October 1994, IRS-1C in December 1995, IRS-P3 in March 1996, IRS-1D in September 1997, IRS-P4 in May 1999; Technology Experiment Satellite (TES) in October 2001, RESOURCESAT-1 (IRS-P6) in October, 2003, Cartosat-1 in May, 2005, Cartosat-2 in January, 2007, Cartosat-2A and Indian Mini Satellite (IMS-1) on 28th April, 2008. The Cartosats 2 & 2A together will help in providing more frequent revisits.

Remote sensing satellites are polar-orbiting and encircle the earth passing over or near to the north or south poles. These are launched in the near polar, sun synchronous orbits, i.e.

satellite always crosses the Equator precisely at the same local time. Indian remote sensing satellites (IRS-1D & P6) launched at an altitude of 817 km with an inclination of 98.7° in the descending mode cross the Equator at 10:30 AM ± 5 minutes. The Indian remote sensing satellite (IRS-P6) takes 101.35 minutes to complete one revolution around the earth and thus completes about 14 orbits a day. The entire earth is covered in 341 orbits during a 24-day cycle. Earlier, the planned life of satellites was three years, but it is five to seven years presently.

A large number of visible and infrared imaging sensors have been flown into space to study the earth. The imaging systems are divided into three general categories: (a) framing camera systems, e.g. Landsat RBV (Return Beam Vidicon) and Shuttle Large Format Camera, (b) scanning systems, e.g. Landsat Multi Spectral Scanner (MSS) and Thematic Mapper (TM), and (c) Pushbroom Imagers as in IRS (Indian Satellite) and SPOT (French satellite) cameras. The Pushbroom Imagers delete the scanning mechanism and use a linear array of detectors to cover all the pixels in the across-track dimension. The ground segment sensed at any instant by individual detector element of Charge Coupled Devices (CCDs) is called the Ground Resolution Element (GRE) or ground resolution cell and its representation on the computer screen is called as PIXEL (Picture-element).

The digital image consists of tiny equal areas or picture elements (Pixels) arranged in regular lines and columns. Size of a pixel depends on the Instantaneous Field of View (IFOV) of sensor, e.g. 23.5 m × 23.5 m in the case of IRS LISS-III (Linear Imaging Self Scanner-3) and 5.8 m × 5.8 m in IRS LISS-IV. The brightness of each pixel has a numerical value ranging from zero (black) and some higher number of white, i.e. 127 or 255 for 7 bit and 8 bit radiometric resolution, respectively. Radiometric resolution is a measure of the capability of the sensor to differentiate the smallest change in the spectral reflectance/emittance between various targets/objects.

The relative intensities of light reflected from objects and features on the Earth's surface, has its distinctive band pattern or "spectral signature". In reference to these properties, it is possible to identify and classify objects by measuring the strength of light reflected from the surface. The radiation from the scene or a particular area that a remote sensor detects is measured as radiance not reflectance.

The spatial and spectral resolutions are important sensor parameters from the point of view of resource surveys. The *Spatial resolution* refers to the size of the smallest object or area that can be discriminated by the sensors. Instantaneous Field of View (IFOV) of the sensor defines the ground resolution of multispectral scanner (e.g. 23.5 m for IRS-P6 LISS-III sensor); on the other hand, *Spectral resolution* is a measure of the discreetness of spectral bands and the sensitivity of the sensor to distinguish between grey levels. The narrow spectral band (e.g. 0.52 – 0.59 μm) in which the image is taken, allows us to observe certain features more prominently.

RESOURCESAT-1 (IRS-P6), the tenth satellite in IRS series launched in October, 2003 helped not only in continuing the remote sensing data services made available by the IRS-1C and IRS-1D, but enhanced also the remote sensing services by providing imagery with improved spatial resolution and additional spectral bands. Resourcesat-1 carries the following three imaging sensors operating on the 'Pushbroom Scanning' concept using linear arrays of Charge Couple Devices (CCDs):

(i) A high resolution Linear Imaging Self Scanner (LISS-IV) operating in mono and multispectral mode. In multispectral mode, data is collected in three spectral bands, two in visible (0.52-0.59, 0.62-0.68 μm) and one in near infrared (0.77-0.86 μm) region (VNIR) with 5.8 metre spatial resolution LISS-IV camera is steerable up to ± 26 degree across the track to obtain stereoscopic imagery and achieve five-day revisit capability. In multispectral mode, sensor provides data corresponding to pre-selected 4096 contiguous pixels (out of full 12k pixels) using electronic scanning scheme corresponding to 23.9 km swath. On the other hand, in mono mode, the data of full 12k pixels of any one selected band corresponding to a swath of 70 km can be transmitted.

(ii) A medium resolution LISS-III camera operating in four spectral bands, three in visible and near infrared (VNIR) regions (as in LISS-IV sensor above) and one in short wave infrared (SWIR) region (1.55 – 1.70 µm). It has a 24-day revisit cycle with 23.5 metre spatial resolution and four CCD arrays (one for each spectral band) with 6,000 detector elements to record the data. Each detector element records the data for each pixel of 23.5 m, resulting in a swath of 141 km (23.5 m × 6,000 = 1,41,000 m or 141 km).

(iii) An advanced wide field sensor (AWiFS) operating in four spectral bands, three in VNIR and one in SWIR region (as in LISS-III camera) with 56 metre spatial resolution, 5-day revisit cycle and a swath of 740 km.

RESOURCESAT-1 also carried a solid state recorder with a capacity of 120 giga bytes to store the images taken by its cameras which could be read out later to the ground stations.

Imaging from space has two important advantages; firstly, a large area (thousands of square kilometres) can be examined from a single point in the orbit (IRS-1D/P6-LISS-III scene covers an area of 141 km×141 km); secondly, any area can be repeatedly examined on a regular basis for monitoring.

Remote sensing technology provides, accurate, timely and cost-effective information on natural resources. The medium resolution IRS LISS-III (23.5 m) or Landsat TM (30 m) data (digital and analogue), serves as an excellent base for 1:50,000 scale mapping at the district level. The coarse resolution AWiFs (56m) or Landsat MSS (79 m) data can be used as a base map for reconnaissance soil surveys for regional level planning. The high resolution (5.8 m) multispectral data from LISS-IV sensor on board RESOURCESAT-1 (IRS-P6) is useful for detailed and intensive soil surveys. The stereoscopic imagery from IRS-P6 LISS-IV sensor can help in delineating various land forms, micro-depressions, sloping lands, erosion types and drainage pattern and thus facilitates the delineation of boundaries between various soil types.

The availability of high resolution data from WorldView-1 (0.55 m panchromatic-PAN); Quick Bird 1 & 2 (0.61 m PAN; 2.5 m Multispectral-Mx); Orb View 3 & 4 and IKONOS 1 & 2 (1.0 m, PAN; 4.0 m, Mx) of USA and Indian satellites, namely Cartosat-1 (2.5 m PAN) and Cartosat 2 & 2A (around 1.0 m – PAN) enables the generation of cartographic quality products as an alternative to aerial photographs. The high resolution single band (0.5 – 0.75 µm) Panchromatic data from Cartosat 1, 2 & 2A as well as Multispectral and Panchromatic data from Quick Bird 1 & 2, Orb View 3 & 4 and IKONOS 1 & 2 is an asset for cartographic applications at the village level and highly intensive soil surveys.

The high resolution black and white imagery (single band panchromatic from Cartosat 1, 2 & 2A) and False Colour Composites (multispectral data of IRS-P6 LISS-IV sensor) on 1:12,500 or larger scale serve as an excellent base map for large scale mapping as individual fields, field roads, individual trees and well locations, are clearly imaged which serve as effective 'reference points' or local control points during the field work and in demarcating soil boundaries of high local accuracy. The satellite data have the same limitations for soil surveys as in aerial photography, but no difference in scale.

Data from IRS satellites is received, processed and distributed to various users in India by the National Remote Sensing Centre (NRSC), Department of Space (DOS), Hyderabad. The NRSC Data Reception Station at Shadnagar (near Hyderabad) receives data from IRS satellites as well as from foreign satellites (NOAA of USA, ERS 1&2 of European Space Agency). The IRS data is also available to the international users under an agreement between the Antrix Corporation of the Department of Space and the Space Imaging, USA, through a network of ground stations. The National Remote Sensing Centre and Antrix Corporation supply Panchromatic (black & white) and Multispectral (Mx), digital and analog data to various users in India and abroad.

7. Examination and Description of Soils

During field operations, soils are studied by examining the soil material removed by an auger or sampling tube. The soils can also be studied by digging minipits up to 0.50 m depth and going below to a depth of 1.5-2.0 metre through augering. The samples of soils are studied for their colour, texture, consistence, mottling, concretions, pH, and effervescence.

Important properties of a pedon are not clearly observable in the small sample extracted with auger due to mixing, and detailed study of the entire pedon is needed. The study of pedon is based on the examination of a soil profile.

7.1. Soil Profile

A soil profile is a vertical section of soil up to a depth of 1.5-2.0 metres in deep soils (Figure 1). In the case of shallow soils, the vertical cut is made up to bedrock or up to water table in the case of waterlogged soils. Width of profile ranges from 1 metre to several metres. Road cuts or brick kiln or querry sites are several metres wide which can be examined for clear perception of soil properties of a pedon. The description on the entire pedon or a sample within it, should record the kinds of depth and thickness and properties layer. Horizons or layers are studied in horizontal and vertical dimensions.

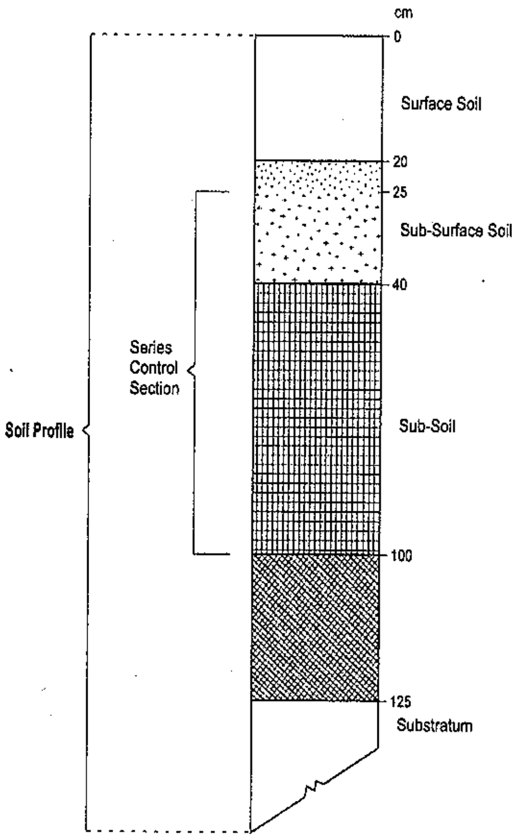


Figure 1. A soil profile

7.2. Soil Horizon

A soil horizon is a layer approximately parallel to the surface of soil, identifiable from adjacent layers by a distinctive set of properties produced by the soil forming processes over a period of time. In soils, where genetic horizons are not developed as in flood plain or sand dune soils and the properties are mostly inherited from the parent material, the term 'layer' instead of 'horizon' is used. The solum (plural sola) of a soil consists of a set of horizons that are related through the same cycle of pedogenic processes. The horizons above the parent material are collectively regarded as solum.

For selecting a profile site, following points should be considered:

- It should be typical of the soil taxa (soil series or families) within the mapping unit,
- It should be away from a tree, an irrigation channel/ditch/river, human settlements and road, as these prevent/obliterate the normal development of a soil
- If possible, a virgin area should be preferred.

8. Map Units

A soil map delineates the areas occupied by different kinds of soils, each of which has a unique set of inter-related properties, characteristic of material from which it was formed, its environment and history. A map unit is a collection of soil components or miscellaneous areas or both. Each map unit differs in some respect from all others in a survey area and is uniquely identified on a soil map. Map units consist of one or more components. An individual component of a map unit represents the collection of polypedons or parts of polypedons that are members of the taxon or a kind of miscellaneous area (inclusion). Soil boundaries are shown on maps by lines. The area enclosed by a boundary is called a "soil delineation".

A map unit consists of all soil delineations which are identified by a unique symbol, colour or name. There are always several map units on a map and an organised list of map unit symbols, colours and names is called map legend.

8.1. Taxonomic Units versus Map Units

The examination of soils in the field and laboratory provides the basis for placing them into taxonomic and mapping units.

Taxonomic units define the specific ranges of soil properties in relationship to the total range of properties measured in the soil. The map units and their individual delineations define areas on a landscape. Almost every map unit has more than one taxonomic units (soil series or phases of soil series, soil families or other taxa).

A *soil series* is a taxonomic unit which represents a group of soils having horizons similar in characteristics and arrangement in a soil profile developed from a particular type of parent material, but they may differ in the surface texture. It is given a geographical name of either the locality where it is well developed or the place where it is recognized first.

Soil phase is a subdivision of a soil series or any other taxa in respect of surface soil texture, degree of erosion, stoniness/rockiness and salinity/sodicity. All these aspects have practical significance in agricultural and engineering interpretations.

8.2. Inclusions within Map Units

In all soil surveys, virtually every delineation of a map unit includes areas of soil components or miscellaneous areas (inclusions) that are not identified in the name of the map unit. Many areas of these components are too small to be delineated separately.

Inclusions reduce the homogeneity of map units and may affect interpretations.

8.3. Kinds of Map Units

Four kinds of map units are used in soil surveys to show the relationships of different soils on the landscape. These are: consociations, complexes, associations, and undifferentiated groups.

8.3.1. Consociation

In a consociation, delineated areas are dominated by a single soil taxon. As a rule, at least one-half of the pedons in each delineation of a soil consociation are of the same soil components that provide the name for the map unit.

8.3.2. Complexes and Associations

Complexes and associations consist of two or more dissimilar components occurring in a regularly repeating pattern. In each delineation of either a complex or an association, each major component is normally present, though their proportions may vary appreciably from one delineation to another.

8.3.3. Undifferentiated Groups

Undifferentiated groups consist of two or more taxa components that are not consistently associated geographically and therefore do not always occur together in the same map delineation. These taxa are included as the same named map unit because use and management are the same or very similar for common uses.

8.4. Naming of Map Units

Map units or groups of map units can be given any name derived from any discipline, one may call a map unit "alluvial soils", 'forest soils', "mountain soils". To be more specific one has to refer *Soil Taxonomy* (Soil Survey Staff, 1975; 1999) or *Keys to Soil Taxonomy* (Soil Survey Staff, 1990; 2003) for map unit names, for example the name "Ustept" could be used to identify a suborder of the order Inceptisol. The objectives of a survey determine the kind of map units and the taxonomic level used to identify components of map units. For example, the name Ludhiana sandy loam, 0-1% slope indicates that the soils of Ludhiana series (a Ustept) are dominant in that mapping unit.

The names of taxa of higher categories that is, suborder (Ustept), great group (Haplustept), subgroup (Typic Haplustept), family (Coarse loamy Typic Haplustept) are also used in map unit names, especially on small scale maps.

9. Kinds of Soil Surveys

All soil surveys are conducted by examining, describing and classifying soils in the field and delineating their areas on the maps. Soil Survey Manual (Soil Survey Staff, 1951; 1993) and Soil Survey Manual of All India Soil and Land Use Survey (AISLUS, 1971) recognize the following three types of surveys, depending on the objectives, methods, types of base material, intensity of field survey and type of map units:

(1) Detailed surveys
(2) Reconnaissance surveys
(3) Detailed - Reconnaissance surveys

To these major kinds, *semi-detailed* and *exploratory or rapid reconnaissance* surveys were added later, these surveys lead to small scale soil maps needed for macro-level planning.

The relationship between scale of soil map and frequency of observations in different kinds of surveys is described in Table 1 and the details of each type of survey are as follows:

9.1. Detailed Survey

In the detailed soil map, the boundaries between mapping units are plotted on base maps (cadastral) or aerial photographs or satellite imagery (high resolution panchromatic data) from observations made throughout their course.

Cadastral maps on 1:2640, 1:7,920 or 1:15,840 scale and aerial photographs on

Table 1. Relationship of scale of soil map and frequency of field observations

Kind of survey	Scale of base map	Area represented by 1 cm^2 on map (ha)	Distance between field observations	Frequency of observation	Mapping unit	Field procedure and accuracy of soil boundaries
Rapid Reconnaissance/ extensive (for selection of area for more intensive study)	1:1,000,000 or smaller	10,000	10 km	1 in 10,000 ha	Phases of soil great groups	Soil identification is done by traversing representative areas to determine soil pattern and composition of map units. Boundaries are plotted mostly by interpretation of remotely sensed data.
Reconnaissance (for regional planning)	1:250,000 1:100,000	625 100	2.5 km 1.0 km	1 in 625 ha 1 in 100 ha Alet	Phases of association of soil series families/great groups	Soil identification is done by traversing sample strips, boundaries plotted by interpretation of remotely sensed data and verified by random observations.
Semi-detailed (for district planning)	1:50,000	25	500 m	1 in 25 ha	Phases of soil series/association of soil series/families	Boundaries in each delineation of sample areas are identified by actual traversing
Detailed (for village/watershed planning)						
• Low intensity	1:10,000	1	100 m	1 per ha	Phases of soil series	Almost all boundaries are checked by actual traversing; remote sensing data are used as an aid in boundary delineation
• High intensity	1:5,000	0.25	50 m	4 per ha	Phases of soil series	All boundaries are checked by actual traversing

1:8,000 to 1:15,000 scale and satellite data on 1:12,500 scale are used, depending on the intensity of survey and the agricultural development needs of an area. Mapping units of this survey are narrowly defined phases of soil series (*refer* Table 1 for more details).

In detailed soil surveys, the maximum distance between route or traverses is 250 m or even closer (50-100 m), depending upon the scale of the map and the complexity of the soil pattern. Although soil boundaries are not actually traversed, they are plotted based on the observations made throughout their courses.

Detailed soil surveys furnish information needed for the proper assessment of soil properties, terrain features, erosional aspects and related factors. Such surveys are time consuming, expensive and are recommended only for priority areas such as pilot projects, agricultural research stations, agricultural farms, micro-watersheds and for areas earmarked for urban development.

9.2. Reconnaissance Survey

This type of survey is undertaken to prepare soil resource inventory of large areas. They furnish information to precede detailed or semi-detailed soil surveys. On a reconnaissance soil map, boundaries between the mapping units are plotted from soil observations made through augar sampling at an interval of 2.5 km to 1 km. The representative profiles of various soils are studied at an interval of 3-6 km or even shorter, depending on the soil heterogeneity or variability. In reconnaissance soil survey, maps are prepared relatively at smaller scale, ranging from 1:250,000 to 1:100,000 depending on the purpose. However, field mapping is frequently done at 1:250,000 or 1:50,000 scale in order to use topographical maps, aerial photographs or satellite imagery for the delineation of land types and planning of field traverses. At reconnaissance level, association of soil series, families and great groups are mapped. The variations in the land type, land use, tone and texture, as observed in aerial photographs or satellite imagery, are used as the basis for boundary delineation.

9.2.1. Rapid Reconnaissance Survey

In a rapid reconnaissance survey, field mapping is done at 1:1,000,000 or still smaller scale using the satellite imagery. Soils are mapped by traversing representative areas. The mapping units are phases of great groups.

9.3. Detailed-Reconnaissance Survey

The detailed reconnaissance survey is not really a separate kind but in this type of survey, a part of the area is covered by detailed survey and the remaining by reconnaissance survey.

It is carried out in individual areas best suited to each of these types. A reconnaissance survey is carried out over an area having limited potentialities for intensive development, in the usual way classifying and grouping the soils into soil series, or association of soil series as necessary, followed by mapping. The remaining areas which show potentialities for priority attention are covered by detailed or high intensity surveys in the standard pattern.

9.4. Semi-Detailed Survey

This survey comprises a highly detailed study of some selected sample strips cutting across many physiographic units and soils. Once the correlation between soils and physiographic units is developed, the rest of the area is checked at random and soil boundaries based on physiographic units are delineated. This kind of survey provides sufficient information about various kinds of soils including problematic or degraded soils. Scale of base maps (aerial photographs or satellite imagery) used is 1:50,000. Mapping unit is the association of soil series or families. The final maps are prepared on 1:50,000 scale.

10. Orders of Soil Survey

Every soil survey is undertaken with a purpose or a set of purposes in mind. Some soil surveys are made to serve users who need precise information about the soil resources of an area, a few hectares or less in size. These surveys require refined distinctions among small, homogeneous areas of soils. Some other surveys are made for users who need a broad perspective of heterogeneous, but distinctive areas of thousands of hectares.

Different intensities of field study and different degrees of details in mapping produce a wide range of soil surveys. The *USDA Soil Survey Manual* (Soil Survey Staff, 1993) recognizes five orders of soil survey. The order of a soil survey is a consequence of field procedures, the minimum size of delineation, and the kinds of map units that are used. The brief details of each type of survey are given in Table 2 (Key for identifying orders of soil survey).

11. Soil Survey and Mapping Procedure

The soil survey methods have undergone large changes during the recent past with the availability of satellite imagery, apart from topographical maps and aerial photographs.

The soil survey and mapping involve the following steps:

(a) Preliminary reconnaissance of the area to investigate the major soils and their pattern of occurrence.

(b) Procurement of required base maps. Aerial photographs, satellite imagery, topographical and other maps are useful references and are used as the mapping base.

(c) Preparation of mapping legend based on the preliminary field studies. The mapping legend is modified as the survey progresses.

(d) Stereoscopic study of aerial photographs and interpretation of satellite imagery or digital data for the identification and delineation of land forms (hills, valleys, terraces, flood plains, coastal plains and sand dunes) and their sub-divisions based on the differences in tone, relief and vegetation. The differences in tone or colour serve as the basis for drawing tentative boundaries and for predicting types of soils. The predictions are verified in the field, but preliminary interpretation can increase the quality of mapping.

(e) The soils are examined at some standard interval along the traverse to locate important differences in soil properties. Interval between traverses and soil observation points cannot be specified. It depends on the scale of mapping and variability of soil properties (Tables 1 and 2 provide some guidelines).

(f) *Plotting of Soil Boundaries*: Some soil boundaries are sharply defined, others are plotted as lines mid-way in zones of gradual transition from one soil to another. The predicted boundaries are checked throughout their course in high intensity surveys and in other cases, the boundaries are plotted mostly by interpretation of remotely-sensed data and verified with some observations.

(g) Classification of soils and naming of map units based on the morphological, physical and chemical properties of soils forming the map unit.

(h) Preparation of final legend and finalization of soil map.

12. Examination and Description of Soil Profile

Different layers or horizons are marked on the basis of characteristics that can be visually observed or measured in the field, such as colour, texture, structure, consistence and presence of carbonates. Each horizon is described for the following characteristics:

(i) Horizon symbol

(ii) Depth of each horizon/layer (cm)

(iii) Soil colour under wet, moist or dry conditions

(iv) Mottling

(v) Soil texture

(vi) Soil structure

(vii) Soil consistence under dry, moist and wet conditions

(viii) Cutans (ped coatings), pressure faces, and slickensides

(ix) Nodules/concretions and cementation

(x) Content of carbonates, and soluble salts

(xi) Roots

(xii) Nature of the boundary with the horizon below

(xiii) pH

(xiv) Hard pans

(xv) Pores

(xvi) Lithorelics

(xvii) Artefacts (pottery pieces)

(xviii) Features of biological origin

Table 2. Key for identifying kinds of soil surveys

Level of data needed	Field procedures	Land area represented by the minimum size delineation (ha)[1]	Typical components of map units	Kinds of map units[2]	Appropriate scales for field mapping and publication
1st order- Very intensive (i.e. experimental plots individual building sites)	The soils in each delineation are identified by transecting or traversing. Soil boundaries are observed throughout their lengths. Remotely-sensed data are used as an aid in boundary delineation.	1 or less	Phases of soil series; miscellaneous areas	Mostly consociations; some complexes	1:15,840 or larger
2nd order - Intensive (i.e. general agriculture, urban planning)	The soils in each delineation are identified by transecting or traversing. Soil boundaries are plotted by observation and interpretation of remotely-sensed data. Boundaries are verified at closely spaced intervals.	0.6 to 4	Phases of soil series; misc. areas; few named at a level above the series	Consociations and complexes; some associations and undifferentiated groups	1:12,000 to 1:31,680
3rd order - Extensive (i.e. range land, forest land, community planning)	The soils are identified by transecting representative areas and by some transects. Boundaries are plotted mostly by interpretation of remotely-sensed data and verified with some observations.	1.6 to 16	Phases of soil series or texa above the series; misc. areas	Mostly associations or complexes; some consociations and undifferentiated groups	1:20,000 to 1:50,000 or 1:63,360
4th order - Extensive (i.e. regional land use planning)	The soils are identified by transecting representative areas to determine soil patterns and composition of map units. Soil boundaries plotted by interpretation of remotely-sensed data.	16 to 252	Phases of levels above the series; misc. areas	Mostly associations; some consociations, complexes and undifferentiated groups	1:50,000 to 1:250,000
5th order - Very extensive (i.e. selection of areas for more intensive study)	The soil patterns and composition of map units are determined by mapping representative areas and applying the information to like areas by interpretation of remotely-sensed data. Soils are verified by occasional onsite investigation or by traversing.	252 to 4,000	Phases of levels above the series; misc. areas	Associations; some consociations, and undifferentiated groups	1:250,000 to 1:1,000,000 or smaller

1. This is about the smallest delineation allowable for readable soil maps. In practice, the minimum size delineations are generally larger than the minimum size shown.
2. Where applicable, all kinds of map units (consociations, complexes, associations, undifferentiated groups) can be used in any order of soil survey.

The description of profile and site characteristics which are used as criteria for placing different soils in various texa in Soil Taxonomy are discussed in *Soil Survey Manual* (Soil Survey Staff, 1993); NBSS & LUP *Field Manual* (Sehgal *et al.*, 1987); and NBSS&LUP *Technical Bulletin* (Sehgal, 1992).

12.1. Horizon Designations

The capital letters O, L, A, E, B, C, R and W represent the master horizons and layers of soils. The letters are the base symbols to which other characters are added to complete the designations. Most horizons and layers are given a single capital letter symbol; some require two.

12.1.1. O-horizons

O-horizons are layers dominated by the organic material. Some of these layers have been saturated with water for long periods or were once saturated but are now artificially drained; others have never been saturated.

12.1.2. L-Horizons or Layers

Limnic horizons or layers include both organic and mineral limnic materials that were either (i) deposited in water by precipitation or through the actions of aquatic organisms, such as algae and diatoms, or (ii) derived from underwater and floating aquatic plants and were subsequently modified by the aquatic animals.

12.1.3. A-Horizons

A-horizons constitute mineral horizons that are formed at the surface or below an O-horizon. These exhibit obliteration of all or much of the original rock structure and show one or more of the following : (a) an accumulation of humified organic matter intimately mixed with the mineral fraction and not dominated by properties characteristic of E- or B-horizons (defined below) or (b) properties resulting from cultivation, pasturing or similar kinds of disturbances.

12.1.4. E-Horizons

E-horizons are mineral horizons in which the main feature is the loss of silicate clay, iron, aluminum or some combinations of these, leaving a concentration of sand and silt particles. These horizons exhibit obliteration of all or much of the original rock structure.

12.1.5. B-Horizons

These horizons are formed below an A, E or O-horizon and are dominated by obliteration of all or much of the original rock structure and show one or more of the following characteristics:

(i) Illuvial concentration of silicate clay, iron, aluminum, humus, carbonates, gypsum or silica, alone or in combination,

(ii) Evidence of removal or addition of carbonates,

(iii) Residual concentration of oxides,

(iv) Coatings of sesquioxides that make the horizon conspicuously lower in colour value, higher in chroma, or redder in hue than overlying and underlying horizons, without apparent illuviation of iron,

(v) Alteration that forms silicate clay or liberates oxides or both and that forms granular, blocky or prismatic structure, if volume changes accompany changes in moisture content,

(vi) Brittleness, and

(vii) Strong gleying.

12.1.6. C-Horizons

C-horizons are layers, excluding strongly cemented and harder bedrock, that are little affected by the pedogenic processes and lack properties of O-, A-, E- or B-horizons. Most are mineral layers. The material of C-layers may be either similar or dissimilar to that from which the solum has presumably been formed. The C-horizon many have been modified even if there is no evidence of pedogenesis.

12.1.7. R-Layers

Strongly cemented to indurated bedrock, granite, basalt, quartzite and indurated limestone or sandstone are the examples of bedrock that are designated as R-layers. A R-layer is sufficiently coherent when moist to make digging with spade impractical, although the layer may be chipped or scraped.

12.1.8. W-layers (Water)

This symbol indicate water layers within or beneath the soil. The later is designated as Wf if it is permanently frozen and as W if it is not permanently frozen. The W (or Wf) designation is not used for shallow water, ice or snow above the soil surface.

For more details one may refer to *Keys to Soil Taxonomy* (Soil Survey Staff, 2003).

12.2. Transitional or Combination Horizons

These are horizons dominated by properties of one master horizon but possess subordinate properties of another horizon also. Two capital letter symbols like AB, EB, BA, BE, BC or CB are used to represent these horizons.

The master horizon symbol which is given first, designates the kind of horizon whose properties dominate the transitional horizon, i.e.

AB/EB - Transition to B, more like A or E than B.
BA - Transition to A, more like B than A.
BE - Transition to E, more like B than E.
BC - Transition to C, more like B than C.
CB - Transition to C, more like C than B.

Horizons in which distinct parts have recognizable properties of the two kinds of master horizons are indicated by the capital letters. The two capital letters are separated by a virgule (/), such as E/B, B/E or B/C.

12.3. Subordinate Distinctions within Master Horizons and Layers

Lower case letters used as suffixes to designate the specific kind of master horizons and layers are given in Table 3

For additional details, *USDA Soil Survey Manual* (Soil Survey Staff, 1993) and *Keys to Soil Taxonomy* (Ninth Edition, 2003) may be consulted.

Table 3. Lower case letters used as suffixes to designate specific kind of master horizons

Letter(s)	Description
a	Highly decomposed organic material
b	Burried genetic horizon
c	Concretions or nodules
co	Coprogenous earth
d	Physical root restriction
di	Diatomaceous earth
e	Organic material of intermediate decomposition
f	Frozen soil and water
ff	Dry permafrost
g	Strong gleying
h	Illuvial accumulation of organic matter
i	Slightly decomposed organic material
j	Accumulation of jarosite (potassium or iron sulphate mineral)
jj	Evidence of cryoturbation
k	Accumulation of carbonates
m	Cementation or induration
ma	Marl
n	Accumulation of sodium
o	Residual accumulation of sesquioxides
p	Tillage or other disturbances
q	Accumulation of silica
r	Weathered or soft bedrock
s	Illuvial accumulation of sesquioxides and organic matter
ss	Presence of slicken sides
t	Accumulation of silicate clay
v	Plinthite
w	Development of colour or structure
x	Fragipan character
y	Accumulation of gypsum
z	Accumulation of salts more soluble than gypsum

13. Geoinformatics

The deep understanding of earth has been limited due to lack of information. Initially, the mapping was undertaken manually and various resource maps generated were overlaid to study the earth resources in an integrated form. Later, this art was taken over by the efficient computers. The voluminous data provided by the satellites in analog and digital format reinforced the use of computers.

Geoinformatics is a fast emerging science encompassing the modern tools of Remote Sensing, Geographic Information System (GIS), Global Positioning System (GPS) and simulation models. The combination of these technologies provides a cost-effective means of acquiring high resolution real time data through remote sensing, georeferencing the ground truth data with GPS, data management, and analysis through GIS and utilisation of the information for a specific purpose. It is a new discipline that integrates elements of various disciplines dealing with geographic data. The key element that differentiates geoinformatics from other areas of information technology is that all input data is geocoded, i.e. has an address in the 3-D space and is linked to some locality on the surface of earth. Thus, geoinformatics is nothing but application of information technology for the study and management of earth resources (soil, land and forest). The details on Remote Sensing is dealt under section 6.4.

13.1. Geographical Information System (GIS)

Until recently, soil maps (usually in paper form) generated through field surveys were used for a wide variety of applications and decision making, e.g. soil conservation and land use planning, selection of sites for water harvesting structures or industrial parks, alignment of roads and drains, etc.

The "spatial" information in map form with proper scale, legend, symbols and colours, enhances the understanding of "Information Inter-relationships" and thus contributes to a more appropriate location-specific developmental strategy. However, it is not easy to analyse information contained in various types of maps (in paper form), viz. soils, landuse, slope and water table depth for the same area and arrive at a logical decision like alignment of a drain for the disposal of rainwater or reclamation of waterlogged area. In recent years, the demand for storage, analysis and display of complex and voluminous data for resources (e.g. soil, water, forest) has led to the use of computers for data handling and creation of sophisticated information and decision support systems. Geographic Information System (GIS) is a new technology which is becoming an essential tool for the analysis of great diversity of data in a short time.

The GIS is computer-based systems that deal with virtually any type of information about features that can be referenced by geographic location. GIS is an integrated database management system in which large volume of georeferenced spatial data derived from field surveys, i.e. soil surveys, aerial surveys, and space remote sensing, in addition to the existing maps and reports, are efficiently stored, organized, manipulated, retrieved, analysed and displayed/presented as per user's requirement. This involves bringing together diverse information from a variety of sources on a common platform. It requires effective matching of similar entities and demand information consistency across the data sets. Any data that can be mapped has both locational and non-locational characteristics. For example, a feature may exist at an X, Y location and possess an attribute Z. The attributes can be both qualitative (soil units, namely soil series, soil family or their associations) or quantitative (e.g. elevation, slope, status of N or Zn in soil).

Many of these data have some type of explicit or implicit geographical reference associated with them. An explicit geographical reference might be a Cartesian or latitude/longitude co-ordinate and an implicit reference might be the name of a town or village or a physical feature, such as a mountain or river. In many cases, it is possible to derive an explicit reference from an implicit reference. The geographical reference has proved to be an effective means of linkage of data sets and this principle perhaps more than any other is the reason for the success of GIS.

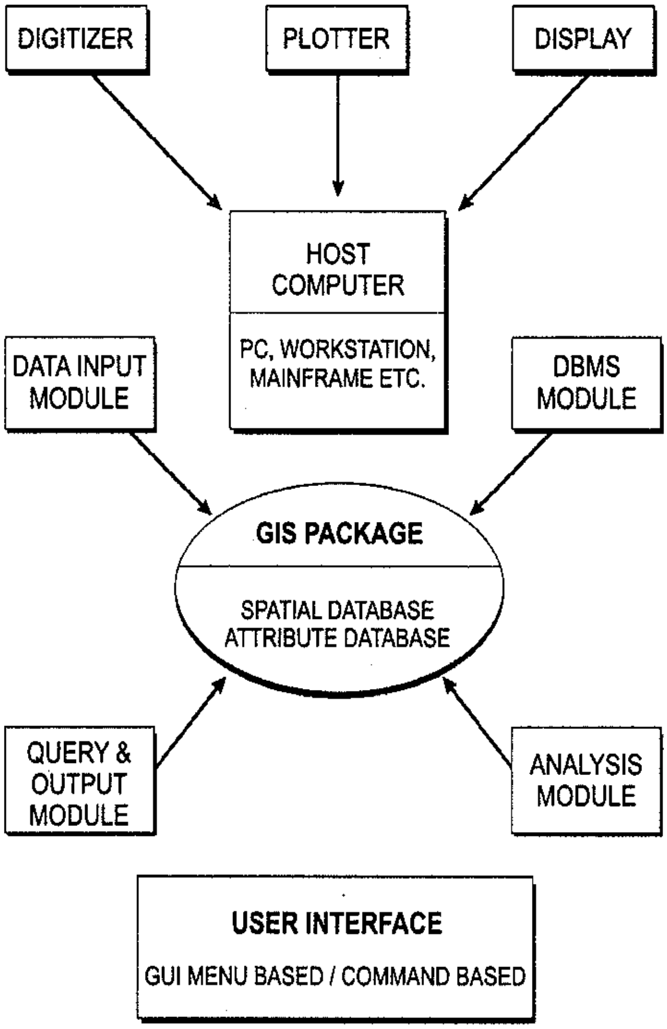
As a technology, GIS has evolved through the following three broad application domains:

(i) **As an information database:** A means of coordinating and accessing geographic data.

(ii) **As an analytical tool:** A means of specifying logical and mathematical relationships among map layers (modelling) to yield derivative maps.

(iii) **As a decision support system:** A means for deciding how to act upon the analysis produced and simulation of after effect.

A GIS database usually has a spatial component for the storage and processing of data. Hence, it has the potential to store the data and create map like products. It also offers the potential for performing multiple analyses or evaluation of scenarios such as model simulations. Any GIS comprises three basic components, viz. computer hardware, application software and a proper organizational context (Figure 2).



GUI - Graphical User Interface
DBMS - Database Management System

Figure 2. Components of Geographic Information System (GIS)

The hardware components include several specialized peripherals, such as digitizer or scanner for converting the resource maps into digital form, a plotter for graphical representation of the maps generated, and a visual colour graphics display unit on which the spatial data editing and display can be performed by the user. In addition to a central processing unit, and standard computer peripherals, computer software is generally designed to undertake particular tasks or solve problems. To use GIS, one has to learn how to apply various tools available in a GIS software as per specific needs.

The salient features of GIS are:

- Large volume of data from a variety of sources and formats can be integrated efficiently.
- Analysis can be carried out speedily and relevant spatial (map form) and non-spatial (attributes) information can be derived accurately with high consistency.
- Provides graphical representation and easily understandable answers to complex questions in rational use of natural resources, infrastructural development, conservation planning and decision-making in a cost-effective manner.
- Spatial modelling can be carried out conveniently through multilayer integration.
- Easy interfacing with remotely sensed data, and socio-economic data.
- Enables alternate scenarios to select the best option.

Table 4. Examples of attributes* for point, line and area features in a GIS

Point feature	Well (depth, chemical constituents)
Line feature	Power line (service capacity, age, insulator type)
Area feature	Soil mapping unit (soil type, texture, colour, permeability)

*Attributes have been shown within the parentheses

The GIS permits the automated mapping or display of the locations of features, and provides capability for recording and analyzing descriptive characteristics about the features. For example, a GIS might contain a "map" of the locations of roads and also a "database" of descriptors about each road. These "attributes" could include such information as road width, pavement type, speed limit, number of traffic lanes, date of construction, and so on. Table 4 lists other examples of attributes that might be associated with a given point, line, or area feature.

In GIS, the data are stored in multiple files. Each file contains data in a co-ordinate system (latitude and longitudes) that defines the position for each data point or entry. Characteristics of the data point are stored as "attributes". The data are associated with their geographic features. For example, water quality data would be associated with a sampling site represented by a point. Data of crop yields might be associated with field or experimental plots, represented on a map by polygons. A database of individual files is developed and the combined files may contain characteristics or attributes such as stream locations, topography, water or soil chemical characteristics, management practices, ownership details, point sources (wells), and any other data that can be collected and have meaning for the analysis.

There are two kinds of databases, viz. spatial and non-spatial that are integrated in the GIS.

- The spatial data is in the form of maps which could be topography, soil types, geology, and forests, and is stored as layers in the digital form in computer.
- The non-spatial data pertains to attribute information in the form of statistics, tables, and lists, which could be on demography, rainfall, wildlife census, etc.

The data sets need to be standardized with respect to formats, exchange, networks and software, etc. The database in a standard format enables different technologies and applications to work together. It is better to involve users at all levels of developments of database standards so that the problems related to each level and theme could be properly taken care of and the users could understand the information attached with each layer in the form of standard codes when these standards are implemented.

The soil survey and mapping help in the classification of soils according to a standard system of classification, delineating the extent of different kinds of soils on a map and making predictions about their behaviour. The soil survey information answers a wide range of soil-related questions in terms of their use, management and environmental protection. Soil survey data make up growing number of geographical information systems and models that deal with regional planning, erosion prediction, crop yields and even modelling the global change. The soil survey data has to be preprocessed and standardized to be put into a form that can be integrated with other data. This involves digitization of soil boundaries and other spatial features into a computer database as points, lines and geographically defined areas called 'polygons'. The analog (paper) maps are digitized using a digitizer or scanner. The soil database attached to different map units (polygons) includes soil profile description, i.e. horizon/layer-wise morphological, physical and chemical properties in the form of SOIL.DAT.

In the standardized database attached to digital soil map, the soil layer is linked to two tables, SOIL.DAT and SOIL.LUT. The SOIL.DAT contains profile description for each soil class. It is linked to soil layer attribute table via SOIL-CODE. SOIL.LUT describes codification scheme of soil classes up to series level. It is linked to the layer attribute table via three key fields, viz. SOIL-CODE, ASS 1 (CODE) and ASS 2 (CODE). SOIL-CODE is a 16-digit number code, with each two digits representing different levels up to soil series (ISRO, 2000).

The Nabha series in Punjab classified as (Fine silty, mixed, hyperthermic family of Typic Haplustepts as per Soil Taxonomy (for details refer Chapter 2) has been denoted by SOIL-CODE: 06-04-05-18-10-07-05-02, in which:

06 represents the order **'Inceptisol'**;
04 represents sub-order, **'Ustepts'**;
05 represents great group, **'Haplustepts'**;
18 represents sub-group **'Typic'**;
10 represents textural class, **'Fine Silty'**;
07 represents mineral class, **'Mixed'**;
05 represents soil temperature regime, **'Hyperthermic'**;
02 represents series, **'Nabha'**.

13.2. Global Positioning System (GPS)

The GPS has revolutionized positioning concepts though it started primarily as a navigation system. The US Navigation System with Time and Ranging Global Positioning System (NAVSTAR GPS) is satellite-based radio navigation system providing precise three-dimensional position, navigation and time information to suitably equipped users. GPS receivers passively receive signals but they do not transmit. There are atleast 24 operational GPS satellites at all times. This is the optimum size of a constellation. The satellites are operated by the US Air Force, with a orbital period of 12 hours. Ground stations are used to precisely track each satellite in orbit. Each GPS satellite has atomic clock on board and transmits data that indicates its location and time. All the GPS satellites synchronize operations so that these repeated signals are transmitted at the same instance. The distance to the GPS satellites can be determined by estimating length of time it takes for their signals to reach the receiver. When the receiver estimates distance to at least four GPS satellites, it can calculate its position in three dimensions (latitude, longitude and altitude).

Most hand held GPS units have about 5-10 metre locational accuracy. To obtain better accuracy, a technique called Differential GPS (DGPS) is used. DGPS requires an additional receiver fixed at a "known" location nearby. Observations made by a stationary receiver (base station) are used to correct the position recorded by rovering units, resulting in an accuracy greater than one metre. Earlier, in order to limit the accuracy for a civilian user, the US Government in 1990 deliberately introduced an error in the orbit data and clock accuracy for L1 signals. This part of GPS operation is called "Selective Availability" and has been discontinued since May, 2000 due to wider civilian applications of GPS.

Global Navigation Satellite System (GLONASS) being developed by Russia is a rival to the US Global Positioning System and Europe's Planned Galileo System. India is a participant in both GLONASS and Galileo programmes. Europe is developing the 30 Satellite Galileo network as a navigational system, independent of any military control. Russia and India are jointly developing a new generation of global positioning satellite (GLONASS-K) for wider navigational applications which will function parallel with the American GPS. Russia intends to operationalize GLONASS by 2010 by completing the cluster of 24 satellites. The GLONASS will provide commercial services to surface transport, shipping and airlines. As per ISRO Chairman, by launching seven satellites, the Indian Regional Navigation Satellite System (IRNSS) is expected to be operational by 2012. The IRNSS will be used for surveying, telecommunication, transport, identification of disaster areas and public safety among others. India is planning to develop its own version of GPS.

Besides the navigational applications, the GPS can be effectively used in location of precise control points, conducting geophysical and cadastral surveys and updating the existing base maps. The wells can be precisely mapped and georeferenced samples of water, soil and plants can be collected. This helps in revisiting the earlier surveyed spots for re-sampling and monitoring. A similar approach can be adopted for mapping the extent of spread of disease in crops and its monitoring.

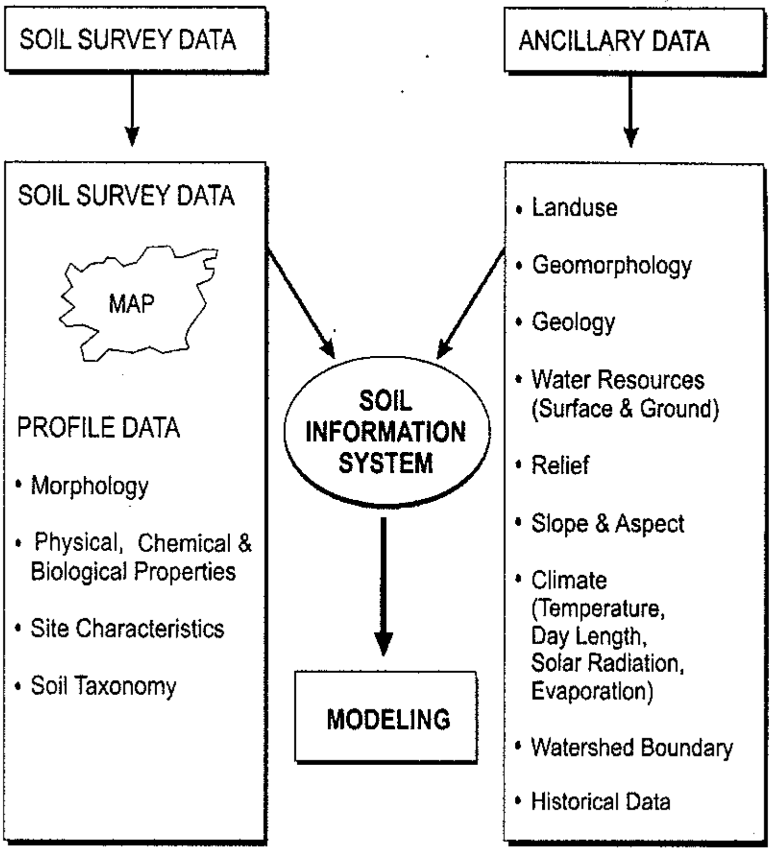


Figure 3. Soil information system: A concept

GPS technology can be applied for mapping soils. Soil surveyors, traditionally, use large-scale base maps or air photos or high resolution imagery to ascertain location on the ground. However, in flat terrain or heavily vegetated areas, these aids are of limited use. GPS has come to the aid of soil mappers to precisely record the geographic co-ordinates of each soil observation point on the ground. The co-ordinates (latitudes and longitudes) given by the GPS receiver for each observation, i.e. auger or profile location are transferred to the base map which in turn help in delineating the location of soil bodies as the surveyor traverses the landscape.

13.3. Soil Information System (SIS)

It is a computerized database system where soil and related data can be organized, stored, retrieved, analysed and processed to make it accessible to the end-users in the form of maps and tables. The SIS is based on a database obtained through remote sensing and ground survey in combination with GIS and Decision Support System (DSS). The concept of Soil Information System is depicted in Figure 3.

The International Society of Soil Science (ISSS), now called as the International Union of Soil Sciences (IUSS), officially endorsed the proposal on the establishment of uniform World Soil and Terrain Digital Database (SOTER) at a scale of 1:1,000,000 during its 13th Congress at Hamburg in 1986. The main function of this database is to provide the necessary data for improved mapping, modelling and monitoring of changes in world soil and terrain resources and presenting a wide range of accurate and timely interpretative analysis for decision- and policy-makers.

Besides soil survey data (soil map and profile data), ancillary data in respect of landuse, geology, geomorphology, water resources, topography (relief, slope, and aspect) and watershed (Figure 3) is collected and used for developing soil information system. Land use/land cover information is essential for the development and management of natural resources. Land use refers to human activities associated with a specific piece of land (i.e.

land used for growing crops, orchards and fodder. On the other hand, land cover is related to the types of features present on the earth, for example houses, factories, lakes, and vegetation).

Information about rocks and minerals is essential to understand the kinds of parent materials from which the soils developed. Both consolidated and unconsolidated materials beneath the solum that influence the genesis and behaviour of soil are described in standard terms (For more details, *see* Chapters 2 and 13).

The information about the land forms is essential as different types of soils are formed on various landforms, e.g. hills, valleys, terraces, flood plains, sand dunes, etc. Before the start of soil survey, aerial photographs or satellite imagery are interpreted to delineate various land forms or physiographic or geomorphic units. The soils developed on various geomorphic units are studied and soil-physiographic relationship is developed.

Information about water resources (surface-water and groundwater) in an area is essential for their rational use and development. Under intensive cultivation, the limited surfacewater resources and precipitation cannot meet the irrigation water requirement, therefore, the groundwater is tapped to augment the surfacewater potential.

Relief, slope and aspect (topography) information is recorded during the course of soil survey as they influence soil information (*see* Chapter 2 for more details).

Development programmes concerning optimum utilization of natural resources are being implemented on watershed basis. Watershed is a natural hydrological entity that covers a specific area within which the entire rainfall runoff, ultimately passes through a specific channel at a particular point. The information about the natural resources of a watershed is very important for watershed management planning. The various parameters of the watershed, viz. stream network (drainage), physiography, land use, vegetation/forest cover and snow cover can be mapped and monitored using remote sensing data.

The SIS developed using soil survey and ancillary data has immense potential in planning judicious management, conservation and sustainable use of soil, land and crop resources. The manifold advantages of the SIS such as ease of handling of voluminous data, reproduction of maps derived suitability and other interpretative maps, easy linkage with other georeferenced coverage to generate new composite overlays, cost-effective and time-saving periodic updation of maps/information and capabilities of quick monitoring and impact assessment of development measures make it a useful tool for generating action plans and its implementation for land resource management of a region/watershed.

14. Agro-ecological Approach for Sustainable Agricultural Development

14.1. Concepts

A proper understanding of potential and limitations of natural resources is necessary for sustainable agricultural development at local, regional and country level. The farm output depends largely on the components like climate, soil and landforms. Therefore, for efficient crop planning in an area and transfer of technology, information concerning requirements of the crops and kinds of soils, their extent, geographic distribution and the local agro-climatic conditions is essential. The delineation of homogeneous agricultural environments, called agro-ecological regions (AER) on the basis of soil characteristics, landforms, climate and biodiversity helps in better crop selection, agro-technology transfer for sustainable land use and land resource planning (Sehgal *et al.*, 1992).

An agro-climatic region is a land unit in terms of major climate and growing period which is climatically suitable for certain range of crops and cultivars (FAO, 1983), whereas an agro-ecological region is characterized by distinct ecological responses to macroclimates as expressed in vegetation and reflected in soil, fauna and aquatic systems. Therefore, an agro-ecological region is the land unit on earth's surface carved out of agro-climatic region when superimposed on different landforms and soil conditions that act as modifiers to the length of growing periods (LGP) and crop environmental needs.

14.2. Concept of Bio-climate and Length of Growing Period (LGP)

14.2.1. Bio-climate

The climate of a particular region is determined by meteorological parameters like rainfall, temperature and potential evapotranspiration (PET). For all practical purposes, the quantification of climatic parameters is done within one metre below the soil surface and few metres above the soil surface where biological life sustains. The bio-climatic profile consists of elements which describe the temperature and moisture condition in the study region. Bio-climatic analysis is done using various climatic and moisture balance indices such as Moisture Index (Im), Aridity Index (Ia), Humidity Index (Ih), Summer Concentration (Sc), and Thermal efficiency type (Thornthwaite and Mather, 1955).

The Water Balance Technique (Thornthwaite and Mather, 1955; Carter and Mather, 1966) and PET values (Penman, 1948) are being used to prepare a bio-climate map. It accounts for the monthly as well as annual water surplus (WS) and water deficites (WD), determining the moisture index (Im) in a particular ecosystem receiving specific amount of rainfall and having specific potential evaportranspiration. The concept of water balance has been illustrated in a flow diagram (Figure 4).

Water deficit and water surplus are calculated from the potential and actual evaportranspiration values. Water deficit is the amount by which the available moisture fails to meet the demand for water and is computed by substracting the potential evapotranspiration from the actual evapotranspiration for the period in question. Water surplus is the excess remaining after the evaporation needs of the soil have been met (i.e. when actual evaportranspiration equals the potential evapotranspiration) and soil storage has been returned to the water-holding capacity level.

The annual water surplus and water deficit help to compute humidity index (Ih), aridity index (Ia) and moisture index (Im), which stand

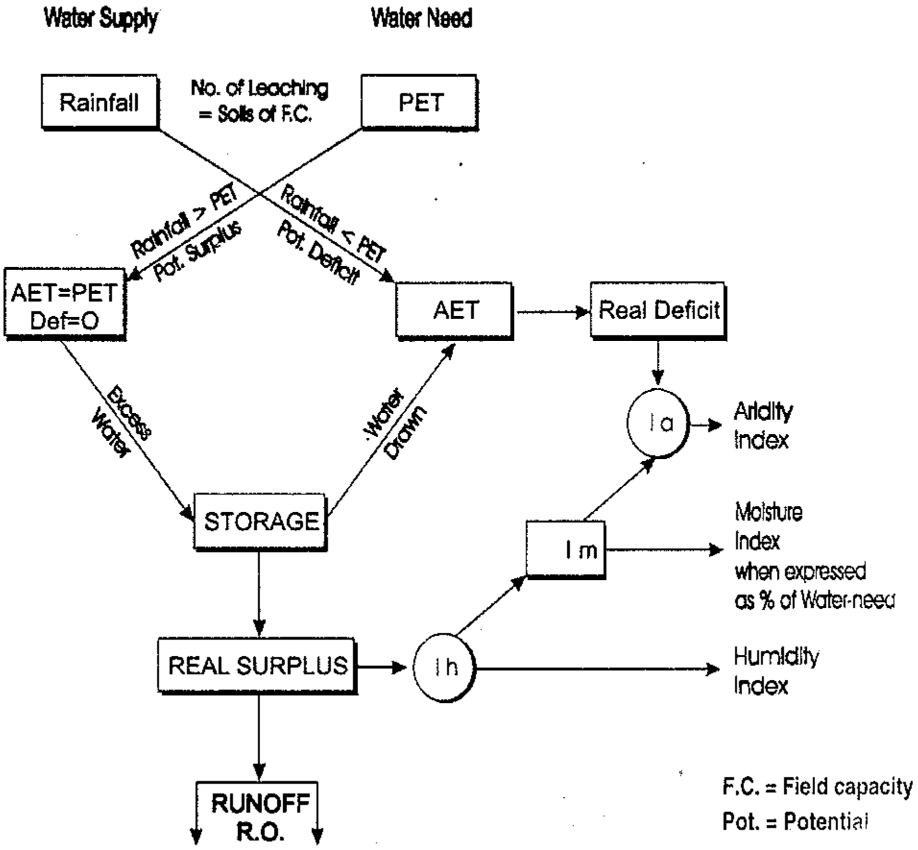


Figure 4. Concept of water balance
After Sehgal (1987)

for a balance between moisture availability and extent of dryness. The moisture index with positive and negative values would indicate moist or dry climate and seasonal variations in effective moisture. The criteria evaluating Moisture Index (Im) are given in Table 5.

14.2.2. Length of Growing Period (LGP)

The growing period or the moisture availability period for crop growth is the period (in days) when the precipitation (P) exceeds 50% of the PET plus the time required to evapotranspire an assumed 100 mm of stored moisture from the deep soil profile. It may be defined as the duration (in days) when both water (moisture in soils) and temperature permit crop growth (Higgins and Kassam, 1981). During a normal growing season, crop experiences a humid period (when P > PET), a moist period (when P > 0.5 PET but < PET) and moderately dry to dry period (when P < 0.5 PET). The concept of growing period has been illustrated in Figure 5.

Table 5. Moisture index limits used for bio-climatic classification

Symbol	Type description	Moisture index (Im)
E	Arid	<- 80
D_1	Semi-arid (dry)	- 60
D_2	Semi-arid (semi-dry)	- 40
D_3	Semi-arid (moist)	- 20
C_1	Sub-humid (dry)	0
C_2	Sub-humid (moist)	+ 20
B_1	Humid 1 (1st degree)	+ 40
B_2	Humid 2 (2nd degree)	+ 60
B_3	Humid 3 (3rd degree)	+ 80
B_4	Humid 4 (4th degree)	+ 100
A(1)	Perhumid 1 (1st degree)	> + 100

Source: Sehgal *et al.* (1992)

Based on the values of P and PET of humid, moist and moderately dry periods, the LGP in a year is determined. Moist period is the duration at the beginning of rainy season when most of the crop establishment operations are usually done. The humid period not only meets

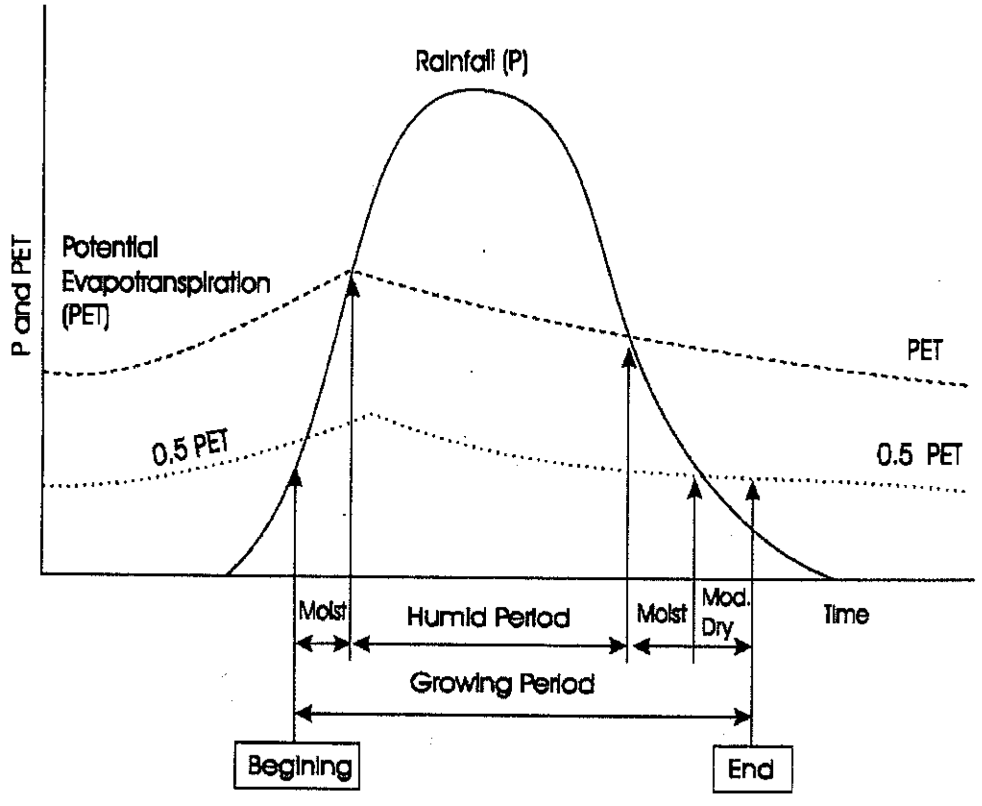


Figure 5. Concept of growing period
Source: Higgins and Kassam (1981)

the full evapotranspiration demand of crop, but also replenishes moisture deficit in the storage (soil profile). During the moderately dry to dry periods, the crop progressively starts drawing moisture from the storage in soil profile.

National Bureau of Soil Survey and Land Use Planning (NBSS&LUP) has delineated 20 agro-ecological regions (AER) in the country using the FAO concept (FAO, 1978) by integrating maps depicting length of growing period, bioclimate and soil scape (soil-physiography) as per the scheme outlined in Figure 6.

The NBSS&LUP has adopted LGP criteria for the delineation of AERs in the country as LGP is the direct indicative of moisture availability of a given landform rather than the total rainfall (Figure 7). For example, both Ratnagiri in western Maharashtra and Nagpur in eastern Maharashtra have LGP of 180-210+ days in a year, but the total annual rainfall of Ratnagiri is more than 2000 mm, whereas that of Nagpur is only 1100 mm. Therefore, the crop planning has to be based on LGP rather than on the total rainfall. The extent, distribution, soils and major constraints of the identified AERs (Sehgal *et al.*, 1992) have been furnished in Table 6.

For sub-regionalization of each AER, the NBSS&LUP has broadened the soil, physiography and LGP concept with the inclusion of soil quality attributes such as soil depth, texture, mineralogy in combination with available water capacity (AWC), cropping pattern and vegetation type (Velayutham *et al.*, 1999). The bioclimatic concept has been extended from Thornthwaite and Mather moisture index to synchronized bioclimate-LGP concept. Arid (E) has been bifurcated into Hyper arid (Eh) with LGP less than 60 days and Typic arid (Et) with LGP 60-90, and Semi-arid (D) into Dry semi-arid (Dd) with LGP 90-120 days and Moist semi-arid (Dm) with LGP 120-150 days, whereas Sub-humid (C) has been bifurcated into Dry sub-humid (Cd) having LGP 120-150 days and Moist sub-humid (Cm) with LGP of 210-240 days. In this way, 20 agro-ecological regions (AER) map prepared in 1992 has been refined by using the length of growing period (LGP) of 30-day interval, starting from LGP of 60 days and, then 90, 120, 150, 180, 210, 240, 270, 300 and > 300 days to generate 60 agro-ecological sub-regions (AESR) map. In the map, the AESRs have been shown with numbers (1.1, 5.2, 8.3, etc.) and mapping unit within each of delineation by alpha numeric codes e.g. in K6Dm4, K stands for physiography (Deccan plateau), 6 stands for soils (mixed red and black soils), Dm stands for bio-climate

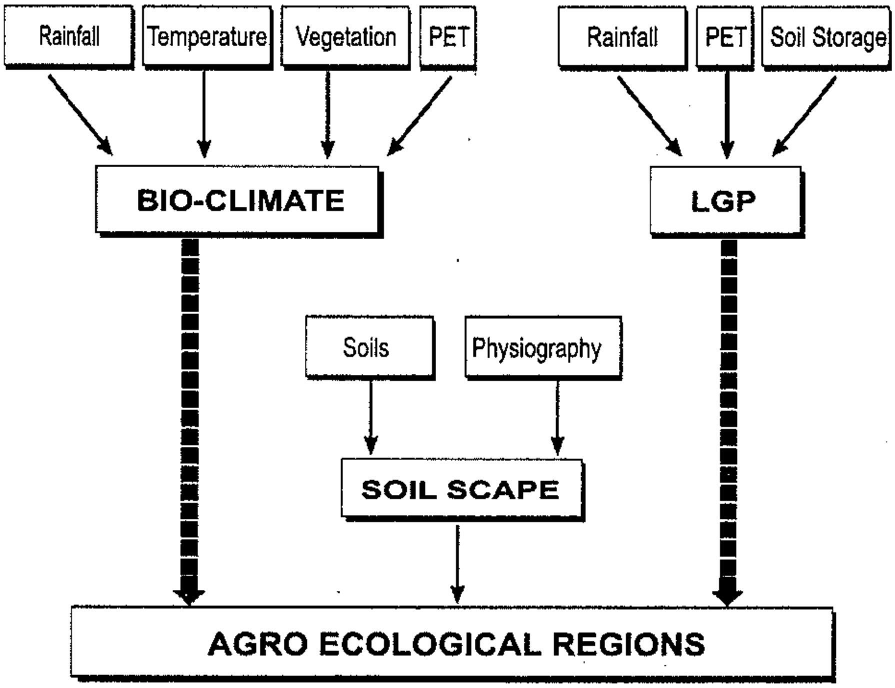
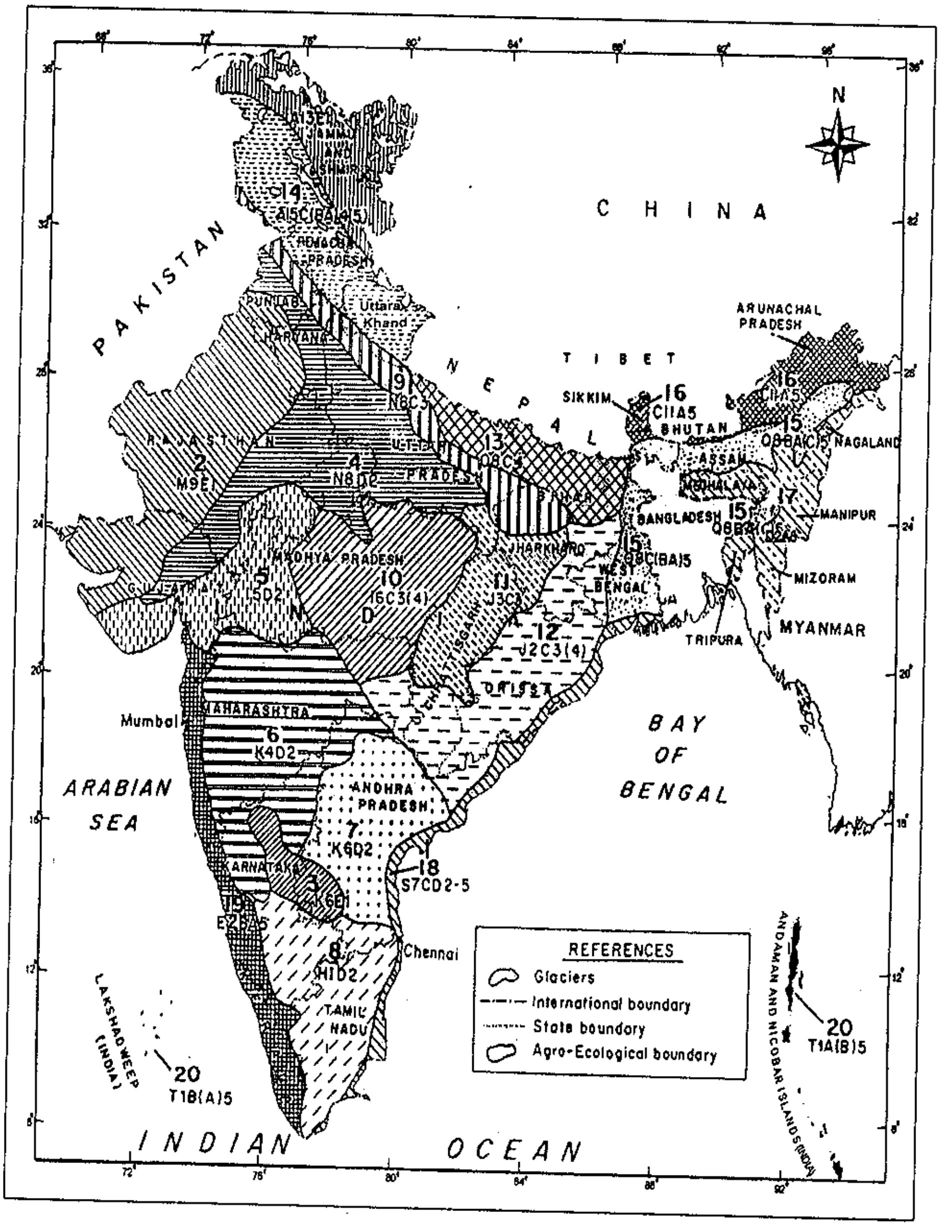


Figure 6. Methodology for agro-climatic regionalization
After Sehgal (1992)



Key for decoding

PHYSIOGRAPHY (1st Letter)

A	Western Himalayas
B	Central Himalayas
C	Eastern Himalayas
D	North-Eastern Himalayas
E	Western Ghats
F	Eastern Ghats & Tamil Nadu Uplands
G	Central Highlands
H	Eastern Plateau
I	Deccan Plateau
J	Kachchh and Kathiawar Peninsula
K	Western Plain
L	Northern Plain
M	Eastern Plain
N	Gujarat Plain
O	Bengal and Assam Plains
P	Western Coastal Plains
Q	Eastern Coastal Plains
R	Eastern Islands
S	Western Islands

SOILS (1st Numeral)

1.	Red Loamy Soils
2.	Red & Lateritic Soils
3.	Red & Yellow Soils
4.	Shallow and Medium (inclusion Deep) Black Soils
5.	Medium & Deep Black Soils
6.	Red and Black Soils
7.	Coastal Alluvium-derived Soils
8.	Aluvial-derived Soils
9.	Desert Soils
10.	Tarai Soils
11.	Brown and Red Hill Soils
12.	Saline and Alkali Soils
13.	Shallow and Skeletal Soils
14.	Grey Brown Soils
15.	Brown Forest and Podzolic Soils
16.	Sandy and Littoral Soils

CLIMATE (2nd Letter)

A	Perhumid
B	Humid
C	Sub-humid
D	Semi-Arid
E	Arid

GROWING PERIOD (2nd Numeral)

1	< 90	(Days)
2	90-150	
3	150-180	
4	180-210	
5	> 210	

Example:	K	6	E	1
	Physiography	Soils	Climate	LGP

Contd...

LEGEND

Ecosystem	Region	Description
Arid Ecosystem	1	Western Himalayas, cold arid ecoregion , with shallow skeletal soils and Length of Growing Period (LGP) <90 days
	2	Western Plain, Kachchh and part of Kathiawar Peninsula, hot arid ecoregion with desert and saline soils and LGP<90 days
	3	Deccan Plateau, hot arid ecoregion, with red and black soils & LGP<90 days
Semiarid Ecosystem	4	Northern Plain and Central Highlands including Aravallis, hot semi-arid ecoregion , with alluvium-derived soils & LGP 90-150 days.
	5	Central (Malwa) Highlands, Gujarat Plains & Kathiawar Peninsula, hot semi-arid ecoregion, with medium & deep black soils & LGP 90-150 days
	6	Deccan Plateau, hot semi-arid ecoregion with shallow and medium (with inclusion of deep) black soils, & LGP 90-150 days
	7	Deccan (Telangana) Plateau and Eastern Ghats, hot semi-arid ecoregion, with red & black soils & LGP 90-150 days.
	8	Eastern Ghats,TN uplands and Deccan (Karnataka) Plateau, hot semi-arid ecoregion with red loamy soils & LGP 90-150 days
Subhumid Ecosystem	9	Northern Plain, hot subhumid (dry) ecoregion, with alluvium-derived soils and LGP 150-180 days
	10	Central Highlands (Malwa, Bundelkhand, & Eastern Satpura), hot subhmid ecoregion, with black and red soils, & LGP 150-180(to 210) days
	11	Eastern Plateau (Chhattisgarh), hot subhumid ecoregion, with red & yellow soils and LGP 150-180 days
	12	Eastern (Chhotanagpur) Plateau and Eastern Ghats, hot subhumid ecoregion, with red & lateritic soils, & LGP 150-180 (to 210) days
	13	Eastern Plain, hot subhumid (moist) ecoregion, with alluvium-derived soils & LGP 180-210 days
	14	Western Himalayas, warm subhumid (to humid with inclusion of perhumid), ecoregion with brown forest and podzolic soils, & LGP 180-210+days
Humid-Perhumid Ecosystem	15	Bengal and Assam Plain, hot subhumid ecoregion (moist) to humid (inclusion of perhumid) ecoregion, with alluvium - derived soils & LGP 210 + days
	16	Eastern Himalayas, warm perhumid ecoregion, with brown and red hills soils & LGP 210 + days
	17	North-eastern Hills (Purvachal), warm perhumid ecoregion, with red and lateritic soils & LGP 210 + days
Coastal Ecosystem	18	Eastern Coastal Plain, hot subhumid to semi-arid ecoregion, with coastal alluvium - derived soils & LGP 90-210 + days
	19	Western Ghats & Coastal Plain, hot humid- perhumid ecoregion, with red, lateritic and alluvium-derived soils, & LGP 210 + days
Island Ecosystem	20	Islands of Andaman-Nicobar and Lakshadweep hot humid to perhumid Island ecoregion, with red loamy and sandy soils, & LGP 210 + days

Figure 7. Agro-climatic regions of India

Table 6. Agro-ecological regions: Extent, distribution, soil orders and major constraints

AER No.	Area (M ha) (% of TGA)	Distribution (Major states)	Soil order(s)	Major constraints
		Arid Ecosystem		
1.	15.2 (4.7)	Jammu & Kashmir	Entisol, Aridisol	Severe climate (Cryic Temperature regime). Shallow, sandy and gravelly soils. Nutrient imbalance
2.	31.9 (9.7)	Rajasthan, Gujarat, etc.	Entisol, Aridisol	Deforestation, Soil salinity. Nutrient deficiency viz. N,P, Zn and Fe
3.	4.9 (1.5)	Andhra Pradesh, Karnataka, etc.	Inceptisol, Vertisol, Alfisol	Soil erosion. Subsoil sodicity
		Semi-arid Ecosystem		
4.	32.2 (9.8)	Haryana, Uttar Pradesh, Rajasthan, Part of Punjab, etc.	Inceptisol, Alfisol, Entisol	Low plant available water capacity (PAWC). Imperfect drainage.
5	17.6 (5.4)	Gujarat, Madhya Pradesh, etc.	Inceptisol, Vertisol, Aridisol	Imperfect drainage. Salinity and alkalinity hazards
6.	31.0 (9.5)	Karnataka,Maharashtra, etc.	Entisol, Inceptisol, Vertisol	Soil erosion. Nutrient deficiency viz. N, P and Zn
7.	16.5 (5.2)	Andhra Pradesh	Entisol, Alfisol, Inceptisol, Vertisol	Soil erosion, Nutrients deficiency viz. N, P and Zn
8.	19.1 (5.8)	Karnataka, Tamil Nadu, etc.	Entisol, Inceptisol, Alfisol	Soil erosion, low to medium PAWC, Nutrient deficiency viz. N, P and Zn
		Sub-humid Ecosystem		
9.	12.1 (3.7)	Bihar, Uttar Pradesh, Punjab, etc.	Inceptisol, Alfisol, Entisol	Waterlogging, soil salinity
10.	22.3 (6.8)	Madhya Pradesh and Maharashtra	Vertisol, Entisol, Inceptisol, Alfisol	Soil erosion
11.	14.1 (4.3)	Madhya Pradesh, Jharkhand, etc.	Entisol, Inceptisol, Alfisol	Soil erosion, nutrient deficiency viz. N, P, Zn and B
12.	26.8 (8.2)	Andhra Pradesh, Jharkhand, Orissa, West Bengal, etc.	Inceptisol, Alfisol, Ultisol	Soil erosion, nutrient deficiency (viz. N, P, Zn) and P fixation
13.	11.1 (3.4)	Jharkhand and Uttar Pradesh	Entisol, Inceptisol, Alfisol	Flooding and imperfect drainage. Salinity and/or sodicity. Deficiency of N, P and Zn
14.	18.2 (5.6)	Jammu & Kashmir, Uttarakhand, Himachal Pradesh, etc.	Inceptisol,Alfisol, Mollisol, Ultisol	Severe climate (Cryic temperature regime). Soil erosion. Soil acidity
		Humid-Perhumid Ecosystem		
15.	12.1 (3.7)	Assam, Tripura and West Bengal	Inceptisol, Alfisol	Flooding, low base status, soil acidity
16.	9.6 (2.9)	Arunachal Pradesh, Assam, Sikkim and West Bengal, etc.	Inceptisol, Alfisol, Ultisol, Mollisol	Soil erosion, deforestation
17.	10.6 (3.3)	Assam, Manipur, Mizoram, etc.	Inceptisol, Ultisol, Alfisol	Soil erosion, depletion of soil nutrients
		Coastal Ecosystem		
18	8.5 (2.6)	Andhra Pradesh, WestBengal, Tamil Nadu, etc.	Entisol, Inceptisol, Vertisol	Poor drainage, soil salinity and/or sodicity
19.	11.1 (3.6)	Karnataka, Kerala, Gujarat, etc.	Inceptisol, Ultisol,	Depletion of plant nutrients, waterlogging
		Island Ecosystem		
20.	0.8 (0.3)	Union Territory (Andaman & Nocobar Islands and Lakshadweep groups of Islands)	Alfisol, Inceptisol, Entisol	Soil erosion

*TGA= Total Geographical Area.

(Semi-arid, moist) and 4 stands for length of growing period (120-150 days), respectively. This map was published in colour on a 1:4.4 million scale, showing distinct boundaries of the country.

The AESR map prepared in 1999 by NBSS & LUP, Nagpur, can only cater to the needs of regional planning. However, for the implementation of development projects at the district level, delineation of agro-ecological units by incorporating details of soils and soil degradation status, crop zones, LGP and biodiversity is necessary. The degree of success in the growth of crop is largely dependent on how well its optimum length of growth cycle fits with the LGP. Curtailment of the growth cycle is naturally reflected by decreased yields and the same is true for enforced extended growth cycle.

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Chapter 5

16/7/2013

Drainage
ease of penetration
by roots

Physical Properties of Soils

D.K. DAS and R.P. AGRAWAL

1. Introduction

The physical properties of a soil play an important role in determining its suitability for crop production. The characteristics like supporting power and bearing capacity, tillage practices, moisture storage capacity and its availability to plants, drainage, ease of penetration by roots, aeration, retention of plant nutrients and its availability to plants are all intimately connected with the physical properties of a soil. Soil as a medium of plant growth should also be physically fertile. The soil which supports plants is a variable mixture of solids (mineral and organic matter), liquid (water) and gases (air) and is called a three phase system (Figure 1). In a representative silt loam soil, about 50% of the total volume is occupied by solids. At optimum moisture for plant growth, 25% of the volume is occupied by water and 25% by air. The inorganic solid phase is composed of discrete mineral particles of various shapes and sizes as well as of amorphous compounds such as hydrated iron and aluminium oxides. The proportion of amorphous material is generally small. The large soil particles are generally visible to the naked eye, whereas the smaller ones are colloidal and can be seen only with the aid of an electron microscope. The liquid phase, consisting of soil water, also contains dissolved salts and thus it is called 'soil solution'. The gaseous phase consists of soil air of varying composition of oxygen and carbondioxide, different from that of atmospheric air.

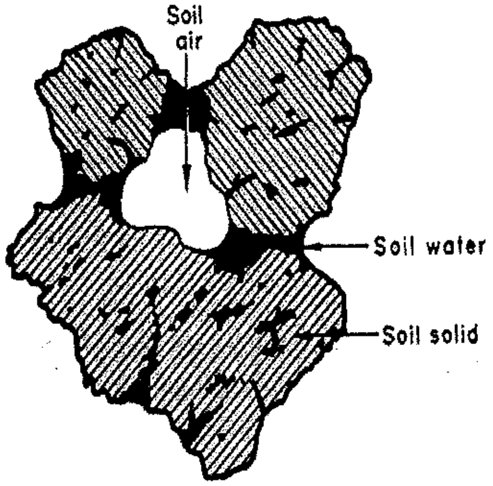

Figure 1. Different components of soil — A schematic diagram

2. Relationships between Different Soil Constituents

The quantitative interrelationships of the solid, liquid and air components of soil are defined in terms of many useful physical parameters of soil (Hillel 1998). These are briefly stated below:

2.1. *Particle Density*

The particle density (ρ_s), also called density of soil solids, is the ratio of total mass of soil solids (M_s) to total volume of soil solids (V_s) and is expressed in g/cm^3 or Mg/m^3 (Mg = mega gram i.e. 10^6 g)[Equation (1)] :

$$\rho_s = M_s / V_s \qquad ...(1)$$

The particle density depends on the chemical and mineralogical compositions of soil.

In most mineral soils, the particle density varies between 2.60 and 2.70 Mg/m³. The mean value of 2.65 Mg/m³ is usually used for all practical purposes. The presence of organic matter lowers the value of ρ_s.

2.2. Dry Bulk Density

The dry bulk density (ρ_b) or simply the bulk density is the ratio of the mass of oven dried soil solid particles (M_s) to the total volume of the soil (V_t). This volume includes the volume of soil solids (V_s), soil water (V_w) and soil air (V_a). The latter two, i.e. volume of water and volume of air constitute the total volume of pores (V_f). So bulk density is expressed by Equation (2):

$$\rho_b = \frac{M_s}{V_t} = \frac{M_s}{V_s + V_w + V_a} \qquad \ldots(2)$$

The bulk density is expressed as g/cm³ or Mg/m³. Bulk density of soil is influenced by soil texture, structure, organic matter content and land management practices. The bulk density of the coarse-textured soils varies from 1.40 to 1.75 Mg/m³ and of fine-textured soils normally ranges from 1.10 to 1.40 Mg/m³. Increase in organic matter content lowers the bulk density of soil. High bulk density indicates compactness of the soil. The bulk density is generally higher in lower profile layers. In swelling soils, bulk density decreases with increase in moisture content and vice versa. In soils, the value of ρ_b is obviously lower than the value of ρ_s.

2.3. (Total) Wet Bulk Density (ρ_t)

It is the ratio of the total mass of a moist soil (M_t) to the total volume of the soil (V_t) [Equation (3)]:

$$\rho_t = \frac{M_t}{V_t} = \frac{M_s + M_w}{V_s + V_w + V_a} \qquad \ldots(3)$$

where, M_w and V_w are the mass and volume of soil water, respectively and V_a is the volume of soil air. The wet bulk density depends more on the wetness or moisture content of a soil.

2.4. Specific Volume (v_b)

It is the ratio of total volume of soil (V_t) to the total mass of dry soil (M_s), i.e. it is the volume of unit mass of dry soil and is expressed as cm³/g or m³/Mg [Equation (4)].

$$v_b = V_t / M_s = 1/\rho_b \qquad \ldots(4)$$

The v_b is an index of the degree of compaction or looseness of a soil. A higher value of v_b indicates lower levels of compaction. The values of v_b for agricultural soils may vary from 0.55 to 0.70 m³/Mg for coarse-textured soils and from 0.70 to 0.90 m³/Mg for fine-textured soils.

2.5. Porosity (f)

It is the ratio of total volume of pore spaces (V_f) to the total volume of soil (V_t) and is expressed as a fraction or as percentage [Equation (5)]:

$$f = \frac{V_f}{V_t} = \frac{V_w + V_a}{V_s + V_w + V_a} \qquad \ldots(5)$$

Thus, porosity refers to the volume fraction of pores and is an index of the relative pore volume in a soil. Its value usually varies from 0.30 to 0.60, i.e. 30% to 60%. Although the size of individual pores may be bigger in coarse-textured soil than in fine-textured soils, the former is less porous than the latter .

Porosity is related to bulk density of the soil and is given by Equation (6):

$$f = \frac{\rho_s - \rho_b}{\rho_s} = \left(1 - \frac{\rho_b}{\rho_s}\right) \qquad \ldots(6)$$

Two types of pore spaces — macro and micro — occur in soils without any clear-cut demarcation. Usually, pores larger than about 0.06 mm in diameter are considered as macropores and those smaller than this, as micropores.

2.6. Capillary and Non-capillary Porosity

The pore spaces in a soil contain both capillary and non-capillary pores which remain filled with water when the soil is saturated. As the soil dries, the non-capillary pores are emp-

29.7.2015

tied first. Thus, capillary porosity is determined by finding the volume of water retained in soil at 50-cm tension. The non-capillary porosity is determined by subtracting the value of capillary porosity from the total porosity value. Capillary pore spaces are important since water retained in these pore spaces are used by the plants for their growth.

2.7. *Void Ratio* (e)

As a result of swelling, shrinkage or compaction, a soil undergoes a change in volume. The V_t in Equation (2) is not constant. In such case, it is advantageous to use the void ratio, e, instead of porosity.

The void ratio is the ratio of total volume of pores (V_f) to the total volume of soil solids (V_s) and is expressed as a fraction, as shown in Equation (7):

$$e = \frac{V_f}{V_s} = \frac{V_w + V_a}{V_s} = \frac{V_f}{V_t - V_f} \qquad \ldots(7)$$

Void ratio is also an index of the relative volume of soil pores. While porosity is largely used in agriculture, void ratio is preferred in engineering. The value of 'e' usually varies between 0.3 and 2.0.

2.8. *Gravimetric Water Content or Mass Wetness* (w)

It is the mass (or weight) of water (M_w) relative to the mass of oven dried soil particles (M_s) and is expressed as a fraction or as percentage, as per Equation (8):

$$w = \frac{M_w}{M_s} \qquad \ldots(8)$$

2.9. *Volumetric Water Content or Volume Wetness* (θ)

It is the ratio of total volume of water occupied in the pore spaces at a specific time to the total volume of soil and is expressed as a fraction or percentage (Equation 9):

$$\theta = \frac{V_w}{V_t} = \frac{V_w}{V_s + V_f} \qquad \ldots(9)$$

Volumetric water content (also called volume wetness) can be computed from gravimetric water content by multiplying the value with bulk density, as shown in Equation (10):

$$\theta = w\rho_b \qquad \ldots(10)$$

The volumetric water content of soil has wider applications in computation of quantity of water added to soil through irrigation or rain or the amount of water used by crop or lost through drainage, etc. The volumetric water content, expressed as a fraction, when multiplied by the depth of soil gives the amount of water in terms of depth.

In swelling soil where volume is not constant, water content is also expressed as the ratio of the volume of water (V_w) to the volume of soil solids (V_s). This is called water volume ratio or liquid ratio (v_w).

Thus,

$$v_w = \frac{V_w}{V_s} \text{ or } v_w = w.\rho_s \qquad \ldots(11)$$

2.10. *Degree of Saturation* (θ_s)

It is the ratio of the volume of water present in the soil at a particular time to the volume of pores [Equation (12)]:

$$\theta_s = \frac{V_w}{V_f} \qquad \ldots(12)$$

2.11. *Air-filled Porosity* (f_a)

It is the ratio of volume of air space to the total volume of soil, as given in Equation (13):

$$f_a = \frac{V_a}{V_t} = \frac{V_a}{V_s + V_w + V_a} = (f - \theta) \qquad \ldots(13)$$

This index is a measure of the relative air content of the soil. It is a useful criterion of soil aeration.

3. Soil Texture

3.1. *Definition*

The soil solid phase as a whole can be characterized in terms of the relative proportions of its particle size groups (soil separates).

Table 1. Classification of soil particles according to size

<table>
<tr><th>System</th><th colspan="8">Soil particles and sizes (diameter, upper limit, in mm)</th></tr>
<tr><td rowspan="2">International Union of Soil Sciences (IUSS)</td><td>Clay</td><td>Silt</td><td colspan="5">Sand</td><td>Gravel</td></tr>
<tr><td>0.002</td><td>0.02</td><td colspan="2">Fine sand
0.2</td><td colspan="3">Coarse sand
2.0</td><td>> 2.0</td></tr>
<tr><td rowspan="2">United States Department of Agriculture (USDA)</td><td>Clay</td><td>Silt</td><td colspan="5">Sand</td><td>Gravel</td></tr>
<tr><td>0.002</td><td>0.05</td><td>Very fine
0.10</td><td>Fine
0.25</td><td>Medium
0.50</td><td>Coarse
1.0</td><td>Very coarse
2.0</td><td>> 2.0</td></tr>
</table>

The relative size-range of soil particles is expressed by the term 'texture' which refers to the fineness or coarseness of the soil. Soil texture is defined as the relative proportions of the different particle size fractions, specifically referred to as sand, silt and clay. This has both qualitative and quantitative connotations. Qualitatively, it refers to the "feel" of the soil material, whether coarse and gritty, or fine and smooth. An experienced soil classifier can tell the soil texture by feel, i.e. by kneading or rubbing soil with his fingers. Quantitatively, soil texture refers to the relative proportions of various sizes of particles in a given soil. The soil texture, typically permanent, is an intrinsic attribute of the soil and the one most often used to characterize its physical make-up, having a bearing on soil behaviour.

3.2. *Textural Fractions*

The traditional method of characterizing sizes of particles in soils is to divide the array of possible particle diameters into three conveniently separable size ranges known as textural fractions or separates, namely sand, silt and clay. The actual procedure of separating out these fractions and of measuring their proportions is called particle size analysis or mechanical analysis. The results of this analysis yield the mechanical composition of a soil, a term often used interchangeably with soil texture.

3.3. *Particle Size Classification*

The different particle size fractions are named and classified arbitrarily. Many particle size classification schemes exist, each of which having different class limits for each size fraction. The classifications of the International Society of Soil Science (ISSS), renamed as the International Union of Soil Sciences (IUSS) and the United States Department of Agriculture (USDA) are widely followed (Table 1). The IUSS system has a geometric proportion with a common ratio of 10, starting from the clay fraction 0.002 mm, while the USDA system has a geometric progression with a common ratio of 2 in the sand fraction, except an irregularity in the fine sand fraction (0.10-0.25 mm). For particles of larger than 2.0 mm diameter, US Soil Conservation Service (1981) provides further subdivisions into gravel, cobble, stone, etc. based on their shape and size (Table 2). The 75 mm upper limit is commonly used for engineering purposes. Various rock fragments up to 250 mm can be obtained by the appropriate sieves with the required apertures.

3.4. *Characteristics of Different Size Fractions / Soil Separates*

The largest group of particles generally recognized as soil material is sand which is defined as particles ranging in diameter from 2 mm to 0.02 mm (IUSS classification) or to 0.05 mm (USDA classification). The sand fraction in IUSS classification is further subdivided into coarse (2-0.2 mm) and fine sand (0.2-0.02 mm) or as coarse, medium and fine sand. Sand particles are primary minerals generally rounded or angular. Sand feels gritty when pressed between the fingers and the particles are generally visible to the naked eye. The particles of sand have relatively lower surface area per unit mass or volume. Sand particles can hold little water. Soils dominated by sand are prone to drought.

Table 2. Size and shape classes for rock fragments

Shape and size*	Name	Quality
Rounded, subrounded, angular or regular or irregular		
0.2-0.5 cm diameter	Fine gravel	Fine gravelly
0.5-2.0 cm diameter	Medium gravel	Medium gravelly
2.0-7.6 cm diameter	Coarse gravel	Coarse gravelly
7.6-25 cm diameter	Cobble	Cobbly
25-60 cm diameter	Stone	Stony
> 60 cm diameter	Boulder	Bouldery
Flat		
0.2-15 cm long	Channer	Channery
15-38 cm long	Flagstone	Flaggy
38-60 cm long	Stone	Stony
> 60 cm long	Boulder	Bouldery

*If significant for classification or interpretation, the shape of fragments is indicated such as "angular gravel" or "irregular boulders".

Source: USDA Soil Conservation Service (1981)

The next fraction is silt (0.02-0.002 mm as per IUSS classification) which is intermediate in size between sand and clay. Mineralogically and physically, silt particles generally resemble sand particles but have a greater surface area per unit mass.

The clay fraction, with particles ranging from 0.002 mm or 2 microns downward, is the colloidal fraction. Clay particles are plate-like or needle-like and are secondary minerals generally belonging to a group of minerals known as the aluminosilicates. Clay is the fraction that has negative charge and greater surface area per unit mass and influences the soil behaviour most. Clay particles absorb water and hydrate, thereby causing the soil to swell upon wetting and shrink upon drying.

The relatively inert sand and silt fractions can be called the soil "skeleton", while the clay by analogy, can be regarded as the "flesh" of the soil. Together, all the three fractions of the solid phase constitute the *matrix* of the soil.

3.5. *Influence of Soil Separates on Properties and Behaviour of Soils*

The soil separates have profound influence on different properties and behaviour of soils. Different soils contain different proportions of sand, silt and clay and exhibit properties as determined by the dominant fraction.

Coarse-textured or sandy soils are loose, low water retentive, well-drained, well-aerated, easy to cultivate and are called *light* soils. On the other hand, fine-textured or clayey soils tend to absorb and retain much more water, become plastic and sticky when wet, tight and cohesive when dry, difficult to cultivate and are called *heavy soils*. These expressions can be misleading as coarse-textured soils are generally more dense, that is, have a lower porosity than the fine-textured soils, and thus are heavier in weight per unit volume (at least in the dry state). Energy required for tillage is much less in light soils as compared to that in heavy soils.

In general, sandy soils have low water and nutrient holding capacity, low organic matter content, little or no swelling and shrinkage, poor sealing properties for ponds and dams, high leaching of nutrients and pollutants. The fine sands are easily blown by wind, while coarse sands resist erosion by water.

The silty soils have medium to high water and nutrient holding capacity, moderate aeration, slow to medium drainage, medium to high organic matter content, usually good supply of plant nutrients, moderate leaching of pollutants and nutrients. These soils are easily blown by wind and are susceptible to water erosion, easily compacted, have little swelling and shrinkage and are moderately difficult to till after rain.

A loam soil contains a balanced mix of coarse and fine particles with properties intermediate among those of a sand, a silt, and a clay. A loam soil is often considered to be the optimal soil for plant growth and agriculture. Its capacity to retain water and nutrients is superior to that of sand, while its drainage, aeration and tillage properties are often favourable than those of clay.

The clayey soils have high water and nutrient holding capacity, are poorly aerated, have very slow drainage unless cracked, high to medium organic matter content, medium to excellent supply of plant nutrients and high swelling and shrinkage. These soils resist wind erosion; aggregated clays also resist water erosion. They have excellent sealing properties. They are easily compacted and retard leaching of nutrients and pollutants.

3.6. Mechanical Analysis

Mechanical analysis is the procedure for determining the particle size distribution of a soil sample. Particles can be separated into different size groups by sieving through graded sieves, up to a particle of approximately 0.05 mm diameter. For separating the finer particles, the method of sedimentation is generally used. The first step is to disperse the soil sample in an aqueous suspension. After complete dispersion, the settling velocity of the particles or the density of the suspension from which the particles are settling is measured based on the principle of Stokes' law.

3.6.1. Stokes' Law and its Derivation

According to Stokes' law, the terminal velocity of a spherical particle settling under the influence of gravity in a fluid of a given density and viscosity is proportional to the square of its radius, and is represented by Equation (14):

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$$v = \frac{2}{9}\frac{r^2 g}{\eta}(\rho_s - \rho_f) \qquad \ldots(14)$$

where, v is the settling velocity (cm/sec or $m \times 10^{-2}$/sec); r is the equivalent spherical radius of the particles (cm or m); η is the viscosity of the suspending fluid (g/cm sec or kg/m sec); g is acceleration due to gravity (cm/sec^2 or m/sec^2); ρ_s and ρ_f are the densities of the solid particles and of the fluid (g/cm^3 or Mg/m^3), respectively.

Derivation — A particle falling in the fluid encounters a frictional resistance (F_r) proportional to the product of its radius (r), velocity (v) and viscosity of the fluid (η). The resisting force due to friction F_r was shown by Stokes (1851) to be

$$F_r = 6\pi\eta rv \qquad \ldots(14a)$$

Initially, as the particle begins to fall, its velocity increases. Eventually, a point is reached at which the increasing resistance force equals the constant downward force and the particle then continues to fall without acceleration at a constant velocity, known as terminal velocity (V_t).

The downward force due to gravity (F_g) is given by Equation (14b):

$$F_g = 4/3\pi r^3(\rho_s - \rho_f)g \qquad \ldots(14b)$$

where, $4/3\pi r^3$ is the volume of the spherical particle.

Setting the two forces (i.e. F_r and F_g) equal, we can obtain Stokes' law as,

$$6\pi\eta rv = 4/3\pi r^3(\rho_s - \rho_f)g \qquad \ldots(14c)$$

or $$v = \frac{2}{9}\frac{r^2 g}{\eta}(\rho_s - \rho_f) \qquad \ldots(14)$$

In the case of systems where ρ_s, ρ_f, η and g are constant at specified temperature, the Equation (14) simplifies to Equation (15):

$$v = K.r^2 \qquad \ldots(15)$$

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where, K is a constant. Thus, the sedimentation velocity being directly proportional to the square of the radius of the particles is a sensitive function of r. In aqueous medium at 20 °C, K assumes a value of 34,700.

If d is the diameter of the particle and assuming that the terminal velocity is attained almost instantly, we can obtain the time t needed for the particle to fall through a height h using Equation (16a) or (16b):

$$v = \frac{h}{t} \text{ or } t = \frac{h}{v} = \frac{9h\eta}{2r^2 g(\rho_s - \rho_f)} \qquad \ldots(16a)$$

$$t = \frac{18h\eta}{d^2 g(\rho_s - \rho_f)} \qquad \ldots(16b)$$

3.6.2. Assumptions and Limitations of Stokes' Law

The use of Stokes' law for measurement of the size of soil particle depends on certain simplifying assumptions. These are:

(i) Particles must be spherical, smooth and rigid. But, soil colloidal particles are plate-shaped and fall slower than spherical particles of the same mass.

(ii) Size of particles must be large compared to the size of molecules of the liquid, so that the medium can be considered homogeneous, i.e. no Brownian movement occurs. The larger limit of particles exhibiting Brownian movement is approximately 0.0002 mm.

(iii) Fall must be unhindered. Particles falling very near the wall of the vessel (0.1 mm distance) are slowed down in their descent. Many fast falling particles may drag finer particles down along with them (concentration up to 3% solids).

(iv) Particles must be of uniform density.

(v) The suspension must be still without any turbulence. Particles of > 0.08 mm diameter settle quickly and cause turbulence and therefore, are analysed by other procedure.

3.6.3. Methods of Mechanical Analysis

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The international pipette method and the hydrometer method are usually used for mechanical analysis of soils.

The international pipette method is based on the principle of sedimentation, i.e. different sized particles having different weights fall at different velocities. If a sample of soil suspension is taken at a given depth at a particular time, this will contain all the particles which are still in suspension at that depth.

The pipette method is regarded as a standard method for particle size analysis because of its accuracy. It is, however, very time consuming and difficult to be employed in the mechanical analysis of a large number of samples.

The hydrometer method is based on the principle that there is a continuous decrease in the density of soil suspension over time at the rate the particles fall below the level of the hydrometer. So by knowing the density of the soil suspension at required times with a calibrated hydrometer, the proportion of different sized particles can be determined.

The hydrometer method is rapid but less accurate than the pipette method. This method gives erroneous results in soils having high $CaCO_3$ and organic matter contents and high salinity.

3.7. Textural Classes

Within each of the three broad groups of soil textural classes, i.e. *Sandy soils*, *Loamy soils* and *Clayey soils*, specific textural classes have been devised based on the relative proportion of sand, silt and clay particles.

In sandy soils, the sand separate comprises more than 70% of the material by weight (less than 15% of the material is clay). Two specific textural classes are recognised— *sand* and *loamy* sand.

The loamy soil group contains many subdivisions. An ideal loam is defined as a mixture of sand, silt and clay particles that exhibit the properties of these separates in about equal proportions. The various subdivisions are: *sandy loam*, *loam*, *silt loam*, *silt*, *sandy clay loam*, *silty clay loam*, *clay loam*, etc. To qualify for the modifier sandy or silt, a soil must have at least 40 to 45% of these separates. Thus, a loam in which sand is dominant is classed as sandy loam.

In clayey soils, the characteristics of clay separate are distinctly dominant. Three distinct classes exist, viz. *sandy clay* (at least 35% clay), *silty clay* (at least 40% clay and 40% silt) and *clay* (at least 40% clay and less than 40% silt).

The particle size distribution and textural classes of some bench mark soil series of India are given in Table 3.

The textural class is determined on the basis of different proportions of sand, silt and clay by using the textural triangle. There are many textural classification schemes; however, the International Society of Soil Science (ISSS 1929), renamed as International Union of Soil Sciences (IUSS) and USDA Soil Survey Staff (1975) schemes are the most common ones.

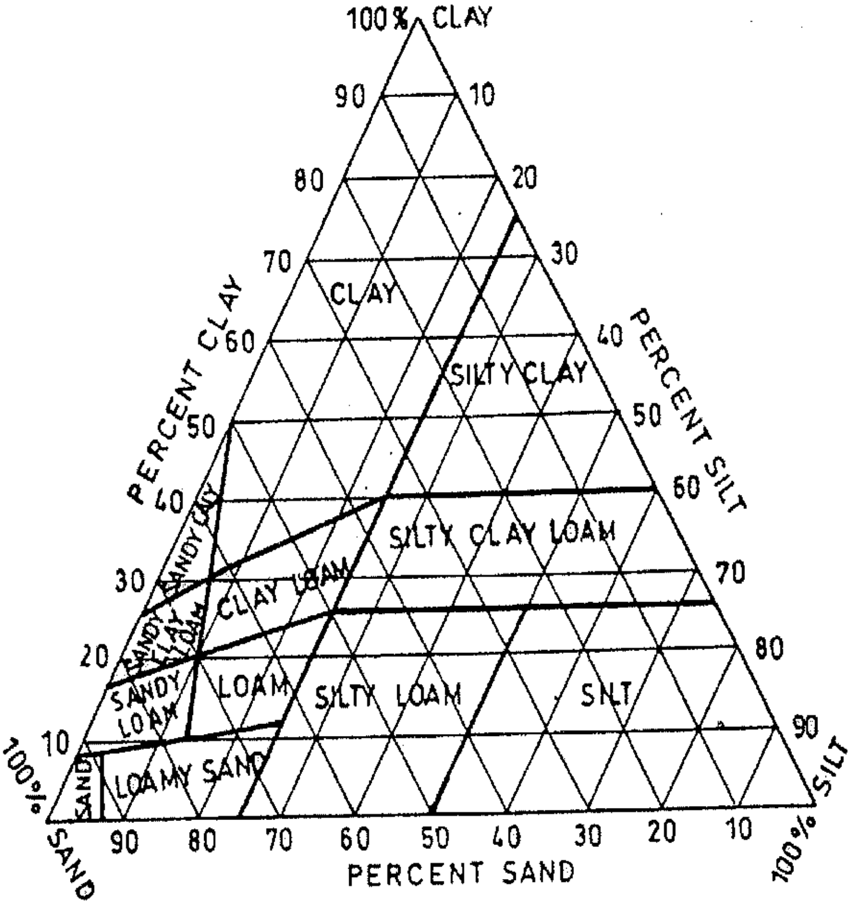


Figure 2. Triangular textural diagram (sand, silt and clay particle sizes of 2-0.02 mm, 0.02-0.002 mm and < 0.002 mm, respectively) (ISSS scheme, 1929)

To illustrate, assume that a soil contains 50% sand, 20% silt and 30% clay. The lower left apex of the triangle (ISSS Scheme, Figure 2) represents 100% sand and the right side of the triangle represents 0% sand. Find the point of 50% sand at the bottom edge of the triangle and follow the diagonally leftward line rising from that point and paralled to the zero line for sand. Then identify the 20% line for silt which is parallel to the zeroline for silt, namely, the left edge of the triangle. The point at which the two lines intersect and meet the 30% line for clay is the point we are seeking. In this particular example, it happens to fall within the realm of "clay loam".

Other textural terms such as peat (fabric), muck (sapric) and mucky peat (hemic) are used to describe organic materials. Peat is a raw undecomposed organic material, while muck is well-decomposed organic material. Mucky peat is an intermediate material between muck and peat. Deposits or soils containing 20% to 50% organic matter are called muck; and those containing more than 50% are classified as peats. In Malaysia, the term organic clay is used in addition to the above terms and the differentiation between the various organic textural classes is essentially based on per cent weight loss after ignition.

The naturally aggregated primary soil particles are separated by removing cementing agents, such as organic matter, calcium carbonate, or iron oxides. Organic matter is removed by oxidation with hydrogen peroxide and $CaCO_3$ is removed by treating with hydrochloric acid. The particles are made discrete by deflocculating the clay with a chemical dispersing agent such as sodium hexametaphosphate and by mechanical agitation (shaking, stirring or ultrasonic vibration). Failure to disperse the soil completely results in flocs of clay or aggregates settling as primary particles and vitiating the results of mechanical analysis.

Table 3. Particle size distribution, textural class, aggregate stability and soil water retention of some benchmark soil series of India*

Horizon	Depth (cm)	Particle size distribution (%)			Textural class	Aggregate stability			Soil water retention (w/w, %)		
		Sand	Silt	Clay		*MWD	**MWD	***% WSA	0 bar	0.33 bar	15 bar
			Patancheru series (Udic Rhodustalfs), Patancheru, dist. Medak, Andhra Pradesh								
Ap	0-10	72.1	5.1	22.8	SClL	0.67	0.63	28.21	36.59	13.36	5.94
A	10-20	75.9	2.6	21.5	SClL	0.80	0.48	30.75	35.52	13.46	5.50
BA	20-30	65.7	1.3	33.0	SCl	0.61	0.49	57.19	46.73	-	-
Bt1	30-49	50.3	3.8	45.9	Cl	3.61	0.99	63.50	59.37	21.59	12.66
Bt2	49-102	36.2	2.6	61.3	Cl	5.54	4.34	65.38	65.26	27.41	18.28
BC	102-145	79.8	2.6	17.7	SL	3.49	2.86	84.90	37.27	12.83	6.28
C	145-160	81.1	1.3	17.7	SL	2.13	2.21	90.37	39.87	12.94	6.35
			Vijayapura series (Typic Kandiustalfs), vill. Kodihilli, dist. Bangalore, Karnataka								
Ap1	0-7	59.7	7.6	32.7		0.50	0.61	28.35	30.68	9.21	4.17
Ap2	7-21	59.7	5.1	35.2	SCl	0.51	0.60	61.09	38.40	14.13	7.61
Bt1	21-46	54.6	5.1	40.3	Cl	0.72	0.87	63.06	44.22	17.33	9.61
Bt2	46-87	54.6	5.1	40.3	Cl	3.31	1.44	62.97	44.56	17.53	10.23
Bt3	87-104	54.6	12.7	32.7	ClL	2.70	1.62	71.60	43.26	19.41	11.65
2C1	104-135	67.3	5.1	27.6	SClL	1.15	1.15	44.78	50.11	24.14	11.77
2C2	135-152	67.3	3.1	30.1	SCl	3.87	2.93	59.89	47.11	23.68	12.93
			Trivandrum series (Ustoxic Dystropepts), vill. Srikriyam, dist. Trivandrum, Kerala								
Ap	0-9	60.8	5.2	34.1	SCl	4.87	2.23	60.36	48.53	17.85	12.68
A	9-25	42.7	5.2	52.1	Cl	5.32	2.25	50.06	53.19	26.43	19.36
B	25-52	32.4	5.2	62.4	Cl	5.57	2.35	40.87	60.58	31.00	22.86
C	52-84	24.7	5.1	70.1	Cl	4.29	2.72	70.71	61.67	34.78	24.92
			Torkewadi series (Lithic Ustorthents), Rahuri, dist Ahmednagar, Maharashtra								
A	0-15	56.01	15.9	28.09	ClL	4.81	1.95	82.13	59.4	26.8	14.3
C	15-23	56.01	5.3	38.69	Cl	5.35	4.75	98.21	62.6	38.1	26.0
			Madhpur series (Typic Endoaqualfs), vill. Madhpur, P.O. Bhatar, dist. Burdwan, West Bengal								
Ap	0-14	52.5	26.1	21.5	SiL	0.69	0.76	50.83	40.85	21.71	5.07
BA	14-38	52.5	18.2	29.3	ClL	0.60	0.33	42.92	43.64	17.99	6.97
Bt1	39-98	44.7	18.2	37.1	Cl	1.30	1.48	74.57	48.49	19.26	9.21
Bt2	98-150	29.0	23.4	47.5	SiCl	1.39	1.48	77.84	53.96	24.67	12.42
P4/5		29.0	23.4	47.5	SiCl	1.49	1.61	65.66			
			Lukhi series (Typic Ustochrepts), vill. Uncha Majra, dist. Gurgaon, Haryana								
Ap	0-8	72.5	10.1	17.4	SL	0.48	0.69	21.30	44.53	8.75	3.97
A	8-27	77.5	5.1	17.4	SL	0.25	0.33	13.63	44.81	6.62	3.62
Bw1	27-55	80.1	2.5	17.4	SL	0.28	0.32	7.73	42.01	6.81	3.81
Bw2	55-86	80.1	2.5	17.4	SL	0.23	0.28	7.48	43.41	6.95	3.72
Bw3	86-125	80.1	2.5	17.4	SL	0.14	0.16	4.11	43.98	7.37	3.90
Bw4	125-178	83.9	3.8	12.3	SL	0.17	0.20	9.18	45.28	7.99	4.06

Contd

Table 3. Particle size distribution, textural class, aggregate stability and soil water retention of some benchmark soil series of India⁺ — *Contd*

Horizon	Depth (cm)	Particle size distribution (%)			Textural class	Aggregate stability			Soil water retention (w/w, %)		
		Sand	Silt	Clay		*MWD	**MWD	***% WSA	0 bar	0.33 bar	15 bar
Mataur series (Dystric Eutrochrepts), vill. Kanra, dist. Kangra, Himachal Pradesh											
Ap	0-21	50.6	35.9	13.5	SiL	0.66	0.72	35.66	54.46	25.73	5.71
BA	21-38	53.1	25.7	21.2	SiL	0.66	0.45	49.78	45.31	19.41	6.72
B1	38-68	55.7	18.0	26.3	ClL	1.15	0.99	53.18	46.28	19.17	8.67
B2	68-90	58.3	17.9	23.8	ClL	0.55	0.53	37.40	44.34	18.98	7.77
Zarifa Viran series (Typic Natraaqualf), Karnal, Haryana											
A1	0-5	48.6	34.3	17.1	SiL	0.86	1.22	39.94	45.85	24.13	5.49
A2	5-24	46.1	34.3	19.7	SiL	0.31	0.26	26.76	45.70	24.18	6.70
Bt1	24-56	43.5	33.0	23.5	SiL	0.31	0.38	14.57	46.25	25.28	8.53
Bt2	56-85	37.2	38.1	24.7	SiL	0.40	0.31	9.25	47.46	28.58	9.58
BCk	85-118	43.5	34.3	22.1	SiL	0.48	0.25	13.38	47.20	28.97	9.11
Ck	118-140					1.93	0.26	8.42	45.44	29.10	10.68
Khatki series (Typic Haplustalfs), Modipuram, dist. Modipuram, Uttar Pradesh											
Ap	0-12	54.9	12.7	32.4	ClL	0.24	0.25	7.53	48.60	21.41	5.44
A3	12-28	52.4	22.9	24.7	ClL	0.19	0.21	5.40	44.97	18.59	5.72
B1t	28-45	42.2	21.6	36.2	ClL	0.22	0.26	15.27	48.51	20.93	9.40
B21t	45-78	38.4	21.6	40.0	Cl	0.25	0.31	24.14	49.99	22.54	10.58
B22t	78-99	35.9	22.9	41.2	Cl	0.39	0.44	31.80	49.54	23.52	13.68
B3t	99-140	35.9	22.9	41.2	Cl	0.40	0.39	44.90	49.17	25.34	12.45
Jagdishpur Bagha series (Typic Ustifluvent), vill. Balua, dist. Muzaffarpur, Bihar											
Ap	0-15	57.8	24.0	18.3	L	0.35	0.43	0.43	49.99	27.45	3.80
A3	15-42	59.0	18.9	22.0	L	0.13	0.23	0.23	48.96	29.15	4.14
B_1	42-76	54.0	15.1	30.9	ClL	0.10	0.14	0.14	48.01	29.14	2.50
C_{11}	76-115	38.9	24.0	37.2	ClL	0.12	0.22	0.22	40.88	15.67	1.37
C_{12}	>115	40.1	21.4	38.4	ClL	0.08	0.19	0.19	52.04	31.04	6.11
Coimbatore series (Vertic Ustropepts), TNAU Campus, dist. Coimbatore, Tamil Nadu											
Ap	0-15	49.5	5.3	45.3	Cl	0.38	0.29	17.72	49.63	24.10	13.62
Bw	15-42	49.5	5.3	45.3	Cl	0.55	0.64	65.53	46.84	24.13	14.48
BC	42-75	49.5	5.3	45.3	Cl	0.46	0.43	55.47	48.41	23.92	14.19
Ck	75-124	43.6	20.3	36.1	ClL	5.76	3.34	81.41	52.75	36.29	17.52

+K.M. Hati and A.K. Misra (personal communication);
S = Sand, Si = Silt, Cl = Clay, L = Loam; SClL = Sandy clay loam; *MWD, Mean weight diameter of water stable aggregates including the sand and concretions; **MWD, Mean weight diameter of water stable aggregates excluding sand and concretions; ***%WSA, per cent water stable aggregates of more than 0.25 mm diameter.

4. Specific Surface of Soils

The specific surface is an important property of soil grains that results from their sizes. It is defined as the amount of surface area per unit weight or volume of a soil and is expressed in cm^2/g or per cm^3. This is important for chemical and physical reactions.

Specific surface of a sphere is given by Equation (17):

$$\frac{4\pi r^2}{4/3\pi r^3} = \frac{\text{(Surface area)}}{\text{(Volume)}} \text{ or } \frac{3}{r} \qquad \text{...(17)}$$

The specific surface of different soil particle size fractions, soil types and clay minerals are given in Table 4. Besides size, the shape and type of clay minerals also affect specific surface of a soil. The specific surface of soil greatly influences the physical and chemical properties such as retention of water at high suction, swelling, plasticity, soil strength, cation exchange capacity and availability of nutrients.

5. Soil Structure

5.1. *Definition*

Physically, a soil is a mixture of inorganic particles, decaying organic materials, water and air. The inorganic primary particles of various sizes (sand, silt or clay fraction) generally cluster together to form complex and irregular patterns of secondary particles which are called aggregates or peds. **The term 'soil structure' refers to the arrangement of these primary and secondary particles into a certain structural pattern.** Soil structure greatly influences many soil physical processes such as water retention and movement, porosity and aeration, transport of heat, etc. The various soil management practices such as tillage, cultivation, application of fertilizer and manures, amendments (liming, gypsum) and irrigation, bring about changes in soil structure that influences other soil properties, thereby affecting root growth, water and nutrient uptake, crop growth and yield.

5.2. *Classification of Soil Structure*

④

Classification of soil structure for field description is based on (i) the type, as determined by the shape and arrangement of the peds; (ii) the class, as differentiated by the size of the peds; and (iii) the grade, as determined by the distinctiveness and durability of the peds.

5.2.1. Type of Soil Structure

Based on the shape and arrangement of peds or aggregates, soil structure is classified into four principal types— platelike, prismlike, blocklike and spheroidal with a few subtypes in each category (Figure 3).

(i) *Platelike* — In this structural type the aggregates are arranged in relatively thin horizontal plates, or leaflets. *Platy* structure is often formed from parent materials and can also result due to compaction by heavy machinery on clayey soils.

(ii) *Prismlike* — Two subtypes of this structure, **prismatic** and **columnar**, are vertically oriented aggregates, occurring commonly in

Table 4. Specific surface of soil particles and clay minerals

Size fraction	Diameter (mm)	Specific surface (cm^2/g)	Clay minerals**	Specific surface (m^2/g)
Coarse sand	2-0.2	45	Kaolinite	37-45
Fine sand	0.2-0.02	446	Illite	120-170
Silt	0.02-0.002	4,458	Montmorillonite	580-750
Ultra clay	10^{-4}-10^{-6}	9,890,000 (9.8millions)	Chlorite	130-180
Sandy loam soil		10-40*	Vermiculite	780-900
Loam soil		50-100*		
Clay soil		150-250*		

* (in m^2/g),

**Source: Raman and Ghosh (1974)

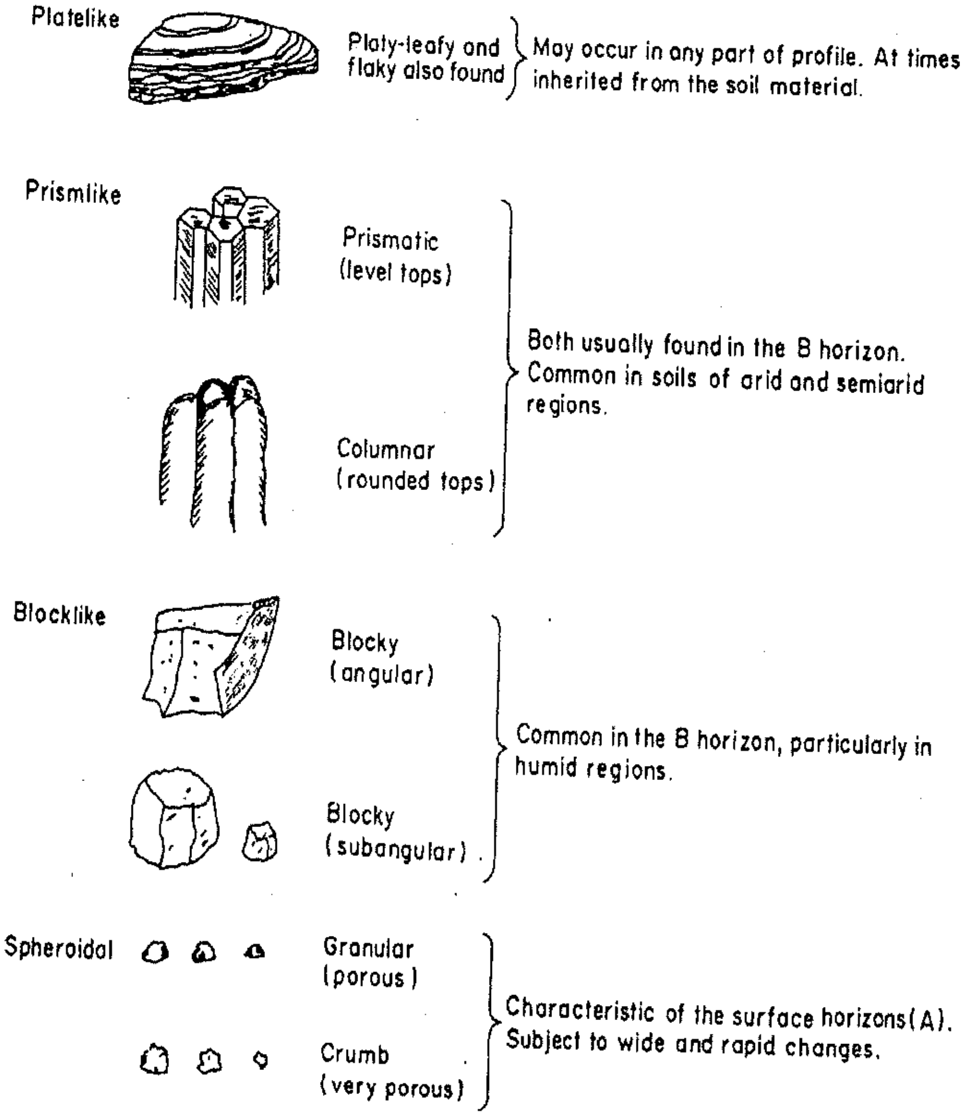


Figure 3. Various structural types found in soils
Source: Brady and Weil (1996)

subsurface horizons of semi-arid and arid regions. These are distinct features in well developed profiles of arid soils of Rajasthan. They are also associated with swelling type of clay and occur in poorly drained soils of humid region too. The prisms having rounded tops are called *columnar* structure, and mostly occur in subsoils of salt-affected/ sodic soils (natric horizon). The *prismatic* structures have the tops of the prisms angular and are relatively flat horizontally.

(iii) *Blocklike* — These aggregates look like blocks, irregularly six-faced and having their three dimensions more or less equal. The peds have sizes varying from 1 cm to 10 cm. Two subtypes of structure exist— *angular blocky* and *sub-angular blocky*. In the former, the cubes have sharp edges and distinct rectangular faces, whereas in the latter, some rounding of the cubes occurs. Formation of these types of structures is influenced by root penetration, soil drainage and aeration. They mostly occur in the subsoil.

(iv) *Spheroidal* — Two subtypes structures— *granular* and *crumb*— are put in this category. When the peds or aggregates are relatively non-porous, they are called *granules* and the porous granules are termed as *crumbs*. These two types of structures occur in surface soils high in organic matter, in grasslands and are greatly influenced by farming practices.

5.2.2. Class of Soil Structure

The various sizes of peds are designated by class of soil structure as very fine, fine, medium, coarse and very coarse. For example, crumb structures having peds less than 1 mm size are very fine, 1-2 mm size are fine and 2-5 mm size are of medium class.

5.2.3. Grade of Soil Structure

The degree of aggregation or grade of soil structure is the distinctness or durability with which the peds are observed, viz. weak, moderate and strong.

The soil is structureless when there is no observable aggregation or there is no line of cleavage indicating the presence of peds, e.g. *single grain* soil particles in sand dune areas and *massive* structure in puddled soil from a rice field.

Soil structure is a very useful criterion in field study of soil profiles and in soil classification. Soil structure is described in terms of shape of the peds present, their relative size and also degree of development. For example, a soil horizon might have a weak, medium and subangular blocky structure.

5.3. Evaluation of Soil Structure

Evaluation of soil structure assumes special significance in view of its important role in influencing soil-plant relationships. Soil structure can be evaluated by direct and indirect methods (Biswas and Mukherjee, 1987).

5.3.1. Direct Methods

The direct methods including the microscopic evaluation in the laboratory and the macroscopic or field observation, characterize the shape, size and arrangement of soil aggregates. In the microscopic method, thin soil sections are examined under a petrographic microscope with respect to the nature, shape and size of the secondary particles and voids. In the macroscopic method, when a chunk of dry soil excavated from soil in the field is allowed to fall gently on a smooth surface, it breaks into small pieces of peds of different sizes and shapes. The shapes and sizes can also be assessed in soil profiles from the cleavages and the *type*, *class* and *grade* of soil structure are determined.

5.3.2. Indirect Methods

The indirect methods of soil structure evaluation involve measurement of (i) size distribution of stable aggregates, (ii) stability of aggregates, and (iii) soil property which is a function of soil structure.

(i) Size Distribution of Stable Aggregates— This is measured by dry or wet sieving techniques. In dry sieving technique, the proportion of aggregates which is stable against vibrating action simulating the scouring effect of wind is determined. Dry sieving gives a better picture of aggregation where the aggregates are weakly held together in the moist condition and the mechanical action of sieving is sufficient to destroy them. Dry sieving of aggregates gives an important index for characterizing the susceptibility of soils to wind erosion.

The wet sieving technique used by Yoder (1936) and subsequently improved by the Soil Science Society of America's Committee on Physical Analysis (van Bavel, 1953) is generally used for determining the size distribution of water stable aggregates. Wet sieving is well adapted to the separation of large aggregates. It can be used to screen out aggregates as small as 0.1 mm, although 0.25 mm is more satisfactory as the lower limit of size.

Indices of Soil Structure — The quantum of aggregates of different size-ranges is to be represented by a single value index. Size and weight being the variables, weighted mean diameter is the widely used index. The commonly used forms of mean diameter are: *Mean Weight Diameter, Change in Mean Weight Diameter, Geometric Mean Diameter*, and *Log Standard Deviation* and *Coefficient of Aggregation*. Also, the *percentage of aggregates greater than 0.25 mm* diameter is a widely used index. In wetland rice soil, the change in mean weight diameter of water stable aggregates before and after puddling as well as clay dispersion are useful for characterizing the change in soil structure due to puddling.

The Mean Weight Diameter (MWD) — It gives an estimate of weighted percentage of average size of all the aggregates. The proportion by weight (w_i) of a given size fraction of aggregates to the total sample weight (W) is multiplied by the mean diameter x_i of that fraction. The sum of these products for all size fractions is called the MWD.

$$\text{MWD} = \sum_{i=1}^{n} x_i w_i \qquad \ldots(18)$$

where, n is the number of fractions; $w_i = \frac{W_i}{W}$, where, W_i is the weight of each size fraction and W is total sample weight.

MWD may also be estimated by plotting the accumulated percentages of aggregates against average diameter and determining the area atop the curve.

Change in Mean Weight Diameter (CMWD): It takes into account the stability of aggregates both under dry and wet sieving conditions. The difference between the two MWDs is the CMWD. Within certain limits, the lower the CMWD, the better is the soil structure.

In *Geometric Mean Diameter* (GMD) the weight of the aggregates in a given size fraction (W_i) is multiplied by the logarithm of the mean diameter (x_i) of that fraction. The sum of these products for all the size fractions is divided by the total weight of the sample (W). GMD is calculated using the Equation (19):

$$\text{GMD} = \exp\left[\sum_{i=1}^{n} W_i \log x_i / W\right] \qquad \ldots(19)$$

The mean weight diameter of water stable aggregates and the percentage of water stable aggregates greater than 0.25 mm diameter of some bench mark soil series of India are given in Table 3.

(ii) Measurement of Stability of Aggregates: This is evaluated by the degree to which soil aggregates resist dispersion. Several indices have been developed such as *Stability index, Structural coefficient, Dispersion coefficient* and *Water drop method*. Stability index is the difference between per cent clay and silt as determined by the mechanical analysis and that obtained by suspension of soil sample in water. The greater the difference, the better is the soil structure. Structural coefficient is given by (D–S)/S, where, D is the percentage of particles of < 0.25 mm diameter, as determined by the mechanical analysis and S is the percentage of aggregates smaller than 0.25 mm diameter, as determined by wet seiving technique. The higher is this value, the better is the structure.

(iii) Measurement of Soil Properties: A number of soil properties such as bulk density, rate of water infiltration, hydraulic conductivity, rate of aeration and aeration porosity, available soil water and degree of compaction are used as indicators of the suitability of soil structure for plant growth. A compacted soil with higher bulk density indicates poor structural condition.

5.4. Genesis of Soil Structure and Stable Aggregate Formation

The genesis of soil structure refers to the causes and methods of formation of the structural units or aggregates. An aggregate consists of grouping of a number of primary particles into a secondary unit. The mechanism of formation of these aggregates involves several factors such as vegetation, soil fauna, microorganisms, impact of cations, clay particle interactions in relation to moisture and temperature as well as organic matter and clay-organic matter interactions (Baver *et al*., 1972).

5.4.1 Flocculation and Aggregate Formation

In elucidating aggregate formation it is important to distinguish between flocculation and aggregate formation, which are not synonymous. In a suspension, the primary particles with high electrokinetic (zeta) potential repel each other. With the addition of flocculating agent, the zeta potential is lowered, the particles collide, mutually attract each other and settle in the form of a *floccule*. The floccules are stable as long as the flocculating agent is present. However, aggregate formation requires the cementation or binding together of flocculated particles so that the primary particles do not disperse in water. Hence, stable aggregate formation or granulation is flocculation plus its cementation which are brought out by interplay of several factors as stated below.

5.4.2. Effects of Vegetation, Soil Fauna and Microorganism

During growth plant roots pushing through the soil, tend to compress soil particles into small aggregates and break the larger aggregates present in the soil. Root exudates help to bind the soil particles together into aggregates. The dehydration of soil in the vicinity of the root system as water is absorbed by the plants, causes local shrinkage and formation of surfaces of fracture.

The beneficial effects on soil aggregation and its stability originating from the integrated activity of soil fauna, microorganisms and vegetation are: (i) The fungi and actinomycetes cause mechanical binding of the aggregates by the mycelia they produce. (ii) The metabolic processes of the mircroorganisms synthesize complex organic molecules which have cementation effects. Thus, microbial products like bacterial gum and microbial polysaccharides, play a major role in soil aggregate stabilization. (iii) Products of microbial decomposition of organic materials added to soil, such as humic acids, colloidal proteins and cellulose materials, also produce stabilizing effect.

5.4.3. Cationic Effects

Aggregate formation is highly influenced by the nature of cations adsorbed by the soil colloids. For example, when Na^+ is a dominant adsorbed ion, as in soils of arid and semi-arid areas or alkali soils, the colloids continue to repel each other causing a dispersed condition. In such a state, soil particles do not come together to form structural aggregates. The soil becomes impervious to water and air. The divalent cations like Ca^{2+}, Mg^{2+}, on the other hand, form electropositive links between the electronegative soil particles which cause the individual colloidal particles to come together and form small aggregates called floccules. Calcium affects the production and decomposition of organic matter in soil. It also helps in the binding action between organic colloids and clay particles.

5.4.4. Effects of Organic Matter

Organic matter plays an important role in stimulating the formation and stabilization of granular and crumb type aggregates. The role of organic root exudates, microbial and decomposition products of organic materials in formation of stable aggregate has already been stated. Organic compounds, such as polysaccharides, chemically interact with the clays and form bridges between the individual soil particles and bind them together in water-stable aggregates.

5.4.5. Clay Particle and Clay-Organic Interaction

Three distinct groups of soil colloidal materials have cementation and aggregating effects— clay particles themselves, inorganic colloids of iron and aluminium oxides, and organic colloids.

Clay-to-clay particle interaction, particularly under dry condition, takes place due to electrostatic and van der Waal's forces. It leads to the formation of secondary particles. Aggregate formation is dependent upon the linkages established by polyvalent exchangeable cations on the clay particles. Polyvalent cations, in fact, serve as bridges to form clay-organic complexes, leading to the formation of stable aggregates.

Colloidal hydrated iron oxides become almost completely irreversible on dehydration, which is an important factor in the production of stable aggregates. This is observed in lateritic soils which have high degree of aggregation. Sesquioxides form complexes with humus, resulting in stable aggregate formation.

The bonding of organic polymers to clay surfaces by cationic bridges, hydrogen bonding, van der Waal's forces and sesquioxide-humus complexes are important mechanisms by which organic colloids stabilize soil structure. As a result of the interaction, the properties of the colloidal clay surfaces change. The organic colloids existing in association with the clay particles may tend to reduce wetting by water as well as swelling.

5.5. Management of Soil Structure

Soil structure management aims at the improvement and maintenance of soil structure, which are the major challenges in cultivated lands. The general principles relevant to structural management are :

(i) Tillage activities need to be restricted to periods of optimum soil moisture condition to ensure least destruction in the soil structure;

(ii) Adoption of suitable tillage or minimum tillage to reduce the loss of aggregates stabilizing organic matter;

(iii) Soil surface should be kept covered with crop residues or plant litter to protect aggregates from the beating action of rain and to add organic matter to soil;

(iv) Incorporation of crop residues and animal manures (FYM, poultry manure, etc.) into the soil would stabilize soil aggregates through supply of decomposition products;

(v) Suitable cropping systems, application of phosphate fertilizers, inclusion of grasses and sod crops in rotation, would enhance organic matter and favour stable aggregation;

(vi) Green manuring and cover crops are good sources of organic matter.

Each soil has distinct problems and requires specific soil and crop management practices for soil structure management.

6. Dynamic Properties of Soils

The behaviour of soil to an applied stress is expressed in terms of dynamic properties of soils which are mostly governed by two physical properties—adhesion and cohesion. *Adhesion* refers to the attraction of two dissimilar phases, e.g. attraction of a liquid phase such as water on the surface of a solid phase such as soil solid particles. *Cohesion* is the attraction between two similar phases. In soils, cohesion is bonding of the particles due to attractive forces between them due to van der Waal's forces, electrostatic attraction of negatively charged clay surfaces and positively charged clay edges, cationic bridges, cementation effects of organic matter and surface tension forces, etc. Cohesion also takes place between the water molecules which remain as films between the adjacent soil particles.

6.1. Soil Consistency

The manifestations of the physical forces of cohesion and adhesion acting within the soil at various moisture contents are designated by the term *soil consistency*. It includes such properties of the soil as resistance to compression, friability, plasticity, stickiness, etc. Thus, most soils exhibit four forms of consistency from progressively wet to dry soil moisture conditions.

(i) Hard or Harsh Consistency — It has the pronounced characteristics of hardness. At low moisture contents, the soil remains very hard and coherent due to cementation effect between the dried particles.

(ii) Friable Consistency — As the moisture content of the soil increases, water molecules are adsorbed on the surface of the soil particles and decrease the coherence. The soil mass becomes friable. Friability characterizes the ease of crumbling of soils. The range of soil moisture contents in friable condition is optimum for tillage operation.

(iii) Plastic Consistency — It is manifested by the properties of toughness and the capacity of the soil to be moulded into any desired shape.

(iv) Sticky Consistency — It is evident by the property of stickiness to various objects. The sticky point is defined as the moisture content of the soil when it ceases to stick to any foreign object.

6.2. Soil Plasticity

Soils containing more than 15% clay exhibit plasticity. Plasticity is defined as the property which enables a clay/ soil to take up water, to form a mass that can be deformed into any desirable shape and to maintain the shape after the deformation pressure is removed. Plasticity results from the plate like nature of the clay particles and the combined binding/ lubricating effect of the adsorbed water. With the adsorption of water, thin films are formed around the soil particles. With applied pressure or force, the particles slide over each other and are held in that condition by the tension of the moisture films even after the pressure is removed.

6.2.1. Indices of Plasticity and their Significance

Plasticity is exhibited over a range of moisture contents referred to as plasticity limits. There are three indices called the *lower plastic limit* or simply the *plastic limit*, the *upper plastic limit* or *liquid limit* and the *plasticity index*. The *plastic limit* is the lowest moisture content at which a soil can be deformed without cracking. It is the upper limit of moisture content for tillage operation for most crops, except rice. Tilling at moisture content above plastic limit results in smearing and puddling of soil. The *upper plastic limit* or *liquid limit* is the moisture content at which a soil ceases to be plastic. It becomes semifluid and tends to flow like a liquid under an applied force. This limit is used for classfication of soils for engineering purpose. The difference in the moisture content between the upper and lower plastic limits is the range over which a soil remains plastic and is called *plasticity index*. Soils with high plasticity index are difficult to plough. Soils with expanding lattice clays such as smectites have high liquid limits and plasticity indices. Clay minerals like kaolinite have low liquid limit values. Soil plasticity is determined by an apparatus called *liquid limit device*.

7. Soil Compression and Compaction

7.1. Soil Compression

Soil compression is defined as the change in volume of a soil under an applied stress, whereas soil compaction refers to the increase in density of a soil as a result of applied pressure or load.

Volume of soil is consisted of solid phase and the voids between it, which are occupied by water and air. So compression denotes the decrease in the void ratio per increment of applied pressure or load. The increase in compression with each increment of pressure can be expressed by the Equation (20):

$$y = ae^{-bx} \qquad \ldots(20)$$

where, 'y' is the amount of compression, 'x' is the pressure, and 'a' and 'b' are constants.

Compression takes place with increment in pressure due primarily to particle orientation and changes in the size of the colloidal micelles. Soils may be compressed under low or high pressures. In the latter case, the soil expands when the pressure is removed because of swelling of the micelles. Compression is affected by the nature of clay mineral, the type of exchangeable cations and the degree of polarity of organic liquids. With increase in soil moisture content, compression increases to a maximum and then decreases with further increase in moisture content. The maximum compression occurs within the plastic range of soil moisture content.

7.2. Soil Compaction

Soil compaction encompasses compression plus increase in density of a soil. It is the dynamic behaviour of soil. The degree of compaction depends upon the nature of soil, amount of energy applied, water content and extent of manipulation of the soil. Compaction is also associated with the rearrangement of the soil solid particles so that soil water and soil air are compressed within the pore spaces.

Because of the imcompressible nature of soil particles and high internal friction, dry soils cannot be compacted to high densities. An increase in water content decreases cohesion between the particles and internal friction, thereby facilitating compaction. During compaction, the density of soil under a load increases with the increase in soil water content up to a certain limit, beyond which further addition of water does not increase compaction because of imcompressible nature of soil solids and water. This critical limit is called *procter moisture content*.

In many soils, a compacted layer is commonly found at the bottom of the zone of ploughing. This layer is termed as '*plough-sole*'. Age-old practices of tillage using wooden plough and other farm practices including use of tractor and other heavy farm equipments, create the problem of surface and sub-surface compaction in soils. These hard compact layers often restrict root penetration and growth and also reduce water and nutrient uptake by crops. Soil compaction changes soil moisture retention, soil thermal regimes and mechanical resistance in soils. For enhancing crop growth, the management practices should be able to break the hard compacted layer and should avoid or reduce its formation. However, in highly coarse-textured sandy, loamy sand soils, compaction may be a boon to enhance the water retention and reduce percolation loss of water. This is elaborated in this chapter in section No. 11.1.

8. Soil Crusting

Soil crust is the thin compact layer of higher bulk density formed at the soil surface following dispersion of natural soil aggregates as a result of wetting and impact of raindrops and its subsequent rapid drying due to radiant energy of the sun.

8.1. Crust Formation

When the raindrops strike the exposed dry soil surface, there is disintegration and dispersion of the aggregates. The finer clay particles move down along with infiltrating water and clog the pores immediately beneath the surface, thereby sealing the soil surface. Also, the dispersed soil may remain in suspension, coarse particles start to settle out, but fine clay particles remain in suspension. As the water evaporates, clay settles on the top of coarse particles, forming a crust on drying. The soil particles tend to pull together due to surface tension forces and form a dense strong soil layer with decreased porosity. Soil crusting is a major structural feature of soils of arid and semi-arid regions. The problem of soil crusting is severe in silty clay loams of older alluvial terraces and levees due to their unstable soil structure.

8.2. Properties and Effect of Soil Crust Formation

The strength of soil crust increases linearly during the first few days of formation. The thickness of the soil crust formed depends on the size of raindrops. Larger raindrops with more energy destroy the original soil structure to a greater depth. The crusts formed are thicker, varying from 4 to 5 mm. In a cloddy soil where fine particles removed from the surface of the clods by rain-drop impact are deposited in inter-clod areas, the crusts become thinner and weaker. The thickness of the crust also depends upon the amount and type of clay and silt present in the soil. The small amount of kaolinite type of clay tends to form a thin crust which curls up and breaks on drying, but montmorillonite type of clay tends to form a thick and hard crust. The thickness of the crust increases with increase in clay content.

In addition to size and intensity of rain drops, soil factors that result in low aggregate stability, encourage soil crust formation. Soils having low organic matter, high silt content and high exchangeable sodium percentage are more susceptible to soil crusting.

Soil crusts have high bulk density, low non-capillary porosity and high soil strength. Stratification and orientation of soil solids and subsequent cementation of particles when dry, make the crusts harder than the rest of soil mass. Infiltration through the crusted layer and the hydraulic conductivity of the crusted layer become very low (Figure 4). As a result, run-off and soil loss increase. Redistribution of water in the soil profile is also greatly affected. The most important effect of soil crusts is the emergence and growth of seedlings which are greatly affected. These, in turn, affect crop stand and ultimately the yield.

8.3. Evaluation of Soil Crust Strength

Soil crust strength can be evaluated by using a penetrometer, balloon pressure technique or modulus of rupture test. A pocket penetrometer or a cone penetrometer is pushed steadily into the soil and the penetration resistance is measured by directly taking the reading on the body or dial of the penetrometer, which is expressed in kg/cm^2. In balloon pressure technique, the balloons are burried in the soil and the pressure required to inflate the balloon at a

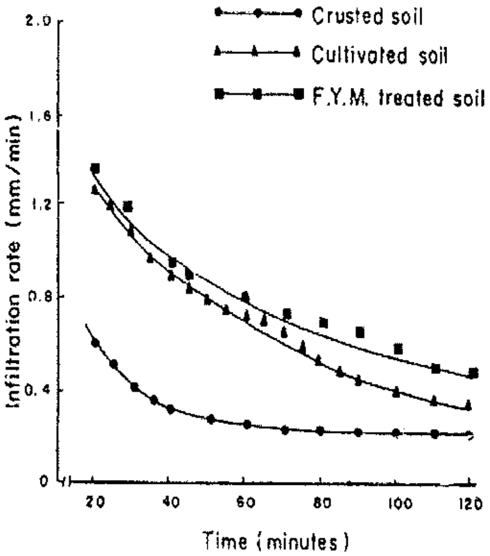


Figure 4. Infiltration rate *versus* time relationships for crusted, cultivated and FYM-treated soils

point where it ruptures the soil surface is measured. In the modulus of rupture test, a briquette of soil sample is prepared and the force required to rupture it is measured. For a rectangular briquette, the modulus of rupture S (dynes/cm^2) is calculated from the Equation (21):

$$S = \frac{3FL}{2bd^2} \qquad \ldots(21)$$

where, F (in dynes) is the breaking force, L is the distance (in cm) between the bars supporting the briquette, b is the width, and d is the thickness of the briquette (in cm).

8.4. Reducing Soil Crust Formation and Increasing Emergence of Seedlings

Soil surface-covers such as mulches, plant residues, etc. reduce the impact of raindrops, prevent dispersion and breakdown of structure of the surface soil, reduce crust formation and maintain high infiltration rate. Close growing crops, grasses and legumes that cover the soil to a large extent also prevent crust formation. Crusting tendency of soils can be reduced by using farmyard manure and chemical amendments like cationic, anionic and non-ionic surfactants and use of gypsum in salt-affected soils, which in turn enhance the seedling emergence (Figure 5). Crop rotation and residue management increase the soil organic matter content and help in formation of low strength crusts. Keeping the soil moist by irrigation also helps in reducing the crust formation. In crust-affected soils, seedling emergence can be enhanced by mechanical breaking of the crusts, planting seeds in furrows and dibbling 2-3 seeds per hill where the seedlings exert more thrusts to overcome the physical restraints imposed by the overlying soil crusts (Figure 6).

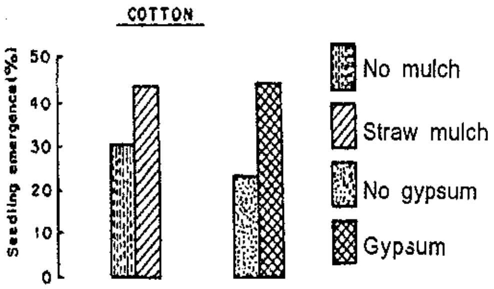


Figure 5. Seedling emergence of cotton as influenced by mulch and gypsum application in crust-affected soils

Figure 6. Seedlings exert thrust to emerge through soil crusts

9. Soil Colour

Soil colour often gives a ready clue to its condition and some important properties. For example, dark-colour surface soils absorb more solar radiation than light-colour soils and so get warm up faster. Colour is often a diagnostic mode of major soil classification and interpretation. Soil colour is included in the description of a soil profile. Surface colour that differs from that of the parent material usually serves as an indicator of the processes involved in the soil formation. It is also indicative of other factors such as presence of excessive salts (white), erosion, etc.

9.1. Determination of Soil Colour

For determination of soil colour, standard system using Munsell colour chart is used. A small piece of soil is compared to the standard colour chips in the soil colour book. Each colour chip is described by three components of colour, namely, hue, value and chroma. Hue is the dominant spectral colour. Value refers to the relative brightness (lightness or darkness) of the colour and is a function of the total amount of light reflected. Chroma is the relative purity or strength (intensity) of the dominat spectral colour.

9.2. Factors Influencing Soil Colour

Soil colour varies from place to place in the landscape. Even adjacent soils have different surface horizon colours such as in black and red soils existing side by side in Andhra Pradesh. Within a soil profile, the colour may change with depth through the different horizons. Even within a single horizon, colour may vary from spot to spot.

Most important factors influencing the soil colour are mineralogy and chemical constituents, organic matter content, soil moisture, soil structure and particle size. Red, yellow or brown colours are mostly related to different degrees of oxidation, hydration and diffusion of iron oxides in the soils, which form coatings on the soil particles. Thus, yellow, red and brown colours are mostly due to the presence of goethite, hematite and maghemite, respectively. The dark colour of soils is associated with a combination of several factors, including the content and decomposition of organic matter, impeded drainage condition and the presence of titaniferous magnetite. Minerals like manganese oxide and glauconite impart black and green colour, respectively to soils. Carbonate, such as calcite accumulating in soils of semi-arid regions imparts a white colour to it. Under prolonged wet anaerobic conditions, the coatings of reduced iron oxide change the soil colour to gray or bluish, a condition of *gley* formation.

10. Soil Physical Constraints that Affect Crop Production

In India, about 85.65 Mha of land produce very low yield of crops due to unfavourable soil physical conditions. The major soil physical constraints identified are: low water retention and high permeability, slow permeability, surface and sub-surface mechanical impedence, hardening and shallow depth of soils, which either restrict crop growth or reduce efficiency of basic inputs, such as water, fertilizer, etc. (Figure 7). The physical properties of representative physically-constrained soils are given in Table 5 (Gupta *et al.*, 1984).

10.1. Low Water Retentive and Highly Permeable Soils

These soils covering about 10.77 Mha, occur mostly in Rajasthan and some parts of Haryana and Punjab. The high permeability of these soils are associated with their sand and loamy sand texture. The soil has low bulk density but high hydraulic conductivity and infiltration rates (as high as 36.5 cm/h for some profiles), which indicate high permeability and low water retention capacity of the soil. The fertilizer and water use efficiency of these soils is very low and the nutrient losses are very high. These problems do not encourage the farmers to use high levels of inputs. The major crops grown on these soils are: pearl millet (*bajra*), maize, wheat and barley in the western parts of India and sorghum, maize, *ragi* (minor millets) and sugarcane in the southern parts of India.

10.2. Slowly Permeable Soils

The slowly permeable soils of about 9.43 Mha occur in Madhya Pradesh, Maharashtra and also in parts of Rajasthan, Uttar Pradesh, Bihar, and Tamil Nadu. The infiltration rate is as low as 0.2 cm/h and hydraulic conductivity is less than 0.15 cm/h for some of the profiles, which indicate slow permeability of the soil and possibility of submergence during rainy season. The very low permeability, which is associated with black clay soils, creates oxygen stress in the root zone due to stagnation of water. The prevailing anaerobic conditions cause the accumulation of carbon dioxide and other by-products in this zone, which restricts the root growth. These black clay soils are sticky when wet and very hard when dry often forming big cracks (Figure 8), thus, these soils could be cultivated or tilled only within a limited soil moisture range.

In the valley lands where the topography is flat, weed menace associated with humid conditions combined with limited range of workability of these soils, prevents the farmers from growing crops during the rainy period. On the undulating and rolling topography, the poor vegetative cover during most of the rainy season exposes the surface soil to the impact of high intensity storms causing loss of large quantities of soil along with run-off water. Under these conditions, a shallow or deep *havali* system is followed by the farmers on low lands to conserve maximum amount of moisture in the soil for the cultivation of crops

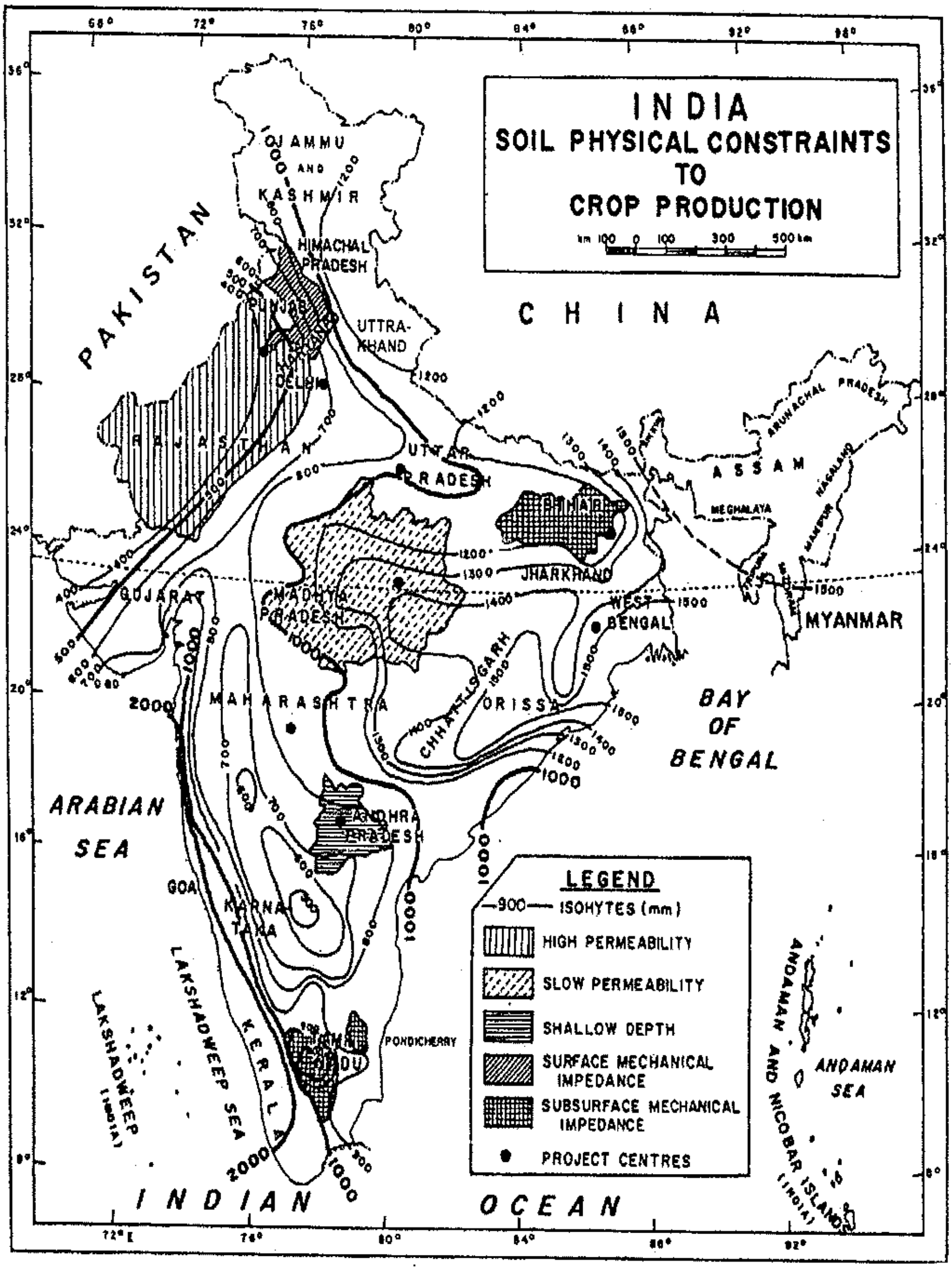


Figure 7. Map of India showing soil physical constraints to crop production

on stored moisture during the post-rainy season, which keeps most of the black soil under monocrop.

Sorghum, cotton, soybean and pigeonpea are grown on uplands, while rice for grain and maize and sorghum for fodder are grown on lowlands during the rainy season.

10.3. Crusting, Hardening and Shallow Soils

The shallow soils cover about 25.02 Mha, hardening soils 20.35 Mha and soils having other physical constraints 9.45 Mha. These soils occur widely in Haryana, Andhra Pradesh and Tamil Nadu. Profile 3 (Table 5) is an example of the crusting soil. It is to be noted that surface soil layer consists of 60% coarse and 40% fine fractions, a proportion optimum for crust formation when organic carbon is less than 1%. Due to surface mechanical impedence, the emerging plumule faces resistance, bends below the crust and tries to come out at weak points of the crust; some of the seedlings injure their tips and fail to emerge. The emergence of pearl millet, cotton and jute seedlings is adversely affected if the crust is formed on the soil surface by the occurrence of rainfall within 48 hours of sowing.

Table 5. Physical characteristics of representative physically constrained soils

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)	Texture (USDA classification)	Bulk density (Mg/ m³)	Moisture retention (g/100 g) at			Soil water retention between 0.1 and 15 bars	Infiltration rate (cm/h)
							1/10 bar (%)	1/3 bar (%)	15 bar (%)		
(a) *Highly permeable soil*											
Profile 1. Jobner sand, desert soil, Entisol/ Ustipsamment, Jobner (Jaipur), Rajasthan											
0-40	89.9	4.5	4.5	0.11	S	1.50	9.8	3.8	1.1	12.9	36.5
40-95	86.9	6.3	6.8	0.15	LS	1.56	10.0	4.2	1.5		
95-158	87.9	5.9	5.3	0.06	S	1.55	9.3	4.0	1.3		
158-215	88.9	5.8	4.2	0.06	S	1.54	9.9	3.9	1.1		
(b) *Slowly permeable soil*											
Profile 2. Black clay soil, Vertisol, Kuthuliaya (Rewa), Madhya Pradesh											
0-15	25	30	45	0.31	C	1.36	44.5	36.8	21.7	24.9	0.2
15-30	27	27	45	0.24	C	1.48					
30-45	25	30	45	0.16	C	1.49	46.0	38.1	21.7		
45-60	35	40	25	0.17	L	1.52					
60-75	32	40	27	0.24	L	1.55	48.5	39.8	21.9		
75-90	35	42	22	0.11	L	1.52					
(c) *Crusting soil*											
Profile 3. Barwala sandy loam, Inceptisol/Ustochrept, University Farm, Hisar, Haryana											
0-15	59.7	24.1	16.2	0.54	SL	1.52	35.1	29.2	8.1	21.5	0.4
15-45	69.8	13.8	16.4	0.60	SL	1.59	35.3	29.8	8.5		
45-80	68.3	13.9	17.8	0.77	SL	1.55	35.8	30.1	8.7		
80-120	69.4	12.8	17.8	0.81	SL	1.54	36.1	31.2	8.8		
120-185	70.0	14.0	16.6	0.77	SL	1.67	37.1	31.5	8.9		
(d) *Hardening soil*											
Profile 4. Hyderabad red sandy clay loam, Alfisol/ Paleustalf, Hyderabad, Andhra Pradesh											
0-10	62.4	12.5	23.5		SCL	1.5		18.7	8.9	5.8 (for 32 cm)	2.8
10-32	47.2	14.8	35.7		SCL	1.7		22.2	10.8		
32-65	Loose calcareous gravelly and murrumy layer admixed with soil										
(e) *Highly subsurface mechanical impedence soil*											
Profile 5. Pichanur red clay loam, Entisol/ Ustorthent, Pichanur (Coimbatore), Tamil Nadu											
0-12	66	11	23	0.60	SCL	1.55	25.6	16.2	6.8	15.9	4.0
12-32	37	13	48	0.35	C	1.62	40.6	31.8	16.8		
32-108	55	22	22		GSCL	1.72	25.6	18.4	10.5		

S= Sand, LS = Loamy sand, L = Loam, SL = Sandy loam, C = Clay, CL = Clay loam, SCL = Sandy clay loam, GSCL = Sandy clay loam mixed with gravel

The red sandy clay loam 'Chalka soil' of Andhra Pradesh dries out very quickly due to low water-retention capacity and becomes very hard. The maximum root growth of most of the crops is confined to the surface layer, and the crop growth suffers due to hardening. The crops grown on this soil include pigeonpea, maize, castor, groundnut and sorghum. The yield of groundnut is very low due to reduced size of pods caused by hardening of the soil.

Profile 4 (Table 5) is an example of hardening of soils. The surface soil layer contains about 62% coarse and 36% fine fractions, a proportion optimum for hardening and crust

Figure 8. Big cracks formed in dry black clay soil (Vertisol)

formation when the organic carbon is less than 1%. The soil is shallow in nature with water retention capacity of 5.8 cm.

The shallow soils of less than 20 cm depth are associated with the problem of erosion. The coarse-textured surface soil is underlain with soft disintegrated weathered rocks mixed with clay. The root growth is very poor due to quick drying of the soil. Most of the roots remain confined to the surface layer as in the case of soils with high subsurface mechanical impedence, but some roots do grow into *murrum* layer and extract water.

10.4. Soils with Subsurface Mechanical Impedence

The subsurface mechanical impedence in soils covering about 10.63 Mha, may be developed either due to the formation of plough sole, as in the case of rice fields on medium-textured soil, use of heavy machinery on moist soil, accumulation of clay in B-horizon under sub-humid conditions or the presence of *kankar* layers.

These high mechanical impedence layers are relatively impervious with the result that water stagnates on the soil surface after heavy rainfall or irrigation and the crops turn yellow due to oxygen stress. These layers do not allow the roots to penetrate deep into the soil. Shallow root system makes the plant drought-prone during dry spells and promotes lodging during unusally wet conditions. In high rainfall areas, the presence of such layers at shallow depth reduces the water storage capacity of the soil with the result that runoff starts even after a short shower, which causes floods in low lying areas.

Profile 5 is an example of the soils with high subsurface mechanical impedence for root growth. The bulk density increases to 1.62 Mg/m^3 at 12 cm depth which is higher than the critical value of 1.40 Mg/m^3 for clay and clay loam soils. Thus, farming systems and soil management practices have to be developed to ameliorate the soil physical constraints of soil and enhance crop production.

11. Management of Physically Constrained Soils

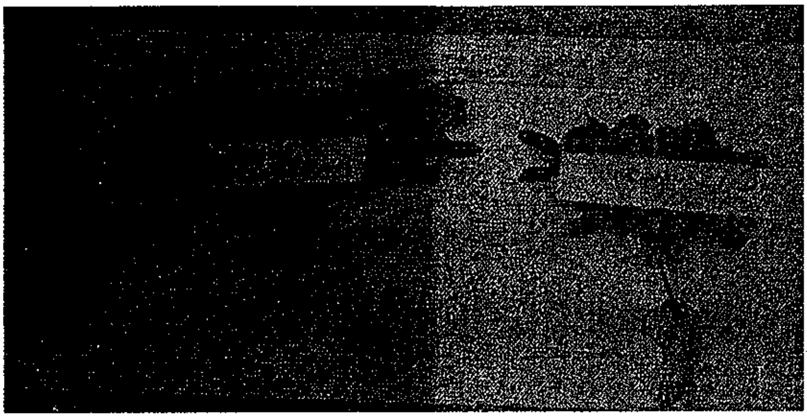
11.1. Highly Permeable Soils

For management of highly permeable coarse-textured sandy and loamy sand soils, adoption of compaction technology to attain sub-surface compaction is very useful. This involves making 4-6 passes of a tractor or bullock-drawn roller (depending upon its weight) at optimum soil moisutre or within 24 hours of irrigation/rainfall (Figures 9a&b). Compaction of such soils increases the proportion of micropores, reduces infiltration rate by 30-75% requiring less water in each irrigation, improves germination, provides anchorage to plant roots, reduces attack of white ants and white grab, enhances water and nutrient retention in the root zone for a longer period and their uptake by crops and thereby enhances the productivity potential of these soils (Figure 9c). The other management practices for such light-textured soils include the application of organic manures, pond sediments or mixing of clay which decreases the bigger pores and increases the smaller pores. This reduces hydraulic conductivity and increases water retention, which helps in enhancing crop yields and water and nutrient use efficiency (Das *et al.*, 1997).

11.2. Slowly Permeable Soils

In the case of fine-textured slowly permeable soils, adoption of 'raised and sunken bed technology' is useful. This involves growing of upland crops in 20 cm high and 3 m wide raised beds adjacent to 20 cm deep and 6 m wide sunken beds growing rice crop is useful

(a) Tractor-drawn roller (b) Bullock-drawn roller



(c) Groundnut growth (i) with and (ii) without compaction

Figure 9. Compaction technology for management of highly permeable soils

(Figure 10). Furrow irrigated raised bed planting system (FIRBS) for improving soil physical environment and resource-use efficiency has been found to be a useful technology. Application of organic manure, crop rotation and use of phosphatic fertilizers are also useful for such soils.

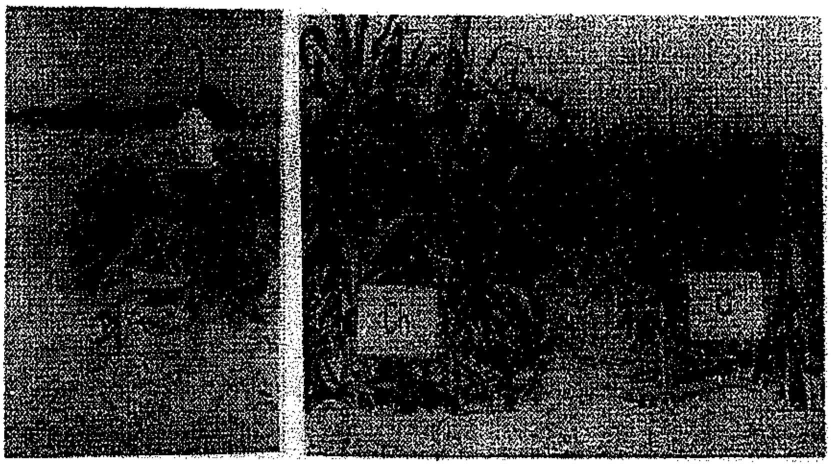
11.3. High Mechanical Impedance

For the management of soils having layers of high mechanical impedence at shallow depths such as plough soles or pans of clay accumulation in B-horizon, adoption of chisel technology or profile modification is a useful practice. The technology involves chiselling of the dry soil to 30-45 cm depth at 50-120 cm intervals, depending on the location of impedance layer and row-to-row spacing of the plants. A chisel, generally mounted in place of a plough, is used to break subsurface compacted soil layer (Figure 11). This (i) increases infiltration of rain and irrigation water which increases water storage in the sub-surface soil, (ii) improves aeration in the root zone, and (iii) encourages deeper root growth.

Figure 10. **Raised and sunken bed technology — Rice grown in sunken bed and soybean and other pulses in raised bed**

11.4. Acid and Sodic Soils

The structural management of acid soils involves application of lime, followed by



(a) Tractor-drawn chiseller (b) Maize growth with (Ch) and without (C) Chiselling

Figure 11. Chiseling technology for management of soils having mechanical impedance at shallow depths

organic manures. To improve the structure and reclaim highly dispersed sodic (alkali) soils, application of gypsum/pyrites in combination with organic manures, green manuring or incorporation of crop residues is successful.

11.5. *Chalka Soils*

The 'crop residue recycling technology' involving incorporation of high C:N ratio organic materials, viz. powdered groundnut shells or paddy husk has been recommended for the management of red sandy loam '*Chalka*' soils, which become very hard on drying. The 'seed line mulch technology' involving application of FYM or wheat *bhusa* @ 25 q/ha on seedlines immediately after sowing of pearlmillet and cotton seeds has been useful for the management of soils suceptible to form a crust.

11.6. *Rice-Wheat Cropping System*

Management of soil structure and enhancing and sustaining crop yields under rice-wheat cropping system in alluvial soils of Indo-Gangetic Plains are formidable tasks. Deep ploughing along with incorporation of crop residues, FYM, leguminous green manure crops during puddling for growing of paddy have been found successful (Das *et al.*, 1997). For subsequent wheat crops, tillage must be timed carefully with respect to soil moisture content to reduce and avoid large clod formation. Adoption of resource conservation technology such as zero tillage or minimum tillage for growing wheat subsequent to rice has been found to be very useful.

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Sample Problems

(In calculation of numericals, use either C.G.S. units or S.I. units. The two units should not be mixed up)

Question 1. A soil sample collected with a cylindrical core sample having height of 15 cm and diameter of 6 cm, has a fresh weight of 675.0 g and oven dry weight of 550.0 g. Calculate bulk density, specific volume, porosity, void ratio, mass wetness, volume wetness, degree of saturation, water volume ratio, airfilled porosity and depth of soil water in 0-15 cm soil layer (assume particle density $\rho_s = 2.65$ g cm^{-3}).

Solution:

Volume of core sample i.e. soil core $V_t = \pi r^2 h = 3.143 \times (3)^2 \times 15 = 424.3$ cm^3

Weight of moisture = Fresh weight of soil (M_t) – Oven dry weight of soil (M_s)

$= 675.0 - 550.0 = 125.0$ g

(i) using Eq. (2), Bulk density $\rho_b = \frac{M_s}{V_t} = \frac{550.0}{424.3} = 1.30\,\mathrm{g\,cm^{-3}}$;

(ii) using Eq. (4), Specific volume $v_b = \frac{V_t}{M_s} = \frac{424.3}{550.0} = 0.77\,\mathrm{cm^3 g^{-1}}$;

(iii) using Eq. (6), Porosity $f = 1 - \frac{\rho_b}{\rho_s} = 1 - \frac{1.30}{2.65} = 0.509$ or 50.9%;

Alternately, $f = \frac{\text{Volume of pores}}{\text{Total volume}} = \frac{V_f}{V_t} = \frac{V_t - V_s}{V_t}$

where, V_s = volume of soil solid $= \frac{M_s}{\rho_s} = \frac{550.0}{2.65} = 207.6\,\mathrm{cm^3}$

So $f = \frac{424.3 - 207.6}{424.3} = \frac{216.7}{424.3} = 0.511$ or 51%

(iv) using Eq. (7), Void ratio $e = \frac{V_f}{V_s} = \frac{424.3 - 207.6}{207.6} = 1.044$

(v) using Eq. (8), Mass wetness or gravimetric water content

$$w = \frac{M_w}{M_s} = \frac{125}{550} = 0.227 \text{ or } 22.7\%$$

(vi) using Eq. (10), Volume wetness or volumetric water content

$$\theta = w.\rho_b = 0.227 \times 1.30 = 0.295 \text{ or } 29.5\%$$

Alternately, $\theta = \frac{V_w}{V_t} = \frac{M_w/\rho_w}{V_t} = \frac{125/1.00}{423.3} = \frac{125}{423.3} = 0.295$

where, ρ_w = Density of water

(vii) Water volume ratio or liquid ratio (using Eq. 11) $v_w = \frac{V_w}{V_s} = \frac{125}{207.6} = 0.602$ or 60.2%

(viii) Degree of saturation (using Eq. 12) $\theta_s = \frac{V_w}{V_f} = \frac{0.295}{0.509} = 0.58$ or 58%

(ix) Air filled porosity (using Eq. 13) $f_a = \frac{V_a}{V_t} = \frac{V_t - V_s - V_w}{V_t}$

$$= \frac{424.3 - 207.6 - 125.0}{424.3} = \frac{91.7}{424.3} = 0.216$$

Alternately, (using Eq. 13) $f_a = (f - \theta) = 0.510 - 0.295 = 0.215$

(x) Depth of soil water in 15 cm soil layer

Depth of soil water (W_d cm) = Volume wetness θ × profile depth (d)

i.e. $W_d = \theta.d = 0.295 \times 15 = 4.43$ cm

Question 2. If bulk density of soil is 1.5 Mg m^{-3}, find the weight of 0.10 metre depth of 1 ha of soil.

Solution:

Volume of 1 ha of soil up to 0.10 cm depth

$V_t = 10000 \times 0.1\ m^3 = 1000\ m^3$

So weight of soil ($M_s = V_t . \rho_b$) = $1000 \times 1.5 = 1500$ Mg = 15×10^5 kg

Question 3. Derive the following useful interrelationships:

(a) Mass wetness (w) and volume wetness θ i.e. $\theta = \frac{w.\rho_b}{\rho_w}$

(b) Porosity (f) and void ratio (e), $e = f/(1-f)$, $f = e/(1+e)$

(c) Degree of saturation (θ_s) and volume wetness (θ), $\theta_s = \theta/f$

(d) Airfilled porosity (f_a) and volume wetness (θ), $f_a = (f_a - \theta) = f(1 - \theta_s)$

Question 4. A soil 80 cm deep has a volume water content $\theta = 0.12$. Find out the quantity of water that must be added to bring the volume water content to 0.30.

(Ans: 14.4 cm)

Question 5. A soil core sample has a fresh weight of 1450 g and ovendry weight of 1200 g. The bulk density of soil is 1.2 Mg m^{-3}. Find out the volumetric water content of the soil sample

(Ans: 25.0%)

Question 6. A soil has a bulk density and particle density of 1.30 and 2.60 Mg m^{-3}, respectively. The volumetric water content is 30.0%. What is the air-filled porosity of the soil?

(Ans: 20.0%)

Question 7. The gravimetric water content in 0-15 cm soil layer in a wheat field is 15.5% before irrigation and 35.5% after irrigation. If the bulk density of the soil is 1.5 Mg m^{-3}, find out the amount of irrigation water stored in the 0-15 cm soil depth.

(Ans: 4.5 cm)

Question 8. Calculate the volume of water present in the root zone i.e. 1 m depth of 1 ha soil having mass water content 20% and bulk density 1.4 Mg m^{-3}.

(Ans: 2800 m^3)

Question 9(a). Using Stokes' law calculate the settling velocity of particles corresponding to the upper size limit of clay fraction (2 μm diameter) at 20°C.

Solution:

We assume particle density $\rho_s = 2.65 \times 10^3$ kg m^{-3}, fluid density ρ_f at 20°C = 1.00×10^3 kg m^{-3}; Viscosity η of fluid at 20°C = 1.00×10^{-3} pascal sec (Pa s) and g = 9.81 m sec^{-2}

N.B. (Note in this example the values of all the parameters are in SI units)

We use Eq. 5.14 and substitute the values of η, g and r

$$v = 2(\rho_s - \rho_f)\, gr^2/9\eta$$

$$= 2(2.65 \times 10^3 - 1.00 \times 10^3) \times 9.81 \times (1.00 \times 10^{-6})^2/9(1.00 \times 10^{-3})$$

$$= 3.30 \times 1.09 \times 10^{-6} = 3.6 \times 10^{-6}\ m\ sec^{-1}$$

Question 9(b). Also calculate the time required for collection of sample through pipette at 10 cm depth of the suspension for determination of clay content.

$$\text{Using Stokes' law, } v = \frac{h}{t} \text{ or } t = \frac{h}{v} = \frac{10 \times 10^{-2}}{3.6 \times 10^{-6}} = 7\,\text{hr}\ 43\,\text{min}$$

Question 10(a). Using Stokes' law, calculate the time required for all sand particles (diameter > 0.05 mm) to settle out of a depth of 15 cm in an aqueous suspension at 20°C ($\eta = 0.01005$ poise).

Here we use C.G.S. units;
$h = 15$ cm, η at 20°C = 0.01005 poise = 0.01005 g cm^{-1} sec^{-1}, $\rho_s = 2.65$ g cm^{-3},
ρ_f at 20 °C = 1. g cm^{-3}, g = 981 cm sec^{-1}, r = 0.0025 cm;
Use equation (16a) to calculate t

(Ans: 67 sec)

Question 10(b). Also calculate the time required for all silt (diameter > 0.02 mm) of the above sample to settle out of 15 cm.

(Ans: 1 hr 9 min 51 sec)

Question 11. The following data were obtained by wet sieving of 25 g of clod soil samples (initially retained on 5 mm sieve) by Yoder's wet sieving method for aggregate analysis. Calculate the mean weight diameter and geometric mean diameter of the water stable aggregates.

Sieve size class (mm)	5.0	5.0-2.0	2.0-1.0	1.0-0.5	0.5-0.25	0.25-0.10
Weight of aggregates retained in each size (g)	14.08	5.31	2.25	2.15	1.06	0.15

Solution:

Sieve size class (mm) (X_i)	Weight of aggregates retained (g) (W_i)	Mean diameter of each size fraction (mm) (x_i)	Fraction of total weight (w_i)	x_iw_i	$\log x_i$	$W_i.\log x_i$
5.0	14.08	5.0	0.563	2.816	0.699	9.841
5.0-2.0	5.31	3.5	0.212	0.743	0.544	2.889
2.0-1.0	2.25	1.5	0.090	0.135	0.176	0.396
1.0-0.5	2.15	0.75	0.086	0.065	-0.125	-0.269
0.5-0.25	1.06	0.375	0.040	0.016	-0.426	-0.452
0.25-0.1	0.15	0.175	0.006	0.001	-0.757	-0.114
Summation	25.0			3.776		12.291

$$\text{Using Eq. (18), } \text{MWD} = \sum_{i=1}^{n} x_i w_i = 3.78\,\text{mm};$$

$$\text{Using Eq. (19), } \text{GMD} = \exp\left[\frac{12.291}{25}\right] = \exp(0.492) = 1.64$$

Question 12. Calculate the mean weight diameter and geometric mean diameter of water stable aggregates of a black clay soil. The sieve sizes and the weight of aggregates retained in each sieve after wet sieving of 25 g of clod soil sample are given below:

Sieve size class (mm)	5.0	5.0-2.0	2.0-1.0	1.0-0.5	0.5-0.25	0.25-0.10
Weight of retained aggregates (g)	19.10	1.39	0.25	0.125	0.062	0.025

(Ans: MWD = 4.03 mm; GMD = 1.76 mm)

Chapter 6

Soil Water

S. KAR, M.C. OSWAL and USHA KIRAN CHOPRA

1. Introduction

Water is an essential constituent of the terrestrial ecosystem. In soil, water is held on the surfaces of its particles as adsorbed water and in the intervening voids as pore water. Soil water plays a significant role in controlling the energy balance of the soil and of its overlying micro-environment by modifying its radiation exchanges and thermal properties. Its content in variable amounts changes the volume of the air-filled pore space and regulates the gaseous exchange in the upper layer of the soil. When present in available form, soil water helps plants to carry out their basic physiological and metabolic processes, including nutrient absorption from soil. It dissolves salts and nutrient compounds and controls their transport processes in soil. Water is also important for various activities of the soil microorganisms leading to the decomposition of organic matter and fixation as well as release of soil nutrients. The presence of water in different amounts in soil governs its mechanical, physical and chemical properties. The soil properties like consistency, compactibility, strength, swelling and shrinkage are strongly influenced by its water content. In order to understand the availability of soil water as well as its role in controlling various soil properties and processes, it is essential to study the energy status, retention and movement of water in soil.

2. Hydrological Cycle

The cyclic process in which water moves from the earth's surface to the atmosphere and back to the earth is termed as the hydrological cycle. In this process, water is evaporated from the water bodies such as ponds, rivers and oceans, as well as from the wet surfaces of soils and plants. The water vapour migrates to the atmosphere where it gets condensed. The condensed water vapour falls as precipitation or snow on the soil surface. A portion of this precipitation runs off laterally over and below the soil surface and reaches the water bodies from where it is evaporated again. The hydrological cycle thus formed is repeated continuously. The remaining portion of precipitation enters the soil and is subjected to the processes of infiltration, redistribution, percolation, drainage and seepage. The net result of these flow processes is water storage or loss from the soil profile. The entire soil profile is categorized in three zones. The upper zone known as 'Soil Water Zone/ Root Zone' extends from the soil surface to the lower boundary of the root zone. Below the soil water zone, there is an unsaturated zone called 'Vadose Zone' which extends up to the upper boundary of the next zone which is called 'Capillary Fringe Zone' and is a near saturated zone occurring over the water table. The recharging of groundwater depends on the water flow through this unsaturated Vadose Zone.

3. Structure and Properties of Water

A molecule of water is formed from two atoms of hydrogen and one atom of oxygen by sharing of electrons in a tetrahedral charged structure (Figure 1). An excess of negative

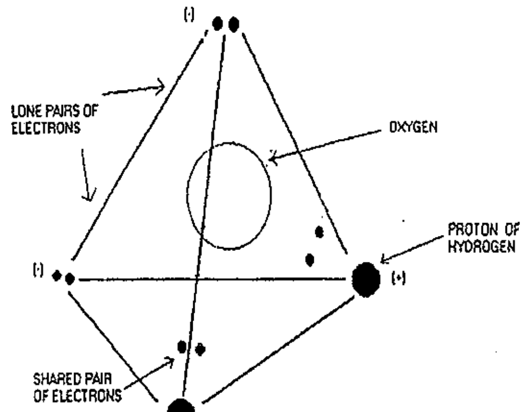


Figure 1. Tetrahedral charge structure of water molecule

charge prevails on one side of the molecule due to the unshared lone pair of electrons, while an excess positive charge prevails on the other side of the molecule due to the unscreened positive charge of the protons of hydrogen atoms, as shown in this figure. Such an arrangement makes a water molecule a dipole which helps it to link with the neighbouring molecules through H-bonding, which is a weak bond developed between hydrogen and an electronegative element like oxygen.

In the liquid state, a molecule of water is surrounded by five or more water molecules, while in the solid state, each molecule of water is linked to four other molecules in a hexagonal type arrangement. This makes the water lighter in solid form than in liquid state. Since water molecules are dipoles, liquid water has a high dielectric constant, whose value is about 80 for the pure water. Due to H-bonding, liquid water has a higher values of melting point, boiling point, dielectric constant, specific heat and viscosity as compared to other compounds of similar molecular weight. However, soil water, due to the presence of solutes, has a lower freezing point and higher boiling point than pure water. The depression in freezing point is sometimes used to characterize the wilting point of soil.

Soil water is a viscous fluid. It experiences resistance from the surface of soil particles while it moves through soil pores. The frictional force (F) is proportional to surface area (A) and velocity gradient $(\delta v/\delta x)$, as given by Equation (1):

$$F=\eta A\frac{\partial v}{\partial x} \qquad ...(1)$$

If force (F) is expressed in dynes, surface area (A) in cm^2, velocity of water (v) in cm/sec, and thickness of water layer (x) in cm, then coefficient of viscosity (η) has the dimension of dyne/sec/cm^2 or poise. At 25 °C, the viscosity of water is 0.0089 poise.

4. Soil Water Content

The amount of water present in soil at a particular point of time is called soil water content. When it is expressed on mass basis, it is called water content by weight (θ_w) and is equal to the mass of water divided by the dry mass of the soil expressed as per cent. It is also expressed on volume basis as volume of water divided by the total volume of soil (θ_v) multiplied by 100. One form can be converted to the other form using the relation (2):

$$\theta_v = \theta_w \text{ (Bulk density of soil/ Density of water)} \qquad ...(2)$$

4.1. Soil Moisture Constants

There are many terms that are associated with the water that is retained by the soil. The common ones are saturation water content, field capacity, permanent wilting point and hygroscopic coefficient.

(1) ***Saturation Water Content*** **(θ_s):** Soil is a porous medium and when all the pores of the soil are filled with water, it is referred to as saturated soil. The saturation water content refers to the water content at which all the pore spaces, including the expanding space of clay minerals, are filled with water and the matric suction is zero. It can be determined with the help of tension plate assembly where the soil core/soil sample is brought in contact with water column at a height equal to the mid-point of the sample and the moisture held by soil in equilibrium with the water column is determined. Since in saturated condition all the pores are filled with water, the total porosity would be same as the volumetric water content. Therefore, it can also be calculated using the formula (3) for porosity:

$$\theta_s = P = \{1 - BD/PD\} \times 100 \qquad ...(3)$$

where, P is the porosity in per cent, BD is bulk density (g/cm^3) and PD is particle density (g/cm^3) of soil. PD is generally assumed to be 2.65 g/cm^3.

(2) ***Field Capacity (FC)***: When a saturated field soil is allowed to drain, soil moisture decreases exponentially with time. After 2 to 3 days, the moisture in the surface layer attains a steady state. At this stage, the water retained in the soil is known as 'Field Capacity'. Thus, field capacity is defined as the amount of water retained in the soil after the downward water movement from a pre-saturated soil has 'materially' ceased. The matric potential corresponding to this moisture content varies with soil texture from -1/10 bar for coarse-textured soils to -1/3 bar for medium- to fine-textured soils. It is, therefore, best estimated in the field by saturating the root zone and determining the soil moisture after free internal drainage ceases. It takes about 24 to 36 hours for coarse and 2-3 days for medium-textured soils in field.

(3) ***Permanent Wilting Point (PWP)***: It refers to the soil moisture content at which plant roots cannot extract water at a rate sufficient to meet the transpirational needs. At this moisture content, plants lose cell turgidity and show symptoms of wilting. The permanent wilting point (PWP) corresponds to the water content of soil when an indicator plant such as sunflower growing on it get wilted so severely that they do not regain their turgidity even when placed in water vapour-saturated atmosphere. The matric potential corresponding to this moisture content is -15 bar. Water retained by soil at -15 bar matric potential is generally estimated in the laboratory using either a pressure plate or a pressure membrane apparatus.

(4) ***Hygroscopic Coefficient***: It is the water held by the soil at -31 bar (3.1 MPa) soil moisture matric potential and is determined using a pressure membrane assembly meant for higher pressures.

4.2. Forms of Soil Water

In soil, the water is held in three forms, depending on the tenacity with which it is adsorbed: (i) Gravitaty or Free water, (ii) Capillary water, and (iii) Available water. The water between saturation and field capacity is called *gravity* or free water. It flows out under the influence of gravity and is considered unavailable to plants. The water between field capacity and hygroscopic coefficient is referred to as *capillary water* as it is bound to the soil by capillary forces. The water held by the soil between field capacity and permanent wilting point is termed as *available water* for plants, while the water held between permanent wilting point and hygroscopic coefficient is considered unavailable to plants.

Some plants are able to survive even at moisture contents below PWP for short periods. The availability of capillary water to plant roots depends on pore diameter which controls the pressure of water as measured by the height of water in capillaries. The narrower the capillary pore, the lower is the water pressure and lesser is its availability. With further increase in water content, when the macropores also get filled with water, it is more and more loosely held. This loosely held water has a suction ranging from 0.01 to 0.05 bar. Under the action of gravitational force, this loosely held water is liable to move downwards and hence it is known as *Gravity water* or free water. The drainage or deep percolation loss of water following irrigation results from the downward movement of the gravity water.

5. Energy Status of Soil Water

Knowledge of different forms of soil water content is not sufficient to characterize the state of water in soil. For example, the water content at which water is 100% available to plants in sandy loam soil, may impose permanent wilting to plants in clay soil. This is due to the higher energy with which water is retained in clay than in sandy loam soil. The energy status of water governs not only its availability but also its mobility in various transport processes occurring in soil. Information on energy status of water is thus essential to quantitatively describe the net force of retention and flow of water in soil.

5.1. Concept of Water Potential

The total energy of water in soil is the sum of potential energy as well as kinetic energy.

Since kinetic energy is very small in comparison to its potential energy, the potential energy is considered as the total energy of soil water, which is expressed by soil water potential. Potential energy represents the capacity to do work. According to the International Soil Science Society, total soil water potential is defined as the amount of work done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of water at a specified elevation at atmospheric pressure to the soil water at the given point. Pure free water has the maximum capacity to do work. Water in soil being held by adsorptive, osmotic and pressure gradient forces, has relatively lower capacity to do work. Rather, work needs to be done on water to move it from one position to another in soil against the force fields to which it is subjected. Therefore, the water potential is negative in soils. Extraction of water by plant roots is an example of work being done on soil water. If a unit quantity of water is moved against a force field (F) from the reference point (R) to a point in question (P), the total work done (W) is given by Equation (4):

$$w = \int_{R}^{P} F.ds.\cos\theta \qquad ...(4)$$

where, F is the force acting on water, ds is the infinitesimal distance along the flow path, and θ is the angle subtended by the flow path with the direction along which the force is acting.

5.2. Components of Total Soil Water Potential

The force fields acting on soil water are short-range adsorptive forces (matric forces), osmotic forces if salts are present, pressure gradient force, and the universal gravitational force. For each of the forces there is an associated potential. This means that the force of gravity will lead to gravitational potential (Ψ_g), hydrostatic and gas pressure gradient force to pressure potential (Ψ_p), osmotic force to osmotic potential (Ψ_{op}), and adsorptive force including air-water interfacial tension to adsorptive or matric or capillary potential (Ψ_m). The total potential (Ψ_t) of soil water at any point of equilibrium would be equal to the algebraic sum of all the component potentials (Scott, 2000):

$$\Psi_t = \Psi_g + \Psi_p + \Psi_m + \Psi_{op} \qquad ...(5)$$

Each of the component potentials may be defined, in principle, in terms of work done against the respective force field, as described by Equation (5). At macroscopic level, the total potential is often considered as the sum of gravitational and pressure potentials only, the latter incorporating the matric and pressure potential components.

5.3. Units of Water Potential

Water potential may be expressed on volume, mass or weight basis. If E is the potential energy of a volume V, mass m and density ρ of soil water, then different forms of water potential are as follows:

Potential energy per unit volume =

$$\frac{E}{V} = \frac{mgh}{\left(\frac{m}{\rho}\right)} = \rho gh$$

$$= \Psi \text{ (pressure unit)}$$

Potential energy per unit mass =

$$\frac{E}{m} = \frac{mgh}{(m)} = gh$$

Potential energy per unit weight =

$$\frac{E}{mg} = \frac{mgh}{mg} = h \text{ (head unit)}$$

5.4. Hydraulic Head Concept

In the study of soil water movement, the soil water potential is generally expressed on weight basis i.e., in head units. The hydraulic head (H) term used in the Darcy's equation consists of soil water pressure/suction head (h) and gravity head (z) at the point in question, as shown in Equation (6):

$$H = h + z \qquad ...(6)$$

The water pressure head at a particular soil depth can be measured by a piezometer in saturated soil and by a tensiometer in unsaturated soil, as shown in Figure 2. It is positive in

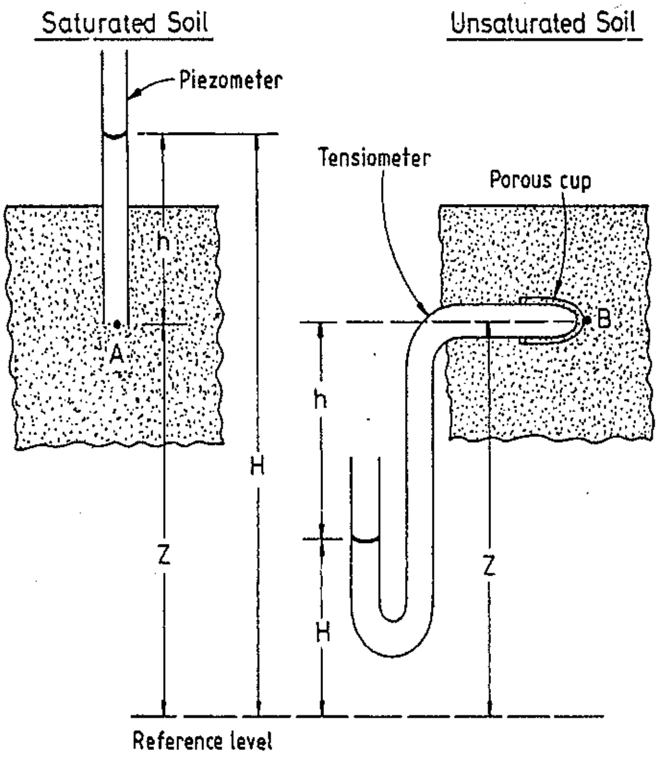


Figure 2. Concept of hydraulic head for saturated and unsaturated soils

saturated soil and negative (tension head) in unsaturated soil. The gravity head is estimated from the difference in elevation between the reference level, chosen arbitrarily at the soil surface, and the soil depth under consideration. It is positive above the reference level and negative below the reference level. The distribution of gravity, water pressure and total pressure heads in a 20-cm soil column which is immersed up to 5 cm in water, is illustrated in Figure 3.

6. Soil Water Availability to Plants

Veihmeyer and Hendrickson (1955) gave the concept of plant available water. The soil water storage capacity is generally expressed in terms of Available Water Capacity (AWC). The total available water in soil is regarded as the difference between soil moisture content of "field capacity" and "wilting point", i.e.

$$AWC = FC - PWP \qquad ...(7)$$

It is customary to express available water capacity in terms of head dimensions so that it is analogous with irrigation, evaporation rate and rainfall units, which are generally expressed in terms of head units. The available water capacity of a specific layer can be expressed in 'cm' if bulk density values and depth of soil layer of the root zone are known as illustrated below:

$$D_w = \{(FC - PWP) \times BD \times D_s\}/100 \qquad ...(8)$$

Table 1. Units, dimensions and common symbols of soil water potential

Form	Symbol	Common name	Dimensions	SI units	CGS units
Energy/volume	ψ	Soil water potential, suction or tension	$ML^{-1}T^{-2}$	N m^{-2} (Pa*)	erg cm^{-1}
Energy/mass	μ	Chemical potential	L^2T^{-2}	J kg^{-1}	erg g^{-1}
Energy/ weight	h	Pressure head	L	m	cm

*Pa = Pascal = 10^{-5} bar

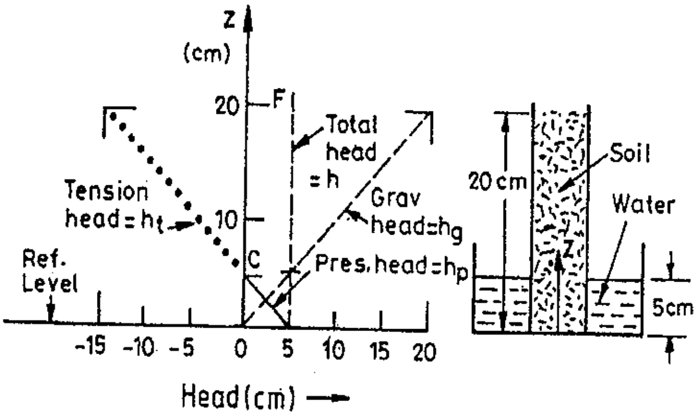


Figure 3. Gravity, tension and total pressure head distribution in soil

where,

D_w = Depth of water contained in a specific soil layer (cm)

D_s = Thickness of that soil layer (cm)

BD = Bulk density of the particular soil layer (g cm^{-3})

FC = Soil water content at Field Capacity (% by wt), and

PWP = Soil water content at Permanent Wilting Point (% by wt).

The profile water available capacity (D_p) is computed by first determining D_w for each soil layer and then adding it for all the soil layers.

$$D_p = \Sigma D_w \qquad ...(9)$$

However, the values of BD, FC and PWP vary from soil to soil and location to location, even under the same major soil group for the simple reason that there will be a variation in soil depth and available water capacity limits also. Therefore, as already emphasized earlier, the actual determination has to be made for the specific soil under consideration.

A school of thought led by Veihmeyer and Hendrickson (1955) maintain that soil moisture is available for plant growth equally over the range between field capacity and permanent wilting point. According to this view, transpiration/plant growth is unaffected by the magnitude of soil moisture content unless PWP is reached when the water suddenly becomes non-available. Another view point states that the water held by the soil becomes progressively less available with a linear decreasing trend as the water content decreases from FC to PWP (Thornthwaite and Mather, 1955). Yet another school of thought maintains that transpiration/plant growth is unaffected by the magnitude of soil moisture content from field capacity up to certain threshold value below which almost linear decrease in rate of transpiration occurs (Ritchie *et al.*, 1972). The magnitude of the threshold value would, however, depend upon a variety of factors related to soil, plant and atmospheric conditions. In general the threshold potential is -1.0 bar for a coarser soil and -5 bar for a finer soil. This approach is the one generally subscribed to by most workers for its practicality. All the three approaches have been depicted in Figure 4.

7. Water Retention by Soils

In an unsaturated soil, water is retained by the forces of capillarity and adsorption. The adsorption of water occurs through the hydration of dry soil matrix surface and exchangeable cations. With further intake of water, it gets into the soil pores where surface tension and radius of curvature of the air-water interface determine its content. The capillary concept is, therefore, often utilized to describe water retention in soil pores. In coarser soils, capillary action is more important than adsorption, while the reverse is true in the finer soils.

7.1. Capillarity and Water Retention

The water rises in a capillary tube when it is partially immersed in water. If the tube is made of glass or quartz, water makes contact with the tube at an angle close to zero, and forms a concave air-water meniscus (Figure 5a). Since the pressure at the water

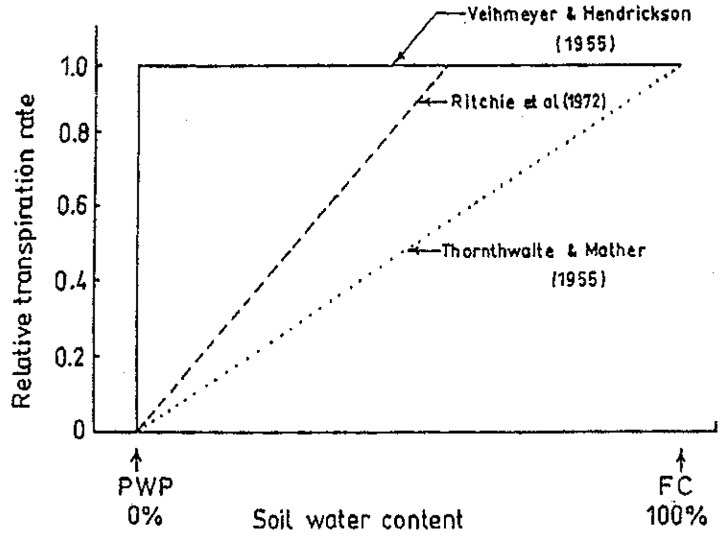


Figure 4. Concepts of soil water availability to plant

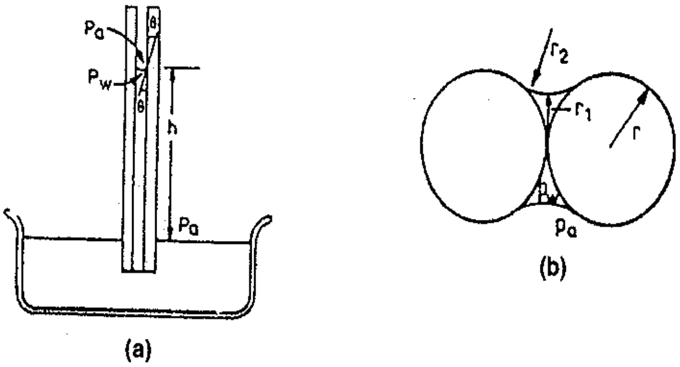


Figure 5. (a) Capillary rise of water, and (b) Principal radii of curvature at air-water interface in soil

surface outside tube is the atmospheric pressure, water rises in the tube till the hydrostatic pressure of water column equals the pressure difference across the air-water meniscus. The force due to the hydrostatic pressure of the rise in capillary water is $\pi r^2 h \rho_w g$, where, r is the radius of the capillary tube, h is the height of water in capillary, ρ_w is the density of water and g is the acceleration due to gravity. This downward force is balanced by the upward force due to surface tension which is estimated as $2\pi r\gamma\cos\theta$, where, $2\pi r$ is the circumference of the capillary tube, γ is the surface tension and θ is the contact angle between water and glass tube.

At equilibrium, the downward force will be balanced by the upward force as represented in Equation (10):

$$\pi r^2 h \rho_w g = 2\pi r \gamma \cos\theta \qquad \text{...(10)}$$

From this, water height (h) can be determined by Equation (11):

$$h = \frac{2\gamma\cos\theta}{r\rho_w g} \qquad \text{...(11)}$$

For water and glass interface, θ being close to zero, $\cos\theta$ may be taken as equal to unity and Equation (11) simplifies to Equation (12):

$$h = \frac{2\gamma}{r\rho_w g} \qquad \text{...(12)}$$

or

$$h = \frac{4\gamma}{d\rho_w g} \qquad \text{...(13)}$$

where, d is the diameter of capillary tube.

Considering $\theta = 0$, $\gamma = 72.75 \times 10^{-3}$ N/m, $\rho_w = 0.998$ Mg/m^3 and $g = 9.81$ m/s^2 at 20 °C, we get the simplified Equation (14):

$$h = \frac{0.279}{d} = \frac{0.3}{d} \qquad ...(14)$$

Equation (14) gives a relation between capillary rise (h in cm) and pore diameter (d in cm) which can be used to estimate capillary or matric potential for a known pore size, or to calculate the diameter of the largest effective pore of a soil for which the capillary rise is known.

In soil, the capillary pores are not uniform in size. The variation in size of pores and the degree of saturation lead to air-water interfaces of varying radii of curvature, which also affect the matric potential by altering the pressure difference across the air-water interface. The relation of the curvature of an air-water interface to the pressure difference across the interface is given by the Laplace equation [Equation (15)]:

$$P_w - P_a = 2\gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \frac{2\gamma}{r} \qquad ...(15)$$

where, P_w and P_a are the pressure of water below and above air-water meniscus, respectively and r_1 and r_2 are the principal radii of curvature (Figure 5b) formed above and below the air-water meniscus. The mean radius of curvature r is positive if it lies within the water phase and negative if it lies in the gas phase.

7.2. Soil Moisture Characteristics

The retention and release of water in soil are the functions of its energy status. When a field soil is saturated with irrigation or precipitation, its water potential becomes zero. Subsequently, on cessation of water application, soil water depletes due to drainage and evaporation, at a faster rate initially from the non-capillary pores where the potential of water is relatively high and then at a slow rate from capillary pores where water potential is relatively low. In other words, water retention in a soil is a function of its matric potential or suction. A soil moisture characteristic (SMC) curve describes the functional relationship between soil water content and its energy status in terms of its matric potential under equilibrium conditions. The SMC is an important property of a given soil controlled by soil pore size distribution which is strongly affected by texture, structure and organic matter content.

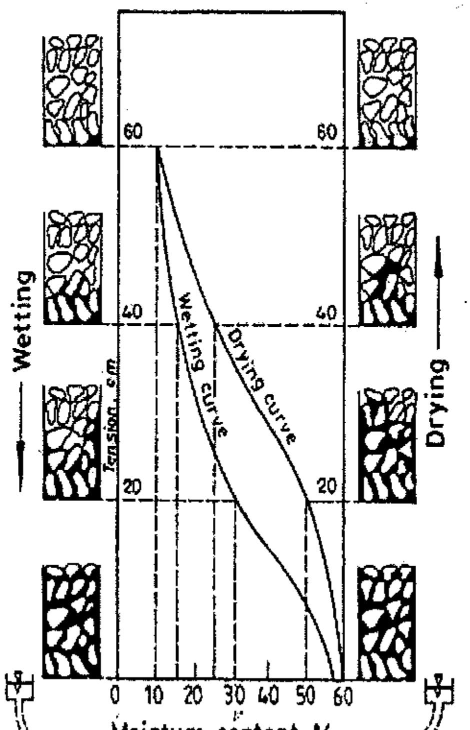


Figure 6. Drying and wetting curves of soil illustrating the effect of hysteresis (redrawn from Ghildyal and Tripathi, 1987)

7.2.1. Soil Water Hysteresis

It is important to note that the SMC relationship is not unique but depends on the sorption or desorption pathways of soil water. When SMC is obtained by taking an initially saturated soil which loses its moisture to become dry, desorption pathway is followed and a unique SMC curve is obtained. However, when a dry soil is gradually wetted and its suction-water content relationship is obtained, sorption pathway is followed which may be a different curve from the desorption curve with the coinciding end points (Figure 6). At a particular suction, the soil water content during drying is generally higher than during wetting. This phenomenon is referred to as 'Hysteresis'. The hystersis in SMC occurs due to various factors: (1) the ink bottle effect resulting from non-uniformity in shape and size of interconnected pores, (2) different contact angles for advancing and receding water menisci, (3) entrapped air during adsorption, and (4) swelling and shrinking of soils under wetting and drying, which alter the pore size distribution and porosity.

7.2.2.Determination of Water Retention Characteristics

In high potential range, the soil moisture characteristics can be determined with the help of 'Tension Plate Assembly'. It consists of a fritted glass plate which is connected to a graduated U-type manometer filled with water (Figure 7). Let us now consider a thin layer of air-dry soil placed over the plate. The soil is saturated by maintaining the water level on the right hand limb of the manometer at par with the fritted glass plate. Since the saturated soil is in equilibrium with the free water level in the manometer at atmospheric pressure, the matric suction or tension on soil water would be zero. Considering this initial level of water as zero suction level, if the suction is gradually increased by lowering the water level slowly, there would be no outflow from soil water system till a critical suction is reached at which point the largest soil pore would begin to drain. This critical suction is known as '*air entry suction*'. As suction is further increased, more water will drain out of the soil pores having smaller radii. The radius of pore drained at a given suction can be estimated by Equation (12) or (14). If an increase in the suction from h_1 to h_2 results in a release of V volume of water, then V must be the pore volume having the largest and smallest effective pore radii of r_1 and r_2, respectively. Thus, the moisture retention characteristics of a soil can be utilized to calculate the pore volumes of different size ranges.

In the broad range of suction from 0 to 15 bar, the soil moisture characteristics can be determined with the help of 'Pressure plate apparatus'. It consists of a ceramic plate cell on which the soil cores are saturated, and a pressure chamber in which positive pressure is applied by an air compressor to desorb water from initially saturated soil. The significance of moisture characteristics, as depicted by curves in Figure 6, is best visualized by the variation in slope of the curve with changes in suction or moisture content. The inverse of the slope of the water retention characteristic curve is referred to as 'Differential Water Capacity', C_θ ($c_\theta = -\frac{\partial\theta}{\partial\psi}$) which is a function of water content. A vertical trend indicating a steep slope of the curve, represents a soil containing large number of pores of the same size range, while a horizontal trend with little slope reveals that the soil has almost no drainable pore in the suction range under consideration. The trend with intermediate slope represents soil with uniform distribution of pores which results in uniform release of water per unit change of suction.

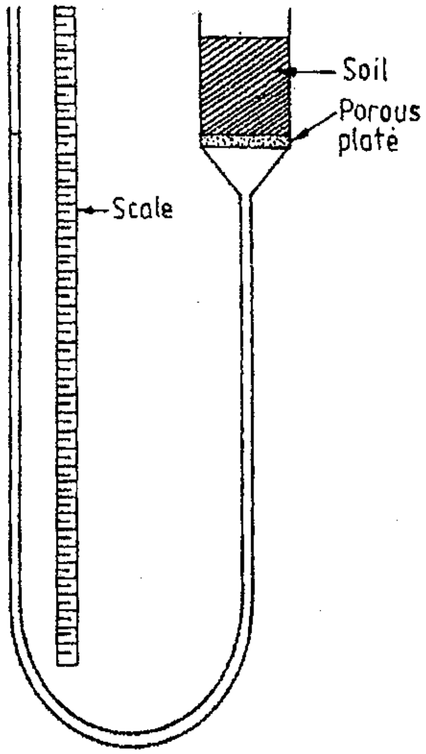


Figure 7. Tension plate assembly

7.2.3. Factors Affecting Soil Water Retention Characteristics

In the high potential range (low suction), water retention is largely controlled by the capillary effect as a function of pore size distribution of soil. Since the size distribution of pores is a consequence of arrangement of particles, water retention at relatively high potentials is primarily controlled by soil structure and related properties. On the other hand, water retention in low potential range (< –1 bar) depends primarily on adsorption of water as a function of surface properties of soil matrix.

Hence, soil texture is more important than soil structure in controlling water retention at low potentials.

Water retention is higher in finer (clayey soils) than coarser (sandy soils) soils, irrespective of water potential (Figure 8). The release of water is, however, gradual in a finer soil and relatively rapid in a coarser soil. Among the mechanical separates, clay and silt fractions are strongly related with water retention. With increase in clay content, water retention increases at all potentials. Water retention is favoured by organic matter content, particularly at high potentials, but at low potentials, organic matter has little influence on water retention. The water retentivity of the soil is also affected by the nature of clay minerals. Black clay soils having smectitic clay minerals retain more water than the kaolinitic lateritic soils (Biswas and Mukherjee, 1990). The presence of soluble salts in soil solution also influences retention and release of water in soil. The diurnal and seasonal variations of soil temperature also affect the water retention of a soil.

8. Measurement of Soil Water

Soil moisture is measured directly by the gravimetric method and indirectly by several improved techniques based on the determination of electrical resistance, slowing down of fast neutrons, gamma-ray attenuation, electrical capacitance and backscattering coefficient as a function of water content.

8.1. Gravimetric Method

In the thermogravimetric method, soil is sampled from the field location, weighed immediately to determine fresh weight and dried in an oven to a constant weight at 105 °C for 24 hours to estimate the oven-dry weight. The per cent soil water on weight basis is estimated by dividing the water content by oven-dry weight of soil and multiplied by 100.

8.2. Electrical Resistance Method

One of the non-destructive, indirect and *in-situ* measurement methods of soil water content is the widely used electrical resistance method, using gypsum or nylon or fibre glass blocks. In this method, two platinum electrodes are embedded in a gypsum block which is placed in soil and allowed to equilibrate. The electrical resistance of the porous block is then measured using a Wheatstone bridge. The electrical resistance of the soil decreases with increase in water content. A calibration curve

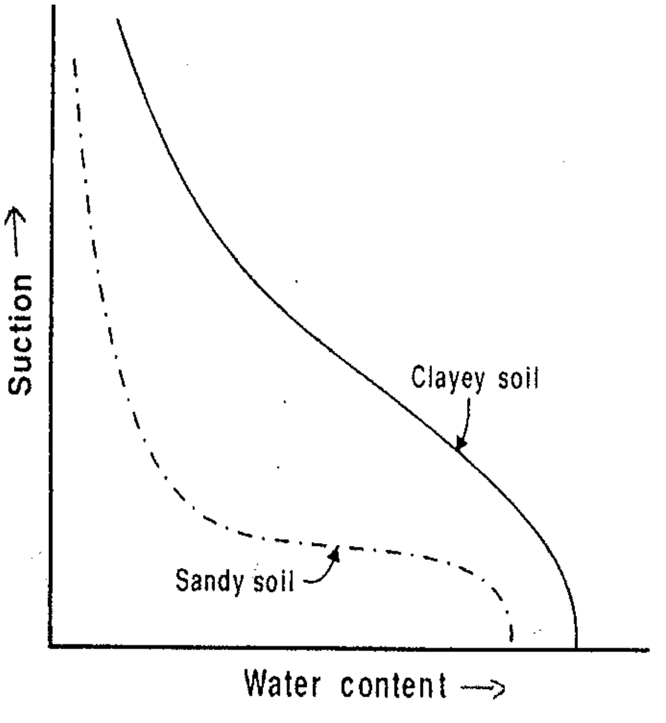


Figure 8. Effect of soil texture on soil water characteristics

between the resistance and water content of the block is determined. The soil water content is obtained with the help of this calibration curve, from the measured electrical resistance of the block.

8.3. *Nuclear Techniques*

The neutron scattering and gamma-ray attenuation are two nuclear techniques that can be used for non-destructive *in-situ* measurement of soil water content.

8.3.1. Neutron Moisture Meter

In the neutron scattering technique, the instrument used is called Neutron Moisture Meter. It consists of Amerecium and Beryllium or Radium and Beryllium as the neutron source. In case of Amerecium and Beryllium, fast neutrons are produced from the following reactions:

$$\underset{\text{Americium}}{{}^{241}_{95}\text{Am}} \longrightarrow \underset{\text{Neptunium}}{{}^{237}_{93}\text{Np}} + \underset{\text{Alpha particle}}{{}^{4}_{2}\text{He}} \quad \ldots(16)$$

$$\underset{\text{Beryllium}}{{}^{9}_{4}\text{Be}} + \underset{\text{Alpha particle}}{{}^{4}_{2}\text{He}} \longrightarrow \underset{\text{Carbon}}{{}^{12}_{6}\text{C}} + \underset{\text{Fast neutron}}{{}^{1}_{0}\text{n}} \quad \ldots(17)$$

The instrument works on the principle that when fast moving neutrons are emitted from the source into the soil, they undergo elastic collisions with hydrogen nuclei. The hydrogen nucleus contains a proton having mass equal to that of the neutron causing an elastic collision in which neutron loses energy and gets scattered. Thus, its energy is reduced and speed is slowed down. The process is called 'thermalization' and the slowed neutrons are called 'thermal neutrons'. The density cloud of thermal neutron so formed around the source (probe) is proportional to the concentration of hydrogen nuclei in the soil. Since water is the main source of hydrogen in soil, the density of slowed neutron is proportional to the volume-fraction of water present in the soil. The thermalized neutrons (fast neutrons slowed down by repeated collisions) are captured by the detector, which is placed just behind the source. The detector consists of a metallic tube containing boron tri-fluoride (BF_3) gas enriched with Boron-10 (^{10}B). The thermalized neutrons react with the boron producing alpha particles according to the following reaction.

$$\underset{\text{Boron}}{{}^{10}_{5}\text{B}} + \underset{\text{Thermal neutron}}{{}^{1}_{0}\text{n}} \longrightarrow \underset{\text{Lithium}}{{}^{7}_{3}\text{Li}} + \underset{\text{Alpha particle}}{{}^{4}_{2}\text{He}} \quad \ldots(18)$$

The detector is able to register thermal neutrons only. The alpha particles thus produced in the detector cause ionization which generates electrical pulses. These pulses are amplified by a pre-amplifier housed in the probe itself and then transmitted to the scalar. The scalar counts the number of pulses (or neutrons) in a pre-set time interval and these counts are converted to moisture content with the help of a calibration curve. The neutron moisture meter has to be calibrated for each soil. The advantages of this method are : it is rapid, less laborious, non-destructive and repeated measurements can be made at the same depth. The probe has to be lowered into the soil through an aluminum access tube. The main disadvantages are that it cannot be used for surface soil moisture content measurement since neutrons escape into the atmosphere and secondly, it is costly.

8.3.2.Gamma Ray Attenuation Method

In the gamma-ray attenuation technique of soil moisture content measurement, the instrument used is called Gamma-ray scanner or Gamma-ray apparatus. It consists of two aluminum access tubes and in one of these, radioactive isotope ^{137}Cs (Caesium-137) is used. The other tube consists of thallium-activated NaI crystal which acts as a detector. When a narrow beam of gamma-radiation is passed through the soil, the rays are attenuated depending upon the thickness of soil mass, the bulk density and water content of the soil, following the principle of Beer's law. So if the thickness and the bulk density of soil are known, the water content of the soil can be determined. The ratio of the monochromatic gamma radiation flux passing through wet soil (N_w) and through dry soil (N_d) of thickness x is exponentially related to the volumetric soil water content (θ_m) by the following relation (19):

$$\frac{N_w}{N_d} = \exp(-\theta_m \mu_w x) \quad \ldots(19)$$

where μ_w is the mass attenuation coefficient for water. This relation provides measurement of soil water content θ_m from Equation (20):

$$\theta_m = -\frac{l_n(N_w/N_d)}{\mu_w x} \qquad \text{...(20)}$$

The gamma-ray apparatus is most useful in laboratory studies where moisture content of very small depth increments of soil can be determined. However, practical difficulties limit its use in the field.

A number of isotopes are used for soil water movement studies. The isotope tritium (^3H) is largely used for water movement, groundwater recharge and pollution studies. In hydrological studies and seepage, stable isotopes deuterium (^2H) and oxygen (^{18}O) are used.

8.4. Time Domain Reflectometry

NET

A recent development in soil moisture measurement is the Time Domain Reflectometry (TDR). It is based on the estimation of dielectric constant (ε) of soil as varied by its water content. Water has a dielectric constant of 80. The apparent dielectric constant (K_a) of a soil varies from 3 to 6 in the dry state and from 20 to 30 in the wet state. The K_a measured in conjunction with a conversion table, can help estimate the volumetric moisture content. K_a is estimated by measuring the time (t) taken for the propagation of an electromagnetic pulse launched along a transmission line or wave guide of length (L) and reflected back to the origin. Based on the electrical transmission line theory of high frequency, K_a can be estimated from the Equation (21):

$$K_a = \left[\frac{ct^2}{2L}\right] \qquad \text{...(21)}$$

where, c is the propagation velocity of electromagnetic wave in vacuum or free space (equal to the velocity of light, i.e. 3×10^8 m/s).

The wave guide, consisting of two parallel electrode rods spaced at 50 mm, is inserted in the soil. The recently developed microprocessor based and calibrated TDR units directly give the volumetric moisture content and dielectric constant of soil. TDR is gaining more and more acceptance as it overcomes the disadvantages of other time-consuming methods. The technique is also useful in measuring soil salinity in terms of electrical conductivity. TDR gives an average soil moisture content of the soil depth equal to the length of the wave guide.

8.5. Microwave Remote Sensing of Soil Moisture

All the above methods give point measurement of soil moisture content. The recently developed microwave remote sensing technique enables us to estimate soil moisture content over a region or large area. The basic principle is that the microwave backscattering coefficient is greatly influenced by the dielectric property of the soil which is mostly a function of soil water content. The dielectric constant is less than 5 for dry soil, whereas it is 80 for water. As the soil water content increases, the dielectric constant of soil also increases which decreases the emissivity (e) of the wet soil. The decrease in emissivity is approximately linear with increase in soil water content. The back scatter coefficient (σ) is a function of emissivity and is given by Equation (22):

$$\sigma = f(e, \lambda, \phi, \rho, \alpha, R, V) \qquad \text{...(22)}$$

where, e is the emissivity, λ is the wavelength of incident radiation, ϕ is the incident angle, ρ is the polarization, α is the aspect angle, R is the surface roughness and V is the volume scatering.

The back-scattering coefficient (σ) measured in a satellite-based sensor synthetic aperture radar (SAR) is correlated with soil moisture content. However, this technique gives moisture content estimation of only surface soil up to 5-10 cm depth.

9. Determination of Soil Water Potential

Total soil water potential at a point can be estimated by measuring its component potentials: gravitational, pressure, matric and osmotic. The gravitational potential is estimated from the difference in elevation between the reference level and the level of the point in question. The pressure potential is generally considered as hydrostatic pressure in saturated or flooded soil. It is measured by the height of water in the Piezometer, sunk up to the soil depth in question. The Piezometer, a metallic tube with perforated bottom, is subtended to the soil depth. A water level recorder is used to determine the height of water in the piezometer. In an unsaturated soil, the matric potential forms the major component of the total soil water potential. It is evaluated with the help of a tensiometer up to –0.8 bar and below this, the matric potential can be estimated along with osmotic potential by soil psychrometer.

9.1. Tensiometer

The tensiometer consists of a porous cup made of ceramic material and a mercury manometer attached to the water-filled cup through a water reservoir tube. The porous cup has high conductance, low response time and air entry pressure of about 1 bar. Following saturation when the porous cup is placed in soil and equilibrated, water tends to move out of the cup under the suction exerted by soil. As a result, a vacuum pressure develops in the cup dialyzate and to make up this, mercury rises in the manometric tube attached to the water reservoir tube. The vacuum in the porous cup is actually the matric potential (Ψ_m) of soil water. The soil matric potential (Ψ_m) is determined from the relation (23):

$$\Psi_m = -12.6\, Z_{hg} + Z_o \qquad \ldots(23)$$

where Z_{hg} is the height of mercury in manometer and Z_o is the distance between the mercury surface in cup and centre of the ceramic cup.

The use of tensiometer is confined up to the minimum matric potential of –0.8 bar, but much of the available water is retained by soil between –0.8 bar and –15 bar, particularly in fine-textured soils. Beyond the tensiometric range, the matric potential is usually interpolated from the water retention characteristics curve using the measured soil moisture content.

9.2. Soil Psychrometer

The total soil water potential is determined with the help of a soil psychrometer. As liquid water in soil is always in equilibrium with its vapour in the ambient air, the energy status of water vapour (vapour potential) must be equivalent to the energy status of soil water. At constant temperature and gravitational potential, the vapour potential is largely contributed by matric and osmotic potentials. The vapour potential of soil can be precisely estimated with the help of a Thermocouple Psychrometer.

The soil water potential (ϕ) is related to the vapour pressure of soil water (p) and vapour pressure (p_o) of pure and free water at the same temperature and air pressure by the relation (24):

$$\phi = RT \ln (p/p_o) \qquad \ldots(24)$$

where, R is the universal gas constant and T is absolute temperature. This relation is used to determine soil water potential by a thermocouple psychrometer.

10. Movement of Soil Water

10.1. Principles of Soil Water Movement

Water is a highly dynamic component in soil system. It moves in all the three phases: solid, liquid and vapour. In a flooded or saturated soil, water moves in liquid phase, while in a partially dry or unsaturated soil, it moves in both liquid and vapour phases. Movement in solid phase as commonly occurring in the frozen soil is also believed to take place close to the clay surface. In liquid and vapour phases, water movement is governed by the principles of fluid flow.

10.1.1. Bernoulli's Equation

In a flooded soil when water moves under hydrostatic pressure difference through a uniform horizontal pore, the energy state of water at any point is characterized by its velocity (v), mass density (ρ_w), pressure (P) and height above the reference level (Z). At any point on the steady state flow path, the energy state of water, either potential or kinetic, remains constant. In other words, the sum of pressure head ($h_p = P/\rho_w g$), potential head ($mgZ/mg = Z$) and velocity head [$(1/2\ mv^2)/mg = v^2/2g$] remains constant for a non-viscous fluid under steady state flow. This relation is known as

Bernoulli's equation and is represented by Equation (25):

$$Z+\frac{v^2}{2g}+\frac{P}{\rho_w g}=\text{Constant} \qquad \ldots(25)$$

10.1.2. Poiseuille's Law

Poiseuille's law is used to describe the flow of a fluid showing viscous properties. It states that flow of water through a narrow tube is directly proportional to the fourth power of its radius and pressure difference, and inversely proportional to the viscosity and length of tube, it is given by the Equation (26):

$$q=\frac{\pi r^4}{8\eta}\left(\frac{\Delta p}{L}\right) \qquad \ldots(26)$$

where, Δp is the pressure difference in dynes cm^{-2}, r is the radius of tube in cm, L is the length of tube in cm, and h is the coefficient of viscosity of the liquid in dyne-sec cm^{-2} (poise). This relation is true only when the flow is steady or streamline and pressure is constant along the cross-section of the tube.

10.1.3. Reynolds Number

Laminar flow, sometimes known as streamline flow, occurs when a fluid flows in parallel layers, with no disruption between the layers. The Reynolds number is an important parameter that describes whether flow conditions lead to laminar or turbulent flow. The ratio of inertial forces of flow to frictional forces is called Reynolds Number (R) which is a dimensionless number given by Equation (27):

$$R=\frac{\rho_w vd}{\eta} \qquad \ldots(27)$$

where, v is the flow velocity, ρ_w is the density of water, η is the coefficient of viscosity of water and d is the pore diameter. In the case of flow through a straight pipe with a circular cross-section, Reynolds Numbers of less than 2300 are generally considered to be of laminar type: however, the Reynolds Number upon which laminar flows become turbulent is dependent on the flow geometry.

It has been experimentally observed that when water flows through a straight tube of diameter d, the flow remains streamline when R ranges between 1000 and 2000 and the critical velocity v_c, which is the maximum velocity up to which the flow is streamline, corresponds to a highest value of R called, the critical Reynolds number, R_c

$$R_c=2000=\frac{\rho_w v_C d}{\eta} \qquad \ldots(28)$$

or

$$v_c=\frac{2000\eta}{\rho_w d} \qquad \ldots(29)$$

When flow velocity ρ_w is less than v_c, the flow remains streamline.

When the tube is either curved or its diameter varies with its length, the value of R_c reduces. In a porous medium such as soil, due to tortuous structure of pore space, deviations from Equation (28) occur at much smaller values of R_c which is less than one ($R_c<1$). Thus, for a water flow through a soil, the critical velocity for streamline flow is given by the relation (30):

$$R_c=\frac{\rho_w v_c d}{\eta}=1 \qquad \ldots(30)$$

or,

$$v_c=\frac{\eta}{\rho_w}.\frac{1}{d} \qquad \ldots(31)$$

For water, we can approximate

$$\frac{\eta}{\rho_w}\approx 10^{-6}\frac{m^2}{s} \rightarrow v_c=10^{-6}\frac{1}{d}\frac{m^1}{s} \qquad \ldots(32)$$

This gives the effect of pore diameter on the critical velocity of streamline flow. For example:

(a) When pore diameter d = 1 mm = 10^{-3} m

$$v_c=10^{-6}\times\frac{1}{10^{-3}}\frac{m^2}{s}\frac{1}{m}=10^{-3}\frac{m}{s}=1\frac{mm}{s}$$

That is flow will be laminar as long as the flow velocity is less than 1 mm/s

(b) For smaller pores of diameter = 10 μm = 10^{-5}m

$$v_c=\frac{10^{-6}}{10^{-5}}\frac{m}{s}=10^{-1}\frac{m}{s}=10\frac{cm}{s}$$

This indicates that the flow will be laminar for velocities less than 10 cm/s. Thus, as the pore diameter decreases, the flow remains streamline for higher flow velocity.

10.2. Types of Flow

Soil water may be in static equilibrium or dynamic equilibrium state.

10.2.1. Static Equilibrium State of Soil Water

It occurs when mass and energy fluxes in the soil are zero, which implies that the total soil water potential remains constant and does not change with different positions or timings. Therefore, no flow of water occurs under static equilibrium. However, natural soils are never in the static equilibrium state as the water fluxes occur due to rainfall, evaporation and water uptake by roots.

10.2.2. Dynamic Equilibrium State of Soil Water Flow

The state of dynamic equilibrium can occur either as a steady state or stationary flow or transient or non-stationary flow of soil. The steady state flow of soil water system is that where water flux at a given point is constant with time. This means all temporal changes are negligible. If ϕ (t,x,y) is a time (t) and space (x,y) variable representing the state of the soil water (called state variable), then for a steady state or stationary system, we have

$$\frac{d\phi}{dt}=0$$

The water flow in a saturated soil exhibits a steady state flow.

The transient or non-stationary flow of soil water is that where water flux changes with space (position) and time. This implies

$$\frac{d\phi}{dx}\neq 0 \text{ and } \frac{d\phi}{dt}\neq 0$$

The unsaturated flow, in general, is transient flow. The behaviour of soil water flow is different under saturated and unsaturated soils.

10.3.1. Saturated Flow

From the above description it is clear that Poiseuille's law that describes steady state water flow through a tube of uniform radius cannot estimate non-steady state water flow through a large volume of soil containing pores of varying radius and length. In such a heterogeneous system, the flow of water can be reasonably estimated only when the flow velocity is considered as a function of macroscopic water pressure gradient of the soil volume.

Let us consider some laboratory cases of water flow through homogeneous soil. Figure 9(a) shows a saturated horizontal soil column of length x and cross-sectional area A being subjected to h units of pressure head at the inflow end. The outflow end is open to the atmosphere. Considering the reference level z units below the axis of the column, the hydraulic heads at the inflow and outflow ends are h+z and z, respectively. The pressure difference between the ends is h. Thus, gravity head

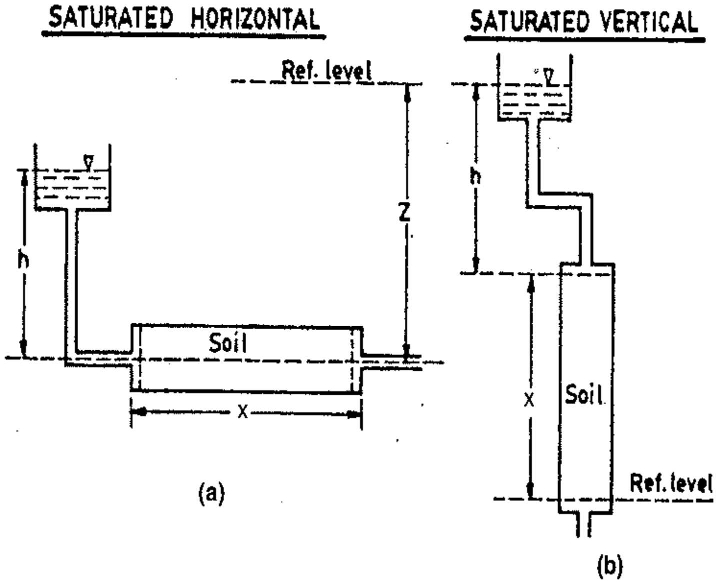


Figure 9. Water flow through (a) saturated horizontal soil column, and (b) saturated vertical soil column

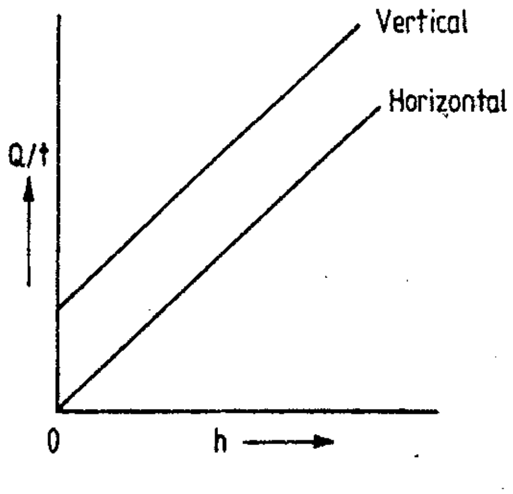


Figure 10. Relationship between water flux and pressure head for saturated orizontal and vertical soil columns

gets nullified in the case of horizontal flow. Water flows under the hydraulic gradient of h/x and the volume of water flowing per unit time (Q/t, water flux) can be measured by collecting the outflow in a measuring cylinder. Now, if we increase the inflow pressure head to 2h and 3h, we will see that outflow increases to 2Q and 3Q, respectively and when it is reduced to 0, the outflow decreases to 0. Similarly, when the cross-sectional area is increased from A to 2A and 3A, the outflow increases to 2Q and 3Q, respectively. In contrast, when the length of the column is increased to 2x and 3x, the outflow decreases to (1/2)Q and (1/3)Q, respectively. Based on these experimental results, we may conclude that Q/t is directly proportional to h and A and inversely proportional to x, i.e.

$$\frac{Q}{t} \propto \frac{Ah}{x} \qquad \ldots(33)$$

Now, if we keep A and x constant and vary h, we will find that Q/t has a 1:1 linear relationship with h (Figure 10). The ratio of hydraulic head to the length of soil column (h/x) is known as 'hydraulic gradient'. The slope of the straight line plot between (Q/At) and h/x is the proportionality constant which is termed as 'saturated hydraulic conductivity' (K) and defined as the velocity (Q/At) of water per unit hydraulic gradient. K is a function of pore size distribution of soil and the properties of flowing water such as density and viscosity. So, the mathematical relationship between Q/t and Ah/x for saturated horizontal flow may be expressed by Equation (34) as:

$$\frac{\theta}{t} = -\frac{KAh}{x} \qquad \ldots(34)$$

The negative sign on the right hand side of Equation (34) indicates that the flow always takes place in the decreasing direction of hydraulic head, implying that the change in head is decreasing with increasing length x.

For saturated vertical soil column (Figure 9b) with the reference level taken at the outflow end, we find that the outflow is not zero even at zero water pressure head. When the water level in the reservoir is brought at par with the inflow end, the hydraulic head becomes equal to x at that end. Since the reference level is considered at the outflow end which is open to the atmosphere, both gravity and water pressure heads become equal to zero at the outflow end. From this, it is clear that the vertical flow in saturated soil is strongly influenced by the gravity. For h water pressure head, as shown in Figure 9b, the flow equation may be given by Equation (35):

$$\frac{Q}{t} = -KA\frac{h+x}{x} \qquad \ldots(35)$$

where, Q/t is the water flux, A is the cross-sectional area of the column, (h+x) is the hydraulic head difference between inflow and outflow ends, x is the length of the soil column, and K is the saturated hydraulic conductivity. The ratio of hydraulic head difference to length of soil column is known as 'hydraulic gradient'.

The equations thus developed are known as Darcy's Law which states that water flux or flow velocity is proportional to hydraulic gradient and the flow occurs in the direction of decreasing water pressure.

If Q/t is measured for varying h and plotted against (h + x) / x, a straight line relationship will be obtained, but unlike horizontal flow, it will not be 1:1. The Q/t will not be zero even at h=0. The above equations for saturated flow may be generalized in terms of velocity of water (v) and hydraulic gradient (*i*) by the Equations (36) and (37) for horizontal and vertical flows, respectively:

Horizontal flow:

$$\frac{Q}{At} = v = -K\left(\frac{h}{x}\right) = -Ki \qquad \ldots(36)$$

Vertical flow:

$$\frac{Q}{At} = v = -K\left(\frac{h+x}{x}\right) = -Ki \qquad \ldots(37)$$

Thus, the general form of Darcy's law for horizontal as well as vertical flow can be written as per Equation (38):

$$q = -K\frac{dH}{dx} \qquad \ldots(38)$$

where, $q = Q/At$ = Soil water flux, and dH/dx is the hydraulic gradient and H is total hydraulic head where $H = h+x$

In a saturated flow, the hydraulic conductivity K is constant as long as pore structure does not change and it is generally represented by K_s, called saturated hydraulic conductivity.

The assumptions made in Darcy's Law are:

(i) Kinetic energy of water is negligible,
(ii) Mass density of water is constant;
(iii) Viscosity of water is constant, and
(iv) Flow is streamline.

The first assumption implies that when the flow velocity is small, the kinetic energy of soil water is negligible in comparison to its potential energy; hence the total energy of soil water is due to its potential energy only. The second and third assumptions are valid so long as temperature does not vary so that the density and viscosity of water remain constant. The fourth assumption is valid when flow velocity is smaller than the critical velocity for streamline flow. As flow velocity increases, the flow becomes turbulent. However in soils, the flow velocity does not reach the critical limit of streamline flow because even when velocity tends to increase, the forces exerted by the turbulent flow on the soil matrix are so strong that matrix begins to disintegrate. Its fragments block the pore space, increasing the resistance to flow and thus reducing the velocity.

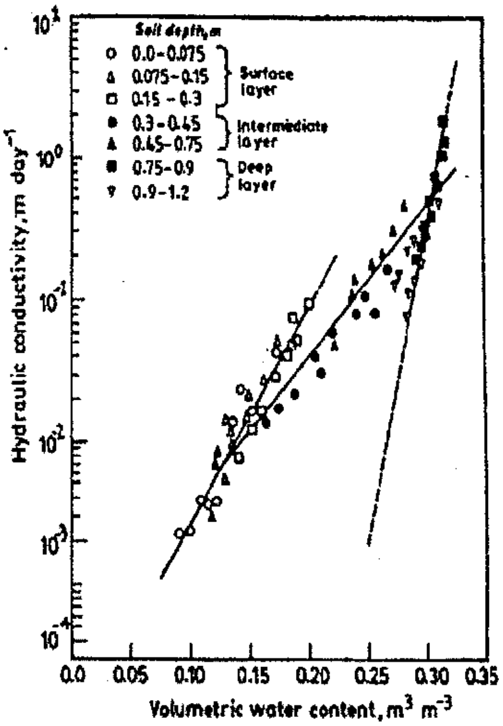
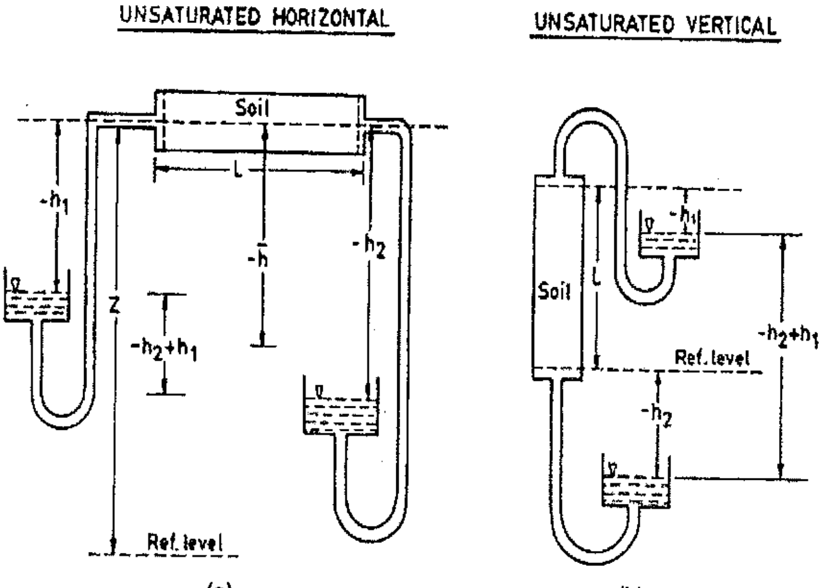


Figure 11. Relationship of hydraulic conductivity with water content for different layers of the Kharagpur lateritic sandy loam soil

10.3.2. Unsaturated Flow

The soils are usually not saturated because some of the pores are always filled with air. In an unsaturated soil, the water pressure is subatmospheric and it decreases with increase in the degree of unsaturation. The hydraulic conductivity is at its maximum in the saturated soil where all the pores are filled with water and take part in water transmission. With increasing degree of unsaturation, more and more soil pores become devoid of water and do not participate in water transmission, and as a result, the saturated hydraulic conductivity, K, decreases with decrease in either water content or water pressure. The functional relationship of K with either water content (Figure 11) or water pressure is essentially needed to estimate K for a specific water content. As observed with saturated soil, the flow velocity of water in unsaturated soil is also a function of hydraulic gradient.

Let us take some laboratory cases to derive flow equation describing water flow through homogeneous unsaturated soil. Figure 12a shows an initially unsaturated horizontal soil column subjected to negative water pressures of $-h_1$ and $-h_2$ units, respectively at inflow and outflow ends through porous plates. As a result, the left half of the column is equilibriated to $-h_1$ water pressure and the right



(a) (b)

Figure 12. Water flow through (a) unsaturated horizontal soil column, and (b) unsaturated vertical soil column

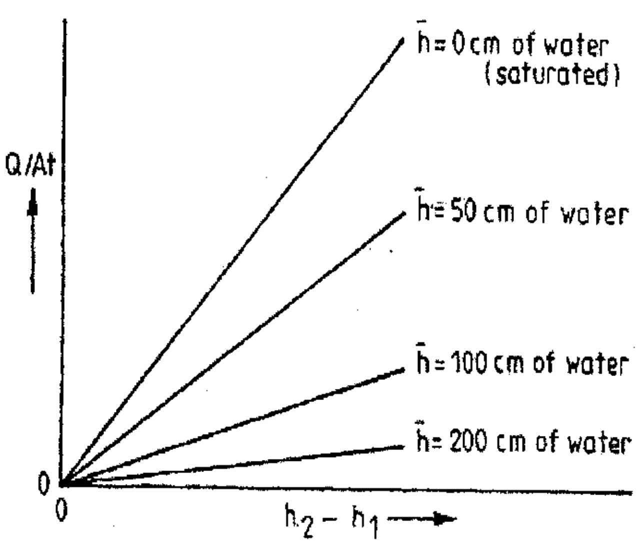


Figure 13. Relationship between flux density of water and pressure head difference for varying average water pressure head of unsaturated soil

half is equilibrated to $-h_2$ water pressure. Water at the central portion of the column would have a mean water pressure of $-\bar{h} = -(h_1+h_2)/2$. As there is no difference in gravity head between inflow and outflow ends, the total pressure head is actually the water pressure head which is higher at the inflow than at the outflow end. Water flows due to pressure head difference, $-h_1+h_2$. The larger the difference in pressure head, the higher is the flow rate, provided the mean pressure head, $-h$, is kept constant. If the flow velocity (Q/At) is plotted against h_2-h_1, the graph is linear and the slope of the graph decreases with the decrease in $-\bar{h}$ (Figure 13). The slope of the graph is proportional to the unsaturated hydraulic conductivity which is a function of $-\bar{h}$. It decreases with the decrease in $-\bar{h}$. Based on these relations, the flow equation for horizontal flow of water through unsaturated soil may be expressed as per Equation (39):

$$\frac{Q}{At} = -K(\bar{h})\frac{h_2-h_1}{x} \qquad \text{...(39)}$$

Applying the same principles, the flow of water through unsaturated vertical soil column (Figure 12b) may be expressed by Equation (40):

$$\frac{Q}{At} = -K(\bar{h})\frac{(h_2 - h_1) + z}{z} \qquad \ldots(40)$$

$K(\bar{h})$ is the hydraulic conductivity of the soil at mean suction head of soil layer and z is depth of soil from surface. In terms of matric suction (ψ) it can be written as $K(\psi)$ and Darcy's law for unsaturated soil water movement becomes:

$$q = -K(\psi)\frac{dH}{dz} \qquad \ldots(41)$$

$K(\psi)$ can be replaced by $K(\theta)$ when θ represents the water content corresponding to suction ψ and the Darcy's Law becomes:

$$q = -K(\theta)\frac{dH}{dz} \qquad \ldots(42)$$

For three dimensional flow, the Darcy's equation can be written as:

$$q = -K(\theta)\,\Delta H \qquad \ldots(43)$$

A general flow equation for unsaturated transient and steady flow is obtained when this Darcy's equation is combined with the equation of continuity

$$\frac{\partial\theta}{\partial t} = -\frac{\partial q}{\partial x} \qquad \ldots(44)$$

which results in Richard's equation for vertical flow of soil water as:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left(K(\theta)\frac{\partial\Psi}{\partial z} + K(\theta)\right) \qquad \ldots(45)$$

where, z is the distance from soil surface downwards.

Richard's equation can be transformed to either Ψ-based or θ-based equation with the use of another paramter defined as hydraulic diffusivity, $D(\theta)$, as:

$$D(\theta) = \frac{K(\theta)}{C(\theta)} \qquad \ldots(46)$$

with $C(\theta) = -\frac{\partial\theta}{\partial\Psi}$ which is differential water capacity and is the slope of θ–Ψ function.

There are few advantages in using $D(\theta)$ in this flow equation. It reduces the determination of two parameters $K(\theta)$ and $C(\theta)$ to one parameter $D(\theta)$. It also transforms the equation into a form for which analytical solutions are possible, especially for horizontal water movement. The range of variation in $D(\theta)$ is much smaller compared to that of $K(\theta)$, thereby reducing the errors introduced while assuming $D(\theta)$ as a constant value of effective diffusivity of a layer.

The θ-based Richard's equation then becomes:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left(D(\theta)\frac{\partial\theta}{\partial z}\right) - \frac{\partial K(\theta)}{\partial z} \qquad \ldots(47)$$

Again Ψ-based Richard's equation for unsaturated soil water flow is:

$$\frac{\partial\Psi}{\partial t} = \frac{\partial}{\partial z}\left(D(\Psi)\frac{\partial\Psi}{\partial z}\right) + \frac{1}{C(\Psi)}\frac{\partial K(\Psi)}{\partial z} \qquad \ldots(48)$$

where, the D, K and C are expressed as a function of matric suction (Ψ) rather than soil water content (θ). The θ based equation has the advantage that $D(\theta)$ does not vary much with θ in comparison to variation in K with Ψ.

10.4. Hydraulic Conductivity

In a saturated flow, hydraulic conductivity is constant since all the pores are filled with water and the water geometry in soil pores remains similar as long as pore structure is rigid. But in an unsaturated flow, the water geometry in pore structure becomes a function of soil water content. Therefore, unsaturated hydraulic conductivity has to be measured as a function of water geometry. There are two variables which represent this geometry in soil, namely soil water content, θ, and soil water suction, Ψ. The different values of water content can correspond to same value of soil water potential. The soil water potential represents the energy status of water due to air-water interface geometry and it does not depend on the entire geometry of water phase, whereas volumetric water content (θ) depends on the entire volume geometry of water phase. Hence volumetric water content (θ) is a better index for geometry of water phase than soil water suction (θ). Moreover, when hydraulic conductivity K is expressed as function of Ψ, hystersis is observed, i.e. $K(\Psi)$ depends on the direction of processes (wetting or drying). This is so again because Ψ is an index of surface geometry which differs while drying and wetting. However, when K is expressed as a function of θ, the hystersis of $K(\theta)$ is negligible because θ is an index of entire geometry of volume of water phase. Therefore, K is also generally expressed as a function of θ rather than Ψ.

Buckingham (1907) was the first to study dependence of K on θ. He proposed the one dimensional Darcy's Law for unsaturated flow as:

$$q = -K(\theta)\frac{dH}{dx} \qquad \text{...(49)}$$

where, $K(\theta)$ is not constant but is a function of θ, termed as unsaturated hydraulic conductivity. This equation is called Buckingham – Darcy's Law.

10.5. Intrinsic Permeability

The hydraulic conductivity (K) is a parameter which is dependent on the properties of the medium (soil) as well as the fluid (water). Intrinsic permeability (κ) is dependent on the properties of the medium (soil) only.

Intrinsic permeability κ, is calculated by the Equation (50):

$$\kappa = \frac{K\eta}{\rho_w g} \qquad \text{...(50)}$$

where, K is the hydraulic conductivity; η is the viscosity of water; ρ_w is the density of water, and g is the acceleration due to gravity. Values of 'η' and 'ρ_w' at a specified temperature can be obtained from any standard handbook. The unit of hydraulic conductivity is cm/sec, while that of intrinsic permeability is cm^2.

10.6. Measurement of Saturated Hydraulic Conductivity

Saturated hydraulic conductivity (K_s) of soil is generally determined in the laboratory on undisturbed soil core with the help of either a Constant Head permeameter or Falling Head permeameter. The constant head method is used for soils having high values of hydraulic conductivity, e.g. coarse-textured soils like sandy loam. Since the flow rates of fine-textured soils like clay are very low, the falling head method is generally used.

10.6.1. Constant Head Method

In this method, a constant head is maintained at the soil surface of a previously saturated sample and water is allowed to flow through the sample till the measured outflow attains a constant value. Undisturbed soil core is collected by depth core sampler. After covering the bottom end with a muslin cloth, the soil core is saturated by placing it in a trough of water. The saturated soil core is then placed in the constant head permeameter where water is allowed to flow through it under a constant head maintained by a constant head reservoir (Figure 14). The steady state outflow through soil core is measured and the following equation is used for calculating K_s:

$$K_s = \frac{Vx}{At(\Delta H + x)} \qquad \text{...(51)}$$

where, K_s is the saturated hydraulic conductivity, cm/sec; V is the volume of water collected, cm^3; A is the cross-sectional area of the sample, cm^2; t is the time interval of collection, sec; and (ΔH+x) is the pressure head difference between inflow and outflow ends.

10.6.2. Falling Head Method

In this method, instead of maintaining a constant head over the saturated soil sample surface, the hydraulic head is allowed to fall (Figure 15). The time interval, t, during which the head falls from a height H_1 to H_2 is recorded. The saturated hydraulic conductivity is given by Equation (52).

$$K_s = \frac{2.3.a.x}{A.t}\log\left(\frac{H_1}{H_2}\right) \qquad \text{...(52)}$$

where, 'a' is the cross-sectional area of the tube in which the falling head is measured; 'H_1' is the initial head in cm; and 'H_2' is the final head in cm, after time t (sec).

In the methods described above, undisturbed core samples brought to laboratory from the field are used for the measurement. Under field conditions, the Auger Hole method is generally adopted if the water table is close to the surface (within 1.5 to 2 metres). It is a very quick method and the calculations are kept to the minimum through the use of nomograms.

10.7. Estimation of Unsaturated Hydraulic Conductivity

The experimental measurement of unsaturated hydraulic conductivity $K(\theta)$ is difficult

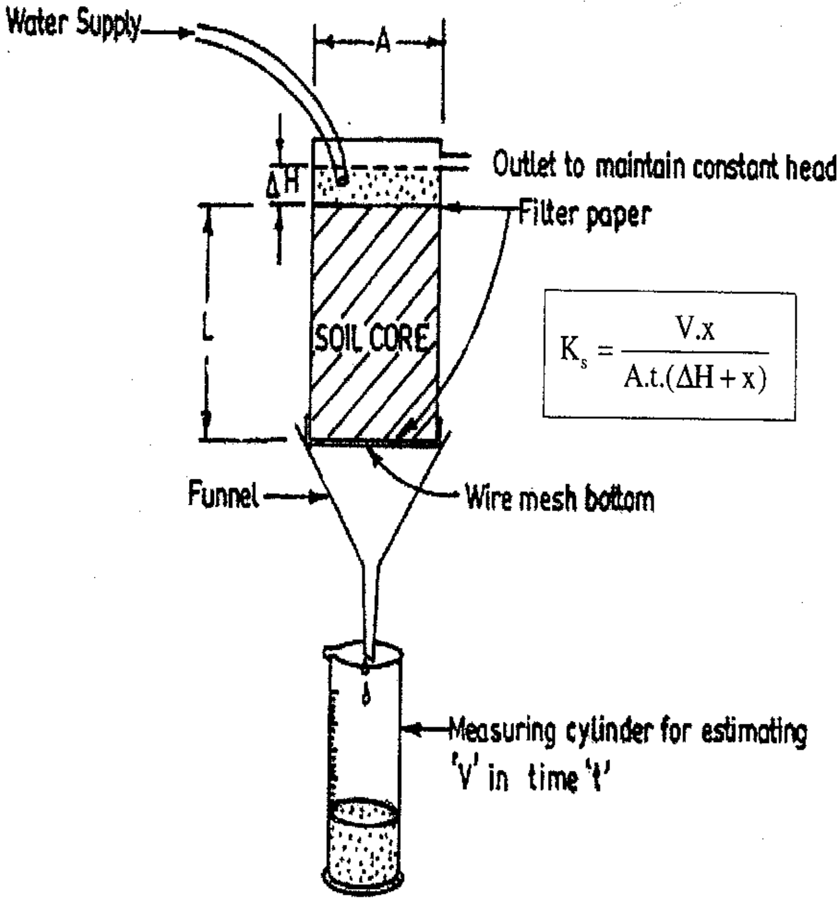


Figure 14. Constant head method for estimating saturated hydraulic conductivity

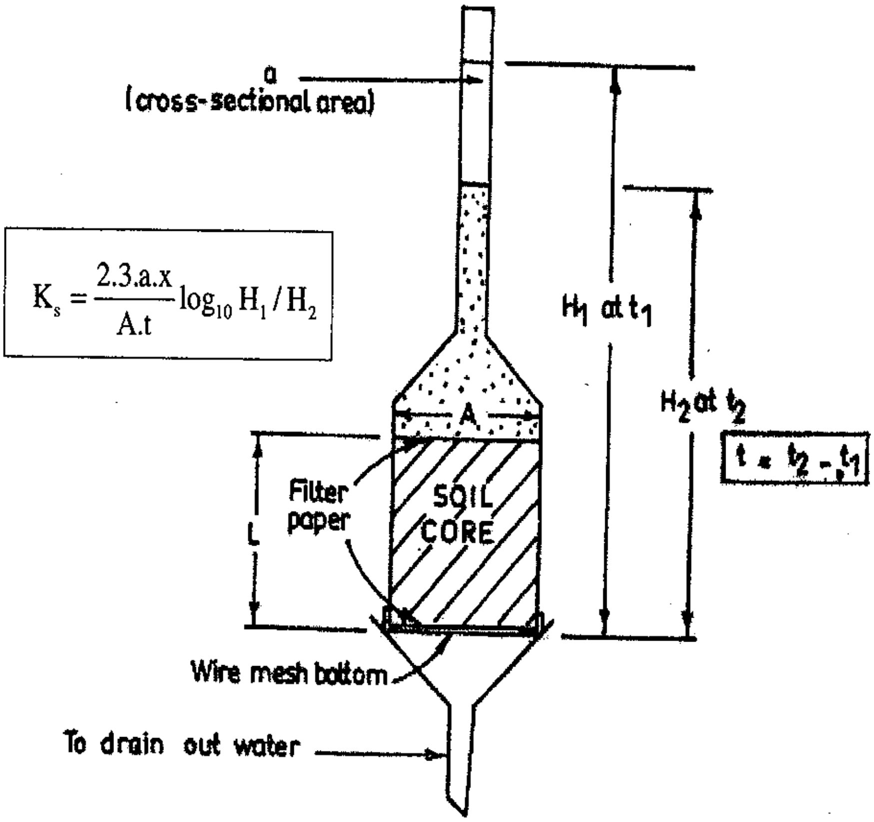


Figure 15. Falling head method for determination of saturated hydraulic conductivity

and complicated. Moreover, at very low θ values, the measurement errors are very high. Therefore, several methods have been developed to estimate K(θ). These estimations are based on three methods:

(i) Empirical and purely statistical regression methods are commonly known as Pedotransfer Functions (PTF), where K(θ) is expressed as a function of several measurable soil properties:

$$K(\theta) = f\ (\text{Bulk density, \% of silt, \% of clay, organic carbon,...})$$

This method has local applications and the accuracy is sufficient for the soil mapping purpose.

(ii) Methods based on dynamics of water flow in soil, where K(θ) is determined by monitoring θ and Ψ as a function of space and time, e.g. instantaneous profile method (Hillel, 1982).

(iii) Method based on parameterization by assuming simplified geometric structure for pore space, the parameters of the geometry are deduced from the measured Ψ–θ characteristics and K(θ) is then estimated from these parameters.

10.7.1. Empirical and Pedotransfer Function Methods

Several empirical equations have been reported in literature for dependence of K on θ or Ψ which can be used to compute K. The most widely used relations are:

$$K(\Psi) = a\,\Psi^{-n} \quad \text{...(53)}$$

$$K(\Psi) = \frac{a}{(b+\Psi^{n})} \quad \text{...(54)}$$

$$K(\theta) = a\,\theta^{n} \quad \text{...(55)}$$

and

$$K(\theta) = K_s\,s^{n} \quad \text{...(56)}$$

where, K(Ψ) and K(θ) are matric suction (Ψ) and soil water content (θ) dependent unsaturated hydraulic conductivities, K_s is saturated hydraulic conductivity of the same soil, s is degree of saturation and a, b and n are empirical constants, which differ from soil to soil. To estimate K(θ) or K(Ψ), first the empirical constants are determined for a given soil from a set of experimentally determined data and then these empirical constants are substituted in the equation to compute unsaturated hydraulic conductivity at any required θ or Ψ.

Apart from these empirical relations, several pedotransfter functions (PTFs) have been developed where K is expressed by a regression equation and easily-measurable soil properties influencing K are taken as independent variables. For example,

$$K(\Psi) = a_1\,(\text{Bulk density}) + a_2\,(\%\ \text{clay}) + a_3\,(\%\ \text{silt}) + a_4\,(\%\ \text{organic carbon}) + \ldots\ldots \quad \text{...(57)}$$

Here, the statistical methods are used to first determine the regression coefficients a_1, a_2, a_3, a_4, ... from a measured data set on K and other soil properties and then with these estimated coefficients, this equation is used to calculate the unsaturated hydraulic conductivity for a given situation with the help of measured soil properties. Such equations are called pedotransfer functions (PTFs).

10.7.2. Instantaneous Profile Method

This method is based on monitoring the transient state internal drainage of a soil profile. The assumptions made in this method are: (i) no evaporation is occurring from the soil surface, and (ii) no horizontal movement of soil water is taking place. In this method, a bare field is selected in which access tube for neutron moisture meter and several tensionmeters in different soil layers are installed. The field is irrigated and is then covered with a plastic sheet. Measurements of soil water content and matric suction of various layers in the profile are made at regular intervals. The rate of change of moisture content per unit time multiplied by the layer thickness determines the drainage flux of that layer. The drainage flux at a depth Z_b can be calculated using Equation (58):

$$q_b = -\frac{dw}{dt} = -Z_b\frac{d\theta}{dt} \quad \text{...(58)}$$

The cumulative drainage flux from all the layers gives the total drainage flux from the bottom of the profile. Under the irrigated conditions of nearly saturated profile, the downward flux is equal to the hydraulic conductivity K(θ). So that we get

$$K(\theta) = q_b \qquad \text{at depth } Z_b \qquad \ldots(59)$$

The instantaneous matric suction measurements allow the determination of hydraulic gradient across the profile. Knowing the flux and hydraulic gradient, the hydraulic conductivity can be calculated.

10.7.3. Parameterization Method

- Parameterization of a Function

If a function or a relation between two variables is represented by an equation having a number of parameters, then how these parameters are to be chosen so as to correctly represent a measured set of data variables is called parameterization.

- Parameterization of Unsaturated Hydraulic Conductivity Models

The objective of parameterization of unsaturated hydraulic conductivity is to interpolate and sometimes extrapolate its value. The various unsaturated hydraulic conductivity models are based on different Ψ–θ relationships. A model given by Mualem expresses the conductivity as:

$$K(\theta_G) = K_s\theta_G^a\left[\frac{\int_0^{\theta_G} h^{-(1+b)}d(\theta_G)}{\int_0^1 h^{-(1+b)}d(\theta_G)}\right]^2 \qquad \ldots(60)$$

where, $h = -\frac{\Psi}{\rho g}$ which represents the suction head in terms of matric suction Ψ, density of soil water (ρ) and acceleration due to gravity (g) and

$$\theta_G = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

where, θ is the actual volumetric water content, θ_s is the saturated water content and θ_r is the residual water content which can be taken as wilting point water content, as this water is not available to plant roots for uptake.

If h is expressed in terms of θ_G using van Genuchten model (1980), the unsaturated hydraulic conductivity can be expressed as per Equation (61):

$$K(\theta_G) = K_s\theta_G^a\left[1 - \left\{1 - \theta_G^{\frac{n}{n-1}}\right\}^{1-\frac{1}{n}}\right]^2 \qquad \ldots(61)$$

In terms of suction head h, it can be written as

$$K(h) = K_s\left[1 + (\alpha h)^n\right]^{-a\left(1-\frac{1}{n}\right)}\left[1 - (\alpha h)^{n-1}\left\{1 + (\alpha h)^n\right\}^{-1+\frac{1}{n}}\right]^2 \qquad \ldots(62)$$

These two equations are called Mualem-van Genuchten model for unsaturated hydraulic conductivity with five parameters to be determined, namely θ_s, θ_r, a, n and α from a measured data set. Once these parameters are known, this model can predict $K(\theta_G)$ or K(h), as the case may be.

Another model for unsaturated hydraulic conductivity is given by Burdine (1953) where he used the Brooks-Corey model (1966) for h–θ_G relation to solve Mualem equation (60). It is called Burdine-Brooks-Corey model for unsaturated hydraulic conductivity and is expressed as Equations (63) and (64):

$$K(\theta_G) = K_S\theta_G^{a+2+\frac{2}{\lambda}} \qquad \text{for } \theta_G < 1 \qquad \ldots(63)$$

or

$$K(h) = K_s\left(\frac{h}{h_o}\right)^{-2-\lambda(a+2)} \qquad \text{for } h > h_o$$

$$= K_s \text{ for } h \leq h_o \qquad \ldots(64)$$

where, h_0 being air entry suction head and λ is a parameter related to the pore geometry of soil. This model needs four parameters θ_s, θ_r, a and λ to be determined for predicting unsaturated hydralic conductivity.

Table 2 shows that the values of saturated water content (θ_s) and air entry suction (h_0) are lowest for sand and are due to large continuous structures in the pore space and narrow distribution of pore sizes. In the case of silt and loam, there is a wider range of pore radii so the maximum radius of water-filled pores decreases more rapidly in fine soil than in coarse-textured soil at moderately high values of θ. This results in comparatively rapid decrease of K(θ) with decreasing θ.

11. Field Water Balance

The field water balance is the balance sheet of inputs and outputs of water in the

Table 2. Mualem–van Genuchten and Brooks-Corey parameters for typical sand, silt and loam soils

Parametrs	Sand	Silt	Loam
Mualem–van Genuchten parameters			
α (m^{-1})	2.3	0.7	1.6
n	4.17	1.30	1.25
θ_r	0.03	0.01	0.00
θ_s	0.32	0.41	0.43
a	-1.10	0.00	0.00
K_s (10^{-5}ms^{-1})	2.2	1.0	0.3
Brooks-Corey parameters			
h_0 (m)	0.43	1.43	0.63
λ	3.17	0.30	0.25

soil-water zone. It begins with the entry of rainfall and/or irrigation water by the process of infiltration, continues with the retention and movement of water in the rooting zone and ends up with its withdrawal by drainage, evaporation and plant uptake. The water balance equation for the root zone depth (z) in the time period t_2–t_1 may be expressed as Equation (65):

$$\int_{t_1}^{t_2}(i-v-q)dt-\int_0^z\int_{t_1}^{t_2}r_z dzdt=\int_0^z\int_{t_1}^{t_2}\frac{\partial\theta}{\partial t}dzdt \quad ...(65)$$

where, 'i' is the rate of infiltration, q is the soil evaporation rate, v is the deep percolation rate at depth z and r_z is the rate of water uptake by plant roots.

11.1. Infiltration

Infiltration is the entry of water at the soil-air interface due to sorption and vertical flow of water through the soil profile. The process is of great practical importance as it determines how much of rainstorm or irrigation water enters the soil, and how much overflows the land surface as runoff. The infiltration rate is helpful in deciding the supply rate of irrigation water. It also helps assess the textural and structural conditions of surface soil and transmission characteristics of the sub-surface layers.

When water is ponded in an Infiltrometer (iron cylinder) sunk in soil up to 15-cm depth, the measured rate of entry of water is faster initially due to higher sorption of water by the dry soil. Subsequently, as the top layer becomes saturated, the sorptivity function decreases to the minimum and the rate of entry slows down considerably. It is then controlled by the rate of advancement of the wetting front through sub-surface layer as a function of unsaturated hydraulic conductivity and matric potential gradient in the wetting zone. Irrespective of soil texture, the infiltration rate reduces exponentially with time and attains a steady rate after a long lapse of time (Figure 17). The final steady rate is also known as basic infiltration rate. The infiltrability of soils is the maximum flux of water that enters the soil with free water ponded at the surface. The total depth of water that infiltrates the soil in a time period gives a measure of cumulative infiltration.

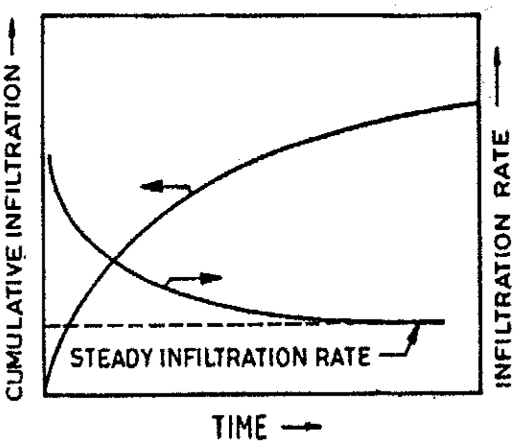


Figure 17. Temporal changes of cumulative infiltration and infiltration rate

The time changes of 'cumulative infiltration' (I) and 'infiltration rate' (i) are better described by the following equations [Eqs (66) and (67)] given by Phillip (1957):

$$I = s\,t^{1/2} + Kt \quad ...(66)$$

$$i = \tfrac{1}{2}s\,t^{-1/2} + K \quad ...(67)$$

where, s is the sorptivity function and K is the hydraulic conductivity of the soil corresponding to the water content prevailing in the transmission zone that occurs below the top saturated zone.

Water infiltrated into soil distributes and redistributes itself in the profile. During the initial stages, the water content of the upper layers of the profile decreases and that of the lower layers increases with time. The process obeys the following relation [Equation (68)]:

$$W = AT^{B} \qquad \ldots(68)$$

where, W is the water storage in a given layer and T is the time after the water supply at the surface is cut off. A is the storage at the start and B, an empirical constant.

The soil moisture content changes further with the lapse of time due to upward and downward movements of water under the influence of evaporation and gravitational pulls. These changes in soil moisture profile are referred to as the 'redistribution of soil water'.

11.2. Soil Water Evaporation

Following infiltration, water present in the soil evaporates as long as there is gradient of vapour pressure between soil surface and atmosphere and supply of heat to meet the latent heat of vaporization (580 cal/g of water at 20 °C). The process continues only when there is a continuous supply of water from sub-surface layers to the soil surface, which is influenced by soil hydraulic conductivity. Initially when the soil is wet, evaporation takes place at a constant but rapid rate, depending on the atmospheric evaporativity. The period of this constant rate of drying varies from a few hours in a coarser soil to a few days in a finer soil. When the soil surface dries out, the evaporation rate reduces exponentially with time and is controlled by the rate at which water is supplied by the sub-surface layer to the evaporation site. This stage of drying, which is known as 'falling rate stage' persists for a few days in a coarser soil and for few weeks in a finer soil. After this stage when the surface layer becomes so dry that the conduction of liquid practically ceases, evaporation continues at a very slow and steady rate, depending on the vapour diffusivity of the surface layer and adsorptive forces holding water in the sub-surface layer.

The evaporation loss during the drying cycle can be approximated from the soil water depletion in a time period after deducting the deep percolation loss. In areas where the water table is very shallow, the rate of soil water evaporation is strongly influenced by the depth of water table. For the steady upward flow from shallow water table, the evaporation rate is directly proportional to saturated K and inversely proportional to the depth of water table.

11.3. Deep Percolation

It is the downward flux of water below the maximum root zone depth. In field water balance this forms an important component. It is an unavoidable loss following irrigation, which is more in the coarser than in fine-textured soils. Under steady state conditions, as in a flooded soil, saturated hydraulic conductivity of the least permeable layer in the root zone helps approximate the deep percolation loss. However, under transient unsaturated condition, as is commonly prevalent in irrigated fields, it can be estimated by the 'Instantaneous profile method' (Hillel, 1982).

11.4. Root Water Uptake

A growing plant extracts soil water for its metabolic and physiological processes. Water enters the root through root hairs, moves through the xylem tissue to the leaf and leaves the plant through stomata to the atmosphere. This flow in soil–plant–atmosphere continuum (SPAC) takes place along the direction of decreasing water potential, which is at its minimum in the atmospheric boundary layer surrounding leaf. The rate of flow is moderated by the resistances in SPAC. Under the steady state conditions, the rate of water extraction (r_z) by plant roots from an unit volume of soil can be described by Equation (69):

$$R_z = (\psi_{soil} - \psi_{plant}) / (R_{soil} + R_{root}) \qquad \ldots(69)$$

where, ψ_{soil} and ψ_{plant} are the total water potential in soil and plant, and R_{soil} and R_{root} are the resistances in soil and plant, respectively.

Soil and leaf water potentials are precisely determined by Soil psychrometer and Leaf psychrometer, respectively. The hydraulic resistance in soil is inversely proportional to K(θ) and rooting density 'L' in the soil layer, while in plant root, it is considered to be the sum of resistances to water absorption and conduction. Knowing transpiration rate (considered equivalent to water uptake), ψ_{soil}, ψ_{plant}, and R_{soil} (=1/BK(θ)L), R_{root} can be approximated.

Resistances in plant including those in root xylem and leaf-air boundary, are higher than soil resistance under wet soil water regime while the reverse is true under dry soil water regime.

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Sample Problems

Question 1. The gravimetric (g g^{-1}) soil water content (%) at field capacity (FP) and Plant Wilting Point (PWP) for four layers of a sandy loam soil along with each layer bulk density (BD) are given as follows:

Soil depth (cm)	Water content (% by weight)		
	BD	FC	PWP
0-15	1.59	15.4	4.7
15-30	1.54	17.9	6.0
30-60	1.51	19.4	6.6
60-90	1.49	18.5	6.2

To determine the available water capacity (AWC) of the soil up to 90 cm depth, first the AWC of each layer in terms of depth of water (D_w) is calculated using Equation (8) and then is added for all the four layers to get the AWC for whole soil profile as given in Equation (9)

$$Dw = \{(FC\text{-}PWP) \times BD \times D_s\}/100 \qquad \ldots(8)$$

Soil layer	Thickness of soil layer, D_s (cm)	FC-PWP (%)	D_w (cm)
0-15	15	10.7	2.55
15-30	15	11.9	2.75
30-60	30	12.8	5.80
60-90	30	12.3	5.50

AWC for 0-90 cm soil layer = ΣD_w=16.60 cm. Therefore, total AWC of soil up to 60 cm depth is 16.6 cm.

Question 2. A soil core of length 7 cm and diameter 10 cm is filled with undisturbed soil sample. Water is ponded on the top of the saturated soil sample to a constant height of 3 cm. Under steady state condition, 42 cm^3 water was collected from the bottom of the sample into measuring cylinder in 30 minutes. The saturated hydraulic conductivity is calculated as follows:

Length of core L = 7 cm
Diameter of core = 10 cm
Radius of core (r) = 5 cm
Cross sectional area of core (A) = πr^2 = $\pi \times (5)^2 = 78.57\ cm^2$
Water height above soil (ΔH) = 3 cm
Water collected in 30 minutes = 42 cm^3
Time (t) = 30 min = 0.5 hr

Using Equation (51), we get

$$K_s = \frac{V.L}{At(\Delta H + L)} = \frac{42 \times 7}{78.57 \times 0.5(3+7)}$$
$$= 0.748 \text{ cm hr}$$

The measured saturated hydraulic conductivity is 0.748 cm/hr.

Question 3. The average volumetric FC of soil A and soil B are 29.4% and 22.5%, respectively, in upper 60 cm of soil layer. The average volumetric PWP for soil A is 10.4%, whereas for soil B is 6.9%. Calculate the AWC for both the soils, in cm of water in upper 60 cm layer and find which soil is better for plant growth.

(Ans: AWC for soil A = 11.4 cm,
AWC for soil B = 9.36 cm
Soil A is better than soil B)

Question 4. A soil sample in a soil core of height 5 cm and cross-sectional area of 10 cm^2, saturated with water has a head of 5 cm of water maintained on its surface. If the volume of water collected at the outflow end is 8 cm^3 in 10 minutes, calculate the saturated hydraulic conductivity of the soil.

(Ans: K_s = 2.4 cm/hr)

Chapter 7

Soil Air and Soil Temperature

R.P. TRIPATHI and V.S. TOMAR

1. Introduction

The physicochemical properties that affect plant growth and biological processes in most of the soils depend on soil air and soil temperature. The aerobic respiration in roots of plants and soil microorganisms involves continuous consumption of oxygen and evolution of carbon dioxide. An inadequate gas exchange may decrease the growth and yield of crops because metabolic processes of roots are impaired immediately if this exchange is interrupted. The rate of organic matter decomposition and mineralization of the organic form of nitrogen increases with temperature. The biological decomposition as well as uptake and movement of water and nutrients practically cease under very low temperature conditions. Similarly, seed germination, emergence, root and shoot growth are slow under low temperature conditions. It is possible to optimize soil air and soil temperature through cultural practices.

2. Soil Air

2.1. Soil Air and its Composition

A typical mineral soil, on volume basis, contains half solid and half pore space. The solid part is consisted of mineral material and organic matter, and space part is filled with water and air interchangeably (Figure 1). In a saturated soil (after heavy rains or irrigation), most of the pore spaces get filled by water, therefore, under such conditions there is a deficiency of aeration in the soil and plant growth may suffer (except rice). As soil dries, air enters into the pore spaces and in a dry soil most of the pore spaces get filled with air. The proportion of air-filled pore spaces, thus, is subjected to rapid and large fluctuations, depending upon soil moisture content.

Soil aeration refers to the exchange of oxygen and carbon dioxide between the soil pore spaces and the atmospheric air (Figure 2). The process controls the deficiency of oxygen consumed during respiration of plant roots and soil microorganisms and prevents toxicity of carbon dioxide evolved during respiration in the soil air. The term '*air capacity*' is used to describe aeration status of soil. According to

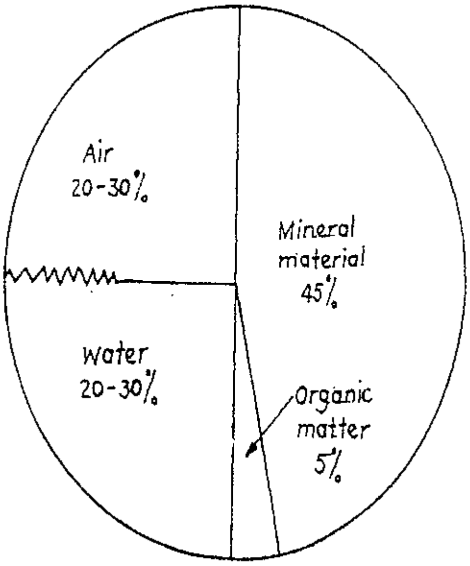

Figure 1. Four major components of a typical mineral soil on volume basis

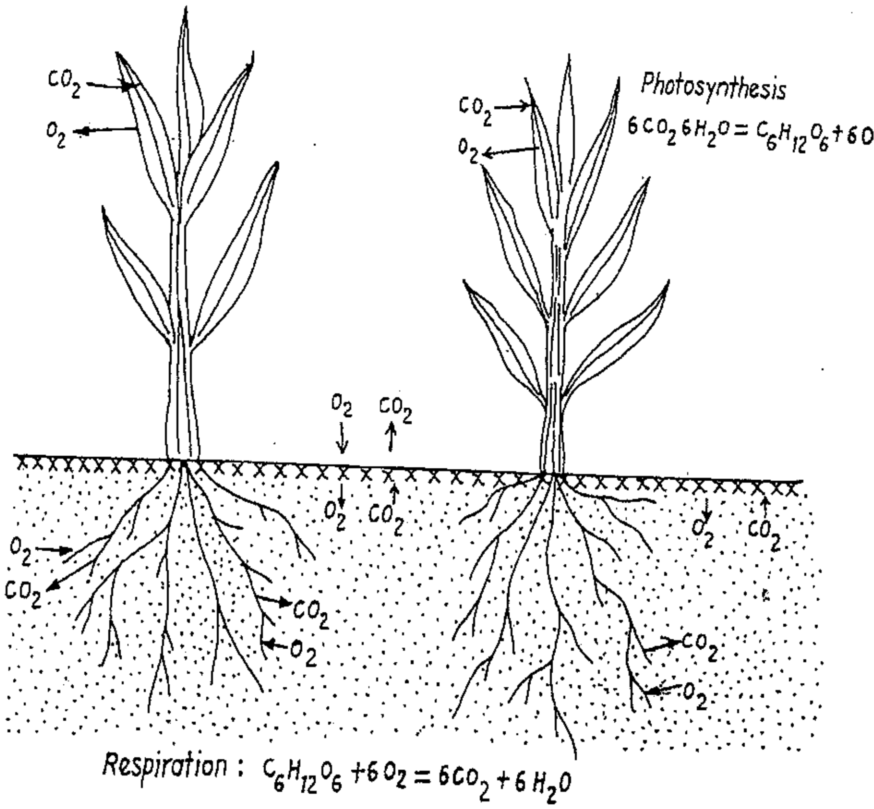

Figure 2. Consumption of oxygen and production of carbon dioxide during respiration by roots of higher plants and microbes. Arrows indicate the exchange of gases between atmospheric air and soil air

Kohnke (1968), the air capacity of soil refers to the volume of pore space filled with air when the soil is under a tension of 50 milli bar. This value is also called as 'non-capillary porosity'. It corresponds to a pore size of 0.06 mm or larger in diameter.

The components of soil air are basically the same as those of the atmospheric air, viz. nitrogen, oxygen, carbon dioxide, inert gases and water vapour. The composition of atmospheric air (by volume) is approximately taken as: nitrogen and inert gases = 79.0 %, oxygen = 20.79 % and carbon dioxide = 0.03 %. The composition of soil air is more or less similar to that of the atmospheric air, except the content of carbon dioxide. In the upper layer of a soil having stable structure and ample macropores, the composition of air is taken as: nitrogen and inert gases = 79.1 %, oxygen = nearly 20.6 %, and carbon dioxide = 0.25%. The plant roots and soil microorganisms consume oxygen and evolve carbon dioxide during respiration. Also, plant roots and microbes decay with the liberation of carbon dioxide. The content of carbon dioxide in soil air is, therefore, several times higher and that of oxygen is slightly less than that in the atmosphere. The composition of soil air is dynamic and varies largely with soil moisture content and from place to place within a given soil.

2.1.1. Factors Affecting Composition of Soil Air

The composition of soil air undergoes rapid changes due to continuous consumption of oxygen by plant roots and soil microorganisms and the production of carbon dioxide and also with renewal of soil air by atmospheric air. Several factors, such as soil characteristics, crop, tillage, organic matter, biological activity, season, etc. affect the composition of soil air.

(i) Soil Respiration – The respiration by roots of higher plants and soil microorganisms is the major cause of consumption of oxygen and production of carbon dioxide in soil. The rate of respiration is influenced by temperature, water supply and the type and amount of respiring tissues.

(ii) Soil Organic Matter – The addition of organic matter to the soil through manures, crop

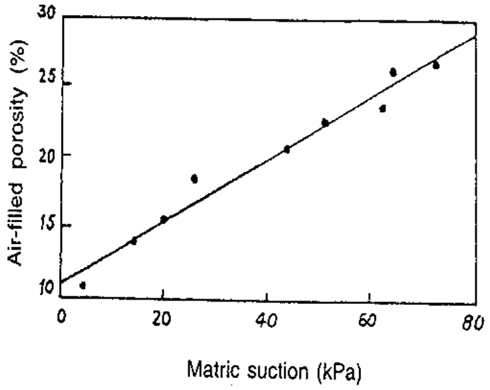

Figure 3. Relationship between air-filled porosity and matric suction in clay loam soil
Source: Bhushan and Sharma (1999)

residues, sewage sludge or other organic materials may affect soil air composition to a large extent. During the process of microbial decomposition of these organic materials, the concentration of oxygen decreases and that of carbon dioxide increases.

(iii) Soil Moisture – The pore spaces in the soil at a given time may be filled by either water or air or by both. These pores get filled by water immediately after heavy rains or irrigation and the oxygen content may fall nearly to zero. When the water from the soil drains or evaporates from the soil surface, air enters into the soil pores (primarily macropores) and oxygen content increases (Figure 3).

(iv) Macropores – The macropore content also affects the total air space and gaseous exchange. Soil texture, bulk density, aggregate stability and organic matter content, all influence the macropore content and, in turn, soil aeration.

(v) Soil Depth – The soil air composition varies with depth. Subsoils are usually more deficient in oxygen than top soils (Figure 4). The total pore space as well as the macropore space are generally much lower at lower depths. The upper layer of a soil having stable structure and large number of macropores, may have oxygen content of nearly 20%. But this oxygen content may become very low, or to near zero, in lower horizons of a poorly-drained soil with few macropores or in waterlogged areas.

(vi) Soil Heterogeneity – It is generally possible that poorly-aerated areas may be found in some well-drained and well-aerated soils. The poorly-aerated portion may be a heavy-textured or compacted soil layer, or it may be located inside a soil structural unit where tiny pores may limit rapid air exchange.

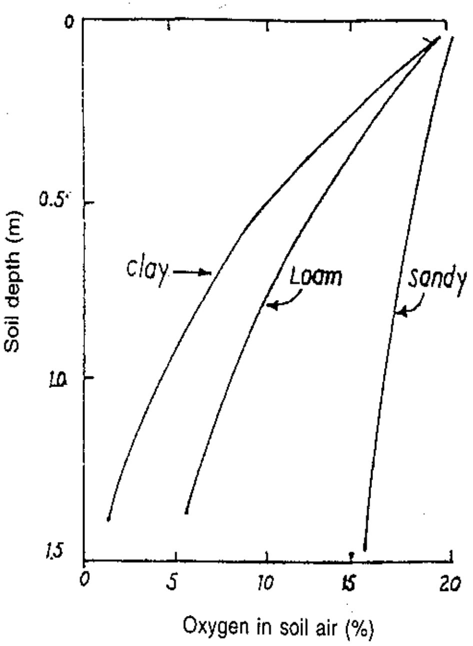

Figure 4. Changes in oxygen content with depth in soils of different texture

(vii) Biological Activity – The carbon dioxide concentration increases with increase of biological activities in soil.

(viii) Effect of Cropping – Cropped fields generally have higher concentration of carbon dioxide than fallow fields. The biological activity associated with crops tends to increase the concentration of carbon dioxide in soil.

(ix) Tillage – Tillage affects the gaseous composition by altering the exchange of gases, which is faster in tilled fields than in untilled fields. The depth of tillage influences the gaseous composition. A shallow tillage encourages formation of carbon dioxide in the top soil in comparison to a deep tillage. Tillage practice, such as puddling or compaction, required to grow lowland rice, decreases the transmission pores (pores greater than 50 μm in diameter). This decrease in larger size pores results in poor aeration for upland crops, such as wheat grown after lowland rice.

(x) Seasonal Effect – The composition of soil air changes with season, primarily due to changes in soil temperature and soil moisture. The concentration of carbon dioxide increases after rains, probably because of increased nitrification and decomposition of organic mat-

ter in addition to slow gas exchange. In summer months, the gaseous exchange is faster causing higher concentrations of oxygen and lower concentrations of carbon dioxide.

2.2. Renewal of Soil Air

The renewal of soil air or the gaseous exchange between soil and atmosphere is a natural process by which carbon dioxide in soil is exchanged by oxygen of atmospheric air. Carbon dioxide is also washed down beyond the root zone by irrigation or rainfall. The renewal of gases is brought about by two mechanisms— the mass flow and the diffusion.

2.2.1. Mass Flow

The mass flow of air occurs due to total pressure gradient of gas. The pressure gradients cause movement of entire mass of air from a zone of high pressure to that of low pressure. Such a flow of air may occur from atmospheric air to soil air or vice-versa. It may also occur from one pocket of soil to another pocket. When water enters the soil, the soil air is forced out. The rain water is often saturated with oxygen. One cm of rain over an area of one hectare contains 4,339 g (3,000 litres) of oxygen at 20 °C at atmospheric pressure. On the other hand, when water is lost from the soil by evaporation, plant uptake and deep drainage, the air is drawn into the soil. Changes in other meteorological factors, such as temperature, wind action and barometric pressure also affect the gaseous exchange. However, the renewal of gases by mass flow is less important than the diffusion in determining the total exchange that occurs.

2.2.2. Diffusion

Diffusion is a process by which each gas molecule tends to move in the space occupied by another gas molecule as a result of difference in partial pressures of the gas. The atmospheric air contains a higher amount of oxygen than the soil air which contains more carbon dioxide than the former. Thus, the partial pressure of oxygen is higher in the atmospheric air than in the soil air, and the partial pressure of carbon dioxide is higher in the soil air than in the atmospheric air, even though the total pressure in the atmosphere and soil may be the same. This results in the movement of oxygen from atmosphere into the soil and carbon dioxide from soil into the atmosphere.

According to Fick's law of diffusion, flux of a gas across a plane is proportional to the concentration gradient [Equation (1)]:

$$q_{gi} = -D\frac{dc}{dx} \qquad \text{...(1)}$$

where, q_{gi} is the flux of gas gi normal to the x-direction, D is the diffusion coefficient, and dc/ dx is the concentration gradient of that gas. The flux refers to the amount of gas diffusing in a unit time across a plane of unit area. D depends on the structure and moisture content of the soil. It is approximately proportional to a fraction of the total soil volume occupied by the gas-filled pores. The rate of diffusion increases with temperature. The diffusion of gases through dry soils of fine texture is higher than that through dry soils of coarse texture. If the soils are moist, the behaviour is reversed because then the air-filled pores will be more in a coarse-textured soil than in fine-textured soil. The value of D in soils is usually between 0.6 and 0.8.

2.3. Factors Affecting Soil Aeration

The process of soil aeration controls the levels of oxygen and carbon dioxide in soil. Factors, such as drainage of excess water and macropore content determine the soil areation status. The soil macropore content is influenced by texture, structure, bulk density and organic matter content of a soil. Respiration by plant roots and soil microorganisms, and incorporation of large quantities of manure, crop residues or other organic materials alter the composition of soil air. The soil aeration also changes with season, soil heterogeniety and depth of soil.

2.4. Characterization of Soil Aeration Status

Several methods have been used to characterize the soil aeration status; some of these are described below:

2.4.1. Air-filled Porosity

The air-filled porosity (f_a) of a soil can be determined by finding total pore space (S) and water content on volume basis (θ) by the Equation (2):

$$f_a = S - \theta \quad \text{...(2)}$$

The air-filled porosity can also be evaluated using air-space pycnometer and tension-table methods.

2.4.2. *Composition of Soil Air*

The oxygen and carbon dioxide contents of the gas samples, taken from soil air, can be determined using chemcial or gas analyzer or gas chromatographic methods.

2.4.3. *Amount of Carbon Dioxide Given off at Soil Surface*

The amount of carbon dioxide is determined for a definite area of the soil surface. It gives an idea about the microbial and root activity in the soil.

2.4.4. *Air Permeability*

Air permeability of soil is a parameter which indicates its readiness to transmit gases when a difference in pressure builds up. The percentage, size and continuity of pores within the soil and occupied by the air determine the permeability of a soil. Special instruments like 'Air Permeameter' and 'Gasometer' are used to determine air permeability under field and laboratory conditions. This method gives a better idea of renewal of soil gases than the actual availability of oxygen to plant roots.

2.4.5. *Apparent Diffusion Coefficient*

Diffusion is the principal mechanism in the exchange of gases between the soil and the aerial atmosphere. Oxygen normally diffuses into the soil and carbon dioxide diffuses out into the atmosphere. The apparent diffusion coefficient is used to characterize a soil for its aeration status.

2.4.6. *Redox Potential*

The oxidized or reduced state of chemical elements in the soil gives an idea about its aeration status. In a well-aerated soil, the oxidized states of elements such as those of iron as ferric (Fe^{3+}), manganese as manganic (Mn^{4+}), nitrate (NO_3^-), and sulphate (SO_4^{2-}) dominate. In poorly-aerated soils, the reduced forms of these elements such as ferrous iron (Fe^{2+}), manganous manganese (Mn^{2+}), oxides of nitrogen (NO_x) and sulphide (S^{2-}) are found.

The oxidation-reduction (redox) potential (E_h) of a soil can be measured by inserting a standard electrode and a platinum electrode in the soil solution. It provides a measure of the tendency of a system to reduce or oxidize substances. The values of E_h can be interpreted up to a certain extent in terms of the ratios of certain oxidizing and reducing organic and inorganic materials present in the soil system. The value of E_h is positive and may be as high as + 0.5 volt under strong oxidizing conditions. It is low and even negative when elements are present in reduced forms. E_h values have the advantage of providing a measure of intensity of reduction under conditions having no molecular oxygen. It is, therefore, useful in characterizing the soil aeration in the range below which the diffusion of oxygen is zero, for example, in rice fields where soils remain saturated or submerged under water. The oxidized and reduced forms of certain elements in soil and the E_h values at which change in the form occurs are given in Table 1.

2.4.7. *Oxygen Diffusion Rate (ODR)*

Analogous to measuring of oxygen movement to a plant root, the rate of oxygen diffusion is measured by inserting a small platinum wire electrode into the soil. The apparatus consists of a platinum microelectrode which is pushed into the soil to a desired depth and an

Table 1. The oxidized and reduced states of certain elements in soil and the redox potential (E_h) at which change in the form occurs

State of element		E_h at which change in form occurs (V)
Oxidized	Reduced	
O_2	H_2O	0.38 to 0.32
NO_3^-	N_2	0.28 to 0.22
Mn^{4+}	Mn^{2+}	0.28 to 0.22
Fe^{3+}	Fe^{2+}	0.18 to 0.15
SO_4^{2-}	S^{2-}	-0.12 to -0.18
CO_2	CH_4	-0.20 to -0.28

Source: Patrick and Reddy (1978)

electrical cell is formed by inserting into the soil nearby a saturated calomel electrode. The calomel electrode through a galvanometer is connected to the positive terminal of an external source of direct current. Its negative terminal is connected to the platinum micro-electrode. The result of measurement is an electric current which is related to the rate of oxygen flux at the electrode surface and is given by Equation (3):

$$i \times 10^{-6} = n\,FAf \qquad \ldots(3)$$

where, i is electric current in microamperes, n is number of electrons required for reduction of one molecule of oxygen which is 4 , F is the Faraday's constant, A is the surface area (in cm^2) of platinum electrode, and f is the flux or ODR to the electrode surface in number of molecules of oxygen per second per cm^2. The ODR is calculated by Equation (4):

$$\begin{aligned} \text{ODR} &= (i \times 60 \times 32 \times 10^{-6}) / (4 \times 96500 \times A) \\ &= (0.497 \times 10^{-8} \times i) / A \ (\text{g cm}^{-2}\ \text{min}^{-1}) \qquad \ldots(4) \end{aligned}$$

The requirement of ODR of a number of crops ranges from 22.9×10^{-8} to 39.5×10^{-8} g cm^{-2} min^{-1} (Table 2). In general, the critical ODR value of soils in which roots of many plants will not grow is of the order of 20×10^{-8} g cm^{-2} min^{-1}.

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2.5. *Effects of Soil Aeration*

The soil aeration may have direct and indirect effects on activities of higher plants and soil microorganisms. The level of soil aeration determines the forms of several inorganic elements, soil reactions, microbial decay of organic matter, symbiotic nitrogen fixation and, in turn, the soil properties and plant growth. The harmful effects of poor aeration are described below:

(i) The growth of plants, particularly the root growth, is adversely affected by poor aeration. Waterlogging for more than 48 hours at knee-high and tasselling growth stages may retard the growth of maize crop. In some cases, an abnormal development of roots may occur, e.g. the de-shaping of sugarbeet and carrots.

(ii) The absorption of nutrients and water gets reduced in poorly-aerated soils.

(iii) Under anaerobic conditions, the formation of inorganic compounds, which are toxic to plants, is favoured.

(iv) The changes in soil oxygen content may affect the susceptibility of plant roots to diseases, and/or the virulence of soil-borne disease organisms, or both, resulting in increased disease incidence.

(v) The absence of sufficient oxygen in soil affects the nitrogen fixation by *Rhizobium.*

(vi) The soil organic matter cannot be decomposed properly by soil microorganisms unless sufficient oxygen is present in the soil. If anaerobic bacteria decomposes soil organic matter, toxic substances like sulphides, methane, organic acids, etc. are liberated which are harmful for plant growth.

(vii) In well-aerated soils, oxidized forms of most of the elements are present, e.g. nitrate-N. These are desirable for most common crops. The reduced forms, specifically of iron and manganese, may be present at toxic levels in the moist acidic soils.

Table 2. Critical oxygen diffusion rate (ODR) for different crops

Crop	ODR (10^{-8} g cm^{-2} min^{-1})
Maize	30.0
Soybean	28.4
Wheat (unirrigated)	26.9
Wheat (irrigated)	26.3
Peas (Unirrigated)	32.9
Peas (irrigated)	39.5
Toria	22.9

Source: Sinha and Ghildyal (1982)

2.6. *Management of Soil Aeration*

The proportion of air-filled pore spaces and the ease with which exchange of gases can take place between atmospheric air and soil air influence the aeration status. The practices encouraging the air-filled pore spaces and the gaseous exchange may improve the aeration status. The variation in tendency of plant species to tolerate water stagnation/ poor aeration can also be utilized to harness better crop yields from such soils. The soil aeration under field conditions can thus be optimized by the following methods:

2.6.1. Improving Soil Structure

An increase in the volume of air-filled pores can be attained by improving soil structure. The practices that help in the maintenance of stable soil aggregates such as use of animal manure, green manure, plant residue manure and growing of legume crops, will, in turn, encourage better soil aeration.

2.6.2. Drainage

An aerobic soil environment can be maintained by providing surface and /or sub-surface drainage. The soil pores get filled with water due to continuous seepage from canals, presence of perched or high water tables, and after heavy rains or irrigation. The drainage of such fields is essential for the supply of sufficient oxygen.

2.6.3. Cultivation

A light cultivation of soil or interculture operation does not only control weeds but helps in the exchange of gases, specially in heavy-textured poorly-drained soils. After rains, an impermeable layer/ crust is formed at the soil surface that hinders the gaseous exchange. A light cultivation will break it and help in improving soil aeration.

2.6.4. Plant Adaptations

Plant roots, in general, are adapted to aerobic respiration. However, some of the plant species develope mechanisms such as increase in the air space of roots (root porosity) or internal aeration through leaves and cortex cells and thereby can grow even in oxygen-deficient soils. The selection of crop species, therefore, is important for growing crops in waterlogged or poorly-drained soils. For example, rice thrives well in submerged soil conditions. Also, soybean crop can tolerate temporarily waterlogged soil conditions better than maize, pigeonpea and other deep-rooted crops.

3. Soil Temperature

3.1. Soil Temperature and Heat

Heat is a form of energy and temperature is a measure of the heat energy. The heat energy refers to kinetic energy of random motion (vibration) of molecules of a substance. The speed of vibration is directly proportional to temperature. The unit of heat is calories or joules and that of temperature is °C. Solar radiation is the source of soil heat. The flux of heat into- and out of the soil determines the soil thermal regime, which is characterized in terms of soil temperature.

3.2. Variation of Soil Temperature

Soil temperature at any time of the day depends on the ratio of solar energy absorbed to energy lost and therefore, depends on the angle of incidence of sun rays on the soil surface. Since position of the sun from the earth and hence the accompanying energy varies both diurnally and annually, the soil profile experiences diurnal and annual variations of soil temperature.

3.2.1. Dirunal Variation

When sun rays strike the ground, the energy it carries is partly absorbed by the soil, thereby the surface soil gets heated and a difference of temperature between the surface soil (hotter) and the subsurface soil (cooler) is created. This difference of temperature causes the heat to flow downward. The difference between maximum and minimum temperature is highest at the soil surface and decreases with depth and becomes small beyond 0.25 m depth (Figure 5).

While the soil surface starts getting heated just after sunrise, heating at lower depth starts much later. The surface soil is heated rapidly between 10.00 and 13.00 hours of a day. But the soil temperature at 0.05 m and 0.1 m depths is maximum around 15.00 and 17.00 hours, respectively. The temperature maxima at still lower depths occur during night time when the upper part of the profile starts cooling rapidly. The progressive delay in the time of occurrence of maximum temperature with depth indicates slow rate of penetration of heat wave into the soil. This time lag in the heating of soil profile at a particular depth is a function of thermal properties, moisture content and structure of the soil. Figure 5 shows that the cooling period of daily cycle in the surface layers is more than twice as long as the warming period. The average temperature of daily cycle in the surface layer of the soil is generally higher than the average air temperature. In

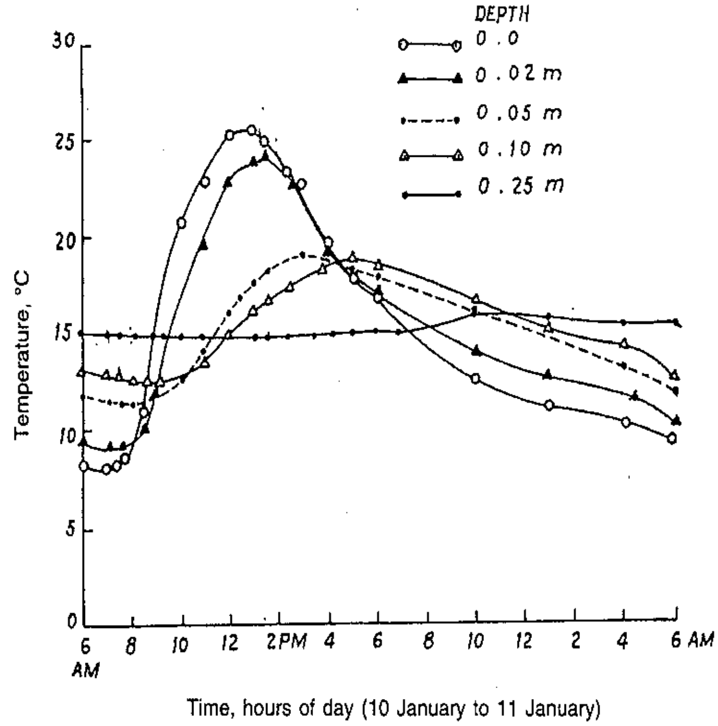

Figure 5. Diurnal variation of soil temperature in a bare soil on a clear day
Source: Tripathi and Ghildyal (1979)

general, the dirurnal changes in soil temperature are lower in moist than in dry soils, in compacted than in loose soils, and in deeper than in shallower soil layers.

3.2.2. Annual Changes

The annual variation of thermal regimes of a Mollisol is depicted in Figure 6. The annual temperatures at 0.05m depth show a progressive increase from 5th week of the year to 24th week (onset of south-west monsoon), followed by a rapid decrease until the 28th week and thereafter a partial stability until the 35th week (end of monsoon). The soil temperature tends to increase slightly during 35th and 42nd weeks of the year and then declines, completing the annual cycle. The sudden drop in temperature between 24th and 41st weeks is associated with excessive wetness due to rainfall, rise in groundwater table and cloudy conditions. The annual changes in soil temperature may occur even beyond 1.0 m depth.

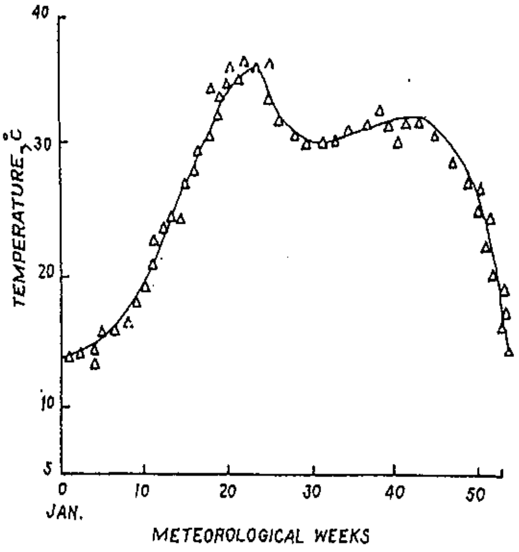

Figure 6. Annual variation in average soil temperature at 7 AM and 2 PM in a bare soil at 0.05 m depth

3.3. Factors Affecting Soil Temperature

Soil temperature is controlled largely by the factors which affect energy balance on and within the soil. Incoming and outgoing solar radiations, albedo, soil colour, slope, soil composition, mulches and vegetation, irrigation and drainage and evaporation affect the soil temperature.

3.3.1. Solar Radiation

The amount of solar energy received by soil depends on the constituents of the atmosphere and the aspect. Clouds, water vapour, dust particles and aerosols reduce the solar energy reaching the soil surface. Only 35-40% of the solar radiation actually reaches the earth in cloudy humid regions and about 75% in the cloudless arid regions. Out of this, only 10 % is actually absorbed to warm the soil and the remaining is lost as heat of vaporization from soil or leaf surfaces and is re-radiated as long wave radiation or reflected back to sky. The aspect differences result in warmer south-facing and west-facing slopes than their respective opposite faces.

3.3.2. *Albedo*

Albedo, which generally, refers to short wave reflectivity, is related to colour and angle that sun rays make with the striking surface. A higher albedo at the dawn and dusk than at other times of the day (Figure 7) and in winter than in summer, causes a continuous change in absorption of heat by soil which, in turn, leads to diurnal and annual variations in soil temperature. A lower albedo means a higher absorption of solar energy. Moist soils which are relatively darker have lower albedo than drier ones.

3.3.3. *Soil Colour*

Light-colour soils have twice the albedo of the dark-colour soils. Consequently, a dark-colour soil is warmer on clear days because it absorbs more solar energy than a light-colour soil. However, since a good absorber is also a good emitter, dark-colour soils emit more energy during the night and, thus, allow a wider daily variation in temperature. Also, dark-colour soils are generally associated with high humus and high retention of water and, therefore, have high heat capacity.

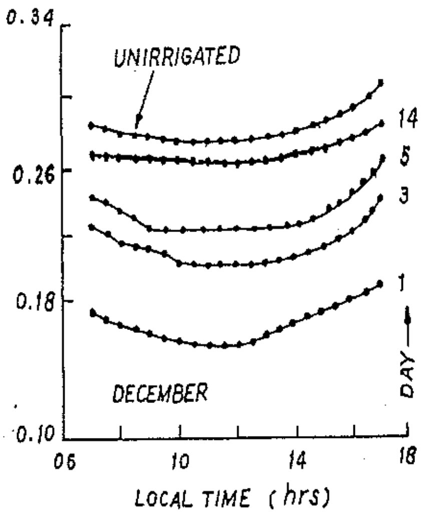

Figure 7. Diurnal variations of bare soil albedo on 1, 3, 5 and 14 days after irrigation and in unirrigated plot

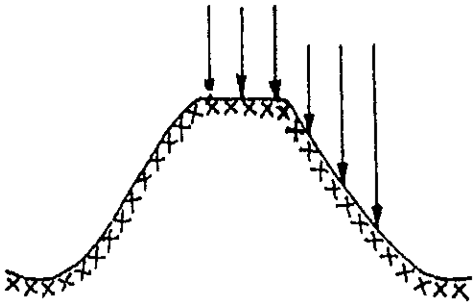

Figure 8. Soil area warmed by sun rays striking on level surface and on slopes

3.3.4. *Slope*

Solar radiations reaching soil perpendicular to the soil surface level heat it more as these concentrate on a smaller area than when the same amount of radiations reach a slope where these get spread on a larger area (Figure 8). This is the reason why temperature on crest of the ridges is higher than on sides and furrows. In northern hemisphere, a south-facing slope is warmer than the north-facing slope and horizontal surface. Similarly, a west-facing slope is warmer than the east-facing slope.

3.3.5. *Soil Composition*

The specific heat of soil components (Table 3) indicates that the soils rich in humus will be cooler than those poor in organic materials in an environment for the same incoming radiations. Because of high thermal conductivity, a compacted soil is cooler than a loose soil.

3.3.6. *Mulches and Vegetation*

Mulches affect the amount of heat received by the soil and its dissipation. For example, straw mulch highly immobilizes the air within the mulch and since the still air has very low thermal conductivity, heat flow from surface of the mulch to the soil and vice-versa is reduced to a large extent. This, in turn, lowers the maximum temperature and raises the minimum temperature of a soil. The vegetation has effects

Table 3. Average density and specific heat of some soil constituents at 25 °C and 1 atmosphere pressure

Soil constituents	Density (Mg/m³)	Specific heat (J/kg/°C)
Quartz	2.65	733.2
Many soil minerals	2.65	733.2
Organic matter	1.30	1927.4
Water	1.0	4190.0
Ice at 0 °C	0.917	2107.6
Air	0.0012	1005.6

similar to those of the straw mulch. Both, the canopy height and thickness of vegetation affect the heat flux into and out of the soil. A thick vegetation highly resists the movement of air within its canopy and therefore, insulates the soil surface against appreciable heat fluxes.

3.3.7. Irrigation and Drainage

For the same incoming solar radiation, irrigation stabilizes the soil temperature by increasing its heat capacity, whereas the drainage, which leads to the removal of water from soil, decreases its heat capacity and raises the soil temperature. A dry soil is heated more easily than a wet soil because the specific heat of water is nearly five-times that of dry soil. The high specific heat of water prevents the sudden changes in temperature of irrigated soils during winter. The effect of irrigation on temperature also depends on the relative temperature of irrigation water and soil, atmospheric condition, and nature and extent of crop cover.

3.3.8. Evaporation

The evaporation causes significant cooling of soil because the heat of vaporization of water is high (580 kcal/kg of water at 25 °C). The low temperature of a wet soil is due partially to its high heat capacity and evaporative cooling.

3.4. Thermal Properties of Soil

The thermal properties of soil are characterized in terms of heat capacity, specific heat, thermal conductivity and thermal diffusivity.

The heat capacity of a soil is defined as the ratio of heat supplied to a body to the corresponding rise in its temperature, and is given by Equation (5):

$$C = \frac{\Delta Q_h}{\Delta T} \qquad \ldots(5)$$

where, C is the heat capacity, ΔQ_h is the quantity of heat supplied to the body and ΔT is the increase in its temperature (°C).

The heat capacity per unit mass of a body is called the specific heat (c) and is defined as the quantity of heat required to raise the temperature of a unit mass of the substance through 1 °C [Equation (6)]:

$$C = \frac{\text{Heat capacity}}{\text{Mass}} = \frac{\Delta Q_h}{m\Delta T} \qquad \ldots(6)$$

where, m is the mass of the substance.

The values for specific heat of some soil constituents and certain soils are given in Tables 3 and 4, respectively. If m_1, m_2, m_3 and m_4 are masses of mineral matter, organic matter, water and air in soil and c_1, c_2, c_3 and c_4 are their specific heats, respectively, then the heat capacity C (J/kg/°C) is given by Equation (7):

$$C = m_1c_1 + m_2c_2 + m_3c_3 + m_4c_4 \qquad \ldots(7)$$

The heat capacity of a soil is expressed as quantity of heat required to raise the temperature of unit volume of soil by 1 °C and is known as volumetric heat capacity or simply the heat capacity, C_v (J/m³/°C) and is given by Equation (8):

$$C_v = \rho c\,(1 + \theta) \qquad \ldots(8)$$

where, ρ is the bulk density of soil and c is the specific heat of soil and θ is the volumetric water content in soil

The thermal conductivity of soil, λ (J/m/s/°C) is defined as the quantity of heat passing in a unit time through a unit area of soil under a unit temperature difference between the faces. The thermal conductivity of a soil depends on its water content, texture, structure, mineralogical composition, organic matter content and compaction, but is independent of the tempera-

Table 4. Specific heat of some soils

Soils	Specific heat (J/kg/°C)
Kharagpur sandy clay loam	963.7
Phoolbagh clay loam	967.9
Beni silty clay loam	936.6
Haldi loam	867.3

tures encountered by it. The thermal conductivity of soil increases with increase in the water content, till about 50% of the soil saturation. In general, the thermal conductivity of soil varies in the order: sand > loam > clay > peat. The thermal conductivity of quartz, water and air are in the ratio 333 : 23 : 1.

The thermal diffusivity, α (m^2/s), is defined as the ratio of thermal conductivity, λ, to heat capacity, C_v [Equation (9)]:

$$\alpha = \frac{\lambda}{C_v} \qquad \ldots(9)$$

The thermal diffusivity, α, is a measure of the rate at which changes in temperature occur in the body.

3.5. Heat Flow in Soil

The heat flow in a soil occurs mainly through conduction. The flow of heat by convection and radiation is of little importance. In conduction, heat flows by the transfer of momentum of individual faster-moving molecules at the hot end to their slower-moving neighbouring molecules at the cool end by collision. Heat flow by convection occurs due to differences in the density of fluid as a result of temperature gradients in soil profile and vaporization of water molecules from the hotter end of a partially saturated soil pore and their condensation at the cooler end, where it releases latent heat. The radiative transfer of heat in a soil occurs in empty pores as thermal radiation. The heat flow in a soil through conduction is described by Fourier's law, according to which the heat flux in a slab of soil (Figure 9) is directly proportional to the ratio of temperature difference ($T_1 - T_2$) between the hot and cool ends of the slab and its thickness ($x_1 - x_2$). The proportionality constant is given by thermal conductivity λ (J/m/s/°C). The Fourier's law in the differential form is written by Equation (10):

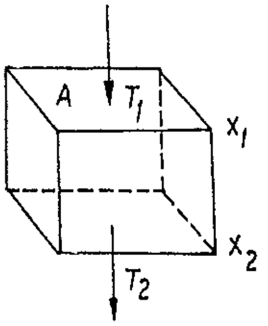

Figure 9. A soil slab

$$q_h = -\gamma \frac{dT}{dx} \qquad \ldots(10)$$

where, q_h is the heat flux ($J/m^2/s$) or quantity of heat, Q_h (J), passing through a unit area, A (m^2), of soil in unit time, t (s); and dT/dx is the temperature gradient, °C/m. The negative sign indicates that flux and gradients are in opposite direction. A principal factor influencing the heat conduction in a soil is its water content. A dry and loose soil is a poor conductor of heat than a wet and compact soil.

3.6. Measurement of Soil Temperature

The measurement of soil temperature is based on the change in thermometric properties of a subsidiary system which is in thermal equilibrium with the soil. The thermometric methods are both contact and non-contact types. The contact type methods include measurement using thermometers in which thermal expansion of a solid, liquid or gas is measured, the corresponding examples are: bimetallic strip thermometers, mercury or alcohol (in glass) thermometers, and constant pressure or constant volume thermometers. Other common contact type thermometers are based on the changes in electrical properties of the material with change in temperature; common examples being thermistors and thermocouple thermometers. In most of the commonly used contact methods, changes in temperature are recorded using mercury (in glass) thermometers, thermistors and thermocouple thermometers. The non-contact type methods include optical pyrometers, total intensity radiometers and infrared thermometers. All thermometers must be carefully calibrated and installed at the point of measurement.

3.7. Soil Temperature and Plant Growth

Soil temperature influences the plant growth only indirectly, by affecting the physical, chemical and biological processes in soil and plants. Soil temperature influences the cell activity, biochemical reactions and phsiological processes necessary for the overall growth and development of a plant. Seeds of most of the crop species germinate within a reasonable time period between 10 °C and 35 °C. Unfavourable temperatures prevent the emergence of many tender seedlings.

Some plant species are adapted to low temperatures only while some are adapted to high temperatures. At higher soil temperatures, the roots of low-temperature crops start decaying and are damaged by soil organisms and plant diseases, but the reverse is not true for a high temperature crop. The temperature optima for root growth of most crop species is between 20 °C and 25 °C. The optimum temperature for the root growth is often lower than for shoot growth. The optimum temperature for the activity of most of the microorganisms is between 25 °C and 35 °C. A low temperature produces toxic substances which are injurious to plants, whereas a high decomposition rate at optimum temperature usually results into the products which are beneficial to plants.

For many crops, particularly cereals, the shoot meristem, which is the site of temperature perception, lies below the soil surface for an appreciable period. The plant growth is initiated only when the minimum (or base) temperature is reached and the rate of growth increases up to the optimum temperature, followed by a decline at the maximum tolerable temperature. The minimum and maximum temperatures differ in different crop species and at different stages of crop growth.

3.8. Management of Soil Temperature

The primary source of heat energy to soil being the sun, practices encouraging the heat absorption and the flow in soil and those discouraging heat loss to the atmosphere would help in heat storage and temperature rise. The soil temperature under field conditions can thus be altered by mulching and vegetation, tillage, compaction, irrigation, and drainage.

3.8.1. Mulching and Vegetation

Mulches, such as straw, tend to buffer the extremes in soil temperatures (Figure 10). Mulching with the polyethylene sheets raises the soil temperature during the day. Mulches also conserve soil moisture. A polyethylene film laid on a soil surface is transparent only to the incoming radiations. The outgoing radiation is inhibited due to the condensation of water vapour and the presence of dust particles on soil side of the polythene surface.

The vegetation, like straw mulch also intercepts both the incoming as well as the outgoing radiation from soil and therefore, reduces the temperature fluctuations. The overall effect depends on the proportion of shaded soil. Air temperature above a crop is lower than at the surface of soil on a clear night. Soil under vegetation warms up more slowly in winter than a bare soil. A soil under a dense vegetative canopy may remain at a uniform temperature in surface layers.

3.8.2. Tillage

Tillage of any kind affects the pore-size distribution and wetness and consequently, the soil temperature. The tillage forming ridges often create a range of soil temperature regime (Figure 11). Rapid changes in soil temperature are observed on ridges, whereas furrows are generally cooler. In poorly-drained soils, ridging improves the soil aeration. A tilled-surface soil is generally warmer during the day time because of its higher porosity and low thermal conductivity than a compacted-untilled soil.

3.8.3. Soil Compaction

Compaction in soil brings its particles closer and regulates temperature in the root zone. The abrupt changes in soil temperature, as observed in the surface layers of a loose soil, do not occur in a compact soil due to its high thermal conductivity. The soil compaction under field conditions is often achieved using a tractor or bullock-drawn roller.

3.8.4. Irrigation and Drainage

The soil water controls absorption of solar radiation, loss of heat energy to the atmosphere,

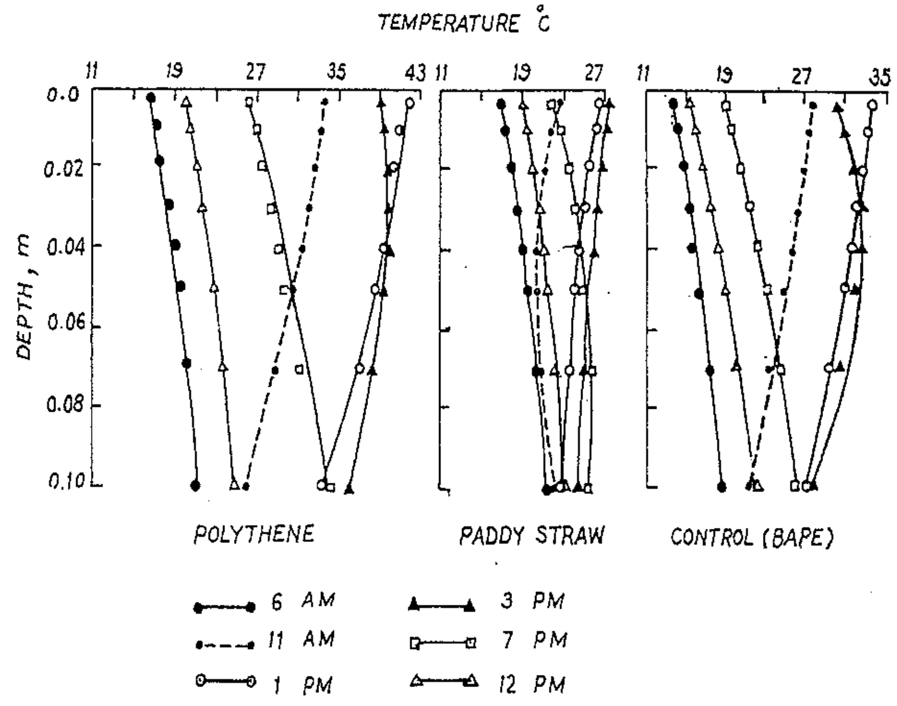

Figure 10. Effect of mulches on soil temperature profiles, 19 days after irrigation
Source: Tripathi and Katiyar (1984)

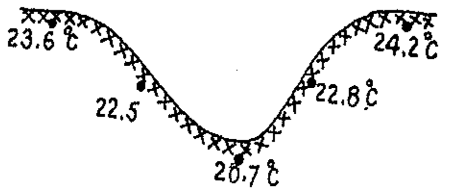

Figure 11. Soil temperature at 0.02 m depth in a north-south running ridge-furrow system at Pantnagar (Uttrakhand)

and movement of heat in soil. Water resists changes in soil temperature because of its high specific heat and high heat of vaporization. A wet soil conducts heat faster than a dry soil and therefore, temperature fluctuations in the surface layers are rapid and approach extreme values easily in drier soils than in wetter soils. The dry soils prevent heat flow and encourage temperature fluctuations. The raising of soil temperature by draining of waterlogged fields and stabilizing soil temperature by irrigating dry fields are the common practices used by farmers. Irrigation reduces both rise and fall of soil temperature due to high heat capacity of water and evaporative cooling. The irrigation in summer causes large evaporative cooling of the surface soil.

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Chapter 8

Tillage

P.R.GAJRI, S.P. MAJUMDAR and PRADEEP K. SHARMA

1. Introduction

The world is facing population explosion and there is an urgent need to increase farm productivity and total food production on sustainable basis, without compromising on natural resources and environment. Several innovations have gone into improving the efficiency of farming systems, with variable results. Tillage is the first step in agriculture. It is an integral part of crop production. Tillage includes operations of planting; weed control; incorporation and mixing of crop residues, manures, fertilizers and pesticides in soils; compaction of loose soils; managing the problems of soil compaction; terracing; mulching and other soil management practices.

The basic objective of tillage is to modify soil conditions in such a way that they become most favourable for the growth and yield of the crop. Tillage practices, in fact, started when man first planted seed in soil. In the process of evolution, tillage has gone through modifications, starting with manipulation of soil with simple hand-operated stone and wooden tools, through animal-drawn metal tools to modern heavy tractors and machines. Each tillage system has its own merits and demerits. Tillage requirements are highly crop- and site-specific. Tillage is the single most expensive component of crop production. The cost of cultivation may be reduced if tillage operations are minimized. This, along with the introduction of chemicals (herbicides) in agriculture in the 1960s, led to the change in the concept of tillage from more intensive to less intensive tillage operations, i.e. conservation tillage, reduced tillage or zero tillage. However, several health risks are associated with chemical agriculture. Further, climate change and global warming have become issues of immediate concern to mankind. In modern agriculture, increased emphasis is being laid on carbon sequestration in soils to arrest global warming and climate change. These factors have once again forced the agricultural scientists to rethink about the utility of tillage in safe crop production.

2. Definition

Tillage is usually defined as the mechanical manipulation of soil aimed at improving soil conditions affecting crop production. In the true sense of words 'mechanical manipulation' includes all soil-handling operations in agriculture, earth moving, mining and construction. However, from crop production point of view, tillage is a process in which human, animal and/or machine energy is applied for physical manipulation of soil to provide soil environment favourable for the growth and production of plants (food, pulses, oilseeds, fibre, timber, medicinal and aromatic plants, etc.). During tillage operations, the soil is subjected to shearing, compressive and tensile stresses. A pure shear stress changes the shape without changing the volume, whereas pure compression leads to the change in volume without changing shape. Practically, shear and compression usually occur together in soil during tillage.

Traditionally, tillage process involves a series of primary (to break soil surface into clods) and secondary (to pulverize, repack and/or smoothen soil surface) operations; some of them are operated repeatedly for getting the desired result. The entire field is tilled. The entire process involves considerable amount of time, energy, labour and cost. In modern agriculture, the concept of tillage has changed, and tillage operations are performed considering two distinct zones in the field: (i) planting zone (where soil conditions must be optimum for seed to germinate and grow), and (ii) management zone (i.e. the inter-row space, which must have maximal infiltration and minimum soil erosion and weed infestation). Modern mechanized farming considers a third zone as well, which is the passage for tractor tyres. Special tracks are specified in the field for the movement of tractors and other farm machinery to avoid their random movement. It is more relevant in the case of row crops, nurseries and orchards.

3. Soil Tilth

Discussion on tillage shall remain incomplete if no description is made about the soil tilth, as tillage is done to obtain a desirable soil tilth. Tillage is the cause and tilth is the effect.

Soil tilth is generally used to describe the fitness of soil to plant growth and yield. The Soil Science Society of America defined soil tilth as "the physical condition of soil as related to its ease of tillage, fitness as a seedbed, and its impedance to seedling emergence and root penetration".

The significance of soil tilth in crop production was known to the farmers long ago. The first recorded evidence about soil tilth was given by Fitzherbert in his book on '*Boke of Husbandry*' (1523), as reported by Keen (1931). Fream (1890) narrated a childhood story to explain the concept of soil tilth. An old man while on death bed called his sons and told them that if they would diligently dig the garden, they would find hidden treasures. The sons dug the garden deeper than the garden had ever been dug before, but alas! they found no treasures. But, the subsequent harvest from the well-dug garden was so large that the sons could understand the meaning of their father's saying. They gradually realized that the words of their father were the words of wisdom. Fream (1890) also illustrated the importance of soil tilth through a 17th Century quote, attributed to Thomas Tusser, that "*Good tilth brings seeds, ill tiltures weeds*".

Soil tilth is a multifaceted soil characteristic reflecting a dynamic combination of physical properties, including texture, structure, permeability and consistence that can be sustained, improved or destroyed by many chemical and biological processes depending on the way the soil is managed. Several studies have been conducted and published on soil tilth (Karlen *et al.*, 1990), yet soil tilth remains an elusive parameter. Defining the optimal physical state of soil for crop growth is very difficult, and determining the most feasible means to achieve this is still more difficult.

A good soil tilth must meet biological, agronomical and engineering objectives. A soil with good tilth, in general, should have the following elements (Slipher, 1932; Yoder, 1937):

- Offers minimum resistance to root penetration
- Permits free intake and moderates retention of water (rainfall and irrigation)
- Provides an optimal soil-air supply with moderate gaseous exchange between soil and atmosphere
- Holds to a minimum the competition between air and water for occupancy of the pore space volume
- Provides maximum resistance to erosion
- Facilitates the placement and coverage of green manures and organic residues
- Promotes microbial activity, and
- Provides stable traction for farm implements.

The following methods help in improving/sustaining soil tilth:

- ♦ Adoption of reduced tillage for crop production
- ♦ Management of crop residues
- ♦ Use of environmentally acceptable drainage programmes
- ♦ Implementation of nutrient management practices that maintain favourable fertility and soil pH

- Stimulation of soil microbial and faunal populations
- Use of animal manures, green manures, cover crops or rotations involving grasses, forages or other crops with fibrous root system, and
- Organic farming.

4. Objectives of Tillage

The objectives of tillage and tillage operations vary with soil, crop and climatic conditions, and are also influenced by the socio-economic status of the farming community. The basic objective of tillage is to obtain good soil tilth for crop growth and yield. Tillage benefits crop production primarily by improving soil environment (mainly the air-water relations in the seed bed), controlling weeds and reducing mechanical impendence to root growth.

Accordingly, there are three primary aims of tillage:

(i) preparation of seed bed with optimum tilth,
(ii) weed control, and
(iii) reduction of mechanical impedance to root growth.

Other objectives of tillage may include, soil incorporation of organic/inorganic matter (crop residues, manures, fertilizers, amendments), soil moisture conservation, modification of infiltration characteristics, land shaping for irrigation, terracing on sloping lands, compaction of loose soils, breaking hard pans in root zone, breaking surface soil crust, control of insect, pests and disease incidence, etc. The overall objective of tillage, however, is to minimize erosion losses by wind and water, maximize soil carbon sequestration, and maximize crop productivity on sustainable basis.

The different objectives of tillage are explained below:

4.1. Seedbed Preparation

As stated above, the basic objective of tillage is to prepare seedbed with soil tilth optimum for plant growth and yield. Tillage improves soil environment by imparting desirable soil-air-water relations in the seedbed. Seedbed with proper tilth has a bearing on planting, germination and water and air exchange. Tillage is often performed to loosen, granulate or otherwise condition soils. Soil may be cut, loosened, or broken-up to facilitate placement of seed in soil at the desired depth, and improve water and air movement through soil. Soil may be loosened to promote drying or reduce mechanical strength of soil mass.

Proper timing with respect to soil water content is very essential to obtain good soil tilth. Tillage operations performed in dry moisture range consume higher energy and lead to clod formation, while those in the wet range, destroy soil aggregation and cause soil compaction. As a thumb rule, for proper soil aggregation, tillage should be performed when soil is in the friable consistency.

It may be noted that improvement in soil tilth is the short-range effect of tillage. In the long-run, especially without proper organic residue management, tillage causes deterioration of soil tilth by increasing rate of oxidation of organic matter. Use of heavy tractors and machinery for tillage in mechanized farms generally leads to soil/sub-soil compaction, thus, destroying soil tilth.

4.2. Weed Control

Tillage is frequently performed to control weeds during crop production. Tillage helps in controlling weeds in many ways. It destroys the growing weeds by uprooting, smothering, desiccating or decomposing them. Tillage improves the effectiveness of herbicides. It brings out the regenerative organs of a plant (seeds, stolens, etc.) to the surface where they may dry out and lose their viability. The exposed seeds of weeds may also be picked up by birds. Tillage also reduces or eliminates the weed competition by way of enhancing the crop growth. Gajri *et al.* (1999) reported that disc plough (soil inversion) and disc harrow were more effective for weed control than strip-till system.

The advent of chemical herbicides about five decades ago appeared to reduce the significance of tillage as a method of weed control. However, due to health hazards associated with the use of chemical herbicides (application hazards, residual effects, environmental hazards) and consumers becoming more and more health conscious, and increasing cost of herbicides, the interest now again is shifting towards weed-controlling aspects of tillage.

4.3. Incorporation of Materials in Soil

Several organic and inorganic materials, such as crop residues, manures, fertilizers, soil amendments, etc. are incorporated and/or mixed with soil in tillage operations. Special implements have been designed to invert soil for covering materials lying on soil surface.

4.4. Soil Mixing

Sometimes, tillage operations are performed to mix soil layers to enhance soil drying, or to mix moisture throughout the depth of soil, or to distribute amendments such as soil conditioners, fertilizers, and soil-stabilizing materials. In special cases, several layers of soil may be mixed to form more desirable soil texture.

4.5. Land Shaping

Tillage is also performed for changing configuration of surface soil for planting (ridge-furrow system or raised/sunken bed system), irrigation, drainage and landscaping, etc. Ridge-furrow planting is recommended in rainfed areas, for *in-situ* moisture conservation. Under the excessive water conditions (marshy lands), raised-bed planting helps in improving the air-water relations of soil; thus, benefitting crop growth and yield.

4.6. Segregation

Tillage may be used to move soil or other materials from one layer of soil to another such as when deep tillage is used to create clods and to move these clods to the surface to minimize wind erosion. Segregation may also involve the removal of materials from the soil. Rock picking and root harvesting are some of the examples.

4.7. Soil Compaction

Soil compaction is required to decrease infiltration and improve water retention in loose (sandy) soils. It is also used for decreasing percolation losses in water channels or water reservoirs. The soil compaction may be achieved by using cement/metal rollers or even road rollers (Sharma *et al.*, 1995). Soil compaction benefits crop production in sandy soils.

4.8. Soil Conservation

On sloping landscapes in high rainfall areas, cultivated soils are exposed to excessive water erosion. It is recommended to go for terracing if the soil slope exceeds 7%. Tillage (cut-fill) operations are performed for terracing such lands to reduce soil erosion hazards. Use of organic mulches is another way of soil conservation in hills. Special tillage practices are required that help in planting seeds and at the same time maintain mulches at the soil surface.

5. History of Tillage

Mother Nature is a no-till farmer since it never leaves the earth bare of vegetation provided basic ingredients of soil, sunlight and moisture, are not limiting. Every plant species has evolved a method of reproducing itself in an environment suited to its needs with no aid from man in the form of tillage. For thousands of years, man used only his hands and possibly a sharpened stick to dig a hole or cut a slot in the soil, bury a seed and cover it with earth.

Slowly, man started to realize that tilling the land produced more crop yield than without tillage. It probably happened as fertilizers were not known and tillage increased mineralization of organic nitrogen. For centuries, farmers kept on tilling their lands with primitive ploughs. The eighteenth century saw the introduction of more specialized metal tools for performing tillage operations, like disks, harrows and cultivators. Thomas Jefferson (1784) gave a mathematical formula for a moldboard plough for complete turning over of the soil prior to planting. In 1796, Charles Newbold patented a cast iron plough. John Deere (1837) introduced manufactured steel plough. The early horse- or oxen-drawn plough was a boon to farmers of the time. The use of moldboard plough spread westward in the United States to break the virgin prairie sod in the 19th century. The horse-drawn straddle row cultivator was another notable tillage development of the 19th century. Development of steam engine and later, gasoline and diesel engines, led the farmers to turn from horses to horse power in the early 20th century. The tillage tools became larger and much sophisticated and more productive.

In early-1930s, the United States experienced economic depression. Simultaneously, millions of hectares of land, which formerly was protected by natural grasses, was now exposed to the fury of weather — thanks to the cultivation by moldboard ploughs. The 1930s experienced the country's first environmental crises, when tonnes and tonnes of soil was blown into the atmosphere by wind erosion. It was observed that although there were several other factors responsible for the dust storm, excessive tillage by moldboard plough and the lack of soil conservation techniques had compounded the problem.

Edward H. Faulkner has criticized moldboard ploughing in his 1934 book, *Plowman's Folly*. Faulkner received very little scientific support at that time. It was in the late-1940s and early-1950s that scientists began to experiment with a revolutionary alternative to tillage. Introduction of herbicides gave farmers for the first time a practical tool other than plough, disc, cultivator and hand hoeing to control weeds and to prepare environment-friendly seedbed. The introduction of Paraquat herbicide became the chemical foundation for no-tillage farming, which led the scientists to think that crop could directly be drilled into the soil with minimum of tillage or no-tillage at all, when weeds are controlled chemically. However, increased health hazards associated with the use of chemicals in agriculture, including herbicides, has once again shifted focus on tillage as a weed control practice.

6. Different Tillage Systems

Depending upon the kind, amount and sequence of soil disturbance during seedbed preparation, tillage systems may be grouped into two classes:

(a) Conventional tillage, and

(b) Conservation tillage.

Tillage terminology can be better explained with a triangle given in Figure 1. At the broad base is the conventional tillage, indicating a full tillage package. As the triangle narrows down, tillage operations are reduced, and it leads to reduced or minimum tillage. At the upper point of triangle, tillage is eliminated completely, indicating no-tillage.

6.1. Conventional Tillage

It refers to a tillage system that has been developed traditionally and followed by the farming community depending on the type of soil, climate, crop and socio-economic status. It includes a combination of primary and secondary tillage operations normally performed to grow a particular crop in a given geographical area. It is also known as 'clean tillage'. SSSA (1987) defines conventional tillage as "a process of ploughing and cultivation which incorporates all residues and prevents growth of all vegetations, except the particular crop desired during the growing season".

Conventional tillage is a system that involves maximum tillage operations in two steps: primary tillage (cutting and loosening of soil, and incorporating crop residues/stubbles into the soil), and secondary tillage operations (pulverization and compaction of pulverized soil, sowing, weed controlling, intercultural opera-

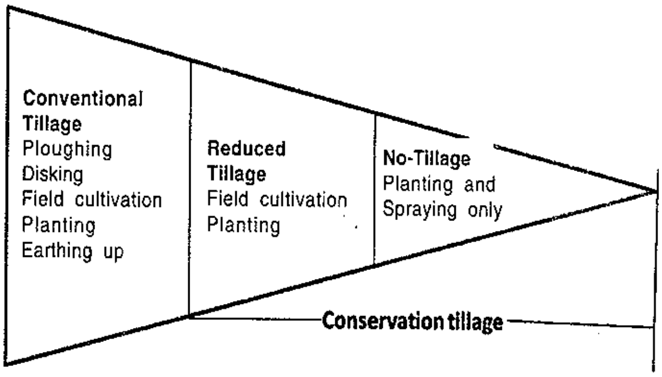

Figure 1. Flow chart showing three basic types of tillage systems

tions, etc.). Although definition of conventional tillage (clean tillage) by SSSA (1987) emphasizes the soil incorporation of all crop residues, conventional tillage also includes systems in which crop resides are either removed as cattle feed, fuel or fencing material, etc. or heaped in the field and burnt before tilling the land.

The resource-poor farmers in developing countries traditionally use animal-drawn ploughs consisting of an iron blade attached to a wooden log (country-side ploughs) for opening the land, followed by wooden planks, with or without iron nails, etc., moved repeatedly on the soil surface to break clods, pulverize soil, level field and slightly compact the soil surface. Seed is sown by broadcast method or in rows behind the plough manually or by using animal-drawn seed drills. Light planking follows the sowing of seed. Because of limited draught power, animal-drawn ploughs cause very little soil inversion. In the mechanized farming, as in developed countries, tractor-drawn heavy ploughs, such as moldboard or disc ploughs, are used for cutting, loosening and inverting the soil. The large clods are broken and soil is pulverized by using disc harrows or rotary tillers. In the conventional tillage system, the soil surface at the time of seeding is practically bare.

The advantages of conventional tillage are:

- No or minimum interference of crop residues with sowing
- Incorporation of fertilizers and other amendments is facilitated
- Water infiltration is improved
- Increased roughness at soil surface enhances temporary surfacewater storage, thereby decreasing surface runoff and increasing infiltration
- Decreases mechanical impedance in the seedbed and root zone
- Incorporation of organic residues favours microbial activity in soil
- Controls proliferation of insect, pests and diseases by burying residues in soil

Following are the disadvantages of conventional tillage:

- ♦ It makes soils loose and bare, and thus increases their vulnerability to erosion by water and wind
- ♦ Repeated conventional tillage results in decline in soil organic matter content
- ♦ Destroys soil aggregates and deteriorates soil structure
- ♦ It is cost-intensive

6.2. Conservation Tillage

Conservation tillage in a broad sense is any tillage system that is less intensive than conventional tillage. In this tillage system, either land preparation and sowing operations are combined in one operation or tillage operations for land preparation are eliminated altogether. The most important component of conservation tillage is the retention of crop residues on soil surface.

The Conservation Technology Information Centre (CTIC, 1993) in Indiana, USA, has defined conservation tillage as "tillage and planting system in which at least 30% of the soil surface is covered by plant residue after planting to reduce erosion by water. Where soil erosion by wind is the primary concern, at least 1000 lbs of flat small grain residue per acre (1120 kg/ha) should be put on the surface during the critical erosion period". Conservation tillage is an umbrella-term and covers all tillage systems that are less intensive than the conventional tillage. The CTIC has sub-divided the conservation tillage into four systems:

(a) no-tillage (also called no-till, zero tillage, slot planting, sod planting, ecofallow, chemical fallow, direct drilling),

(b) reduced tillage,

(c) stubble mulch tillage, and

(d) ridge tillage (Parr *et al.*, 1990).

Some researchers are of the view that reduced/minimum tillage or zero/no-till system should be considered under conservation tillage only if it does not destroy or burry all plant residues, and leaves some residues as soil cover.

The success or failure of conservation tillage depends on the use of herbicides, crop residue management and efficiency of planting equipments to place seed in soil below the residues.

Conservation tillage has the following advantages:

- Protects land against erosion
- Increases soil organic matter content
- Increases activity of soil flora and fauna
- May control some plant diseases by encouraging activity of organisms in soil that are antagonistic to pathogens, or may modify soil environment to favour multiplication of selected organisms
- Improves soil structure and associated soil physical properties
- Lowers cost of cultivation

Conservation tillage may have the following limitations:

- ♦ The residues left on soil surface may lead to phytotoxicity or allelopathy on the subsequent crops.
- ♦ It may increase the incidence of plant diseases by providing crop residues left on soil surface as a source of overwintering disease inoculums, thereby increasing overwintering survival rate of pathogen propagules.
- ♦ Sowing of seed under crop residues requires special planting equipments.

6.2.1. No-tillage

It is a method of planting crops that involves no seedbed preparation, other than the opening of soil for placing seed at the intended depth (SCSA, 1982). In this tillage system, crop residues are largely retained on soil surface by avoiding their removal, burning or animal grazing, etc. The seed is placed in soil by cutting small slits or by punching holes in the soil. In extreme cases, seed is broadcast on untilled soil, and the germination is assured by covering seed with residues (protected against bird damage) and by regulating optimum soil moisture regime through irrigation management. This practice is being followed in the rice growing areas of Nepal, where wheat is broadcast-seeded in wet/moist soil in the stubbles of recently harvested rice crop (called surface seeding of wheat). In the north-western parts of India, planting of linseed immediately after rice harvest in untilled-wet soil is a common practice. The weeds are controlled by use of herbicides or maybe manually.

One may argue that if crops can be grown without tillage why farmers traditionally have been performing different tillage operations to grow crops. Different tillage operations are performed by farmers basically for two reasons: weed control and optimum environment for seed to germinate and grow. In no-till system, herbicides replace tillage for weed control, and favourable environment to seeds is provided by the decaying residues on soil surface, which act as mulch to conserve soil and moisture and improve soil productivity (chemical, physical and biological). Thus, basic needs of plants are met without tillage.

No-tillage system has the following advantages:

- Saving in time, energy and labour and cost effective
- Favours timely sowing of crops; particularly useful in rice-wheat system, where wheat yields are low due to its late planting because of large turn-around time between rice and wheat caused by slow drying of wet rice soils
- Increase in soil organic matter content
- Moisture conservation, by decreasing evaporation losses and increasing water retention properties of soil
- Soil conservation, by reducing water and wind erosion
- Improvement in soil structure and associated soil physical properties (aeration, water retention, infiltration, drainage)
- Favours prolific growth of soil flora and fauna beneath the litter. Increased earthworm and arthropod activities have been observed under no-till system. They improve soil quality in the long-run by improving soil structure and other soil properties.
- In hot climates, residues with no-tillage system keep the soil temperatures cooler than under conventional/clean-tillage system by increasing albedo. Crop residues also reduce heat fluxes into soils as the thermal conductivity is lower of residues than of a mineral soil. It benefits crops by avoiding high temperatures that may be detrimental to root growth and soil faunal activities.

No-till may have the following limitations:

- May increase incidence of crop diseases and pests by providing excellent substrate to inoculums and overwintering source in the form of residues.
- In cold climates, surface residues under no-till system may delay soil warming, resulting in delayed planting, germination, emergence and crop establishment.
- Reduction in the surface flow of water and the reduced evaporation rates under crop residues may increase excess water conditions and problems related to poorly-drained soils. Enhanced nitrate leaching and denitrification have been observed in wet soils under no-till system (Rice and Smith, 1982; Blevins *et al.*, 1985).
- No-till without adequate surface cover (or no crop residues) decreases infiltration and increases surface flow of water, especially in hard-setting soils or sandy soils in arid/semi-arid regions due to formation of surface crusts after rainstorms.
- In many developing countries, particularly in tropics and semi-arid tropics, major constraint to adoption of no-till system is non-availability of adequate surface residues, as there is increased demand of crop residues as cattle feed, fuel or fencing material. Under such circumstances, it is emphasized that the farmers may remove crop residues selectively, grow fodder for animals, put waste lands under forage cultivation, adopt alley cropping or may control the number of livestock.
- Requires special equipments for sowing of seeds under crop residues.

6.2.2. Reduced Tillage

As the name indicates, it is a tillage system less intensive than the conventional tillage. Attempts are made to minimize tillage operations by elimination of one or more tillage operations from a conventional tillage programme. Only those tillage operations are performed that are absolutely necessary for crop production under a given set of soil, crop and climatic conditions. The primary and secondary tillage operations are generally combined together. Land preparation and seeding is completed in one operation. Ploughing is normally eliminated, but the total field surface is still worked by tillage equipment. Crop residues may or may not be retained on the soil surface. The crop residues are retained on soil surface for as long as possible if the objective is to conserve soil and soil moisture during the rainy season. Under irrigated conditions, reduced tillage system may be practised after removing residues from the soil surface. The practice has largely been adopted in alluvial soils of the Indo-Gangetic Plains, where wheat is planted with minimum tillage operations in lean fields. Several variations of minimum tillage system are in use globally, varying in degree from almost no tillage to nearly full conventional tillage (Unger, 1984).

The major advantages of minimum tillage over conventional tillage may include:

- Better soil and water conservation
- Time, energy, labour and cost effective

Some of the disadvantages associated with minimum tillage system are:

- Lower soil temperature which may delay germination, emergence and crop establishment
- Poor seed placement in the presence of residues on surface
- Problems of diseases and pests

6.2.3. Stubble Mulch Tillage

Any tillage operation that retains crop residues on the soil surface may be classified under mulch tillage. It may be defined as "tilling the soil so that plant residues or other materials are retained to cover soil surface" (SCSA, 1982). It is also known as mulch farming, mulch tillage or ploughless farming.

In the stubble mulch tillage system, the soil surface is undercut to control weeds and prepare the seedbed in such a way that most of the crop residues are retained on the soil surface. Generally, subsurface tillage implements such as chisel ploughs are used for the purpose. The presence of residues may also enhance infiltration and reduce evaporation. Stubble mulch tillage was basically designed to control wind erosion, but it controls water erosion as well.

Advantages of stubble mulch tillage are:

- Wind and water erosion control
- Cost effectiveness

The main disadvantages of this system are:

- Difficulty in performing tillage operations in the presence of large amounts of residues
- Difficulties in tilling due to higher soil water content as a result of reduced evaporation and poor weed control when precipitation occurs soon after tillage

6.2.4. Ridge Tillage

Ridge tillage is "a method of land preparation whereby the top soil is scraped and concentrated in a defined region to deliberately raise the seedbed above the natural terrain" (Lal, 1990). In this system, crops may be grown on ridges or in furrows depending on the moisture status of soil. In poorly-drained, wet soils, crops are grown on ridges with one or more rows per ridge. In dry and sub-humid areas, crops are grown in furrows, which favour *in-situ* moisture conservation by retaining rain water and decreasing evaporation losses.

Ridge tillage is adapted to a wide range of soils, crops, rainfall regimes, ecological environment, socio-economic and cultural conditions (Lal, 1990). On sloping landscapes (with usually less than 7% slope), ridge planting is particularly effective in soil and water conservation. The excess surface water can easily and safely be disposed off on sloping lands via furrows. However, ridge-furrows need to be properly designed and constructed, otherwise surface water may concentrate at spots above the ridges and cause their breaching, resulting in severe erosion damage.

The concept of raised-bed planting, another variation of ridge tillage, was recently experimented by Rice-Wheat Consortium (CIMMYT, IRRI, NARS and IARCs) in the Indo-Gangetic Plains cultivating rice-wheat system. The objective was to economize on irrigation water in rice cultivation and increase water productivity in wheat cultivation. In this system, rice is planted on permanently maintained broad-beds (30-40 cm), 2-3 rows per bed. Irrigation is applied in furrows at the defined intervals. The furrows cover about 40% area in the plot. Since rice is sown on about 60% area of the plot, there is a saving of seed. The yield loss due to decrease in plant population is expected to be compensated by realizing the border effect on raised beds. The studies have revealed that growing rice on permanently raised beds, under aerobic conditions, may save 35-40% of irrigation water, without showing a significant yield decline. The saving in water could be more if the technology is combined with (LASER) field levelling and better farm layouts. Coupled with water saving, bed planting shows promise for better N management. The technique, however, needs thorough investigation to answer several questions on irrigation scheduling, weed control, suitability of rice cultivars for bed planting, salt dynamics in normal and salt-affected soils, etc.

Significant advantages of ridge-tillage system are:

- Effective soil and water conservation technique on sloping lands
- Effective in conserving water in root zone in semi-arid to sub-humid regions; in dryland farming helps to conserve soil moisture
- On shallow soils, cultivating crops on ridges increase the effective rooting volume
- On poorly-drained soils, ridge tillage improves soil aeration and makes possible the successful cultivation of upland crops

The limitations of ridge tillage include:

- ♦ Requirement of special equipments for establishing ridges
- ♦ If ridges are maintained permanently for few cropping seasons, especially under low rainfall conditions, there is danger of increase in salt content in ridges due to upward flux of salts along with water
- ♦ Involves additional cost if ridges are to be constructed every cropping season

6.3. Special Tillage Systems

6.3.1. Wet Tillage

Wet tillage is performed during cultivation of aquatic/semi-aquatic plants. Rice is the best example. For transplanting rice, the most common rice culture, land is repeatedly tilled under wet conditions to convert soil into a soft mud, a process called puddling. Buehrer and Rose (1943) defined puddling as "the destruction of aggregated condition of the soil by mechanical manipulation within a narrow range of moisture content above and below the field capacity, so that soil aggregates lose their identity and the soil is converted into a structurally more or less homogeneous mass of ultimate particles". According to Bodman and Rubin (1948), "puddling is the mechanical reduction in the apparent specific volume of soil".

The objective of puddling is to destroy macro-pores so as to minimize percolation losses from the rice fields. Puddled soil is a two phase system: the solid phase and liquid phase; and the gaseous phase is practically eliminated (some air may be present occluded in blocked soil pores). During puddling, at least three processes occur that reduce percolation, viz. (i) destruction of soil aggregates and elimination of macro-pores, (ii) clogging of soil pores by clay particles, and (iii) sub-soil (below puddled soil layer) compaction caused by implements used during puddling. Maximum destruction of soil aggregates occurs when tillage is performed at moisture contents between field capacity and saturation. At this moisture content (a) cohesion within soil aggregates is minimal, which helps in increasing the shear planes in soil aggregates, and (b) cohesion between the aggregates is maximum, which restricts the movement of aggregates along each other and along the implement, thereby, transferring maximum energy for the destruction of aggregates. The clay particles suspended in the floodwater during puddling settle down with time, blocking the soil pores further to reduce percolation. Thus, best puddling occurs when tillage is performed at moisture contents at or slightly below saturation, followed by tillage under submerged conditions.

The ease and degree of puddling depend on soil wetness, soil type, nature of implement used and cultural practices. Saturation/near-saturation moisture content, less aggregate stability, more silt and clay, more swelling-type clay minerals, and rotary implements give a better soil puddle.

Puddling causes a series of physical, chemical and biological changes in soil (Sharma and De Datta, 1986). The soil effects of puddling may be classified into two categories: short-term and long-term effects.

A. *Short-term Effects of Puddling*

- Destruction of soil structure due to destruction of soil aggregates
- Elimination of macro-porosity
- Decreases in bulk density; bulk density increases with time, and the puddled soil when dry has higher bulk density
- Soil strength follows the trend in bulk density; puddled soil has very low soil strength/ mechanical impedance, which increases as the puddled soil dries
- Reduction in saturated hydraulic conductivity and percolation rates
- Increase in soil water retention
- Decrease in evaporation losses; puddled soils take more time to dry than the aggregated soils
- Puddling and water submergence increase the volumetric heat capacity, decrease the thermal conductivity, thermal diffusivity and net heat flux into soil, and increase the time lag for peak temperatures between air and soil. In one study, the time lag between temperature peaks at soil surface (flood-water) and at 30-cm depth of puddled soil was about 11 hours as compared to less than 7 hours in an upland soil (Singh and Sandhu, 1979; Sharma and De Datta, 1991).
- Reduction in gaseous exchange between soil and outer atmosphere
- Decrease in soil redox potential, resulting in increased solubility of several plant essential elements in soil (P, Fe, Mn, etc.), and increase in the production and accumulation of (phyto-toxic) organic acids
- The pH of puddled and submerged soils tends towards neutrality

B. *Long-term Effects of Puddling*

- Development of sub-surface hard pans due to physical compaction caused by tillage implements and human beings, and illuviation/precipitation of Fe and Mn in the subsurface layers

Puddling is favourable for the rice crop as it eases transplanting, reduces percolation of water and nutrients, increases water stagnation, controls weeds and increases availability of essential plant nutrients in soil. However, puddling is not favourable to upland crops that follow wetland rice, as puddling destroys soil structure, increases draft power requirement to pulverize puddled dry soils, impairs drainage, creates aeration problems and increases mechanical impedance to root growth. Hence, if soils are not properly managed, yields of upland crops in a wetland (lowland)-upland culture are lower than in upland-upland culture.

6.3.2. Soil Compaction

Soil compaction refers to the increase in density of a soil by a dynamic load. Under natural conditions in certain soil types, hard pans or compact horizons are recognized in a soil profile. These hard layers of soil may be genetically induced or developed due to improper tillage practices. In recent years with the increase in mechanization, uses of heavy machines have created a serious problem of artificial soil compaction. The compact soil layer at the bottom of the zone of ploughing is termed as the 'plough sole'. Since all agricultural implements may create some kind of sole under favourable soil conditions, these have been named on the implement used, i.e. the plough soles, sub-soiler soles, disc harrow soles, traffic soles, etc. The last one is caused by the tractor tyres and vehicular traffic. The artificial compaction is achieved by rolling, tamping, vibrating or compressing the soil by any means. The degree and depth of compaction depend on soil texture, antecedent soil moisture, load applied at soil surface., i.e. compactive energy and the amount of soil manipulation. Sandy soils are difficult to compact than clayey soils. Under the same load, the depth of compaction is more in sandy than clayey soils. Dynamic load is more effective in compacting soils than static load. Best moisture content for achieving maximum compaction under a given load is at or slightly below the field capacity (called 'proctor moisture content'). The state of compaction affects the soil-air-water-temperature relationships profoundly and determines the physical, chemical and biological properties of soil.

In the compaction process, soil particles are packed together in a closer state of contact indicated by a change in bulk density, porosity, etc. Under a dynamic load sufficient to increase the density of soil, the following changes may occur:

(a) Compression of soil solids

(b) Compression of liquid and gas within the soil pore spaces

(c) Change in liquid and gas contents in the soil pore spaces

(d) Re-arrangement soil solids.

Soil compaction generally interferes with root development of crops and is, therefore, not a desirable soil property. However, under certain conditions, soil compaction is desirable. Soils in the arid and semi-arid regions are generally coarse-textured, having high permeability, low water-retention and low fertility. Same is true with sandy soils of other eco-systems. The crops suffer in these soils mainly from the moisture stress. Compaction of such soils has shown positive effect on the crop yields. Soil compaction compresses larger pores into smaller ones, favouring water retention over drainage.

The benefits of compaction of sandy soils may be summarized as follows:

- Soil compaction reduces
  - o Nutrient and water losses through leaching
  - o Time taken for each irrigation
  - o Depth of water required in each irrigation
  - o Evaporation losses, and
  - o Soil erosion
- Soil compaction increases
  - ♦ Soil moisture retention
  - ♦ Effectiveness of fertilizer
  - ♦ Nutrient uptake by crops
  - ♦ Uniformity in seed germination, and
  - ♦ Soil productivity
- Single time compaction lasts for two to three crops (Majumdar, 1994).

Soils may be compacted by moving manual, animal-drawn or tractor-drawn metal or cement rollers on soil surface. Majumdar (1994) used a 500-kg or 1000-kg iron roller for soil compaction. A loamy sand soil with 3-6 passings of iron roller at proctor moisture content could be compacted to more than 45 cm depth. Heavy machines like road roller can also be used to compact soils. In one study, nine passes of 12-tonne road roller (Dynapac CA25) at about 12% soil moisture content compacted a loamy sand soil (75% sand content) up to a depth of about 60 cm, thereby decreasing percolation rate from 11.8 mm/d in control to 1.4 mm/d and increasing rice yield from 0.9-2.4 Mg/ha to 2.1-4.0 Mg/ha (Sharma *et al.*, 1995).

Majumdar (1994) observed increase in bulk density and soil water retention, and decrease in saturated hydraulic conductivity of a sandy loam soil with 6 passings of 1000-kg iron roller at about proctor moisture content (Table 1). The 8 passings of the roller decreased infiltration rate of soil from 33.2-37.2 cm/h to 20.0-23.1 cm/h, and increased yield of various crops (pearl-millet, guar, cow-pea, wheat, barley, raya, taramira, fenugreek, tomato and chilli) by about 2-64% (Majumdar, 1994; Majumdar *et al.*, 2000). The increase in yield was attributed to the favourable root growth and nutrient availability in compacted soil. In another experiment, soil compaction increased water expense efficiency of mung-bean and pearl millet by about 15-31% (Yadav and Jakhar, 2001; Yadav and Yadav, 2004). Yadav and Vyas (2006) have reported about 14% increase in N-use efficiency and 21% increase in apparent nitrogen recovery by wheat in a loamy sand soil due to soil compaction.

7. Tillage and Edaphic Environment

Tillage influences soil organic matter content and soil structure, and all other associated soil properties, including bulk density, soil strength, porosity, pore-size distribution, infiltration, hydraulic conductivity, water retention, drainage, evaporation, gaseous exchange, soil thermal properties, soil microbial activities, etc. Tillage may loosen or compact the soil, and may enhance or retard the rate of decomposition of soil organic matter. Tillage systems also influence hydrological soil properties, such as surface runoff and soil erosion, through their influence on soil structure. The modifications in hydraulic properties of soil significantly influence nutrient availability, leaching losses, groundwater contamination, plant growth and crop productivity.

7.1. Soil Organic Matter Content

Continuous ploughing and other tillage operations stimulate organic matter losses by increasing aeration, changing temperature and

Table 1. Effect of compaction on the average bulk density, saturated hydraulic conductivity and moisture content of a loamy sand soil immediately after compaction

Soil properties	Depth (cm)	Treatment	
		Control	Compaction*
Bulk density (Mg/m^3)	0-15	1.48 ± 0.02	1.57 ± 0.02
	15-30	1.51 ± 0.02	1.63 ± 0.03
	30 -45	1.53 ± 0.01	1.59 ± 0.03
Saturated hydraulic conductivity (cm/h)	0-15	10.85 ± 0.02	8.16 ± 0.02
	15-30	9.20 ± 0.02	6.60 ± 0.02
	30-45	8.75 ± 0.01	6.80 ± 0.01
Soil moisture content (%)	0-15	8.11 ± 0.02	13.09 ± .02
	15-30	8.61 ± 0.02	13.79 ± .01
	30-45	8.96 ± 0.04	13.66 ± 0.01

*Compaction of loamy sand soil by 8 passes of 500-kg iron roller

Source: Majumdar (1994)

Table 2. A comparison of soil organic matter distribution after 10 years of no-till and conventional tillage in corn production

Soil depth (cm)	Soil organic matter content (%)		
	No-tillage	Conventional tillage	Untreated bluegrass sod
0-5	4.82	2.40	6.55
5-15	2.34	2.31	2.98
15-30	1.15	1.22	1.55

Source: Blevins (1986)

moisture conditions, and thus favouring microbial decomposition. In addition, soil aggregate disruption by tillage exposes once protected organic matter to decomposition. Hence, intensive conventional tillage system in the long-run may cause a decline in soil organic matter (SOM) content. Conservation tillage systems, with proper residue management, are expected to maintain or increase SOM by maintaining relatively slow decomposition rate of surface residues. Blevins (1986) observed significantly higher SOM under no-till system compared to conventional tillage system in operation for 10 years (Table 2).

7.2. Bulk Density, Porosity and Mechanical Impedance

The magnitude of change in bulk density of soil depends on its antecedent properties, time of measurement, depth and intensity of tillage operations. Soil loosening decreases and compaction increases the bulk density. The studies on the impact of tillage systems on soil bulk density have shown variable results. For example, Lal (1976) reported that no-tillage with mulch improved the soil porosity, soil structure and water transmission in an alfisol. Sharma and Acharya (2000) have observed lower bulk density at maize harvest under conservation tillage (no-till + mulch) than conventional tillage, and the effect was associated with higher soil organic carbon (SOC) under the former than the latter (Table 3). Blevins *et al.* (1985), on the other hand, did not observe any change in bulk density of a medium-textured soil under no-till system, Gantzer and Blake (1978) reported increase in bulk density of a fine-textured soil with no-tillage compared to conventional tillage. The soil strength generally follows the bulk density trends.

The total porosity of soil would change with tillage depending on the change in bulk density. Tillage operations increase macro-porosity, while the compaction increases the micro-porosity of the soil. Kar (1994) has reported significant increase in the proportion of non-capillary pores with conventional tillage compared to zero-tillage in a lateritic sandy loam soil (Table 4). In contrast to conventional tillage, conservation tillage system results in a more continuous pore system because of increase in earthworm activity, old root channels and vertical cracks between peds.

Table 3. Soil organic carbon (SOC) and bulk density at maize harvest under different tillage treatments

Treatment	SOC (g/kg soil)	Bulk density (Mg/m^3)
Conventional tillage*	9.0	1.37
Zero tillage + Residue mulch**	12.3	1.31
LSD (0.05)	1.1	0.04

Notes: *Fine seed-bed prepared by digging top 12-15 cm soil layer manually
**Furrows opened in mulched plots with hand plow for sowing
Lantana was used as mulch at about 15 Mg/ha fresh biomass
These data were recorded after four maize-wheat cropping cycles
Source: Adopted from Sharma and Acharya (2000)

Table 4. Effect of tillage treatments on proportion of non-capillary pores in tilled layer of a lateritic sandy loam soil

Treatment	Non-capillary porosity (%)
No tillage	15.8
Moldboard plough + Disk harrow	42.9
Disc harrow	37.1
LSD (0.05)	0.9

Source: Kar (1994)

7.3. Soil Hydraulic Properties

A change in the soil pore system (total porosity, pore geometry, continuity of pores), and maintenance of surface residues and associated soil faunal activities (e.g., earthworms) due to tillage system have significant effect on all soil hydraulic properties, viz. infiltration, hydraulic conductivity, water retention, drainage and evaporation. Tillage affects the soil-water status as well as capacity of plants to utilize it. Tillage also influences the soil wetness through weed control.

Conservation tillage is an excellent technique of *in-situ* soil moisture conservation in rainfed areas (Sharma and Acharya, 2000). Creation of dust mulch through repeated tillage is a common practice of moisture conservation in rainfed farms (Sharma *et al.*, 1990). However, zero tillage with mulch has been found superior to dust mulch in soil moisture conservation in a sandy loam soil; best results have been observed with conventional tillage with mulch (Table 5).

7.4. Soil Aeration

The impact of tillage system on soil aeration depends on the tillage intensity, residue management, soil aggregate stability and soil moisture regime. Tillage operations generally increase total soil porosity. The conventional tillage supports a relatively higher proportion of macro-pores in the tilled layer, which is able to restore adequate water-free porosity more rapidly after heavy rains or irrigation by rapidly draining the excess water. A decrease in the volume-water fraction increases the volume of air-filled pores, thus, enhancing soil aeration. In fact, the effect of tillage on aeration of soil is directly linked to its effect on enhancing the infiltration rates, which considerably reduces the time for which the surface remains sealed to air exchange. Tillage is likely to affect the oxygen diffusion rate (ODR) in soil.

In soils with stable structure, conventional tillage generally supports higher aeration status than conservation-tillage system; more so under the excess water conditions (say close proximity to water table). In one study at IRRI, Philippines, aeration porosity was significantly higher with conventional than with no-till system in two different soils (Table 6).

Table 5. Effect of different tillage systems on soil moisture conservation and grain yield of wheat

Treatment	Soil moisture at sowing of wheat (mm)		Soil moisture conservation over control (mm)	Wheat grain yield (Mg/ha)
	0-7.5 cm soil	0-45 cm soil	0-45 cm soil	
Control	4.8	33.8	-	1.22
Dust mulch*	8.3	64.6	30.8	1.53
No-tillage + mulch**	9.3	75.2	41.4	1.46
Conventional tillage + mulch	14.4	101.5	67.7	1.88
LSD (0.05)	-	-	-	0.23

Notes: *Soil was repeatedly ploughed with animal-drawn plough, followed by planking at about weekly interval, starting from maize harvest in the last week of September until sowing of wheat in mid-November (local farmers' practice)

**Dry leaves of sal (*Shorea robusta*) were used as mulch at about 10 Mg/ha

Tillage and mulch treatments were imposed after maize harvest in the last week of September

Source: Adapted from Sharma *et al.* (1990)

Table 6. Effect of tillage systems on air-filled porosity of soil at 4 weeks after planting (4 WAP) and at harvest of summer mungbean

Tillage treatments	Air-filled porosity (%)			
	Clay loam		Sandy loam	
	4 WAP	At harvest	4 WAP	At harvest
No-till	8	12	27	27
Minimum tillage	17	21	43	42
Conventional tillage	18	25	44	39
LSD (0.05)	4	7	5	3

Note: Clay loam soil had water table with 20 cm depth
Source: Sharma *et al.* (1988)

7.5. Soil Temperature

The changes in soil surface roughness and the presence of plant residue cover under a given tillage system influence the thermal regime of soils. A change in bulk density alters the specific heat capacity of a soil, primarily by changing the relative amount of mineral matter and water per unit volume of soil. Compaction increases thermal conductivity of the soil because of decreased porosity and increased contact between particles. Tillage systems, that maintain better soil cover with residues, lower the soil temperature by increasing albedo. In a field study, no-tillage maintained 1-2 °C higher maximum soil temperature at 10-cm soil depth than tillage with moldboard plough; the application of surface mulch maintained 2-8 °C higher maximum temperature in each case (Sharma, 1991). The presence of residue mulch at soil surface keeps the soil cooler, irrespective of tillage.

7.6. Chemical and Biological Properties

Tillage influences several chemical and biological properties of a soil by modifying its hydro-thermal regime and aeration status. The conventional tillage (plough-based) incorporates crop residues and distributes organic matter almost evenly throughout the ploughed layer. Conservation tillage does not completely incorporate the crop residues and results in accumulation of organic matter at the soil surface.

The effect of tillage on biological and chemical properties of a soil depends upon climate, soil type, quantity and quality (mainly C/N ratio) of crop residues and management practices. Ploughing of a soil often stimulates nitrogen mineralization. Conservation tillage system tends to immobilize the applied nitrogen. The phosphorus distribution under different tillage systems follows a similar pattern as depicted by the organic matter.

Tillage operations disturb soil and affect several changes in soil microbial population and their activities. The effect of tillage on soil microbes occurs largely through the changes it brings about in organic matter, moisture and thermal regime of soil. Since different tillage systems affect these factors differently, they have different effects on soil biology. The microbial population generally follows the trend of soil organic matter contents. Conservation tillage increases the heterotrophic bacteria and has higher activity of denitrifiers than the conventional tillage. There is a higher earthworm activity under conservation tillage than conventional tillage.

8. Tillage Effects on Crop Growth and Productivity

Tillage affects seed germination, emerging of seedlings, root growth, and crop yields as described below.

8.1. Seed Germination and Seedling Establishment

The basic requirements for seed germination and seedling emergence are that the seed should be placed at a uniform depth, in good contact with soil so that it may absorb water easily, yet the soil must be well aerated. The soil above the seed must remain sufficiently loose for the seedling to grow up through the soil. Further, the soil must maintain optimum temperature in the seed zone. As described earlier, tillage influences all these factors significantly.

The tillage system that leaves residues on the surface of soil may cause low soil temperature and may delay seed germination and seedling emergence in temperate regions. However, in tropics and sub-tropics, reduction in super-optimal temperature with residue may facilitate seed germination.

Tillage practices also play an important role in controlling the surface crust and in affecting the seedling emergence. Any tillage system that results in a stratified seedbed with finer aggregates in the seedbed covered by coarser aggregates on the surface helps in combating the adverse effects of crusting.

8.2. Root Growth

The access of crop to water and nutrients is directly related to the size of its root system. Tillage affects the depth and density of rooting by modifying the mechanical impedance, continuity, stability and size distribution of pores, air-water dynamics and thermal regime of soil (Prihar *et al.*, 2000). Roots grow into the soil pores or root channels (of decomposed roots of previous crops) which are bigger than the size of the root tips. Where such pores do not exist, the growing roots make their own path by displacing the soil particles. The role of tillage is to provide space for the growing roots in soil profile by reducing the soil strength and increasing the macro-porosity. Loosening of root-restricting hard soil layers by tillage promotes root growth into deeper soil layers. The effect of tillage on root growth is governed by the soil type, climate and other management practices. Deep tillage (sub-soiling to 40-cm depth) has been found to increase the depth and density of maize roots even in sandy soils (Arora *et al.*, 1991).

8.3. Crop Yields

For a tillage system to have a positive effect on growth and yield of crops, there must exist in soil some constraint(s) to crop growth and the tillage operations must be able to alleviate that constraint(s). If the soil has air-water relations and soil strength optimum for plant growth, the type of tillage may not affect much crop growth and yield.

Deep tillage to 40-cm depth without inversion with a chisel has been found beneficial in increasing crop yields of maize, wheat, mustard and sunflower in a coarse-textured soil that exhibited increase in soil strength on drying (Table 7). The magnitude of yield increase was more in summer than winter season, and was more in sand and loamy sand than in sandy loam soils.

Table 7. Effect of deep tillage (chiseling 40-cm deep, 35-40 cm apart) on crop yields in relation to soil type and season

Crop	Season	Soil	Crop yield (Mg/ha)	
			Conventional tillage	Deep tillage
Maize	Winter	Sand	3.2	4.9
		Loamy sand	4.6	5.0
	Summer	Sand	0.9	2.2
		Loamy sand	1.1	2.2
		Sandy loam	4.0	4.8
Wheat		Sand	2.8	3.3
		Loamy sand	4.9	5.3
		Sandy loam	5.2	5.4
Sunflower		Loamy sand	1.7	2.0
		Sandy loam	1.9	2.2

Source: Prihar *et al.* (2000)

In loose sands, compaction of soils increases micro-porosity and consequently, there is an increase in water and nutrient retention, leading to an increase in the yield of crops, as has been observed in pearl millets and other crops (Majumdar, 1994). Depending on the depth and density of sub-surface layer, subsoiling with chisel to 40 cm depth or profile modification increases the infiltration of water and water storage in the profile by breaking the restricting layer. These tillage practices also encourage deeper rooting and hence better mining of water by the crops, resulting in high yields.

Conservation tillage which retains the crop residues at or near the surface is most suited for erosion-prone soils in the arid and semiarid regions for increasing crop yields. The maximum benefits occur on well-drained soils and in crops grown in rotation. In the rainfed areas where water stress conditions prevail, conservation tillage shall improve crop yields. In poorly-drained soils in humid areas or in soils with shallow water table, especially in temperate regions, conservation tillage generally gives lower yields than conventional tillage by keeping soils relatively cool and wet, which causes aeration stress.

In areas where there is a short window period for planting wheat after rice harvest, direct drilling may benefit wheat crop, provided it advances the seeding time in comparison with conventional tillage. If seeded at the same time, for equivalent yields, the direct drilled wheat crop requires more nitrogen and water input than by the conventional tillage.

It is thus seen that all types of tillage systems are not suited to all soils, crops and climatic conditions. Tillage requirements are highly crop- and site-specific. Therefore, the selection of type of tillage must consider the soil and climate conditions, and identify constraints that limit crop yield. There is a need to assess the soil/crop specific factors that limit the potential yields, which can be modified through tillage. The wrong choice of tillage system would not only lower the crop yields but would unnecessarily cause wastage of money and other resources.

8.4. Tillage Indices

One or more soil properties, alone or in combination, that guide the selection of the type of tillage in a given soil and climate and for a given crop is called a tillage index. Tillage indices help in deciding the type of tillage system that is required under a given set of conditions.

Lal (1985) has developed a rating system to assess tillage requirements for diverse soil conditions in the tropics. Soil and climatic properties considered in developing the rating system include erosivity, erodibility, soil loss tolerance, compaction, soil temperature regime, available water holding capacity, cation exchange capacity, soil organic matter content and crop residue at soil surface at seeding. The minimum and maximum cumulative rating values for all factors range from 14 to 70. No-till is applicable for soils with cumulative ratings of < 30, and conventional tillage system of ploughing and harrowing for soils whose cumulative rating values exceed 45. For soils with intermediate ratings, some form of minimum or reduced tillage is suggested. Separate rating systems are suggested for rice and tropical root crops. These are the tentative guidelines that should be evaluated for local soils and environments.

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Chapter 9

Water Management

ANIL K. SINGH, S.S. PRIHAR, RAM K. GUPTA and C.L. ACHARYA

1. Introduction

Water, seemingly, is an abundant natural resource as three-fourths of the earth's surface is covered with it, but only 2.7% of the global water available is fresh water and of this, only 30% is available to meet the water demands of the human and livestock population, both of which are increasing at an alarming rate. The rest of the fresh water is locked up in glaciers and snow covers. On 2.3% of the world's land area, India supports almost 17% of the world's population with only 4% of the world's fresh water resources. Not only the per capita land availability but also the per capita water availability is decreasing day by day. It was more than 5300 m^3 in 1951, but decreased to 1905 m^3 in 1999 and is likely to be less than 1500 m^3 by 2025. The per capita availability of water less than 1700 m^3 is considered as the 'stress' level. Below this level, availability of water is classified as "scarce" and is considered a severe constraint on socio-economic development and environment quality.

Considering the wide spatial and temporal variations in the water availability within the country, several regions are already facing severe water crisis. Rain is the primary source of water — be it irrigated or rainfed agriculture. It is the precipitation in the catchment area that finally fills the dams and reservoirs so vital for irrigation and it is rainfall again that recharges the groundwater.

2. Water Resources

The major source of water to Indian agriculture is the monsoon system. India annually receives about 400 Mha-m of rainwater, which is 4% of the global precipitation. Out of this, 24 Mha-m equivalent rainwater is available for harvesting. Most parts of the country receive rains during south-west monsoon, except parts of Andhra Pradesh and Karnataka which receive rains from the north-east monsoon also.

Extensive efforts were made in the country to develop water resources for agriculture before independence through construction of village tanks and small harvesting structures. Post-independence, the Government of India has developed a huge infrastructure of canal-based irrigation system. Since 1970s, with the availability of electricity supply and water-pumping technologies, there has been a massive increase in groundwater utilization through tubewells, though largely under private investment. Groundwater today provides about 70% of irrigation and 80% of drinking water supplies. At present, the total irrigated area in the country is 60 Mha, out of which the canal system, tanks and tubewells + open wells constitute 30%, 4.1% and 62%, respectively. During the past 60 years, the management of water resources has changed from the hands of some communities (tanks and small water structures) to government (major and medium irrigation projects), and private domain (groundwater). Though, the net irrigated area in the country has reached 60 M ha, there is a wide spatial variability in availability of water to agriculture in view of the rainfall pattern, land forms, and the river systems. The current status of water resources is shown in Table 1.

3. Water Management Issues

Water management is a highly critical area for sustaining agriculture productivity. It is estimated that by 2050 about 22% of geographical area and 17% of the population would be under absolute water scarcity (< 500 M^3 per capita per year), and about 70% of the area and 16% of the population will be on the verge of economic scarcity and health risk with water availability of less than 1000 M^3 per capita per year. Declining water availability to agriculture and use of poor quality waters are the key constraints. The present water management practices are beset with many problems of wastage and poor productivity for unit water used. There has been an alarming increase in the exploitation of groundwater. While in the northern, western and southern states, the groundwater is being fully exploited, the eastern and north-eastern parts, offer some untapped potential.

Table 1. Water resources of India

Estimated utilizable water	
Surface water	690 km^3
Groundwater	432 km^3
Total	**1,122 km^3**
Irrigation potential	
Major and Medium (Surface water)	
Ultimate	58.50 Mha
Created	40.85 Mha
Utilized (up to 2005-06)	33.45 Mha
Minor irrigation	
Surface water	
Ultimate	17.40 Mha
Utilized (up to 2005-06)	8.17 Mha
Groundwater	
Ultimate	64.00 Mha
Utilized (up to 2005-06)	47.93 Mha
Total (surface and ground)	
Ultimate	81.40 Mha
Created (up to 2005-06)	80.01 Mha
Utilized (up to 2005-06)	56.10 Mha
Total (Major and Medium + Minor)	
Ultimate	139.90 Mha
Created (up to 2005-06)	120.86 Mha
Utilized (up to 2005-06)	89.55 Mha

Source: Central Water Commission (2008)

A. WATER MANAGEMENT OF RAINFED SOILS

A major portion of rainfall received in India is restricted to a period from June to September (Table 2), and it is received in four or five major wet spells. This feature of rainfall leads to generation of sizeable runoff with associated soil erosion and nutrient loss. Crops grown on soils with internal poor drainage and on low lands suffer because of surplus water, whereas the post-rainy season crops often encounter water stress. It is mainly because of these reasons that the agricultural productivity of rainfed regions is generally low (Table 3) and unstable. Scientific management of natural resources including rain water is therefore, called for.

An efficient rain-water management is important for enhancement of agricultural productivity on sustainable basis in rainfed soils which are distributed in most of the states of India. They occupy almost 60% of the area cultivated and contribute more than 40% to India's total food production. Out of the total area used for growing different crops in our country, the rainfed soils cover more than 80%

Table 2. Distribution of annual rainfall according to seasons in India

Rainfall	Duration	Approximate percentage of annual rainfall
Pre-monsoon	March-May	10.4
South-west monsoon	June-September	73.7
Post-monsoon	October-December	13.3
Winter or north-east monsoon	January-December	2.6

Source: Reported from India Meteorological Department, Pune

Table 3. Area, productivity and major growing regions of principal rainfed crops

Crops	Area (Mha)	Productivity (t/ha)	Principal growing areas
Sorghum	15.79	0.690	Maharashtra, Karnataka, Madhya Pradesh, Andhra Pradesh
Pearlmillet	10.69	0.522	Rajasthan, Maharashtra, Gujarat, erstwhile Uttar Pradesh
Maize	5.88	1.325	Erstwhile Uttar Pradesh, Rajasthan, Madhya Pradesh, Bihar
Pulses, including chickpea and pigeonpea	23.83	0.540	Madhya Pradesh, Rajasthan, erstwhile Uttar Pradesh, Maharashtra
Oilseeds, including groundnut, rapeseed and mustard	18.87	0.650	Madhya Pradesh, Gujarat, Maharashtra, erstwhile Uttar Pradesh, Rajasthan, Karnataka, Tamil Nadu
Cotton	7.58	0.175	Maharashtra, Gujarat, Karnataka

Source: Abrol (1988)

area of coarse cereals, 87.5% of pulses, 77% of oilseeds, 65% of cotton and 45% of rice. Thus, the nature, characteristics and management of these soils and rain-water resources hold a key to their long-term productivity.

4. Rainfed Soils of India

The rainfed regions of India encounter different soil types besides the climatic features (Figure 1). Consequently, the problems associated with management of soil and water also differ in nature and severity. The characteristics of the major soil groups in the regions with respect to water management problems are briefly described below and have been depicted in Table 4.

4.1. Sierozems (Aridisols)

These soils are found in about 90% of the geographical area in the north-western part of the country, particularly Rajasthan, parts of Gujarat, west Haryana and west Punjab. The rainfall received in these regions is not only low (less than 500 mm) but also varies highly from year to year. These soils are coarse-textured, often containing a layer of calcium carbonate concretions at different depths. The solum thickness varies from 70 cm to 100 cm. These soils can retain only low amounts of water and plant nutrients and are highly prone to wind erosion. The prospects of intensive agriculture and enhanced crop productivity are low owing to their low water and nutrient retention capacity.

4.2. Sub-montane Soils

This group comprises Mollisols, Inceptisols and Entisols. These soils cover about 9% of the geographical area of India and occur on gently sloping lands, lower elements of slope and steep slopes, respectively, in the hill and foot-hill regions of India. The soils are silty loam to loam in texture, generally deep and retain about 300 mm of water per metre of soil profile. A relatively light texture, slopy terrain and moderate to high rainfall (700-2000 mm) make these soils prone to runoff-induced erosion and landslides.

4.3. Alluviums

Alluviums occupying rainfed regions include Inceptisols, Alfisols and Entisols. These soils are predominantly coarse-textured and occupy 21% of the geographical area of India. They are widely spread across the states of Punjab, Haryana, erstwhile Uttar Pradesh, Bihar, Delhi and Rajasthan. The soils are generally deep and possess high production potential, particularly under irrigated conditions.

4.4. Red Soils (Alfisols)

Red soils occupy 20% of the geographical area of our country. These soils are highly prone to crusting after heavy rains. This leads to high runoff and erosion as the annual rainfall in these areas ranges from 700 mm to 2000 mm. The water retention capacity of these soils ranges from 0.15 to 0.20 m^3 per m^3 at field capacity.

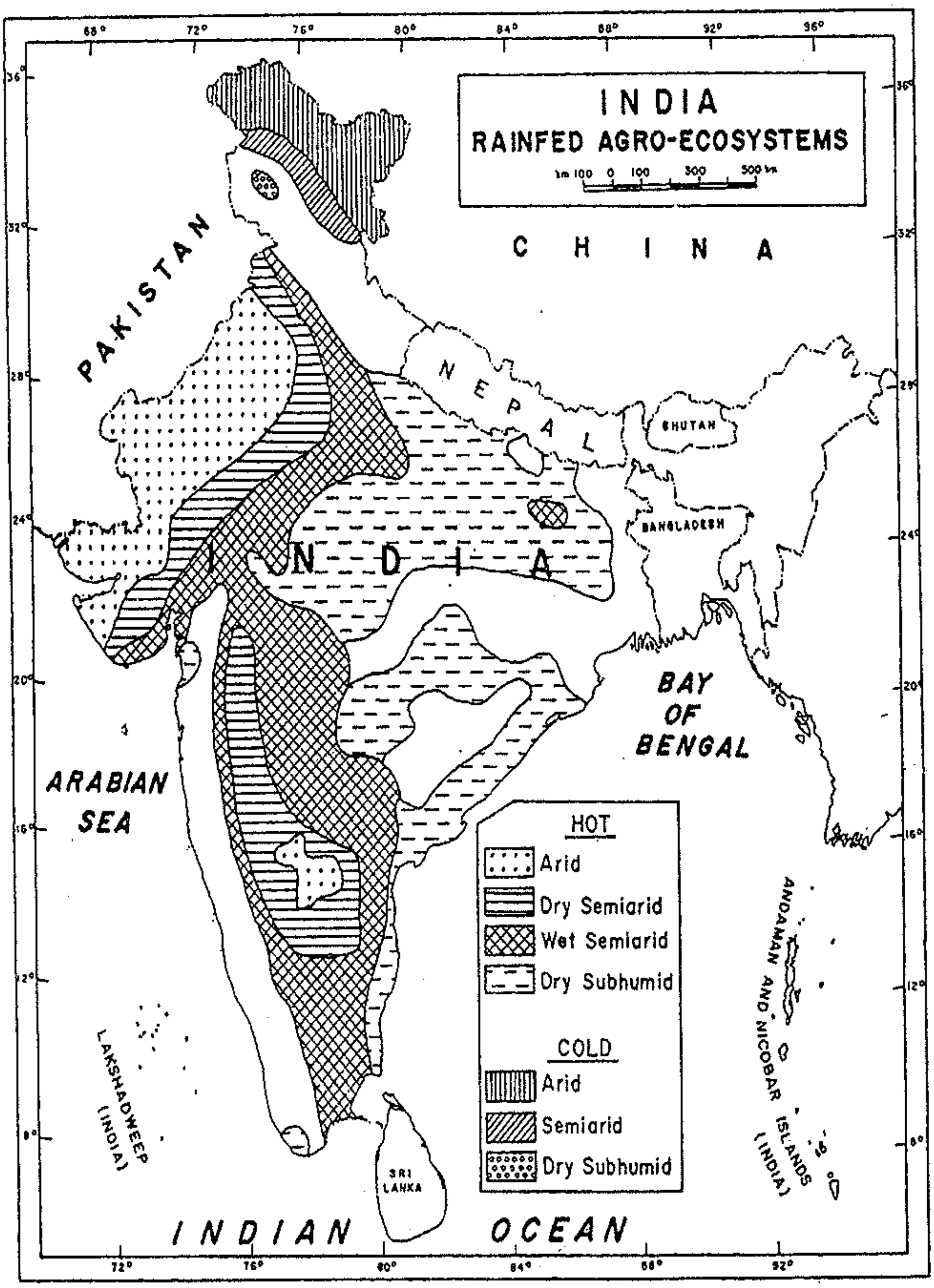

Figure 1. Rainfed agro-ecosystems of India
Source: Sehgal and Sharma (1994)

4.5. Black Soils (Vertisols)

Black soils are mainly Vertisols with associated soils and cover almost 22% of the geographical area of India. They are extensively spread across the states of Maharashtra, Madhya Pradesh, Gujarat, Andhra Pradesh, Karnataka and Tamil Nadu. These soils are characterized by high clay content and consequently, high available water holding capacity. Because of the dominance of the smectite mineral, these soils exhibit swell-shrink properties during a wetting-drying cycle. High water retention and differential water capacity over an extended range of soil water suction render these soils most suitable for rainfed farming. The soils are by and large highly productive. However, they require special soil and rainwater management practices owing to their low permeability, swell-shrink nature and narrow workable moisture range.

5. Water Management Practices

Areas practising rainfed agriculture are diverse with regard to soils and rainfall pattern. The improved farming practices in these areas could enhance the productivity and

Table 4. Distribution, characteristics and water management problems of rainfed soils of India

Agro-ecoregion	Area (Mha)	Soil characteristics	Land utilization type	Water management problems
Western Himalayas	15.2	Shallow, sandy to loamy, skeletal soils with low available water capacity (AWC)	Millets and wheat (in patches)	Severe climatic limitations, viz. cryic temperature regime. Short crop growing period because of low water storage capacity of soils
Western Plains and Kachchha Peninsula	31.9	Deep, sandy and coarse loamy, desert soils with low AWC, deep, loamy, saline and alkali soils with medium AWC	Millets and pulses	Erratic and scanty rainfall, leading to high water deficit. Soil salinity and sodicity, resulting in physiological droughtiness. Acute droughtiness at the time of grain formation
Deccan Plateau	4.9	Deep loamy red soils and clayey, black soils with medium and high AWC	Millets, cotton and oilseeds	High runoff and erosion hazard during stormy cloud bursts. Prolonged dry spells during crop growing period. Poor internal drainage and narrow workable soil moisture range. Subsoil sodicity affecting water availability to plants.
Northern Plain and Central Highlands including parts of Gujarat Plains	32.2	Deep, loamy, alluvium-derived soils with medium AWC and shallow to medium, sandy to loamy, gray brown soils with low to medium AWC	Millets, oilseeds wheat, pulses and maize; sugarcane and cotton under irrigation	Low AWC because of coarse texture. Lowering of groundwater table in some areas because of over-exploitation. Imperfect drainage conditions at some places, leading to surface and sub-surface salinity and/or sodicity.
Central (Malwa) Highlands, Gujarat Plains and Kathiawar Peninsula	17.6	Medium and deep, fine loamy and clayey, black soils with medium and high AWC	Millets, wheat, pulses and oilseeds	Droughtiness during the intermittent dry spell period. Imperfect drainage conditions that limit optimum root ramification and oxygen availability in low lying areas.
Deccan Plateau	31.10	Shallow and medium loamy to clayey, black soils with low and medium AWC, inclusive of deep, clayey, black soils with high AWC	Millets, cotton and pulses; Sugarcane under irrigation	Prolonged dry spell periods, adversely affecting the crop growth and leading to crop failure in some areas. High runoff during stormy cloud bursts in the rainy season.
Deccan Plateau (Telangana) and Eastern Ghats	16.5	Medium, red loamy soils with slow and medium AWC and deep, clayey, black soils with medium and high AWC	Millet, and oilseeds, rice; cotton and sugarcane under irrigation	High runoff during rainy season leading to severe soil loss in both red and black soil areas. Under-irrigated agriculture, unjudicious use of irrigation water and imperfect drainage

Contd

Table 4. Distribution, characteristics and water management problems of rainfed soils of India— ***Contd***

Agro-ecoregion	Area (Mha)	Soil characteristics	Land utilization type	Water management problems
				conditions result in high ground-water table, leading to subsoil salinity and sodicity, especially in black soil areas. Frequent droughtiness, resulting in crop failure in some years.
Eastern Ghats (Tamil Nadu uplands) and Deccan Plateau (Karnataka)	19.1	Shallow to deep, loamy, red soils with low to medium AWC; inclusive of deep clayey black soils with high AWC	Millets, pulses and oilseeds; sugarcane and rice under irrigation	High runoff resulting in severe erosion. Coarse soil texture and low to medium AWC, resulting in severe droughtiness during crop growth period.

Source: Sehgal *et al.* (1990)

sustainability. Several water management practices are in vogue in the rainfed regions. They include contour cultivation, bench terracing, strip cropping, and different types of land configurations which are described below. More details about these practices are provided in Chapter 10.

Contour cultivation increases the opportunity time, and hence, the infiltration of rainwater into soil profile. It forms a multitude of mini-barriers across the flow path of runoff which vastly improves the detention and storage *in situ.* Contour cultivation is most effective on deep permeable soils with moderate slopes of 2-7%, whereas it is least effective on flat and steep slopes.

Bench-terracing is practised in areas with 16 to 33% slope (*see* colour plate at the end of this book). It helps in the conservation of soil, rainwater and plant nutrients besides ensuring uniform application of irrigation water. Table top or level terraces are made where rainfall is good. The outward sloping terraces are recommended for areas with relatively low rainfall and shallow soils. The inward sloping bench terraces are suitable for high rainfall tracts with deep permeable soils. Here, even the intra-terrace runoff can be harvested and stored at the end of slope of a terrace in a small dug-out pond. The stored water is conveyed through gravity flow to irrigate the next lower terraces. The percolation losses from these ponds can be reduced by poly-lining (*see* colour plate at the end of this book) as cement-concrete structures develop cracks and fail to store water.

The flat contour cultivation and the ridge and furrow system at 0.4% grade are effective in reducing the runoff and soil loss and in increasing the crop yields (Table 5), particularly on Alfisols having slope less than 1.5%. The raised land configurations (broad bed and furrow, raised and sunken bed system, and narrow ridge and furrow) are useful in low permeable soil regions receiving moderate to high rainfall. They, in some cases, pose the problem of low stability and complications in accommodating certain crop combinations.

For soils occurring on slopes of more than 1.5% in low rainfall regions, a modified contour bund system holds promise (Table 5). This system differs from the original system in that it has outlets in the lower field sections, land is smoothened and the crop is planted on grade instead of on contour. The system allows runoff water to be stored above the bund for a certain period and then released at the desired rate through an outlet. The graded bunds and vegetative barriers spaced at 0.75 m vertical interval have been observed to be useful in conserving soil, rain-water and plant nutrients, besides being cost-effective (Table 6) on moderate slopes.

Table 5. Effect of alternative land surface configurations on crop yield, runoff, and soil loss on Alfisols at ICRISAT Centre, 1981-84

Land treatment	Crop yield (kg/ha) Intercrop system		Runoff (mm)	Soil loss (tonnes/ha)
	Sorghum	Pigeonpea		
(A) Land slope <1.5%				
Broadbed and furrow at 0.4% slope	2740	825	315	3.79
Ridge and furrow at 0.4% slope	2910	870	282	3.02
Flat contour cultivation	2960	875	172	2.05
Flat-on-grade at 0.4% plus ridging up later	2880	840	180	2.78
SE (±)	**151**	**65**	**16**	**0.24**
(B) Land slope > 1.5%				
Contour bund*	2520	710	75	0.97
Modified contour bund with gated outlet*	3020	970	160	0.92
Flat-on-grade with field bunds*	2810	900	215	3.35
Traditional flat with field bunds**	2380	220	256	4.79
SE (±)	**175**	**60**	**23**	**0.19**

Notes: * Treatment with recommended crop management practices which implies the use of acceptable or recommended variety, cropping system, chemical fertilizer and other practices for weed, pest and insect control.

**Treatment with traditional management practices which implies the use of variety, cropping system, farmyard manure, implement and other practices.

Source: Pathak *et al.* (1989)

6. Structural Conservation Measures

The runoff water is a significant component of water balance of rainfed regions in India (Table 7). The rainfall is usually concentrated over a period of 90 to 100 days and has a few high intensity and stormy events, leading to substantial runoff volumes, depending on topographic features, rainfall characteristics and other associated factors. The volumes of runoff water can be conserved/ stored and recycled for supplemental irrigation during a prolonged dry-spell. The estimated potential of rainwater storage in the various rainfall zones is given in Table 8. The following types of storage structures are commonly used.

Table 6. Effect of inter-terrace land treatments on runoff, sediment and nutrient loss from a Vertisol at Indore

Treatment	Runoff (mm)	Soil loss (kg/ha)	Nutrient loss (kg/ha)	
			N	S
Check	66.4	626.3	13.90	3.94
Graded bund	47.3	387.5	8.25	2.25
Vegetative barrier (Vetiver)	47.3	369.1	7.68	1.54

Source: Annual Progress Report (1993-94)

6.1. Farm Ponds

These are bodies of water made by constructing an embankment across a water course or by excavating a pit or by combining both. The dug-out ponds are recommended for areas with flat topography, whereas the impounding type farm ponds are developed on water courses in the regions with rolling topography.

The size of farm ponds is governed by the runoff potential. It may be half of the total amount of annual runoff expected from the catchment so that more than one filling can be obtained during the season/ year and the construction cost is minimized. The permissible depth of a pond and side slopes are decided on the basis of soil characteristics of the site such that water retention in the pond and stability of the side walls is ensured. The side wall slopes are kept flatter than 1:1.

Among different shapes, cylindrical ponds offer geometrical advantage of maximum
age per unit perimeter. This minimizes
age losses from side walls and also the cos

Table 7. Expected water yield in different regions of India

Location	Soil Type	Annual rainfall (mm)	Land slope (%)	Expected water yield (%)
Dehradun (Uttaranchal)	Silty loam	1600	2.4	16.5
Bellary (Karnataka)	Deep black	508	1.2	20.0
Shiwalik region	Sandy loam	1150	10.15	55.0
Anantapur (A.P)	Shallow red	540	3.5	20.0
Hyderabad (A.P.)	Red sandy loam	770	2.5	10.0
Bangalore (Karnataka)	Red soil	830	2.3	20.0
Karnal (Haryana)	Sodic soil	650	0.2	40.0
Chitradurga (Karnataka)	Red loam	612	5.1	10.0
Bunga (Haryana)	Silty clay loam	1116	10.12	50.0

Source: Sastry *et al.* (1985)

Table 8. Estimated potential volume of rainwater storage for small-scale water harvesting structures

Rainfall zone (mm)	Geographical area (Mha)	Rainfall for effective surface storage (%)	Harvestable *runoff* in water harvesting structures (Mha-m)
100-500	52.07	5	0.78
500-750	40.26	6	1.51
750-1000	65.86	7	4.03
1000-2500	137.24	6	14.61
>2500	32.57	4	3.26
Total			23.99

Soruce: Katyal (1997)

lining. All farm ponds must be provided with a spillway for safe disposal of overflows. Spillways provided on ponds with small catchment could be of vegetative nature, whereas for ponds with large catchments, a well-designed mechanical structure has to be provided. Gabion structures (*see* colour plate at the end of this book) (made from boulders arranged in wire mesh boxes) are suitable for black soil region as they are cost-effective and flexible enough to withstand swelling pressures from the underneath soil.

The percolation losses from farm ponds are a major impediment in their popularity in the rainfed regions. Several lining materials have been used with varied success. Bentonite, soil + cement mixture, soil + dung + straw slurry and plastic lining could be used. "Silpaulin", a plastic of 120 g/m^2 density, has been observed to be quite promising, cost-effective and reasonably durable (*see* colour plate at the end of this book).

6.2. Low Earthen Dams

These are commonly used in the areas with preponderance of water streams. They are constructed on the basis of engineering principles across water courses for creating a water reservoir.

6.3. Nala Bunds and Percolation Tanks

These structures are constructed across *nalas* for reducing the velocity of runoff, increasing the water percolation and improving the soil moisture regime in the watershed areas.

7. *In-situ* Conservation

The conservation of water where it falls by means of appropriate moisture conservation practices is termed as *in-situ* conservation. Some of the practices include off-season tillage, deep ploughing, mulching, dead furrows, keyline cultivation, compartmental bunding, cover crop strips, and interplot water harvesting.

Off-season tillage facilitates infiltration of rain-water into the soil profile and reduces the weed infestation. Off-season tillage, however, is not suggested for Aridisols as this would accelerate wind erosion. Deep ploughing (> 22 cm), once every two or three years, promotes infiltration of water and improves the productivity of rainfed crops, particularly in soils with hard pan. The deep tillage immediately following the harvest of post-rainy season crops, encourages the conservation of water in the soil and reduces the incidence of insects and pests. Mulching impedes the movement of moisture from the soil into the atmosphere. Vertical mulching (sorghum stalks placed in 40 cm deep, 15 cm wide trenches and protruding 10 cm above the ground level) can be practised to increase infiltration in the low permeable soils. "Dead furrows" laid out at 3 to 6 m interval help in improving the water retention.

The inter-row water harvesting system is a practice suitable for light-textured soils occurring in low rainfall regions. Significant yield increase can be obtained in crops like pearl-millet by adopting this practice in combination with recycling of harvested water for supplemental irrigation.

8. Agronomic Practices for Improving Water Use Efficiency (WUE)

8.1. Tillage Practices

Tillage refers to mechanical manipulation of soils in a way that it promotes root activity and plant growth. The objective of tillage in rainfed/ dryland areas is to provide a suitable environment for seed germination and root growth, control or minimize weed infestation, reduce soil erosion, conserve moisture *in situ* and reduce runoff. The common tillage practices in rainfed/ dryland areas are minimum or optimum or reduced tillage, conservation or mulch tillage and zero tillage.

The goals of minimum/ optimum/ reduced tillage systems include (a) reducing the energy input and labour requirement for crop production, (b) providing optimum seedbed condition rather than homogenising the entire soil surface, (c) minimizing soil compaction, and (d) conserving soil moisture and reducing erosion.

The objectives of conservation/ mulch tillage are: (i) achieving soil and water conservation, and (ii) saving energy through reduced tillage operations. Both systems usually involve continuous soil coverage by crop residues. Conservation tillage modifies energy balance of soil and reduces diurnal changes in soil temperature besides minimizing runoff and evaporative losses.

In zero tillage or no-till system, planting is practised without seedbed preparation. No-tillage system leads to the saving of energy, conservation of soil moisture and early planting of post-rainy season crop. It, however, allows weed infestation of the crop, particularly in the later stages of crop growth.

8.2. Fallowing

Fallowing, whereby the land is cropped in alternate seasons, is traditionally practised in many dry/ rainfed areas. Rainy season fallowing is usually practised with a view to conserve rainwater in the soil profile, restore soil fertility to some extent and reduce incidence of soil-borne pathogens.

The efficiency of fallowing (E) can be computed using Equation (1):

$$E = \frac{M_2}{M_1 + \text{R or Sc (whichever is less)}} \qquad \ldots(1)$$

where,
E is the efficiency of moisture conservation,
M_1 is the available moisture at the beginning (mm),
M_2 is the available moisture at the end of the period (mm),
R is the rainfall received (mm), and
Sc is the storage capacity of the profile (mm).

To make fallowing more effective, it should be combined with conservation tillage systems that leave crop residues on the surface.

With increasing pressure on land resources, the practice of fallowing is being abandoned even in the traditional areas. The availability and use of improved dryland technology have enabled farmers to judiciously utilize land and rain-water resources and maintain soil fertility without resorting to fallowing.

8.3. *Crops and Cropping Systems versus Water Availability Period*

The problems that are common to crop production in rainfed areas are: (i) often inadequate and erratic water availability, leading to moisture stress, (ii) generally poor resource base of the farmers and therefore, low risk-bearing capacity, and (iii) low and unstable crop productivity. The water availability period, which accounts for both rainfall and stored soil moisture and the recommended cropping systems for different dryland areas of India are presented in Table 9.

The water availability period ranges from 75-90 days in the western Rajasthan and parts of Haryana (Aridisols zone) to 260-280 days in the sub-mountain regions of Punjab and Himachal Pradesh in Inceptisols and related soil zone. In regions receiving 350-600 mm rainfall and having 20 weeks of effective growing season, only single cropping (100% cropping intensity) in *kharif* (red and shallow black soils), or in *rabi* (deep black soils) is possible. Intercropping is possible in regions with 20-30 weeks of effective growing season. In areas receiving more than 750 mm rainfall and having an effective growing season of more than 30 weeks, double cropping is assured.

8.4. *Use of Mulches*

A mulch is a material used to cover soil surface with the primary objective of reducing water evaporation. Mulches improve the infiltration of rainwater into soil through runoff control (Table 10), increase infiltration, moderate soil temperature, decrease evaporation and reduce weed infestation. Since major difference in moisture content between the mulched and the bare soils occurs near the surface, they are very useful in seedling establishment.

Several types of materials can be used as a mulch in the rainfed areas. However, crop residue mulches are economical, effective and widely used. Stalks of various crops like maize and pearlmillet, groundnut haulm and shells, paddy husk, wheat and soybean straw, twigs of wild bushes, pine needle and coir pith dust have been used successfully as mulches in the rainfed areas. Soil mulch is also of importance in the Indian context. Soil mulch can be practical in both *kharif* as well as *rabi* crops. In *kharif* crops, it helps in reducing the weed population and increasing the infiltration, whereas in *rabi* crops, its main function is to reduce evaporation. Use of soil mulch in black soils is of special significance as it minimizes the evaporation from shrinkage cracks also.

8.5. *Planting Geometry*

The geometry of crops can be suitably manipulated to offer resistance to the overland flows. An optimum plant population is essential for ensuring efficient use of land and soil water. The excessive plant population may lead to severe moisture stress and consequently, to crop failures under rainfed conditions.

The practices discussed above may require some modification/ refinement depending on the location and site characteristics. Best results in terms of resource conservation, their use efficiency and enhanced biomass production, and sustainability are achieved through adoption of "watershed management" approach.

B. WATER MANAGEMENT OF IRRIGATED LANDS

In areas where natural rainfall is insufficient – in time and space – the crops are supplied with additional water through artificial means to secure potential crop yields. This process is called irrigation. It enhances crop yields by eliminating crop water stress and increasing possibility of using other inputs affecting the crop growth such as fertilizers, tillage, better seeds and plant protection measures. An assurance against crop failures with irrigation gives sufficient confidence to the grower to use these costly inputs. Recognizing that irrigation holds the key to increasing agricultural production, most nations of the world have invested huge sums of money for developing their surface water and groundwater resources for irrigation.

The availability of water for irrigation is by no means unlimited. Moreover, the increasing demand of water for other uses, viz. civic and industrial uses, hydropower generation, navigation, recreation, fisheries, etc. would decrease

Table 9. Water availability period and efficient cropping systems for different dryland areas in India

Soil zone and region	Water availability period (days)	Crop sequences	Intercropping system (with row ratios)
1. Vertisols and related soil zone			
Malwa Plateau (Madhya Pradesh)	210-230	Maize-safflower/chickpea Soybean-wheat	Maize + soybean (2:2) Soybean + pigeonpea (4 or 6:2)
	190-210	Sorghum-safflower/ chickpea	Sorghum + pigeonpea (2:1)
Baghelkhand (Madhya Pradesh)	210-230	Rice-chickpea/lentil	Wheat + chickpea (2:1) Chickpea + linseed (2:1)
	190-210	Sorghum-chickpea Black gram/ green gram-wheat Groundnut-chickpea	Sorghum + pigeonpea (2:1)
Bundelkhand (Uttar Pradesh)	190-220	Sorghum-chickpea Black gram-mustard/ safflower Fodder cowpea-mustard	Pearlmillet + fodder legume (1:1) Sorghum + pigeonpea (2:1)
Vidharbha (Maharashtra)	190-210	Groundnut-safflower Sorghum-safflower	Sorghum + pigeonpea (2:1) Cotton + pigeonpea (2:1 or 2) Cotton + green gram/ cowpea (1:1) Pigeonpea + green gram (1:3) Pearlmillet + pigeonpea (2:1)
	170-190	Greengram-sorghum/ safflower	Sorghum + greengram/ black gram (2:1)
Southern Maharashtra	160-180	Greengram-sorghum /safflower	Pealmillet + pigeonpea (2:1) Sunflower + pigeonpea (2:1 or 2) Groundnut + sunflower (2 or 3:1) Chickpea + safflower (3:1)
	120-130	–	Pearlmillelt + mothbean (2:1)
Southern Rajasthan	160-180	Green gram -safflower	Maize + pigeonpea (1 or 2:1) Sorghum + green gram (2:2) Groundnut + pigeonpea (2:2) Chickpea + mustard (4 or 7:1)
Northern Central Karnataka	130-150	Cowpea-sorghum Greengram-safflower	Pearlmillet + pigeonpea (1:1) Groundnut + pigeonpea (3 or 4:1) Sunflower + pigeonpea (2:1) Chickpea + safflower (2 or 3:1) Sorghum + pigeonpea (2:1) Sorghum + coriander (2:1)
	100-120	–	Safflower + coriander (2:1)
Saurashtra (Gujarat)	130-140	–	Groundnut + castorbean/ pigeonpea (3:1) Pearlmillet + pigeonpea/ castorbean (2 or 4:1)

Contd

Table 9. Water availability period and efficient cropping systems for different dryland areas in India— Contd

Soil zone and region	Water	Crop sequences availability period (days)	Intercropping system (with row ratios)
Southern (Tamil Nadu)	120-130	–	Sorghum + black gram/ cowpea (2:1) Cotton + black gram (2:2)
2. Inceptisols and related soil zone			
Jammu region of Jammu and Kashmir	280-320	Maize-wheat	Maize + green gram/ black gram/cowpea (1:2) Wheat + mustard (4:1) Chickpea + mustard (4:1) Barley + chickpea (2:2)
Sub-mountain region of erstwhile Uttar Pradesh	240-280	Rice-wheat/chickpea Soybean-wheat Maize-chickpea	Maize + soybean (2:8) Rice + soybean (1:2) Wheat + mustard (9:1) Wheat + chickpea (2:2)
Sub-mountain region of Punjab and Himachal Pradesh	260-280	Maize-mustard/chickpea Pearlmillet-chickpea	Maize + blackgram (1:2) Chickpea + mustard (4:1) Pearlmillet + blackgram (2:1)
	240-260	–	Chickpea + mustard (4:1)
Plains of Uttar Pradesh	200-230	Rice-chickpea/lentil Maize-lentil	Maize + blackgram (1:1) Pigeonpea + blackgram (1:1) Pigeonpea + sesame (1:1) Groundnut + pigeonpea (2:1) Barley + mustard (6:1)
	180-200	Pearl millet-chickpea Greengram / black gram mustard/ barley	Pearl millet + greengram /blackgram (2:1) Pleari millet + pigeonpea (2:1) Chickpea + mustard (4-5:1) Chickpea + barley/linseed (2-3:1)
3. Oxisols zone			
Sub-humid region of Orissa	200-220	Rice-horse gram Maize/finger millet-horsegram Groundnut – horse gram	Rice + green gram (2-3:1) Rice + pigeonpea (3-4:1) Finger millet + pigeonpea (1:1) Maize + pigeonpea (2:1)
Sub-humid region of Southern Bihar	160-180	Maize-chickpea/safflower Groundnut-barley Fingers millet/chickpea Rice-chickpea/lentil	Maize + pigeonpea (1:1) Rice + pigeonpea (2-3:1) Groundnut + pigeonpea (2-3:1) Soybean + pigeonpea (3:1) Pigeonpea + black gram (1-2:3)
4. Alfisols and Related soil zone			
Southern Karnataka	190-220	Cowpea-finger millet Soybean-finger millet	Finger millet + pigeonpea (3:1) Groundnut + pigeonpea (4:1) Finger millet + soybean (1:1)
Telangana (Andhra Pradesh)	140-160	– –	Sorghum + pigeonpea (3:1) Castor bean+cluster bean(2:2)
Rayalsaeema (Andhra Pradesh)	110-130	–	Groundnut + pearlmillet (6-8:1-2)

Contd

Table 9. Water availability period and efficient cropping systems for different dryland areas in India— Contd

Soil zone and region	Water	Crop sequences availability period (days)	Intercropping system (with row ratios)
			Groundnut + pigeonpea (6-8:1-2) Groundnut + castorbean (2:1)
5. Arid soil zone			
North-western Gujrat	100-120	–	Pearlmillet + green gram (1:3) Pearlmillet + clusterbean (3:1) Clusterbean + green gram(2:1)
Western Rajasthan and parts of Haryana	75-90	–	Pearlmillet + balck gram/ green gram (2:1) Pearlmillet + clusterbean (1:2) Cluster bean + black gram(1:1) Pigeonpea + black gram (1:2)

N.B. Figures in parentheses are optimum row ratios of inter-cropping system.
Source: Singh (1988)

Table 10. Effect of groundnut shell mulch on crop yield, runoff and soil loss from Alfisols at ICRISAT Center, Patancheru (1981-85)

Rate of groundnut shell mulch (tonne/ha)	Crop yield (tonne/ha) (intercropping)		Runoff (mm)	Soil loss (tonne/ha)
	Sorghum	Pigeonpea		
No mulch	2.07	0.84	282	3.92
2.5	2.27	0.97	147	1.95
5.0	2.42	1.11	88	1.21
10.1	2.63	1.34	26	0.35
SE±	***0.17***	***0.09***	***13***	***0.23***

Source: ICRISAT Annual Report (1986)

the proportion of available water for agricultural usage in future (Table 11). Therefore, the available irrigation water must be used most efficiently. The efficient use of this resource for crop production consists of conserving the resource, allocating it optimally among the competing demands, its application to crop at optimal rates and timing, maximizing the utilization of resource by crop and maximizing returns per unit resource used by the crop. Concerns for sustainability of production systems require that the agricultural practices should not degrade the environmental quality and long-time productivity of the system. Irrigation, unfortunately is only a mixed blessing. Injudicious irrigation is known to cause waterlogging and salinization of soil, which jeopardise the soil productivity. Hence, the objective of water management in irrigated lands is to optimize agricultural production with available irrigation water without adversely affecting the quality of environment and production resources.

9. Basic Aspects of Field Water Management

Water management for irrigation is accomplished in two phases, viz. (i) water development for irrigation, and (ii) utilization of irrigation water for agricultural production. First phase is the realm of civil engineers and is

Table 11. Water requirements for different uses

(Quantity in BCM)

S. No	Uses	Year 1997-98	Year 2010			Year 2025			Year 2050		
			Low	High	%	Low	High	%	Low	High	%
				Surface Water							
1.	Irrigation	318	330	339	48	325	366	43	375	463	39
2.	Domestic	17	23	24	3	30	36	5	48	65	6
3.	Industries	21	26	26	4	47	47	6	57	57	5
4.	Power	7	14	15	2	25	26	3	50	56	5
5.	Inland Navigation		7	7	1	10	10	1	15	15	1
6.	Flood Control		-	-	0	-	-	0	-	-	0
7.	Environment (1) Afforestation		-	-	0	-	-	0	-	-	0
8.	Environment (2) Ecology		5	5	1	10	10	1	20	20	2
9.	Evaporation Losses	36	42	42	6	50	50	6	76	76	6
	Total	**399**	**447**	**458**	**65**	**497**	**545**	**65**	**641**	**752**	**64**
				Groundwater							
1.	Irrigation	206	213	218	31	236	245	29	253	344	29
2.	Domestic & Municipal	13	19	19	2	25	26	3	42	46	4
3.	Industries	9	11	11	1	20	20	2	24	24	2
4.	Power	2	4	4	1	6	7	1	13	14	1
	Total	**230**	**247**	**252**	**35**	**287**	**298**	**35**	**332**	**428**	**36**
	Grand Total	**629**	**694**	**710**	**100**	**784**	**843**	**100**	**973**	**1180**	**100**
				Total Water Use							
1.	Irrigation	524	543	557	78	561	611	72	628	817	68
2.	Domestic	30	42	43	6	55	62	7	90	111	9
3.	Industries	30	37	37	5	67	67	8	81	81	7
4.	Power	9	18	19	3	31	33	4	63	70	6
5.	Inland Navigation	0	7	7	1	10	10	1	15	15	1
6.	Flood Control	0	0	0	0	0	0	0	0	0	0
7.	Environment (1) Afforestation	0	0	0	0	0	0	0	0	0	0
8.	Environment (2) Ecology	0	5	5	1	10	10	1	20	20	2
9.	Evaporation Losses	36	42	42	6	50	50	6	76	76	7
	Total	**629**	**694**	**710**	**100**	**784**	**843**	**100**	**973**	**1180**	**100**

Source: Report of the National Commission for Integrated Water Resources Development (Vol-I), Sept., 1999

beyond the scope of this book. Discussion here pertains only to the second phase. It is assumed that maximum (natural) rainwater is conserved through adoption of soil and water conservation practices and irrigation is applied to supplement the soil-stored water for enhancing crop production. Efficient use of irrigation water calls for an understanding of the soil-water-plant-atmosphere relationships. Water is stored in the root zone and is taken up by plant roots and transported to the foliage to be lost to atmosphere through transpiration (T). Simultaneously, water is also lost through evaporation directly from the exposed soil surface. For optimum photosynthetic activity of the plant, transpiration from its green foliage must meet the atmospheric demand. When actual T falls short of potential T demand of the plant, the rate of photosynthesis is reduced. The potential crop water demand is governed by green-area-index (green surface area per unit land surface) and atmopsheric evaporativity. And the actual T depends on the soil water status and water uptake capacity of the root system. Therefore, in order to develop strategies for efficient water use, it is important to understand the components of the soil-water-plant-atmosphere system. These sub-systems are: (i) soil-water relations, (ii) soil-plant relations, (iii) soil-water-plant relations, and (iv) plant-water relations.

9.1. Soil-Water Relations

Soil-water relationships such as water retention and transmission characteristics, plant available water (PAW), infiltration and redistribution of water in the soil, etc. have been described in detail in Chapter 6. However, it may be reiterated that depending upon the texture, structure and mineralogical composition, soils differ widely in moisture characteristics and water transmission properties. The plant available water capacity is low in coarse-textured soils and it increases with proportion of fine particles up to a point and decreases thereafter.

An important parameter of soil-water relationship from field water management standpoint is the infiltrability of soil which determines the suitability of irrigation methods for assuring efficient water-use. Water infiltrated into the soil redistributes itself in the profile. Soils with slow infiltrability and redistribution may cause aeration stress to crops in the event of heavy rain or irrigation. As already stated, when the rate of water application or rainfall intensity exceeds the infiltrability of soil, excess water accumulates at the surface. It cuts off the process of soil aeration till all the water enters the soil and gets redistributed so as to create sufficient water-free pore spaces for renewal of oxygen in the soil air by diffusion.

9.2. Soil-Plant Relations

A plant uses soil for germination of seeds and seedling emergence and growth and proliferation of its root system. The first step in seed germination is imbibation of water by seed to start the metabolism. The rate of water movement to the seed is governed by soil wetness and hydraulic conductivity of soil together with the properties of the seed-coat. There exists an optimum range of soil water content in each soil or of soil water potential across soils for germination and seedling emergence. On either side of this range, germination and emergence get delayed or beyond a certain threshold, it does not occur at all. Thus, it is important to ensure adequate soil moisture in the seed-zone for establishment of seedlings.

9.2.1. Root Systems and Water Uptake

The plants take up water and nutrients from the soil through their root system. Like seed germination, the process of root growth also requires an optimum range of soil moisture as would supply enough water to the roots, keep the soil strength low and permit adequate soil aeration. For management of irrigation water, it is important to know that in early stages root systems of crops are confined to shallow surface layers and so is the water uptake from soil. But with time, roots penetrate deeper into the profile and may extend down to 2-3 m even in annual crops. In perennial crops and trees, root systems penetrate several metres and derive water from such depths. Under non-limiting soil water content, the rate of water uptake from various layers of soils is proportional to the fraction of roots located in that layer. However, when the upper layers are wetted, they become the zone of maximum water uptake.

It is generally reported that frequent wetting of soil with small amounts of water tends to promote shallow rooting. Infrequent and heavy applications of water induce deep rooting. Practices such as tillage, mulching, nutrient application which influence depth and density of rooting are likely to influence the water management criteria for best returns.

9.3. Soil-Water-Plant Relations

Dynamics of soil-water uptake by plants is an interplay of soil-water status and root proliferation on the one hand, and canopy development and atmospheric evaporation on the other. Water in the soil-water-plant-atmosphere continuum (SPAC) moves in response to difference in the energy status of water in the system. A drop in the energy status of leaf water on exposure to radiation, wind and vapour-unsaturated atmosphere is transmitted through the stem to the root in contact with soil-water. This sets up the energy gradient required for water to flow from soil to root, from root to stem and from stem to leaf and atmosphere.

The flux of water (q) through SPAC can be expressed by Equation (2):

$$q = (\psi_s - \psi_l) / R_t = T \qquad ...(2)$$

where, ψ_s and ψ_l are soil-water potential and leaf-water potential, R_t is the total resistance in the soil and plant, and T is transpiration.

Since during nights, T is negligible, the pre-dawn values of ψ_l are considered equal to ψ_s values. As the day advances, the stomata open up and the evaporative demand increases; the ψ_l decreases till afternoon and then the cycle reverses.

9.4. Plant-Water Relations

To remain fully turgid and photosynthesize at potential rate, the plant foliage must lose water fast enough to meet the atmospheric evaporative demand. When the transpirational loss falls short of the evaporative demand, the plant develops water stress. This stress is reflected in the loss of turgidity, increase in leaf diffusion resistance and decrease in leaf water potential. Before describing the effect of stress on plant growth and yield, it is important to know about the commonly used indices of plant-water stress.

10. Indices of Plant-Water Stress

10.1. Relative Leaf-Water Content

The relative turgidity measured as relative leaf-water content (RLWC) is computed from the fresh weight, turgid weight and oven-dry weight of leaf discs using Equation (3):

$$\text{RLWC} = \frac{\text{Fresh weight} - \text{Oven dry weight}}{\text{Fully turgid weight} - \text{Oven dry weight}} \qquad ...(3)$$

The turgid weight is obtained by keeping the leaf discs in free water till they acquire maximum weight. In the case of rice, the leaf discs must float on water for 4 to 6 hours before water deficiency is completely removed. Plants generally start wilting at RLWC of 75-85%.

10.2. Leaf-Water Potential

Plant-water potential is a measure of energy status of plant water and has three components as depicted by Equation (4):

$$\psi_l = \psi_m + \psi_p + \psi_o \qquad ...(4)$$

where, ψ_l is the leaf water potential, and ψ_m, ψ_p and ψ_o are matric, pressure and osmotic potentials. Since the contribution of ψ_m is not known, it is lumped with ψ_p and the relation is expressed by Equation (5):

$$\psi_l = \psi_p + \psi_o \qquad ...(5)$$

The leaf-water potential, also called the 'xylem water potential', is intimately related to RLWC. For example, in rice leaves, y_l decreases sharply as RLWC falls below 100%; in the intermediate RLWC range, the drop of y_l is gradual, but below RLWC of 35%, the y_l drops sharply (Tomar and Ghildyal, 1973).

10.3. Leaf Diffusion Resistance

In a fully turgid leaf in the presence of day-light, the stomata are fully open. Water vapour and carbon dioxide diffuse across the open stomata without any resistance. Functioning of gaurd cells which regulate the stomatal opening is controlled by the tissue water status. When the plant tissues develop water-deficiency, stomata begin to close partially and may be completely when water stress reaches a critical level. The closure of stomata reduces their apertures which increases the resistance to the diffusion of water vapour and carbon dioxide across stomatal openings and thus, the rate of transpiration from plants decreases. The leaf diffusion resistance (LDR) increases with a decrease in RLWC.

11. Water Use Efficiency

Agronomists define water-use efficiency (WUE) as the ratio of produce per unit area to the water used by the crop [Equation (6)]:

$$\text{WUE} = \frac{\text{Biomass(kg)} / \text{area}(\text{m}^2)}{\text{Water used(m)}} = \text{kg.m}^{-3} \qquad ...(6)$$

The water use in this relationship represents the evapotranspiration (ET) loss from the crop. In other words, it includes direct evaporation from the exposed surfaces in the field.

The plant physiologists define WUE as the ratio of biomass per unit area to transpiration (T) loss from the crop [Equation (7)]:.

$$WUE = \frac{Biomass(kg) / area(m^2)}{T(m)} = kg.m^{-3} \qquad ...(7)$$

In this case, water lost as direct evaporation is excluded.

An integrated approach has also been developed to express WUE, where it is defined as biomass (B) or grain (G) yield in terms of evapotranspiration (ET) or transpiration (T) on daily or seasonal basis. For example, WUE (G, ET, s) means WUE is expressed as the ratio of grain yield to seasonal ET. Similarly, WUE (B, T, d) signifies WUE based on biomass per unit T on daily basis.

12. Management of Irrigation Water

In view of the high investment costs of developing irrigation and limited availability of irrigation water, it should be used most efficiently. It has to be transported to the site of use and applied to the fields efficiently at appropriate timing and in adequate amounts.

12.1. Sources of Irrigation

Irrigation water is available as surface storage or as groundwater. The size of surface water reservoirs varies from a few hundred cubic metres in small tanks to several million hectare-metres in big storage dams. Depending upon the site of storage and site of use, the surface water is transported over distances, ranging from a few metres to several hundred kilometres. Groundwater is generally used in the vicinity of the source and conveyed over short distances. The quality of water also differs within and between sources of irrigation.

12.2. Surface Water Conveyance

Water from big reservoirs is carried to the use-site through canal networks consisting of main canal, distributaries and water courses. To permit gravity irrigation, the dug-out canal network is bunded above ground. Therefore, water in the canal system is lost as downward percolation from bottom and seepage through the sides of the channels. In unlined channels, the seepage losses from the main canal, distributory and field water courses depend upon the water transmission properties of the terrain through which the channels pass.

The major loss of water occurs in the field water courses (Table 12). If seepage losses are high, canals are lined with various materials such as bricks, concrete and stones, etc. to reduce the same. Since the seepage near the head-end is more than near the tail-end, it is not necessary to line the entire length of a water course. The lining of 50-60% of the total length may reduce the seepage loss by 80-85%. A plot of the ratio of annual benefits to annual costs versus the length of lining can help decide about the length to be lined for best returns.

Water from pumps and tubewells and small tanks is transported over short distances. The lining of water courses is effective in reducing seepage loss in these cases also. Conveyance of water through underground pipes has also

Table 12. Conveyance losses from unlined, partially-lined and lined irrigation system as per cent of water released from a reservoir

System characteristics	Main canal (%)	Distributory (%)	Field water courses (%)	Total conveyance losses (%)	Conveyance efficiency (%)
Entire system unlined	15	7	22	44	56
Only canal lined	4	7	25	36	64
Canal and distributories lined	4	2	26	32	68
Whole system lined	4	2	6	12	88

Source: Aggarwal and Khanna (1983)

been recommended. It is especially useful for undulating lands and highly permeable soils. Apart from reducing seepage losses, it has the added advantage of saving land. It decreases the maintenance costs and increases the freedom of farm operations.

13. Methods of Water Application

Once irrigation water reaches the field, the next task is to apply it efficiently. Attributes of judicious application are: application efficiency, storage efficiency and distribution efficiency. Water application efficiency (WAE) is the ratio of water stored in the root zone to water delivered to the field during irrigation [Equation (8)]:

$$\text{WAE(per cent)} = \frac{\text{Water stored in root zone}}{\text{Water delivered to field}} \times 100 \qquad \ldots(8)$$

Water storage efficiency (WSE) is the ratio of actual irrigation water stored in root zone to water storage needed in the root zone before irrigation [Equation (9)]:

$$\text{WSE (per cent)} = \frac{\text{Water stored in root zone}}{\text{Root zone water deficit before irrigation}} \times 100 \qquad \ldots(9)$$

Similarly, water distribution efficiency (WDE) is given by Equation (10):

$$\text{WDE} = \left(1 - \frac{N}{D}\right) \times 100 \qquad \ldots(10)$$

where, N is the average numerical deviation in depth of water stored at different locations from the average water storage depth of field following irrigation, and D is the average water storage depth of field.

Irrigation methods fall under two categories, viz.

(i) Surface methods, and

(ii) Pressurized irrigation systems

13.1. Surface Irrigation Methods

In India, systems of surface methods of irrigation have been developed in the past years. Among them, the check basin method of irrigation is the most popular one. It is very important to employ the correct method of water application to minimize adverse effects of irrigation. The soil type, land topography, crops to be grown, quality and quantity of water available for irrigation and other site-specific variations influence the selection of the right method of irrigation. Proper land levelling and channel linings are some of the management options that are generally ignored. Land levelling increases the water application efficiency, which leads to higher yields as well as increase in water-use efficiency (Table 13). It also has a direct impact on the nutrient-use efficiency.

13.1.1. Check Basin Method

It is the most common method of surface irrigation. Several lateral field channels are taken off from the main irrigation channels running along the side of the field. Each lateral channel feeds on both sides, a row of several small plots surrounded by ridges — termed as check-basins. More lateral channels facilitate rapid spread of water over the enclosed area of land. This method is preferred and practised over level lands. The spread time is kept generally low to minimize percolation losses near the head-end of the basin. Therefore, on highly permeable soils, high stream size and small check basins are desirable. However, an adequate water depth to make up the soil water deficit should be ensured.

13.1.2. Border Strip Method

Water is applied from one end (head-end) to borders of suitable dimensions with appropriate slope. The design criteria of borders depend on the infiltrability of soil, border slope, border length and stream size. Narrow strips help achieve uniform advance of water front from head-end to tail-end. Similarly, a gentle and uniform slope improves the water application efficiency. Slope generally varies between 0.05% and 0.5% for most crops. The recommended design dimensions of borders for various soils, stream size and slopes are given in Table 14. During application, water supply is cut off when the advancing water front is still some distance away from the tail end. The cut-back point on the strip length depends on strip width, soil slope, stream size and soil characteristics.

Table 13. Effect of land levelling on yield and water use efficiency

Levelling Index (cm)	Water use efficiency (kg/ha-cm)		Yield (q/ha)	
	Wheat	*Bajra*	Wheat	*Bajra*
1.2	166	120	46.6	37.3
2.0	138	106	42.2	34.2
2.5	128	99	39.3	32.9
3.0	116	92	36.5	31.4
3.7	110	84	34.9	27.9

Table 14. Recommended design dimensions of border strips for various soils, slopes and stream sizes

Place	Soil	Slope (per cent)	Stream size (L/s)	Border dimensions (m)	
				Width	Length
Hissar	Sandy loam	0.1-0.2	14.0	7.5	50-70
Jobner	Sand	0.3-0.5	3.5	1.5	20
Karnal	Clay loam	0.1-0.15	10-12	6.0	70
Kharagpur	Sandy loam	0.3	6-8	3.5	50-70
Kota	Clay loam	0.2	10.0	6.0	50
Pantnagar	Clay loam	0.3-0.4	12-15	7.5	100

Source: Yadav (1982)

13.1.3. Furrow Method

The furrow method of irrigation is generally used to irrigate row crops and vegetables, and is suited to soils in which the infiltration rates are between 0.5 and 2.5 cm/hr. It is ideal for slopes varying from 0.2% to 0.5% and a stream size of 1-2 L/sec. Many of the field crops in which water is applied through check basin or border strip methods, can easily be adapted for furrow irrigation. In areas requiring surface drainage, furrows are more effective. Scientific studies suggest that irrigation in alternate furrows for the cotton and maize crops saves irrigation water to the tune of 30%, without compromising the crop yield

Water from the main or lateral channel is directed into small parallel furrows drawn along the slope in between the small ridges or broad checks. Water in the furrow moves both laterally and vertically to moisten the ridges and sub-soil layers. On soils with slope, furrows are made along the contour. Furrow irrigation is more efficient than either border strip or check-basin methods. Furrow dimensions depend upon the soil type, stream size, land slope, and nature of crop and implements available for cultural operation.

13.1.4. Surge Flow Irrigation

Excessive water intake and deep percolation losses are major limitations for irrigation applications through furrows and border strips. Surge flow irrigation, the intermittent application of water in a series of on and off modes of constant or variable time spans has the potential of reducing intake and percolation losses, increasing the irrigation efficiencies and conserving irrigation water. Field experiments have corroborated that surge flow furrow irrigation results in faster water front advance and reduces the volume of water required to complete the advance phase. The studies have also confirmed that it increases water distribution efficiency, reduces infiltration rate and the cumulative infiltration depth, and consequently, reduces the percolation losses.

13.1.5. Raised Bed Planting Systems

This system of crop establishment is a modification of the ridge-furrow system in which the ridges are replaced by flat beds. Crops are cultivated on the raised beds, while the furrows are used for irrigation. Fertilizers can be placed on the raised beds. The width of raised beds depends on the crops to be grown. This crop establishment technique has many advantages as it improves both water and nutrient use efficiency, requires lower seed rates and the furrows act as the drainage channels in the case heavy rainfall, preventing temporary waterlogging. Several crops, particularly vegetables, are ideally suited for this method of crop establishment.

13.1.6. Water Management in Rice

Rice is the staple food in Asia, the most populous continent, which accounts for almost 90% of the global production and consumption of rice. This demand is likely to increase by 70% in the next three decades for the ever-increasing Asian population. Asia produces more than 530 million tonnes of paddy rice every year. More than 75% of this comes from the irrigated area, which accounts for 55% of the total rice area. Irrigated low land rice constitutes the major economic activity, source of employment and income for the rural population. In India, out of the 43 million hectares under rice cultivation, almost 55% is irrigated, which consumes almost 50% of the irrigation water resources. The growing water shortage has threatened the sustainability of irrigated low land rice production systems, which consume up to 3000-5000 litres of water to produce 1 kg of grain. Fresh water consumption for irrigated low land transplanted rice in most Asian countries is, therefore, very high. Since rice is the staple food of billions, it is imperative to devise technologies for growing rice with less water, reducing dependence on traditional methods of rice growing, without compromise on its production.

Traditionally, it is thought that for maximum production rice needs continuous submergence/flooding throughout its life-cycle. As a result, the water requirement of rice is many times more than other crops. This practice not only leads to wastage of water but also causes environmental degradation and reduces fertilizer-use efficiency. Years of research conducted on varying soils all over the country has conclusively established that irrigating rice one to three days after disappearance of ponded water can save 20 to 30% of irrigation water applied without any significant effect on the yield (Table 15). The saving in irrigation water could be used to bring additional area under irrigation or diverted to dry and/or water scarce areas.

Table 15. Effect of irrigation on the yield of paddy at various locations in the country

Place	Yield (t/ha)			
	Continuous submergence	Irrigation after disappearance of ponded water from the surface		
		One day	Two days	Three days
Pusa (Bihar)	3.59 (81)*	3.47 (60)	3.25 (46)	2.85 (35)
Chiplima (Orissa)	7.21 (99)	6.66 (90)	6.47 (76)	5.85 (68)
Kharagpur (W.B.)	6.11 (197)	5.98 (150)	5.89 (129)	4.99 (108)
Bilaspur (M.P.)	5.86 (98)	5.59 (77)	5.13 (70)	4.62 (56)
Pant Nagar (Uttranchal)	8.09 (121)	7.57 (112)	7.38 (90)	6.92 (60)
Ludhiana (Punjab)	5.52 (190)	5.44 (145)	5.12 (113)	5.20 (96)
Hisar (Haryana)	5.66 (220)	5.15 (196)	4.69 (126)	-
Kota (Rajasthan)	5.41 (145)	5.33 (86)	5.05 (68)	-
Mudrai (T.N.)	6.59 (128)	6.66 (104)	6.18 (82)	-
Bhavanisagar(T.N.)	4.57 (136)	5.09 (110)	4.95 (80)	4.19 (55)
Chalakudi (Kerala)	3.47 (14)	3.44 (63)	3.45 (49)	-

Note: *Figures given in brackets show the quantity of irrigation water applied (cm)

Source: Chaudhary (1997)

Efforts are being made to devise and develop new management options and varieties using modern tools like marker aided selection to increase water-use efficiency of rice crop. Aerobic rice cultivation and location-specific modified versions of system of rice intensification (SRI) are some of the options that are being explored.

13.2. Pressurized Irrigation Systems

Considering the need of irrigation methods that are more efficient, efforts are being made to develop water-efficient methods. Two of these methods are sprinkler and drip irrigation systems, which are more efficient than the conventional surface methods (Table 16). Since these methods need water under pressure, they are classified as 'Pressurized Irrigation Systems', in contrast to the surface irrigation methods which are generally gravity-driven. The pressurized methods of irrigation provide many advantages over the gravity surface irrigation methods in terms of water savings and crop yields. The quality of produce is also considered generally superior than in conventionally irrigated crops. These pressurized irrigation systems are very useful, particularly in undulating and uneven lands or coarse-textured soils. The use of these techniques can be promoted for adoption in irrigation commands also under specific conditions. The total potential area where these methods could be applied is very large (Table 17) and Government of India is making several efforts to popularize these methods among the farmers.

13.2.1. Sprinkler Irrigation

In the sprinkler method of irrigation, water is sprayed through nozzles connected to a network of pipes through which water is supplied

Table 16. Irrigation efficiencies (per cent) under different methods of irrigation

Irrigation efficiencies	Methods of irrigation		
	Surface	Sprinkler	Drip
Conveyance efficiency	40-50 (canal) 60-70 (well)	100	100
Application efficiency	60-70	70-80	90
Surface water moisture evaporation	30-40	30-40	20-25
Overall efficiency	30-35	50-60	80-90

Source: Sivanappan (1998)

Table 17. Theoretical potential area for drip and sprinkler irrigation in India (Mha)

Crop	Area		
	Drip	Sprinkler	Total
Cereals	-	27.6	27.6
Pulses	-	7.6	7.6
Oilseeds	3.8	1.1	4.9
Cotton	7.0	1.8	8.8
Vegetables	3.6	2.4	6.0
Spices & condiments	1.4	1.0	2.4
Flowers & medicinal and aromatic plants	-	1.0	1.0
Sugarcane	4.3	-	4.3
Fruits	3.9	-	3.9
Coconut & plantation crops, Oil palm	3.0	-	3.0
Total	27.0	42.5	69.5

Source: Government of India (2003), Agricultural Statistics at a glance 2003, Directorate of Economics and Statistics, MoA, New Delhi; NHB (2002), Indian Horticulture Database: 2002, National Horticulture Board, MOA, GOI, Gurgaon under pressure. The rate of spray of water can be regulated and natural rainfall may be simulated. This method has higher application and distribution efficiency, effects considerable savings of water, and provides complete control on timing and quantity of irrigation water to be applied. The overall efficiency of sprinkler method can be as high as 60%, compared to around 30% of surface method of irrigation. Water can be applied in quantities required to adequately wet the root zone of the crop, thus avoiding wastage of water through percolation. As the water is conveyed through a closed pipe system, conveyance losses are minimum in sprinkler method of irrigation. Run-off losses are also reduced considerably. As the time of application of water can be controlled effectively, light and frequent irrigations can be applied and a healthy moisture regime can be maintained in the root zone of the crop, thus leading to healthy crops and higher levels of production of good quality produce. Further, this method leads to considerable savings in the irrigation water and increase in area covered and, hence, higher irrigation intensity can be achieved.

In spite of above-mentioned advantages, very limited cropped area in the country is under this method of irrigation. High initial capital cost, and lack of expertise in its operation and maintenance have limited the use of this system to crops. This technology is being gradually adopted in water-scarce areas and for cultivation of high-value export-oriented commercial crops like flowers, vegetables and horticultural crops. The sprinkler method of irrigation could be introduced for a large number of crops, depending upon the soil, slope, water resource, farmers' capacity for investment, etc.

Historically, development of sprinkler irrigation got a boost mainly after the Second World War, with the introduction of lightweight, portable aluminum pipes. At the same time, improved sprinklers and quick couplers, that facilitate convenient uncoupling and recoupling of pipes, has been a remarkable development. The farming community in India was not familiar with sprinkler irrigation till mid-1950s. Even today, the area under sprinkler method of irrigation is too low in India compared to several other countries. It is largely because an average Indian farmer is resource-poor and cannot invest in the system.

The plantation owners in the hills use sprinkler irrigation to irrigate tea, coffee and cardamom crops during dry seasons and dry spells of the monsoon period. In mid-1970s, progressive farmers in the Narmada valley in Madhya Pradesh, southern parts of Haryana and north-east parts of Rajasthan started using sprinkler system to overcome problems of water-shortage, particularly during summers. Adoption of this system gradually spread to larger areas in the states of Haryana, Rajasthan, Madhya Pradesh, Maharashtra and Karnataka. However, in major agricultural states like Punjab, Uttar Pradesh and Bihar, this system of irrigation is extremely limited. About 60% of area irrigated by sprinkler system is under field crops like cereals, pulses, oil seeds, cotton, sugarcane and vegetables, the rest being under tea, coffee, cardamom gardens in the western ghats and north-eastern states.

The developmental work on sprinkler irrigation system has been mainly aimed at reducing the cost of the equipment and introducing smaller low pressure sprinklers. Till recently, the most popular piping material has been aluminum but to reduce the cost of the systems 'High Density Polyethylene' (HDPE) pipes with suitable modifications have been introduced. The spread and popularization of sprinkler irrigation method among farmers has received significant support under the various schemes, involving subsidy of the central and state governments in the recent years.

13.2.2. Drip Irrigation

Drip irrigation involves application of water only at the roots of the plant where it is required and thereby saving more water and brings more area under irrigation. The crop yields by this method of irrigation are higher with reduction in cost of fertilizers, pesticides and power-use for irrigation. In drip irrigation, water is directly applied into the root zone of plants and it permits the irrigator to limit the watering closely to the consumptive use of the plants. This method is well-suited for wide-spaced high-value crops like coconut, grapes, banana, lime, etc. The required quantity of water is provided to each plant daily or at short intervals at the root zone through a network of piping system. Hence, there is no loss of water in either conveyance or application. Evaporation losses from the soil surface are also minimal, since water is applied only to the root zone and crop canopy provides the shade to prevent evaporation. Research studies have indicated that the water savings can range from 40% to 70% or higher with enhanced yield in various crops, if the drip method is used.

Considering the irrigation needs in Indian agriculture, emphasis is being laid on promoting drip irrigation which helps conserve water, reduces fertilizer inputs and ensures higher productivity. This technology though was introduced in early-1970s in India, its adoption took off in the 1980s, particularly in fruits, vegetable and cash crops. Drip irrigation is becoming increasingly popular in water-scarce and salt-affected areas. In India, almost 1.5 lakh hectares of fruit crops and 2.5 lakh hectares of vegetable crops are being added annually under drip irrigation. As per the estimates of Ministry of Agriculture, Government of India, about 27 Mha area in the country can be brought under drip irrigation (Table 17).

To tap this potential, the Government of India has initiated various schemes for motivation of farmers, ensuring availability of material, technical support and credit availability. This has helped in promoting the technology in a big way.

13.2.3. Rainguns

Rainguns are the modified form of sprinklers and are less capital-intensive compared to conventional sprinkler systems and can be modified to cater to many other crops. They support the highly recommended practice of trash mulching in sugarcane, enriching the soil with nutrients. They also hold a lot of promise as an efficient tool for application of irrigation water.

13.2.4. Micro Sprinklers

The micro sprinkler method of irrigation has the advantages of both the sprinkler and drip irrigation methods. Water is sprinkled or sprayed around the root zone of the trees with small sprinklers that work under low pressure. This unit is fixed in a network of tubings, but can be shifted from place to place. The exact quantity of water can be delivered to each plant daily at the root zone. Water is given only to the root zone area as in the case of drip irrigation unlike to the entire ground surface as in case of sprinkler irrigation method. This method is highly suitable for tree/orchard crops and vegetable crops and is suited for protected agriculture.

13.2.5. Fertigation

It is also possible to supply the nutrients to the crops through the pressurized system of irrigation popularly called as fertigation. Supplying liquid-soluble fertilizers through a drip system can lead to savings in fertilizer applied to the extent of 40% to 60% without affecting the yield and a much higher application efficiency compared to the conventional methods. This is in addition to the savings in water applied which could be anywhere from 40% to 70%. The quality of produce is also superior. These aspects will play a decisive role in the adoption of these technologies when the subsidies to the two vital inputs to agriculture, water and fertilizer, are reduced which is inevitable in future.

13.2.6. Use of Poor and Marginal Quality Waters for Irrigation

Due to intense competition with domestic, industrial and power sectors, agriculture will have to depend more on the use of marginal/poor quality of water, as it is projected that the share of water allocated to agriculture is likely to decrease by 10-15% in the next 20-30 years. One of the advantages of pressurized irrigation systems is that they can be used with poor quality waters also. In addition to the specific maintenance requirement of the system, it is important to ensure removal of salts or other chemicals periodically to prevent their critical concentrations, which will ultimately affect production. If the field can be saturated or flooded at the time of seed germination, much of the salinity can be leached out, if only for a brief period. Most species are more susceptible to salt effects during germination and are more resistant during other portions of their life-cycle. With this system, the soil salinity will remain below the crop's damage threshold throughout the year, although during sometimes in the season salt levels may become quite high. In case of drip/sprinkler irrigation systems, it is also essential to follow an application schedule that encourages deeper root system in trees (horticulture/orchard crops) for anchorage in regions which are prone to high wind speeds.

14. Scheduling of Irrigation to Crops

Irrigation scheduling — the timing and amount of irrigation to crops — plays a significant role in optimizing crop production with a given amount of water and avoiding the adverse effects of either over-irrigation or under-irrigation on soil environment. These objectives are achieved through optimum scheduling of irrigations based on sound scientific principles of soil-water-plant-atmosphere relationships. Approaches to irrigation scheduling vary depending on situations, e.g. (i) where adequate irrigation water is available on demand to secure potential yield, and (ii) where available supplies fall short of the full irrigation water requirement of crops over the entire command area.

14.1. Plentiful Water

Where ample water supplies are available for meeting the water requirements of crops over the entire command area, growers' aim is to secure potential yields without wasting water. For such a situation, an optimum irrigation schedule is that time sequence of the amounts of needed minimum irrigation which may eliminate under- and over-irrigation and ensure high water-use efficiency. For securing potential yield, the following points need consideration:

(i) Irrigation must be repeated while soil water content is sufficiently high, and
(ii) Soil can and does supply water sufficiently fast to meet the atmospheric evaporative demand without putting the plants under stress that will reduce yield or quality of produce.

In any irrigation practice we have to answer two questions, viz.

(i) When to irrigate? and
(ii) How much to irrigate?

For optimum irrigation scheduling, we have to first look for the point on the yield versus soil water status curve at which yield starts declining so that the irrigation is applied before this point is reached. Also, we should have means of knowing the soil-water deficit in the root zone when this point is reached. Several criteria that are used for finding out this point can be classified into three categories. These are based on:

(i) Soil-water regime,
(ii) Meteorological parameters, and
(iii) Plant indices.

14.1.1. Soil-Water Regime

The criteria for scheduling irrigation based on soil-water regime use soil water content, available soil water depletion and soil water tension to find the threshold point for irrigation.

Soil-Water Content — Yields are related to soil-water contents in assumed root zone at which irrigations are applied and the soil-water content is identified where yields begin to decline. Alternatively, fixed time intervals between successive irrigations are tried experimentally and the most suitable interval is identified. These criteria suffer from lack of generalization because both threshold soil-water content and fixed time intervals for a given crop vary widely with soil-water characteristics. It has been suggested that the soil-water content at which the ratio of actual to potential evapotranspiration (ET) falls below a threshold value for potential yield is the point before which irrigation must be applied. This soil-water content has been termed as lower limit for potential ET (LLE_0). Once the threshold limit for application of irrigation is established, irrigation could be repeated any time before this point is reached. Water addition should be only sufficient to make up the soil water deficit and keep the salts below the root zone.

Available Soil-Water Depletion — Irrigation is advocated on the basis of the fraction of plant available soil-water depletion from a fixed root zone usually the upper 15 cm. In view of the ever-deepening characteristics of the root system, at least till flowering, the assumption of fixed shallow root zone is not valid.

Soil-Water Suction — The soil-water suction measured by tensiometers has also been used as a criterion for scheduling irrigation to crops. Tensiometers are installed at specified depths to monitor soil water suction (or tension) for irrigation purpose. Soil water suction integrated across the root zone depth is a more dependable criterion than soil water suction of a shallow layer. The traditional tensiometers have a narrow working range of 0-80 kPa which render this method unsuitable for fine-textured soils, but now new devices with higher range are also available. It may be noted that this technique does not measure the amount of water needed at each irrigation. This has to be assessed through other means.

The response of crops to irrigation is better correlated with soil moisture tension than with soil-water content. Crop yield is related to soil moisture tension at which irrigation is repeated and the period is chosen when yield starts declining. This approach is applicable to fruit and vegetable crops which require more frequent irrigations and on sandy soils in which most of the available water is depleted at tensions well below 80 kPa.

14.1.2. Meteorological Parameters

Irrigation can be scheduled on the basis of water lost from the canopy and the permissible soil water depletion for potential yield. The former is determined by the ambient environment and the degree of crop cover and is obtained from the potential ET and the crop cover factor. Now computers can be used to advise the farmers about the timing of irrigation based on water budgets of individual fields prepared from the potential evapotranspiration (PET) rates and initial soil water storage. A serious problem with this approach is one of establishing the suitable crop factors. Moreover, it is now being increasingly recognised that under field conditions soil-water depletion does not necessarily equal ET by the crop. Water is also lost by deep percolation between irrigations. Another approach based on pan evaporation has been suggested. In this approach the ratio of fixed amount of water (in each irrigation) and evaporation from open pan is used as the basis for irrigation. It is mathematically denoted as:

$$\frac{\text{IW}}{\text{Pan} - \text{E}}$$

where, IW denotes the fixed amount of water in each irrigation (based on the permissible profile water depletion) and Pan–E is the net cumulative evaporation from open pan since previous irrigation. It is particularly convenient during low rainfall *rabi* season. Wheat sown on deep alluvial soils after pre-sowing irrigation and given first irrigation after four weeks could be irrigated on the basis of IW/(Pan–E) ratio of 0.75 to 0.90 in northern India. This approach could save irrigation water without reducing the yield (Table 18).

Intervals between successive irrigations, based on the optimum IW/(Pan-E) ratio, can be worked out using average pan-evaporation

Table 18. A comparison of irrigation schedules in wheat (average of two years)

Irrigation		Mean irrigation water (cm)	Mean profile water depletion (cm)	Mean grain yield (kg / ha)
Amount	Basis of timing			
7 cm	5 growth stages	35	15.5	4260
0.9 PAN-E	5 growth stages	27	14.6	4060
0.10 PAN-E	5 growth stages	23	15.4	4145
7 cm	IW / (PAN–E) = 0.9	23	18.5	4080
7 cm	IW / (PAN–E) = 0.75	22	15.6	4125
L.S.D. (0.05)		–	–	NS

The mean rainfall during these seasons was 800 mm for a few years and time tables of the type given in Table 19 can be recommended for different crops for various locations (Prihar and Sandhu, 1987).

14.1.3. Plant Indices

Several plant indices ranging from simple appearance of plants, their rates of growth, plant water stress measured as relative leaf water content, xylem water potential, leaf diffusion resistance and canopy temperature in relation to ambient air temperature have been investigated as the criteria for scheduling irrigations to crops. It is generally agreed that the plant integrates the effects of soil-water availability and the evaporative demand and the growth and yield are also found to relate with certain plant-water stress. However, it has not been possible so far to exploit these indices for the practical irrigation scheduling. These parameters only indicate when to irrigate but not how much to irrigate.

Canopy temperature appears to be the most promising index which could be exploited for scheduling irrigations (Jackson, 1982). Certain instruments like infrared thermometers are easy to operate and permit rapid determination of canopy temperature.

14.2. Limited Water Supplies

Irrigation scheduling for optimizing production with limited water supplies is a bigger challenge than that with adequate water supplies. As stated earlier, the first step in scheduling irrigations with limited water is to assess the relative sensitivity of different growth stages of a crop to water stress.

15. Special Purpose Irrigation

Irrigations are often applied to save crops from frost damage, even if the soil is sufficiently moist to meet transpirational requirements of crops. Similarly, irrigations are applied to soften the crust that develops on seedbeds before the emergence of seedlings. Early post-seeding irrigations which do not conform to the given criteria of scheduling irrigation are reported to enhance availability of surface applied nutrients and promote root extension to deeper layers.

16. Adverse Effects of Irrigation

While irrigation does help in increasing and stabilizing the crop production in water deficient areas, it may have short-term and long-term adverse effects on crop yields and soil productivity. Heavy irrigation (or rain) on soils of low permeability may cause anaerobic conditions resulting in aeration stress to plant roots for variable lengths of time which reduces crop yields. Similarly, over irrigation on excessively permeable and low retentivity soils may leach down the native or applied plant nutrients out

Table 19. Irrigation time table for wheat sown after a heavy pre-sowing irrigation on deep alluvial soil in Punjab

Date of sowing	First irrigation	Second irrigation 7.5 cm	Third irrigation 7.5 cm	Fourth irrigation 7.5 cm
		Days after sowing/previous irrigation		
Nov. 1-7	28	36	43	26
Nov. 8-21	28	41	38	25
Nov.22-Dec.5	28	44	30	15
Dec.6-20	28	35	25	15
Dec.21-Jan.4	28	30	20	14
Jan.5-Jan.15	28	28	18	12

* First irrigation should be comparatively lighter

Notes: This time-table is not applicable if any one or more of the following conditions prevail:

(a) A crop has been sown without giving a heavy pre-sowing irrigation

(b) A hard impervious layer of lime concretions (*kankar*) or clay lies in soil profile within one metre from the surface

(c) The soil is excessively sandy or saline of the root zone and, thus, make them physically inaccessible to crop. This, too, results in reduced yield.

The long-term adverse effect of irrigation is one of raising the groundwater table. The rising water, if not intercepted, ultimately causes waterlogging, often accompanied by salinity. The development of waterlogging and salinity in some areas of Punjab, Indira Gandhi Canal Command Areas of Rajasthan, several parts of Haryana and low-lying areas of Tungabhadra canal region are examples of such an effect (Bhumbla, 1984) (Table 20). Provision of canals is essential for agriculture in arid and semi-arid areas, but permanent irrigated agriculture is not possible unless effective steps are taken to control the rise of water table. The surface drainage is of limited avail in this regard and the water table can be controlled through sub-surface drainage. Where quality of ground water is good, shallow tubewells may be sunk to augment irrigation water supplies and prevent rise of water table. Shallow water tables with good quality ground water can be exploited *in situ* to partly or fully meet the water requirements of crops.

17. Irrigation with Poor Quality Water

It is estimated that in India about 25% of ground water is of poor quality. The use of saline and sodic water has till recently been guided by the standards laid down in the U.S. Salinity Laboratory Handbook 60. However, these standards are not applicable under Indian monsoonal type of climate. We have evolved our own classification of saline and sodic water for arid and semi-arid areas and these are given in Table 21.

The poor quality waters can be used conjunctively with good quality water by either mixing the two or irrigating with poor and good quality water in suitable succession. The quality of water resulting from the blending of good and poor quality waters can be computed from the quality of the respective waters by Equations (10) and (11):

$$EC_{iw} = (EC_{pw} * f_{pw}) + (EC_{gw} * f_{gw}) \quad ...(10)$$

$$RSC_{iw} = (RSC_{pw} * f_{pw}) + (RSC_{gw} * f_{gw}) \quad ...(11)$$

where, EC denotes the electrical conductivity, RSC denote residual sodium carbonate, and the subscript 'iw' stands for irrigation water and 'pw' and 'gw' denote poor quality and good quality waters, respectively and 'f' is the fraction of water. The fractions of poor and good quality water can be adjusted to have an irrigation water within permissible limits.

18. Drainage

The purpose of drainage is to remove the excess water from soil to ensure proper soil aeration. When soil gets saturated with water, the entire pore space is occupied by water and soil aeration is cut off. Also, water ponded at soil surface cuts off gaseous exchange between atmospheric air and soil air even if there are enough air-filled pores in the soil below. Draining out the excess water to create air porosity creates soil conditions favourable for soil aeration. Drainage is of two types, viz. (i) Surface drainage, and (ii) Subsurface drainage.

Table 20. Rate of water table rise in some irrigation commands in India

Name of irrigation command	Water table rise (cm/yr)
Mahi Right Bank Canal Command, Gujarat	28
Rajasthan Canal Command (IGNP), Rajasthan	29-88
Western Jamuna and Bhakra Canal Command, Haryana	30-100
Sirhand Canal Command, Punjab	10-100
Sharda Sahayak Canal Command, Uttar Pradesh	68
Malprabha Canal Command, Karnataka	60-120
Nagarjuna Sagar Irrigation Project, Andhra Pradesh	32

Source: Gupta and Tyagi (1996)

Table 21. Classification of saline waters (RSC <2.5) for irrigation of soils of different textures for crops sensitive, semi-tolerant and tolerant to salinity

Soil texture and percentage of clay	Crop tolerance to salinity	Upper limits of EC_{iw} (dS/m) in different regions, mm		
		< 350	350-500	500-750
Fine > 30%	Sensitive	1.0	1.0	1.5
	Semi-tolerant	1.5	2.0	3.0
	Tolerant	2.0	3.0	4.5
Moderately fine 20-30%	Sensitive	1.5	2.0	2.5
	Semi-tolerant	2.0	3.0	4.5
	Tolerant	4.0	6.0	8.0
Moderately coarse 10-20%	Sensitive	2.0	2.5	3.0
	Semi-tolerant	4.0	6.0	8.0
	Tolerant	6.0	8.0	10.0
Coarse < 10%	Sensitive	-	3.0	3.0
	Semi-tolerant	6.0	7.5	9.0
	Tolerant	8.0	10.0	12.5

Source: Gupta *et al.* (1994)

18.1. Surface Drainage

For the removal of the surface-accumulated water, surface drainage methods are adopted. On a sloping land, water does not accumulate over the land and most of it flows out by gravity. Therefore, surface drainage methods are more applicable in flat lands or lands with mild (<0.5%) slopes. For flat land drainage, a network of drains in a hierarchical order, from field drains to main drain are established. The lowest order drains are constructed in the field or at the lower boundary of the field. These drains are shallow about 15 cm deep and are triangular or trapezoidal in cross-section. They are referred to as "field drains". Their requirement exists in the monsoon season in providing a smooth access of the overland flow into it and carrying this water towards the hierarchically higher order drain. Hence, they need to be constructed or renovated before the monsoon arrives. The distance between adjacent field drains may be between 100 m and 200 m and may have a longitudinal slope of 0.1% to 0.2%. A number of such field drains convey their water to a "collector drain", which further conveys the water towards the main drain. Collector drains are trapezoidal in cross-section, 40 to 50 cm deep with 1:1 side slope and 0.2% to 0.3% longitudinal slope. Generally, the collector drain capacity is between 5 to 10 Lps/ha. A number of collector drains lead their water into a main drain, which takes the excess surface water out of the drained agricultural land. The capacity of the main drain depends on the number of collector drains joining it. The above-mentioned depth, spacing and slope are only general guidelines and they vary depending on local topography, rainfall, field boundary and size, soil type, crops grown and outlet condition. Regular maintenance of surface drainage network is essential to keep them functional at the time of maximum need, mostly in the monsoon season.

18.2. Sub-surface Drainage

Sub-surface drainage is accomplished through a network of pipe drains buried 1 to 2 m below the land surface. This is used for controlling shallow water table and for leaching of harmful salt solutions in the soil profile. The drainpipes are usually of baked clay or plastic material. Baked clay pipes are normally 30 cm to 60 cm long and 10 cm to 15 cm in diameter. The most common plastic drainpipes are made in continuous length of 200 m to 500 m and are corrugated PVC pipes with small perforations on their surface. For commissioning a sub-surface drainage system, a trench is dug to the desired depth, its bottom is smoothened and is given a uniform slope of 0.05% to 0.2%. A layer of filter is placed at the bottom of the trench. A common filter is a mixture of sand and small size gravel. The drainpipe is laid over the filter bed and is covered from sides and top by filter. The trench is then backfilled. Organic filters such as paddy straw or coir fibre may also be used at the top and at the sides of the drainpipe. Synthetic filter of nylon fabric is also used, particularly for the corrugated PVC drainpipes. If clay pipes are used, the fine gaps between the adjacent pipes convey the excess water in the soil profile into the drainpipe.

Like in the case of surface drainage, a sub-surface drainage network also has a hierarchical order of drains, from the lowest level lateral drains to the highest-level main drain. The final outlet drain may be an open drain if topography permits gravity flow into it from a drainage network buried 1 to 2 m below the ground. Otherwise, the sub-surface drained water is collected in a sump well from where it is pumped and disposed in any available shallow surface drain nearby.

The problem of waterlogging and soil salinization is increasing in the commands of many irrigation projects, especially in the arid and semi-arid areas. It is estimated that almost 2.5 Mha are has become waterlogged and 3.3 Mha has been affected by salinity in the irrigation commands. Inefficient use of irrigation water is the primary cause for converting these highly productive lands into wastelands. To improve the soil environment and make it more conducive and favourable for crop growth, surface or subsurface drainage is the only effective alternative (Table 22). Investigations have revealed that the cost of restoring the productivity of these affected lands is very high and can totally upset the economy and durability of the projects.

In many coastal areas, excessive pumping of groundwater through tubewells leads to deterioration of water quality due to seawater intrusion. For skimming fresh water, Dorouv technology/infiltration gallery methods have been found beneficial to prevent seawater intrusion. Similarly, in many island areas overdrawal of good quality groundwater leads to lowering of water table and acute water shortage. Scientific regulation of the intensity of tubewells according to local aquifer characteristics, is highly essential to ensure a proper water balance.

Table 22. Effect of subsurface drainage (SSD) on crop yields in Chambal Command (Rajasthan)

Crop	Yield (t/ha)		
	Without SSD	With SSD	Percent Increase
Wheat	2.2	3.4	55
Mustard	0.8	1.5	84
Berseem	36.0	52.0	44
Paddy Rice	1.9	2.9	53
Soybean	1.4	2.2	56

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Chapter 10

Soil Erosion and Soil Conservation

J.S. SAMRA, U.C. SHARMA and K.S. DADHWAL

1. Introduction

Soil is a dynamic natural body on the surface of the earth and is a critical resource for supporting plant growth. It is composed of minerals, organic materials and living forms and provides the necessary nutrients to the growing plants. Water acts as a nutrient carrier as well as an agent of soil erosion. Mismanagement and indiscriminate use of soil and water resources result in land and environmental degradation and may prove disastrous for humankind as well as animals. Hence, judicious management and conservation of soil and water are essential for realizing sustainable productivity and environmental benefits.

2. Soil Erosion

Soil erosion is defined as the detachment of soil particles, their transportation from one place to another and deposition elsewhere through water, wind, coastal waves, snow, gravity and other forces. Soil erosion involves three steps, viz. (i) detachment of soil particles from the main soil body, (ii) their transportation by splashing, floating, rolling, dragging, and (iii) their deposition at another place. The major factors which encourage detachment of soil particles are: rainfall impact, vegetation destruction, freezing and thawing, flowing water, and wind velocity. Rain drop splash, runoff water and blowing wind facilitate the carrying away of soil to distant places. In gullies, most of the loosening and cutting of soil are due to water flow, while on flat soil surfaces, beating action of rain drops causes the detachment of soil particle.

Soil erosion due to runoff is more on slopping and denuded lands. In high rainfall areas, loss of water may be as high as 50 to 60% of the annual rainfall. The loss of water through runoff could be reduced by suitable methods. The soil erosion accompanying runoff is usually more serious. The surface soil is taken away by the running water causing loss of soil along with nutrients, both native and applied. Since erosion starts with the loss of finer fraction of soil, the soil fertility is depleted. The loss of soil fertility and top soil makes the land unsuitable and unproductive for biomass production. In certain cases, the nutrient losses exceed the gains through renewal by the growing crops.

In deserts, the formation of sand dunes and their erosion due to high wind velocity are common phenomena. Under normal physical, hydrological and biotic equilibria, the erosion or removal of soil should be balanced with soil formation processes. If the balance gets disturbed due to biotic interference or natural factors, the eroding agencies become more active and cause accelerated soil erosion.

2.1. Geological Erosion

It refers to natural or normal erosion. It represents the erosion when the land is in natural equilibrium under the cover of vegetation.

Geological erosion takes place as a result of the action of water, wind, gravity and glaciers and its rate is so low that the loss of soil is compensated by the formation of new soil under natural weathering processes. Geological erosion may be considered a part of the natural soil forming processes which result in the existing form and distribution of soils. This kind of erosion does not pose any problem.

2.2. Accelerated Soil Erosion

When soil erosion exceeds the normal rate and becomes unusually destructive and unproductive, it is called accelerated erosion. When man or animal interferes with the existing balance in nature, by way of removal of vegetative cover, indiscriminate cutting of trees, overgrazing, faulty agricultural practices, etc., there is deterioration and loss of soil. This signifies accelerated erosion. Accelerated soil erosion has been a major process in degradation of land resources and has destroyed about 430 million hectares (Mha) of area in different countries or about 30% of the cultivated land of the world or 50% of the geographical area of India. This erosion often results in vast deposits from sedimentary rocks.

2.3. Extent of Soil Erosion in India

A precise estimation of the extent of land affected by soil erosion is still lacking. As per earlier estimates, out of 305.9 Mha of the reported area, about 50% (145 Mha) needs conservation measures and about 25% of the reported utilizable land is precariously degraded, needing immediate soil-conservation measures. This includes sub-humid and per-humid regions, Western Ghats, coastal and north-eastern hill regions afflicted with severe erosion, and facing soil loss of 20-40 tonnes/ha/year.

Agricultural land in major parts of the country suffers from the decline in fertility due to loss of soil matrix which produces runoff. These areas need conservation for sustaining production. For example, in Maharashtra, over 70% of the cultivated land has been affected by erosion in varying degrees and 32% of the highly eroded land is no longer cultivable. In the Sholapur district, nearly 17% of the land of medium depth (> 45 cm) was converted into shallow soils (< 45 cm) during 1870 to 1945. Similarly, in the districts of Akola, Buldhana and Yeotmal, the number of fields with less than 37.5 cm soil depth increased during the same period by 54%, 16% and 8%, respectively. As much as 2.68 Mha land is already under ravines scattered all over India and is a constant threat to the adjoining fertile cultivated lands.

In the Himalayan region, landslides and landslips pose a very serious problem due to improper land management. The landslide disasters in the winter of 1969 in the Darjeeling district of West Bengal, and in 1998 in the Pithoragarh district of Uttarakhand are eye-openers of future potential hazards. The erosion problem along the mountain roads is assuming alarming proportions. The Border Road Organization spends huge resources to stabilize the slopes along the highways for keeping these important lines of communication serviceable.

2.4. Consequences of Soil Erosion

Soil erosion has both on-site and off-site effects. It is the severest form of land degradation, which has assumed national as well as global importance.

2.4.1. Land Degradation

Soil degradation is a major threat to our food and environmental security. Many thriving civilizations have vanished in the past because of inadequate attention to land care. Various agencies have been constantly inventorizing and characterizing soil resources for drawing up land use and land developmental plans (Table 1). The estimates are at great variance due to differences in approaches and criteria for assessment. The National Bureau of Soil Survey and Land Use Planning, Nagpur (ICAR) has furnished the latest data on soil degradation on 1:250,000 scale for different states of the country. About 45% of the total geographical area of the country is degraded due to different degrading agents, in which

Table 1. Estimates of soil degradation in India by different agencies

Agency	Estimated degraded area (Mha)	Criteria for delineation
National Commission on Agriculture (1976)	148:09	Based on secondary data
Ministry of Agriculture (1978)	175.00	Based on National Commission on Agriculture (NCA) estimates
Society for Promotion of Wastelands Development (1984)	129.58	Based on secondary collected data
National Remote Sensing Agency (1985)	53.28	Mapping on 1:1 million scale based on remote-sensing techniques
Ministry of Agriculture (1985)	173.64	Land degradation statistics for the states
Ministry of Agriculture (1994)	107.43	Elimination of duplication of area
National Bureau of Soil Survey and Land Use Planning (1994)	187.70	Mapping 1:4.4 million scale based on Global Assessment of Soil Degradation (GLASOD) guidelines
National Rainfed Area Authority (NRAA) (2008)	120-72	Harmonization of various maps

more than 65% of the land degradation is due to water and wind erosion (NBSSLUP, 2004).

2.4.2. *Soil Degradation and Loss in Soil Productivity*

Soil degradation through the loss of topsoil is one of the major factors of low and unstable crop yields in the rainfed semi-arid to subhumid subtropics of India. The study on the effect of surface/topsoil depth on the yield of rainfed crops grown in an Alfisol soil has revealed that yield responses are up to 2.5-times higher in soils with deeper topsoils when rainfall in the critical period exceeds evapotranspiration than under drier conditions (Vittal *et al.*, 1990).

Various agronomic experiments have shown significant decline in yield of different crops with increasing degrees of erosion by water, slope per cent and decreasing soil depth. The estimated loss in crop productivity on soils showing different degrees of erosion by water has been shown in Table 2. The reduction in yield is significant when the soil depth decreases. The erosion classes may be modified with availability of more data on kind, degree and extent of problem vis-à-vis loss of productivity of different soils. It may also be noted that a moderate water erosion in alluvium-derived deep soils may show significantly less reduction in soil productivity as compared with the deep Red and Black soils (Table 2). Similarly, in deep alluvial silty loam soils at Dehradun, each centimetre desurfacing of soil caused 76 kg/ha decline in maize yield. This reduction is likely to be more severe in shallow soils.

2.4.3. *Siltation of Reservoirs*

The off-site effects of water erosion include siltation of reservoirs. Multipurpose reservoirs constructed at huge costs under the river-valley projects are getting silted at an alarming rate due to excessive soil erosion. It has been estimated that 5,334 million tonnes of soil (16.35 tonnes/ha/annum) is lost annually, which is 4-times higher than the permissible soil loss (4-5 tonnes/ha/annum). About 29% of the eroded material is permanently lost to the sea, 61% is dislocated from one place to another, and 10% is deposited in the reservoirs, resulting in loss of storage capacity by 1-2% per annum. The data on river valley projects on 17 medium and small reservoirs in India has shown that the rate of inflow of annual sediment rate is 3-fold (9.17 ha-m/100 km^2) in comparison to the designed rate of 2.93 ha-m/100 km^2/annum; thus reducing their life expectancy and hydro-electric power generation capacity to only one-third.

Table 2. Estimated loss of soil productivity due to erosion by water in different soils

Soil erosion class	Soil loss (t/ha)	Loss in productivity (%) in		
		Alluvium-derived soils (Inceptisols)	Black soils (Vertisols)	Red soils (Alfisols)
Nil to very slight	< 5	Nil	< 5	< 10
Slight	5 - 10	< 5	5-10	10 - 25
Moderate	10 - 20	5 – 10	10 – 25	15 – 50
Strong	20 – 40	10 – 25	25 – 50	> 50
Severe	> 40	25 – 50	> 50	N.A.

2.4.4. Floods and Flood Plains

The soil erosion, siltation and reduced transport capacity of rivers, *chos* and drains, and serious catastrophies, viz. floods and landslides cause large-scale damage to animal as well as human life and property. Productive agricultural land might go out of cultivation due to soil and nutrient erosion or silt deposition, in the flood plains. Flood water from the Brahmaputra river has been reported to carry a sediment load of 1500-30000 mg/L of soil, 6.4-25.8 mg/L of NO_3-N, 2.3-8.5 mg/L of PO_4-P, 15.4-33.8 mg/L of K_2O, 2.5-6.4 mg/L of Ca, 6.5-14.0 mg/L of Mg, 5.0-8.5 mg/L of SO_4^{2-} and 7.5-22.7 mg/L of micronutrients (Sharma and Sharma, 2004)

2.4.5. Environmental Pollution

Sediment is one of the major pollutants. In India, the situation is still worse, since the sediment load from agricultural lands not only continues unabated, but is also on the increase due to the fast rate of our developmental activities. If erosion continues unchecked at its present rate, we shall be left with the reclamation of soil rather than its conservation and management.

2.4.6. Changing Forest Cover

India has 2% land, 10% forests and 0.5% grazing area of the world, but has the burden of supporting 18% human and 15% cattle population. The recorded forest area of the country is 67.7 Mha. Out of this, 1.66% is very dense (more than 70% canopy), 10.12% is moderate dense (40-70% canopy) and 8.82% is open forest (10-40% canopy). Apart from that, 3.8 Mha is scrub or non-forest cover (canopy <10%) (FSI, 2005). About 29 Mha area is under degraded forests. The forest cover is declining due to the degradation of permanent pastures and open forests in the desert and arid regions.

2.4.7. Loss of Biodiversity

Loss of biodiversity is one of the major global concerns today. India's biodiversity is unique in the world. As many as 45,000 species of wild plants and over 77,000 of wild animals have been recorded, which comprise 6.5% of the world's known wildlife. An assessment of the loss of wildlife habitat in tropical Asia in 1986 showed that the country had only 615,095 km^2 out of its original wildlife habitat of 3,017,009 km^2, i.e. loss of 20%. Loss of seeds and propagules in the erosion fluxes, washing away of nutrients, run-offs, etc. depletes the biodiversity. During the past few decades, India has lost at least half of its forest, has polluted over 70% of its water-bodies and has degraded most of its coasts.

3. Factors Affecting Soil Erosion

Numerous factors affect soil erosion depending upon the local conditions with regard to physical, chemical and biological nature of the soil. The major factors affecting soil erosion are :

(i) Climate, especially rainfall and wind velocity – Their intensity in time and space

(ii) Topography – Slope of land, its nature, degree and length

(iii) Physical, chemical and biological characteristics of the soil

(iv) Nature of ground cover and land use

(v) Biotic interference due to human beings and animals

(vii) Conservation practices, and

(viii) Mass erosion, such as earthquakes, land slides, torrents (flash) floods, etc.

Mathematically, soil erosion may be depicted by functional Equation (1):

$$\text{Erosion} = f(cl, v, t, s, h, \ldots) \quad \ldots(1)$$

where, f, is the function of climate (cl), vegetation (v), topography (t), soil (s), human and animal activities (h).

3.1. Climate

Rainfall is by far the most important factor causing soil erosion by water. The soil erosion depends on the intensity, kinetic energy, amount, duration and frequency of rainfall. The intensity, duration and frequency of rainfall govern the rate and the volume of runoff. A light rain that can be easily absorbed in the soil causes no runoff and soil loss. When the intensity of rain is more than infiltration rate, it causes runoff and soil loss. The principal effect of rain drops is to detach soil (splash) and the principal effect of surface flow is to transport the detached particles. The interaction of kinetic energy (KE) [$\frac{1}{2} mv^2$] and rainfall intensity (say I_{30}) expressed as erosion index (EI_{30}) could be best related with rainfall erosion as per Equation (2):

$$EI_{30} = KE \times I_{30}/100 \quad \ldots(2)$$

where, EI_{30} is the erosion index; KE is the kinetic energy of storm, 210.3 + 89 log I; I_{30} is the maximum 30-min intensity of storm; and I is the rainfall intensity (cm/hr), which can be computed through automatic raingauge charts. The sequence of storms and rainfall distribution also determines the extent of soil erosion. Wischmeier and Smith (1958) had used precipitation and soil loss data from fallow plots to determine the best characteristics of rainfall for estimating storm soil loss. The results indicated that the rainfall characteristic best for estimating single storm soil erosion was the product of the total kinetic energy of the rainfall and the maximum rainfall intensity over a continuous 30-minute period during the rainstorm. This was also known as EI or the R factor (Laflen and Moldenhauer, 2003).

3.2. Topography

The land slope, its degree and length, is important in determining the extent of soil erosion. Higher the degree of slope and longer is its length, more is the soil erosion due to increased velocity of water running down the slope. If the land slope is increased 4-fold, the velocity of water flowing down the slope becomes approximately doubled. If the velocity of the runoff water is doubled, its energy, i.e. erosive power, increases 4-times, because the latter varies as the square of the velocity. Similarly, the quantity of material of a given size that can be carried is increased 32-fold (varies as the fifth power of the velocity), and the size of the particles that can be transported by pushing or rolling is increased 64-fold (varies as the sixth power of the velocity). Similarly, the velocity of winds and storms also affects soil erosion in the arid regions. Large sand dunes are transported from one place to another within no time due to wind action. Smith and Wischmeier (1957) evaluated the effect of slope and length on soil erosion for several locations. Data evaluated included slopes ranging from 1 % to 25%. The derived relationship was a quadratic relationship expressing the effect of slope on soil loss (Laflen and Moldenhauer, 2003) as:

$$S = (0.43 + 0.30s + 0.043s^2) / 6.613 \quad \ldots(3)$$

where, S is the slope factor and s is per cent slope. Smith and Wischmeier (1957) also evaluated the effect of slope length on soil erosion. They defined slope length as 'the distance from the point of origin of overland flow to either where the slope decreases to the point that deposition begins, or to the point where runoff enters a well-defined channel'. They have also found that soil loss per unit area varies as the

m^{th} power of slope length, expressed as Equation (4):

$$L = (\lambda/72.6)^{m} \qquad ...(4)$$

where, L is the slope length factor, λ is the slope length and m is the slope length exponent. It was observed that the value of m varies widely from year to year, even at times becoming negative. The effect of slope length on soil erosion is influenced by slope, vegetation, soil and management. The Universal Soil Loss Equation (USLE) used a value of 0.5, but values of 0.6 have been recommended for slopes steeper than 10%, and 0.3 for very long slopes under furrow irrigated conditions. For most situations, the length and slope factors have been combined into Equation (5):

$$LS = \lambda^{0.5}(0.0076 + 0.0053\,s + 0.00076\,s^2) \qquad ...(5)$$

3.3. Soil Characteristics

Erodibility of soil is influenced by its physical and chemical properties, including soil texture, structure, organic matter, nature of clay and amounts and kinds of salts present. Soil structure, texture, organic matter, infiltration and permeability influence the runoff and soil loss. Fine soils are more susceptible to erosion than coarse soils. The organic matter helps in binding the soil particles and improves the water holding capacity of soil. The three most significant soil characteristics which influence soil erosion are: (i) infiltration capacity, (ii) structural stability, and (iii) antecedent soil moisture. Various empirical equations like dispersion ratio and erosion ratio based on the ratio of sand + silt to clay and nomographs, have been used to estimate erodibility of soil. In India, the deep lateritic soils of Tamil Nadu and red soils of Bihar have the lowest rate of runoff, whereas, the alluvial soils of Gujarat and Uttarakhand have a very high rate of runoff.

3.4. Nature of Ground Cover and Land Use

The nature of vegetative cover on the soil surface such as crops, cropping systems and the accompanying vegetation, is a major factor influencing soil erosion. A thick mantle of plants reduces erosivity of rainfall and most of the water either quickly percolates through the soil or flows over the surface with non-erosive velocity. The areas which are not protected with thick cover of plants, are not able to absorb water effectively, because the falling rains shatter the soil surface. The fine soil particles go into a suspension and other particles form a thick mixture of water and soil, which quickly fills and clogs the tiny interspaces in the soil, reducing water infiltration and consequently increasing the runoff and soil loss. Moreover, the rooting system of vegetation also improves the binding capacity of the soil particles as well as soil infiltration. The effect of canopy is more when it is closer to the land surface. Hence, mulches being directly in touch with land surface are most efficient in reducing the runoff and soil loss, followed by grasses and crops.

The cropping and management factor (C) for the USLE is defined as the ratio of soil loss from a particular cropping and management to the soil loss from a continuously tilled fallow land.

If the land is left undisturbed under a natural cover, the runoff and soil loss are the least, which increase steeply when the vegetation is removed and the land is cultivated (Table 3).

Along with the loss of runoff water and soil, considerable amounts of plant nutrients are also lost.

3.5. Mass Landslides and Biotic Interference

Soil erosion due to loosening and cutting of soil on the river banks is accelerated during floods. Earthquake shakes and de-stabilizes the soil surface, thereby rendering it prone to erosion in the form of mass landslides. Faulty agricultural practices without proper care for resource conservation like shifting cultivation and free range grazing by cattle cause disturbance and removal of top fertile soil. This results in soil fertility depletion and makes land unsuitable for cultivation. Construction of roads and railway tracks in the hills produce mass wasting.

Table 3. Effect of land use on runoff and soil erosion

Treatments	Runoff (mm)	Soil loss (tonnes/ha)
Alluvial soils : 8% slope (Uttarakhand)		
Bare fallow	339	42.4
Cultivated fallow	889	156.0
Natural grasses	265	1.0
Maize-wheat (up-and-down cultivation)	870	28.5
Black soils : 0.5% slope (Rajasthan)		
Natural cover	33	0.3
Cultivated fallow	111	3.5
Sorghum (*kharif*)	79	2.9
Red soils : 2% slope (Bihar)		
Natural fallow	105	0.6
Overgrazed fallow	222	3.3
Maize (contour cultivation)	64	3.3

3.6. Conservation Practices

The Conservation Practice Factor (P), also called as the Erosion Control Practice Factor, is the ratio of soil loss for a specific practice to the soil loss with up-and-down hill culture. The initial practices considered for the USLE were contouring, strip cropping, contour strip cropping and terraces. These were expanded to include contour listing, controlled-row grade ridge planting contoured residue strips and terraces of various types.

3.7. K- Soil Erodibility

Wischmeier and Mannering (1969), using a rainfall simulator, measured soil loss and computed soil erodibility on the data adjusted to the unit plot as the slope of the linear relationship between the rainfall factor and soil erosion. They related soil erodibility to a number of variables using multiple regression techniques. A major finding was that very fine sand behaves more like silt than like sand. Using these results, Wischmeier *et al.* (1971) developed a soil erodibility monograph that has proven to be easily usable for estimating soil erodibility for most soils.

4. Water Erosion

It is the removal of soil from the land surface by water, including runoff from melted snow and ice and is one of the major causes of soil degradation (Table 4) (Velayutham and Bhattacharyya, 2000). Water erosion has been sub-divided into various types in relation to progressive concentration of surface runoff. Different types of water erosion are described below:

4.1. Splash Erosion

A falling rain drop is capable of generat-ing a force equals to almost 14-times of its weight. A rain drop produces three important effects during splash erosion: (a) its beating action breaks down the soil aggregates, (b) it detaches soil particles, and (c) its splash after touching the ground causes displacement of soil. Under low intensity and low rainfall conditions, if the dispersed material is not removed by the runoff, it forms a hard crust after drying. Under such conditions, germination of seeds is hampered and sometimes, if this condition develops just after sowing, the crop stand remains poor due to very low germination. The rain drops beat the soil with force and splash may take away soil even up to 2 metres.

4.2. Sheet Erosion

The erosion in which soil matrix is lost but remains undetected for a long period and a thin venier of soil is removed from large areas uniformly during every rain, even producing a runoff, is called sheet erosion. The eroding and

Table 4. Land degradation status in India

Type of degradation (million ha)	Area
1. *Water erosion*	148.9
(i) Loss of top soil	132.5
(ii) Terrain deformation	16.4
2. *Wind eorosion*	13.5
(i) Loss of top soil	6.2
(ii) Loss of top soil/terrain deformation	4.6
(iii) Terrain formation/overblowing	2.7
3. *Chemical deterioration*	13.8
(i) Loss of nutrients	3.7
(ii) Salinization	10.1
4. *Physical deterioration (waterlogging)*	11.6
Total degraded area	187.8

transporting power of sheet flow is a function of the depth and velocity of runoff for a given size, shape and quantity of soil particles or aggregates.

Sheet erosion can result from: (a) surface creeping of the soil in uniform layers and its deposition at another place or washing away along with runoff in the drainage system, (b) saltation, which results when water causes soil particles to hop or slip during their downward movement, and (c) suspension of the soil particles in runoff as they do not touch the soil surface. Sheet erosion continuously makes the soil shallower with a progressive decline in crop yields. It is generally neglected, although the soil deteriorates slowly and imperceptibly. Its existence, however, can be detected by the muddy colour of the runoff arising from the fields/areas. The most serious sheet erosion occurs in red and black soils, occupying 69 Mha and 67 Mha of land, respectively in the country.

4.3. Rill Erosion

It is the removal of soil by water from small channels which develop due to concentration of surface flow along the slope. It generally develops on bare and unprotected land where soil conservation measures are not adopted. In advanced stage, it may take the shape of gullies. The rill erosion is an intermediary stage between sheet erosion and gully erosion. The rill can be removed by normal tillage operations. Generally, these rills vanish after cultivation, but may reappear with ensuing rains.

4.4. Gully Erosion

It is the advanced stage of rill erosion which cannot be obliterated by normal tillage operations. Rills with more than 30 cm depth are generally called gullies. Gullies obstruct the operation of farm machinery and tends to deepen and widen with every heavy rainfall. They cut up large fields into small fragments and in course of time, make them unfit for cultivation. The rate of gully erosion depends on several factors, viz. runoff producing characteristics of the watershed, drainage area, soil characteristics, channel alignment, slope and vegetative cover on the ground, etc. Gully erosion indicates misuse, neglect and mismanagement of land over a long period of time.

5. Special Forms of Erosion

Besides the four main water erosions described above, there are some special forms of erosion also. These are discussed below:

5.1. Landslides or Slip Erosion

During monsoon season or heavy down-pour, the hills get saturated with water, resulting in instability of the land mass. The complete surface portion of soil may slips down from its actual position causing landslides. Landslides are very common in hills and huge quantities of soil are washed away in streams and rivers. Hills devoid of vegetation are more prone to slip erosion, causing damage to agricultural lands, orchards, communication systems and human lives. Minor landslips occur during the drying phase in the months of May and June, especially in the sandy hills of Shiwaliks.

5.2. Stream Bank Erosion

It is caused by streams and torrents, also called *chos*, cutting their banks and adjoining fields. It is mainly due to runoff flowing over the side of the stream banks or by scouring and undercutting below the water surface, the latter process being more serious. It is influenced by deforestation and overgrazing. Scour erosion is influenced by the velocity and direction of water flow, depth and width of channel and soil texture.

5.3. *River Bank Erosion*

This is a common phenomenon in the rivers of the eastern and western Himalayan regions. During floods, the rivers undermine their banks and big chunks of land mass are engulfed by flood water. This leads to broadening of river beds and changes in their courses.

5.4. *Slumping*

It is a geological process and is one of the most common types of slippage. It may be defined as the downward slipping of a mass of unconsolidated matter or rock, moving as a unit or as several subsidiary units. It is an important process in widening of the stream channels and gullies under high rainfall areas.

5.5. *Coastal Erosion*

The strong waves of sea strike against the seashore causing large-scale soil erosion. In this case, erosion is a combined effect of wind and water.

6. Estimation of Soil and Water Erosions

Universal Soil Loss Equation (USLE) has been designed to predict soil loss from agricultural lands under various agro-climatic and topographical situations. The essence of the USLE is to isolate each variable and reduce its effect to a number so that when the numbers are multiplied together, the answer is the amount of soil loss.

The Universal Soil Loss Equation is presented by expression (6) (Wischmeier and Smith, 1978):

Net

$$\boxed{A = R \times K \times L \times S \times C \times P} \qquad \ldots(6)$$

where,

A = Computed soil loss per unit area,

R = Rainfall factor, is the number of erosion-index units in a normal year's rain. The erosion index is a measure of the erosive force of specific rainfall,

K = Soil-erodibility factor, is the erosion rate per unit of erosion index for a specific soil in cultivated continuous fallow, on a 9% slope, 22 m long,

L = Slope-length factor, is the ratio of soil loss from the field slope length to that from a 22-m length on the same soil type and gradient,

S = Slope-gradient factor, is the ratio of soil loss from the field gradient to that from a 9% slope,

C = Cropping-management factor, is the ratio of soil loss from a field with specified cropping and management to that from the fallow condition on which the factor K is evaluated, and

P = Erosion-control practice factor, is the ratio of soil loss with contouring, strip-cropping or terracing to that with straight-row farming, up and down slope.

6.1. *Soil Erodibility Factor*

The soil erodibility factor (K) in the USLE is related to the rates at which different soils erode. The soil erodibility is different from soil erosion in the sense that the total erosion may be influenced by other factors like rainfall, crops, management of the lands, etc. However, a soil may erode relatively more than the other, although the rainfall, crop condition, etc. may be the same in these two soils. This difference which is caused by the inherent soil properties is referred to as "soil erodibility". The soil properties that influence erodibility are texture, structure, permeability, infiltration, organic matter and mineralogy. Usually, the deep, permeable, coarse sands are the least erosive.

To obtain the value of K, soil loss is required to be measured from a unit plot of 22.13 m × 1.83 m size having uniform slope of 9% in a continuous fallow, tilled up and down the slope. The soil loss obtained from above unit plot is divided by yearly EI_{30}, where EI_{30} is the cross-product of the total kinetic energy and the maximum 30-minuie intensity (I_{30})

(Wischmeier, 1959) to obtain the soil erodibility factor (K).

In case the plot gradient and length are different than the defined unit plot, the soil loss may be adjusted by dividing it with the topographic factor (LS).

The value of K can be estimated from Equation (7):

$$K = \frac{\text{Total adjusted soil loss}}{\text{Total } EI_{30}} \quad \ldots(7)$$

6.2. Estimation of Sedimentation Yield

For estimation of sedimentation yield in runoff plots/ watersheds, the first runoff is measured through the flumes with the help of stage level recorders. A portion of the total runoff can then be collected with the help of devices like Coshocton wheel and this runoff sample is then used for the determination of soil loss from the plots/ watershed. The runoff is calculated using Equation (8):

$$\text{Runoff (mm)} = \frac{\text{Runoff (litres)}}{\text{Area of plot (m}^2\text{)}} \quad \ldots(8)$$

For estimating the soil loss, the runoff collected in the tank is churned thoroughly and a small runoff sample of about 500 mL to 1000 mL is drawn. The sample is then evaporated in the laboratory and the amount of soil is measured gravimetrically to give soil loss in g/litre. This quantity is multiplied by the total runoff volume and divided by 10^6 to give total soil loss in tonnes per plot. It is further multiplied by the suitable factor as per size of the plot to get the soil loss in tonnes/ha, for that particular storm. The soil losses from all the storms during one year are added to get the annual soil loss in tonnes/ha/year (Singh *el al.*,1990).

7. Development of Universal Soil Loss Equation (USLE)

The evolution of Universal Soil Loss Equation (USLE) is one of the most significant developments in soil and water conservation. It is an empirical technology that has been developed in an evolutionary manner during about past 60 years and is still undergoing evolution with the development of various revisions (Laflen and Moldenhauer, 2003). The USLE is the contribution of many individuals over a very long period of time. The period from 1930 to 1942, was the golden period of conservation research. Most of the work related to erosion prediction was conducted by USDA scientists (Soil Conservation Service). Duley and Ackerman (1934) had mentioned about the effect of slope and length on soil erosion but no relationship was described. Zingg (1940) evaluated data from field experiments under natural rainfall and from rainfall simulation experiments and proposed the relationship (9):

$$X = C\,S^m L^n \quad \ldots(9)$$

where, X is the total soil loss from a land slope of unit width, C is a constant of variation, S is the land slope (%), L is the horizontal length of land slope and m and n are exponents. Soil loss per unit area from a land slope of unit width may be expressed as per Equation (10):

$$A = C\,S^m L^{n-1} \quad \ldots(10)$$

The Zingg's equation was expanded by Smith (1941) to Equation (11):

$$A = C\,S^{1.4} L^{0.6} P \quad \ldots(11)$$

where, P is the ratio of soil loss with a mechanical conservation practice to soil loss without the practice. Smith (1941) used Equation (11) with measured annual values of A, S and L from individual plots to compute C values for various treatments. Browning *et al.* (1947) developed the "erodibility factor". Musgrave (1947) used vegetal cover factor that expressed relative soil erosions for different vegetative covers.

$$\text{Soil loss} = (R)^{1.75}\,(K)\,(L)^{0.35}\,(S)^{1.35}\,(C) \quad \ldots(12)$$

where, R is 30-minute maximum rainfall, K is soil erodibility, L is the length, S is the slope and C is the vegetal factor.

In an example presented for the soil (erodibility of 0.33 inches/year), where 30 minute maximum rainfall was 1.35 inches, slope was 5%, length was 150 feet and the crop was wheat (vegetal factor 0.2), the average predicted soil loss was :

$$\text{Soil loss} = (1.35)^{1.75}\,(0.33)\,(150\text{ ft})^{0.35}\,(5)^{1.35}\,(0.2) \quad \ldots(13)$$

$$\text{Soil loss} = 5.67\text{ tonnes/acre/year} \quad \ldots(14)$$

Gavrilovic (1962; 1970; 1972; as described by Globevnik *et al.*, 2003) proposed an analytical relationship for determining the annual volume of detached soil due to surface erosion, as Equation (15):

$$W_p = {}^\wedge P\,F_w\,K_t\,\sqrt{K_z^{\,3}} \quad \ldots(15)$$

where, P is the average yearly precipitation, F_w is the drainage area (km^2), K_t is the temperature coefficient, and K_z is the erosion coefficient. The equation for K_t is :

$$K_t = \sqrt{(0.1 + T/10)} \quad \ldots(16)$$

where, T is the average yearly temperature. The K_z is given by Equation (17):

$$K_z = K_y\,K_x\,(K_o + \sqrt{F_{sl}}) \quad \ldots(17)$$

where, $\sqrt{F_{sl}}$ is the average slope of the basin (%), K_y is the soil erodibility coefficient, K_x is the soil protection coefficient, and K_0 is the erosion and stream network development coefficient. Various soil loss equations developed by different workers between 1940 and 1997 are presented in Table 5.

8. New Developments in Predicting Soil Erosion

8.1. USLE, RUSLE and WEPP

By 1980, there was considerable interest in updating USLE. There was a successful development of a field-scale model for Chemicals, Runoff, Erosion from Agricultural Management Systems (CREAMS) (Kinsel, 1980). Consensus was arrived to revise the USLE [eventually named as Revised Universal Soil Loss Equation (RUSLE)] and the other to begin planning for a technology [which became Water Erosion Prediction Project (WEPP)] to replace the empirical technology for erosion prediction.

8.2. Developments in Predicting Erosion from Ungauged Areas

Simulating erosion, transport and deposition of sediment involve complex interactions of precipitation, surface and sub-surface hydrological processes, soil properties, land cover and topography. For this kind of complex spatial process, conventional rainfall-runoff models are of little use (Xu *et al.*, 2003). Although much has been achieved in the field of hydrological research, the issue of how to reliably predict the erosion and deposition of sediment

Table 5. Equations in the development of soil erosion prediction

Scientist/Acronymous	Year	Equation
Zingg	1940	$A = C' L^{0.6} S^{1.4}$
Smith	1941	$A = C'' L^{0.6} S^{1.4} P$
Browning *et al.*	1947	$A = C''' L^{0.6} S^{1.4} P$
Musgrave	1947	$A' = (P_{30}/1.25)^{1.75}\,K'\,(L/72)^{0.35}\,(S/10)^{1.35}\,C^*$
USLE	1965	$A = EI_{30}\,K\,(L/72.6)^{0.5}\,(0.065+0.045+0.0065\,S^2)\,C\,P$
USLE	1978	$A = EI_{30}\,K\,(L/72.6)^{0.5}\,(65.4\sin^2\Theta + 4.56\sin\Theta + 0.065)\,C\,P$
RUSLE	1997	$A = EI_{30}\,(L/72.6)^m\,(a\sin^2\Theta + b)\,C\,P$

A = Soil loss in tonnes/acre; A′ = Soil loss in inches/year; C′, C″, C‴ = Coefficients; C*= Vegetal cover factor; P_{30}= Maximum precipitation amount (inches) falling in 30 minutes in a storm; K′, K = Soil erodibility factors; L = Slope length in feet; S = Slope in per cent; Θ = Slope angle in degrees; C = Cropping management factor; E = Storm rainfall energy in hundreds of foot-tonnes per acre; I_{30} = Maximum rainfall intensity in a 30-minute period within a storm in inches per hour; P = Conservation practice factor; M = Exponent on length term-values depend on slope or slope and rill/inter-rill ratio; a, b = Coefficients in function making up slope term-values depend on slope.
Adopted from Laflen and Moldenhauer (2003).

in ungauged river basins is still a big challenge. Simulating erosion and sedimentation usually requires prediction of spatially variable hydrological processes at a fine resolution (Xu *et al.,* 2003). Overland flow generally detaches and transports large amounts of sediment, depending on ground slope, soil characteristics, vegetation cover and conservation practices. In a spatially distributed model, the spatial variability within the basin may be properly accounted for (Wigmosta *et al.,* 1994). An economical and reasonably efficient alternative would be to monitor the major basins with a reliable gauging system and to create a network of representative experimental basins for predictive purposes in medium and small sized basins (Toebes, 1965).

Many countries or certain areas in some countries face shortage of water, and at the same time, lack scientific support for water management. 'Prediction in Ungauged Basins' (PUB) is a recent initiative undertaken by the International Association of Hydrological Sciences (IAHS). Many countries and regions do not have sufficient hydrological stations to construct hydrological models with a high degree of accuracy. The International Hydrological Programme (IHP), World Climate Research Programme (WCRP), and International Geosphere-Biosphere Programme/ Biospheric Aspects of the Hydrological Cycle (IGBP/ BAHC) are all concerned, at some level, with research in ungauged basins (Jun and Ge, 2002; Zhu, 2002). PUB is a unique scientific endeavour that IAHS has conceived, initiated and is implementing. The aim of PUB is to develop hydrological sciences so that basin hydrology can be predicted using the limited information available for any basin, and to reduce uncertainty associated with such predictions (IAHS, 2003). At the same time, PUB has a social mission to provide the necessary hydrological information, especially discharge data, for ungauged or poorly-gauged basins, where those data are urgently needed.

The PUB initiative aims to increase our understanding of how hydrological systems work and can best be described by mathematical models. Success is to be measured by the reduction of uncertainty in the predictions from such models. Mismanagement of the rainwater has caused enormous soil erosion from the basins and silting of river beds, resulting in floods in many parts of the world. We are faced with a major water crisis that has emerged as a result of population growth, increase in water demand, environmental degradation and climate change. Increasing water shortages, flood hazards and groundwater contamination are problems intensifying during the recent past. There are numerous ungauged or poorly-gauged basins. It is especially true in developing countries where data are urgently needed to enable water resources to be developed and managed (IAHS, 2003). Numerical simulation models will be the new way for PUB (Jun *et al.,* 2003).

PUB Science Agenda

1. Exploration of ways to characterize the heterogeneity of landscape properties and climate inputs;
2. Development of general model framework for heterogeneity and predictive uncertainty;
3. Conducting model inter-comparisons in selected gauged basins to investigate uncertainty resulting from the choice of model structure;
4. Investigation of methods for efficient assimilation of gauged and/or remotely sensed data to constrain predictive uncertainty;
5. Promotion of process studies and field experiments to advance process understanding and conceptualizations with the aim of reducing uncertainty;
6. Advancing our understanding and predictions of the effects of hydro-climatological variability and change; and
7. Transforming the available global research products into hydrological information useful for local and regional water resources management.

Objectives of PUB

PUB is a policy-relevant hydrological science activity with the following objectives (IAHS, 2003):

- To advance our ability to predict with confidence the fluxes of water out of drainage basins worldwide in the areas of societal and ecological relevance in different biomes of hydro-climatic regions, and to verify predictions with data from selected basins;
- To advance the scientific foundations of hydrology, including understanding the climatic and landscape controls on the natural variability of hydrological processes, and the impact of human induced alterations to climate and landscape;
- To increase awareness about the value of data, especially of the measurement of hydrological variables, for the management of water resources around the world, and to demonstrate the importance of existing gauging systems and the need for targeted gauging to enhance currently inadequate or non-existent data sources;
- To advance technological capability around the world, so that predictions in ungauged basins are firmly based on local knowledge of the climatic and landscape controls on hydrological processes, along with access to the latest data sources; and
- To promote capacity building activities in the development of appropriate scientific knowledge and technology for areas and communities where they are needed.

Sharma and Sharma (2003) evolved a mathematical model to predict soil erosion from ungauged basins; based on the slope, rainfall, vegetation cover and soil texture. The soil erosion prediction model involves a partial regression equation of the form (18):

$$S_e = a + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 \qquad \text{...(18)}$$

where, S_e is the soil erosion (t/ha) and b_1, b_2, b_3 and b_4 are the partial regression coefficients for slope (X_1) in %, annual rainfall (X_2) in cm, clay content (X_3) in %, and vegetation cover (X_4), respectively.

Equation (18) was developed using the Dolittle method, which gave a reasonably high degree of accuracy in prediction or estimation of soil erosion. The vegetation is the only independent variable for which the values (1-5) have to be based on visual estimates. For uniformity, the classification used for the vegetation values was: 1, bare soil surface with soil stirred or ploughed; 2, scrubs or effective covered area below 25%; 3, cropped soil surface or effective covered area of 25-50%; 4, open forest vegetation or effective covered area of 50-75%; and 5, dense forest with trees and bushes. The model given by Equation (19):

$$S_e = 41.73 + 0.181 \times \text{slope (\%)} + 0.046 \times \text{rainfall (cm)} - 0.387 \times \text{clay (\%)} - 8.125 \times \text{vegetation (1 to 5 scale)} \qquad \text{...(19)}$$

More available data for calculating the values of the coefficients may result in an increase in the predictive power of the equation. In principle, the model can be used for predicting soil loss by flowing water, under a wide range of climatic and physical conditions.

An explicit finite difference scheme for erosion and sediment transport on upland area of a watershed was derived by Aksoy (2003). The derivation ends up with a linear partial differential equation. Calibration of parameters is of great importance for ungauged basins, where data do not exist. Erosion by rainfall is usually related to the rainfall intensity (R) as:

$$E = \lambda P^{\delta} \qquad \text{...(20)}$$

where, λ and δ are parameters to be determined at the calibration stage of the model, λ is the soil detachability coefficient, which has a dimension that depends on the value of δ, which generally equals to 1 or 2 (Aksoy, 2003). The model derived is given by Equation (21):

$$E = \lambda R^{\delta} + \sigma\,[\eta\,(\gamma h S)^{\varepsilon} - \rho_s C_s \alpha h] \qquad \text{...(21)}$$

where, E is erosion; λ and δ are dimensional rainfall erosion coefficient and rainfall erosion exponent, respectively; σ is transfer rate coefficient (m^{-1}); η is dimensional coefficient; γ is the specific weight of water; h is the flow depth; S is the topographical slope (% slope/100); ε is the exponent; ρ_s is the specific mass of sediment (kg/m^3); C_s is the volumetric sediment concentration, and α is the coefficient. The performance of the model on the hill slope indicates that it has potential for application on watershed scale.

8.3. Adjusted Tolerable Soil Loss for Conservation Planning

The tolerable soil loss (T) has been defined in several ways (McCormack *et al.*, 1982; Lal, 1988; ISSS, 1996), but it is generally considered as the upper limit of soil erosion that can be allowed without degrading the long-term productivity of a specific soil. The T-value is also sometimes called "permissible soil loss" (Kok *et al.,* 1995). If erosion rates are higher than T, they are considered unacceptable and should be reduced. In India, a generalized T-value of 11.2 Mg /ha/yr is used for different sets of conditions to develop specific best resource management practices for each specific area. Mandal *et al.* (2006) have applied a quantitative model to sum up the overall soil performance to define the current state of soil resource for the north-west Himalayas of India in which scaling functions were used to convert soil parameters to a 0 to 1 scale. The normalized values were then multiplied by the appropriate weighting factors, based on relative importance and sensitivity analysis of each indictor. A categorical ranking of soil as 1, 2 or 3 was given to a soil group and general guideline was developed by following USDA Natural Resource Conservation Service (NRCS) to calculate soil loss tolerance for each soil group by using effective soil depth. Adjusted T values for the area ranged between 5.0 and 12.5 Mg/ha/yr compared to 11.2 Mg/ha/yr. Hence, the use of adjusted T-values is useful in improving conservation planning, meeting erosion control regulations for the development of sustainable farm operations, and improving watershed management.

8.4. Assessment of Erosion Hazards for Conservation Planning

Globally, vast areas face serious erosion and land degradation problems. Various erosion hazards occurring in the form of rills, gullies and torrents in arable and non-arable areas can be assessed and mapped for the purpose of resource conservation. Remote sensing techniques (Lillesand and Kiefer, 1994) are operationally useful for soil resource inventory and natural resource mapping at a scale of 1:50,000. They provide real lime and accurate information related to landuse/soil (Manchanda and Kudrat, 1999). For mapping the existing land uses and erosion hazards of a hilly watershed from Uttarakhand Himalaya, Dadhwal *et al.* (2007) employed two approaches: (i) visual interpretation of the merged FCC, and (ii) the digital classification of LISS-III data. Erosion hazard sites in the watershed were identified covering topographical variations from top to bottom. Index-based method was used for soil, landuse, slope and proximity to drain for the hazard assessment. Stream bank, rill and gully erosions were found as the dominant form of degradation associated with the drainage net work.

Different land uses, viz. open scrub, mixed forest and agriculture were considered to assess and understand their role towards degradation. Erosion hazard mapped by digital classification showed the maximum area under moderate rill erosion (e_2), followed by high (e_3) and very high (e_4) hazards. The average accuracy of erosion hazards mapped by remote sensing data was > 80%, inclusive of all the available land uses in the watershed. Thus, index based method for assessing erosion hazards has been found satisfactory. The problems in assessment with remote sensing data are mainly due to infrared reflectance of the prevailing vegetation which masks the effect of other reflectance, while interpreting the erosion hazards.

9. Wind Erosion

The south-western desertic zone of India covers about 28.6 Mha of area (about 8.7% of the geographical area of the country). The annual rainfall in the area ranges from 100 to 500 mm against the annual potential evapotranspiration of 1600 to 2000 mm. Wind erosion is mainly due to a strong wind regime, low atmospheric humidity, high solar radiation and single grain structure of sandy soil. About 14% and 28% of the area of the arid zone of Rajasthan suffers from severe and moderately severe form of wind erosion, respectively. The wind erosion under different land-use situations is shown in Table 6 (Dhir, 1989).

It occurs in arid and semi-arid areas which are devoid of vegetation, and where wind velocity is high. The single-grained sandy soil particles on the land surface are lifted and blown off as dust-storms. When the velocity of dust-bearing wind retards, the coarser soil particles are deposited in the form of dunes, sometimes rendering fertile lands unfit for cultivation. The finer particles are carried away to farther distances. The fertile soil is blown away by winds and the subsoil gets exposed, as a result the productive capacity of the soil is considerably reduced. Areas susceptible to wind erosion were delineated on the global as well as country levels. The Thar desert of the western Rajasthan shows high soil losses due to wind erosion. Deep ploughing of sand plains lost more than 3,000 tonnes soil/ha during a sand storm in 1987, whereas similar areas with 10-12% plant cover or with higher cloddy surface, suffered negligible soil loss.

9.1. Wind Erosion Processes

The abrasive action of the wind causes detachment of soil particles, followed by their transportation to distant places. The impact of high speed soil particles dislodges even other soil particles from the soil aggregates. The dislodged soil particles move by three phenomena: saltation, suspension and surface creep, usually occurring simultaneously.

9.1.1. Saltation

The movement of soil by wind in a series of short bounces along the surface of land carrying fine particles of 0.1 to 0.5 mm diameter is called 'saltation'. It is caused by the direct pressure of wind on soil particles and their collisions with other particles. After being pushed along the ground surface by the wind, the particles leap almost vertically in the first stage of saltation. Some grains rise only to small heights and, others leap up to 30 cm or even higher, depending directly on the wind velocity and the rise from the ground. In this process, the particles drop down within the eroded area or its immediate vicinity. Depending on the nature of the soil. wind speed and vegetative cover, saltation accounts for 50 to 75% of the total soil movement through wind erosion.

9.1.2. Suspension

The movement of very fine soil particles of less than 0.1 mm in diameter into the air and remaining suspended there is called suspension. The particles are kicked up into the air by the action of particles in saltation. The movement of fine dust in suspension is completely governed by the characteristic movement of the wind. The suspended material is carried to long distances from its original location and thus there is a considerable loss to the eroded area, accounting for about 40% of total soil movement.

9.1.3. Surface Creep

The soil particles varying between 0.5 mm and 1.0 mm in diameter, are too heavy and move along the surface resulting in the formation of surface creep. The movement through

Table 6. Soil loss due to wind erosion on flat sandy plains under different situations

Land use	Mean soil loss (tonnes/ha)
Cropped and left uncultivated a year before	80
Cropped and ploughed	1000
Long fallow	50
Degraded pasture	90
Dunes	200

surface creep is the outcome of the kinetic energy de-rived from the impact of particles moved in saltation. The particles raised from the ground move by rolling and sliding along the surface of soil drop down within the eroded area or its immediate vicinity. It accounts for about 5% to 25% of the soil erosion through wind.

9.3. Factors Affecting Wind Erosion

The major factors affecting wind erosion are: (i) climate, (ii) soil, and (iii) vegetation. The climatic parameters influencing wind ero-sion are: rainfall. Temperature, wind, humidity, viscosity and intensity of the air. The amount and distribution of rainfall and its effect on soil moisture regime are the most important factors. The principal characteristics of wind affecting erosion are: velocity, direction, duration and turbulence. Soil characteristics affecting wind erosion are: texture, structure, density of soil particles, organic matter, and surface roughness. The vegetative factors that affect wind erosion are: kind of vegetation, height, density, etc. Living plant roots and tops are more effective in retarding wind erosion.

9.4. Control of Wind Erosion

The basic principles in the control of wind erosion are breaking of wind velocity at the soil-atmosphere interface and the reduction in soil erodibility. This can be achieved through vegetation or cultural practices. The wind erosion control measures include: (i) creation of permanent grass strips across the prevailing wind direction, (ii) roughening of the soil surface to trap some of the moving particles, (iii) provision of stubble mulch, (iv) tillage to provide cloddy surface condition which is at right angles to the wind direction, (v) strip cropping which can prove useful in reducing the effect of wind, and (vi) wind-breaks with tree linings which are effective in reducing wind velocity for short distances.

9.5. Estimation of Wind Erosion

Wind erosion can be estimated by using Equation (22), given by Chepil and Woodruff (1963), which predicts the relationship between annual soil loss by wind erosion from a given field and the five factors influencing wind erosion:

$$E = f(I \times K \times C \times L \times V) \qquad \ldots(22)$$

where,

E = Average annual soil loss in tonnes/acre,
I = Soil erodibility index indicated by soil aggregates greater than 0.84 mm in diameter and percentage of land slope,
C = Climatic factor indicated by wind velocity and surface soil moisture,
K = Soil surface roughness,
L = Unsheltered field width measured along the direction of the prevailing wind, and
V = Vegetative cover.

Equation (22) is useful in determining (i) potential wind erosion on any field under existing conditions, and (ii) conditions of surface roughness, soil cloddiness, vegetative cover, sheltering or width and orientation of field necessary to reduce wind erosion to tolerable level.

10. Extent of Soil and Nutrient Erosion due to Shifting Cultivation (*Jhuming*)

Major physical manifestations of the processes causing degradation are the removal of top soil through water and wind erosions, reduced capacity of soil to hold water, increased susceptibility to runoff and gradual increase in the loss of nutrients. The process of soil erosion begins when a farmer enters his field either for selection of site for cultivation or cutting of the forest vegetation. There is a considerable loss of soil even due to the movement of farmers on hill slopes, earthworm castings, dibblings, etc. The problems of soil erosion in shifting cultivation are mainly of splash and wash. Soil erosion from hill slopes (60 to 70%) under first year, second year, abandoned *Jhum* (shifting cultivation) and bamboo forest was 147, 170, 30 and 8 tonnes/ha/yr, respectively. The second year of shifting cultivation is more hazardous than that of the first year. It has been estimated that about 88.3 million tonnes of soil is lost annually in the North-Eastern states of India alongwith 10.7 thousand tonnes of N, 0.4 thousand tonnes of P and 6.0 thousand tonnes of K (Table 7) (Sharma and Prasad, 1995). However, wide variations in soil and nutrients losses are found, depending on the slope gradient, nature of the soil, crop canopy, agricultural activities, etc. Improper land management in hills can cause annual soil loss of about 80 t/ha/yr as compared to the national average of 16.35 t//ha/yr. The permissible soil loss limit is from 4.5 to 11.2 t/ha/yr under different soil types. About 5334 million tonnes of soil is being eroded annually due to agricultural and associated activities in the country and 29% of the eroded material is permanently lost into the sea (Dhruva Narayana, 1993). The loss of soil nutrients through water erosion is estimated to be 5.4 to 8.4 million tonnes.

11. Soil Erosion *vis-à-vis* Carbon Sequestration

Growing of trees and crops as well as rearing of animals on the same piece of land simultaneously or sequentially is viewed an optimum strategy for resource conservation and environmental security. Sustainable development and management of land-use system through such innovations not only meet the multiple needs for food, fodder, fuelwood, fibre, fertilizer, timber, gum, etc. but guarantees economic and environmental security also for safe and protected habitats for human beings and other living organisms. Indian soils are largely carbon depleted but can be brought back to their native carrying capacity by such interventions. Hence, sustainable forest/tree-crop/animal combinations are very important for the environmental conservation, as they help in regulating water cycle, protect against erosion, recharge groundwater, improve soil fertility, conserve soil and water, moderate climate, sequester carbon, conserve biodiversity, combat desertification and degradation, provide perpetual flow of clean water in streams, improve soil health, etc. They play an important role in carbon sequestration and may hold even up to 100-times more carbon per unit area as compared to purely agricultural lands (Houghton and Hackler, 1994). Though the major part of the carbon stored is held in the above-ground biomass, soils are also important reservoirs of carbon. Thus, forest/tree- crop systems serve as carbon sink/source, depending on the management system and also protect the soil from erosion losses (Dadhwal and Kumar, 2004).

11.1. Carbon Emissions

Tropical deforestation is responsible in part for the increasing concentration of CO_2 in the atmosphere (Houghton, 1990). Estimates of net release of carbon at the global level depict wide variations, ranging from 0.4-1.6 GtC/ year (Detwiler and Hall, 1988) to 1.1-3.6 Gt C/ year (Houghton, 1991). Carbon emissions can be from deforested as well as degraded lands also (Ravindranath *et al.*, 1997).

Table 7. Annual soil and nutrient losses in different states of North-Eastern region due to shifting cultivation

State	Soil loss (million tonnes)	Nutrients loss ('000 tonnes)		
		N	P	K
Arunachal Pradesh	14.49	2.04	0.058	1.01
Assam	12.32	0.98	0.061	0.64
Manipur	20.43	2.68	0.082	1.53
Meghalaya	14.15	1.90	0.042	1.06
Mizoram	13.04	1.69	0.065	0.98
Nagaland	7.60	0.87	0.040	0.52
Tripura	5.95	0.51	0.024	0.31
NE Region	88.34	10.67	0.372	6.05

Source: Sharma and Prasad (1995)

As per estimates, 13.5×10^6 t C is released from combustion. There is no balance between the total carbon stored in the felled vegetation and the total carbon released from deforestation. In addition to carbon release from deforestation, degradation of the existing forests also contributes to the carbon release. This degradation may be due to grazing, fire, death due to diseases and pests, illegal removal of timber, non-sustainable harvest of firewood or timber, etc. (Houghton, 1991; Flint and Richards, 1991). The analysis carried out by Flint and Richards (1991) and Houghton (1991) for southern Asia (including northern parts of India) for the period 1950-1980 has indicated a degradation ratio of 1.54, which means that for every tonne of carbon released into the atmosphere through deforestation, an additional 0.54t of C is released from the degradation of standing forests which amounts to 15.4×10^6 t C. Of this, about 50% is assumed to be used as firewood, 25% for long-term purposes, and 25% decomposes.

In India, about 0.99×10^6 ha area is annually subjected to shifting cultivation (FSI, 2005). The fallow period has also been shortened and considering this, a net emission of 1.56×10^6 t C is estimated after accounting for the cutting of secondary forests in fallow areas, uptake in the fallow, and degradation or burning of new areas.

11.2. Carbon Storage and Uptake

Carbon storage is estimated by taking 50% of the biomass as carbon and is based on the soil organic content in the top 30-cm soil. Total carbon stored in Indian forests is estimated at 9585×10^6 t C, of which vegetation accounts for 44% and soil, the remaining 56% (Ravindranath *et al.*, 1997).

While considering the net carbon release, carbon uptake and storage in forests, and tree plantations, e.g. *eucalyptus, casuarina*, etc. are also considered. But, large tracts of forests in India have been subjected to anthropogenic pressures over centuries and thus are at various stages of succession. The C-accumulation is estimated using the data on standing biomass.

11.3. Balance between Carbon Emission and Sequestration

It is established that the carbon flux is nearly balanced in India because of the reason that the Forest Conservation Act, 1980, prescribes that no land should be alienated without the consent of the Central Government. Moreover, in the late-1970s, the high level of subsidies enjoyed by the forest industries were gradually reduced and farmers have been encouraged to plant tree crops. The states like Haryana and Gujarat have initiated measures to create village-based management systems involving local people in sustainable use and restoration of degraded lands (Ravindranath *et al.*, 1997).

11.4. Limitations of Carbon Emission Estimation in India

The carbon emission estimates in India are based on the standing biomass determined using the crown cover estimates and a few published studies on the standing biomass. Similarly, the C-uptake is estimated to be in the range of 1.25-2.84% of the standing biomass. Therefore, any changes in the estimates of crown cover, standing biomass and annual productivity will also change the net emission rates (Ravindranath *et al.*, 1997).

11.5. Agroforestry and Carbon Sequestration

Trees growing on non-forest areas meet a major part of the demand for fuelwood and timber in the rural areas which envisages that agroforestry has great potential in carbon sequestration and resource conservation in India. But, the constraints in agroforestry on marginal lands include low income of farmers, low productivity of land, heavy grazing, insecure tenurial rights, etc. (Singh, 2001). Despite problems, agroforestry is picking up and about 50% of the planting done in India after 1980 is reported under agroforetry (MOEF, 1989). Thus, agroforestry is picking up an important opportunity for C-sequestration. Plantations on marginal and degraded lands, on bunds and boundaries in agricultural lands and growing of trees in homesteads in all parts of the country would be helpful in carbon sequestration (Ravindranath and Somashekhar, 1995).

12. Soil and Water Conservation

Soil and water conservation is a combination of all management and land use practices which protect the soil against depletion or deterioration by natural or man-induced factors and improve the productivity of the natural resources on sustainable basis. It is said that nature takes centuries to produce the soil but man may loose it in a few years due to its indiscriminate exploitation for his need and greed. Soil once lost, is difficult and expensive to replace. The conservation of soil and water is an anti-erosion and anti-runoff approach, and is also a comprehensive and integrated approach for the judicious use of these resources rather than their negligent and wasteful use.

12.1. Soil Conservation Measures

The following soil conservation measures may be adopted for controlling soil erosion, depending on the degree and length of the slope and physical configuration of the land.

12.1.1. Mechanical Measures

(i) Contour Bunds — Contour bunds are mechanical barriers built across the slope for safe diversion of excess runoff and retention of eroded soil. The land area in between the two bunds gets levelled in due course of time. Due to deposition of eroded soil along the bund, the latter takes the shape of a riser. These risers should be planted with grasses to check their erosion.

(ii) Graded Bunds — The graded bund is a small earthen bund with slight grade constructed across the slope for safe disposal of runoff. The graded bunds are recommended up to 10% slope for areas where annual rainfall exceeds 800 mm, particularly on clayey and black soils with poor drainage. However, efficacy of graded bunds gets reduced gradually beyond 4% slope. The purpose of graded bunds is to reduce the velocity of runoff water, for *in-situ* conservation of rain water and to minimize soil erosion.

(iii)Bench Terraces — Bench terraces are flat beds constructed on the hills across the slope. The height of the riser should not be more than one metre and the width of bench terrace depends on the degree of slope. The bench terraces are important because they promote uniform distribution of soil moisture, irrigation water, etc. and control soil erosion. The bench terraces may be table top (level), outward sloping or inward sloping, with or without mild longitudinal grades. On steep slopes, it is better to construct terraces on foot hills for agricultural crops when soil depth is more than one metre.

(iv) Half Moon Terraces — Half moon terraces are semi-circular beds of appropriate diameter with the shape resembling a half moon. These terraces are recommended for fruit trees or other plantation crops on steep slopes.

(v) Grassed Waterways — Grasses are well-known for their soil binding characteristics. They are most effective in moderating the flow and reducing the erosive velocity of runoff water, particularly on the rolling topography. The runoff water moves with high velocity down the slope, carrying with it soil and nutrients. If some suitable grasses are planted on the runoff route or natural channels, the soil and nutrient losses can be reduced. These grassed waterways are laid on the natural drainage lines in the watershed. Stilling basins or water ponds are constructed *en route* at appropriate locations, with earthen and boulder pitched bunds for the retention of runoff water. By reducing the velocity of runoff water, the erosion losses can be minimized.

(vi) Water Harvesting Ponds — Water harvesting structures can be dug out for retaining runoff water on seasonal or perennial basis. These are generally constructed down the slope. Earthen dams should be used for retaining silt loads at appropriate locations on the slope of a watershed. The water thus harvested

or stored can be used for pisciculture and supplemental irrigation.

(vii) Conservation Bench Terraces (CBT) — These are used to stabilize the yield of rainfed crops by inter-field water harvesting. A part of the field is levelled to retain the runoff originating from rest of the field.

(viii) Gully Control Structures — Gully control structures are provided to (i) reduce the erosive velocity of runoff water, (ii) facilitate establishment of vegetation, and (iii) provide protection at points that cannot be adequately protected by other methods. Loose boulder check-dams perform well in gullies which do not carry much runoff and it also helps in silt deposition, thereby helping the stabilization of gully beds. Permanent gully control structures are constructed to control the overfalls either at gully head or in gully bed. Erosion from the extending heads and sides of gully and main channel are the major sources of sediment. There is also a need to construct diversion bunds to divert surplus water to water harvesting structures or to the grassed water ways.

(ix) Contour Trenches — Contour trenches are dug-out, piling up the dug-out earth on lower side of the trench, for trapping sediment and runoff at the early stage of their movement. These trenches also improve soil moisture and favour quick growth of trees and grasses.

(x) *Stream Bank and Torrents Control* — The vulnerable stream banks should be protected by providing spurs and retaining walls, etc. To control torrents, structures like barrages, paved channels, etc. need to be provided.

12.1.2. Agronomical Measures

For preventing soil erosion on cultivated lands, proper choice of crops and cropping patterns is necessary, particularly on hill slopes. The protection through vegetative shield, forest cover, grasses, crops and mulches, etc. are some important measures to prevent soil erosion. Such a protection by absorbing the energy of rain impact prevents the loss of both water and soil. The following crop management practices can be useful in minimizing the erosion of soil and nutrients.

(i) *Cropping Systems* — Crops with the ability to develop canopy quickly provide an early protection to the soil. Inter-planting of ero-sion-resistant crops like cowpea, soybean, etc. are also useful. Strip cropping of erosion-resistant legumes along with cereals can conserve rain water and reduce the velocity of runoff.

(ii) Crop Geometry — It is essential to manipulate the crop layout in the field in a manner which may prevent soil erosion. A closer spacing of rows across the slope can help in this regard.

(iii) Contour Cultivation — Contour cultivation reduces the runoff to a large extent, thereby reducing the soil and nutrient losses. Contour cultivation as well as furrows and ridges have been found useful.

(iv) Tillage — Low intensity tillage favours consolidation of soil through better structure, infiltration and pore distribution. This imparts erosion resistance. A study of conventional method of cultivation of maize with zero tillage, with or without live mulch, has shown that runoff and soil losses are greatly reduced with low intensity tillage (Table 8) (Bharadwaj, 1998).

(v) Grasses — Grasses are perhaps the best friend of soil conservationists. Low and evenly distributed canopy and fibrous root systems with much soil binding capacity make grasses highly effective in controlling soil erosion. The performance of various grass species in controlling soil erosion and runoff losses at 9% and 11% slopes are given in Table 9. The selection of grasses should be based on their production potential considering edaphic conditions and local preferences.

Table 8. Effect of tillage and living mulch on runoff and soil losses

Conservation measure	Runoff (%)	Soil loss (tonnes/ha)
Conventional maize	61.2	15.76
Zero tillage without live mulch	41.8	12.00
Normal tillage with live mulch	31.2	7.00
Zero tillage with live mulch	21.6	3.30

Source: Bharadwaj (1998)

12.1.3. *Agronomical-cum-mechanical Measures*

Depending upon the needs of land and intensity of erosion, bio-engineering measures are sometimes preferred as compared to either mechanical or agronomical measures in isolation. In black soils with 45-50% clay, both agronomical and mechanical measures have been found to reduce runoff and soil losses. These conserve soil moisture and thereby increase crop yield. The treatment of vertical mulch and surface mulch has been found to be most effective in controlling runoff and soil losses, and consequently, could produce maximum sorghum grain yield. Under mechanical measures, the graded bunding has been found to be superior to conservation ditch and contour bunds (Table 10).

12.1.4. *Agroforestry Measures*

Agroforestry has become popular as a useful land-use system on slopes in the recent past. Growing of trees along with agricultural crops satisfies the multifarious needs of farmers. The data presented in Table 11 provide an idea of the usefulness of agroforestry system as a soil conservation measure (Narain *et al.*, 1994). Growing of multipurpose tree species (MPTs) has been recommended alongwith crops.

(a) Soil Health Improvement

Ameliorative effects of agroforestry landuse in marginal and degraded lands have been observed in Doon Valley (Uttarakhand). A decrease in soil pH by 0.4 units and in bulk density (BD) by 0.1 mg/m^3, improvement in organic matter content by 0.16% and in water holding capacity by 1-5% have been observed (Dadhwal and Tomar, 1999). Low pH values and high organic carbon (OC) contents beneath the tree cover than bare soil have also been observed by Aggarwal *et al.* (1975). In another study in the Garhwal Himalaya, improvement in soil health has been recorded over time in minespoil degraded lands. After 14 years with agroforestry interventions, pH of the minespoil decreased to 7.5 from 8.1, OC

Table 9. Runoff and soil losses under different grass species at 9% and 11 % slopes at Dehradun

Land slope	Treatment	Runoff (%)	Soil loss (tonnes/ha)	Reduction (%)		Biomass (kg/ha)
				Runoff	Soil loss	
9%	Bare and ploughed	59.6	155.95	-	-	-
	Bare fallow	71.1	92.42	19.3	40.7	-
	Cynodon dactylon	27.1	2.10	54.5	98.7	-
	Natural grass	21.2	1.02	64.4	99.3	4355
11%	Cultivated fallow	16.2	18.45	-	-	
	Puerara hirsuta	1.8	0.11	88.2	99.4	14962
	Dicanthium annulatum	1.9	0.23	88.1	98.7	6805
	Chrysopogon fulvus	2.5	0.30	84.2	98.4	19170
	Eulaliopsis binata	5.2	0.29	67.1	98.4	16290

Source: Tejwani *et al.* (1975)

Table 10. Effect of conservation measures on runoff and soil losses and yield of sorghum under black soil of Bellary (Karnataka) at 1 % slope (Average of 8 years)

Treatments	Runoff (% of rainfall)	Soil loss (kg/ha)	Sorghum grain yield (kg/ha)
Agronomical Measures			
Up and down cultivation	54.8	2167	685
Vegetative barrier	39.9	1372	848
Contour cultivation	38.6	1640	897
Vertical mulch + surface mulch	23.3	172	1204
Mechanical Measures			
Contour bund	33.6	606	859
Graded bund	26.7	601	943
Conservation ditch	18.4	618	931

Source Rama Mohan Rao *et al.* (1997-98)

Table 11. Runoff and soil loss under different agroforestry systems

Land use	Runoff (%)	Soil loss (tonne/ha)
Maize	18.3	17.70
Maize + *Subabul*	8.9	5.00
Maize + Eucalyptus	3.6	0.91
Chrysopogon fulvus	1.6	0.33
Grass + *Subabul*	0.6	0.13
Subabul	0.4	0.04
Grass + Eucalyptus	0.1	0.02
Eucalyptus	0.1	0.01

Source: Narain *et al.* (1994)

Table 12. Change in minespoil characteristics over time (average of 14 locations) from Uttarakhand Himalayas

Characteristics	Year		
	1985	1991	1997
pH (1:2.5)	8.10	7.90	7.50
Organic C (%)	0.13	0.18	0.42
Total N (%)	0.01	0.01	0.05
$CaCO_3$ (%)	54.60	34.60	31.00
Bulk density (Mg/m^3)	1.63	1.53	1.47

Source: Dadhwal (1999)

increased from 0.13% to 0.42%, whereas $CaCO_3$-content decreased from 54.6% to 31.0% and BD (mg/m^3) decreased from 1.63 to 1.47 (Dadhwal, 1999); it shows that planting of MPTs, shrubs and grasses help in improving soil health and arresting soil erosion (Table 12).

Further, bio-engineering measures applied in the mined watershed at Sahastradhara (Uttarakhand), checked the heavy soil erosion, drastically reduced the surface runoff the surface runoff with attenuation in the flood peaks, increased the lean period flow due to groundwater recharge and improved the biodiversity over time (Table 13) (Juyal *et al.*, 2007).

Leguminous shade trees benefit through shade and nitrogen they provide to tea plants. A shade tree may add as much as 2500-5000 kg leaf, twigs and pods and 63-126 kg N, 18-36 kg P_2O_5, 22-44 kg K_2O, 32-64 CaO and 16-32 kg MgO per ha per annum to the soil.

The accumulation of soil organic matter under trees is the most commonly reported effect of trees on soils (Odum, 1960). Quantity and quality of soil organic matter bring about important changes in physical and chemical properties of soil. Reduction in soil bulk density and concomitant increases in soil aeration and soil hydraulic conductivity are caused by the incorporation of low specific gravity organic matter and metabolic activity of decomposer organisms. Rolfe and Boggess (1973) had found that 30-35 years after pine establishment in Southern Illinois (USA), the soil bulk density had decreased while soil hydraulic conductivity and exchangeable calcium and magnesium contents had increased. It is worth noting that these improvements in soil

Table 13. Impact of rehabilitation measures at minespoil watershed, Sahastradhara, Derhadun (Uttarakhand) (treated since 1984)

Particulars	Pre-treatment (1984)	Post-treatment (1996)
Debris outflow (t/ha/yr)	550	6
Monsoon runoff (%)	57	37
Lean period flow (days)	60	240
Water quality	Not potable	Potable
Vegetation cover (%)	10	80
Cost of debris clearance (Rs/yr)	1 lakh	Nil

conditions under trees have occurred on young soils, which contain weatherable minerals and are dominated by fixed charged clays. In many soils, a large portion of cation exchange capacity (CEC) is associated with carboxyl group in the organic matter. This can have a significant effect on soils that have very low mineral based CEC (Fisher, 1990).

The age-old practice of shifting agriculture takes the advantage of ameliorating effects of a period of forest fallow. This causes organic matter additions greatly in excess of decompositional losses and restores good physical and chemical conditions to the site (Ewel, 1986; Venkataramanan *et al.,* 1983). Singh *et al.* (1994) have reported 6-10 fold increase in organic carbon status of a sodic soil when occupied by trees such as *Prosopis juliflora, Acacia nilotica, Eucalyptus tereticornis, Terminalia arjuna* and *Albizia lebbek* for more than 20 years. Similarly, Shankaranarayan (1984) had reported greater increase in the amount of organic matter, nitrogen and phosphorus under *Prosopis cineraria* than under *Prosopis juliflora* and bare field under arid conditions.

(b) *Carbon Sequestration and Soil Fertility in Tree-Crop Interaction*

Tree legumes are often important component of arid and semi-arid ecosystems. Many of these trees and shrubs have the ability to develop a deep root system and symbiotically fix atmospheric nitrogen. Martin (1977) had noticed significant formation of soil organic matter during active root growth, much of it coming directly from the root tissue without the intervention of soil microfauna. Woody legume trees, which have potential to fix significant quantities of nitrogen, may have an influence on the yield in the nitrogen-deficient soils. Some nitrogen-fixing trees have proved to be very efficient in phosphorus uptake and can effectively serve as nutrient pumps for phosphorus and other mineral nutrients (Balkrishan and Toky, 1993).

Nair (1984) had predicted the possibility of nitrogen fixation in woody legumes to the order of 100 kg N/ha/year in areas receiving 500 mm annual rainfall. Nitrogen fixing trees can achieve the rates of fixation comparable with those of leguminous crops (Young, 1990). The major recognized avenue for addition of organic matter to the soil from the tree standing on it, is through the fall of litter, twigs, branches and fruits (Brinsen *et al.,* 1980).

Kellman (1979) had emphasized that trees also show preferential enrichment of soil below them in terms of N, P, K, Ca, Mg and Na. In some cases, the levels of these nutrients approach or exceed those found in the nearby rain forest. He concluded that gradual accumulation of mineral nutrients by perennial, slow growing trees, and incorporation of these into an enlarged plant-litter-soil-nutrient cycle was the mechanism responsible for this soil enrichment. Similar results of an increase in nutrient content of soils under species *P. cineraria*, growing in the arid and *F. albida* trees in semi-arid environment, were reported by Singh and Lal (1969) and Felker (1978), respectively. By adopting various agroforestry/silvipasture models, degraded soils can be rehabilitated (Pathak and Dagar, 1998).

In the semi-arid conditions at Jhansi, in the silvipastoral systems of *Albizia lebbeck – Cenchrus – Stylo* and *A. procera – Cenchrus – Stylo*, a significant improvement in soil organic matter builds-up was recorded; it was 38% in the former and with 25% in the latter system (Pathak, 1992).

In a nutrient management study conducted at Meghalaya in the north-eastern India, the contents of exchangeable Al and Mg decreased, while those of Ca, K and Bray's P increased in the silvipastoral system (Prasad, 1992). Similarly, in the north-west Himalayas, a study on the dynamics of herbage in *Acacia catechu* and *Punus roxburghii* based natural silvipastoral systems has revealed that as the distance from tree trunk increases, pH and EC enhance and organic carbon, N, P, K, Ca and Mg decrease. Recent studies on soil fertility improvement in *Grevillea robusta, Gmelina arborea* and *Tectona grandis* based silvipastoral systems under semi-arid condition at Mettupalayam, Tamil Nadu, have revealed that due to inclusion of either tree alone or tree + grass, the organic carbon, available N, P and K in the soils increase appreciably as compared to those in open (barren) land and pure grass, except N in *G. robusta* + grass; P with pure trees of *G. arborea* and *T. grandis* + grass, and K with *T. grandis* (Thiyageswari *et al.*, 1998).

In arid condition, Singh and Lal (1969) investigated the profile characteristics and level of fertility under *P. cineraria* and *A. nilotica* canopies and concluded that silvipasture systems enhance organic matter, total N, available P, soluble C and brings down soil pH. Better mechanical composition of soil up to 120 cm depth due to silvipasture systems promote the growth and yield of crops grown in the vicinity of *P. cineraria.* Aggarwal *et al.* (1975) concluded that the status of available micronutrients generally improves under plantation especially under *P. cineraria.*

The soil properties, in general improve with tree-cropping as compared to non-tree situation. Hazara (1990) had observed that field capacity, wilting point, organic carbon, cation exchange capacity and available N and P contents of soils were greatly improved, whereas bulk density, pH and EC values were appreciably decreased under *Albizia lebbeck* plantation as compared to normal cropping. The canopy structure and density of tree species had influenced the grass production underneath. The leguminous shrubs and trees have great influence in building up soil organic matter (0.32-0.91%), available soil N (131-293 kg/ha), available P (6.2-18.5 kg/ha) and field capacity (11-15.8%).

In one of the studies conducted at IGFRI, Jhansi, under seventeen years old silvipastoral systems, it was found that the organic carbon was maximum at the top layer (0-15 cm), followed by 30-45 cm soil depths in pure grasses as well as in *C. ciliaris* + *A. tortilis* and *P. maximum* + *L. leucocephala* based silvipastoral systems (Mishra, 2002). The increase in organic carbon by 10 to 40 per cent under the silvipasture system as compared to the sole pastures may be because of more litter decomposition and available root biomass. The increase in organic carbon under the silvipasture systems has indicated the improvement in soil health, resulting in higher system productivity and sustainability. *L. leucocephala* + *P. maximum* based silvipasture system maintains higher organic carbon content and therefore, the sustainability of production system is maintained over the years. Maximum increase has been estimated in the contents of available N, P and K under the tree pasture canopies than the sole pastures.

13. Watershed Approach

The soil and water conservation measures in the lower catchment areas are prone to dam-age due to uncontrolled runoff from the upper areas. It is therefore necessary to protect the upper catchment areas through the watershed approach.

Watershed can be defined as a topographic hydrological unit draining runoff water at a common or a particular point by a network of channels and streams. Thus, a watershed represents a hydrological unit of area but can also be described as a bio-physical and socio-economic and sometimes a political unit for planning and management of natural resources.

Small watersheds are those where the overland flow is the chief contributor to the peak flows and the overland flows are not affected by the channel characteristics. On large watersheds, the channel flows are highly pronounced and peak flows are influenced by the channel characteristics. The area to be managed for soil and water conservation programme is also important in categorizing a watershed. Thus, these are sub-divided into different levels called as sub-, milli-, micro- and mini-watersheds managing the area of 10000-50000 ha, 1000-10000 ha, 100-1000 ha and 10-100 ha, respectively.

The main objectives of watershed approach for the management of land, water and vegetation resources are: (i) to establish a watershed as a basis to conserve and upgrade crop and degraded lands, (ii) to develop and demonstrate location-specific technologies for soil and water conservation and for crop production stabilization, and (iii) to augment the fodder, fruit and fuel resources through alternate land-use systems. For steep hill slopes, the following aspects are to be considered (Samra, 1997):

(i) Ensuring adequate protection of land against soil erosion with the use of local resources and skill-based soil conservation measures.

(ii) Maximum retention of rainfall within the area without affecting the crops.

(iii) Storage of runoff water, its use for pisciculture and irrigation.

Based on the micro-watershed approach, different land uses such as agriculture, horticulture, agri-horti, agri-horti-silvi-pastoral and livestock based systems, etc. may be adopted for a judicious resource conservation. In the watershed approach, proper land-use systems may be adopted to minimize runoff and soil losses. The data presented in Table 14 show the average runoff and nutrient loss from seven land-use systems under different slopes and soil conservation measures.

13.1. Hydrology of Watershed

A thorough knowledge of the different hydrological phenomena is required in all aspects of soil and water conservation in the watershed. Information about rainfall is needed for in estimating runoff, planning erosion-control measures, planning for irrigation, removal of excess water and conserving water in low rainfall regions. Knowledge of runoff is required in designing structures and channels that will handle natural flows of water. Data on infiltration, evaporation and transpiration are required in planning irrigation and drainage systems, moisture conservation practices, etc.

13.2. Watershed Management

A good watershed management must consider the social, economic, and environmental sustainability and institutional factors operating within and outside the watershed area. The essentials features of watershed-management programmes involve newly emerging paradigms — priority areas should be identified and integrated development approaches should be followed; community-driven involving interaction between users, agencies and developmental departments; bottom-up and flexible approach with the capacity for making interim corrections; execution through village cooperative societies in perfect harmony; peoples' participation is necessary right from planning, execution and monitoring of the programme; judicious and equitable sharing of costs and benefits to landowners and the landless people in the watershed; gender neutrality, women, who play pivotal role in agriculture should be involved in all the decisions without any gender bias; involving non-governmental organizations (NGOs) in watershed management; and the common property resources should be managed by the people with their rights. Joint forest management needs serious thinking/rethinking. Village societies are required to be established for resource management with peoples' empowerment for their effective management.

13.3. Participatory Integrated Watershed Management

Watershed management is an integrated approach, considering the holistic development for all the users of the watershed. It is necessary to protect, conserve and improve the land resources for an efficient and sustained production; to protect and enhance water resource, moderate floods and reduce silting up of tanks, increase irrigation and conserve rainwater for crops and thus mitigate droughts; and to utilize the natural local resources for improving agriculture and allied occupations or industries (small and cottage industries) to improve socio-economic status of the local residents.

It is universally accepted that conservation should be essentially an area approach and the unit of its adoption should be a watershed. Therefore, a combination of few approaches is required to be adopted in a given watershed. Now-a-days, integrated watershed management of the resources with peoples' participation is a well-accepted concept for the management of natural resources.

14. Future Scenario as Affected by Resource Conservation Technologies

Adoption of resource conserving technologies for efficient utilization of land, water, vegetation and human resources following bottom-up integrated watershed management approach is the only solution to meet the ever increasing demand of foodgrains, fodder, fuelwood and fibre for the growing population. Apart from increasing production, integrated watershed management (IWSM) is quite beneficial in generating employment opportunities. The Participatory IWSM approach exhibites long-lasting, people-oriented and environment-friendly impact. Application of multi-objectives decision support system (MODSS) technique to the Himalayan watersheds has revealed great potential in watershed planning, monitoring and evaluation through adoption of optimal watershed management plans. For example, at the Fakot watershed in Uttarakhand, income employment and food sufficiency increased by 18%, 8% and 46%, respectively, with 53% reduction in soil loss. Similarly, based on the experiences of model watersheds developed by CSWCRTI, Dehradun (India), potential of IWSM in increasing production of crops, horticulture, livestock, etc. in terms of rice equivalent yields in the rainfed areas has been analyzed in 11 agro-climatic zones. The average productivity of the predominant rainfed cropping systems and allied agriculture sectors in the model watersheds has been compared with the average productivity at the district level and the concerned agro-climatic region for extrapolation of production potentials based upon the yield gaps. The analysis has revealed that production can be enhanced by 152 million

Table 14. Runoff and soil losses under different land-use systems on micro-watersheds

(Average of 7 years)

Watershed No.	Dominant land-use system	Conservation measures	Average slope (%)	Average runoff (mm)	Soil loss (tonnes/ha)
1	Livestock based	Contour bunds, trenches and grassed water-ways	32.0	12.7	0.02
2	Forestry	-	38.0	80.1	0.11
3	Agroforestry	Contour bunds	32.2	39.7	0.06
4	Agriculture	Contour bunds, bench terraces and grassed waterways	32.4	23.2	0.08
5	Agri-horti-silvi-pastoral	As in watershed No. 4 also half-moon terraces	41.8	12.1	0.19
6	Horticulture	As in watershed No. 5	53.2	29.2	1.89
7	Natural fallow	-	45.8	11.5	0.01

Source: Singh and Singh (1978)

Table 15. Potential of additional production and income generation through integrated watershed management in different agro-climatic regions of India

Sl No.	Agro-climatic region	Additional regional production ('000 tonne)	Additional regional gross return advantage (in lakh Rs)
1.	Western Himalayan Region	13132.7	735433.2
2.	North-eastern Himalayan Region	16234.1	909111.8
3.	Upper Gangetic Plain	1933.8	108293.9
4.	Trans-Gangetic Plain	25791.5	1444321.9
5.	Eastern Plateau and Hill Region	29350.6	1643634.7
6.	Central Plateau and Hill Region	20487.7	1147310.1
7.	Western Plateau and Hill Region	8254.1	462226.8
8.	Southern Plateau and Hill Region	18967.2	1062163.2
9.	East Coast Plains and Ghat Region	10858.4	608068.2
10.	West Coast Plains and Ghat Region	1077.1	60317.0
11.	Gujarat Plains and Hill Region	5790.9	324289.3
12.	All India	151878.1	8505170.0

tonnes, if efficiency of technology transfer is assumed as 100%, similar to the model watersheds (Table 15). Even at 70% efficiency, a significant increase in production (106 Mt) can be achieved, which would be sufficient to meet the demands of growing population by 2025 (CSWCRTI, 2007).

Better inventorization/characterization of natural resources and prioritization of critical areas for erosion control on watershed basis (through application of advanced RS/GIS/GPS techniques), development of area-specific soil loss tolerance limits along with estimation of erosion-fertility-productivity relationships under primary production systems of the country and site-specific land suitability criteria can lead to efficient management of natural resources.

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Chapter 11

Chemical Composition of Soils

D.K. PAL, V.A.K. SARMA and S.C.DATTA

1. Introduction

Soils are the products of many forces and agents. They exist in the lithosphere where geological deposits get affected by the forces of wind, water and climate, and occasionally by earthquakes, volcanic eruptions and glaciation. The climate of a region plays a dominant role in altering the lithospheric materials into soils. But, soils are produced and will continue to support us even in places where climate has little apparent influence, as in very dry regions or in the Arctic. It is because of the past history of the Earth, existing plants and animals, groundwater, and man's multitudinous activities which all contribute to the production of the more or less loose material at the earth's surface that we call 'soil' in which plants grow and on which we live.

Soil composition concerns the geochemistry of that portion of the mantle of the earth which is currently under exposure to the atmosphere and is subjected to biotic influences. Considering soil as a material, its essential ingredients are:

(a) Mineral matter, which is originated from a rock by the action of a series of weathering processes,

(b) Organic matter, which is generated from the residues of organisms (plant and animal),

(c) Soil water, containing substances in colloidal or true solution, and

(d) Soil air.

The solid phases (mineral and organic) generally make up only about 50% of the soil volume, the other half being constituted by the soil solution and soil air (Figure 1).

Since the density of organic matter in a soil is only about 0.5 Mg/m^3, while that of mineral matter is approximately 2.7 Mg/m^3, 5% (by weight) of organic matter occupies nearly 25% of the volume of solids. The liquid and gas phases together often make up as mentioned above, about half of the soil volume, in the relative proportions of each varying rapidly as the liquid phase (water) is drained away or used by the plants.

The gas phase of soils, which often occupies about one-fourth of the soil volume, contains approximately 80% nitrogen, as in the ordinary air, and about 20% (by volume) oxygen. In well-drained soils, the CO_2-content of soil air is less than 0.1% by volume; in poorly-drained soils, it rises to 5-10%, and in extreme cases like frozen soil horizons, it may be as high as 20% and thus can replace all oxygen. Rare gases like Ne, Ar, Kr and Xe also occur in the soil atmosphere, though in trace amounts.

Soils are the products of several chemical, biochemical and physical processes. These processes affect the earth material under various topographic and climatic conditions and the soils formed reflect landforms and climatic and geomorphic history of the region in which they are evolved. Under the control of these factors, chemical compounds are translocated and deposited in deeper soil horizons; sometimes these are returned to the upper horizons by biocycling, and sometimes they are removed from the soil by leaching. In spite of this, most

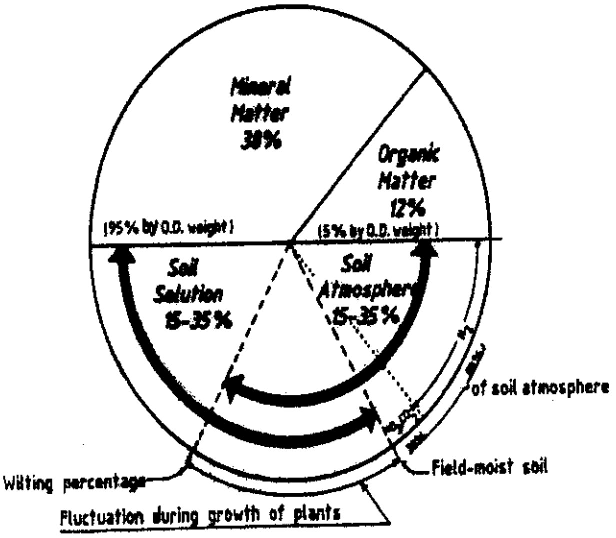


Figure 1. Percentage composition of soil (volume basis)

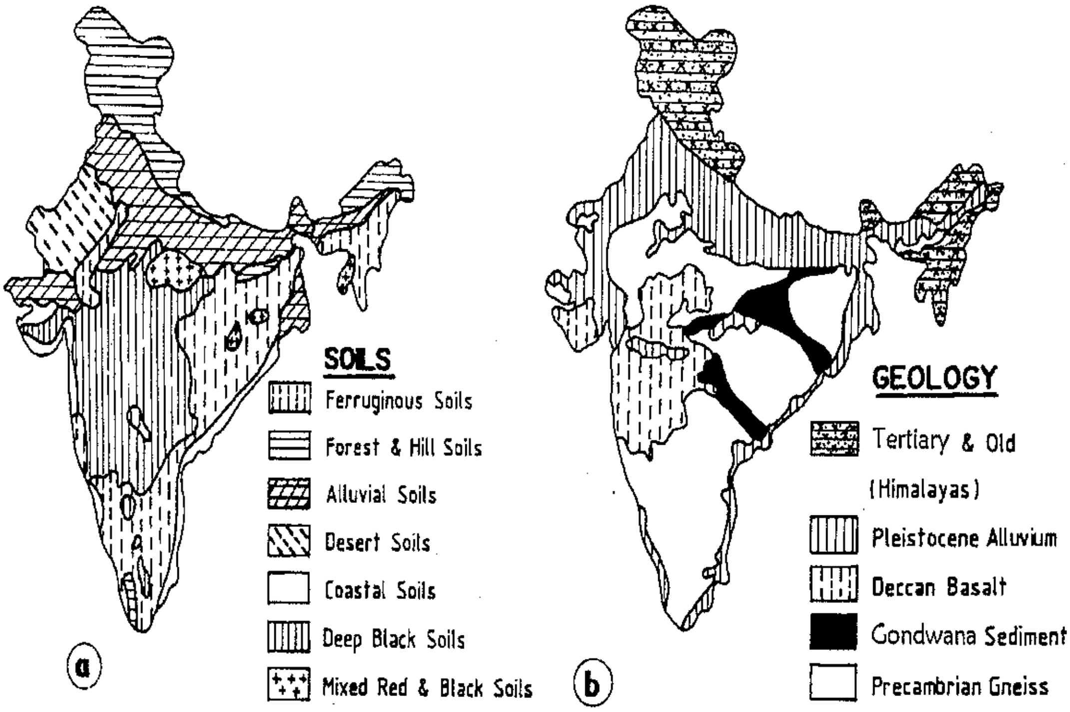


Figure 2. (a) Distribution of different kinds of soil, and (b) the spread of geological formations of India

soils reveal through the chemical composition of their constituent minerals, the nature of their original parent rock.

2. Composition of Earth's Crust

Coarse-grained rocks tend to weather faster than fine-grained ones, and basic rocks weather faster than acid ones. Soils formed from the basic rocks are usually more fertile than those formed from the acid rocks. Distribution of different kinds of soils of India (Figure 2a) and the different geological rock formations (Figure 2b) demonstrate the effect of parent rock on soil formation. The fine-textured Deccan basalt (*see* later) has been responsible for the formation of clayey black soils, whereas coarse-grained metamorphic rocks (*see* later) have given rise to ferruginous soils. However, the occurrence of ferruginous soils in black soil areas, and of black soils in the ferruginous soil areas reflect two contrasting chemical environments that were conducive to the formation of these two groups of soils on the same parent material, presumably under similar climatic conditions. The forest and hill soils on tertiary sediments and desert soils in the Pleistocene sediments, however, indicate the predominant influence of climate and vegetation on the former and climate alone on the latter soils. Both, the rocks and their mineral components are important because their structure, texture and hardness together determine physical resistance to weathering. The significance of the minerals is that their chemical composition, crystal structure and susceptibility to alteration and decomposition are all important factors from both pedologic and agricultural standpoints (Mohr *et al.*, 1972). Therefore, it is useful to note the mineralogical composition of the various rock types, such as igneous, sedimentary and metamorphic rocks, in which the chemical compounds are held in the mineral portion of soils and soil parent materials.

2.1. Igneous Rocks

Igneous rocks range in composition from ultrabasic to acid rocks (Figure 3), and have resulted from the cooling of magma or silica melts of the lithophile elements (which ionize readily or form stable oxyanions). When cooling occurred slowly, coarse-grained, plutonic rocks resulted. In the event of an eruption, when cooling was rapid, finer-grained, volcanic rocks resulted. Of the plutonic rocks, granites and granodiorites are far more plentiful than all the others combined. Among volcanic rocks, basalts and basic andesites predominate largely. When the melt was deficient in silica, nepheline was formed from melts high in Na and K, while olivine was formed at the other extreme when the proportions of Fe and Mg were very high.

Volcanic rocks range in texture from massive to ash, depending on the degree of fracturing that occurred by either gas expansion or chilling in water. Such textural differences lead to enormous alterations in the rate of chemical weathering during soil formation. In addition, chemical variations in various rock types influence directly and indirectly, the elemental and mineralogical compositions of the soil parent material and of the soils developed thereon. The elemental composition of rocks mainly controls the nature of the secondary minerals formed and influences the ionic composition of the weathering solution in contact with the mineral grains.

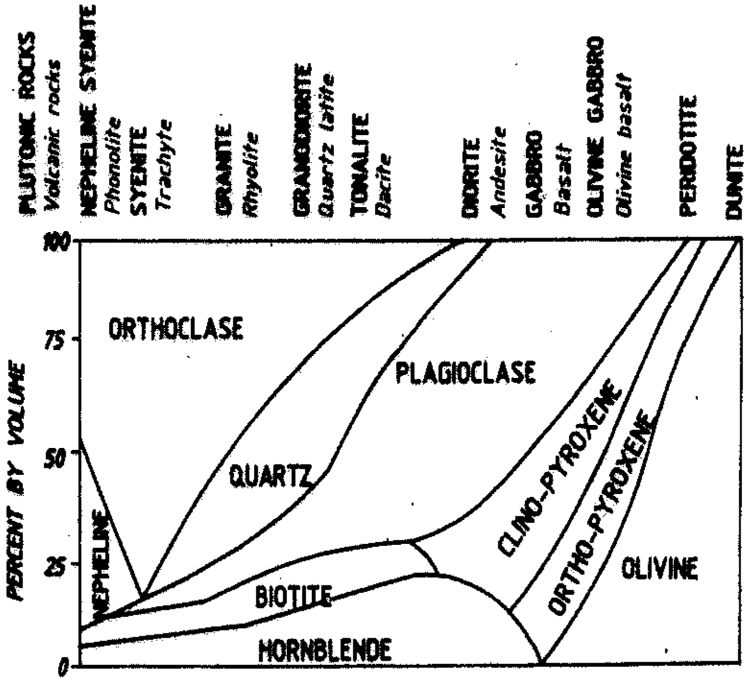


Figure 3. Mineralogical composition of common igneous rocks. Volcanic rocks with names in *italics* consist of fine-grained minerals

Table 1. Some important metamorphic and sedimentary rocks and their predominant minerals

Metamorphic rock	Predominant mineral	Sedimentary rock	Predominant mineral
Gneiss	Varies*	Limestone	Calcite ($CaCO_3$)
Schist	Varies*	Dolomite	Dolomite [$CaMg(CO_3)_2$]
Quartzite	Quartz (SiO_2)	Sandstone	Quartz (SiO_2)
Slate	Clay minerals	Shale	Clay minerals
Marble	Calcite ($CaCO_3$)	Conglomerate	Varies**

* The minerals present are determined by the original rock which has been metamorphosed. Primary minerals present in the igneous rocks commonly dominate these rocks; however, some secondary minerals are also present.

** Small stones of varied mineralogical composition are cemented into conglomerate.

Source: Buckman and Brady (1971)

2.2. Sedimentary Rocks

Sedimentary rocks are formed near the interface of the earth's crust with the hydrosphere and atmosphere, and cover about three-fourths of the land area of earth. This geomorphic fact is of great importance to soils, because the higher specific surface area of the mineral grains and the general nature of sedimentary rocks (less consolidated than igneous rocks) permit more rapid biotic invasion and development of deep, highly productive soils. It is probable that accumulation of hydrous minerals in the sedimentary muds favoured and conditioned the evolutionary development of life forms on earth.

Sedimentary rocks of marine origin are classified as shale, sandstone, and limestone (including dolomite) (Table 1). Terrestrial sediments include glacial drift, loess, dunes, volcanic ash, and stream and lake sediments. Calcium carbonate ($CaCO_3$) and to some extent dolomite ($CaCO_3.MgCO_3$), accumulate in limestones of sedimentary rocks mainly through the chemical and biochemical precipitation in the ocean waters, and also as chemical precipitates (evaporites) in lakes and soils.

2.3. Metamorphic Rocks

Metamorphic rocks are formed by the effect of heat and pressure on sedimentary and igneous rocks. The mineralogical composition and texture of the rocks strongly affect the composition of soils formed. Details about minerals in the metamorphic rocks are given in Table 1.

A gneissic rock is a laminated or banded metamorphic rock similar in mineralogical composition to granite. Mica schists, another metamorphic rock, weather rapidly to give rise to soil high in vermiculite and quartz. The third form, slates are produced by compression and alteration of shales and mudstones, giving fine-grained rocks high in mica and quartz. Marble, another form of metamorphic rock, is the metamorphosed form of limestone. It is resistant to weathering and is often found in different colours due to the presence of minerals. Quartzite is metamorphosed sandstone. It is very rich in SiO_2 and is extremely resistant to weathering. In addition, there are metamorphic rocks that are less extensive in occurrence. They are amphibolite, amphibole schist or hornblende schist, chlorite schist or greenstone and tactite.

3. Soil Minerals

The inorganic components of soils are derived mainly from a limited number of minerals. The composition of minerals can vary widely due to the isomorphous substitution of different ions in similar structural sites in the crystal; each mineral structure may have an isomorphous series of minerals. Thus, many of the essential trace elements are present in host minerals, and constitute sources of the plant available pool of trace metal ions, in addition to that of metal ions present in larger amounts.

A small portion of various ions in soil minerals is readily available in exchangeable or adsorbed form. This form assumes importance in the nutrition of crop plants grown on different soils. However, the renewal of ions in the exchangeable form through weathering of minerals is a slow process. The mineral species in

Limonite Kaolinite
calcite muscovite

soils are many and they influence the release of structural ions and the chemical activity of exchangeable ions. Therefore, the mineral composition of soils has a strong relevance to soil fertility.

Soil minerals are classified as: (a) primary minerals formed at elevated temperatures and inherited from igneous,and metamorphic rocks, and (b) secondary minerals formed by low-temperature reactions and inherited by soils from some sedimentary rocks or formed in soils by weathering (Jackson, 1964). The primary and secondary mineral classes are not mutually exclusive, and some minerals occur in both.

The silicates comprise a bulk of most of the soils. These occur as both primary minerals inherited from igneous or metamorphic rocks, and secondary minerals formed from the weathering products of primary minerals. The fundamental unit of all silicate structures is the SiO_4^{4-} – tetrahedron. Several different arrangements of the SiO_4^{4-} – tetrahedron occur, partly accounting for the large number of silicate minerals and providing a basis for their classification. The tetrahedra may be present as single tetrahedra (nesosilicates), double tetrahedra (sorosilicates), rings (cyclosilicates), single or double chains (inosilicates) or frameworks (tectosilicates) (Table 2). In all these arrangements, adjacent SiO_4^{4-} – tetrahedra share only corners. It means they share only corners. The minerals from each silicate class, commonly found in soils, are listed in Table 2.

3.1. Primary Minerals in Soils

Primary minerals are inherited from the parent rock and constitute a major part of the sand and silt fractions of most of the soils. For a given soil, the sedimentation history of the parent material determines the sand content (2000-50 μm) of the soils, whereas the combined effect of weathering and sedimentation determines the silt content (50-2 μm). The combination of sand and silt determines the percentages of primary minerals in a soil. The primary minerals may also occur in the clay fraction (< 2 μm) of less-weathered soils.

Throughout the world, the most abundant minerals and mineral groups in sand and silt of soils are quartz–SiO_2 (silica), and feldspars–$MAlSi_3O_8$ (silicates of basic cations, M^+). There are other minerals like pyroxene, amphibole, olivine and accessory minerals of primary origin that are present in the soils. Some carbonates, sulphur–bearing minerals and zeolites are also present. Though present only in smaller amounts, they are important to the chemistry of soils.

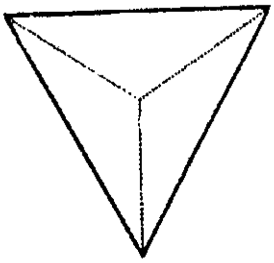
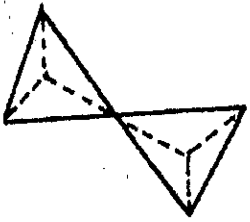
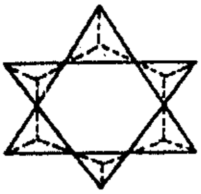
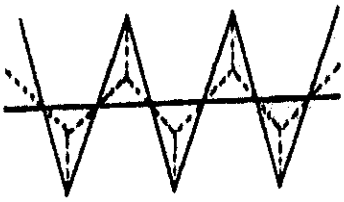
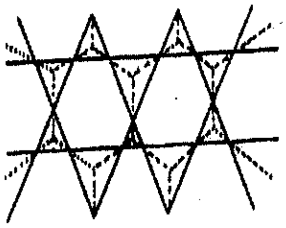
3.1.1. Quartz

Free silica occurs in soils mainly in the form of quartz (SiO_2). It consists of a continuous framework of silica tetrahedra. It is almost ubiquitous in soils and it is only a rare soil that does not contain some quartz. It is often present in coarse clays (2-0.2 μm). Free silica also occurs in some soils as *opal* ($SiO_2.nH_2O$), including opal pseudomorphic after plant cells (phytoliths), chalcedony, agate, flint and chert. The other quartz polymorphs (cristobalite and tridymite) are rare in soils. However, cristobalite has been found in the sand and silt fractions in ferruginous and black soils developed in alluvium of weathering Deccan basalt (Pal and Deshpande, 1987; Bhattacharyya *et al.*, 1993).

Quartz is inherited mostly from the soil parent material. But, aeolian contributions are believed to be widespread and are usually considered to be the source of quartz in soils derived from basalt. However, its presence in soils derived from Deccan basalt, cannot be attributed entirely to the aeolian origin because Deccan basalts contain quartz (Figure 4a) as a secondary mineral.

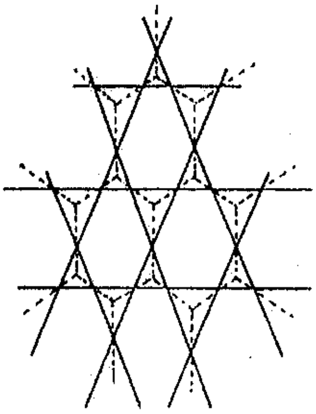
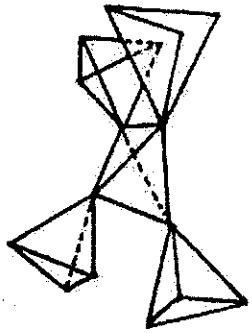
The main process of concentration of free silica is podzolization, under which organic matter chelates the sesquioxidic cations and reduces ferric iron so that these ions are leached out of the bleached A2 (or E) horizons. Despite its stability, quartz may be subject to dissolution under intense weathering, especially when the grains are very small. The tendency for SiO_2 is, therefore, to accumulate as coarser grains of sand, silt, and even coarse clay in highly podzolized horizons. The most common and conspicuous light grey or white E horizons of many podzolic soils consist of sand-sized SiO_2 and other aluminosilicate particles, but a high content of bleached silt and rarely of coarse clay, do occasionally occur in the E

Table 2. Classification of silicate minerals

Silicate class and unit composition arrangement of $(SiO_4)^{4-}$-tetrahedra	Mineral	Ideal formula
Nesosilicates $(SiO_4)^{4-}$	Olivine	$(Mg, Fe)_2SiO_4$
	Forsterite	Mg_2SiO_4
	Fayalite	Fe_2SiO_4
	Zircon	$ZrSiO_4$
	Sphene	$CaTiO(SiO_4)$
	Topaz	$Al_2SiO_4(F, OH)_2$
	Garnets	$X_3Y_2(SiO_4)_3$, where X=Ca, Mg, Fe^{2+}, Mn^{2+} Y=Al, Fe^{3+}, Cr^{3+}
	Andalusite	Al_2SiO_5
	Sillimanite	Al_2SiO_5
	Kyanite	Al_2SiO_5
	Staurolite	$Fe_2Al_9O_6(SiO_4)_4(O, OH)_2$
Sorosilicates $(Si_2O_7)^{6-}$ 	Epidote	$Ca_2(Al, Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$
Cyclosilicates $(Si_6O_{18})^{12-}$	Beryl	$Be_3Al_2(Si_6O_{18})$
	Tourmaline	$(Na, Ca)(Li, Mg, Al)(Al, Fe, Mn)_6$-$(BO_3)_3(Si_6O_{18})(OH)_4$
Inosilicates	Pyroxenes	
(single chains) $(SiO_3)^{2-}$	Augite	$(Ca, Na)(Mg, Fe, Al)(Si, Al)_2O_6$
	Enstatite	$MgSiO_3$
	Hypersthene	$(Mg, Fe)SiO_3$
	Diopside	$CaMgSi_2O_6$
	Hedenbergite	$CaFeSi_2O_6$
	Pyroxenoids	
	Wollastonite	$CaSiO_3$
	Rhodonite	$MnSiO_3$
Inosilicates	Amphiboles	
(double chains) $(Si_4O_{11})^{6-}$	Hornblende	$(Ca, Na)_{2\text{-}3}(Mg, Fe, Al)_5Si_6$-$(Si, Al)_2O_{22}(OH)_2$
	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
	Actinolite	$Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$
	Cummingtonite	$(Mg, Fe)_7Si_8O_{22}(OH)_2$
	Grunerite	$Fe_7Si_8O_{22}(OH)_2$

Contd

Table 2. Classification of silicate minerals — Contd

Silicate class and unit composition arrangement of $(SiO_4)^{4-}$-tetrahedra	Mineral	Ideal formula
Phyllosilicates $(Si_2O_5)^{2-}$ 	Micas	
	Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
	Biotite	$K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$
	Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$
	Chlorites	$(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2$-$(Mg, Fe)_3(OH)_6$
	Clay minerals (selected)	
	Talc	$Mg_3Si_4O_{10}(OH)_2$
	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Smectite	Variable
	Vermiculite	Variable
	Serpentines	
	Antigorite	$Mg_3Si_2O_5(OH)_4$
	Chrysotile	$Mg_3Si_2O_5(OH)_4$
Tectosilicates $(SiO_2)^0$ 	Feldspars	
	Orthoclase	$KAlSi_3O_8$
	Albite	$NaAlSi_3O_8$
	Anorthite	$CaAl_2Si_2O_8$
	SiO_2 Group	
	Quartz	SiO_2
	Tridymite	SiO_2
	Cristobalite	SiO_2
	Zeolites	
	Analcime	$NaAlSi_2O_6 \cdot H_2O$
	Clinoptilolite	$(Na_3K_3)(Al_6Si_{30}O_{72}) \cdot 24H_2O$
	Feldspathoids	
	Nephelene	$(Na, K)AlSiO_4$

Source: Adapted from Schulze (1989)

horizons. Neoformed quartz has also been detected in petroplinthite of ferruginous soils of southern India.

3.1.2. *Feldspars*

Feldspars are anhydrous aluminosilicates of K, Na and Ca and occasionally of other large cations such as Ba. The feldspars make up an average of about 60% (by weight) of igneous rocks and large fractions of sedimentary rocks (Table 3).

Next to quartz, feldspars are the most widespread primary minerals in soils. They may constitute most of the sand and silt in some slightly weathered soils developed from highly feldspathic parent materials. There is usually more feldspar in the coarser soil fractions than in the clay, but it is often reported as a minor component in coarse clay (2-0.2 μm). Feldspars occur as components of the clay fractions in a large variety of Indian soils.

The feldspar structure consists of tetrahedra linked by sharing each O^{2-} ion between the adjacent tetrahedra. The result is a three-dimensional framework or tectosilicate structure. Feldspars are commonly divided into potassic species, or K-feldspar ($KAlSi_3O_8$, polymorphs orthoclase and microcline), and plagioclase series (ranging from albite, $NaAlSi_3O_8$ to anorthite, $CaAl_2Si_2O_8$). Orthoclase and microcline are common in plutonic and metamorphic rocks such as granites, syenites, gneisses, and some pegmatites. The potassium feldspars occur commonly in the silt and sand fractions of soils, but may be abundant in the clay-size fraction of soils which have undergone less weather-

Table 3. An average mineral composition of igneous and sedimentary rocks

Minerals	Average percentage		
	Igneous rock	Shale	Sandstone
Feldspar	59.5	30.0	11.5
Amphibole and pyroxenes	16.8	—	Trace
Quartz	12.0	22.3	66.8
Micas	3.8	—	Trace
Titaniferous minerals	1.5	—	Trace
Apatite	0.6	—	Trace
Clay	—	25.0	6.6
Limonite	—	5.6	1.8
Carbonates	—	5.7	11.1
Other minerals	5.8	11.4	2.2

Source: Jackson (1964)

ing. In the finer silt and clay sizes, they indicate a reserve of K, but the release of K by surface reaction and also by the rupture of Si-O-Al bonds during breakdown of mineral structure is very slow and K-feldspars contribute very little to the soil pool of potassium that can be used by plants. Thus, they are less important than micas as a mineral source of potassium in soils.

The plagioclase feldspars are a series consisting of a solid solution of albite–$NaAlSi_3O_8$ and anorthite–$CaAl_2Si_2O_8$. Classically, the plagioclase series is named by compositional increments. They are albite, oligoclase, andesine, labradorite, bytownite and anorthite. Albite and oligoclase occur commonly in pegmatites and in metamorphic rocks, but do occur in some igneous rocks too. The bytownite and labradorite end of the series becomes more abundant in the less-siliceous rocks such as basalts. These minerals are important sources of available calcium of less-weathered soils.

Anorthite, a product of contact metamorphism of limestones, weathers rapidly in soils even in temperate climates. Thus, the chemistry and dissolution of plagioclase series of feldspars provide an interesting and important relationship between the degree of weathering (Figures 4b and 4c) and the fertility status of soils. The exchange complex of many of the ferruginous soils of southern and central India is dominated by Ca^{2+} ions and the soils are moderately fertile, indicating the importance of the presence of plagioclase. Thus, in many highly-weathered tropical and subtropical soils, the presence or absence of plagioclases in the parent rock makes a clear difference between productive and unproductive soils.

Many minerals have been reported as alteration products of feldspars, depending on the feldspar composition and the weathering environment. The clay-size dioctahedral smectite (*see* later) was the first weathering product of plagioclase of the Peninsular gneiss of southern India during the tropical humid climate of the pre-Pliocene period (Figure 4d) (Pal *et al.*, 1989).

3.1.3. Accessory Minerals of Soils

A wide variety of accessory minerals in small but significant amounts is found in the soils. These minerals occur in the coarser fractions of soils, but are sometimes found in the clay fraction as well. Most of these minerals are heavy minerals falling in the fractions with density greater than 2.95 Mg/m^3 and are used profusely in soil genesis studies to infer the origin of the parent material (Pal and Roy, 1978; Rengasamy *et al.*, 1978).

3.1.4. Pyroxenes and Amphiboles

These two minerals are two groups of ferro-magnesian minerals and their structures consist of long chains of linked silica tetrahedra. The pyroxenes consist of a single chain (two O^{2-} ions shared in each tetrahedron) and the amphiboles of double chains (two and three O^{2-} ions shared alternatively between succes-

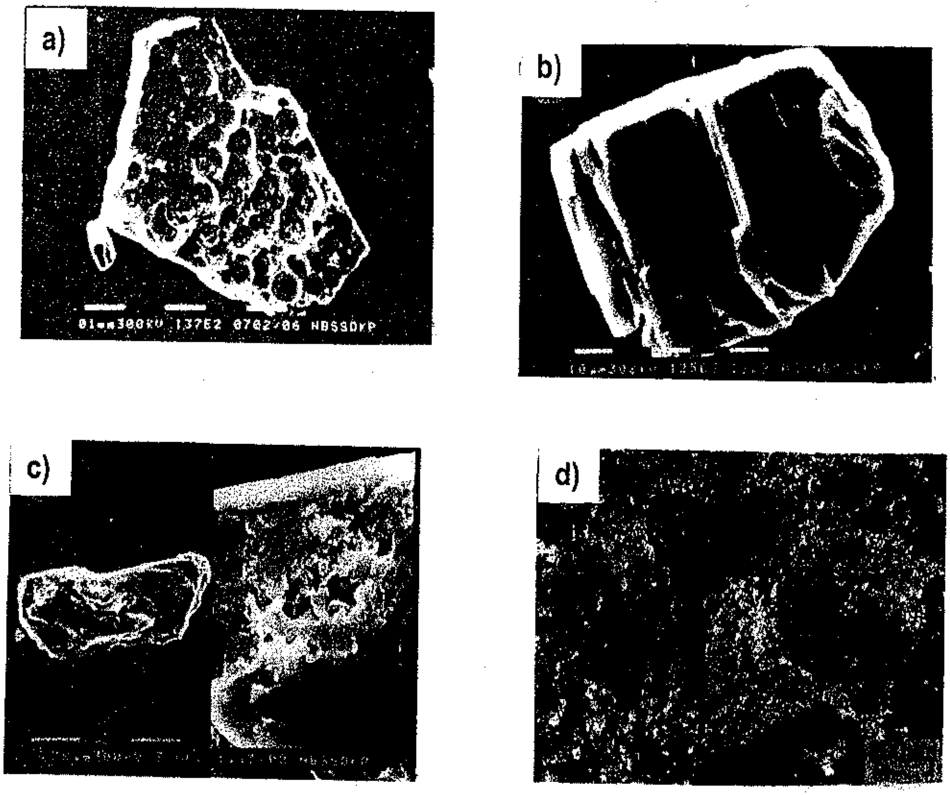


Figure 4. Scanning electron microscope photographs of (a) quartz particle from ferruginous soil, (b) relatively unweathered plagioclase from alluvial soils of the Indo-Gangetic Plains, (c) weathered plagioclase from alluvial soils of the Indo-Gangetic Plains, (d) photomicrographs of smectitic clay mineral pseudomorphs after plagioclase in shrink-swell soils

sive tetrahedra). These chain silicates are classified as inosilicates. Due to a variety of substitutions, these minerals are excellent host minerals for trace elements in soils and also for main constituent cations like Ca, Mg and Fe. Their weathering rate is quite favourable to provide sufficient amounts of these ions in available form for plant nutrition.

The compositions of pyroxene are represented by enstatite — $MgSiO_3$, hypersthene — $(Mg, Fe)SiO_3$, diopside — $CaMgSi_2O_6$, and augite — $(Ca,Na)(Mg,Fe,Al)\ (Si,Al)_2O_6$. Among these, augite is the most important in amounts and compositional significance to soils. This dark-colour mineral is common in the Deccan basalt.

The compositions of amphibole may be represented by the isomorphous series between the end members tremolite — $Ca_2Mg_5Si_8O_{22}.(OH)_2$ and actinolite — $Ca_2Fe_5Si_8O_{22}(OH)_2$ or $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$. Tremolite is characteristic of metamorphosed dolomites; actinolite is also characteristic of metamorphic rocks.

The amphibole group is widely represented in the hornblende series— $(Na, Ca)_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$ and it is widely distributed in igneous rocks from syenite and granite to gabbro (Figure 3), and in metamorphic rocks such as gneiss, hornblende-schist, and amphibolites.

3.1.5. Olivines

Olivines $[(Mg,Fe)_2\ SiO_4]$ are olive-green minerals forming an isomorphous series between the end members forsterite — Mg_2SiO_4, and fayalite — Fe_2SiO_4. The structure consists of independent silica tetrahedra in which oxygen ions are not shared and Al ions are not substituted for Si ions, while alkali ions are excluded. The magnesium and ferrous ions are both surrounded by six oxide ions of two tetrahedra. These minerals are classified as nesosilicates. Large crystals or phenocrysts of olivine are frequently found in the basic rocks (basalt) elsewhere but not in basalt of Deccan (Pal and Deshpande, 1987). On weathering in soils, these crystals yield smectite (nontronite) and free iron oxides. Olivines are relatively easily weathered.

3.1.6. Other Accessory Minerals

The mineral apatite [$Ca_{10}(PO_4)_6F_2$ and its variant], is the most common primary mineral carrier of phosphorus in rocks and parent materials. In basalt, apatites occur commonly as fine mineral grains. They also occur in calcareous sediments. Fluorapatite—$Ca_{10}F_2(PO_4)_6$, is a common form in the igneous and metamorphic rocks. In a few deposits, F has been partially substituted by either Cl^- or OH^-. In most of the sedimentary deposits, PO_4 has been partially substituted by CO_3, causing subsequently a series of inclusion of Na, Mg, and F, leading to the formation of a group of minerals called 'francolites' (also called carbonate apatite). The occurrence of phosphate minerals in the Indian soils is vary rare. The presence of the plumbogummite group of phosphate minerals has been reported in some Indian soils, and therefore, these are considered to be pedogenetic.

Tourmaline—$Na(Mg,Fe)_3Al_6(BO_3)_3.Si_6O_{18}(OH)_4$ has the cyclosilicate (closed ring) structure represented by the $[Si_6O_{18}]^{12-}$ part of the formula. This mineral has relevance to soil chemistry because it contains boron, a plant essential element. Although the mineral is highly insoluble in normal soils, its solubility is enhanced in alkali (sodic) soils to the extent that boron toxicity may occur.

Epidote — $Ca_2(Al,Fe)Al_2O(OH)(SiO_4).(Si_2O_7)$ represents a mineral group in which some of the Ca may be substituted by rare earths and some Mg may be substituted for Fe. Minerals of the epidote group characteristically occur in metamorphic rocks.

Other accessory minerals, used to establish the origin of soil parent material, are: zircon ($ZrSiO_4$), topaz $[Al_2SiO_4(OH,F]_2$, garnets $[X_3Y_2(SiO_4)_3]$, in which X may be Ca^{2+}, Mg^{2+}, Fe^{2+} or Mn^{2+} and Y may be Al^{3+}, Fe^{3+} or Cr^{3+}, and sometimes Ti or Mn^{3+}, magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), sphene ($CaTiSiO_6$), rutile and anatase (TiO_2), kyanite, sillimanite, and andalusite (Al_2SiO_5), and similarly structured staurolite $[2Al_2SiO_5.Fe(OH)_2]$. The presence of some of these minerals has been helpful in establishing a relationship between the parent material and ferruginous soils of the eastern and southern India (Pal and Roy, 1978; Rengasamy *et al.*, 1978).

3.2. Secondary Minerals

3.2.1.Carbonates, Sulphur-bearing Minerals and Zeolites

Carbonates – Calcite ($CaCO_3$) is the most abundant carbonate mineral in dry (subhumid to arid) regions. It may be inherited (Figure 5a) or neoformed (Figure 5b). It often makes up much of the soil mass in thick calcic or petrocalcic horizons (calcretes). In some instances, the isomorph, aragonite ($CaCO_3$), occurs in the sediments and mantle rocks and may, therefore, be found in some soils. Arid and semi-arid climate is the prime factor responsible for the depletion of Ca^{2+} ions from the soil solution in the form of pedogenic carbonates (neoformed calcites) and also in the simultaneous increase of both sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) with pedon depth (Balpande *et al.*, 1996). The impairment of percolative moisture regime due to subsoil sodicity provides an example of a soil where gains exceeds losses. This self-terminating process will lead to not only extreme sodicity but also formation of a calcic horizon.

With the establishment of vegetation on soils, some $CaCO_3$ of soils is dissolved as $Ca(HCO_3)_2$ and this dissolution provides a source of available calcium in soils. This reaction has relevance to reclamation of alkali (sodic) soils of the Indo-Gangetic Plains with or without addition of gypsum (Gupta and Abrol, 1990). Only in rare environments magnesite ($MgCO_3$) can persist in surficial soil and rock layers, because of its relatively high solubility in water.

Dolomite — $CaCO_3.MgCO_3$, in soil parent materials is inherited from dolomitic limestone and mantle rocks derived therefrom. Its dissolution by H_2CO_3 supplies both calcium and magnesium ions that could become available in soils.

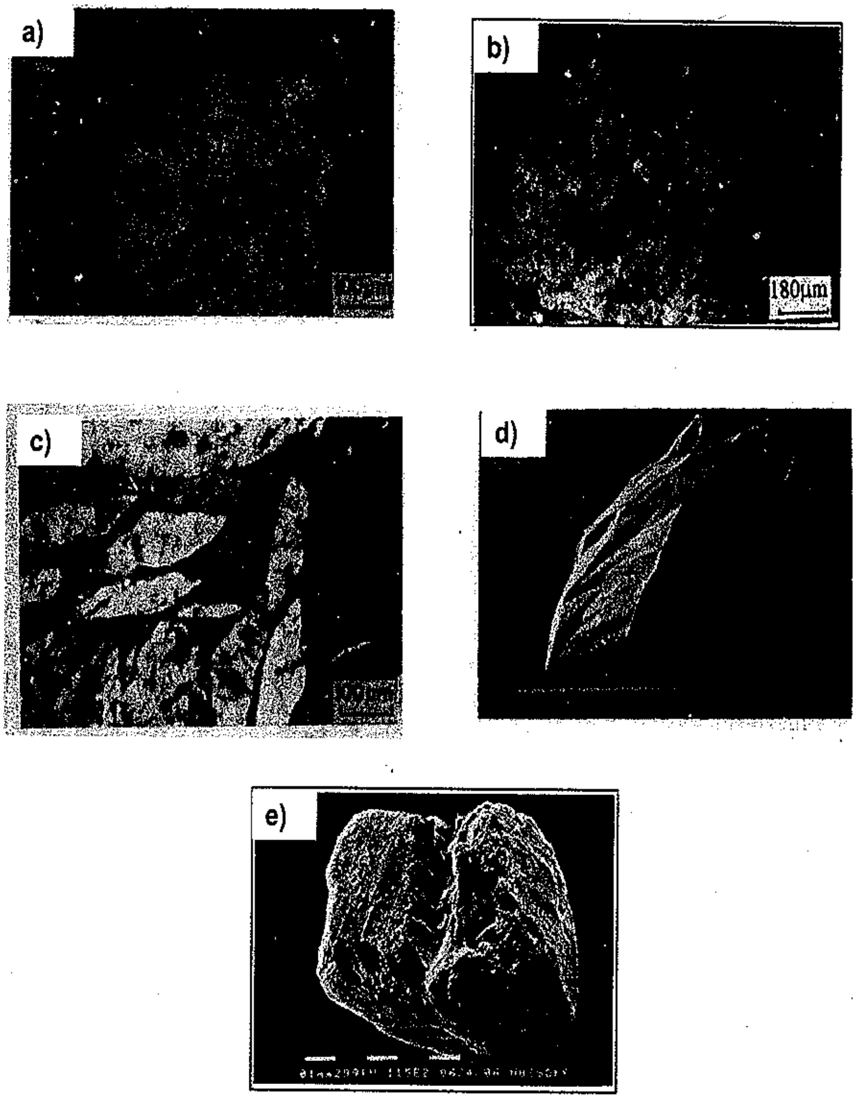


Figure 5. Photomicrographs of (a) lithogenic (parent material) calcium carbonate of shrink-swell soils, (b) pedogenic calcium carbonate of shrink-swell soils, (c) lenticular gypsum crystal of shrink-swell soils; and scanning electron microscope photographs of (d) unweathered heulandite of shrink-swell soils, and (e) weathered heulandite of ferruginous soils

Siderite — $FeCO_3$, is formed by the decomposition of iron-bearing minerals in environments suitable for carbonate accumulation. It is more resistant to the action of H_2CO_3 than $CaCO_3$.

Gypsum — $CaSO_4.2H_2O$ is a relatively common component in soils of arid climates, found frequently in a horizon situated somewhat beneath the horizon in which $CaCO_3$ is accumulated. It occurs sometimes as indurated horizons and as crystals disseminated in surface soil horizons. Gypsum is found in certain subsoils as a weathering product of pyrites (FeS_2), even in soils of humid regions. In arid regions, epsomite ($MgSO_4.7H_2O$) and other soluble sulphates may occur in soils. Minor amounts of the insoluble minerals, namely sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and cobaltite (CoAsS), may also occur in soils. The presence of gypsum in the Indian soils is found very rarely. One such example is its presence in shrink-swell soils of Tamil Nadu (Figure 5c). The presence of gypsum in these soils may have positive implications in water-management practices.

Pyrite and Marcasite — FeS_2 ('fool's gold'), are formed during the reduction phase in the geomorphic cycle of sedimentation when iron of ferric oxides and sulphur of sulphates get reduced [Equation (1)].

$$2Fe_2O_3 + 4Na_2SO_4 + 4H_2O + 9/n\ Cn \longrightarrow 4FeS + 8NaHCO_3 + CO_2 \quad \ldots(1)$$

where, Cn represents organic matter.

The occurrence of sulphides is frequent in shales, underclays of coal seams, and some sedimentary rocks, including limestones. Pyrite is also found in igneous and metamorphic rocks.

The sulphate reduction reaction is extremely fundamental in as much as it utilizes iron of ferric oxide as a cation to replace Na of Na_2SO_4 and to liberate free alkali into the soil solution, lake, or ocean. This reaction occurs under anaerobic conditions. The sulphate ion is reduced in the presence of sulphur reducing bacteria and this reaction is responsible for the development of alkalinity in poorly-drained saline soils. However, in the development of alkali (sodic) soils of the Indo-Gangetic Plains (Pal *et al.*, 2003a) and also of the Purna Valley (Balpande *et al.*, 1996), there has been no role of this reaction.

With time FeS transforms into FeS_2 which on oxidation under good drainage conditions, produces H_2SO_4, resulting in extreme acidity in soils (pH 2.5). Calcium is removed from Ca-bearing minerals by H_2SO_4, and gypsum crystals [$CaSO_4.2H_2O$] are formed. The reaction of sulphuric acid with soil minerals yields jarosite [$KFe_3(OH)_6(SO_4)_2$] and alunite [$KAl_3(OH)_6(SO_4)_2$]. The presence of these minerals in soils has rarely been reported though favourable conditions prevail in some soils of the coastal belt of the country.

Zeolites — Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations. They are further characterized by their ability to hydrate and dehydrate reversibly and to exchange some of their constituent cations, without a major change in structure. Zeolites were discovered in 1756 by the Swedish mineralogist, Cronstedt. Since that time, about 50 natural species have been recognized, and at least 150 species having no natural counterparts have been synthesized in the laboratory (Ming and Mumpton, 1989).

During the past three decades, zeolite minerals have been recognized with increasing regularity as common constituents of Caenozoic volcanogenic sedimentary rocks and altered pyroclastic rocks. Zeolites have also been found as secondary minerals in the Deccan basalt of the Western Ghats in Maharashtra (Sabale and Vishwakarma, 1996).

Along with quartz and feldspars, zeolites are tectosilicates. They consist of three-dimensional frameworks of SiO_4^{4-}-tetrahedra wherein all O^{2-} ions of each tetrahedron are shared with the adjacent tetrahedron. The zeolites may be represented by the following general formula:

$$[M_x^+, M_y^{2+}]\ [\{Al_{(x+2y)}Si_{n-(x+2y)}O_{2n}\}.mH_2O]$$

where, M^+ and M^{2+} are monovalent and divalent cations, respectively. Cations within square brackets are the exchangeable cations, and the others are known as structural cations because with oxygen they make up the framework of the structure.

Zeolites were not believed to be significant in soils until the 1960s, when analcime ($NaAlSi_2O_6.H_2O$) was found in several saline, high-pH soils formed in alluvium in the San Joaquin Valley of California. The analcime in high-pH soils was considered to be authigenic (Baldar and Whittig, 1968). Authigenic analcime has also been found in sodic soils of the Indo-Gangetic Plains. The occurrence of inherited zeolites in soils has been rare. The presence of heulandite [$Ca_4(Al_8Si_{28}O_{72}).24H_2O$] has been found in the sand, silt and clay of red and black soils of the Western Ghats of Maharashtra (Bhattacharyya *et al.*, 1993) (Figures 5d and 5e). It is believed that zeolites can provide adequate amount of bases to prevent the transformation of smectite to kaolinite, and thus enable formation of shrink-swell soils in microdepressions, even in the humid tropical climate of the Western Ghats. The presence of zeolites in acid ferruginous soils of the Western Ghats may be the reason as to why crops do not show response to liming.

3.3. Layer-Silicate Minerals of Soils

Layer silicates or phyllosilicates (Table 4) strongly influence both the physical and chemical properties of soils because of their generally small particle sizes, high specific surface areas, and unique cation exchange properties. Comprehension about phyllosilicate minerals is very basic to soil clay mineralogy. In fact, many clays contain other hydrous silicate and oxide components that may greatly affect soil properties. Layer silicates are also important components of silt and sand and even gravel of soils. Therefore, the layer silicate names need not be restricted in meaning to clays.

3.3.1. Structural Principles

The principal building elements of the layer silicates are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminum or magnesium-oxygen-hydroxyl octahedra. Such sheets of tetrahedra and of octahedra are layered in different fashions in various layered silicates.

In the silicon-oxygen sheets, silicon atoms are coordinated with four oxygen atoms. The oxygen atoms are located on the four corners of a regular tetrahedron with silicon atom in the centre. Three of the four oxygen atoms of each tetrahedron are shared by three neighbouring tetrahedra. The fourth oxygen atom of each tetrahedron is not shared. This arrangement gives hexagonal symmetry to the sheet, in which rings of six oxygen atoms appear. The silicon-oxygen sheet is called the 'tetrahedral sheet' or the 'silica sheet'.

In the Al-, Mg-O-OH sheets, the Al or Mg atoms are coordinated by oxygen atoms or OH groups, forming octahedra. The sharing of oxygen atoms by edges of the neighbouring octahedra results in a sheet. The oxygen atoms and hydroxyl groups lie in two parallel planes with Al or Mg atoms between these planes. The projection of the sheet indicates that the oxygen atoms and hydroxyl groups form a hexagonal close packing. This sheet is called the octahedral sheet or the alumina or magnesia sheet, and is also called as gibbsite layer or brucite layer, respectively.

Phyllosilicates are divided into two groups: 1:1 and 2:1 type minerals, based on the number of tetrahedral and octahedral sheets in each unit layer. Different combinations of these two general structural units, the octahedral and tetrahedral sheets, yield the structures of various layer silicates of importance in soils, including mica, vermiculite, smectite, attapulgite, chlorite, kaolinite, and halloysite, as well as various interstratified and intergradient forms of these layer silicates.

3.3.2. 1:1 Type Minerals

The 1:1 Layer Structure — The 1:1 layer structure consists of a unit made up of one octahedral sheet and one tetrahedral sheet, with the apical oxide (O^{2-}) ions of the tetrahedral sheet being shared with (and becoming part of) the octahedral sheet (Figure 6a). There are three planes of anions. One plane consists of the basal O^{2-} ions of the tetrahedral sheet, and the second consists of O^{2-} ions common to both the tetrahedral and octahedral sheets plus OH^- belonging to the octahedral sheet, and the third consists of only OH^- belonging to the octahedral sheet.

Kaolinite Group — This group includes a number of clay minerals: kaolinite, halloysite, anauxite, dickite, etc. Of these, kaolinite is of maximum importance in soils. The structure of kaolinite minerals consists of 1:1 layers stacked one above the other. Kaolinite is dioctahedral mineral and contains Al^{3+} ions in the octahedral sites and Si^{4+} in the tetrahedral sites (Figure 6b). The 1:1 layer is electrically neutral, and the adjacent layers are held together by hydrogen bonds between the basal oxygens of the tetrahedral sheet of one unit and the hydroxyls of the surface plane of the octahedral sheet of the adjacent unit. Consequently, the structure is fixed and no expansion ordinarily occurs between units when the clay is wetted. Cations and water do not enter between the structural units of the mineral. The effective surface area of kaolinite is thus restricted to its external faces. This is one reason for its low adsorptive capacity for cations. Soils high in kaolinite are generally less fertile than soils in which 2:1 clay minerals predominate.

Kaolinite crystals usually are hexagonal with clear-cut edges (Figure 7a). In comparison with smectite particles, kaolinites are large in size, the diameter generally ranging from 0.1 μm to 5 μm. In contrast to other minerals layer silicate groups, the plasticity, cohesion, shrinkage and swelling properties of kaolinite are very low (Table 4). Kaolinite is abundant in more weathered soils such as Ultisols and Oxisols. It is also commonly present in many ferruginous soils (Alfisols) of southern India. Kaolinites have very little isomorphous

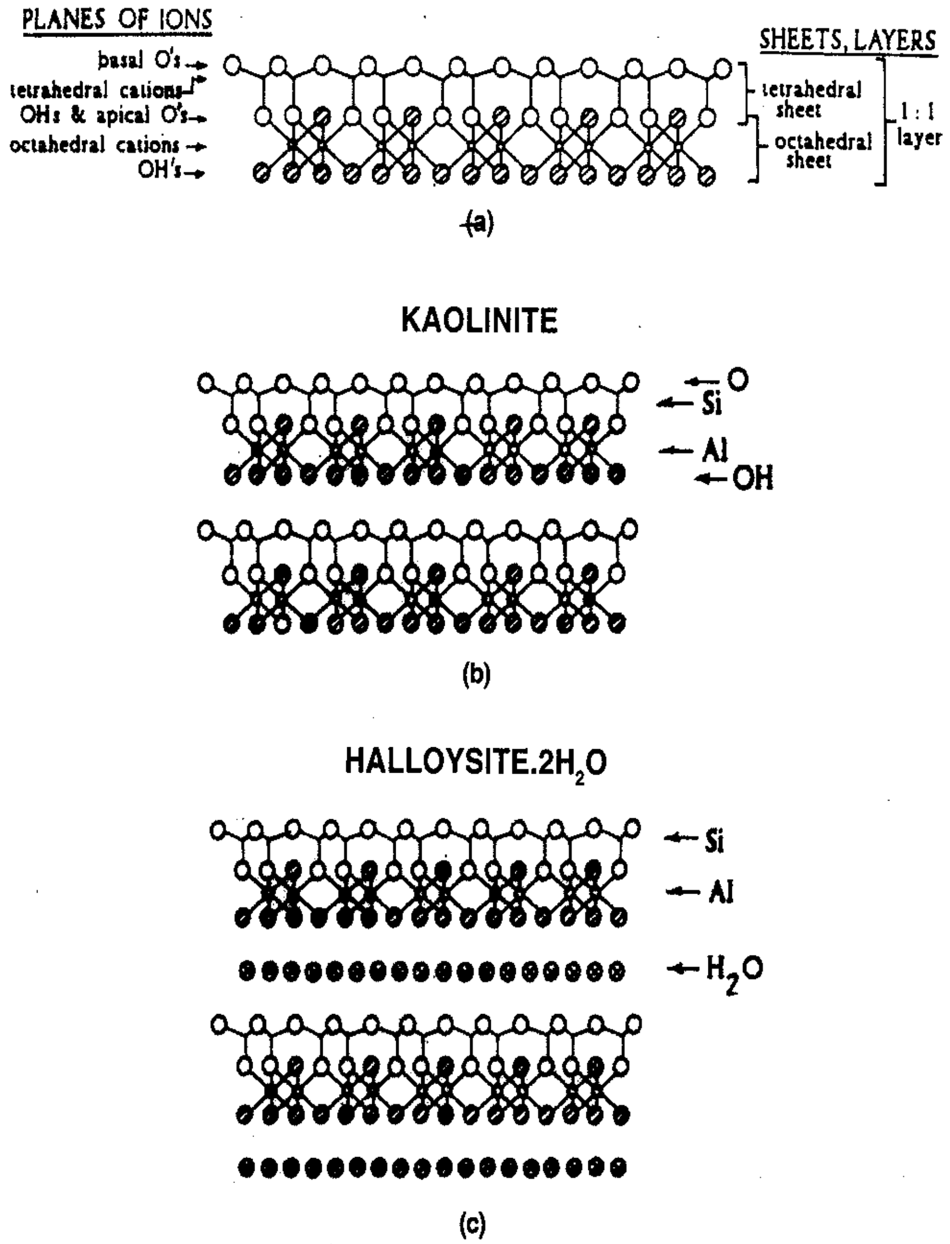


Figure 6. Structural scheme of soil minerals based on tetrahedral and octahedral sheets (a) 1:1 type minerals, (b) kaolinite, and (c) halloysite

Table 4. Properties of three major groups of clay minerals – A comparison

Property	Mineral group		
	Smectite	Mica	Kaolinite
Particle size, µm	0.01-1.0	0.1-2.0	0.1-5.0
Shape	Irregular flakes	Irregular flakes	Hexagonal crystals
Specific surface, m^2/g	700-800	100–120	5–20
External surface area	High	Medium	Low
Internal surface area	Very high	Medium	None
Cohesion and plasticity	High	Medium	Low
Swelling capacity	High	Medium	Low
CEC, $cmol(p^+)kg^{-1}$	80–100	15–40	3–15

Source: Buckman and Brady (1971)

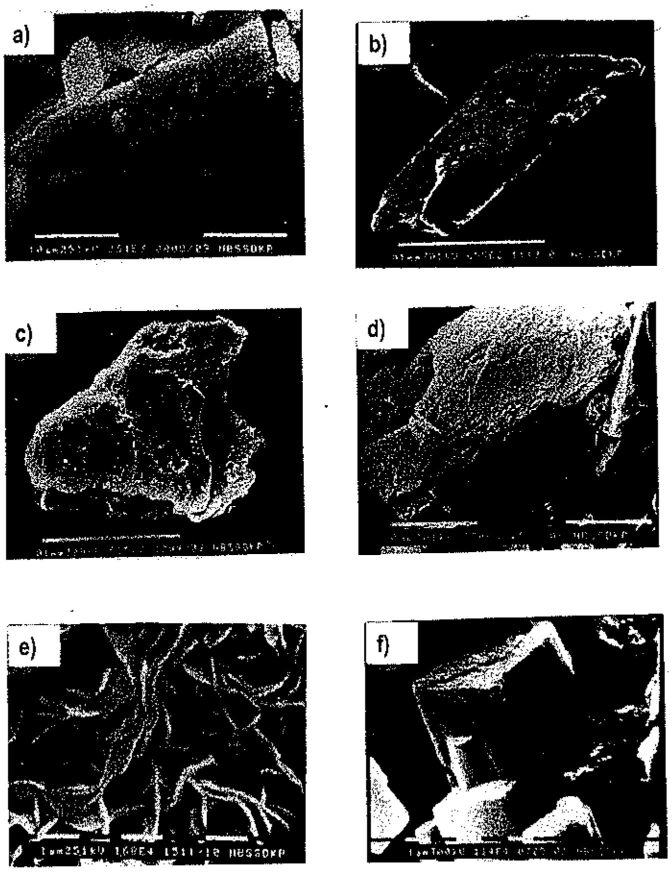


Figure 7. Scanning electron microscope photographs of (a) vermiform kaolinite of ferruginous soils, (b) muscovite, and (c) biotite of alluvial soils of the Indo-Gangetic Plains, (d) vermiculite forming at the edges of biotite mica of ferruginous soil, (e) smectite clay of shrink-swell soil, and (f) gibbsite crystal of ferruginous soil

substitution in the tetrahedral or the octahedral sheet and most kaolinites are close in composition to the ideal formula $Al_2Si_2O_5(OH)_4$. However, the isomorphous substitution of Fe^{3+} for Al^{3+} in the octahedral sheet does occur in ferruginous Alfisols of southern India (Rengasamy *et al.*, 1975).

Kaolinite may be formed in the soils by neosynthesis from the products of hydrolytic decomposition of feldspars and other primary minerals (Rengasamy *et al.*, 1978) and by the conversion of smectite to kaolin by hydroxy Al-interlayering in the expandable minerals and/or mixed layering between 2:1 and 1:1 layers (Pal *et al.*, 1989; Bhattacharyya *et al.*, 1993). The latter process, however, has to provide for the inversion of tetrahedra of alternate tetrahedral sheets so that all the tetrahedra in the crystal are oriented in the same direction. Kaolinite also can be inherited from soil parent materials such as clayey sediments.

Halloysite — Halloysite has a 1:1 layer structure similar to that of kaolinite, except that the 1:1 layers are separated by a layer of H_2O molecules when fully hydrated (Figure 6c), but halloysite often occurs as tubular or spheroidal particles. Halloysite forms early in the weathering process, but it is generally less stable than kaolinite and gives way to kaolinite with time.

3.3.3. 2:1 Type Minerals

In contrast to the 1:1 minerals, the 2:1 minerals are structurally more diverse and are represented by several mineral species.

The 2:1 Layer Structure — The 2:1 layer structure consists of two tetrahedral sheets bound to either side of an octahedral sheet (Figure 8a). There are four planes of anions. The outer two planes consist of the basal oxygens (O^{2-} ions) of the two tetrahedral sheets, while the two inner planes consist of oxygens common to the octahedral sheet and the two tetrahedral sheets, plus the hydroxyls (OH^-) of the octahedral sheet.

Talc and Pyrophyllite — The simple structures of talc and pyrophyllite are a good starting point for discussing 2:1 structures. Both minerals consist of 2:1 layers stacked one above the other. Talc has Mg^{2+} in the octahedral sites and is trioctahedral, while pyrophyllite (Figure 8b) has Al^{3+} in the octahedral sites and is dioctahedral. The tetrahedral sheet in both minerals contains only Si^{4+}, giving ideal formulae $Mg_3Si_4O_{10}(OH)_2$ for talc and $Al_2Si_4O_{10}(OH)_2$ for pyrophyllite. In each case, the charge is balanced within the 2:1 layer, making it electrically neutral. The adjacent 2:1 layers are held together only by weak van der Waal's forces. Both the minerals when found in soils, are usually inherited from low-grade metamorphic rocks.

Micas — The mica minerals have 2:1 layer structure described for talc and pyrophyllite, but with two important differences (Figure 8c), viz.

1. One-fourth of the tetrahedral sites is occupied by Al^{3+} and this substitution causes an excess of one negative charge per formula unit in the 2:1 layer.
2. The excess negative charge is balanced by K^+ ions that occupy interlayer sites between the two adjacent 2:1 layers. This gives an ideal formula of $K(Al_2)(AlSi_3)O_{10}(OH)_2$ for a dioctahedral mica mineral (muscovite) and $KMg_3(AlSi_3)O_{10}(OH)_2$ for phlogophite.

The octahedral sheet of mica may be either dioctahedral or trioctahedral. There are several different mica species because Fe^{2+} and Fe^{3+} can be substituted for Mg^{2+} and Al^{3+} in the octahedral sheet, and Na^+ and Ca^{2+} can be substituted for K^+ in the interlayer. Since the unit layers do not part on addition of water, the K^+ ions between the unit layers are not available for exchange; they are fixed. Only the K^+-ions on the external surfaces can be exchanged for other cations.

The non-swelling character of the micas is attributed to the specific linking effect of the unit layers by the K^+ ions. These ions are of the right size to establish a favourable 12-coordination with the opposite hexagonal oxygen rings of adjoining unit layers. In fact, these rings are not hexagonal in real structure, rather, they are ditrigonal in shape (Rich, 1972). This arrangement is caused by the rotation of adjacent tetrahedral in opposite direction so that the larger tetrahedral sheets can fit with smaller octahedral sheet in between. The coordination number of oxygen about K caused by the ditrigonal arrangement is thus reduced from 12 to 6 and the K-O bond is shortened and strengthened. A larger rotation is found in a dioctahedral structure causing shorter K-O bond length than in a trioctrahedral structure. Thus, the bonding of K is stronger in dioctahedral micas than in trioctahedral varieties of this mineral group. Such properties as hydration, cation adsorption, swelling, shrinkage, plasticity, and ease of dispersion are less developed in soil micas. As to size, soil mica crystals are apparently intermediate between those of smectite and kaolinite (Table 4).

Mica in soils is usually inherited from the parent rocks and is likely to occur in soils derived from various igneous and metamorphic rocks as well as from sediments derived from them. The most common mica group minerals in rocks and consequently in soils are three K-containing micas : muscovite (Figure 7b), biotite (Figure 7c) and phlogopite. The tetrahedral sheets of all the three are similar, but their octahedral sheets differ. Biotite and phlogopite are trioctahedral, with phlogopite containing Mg^{2+} in the octahedral sites, while biotite contains Mg^{2+} and Fe^{2+}. Muscovite is dioctahedral and contains Al in the octahedral sheet.

Soil clay mica often has poorer crystallinity, lower K-content, and higher H_2O-content than the macroscopic muscovite which most closely resembles. This clay-sized mica is often referred to as illite. However, illite is not to be used as a specific mineral name but as a term indicating that it is a mixed assemblage of minerals with mica as the main component. Unless one is using the mineral name in the strict crystallographic sense, for common understanding, soil clay minerals with a dominance of mica can still be called illite (Raman,1984).

Micas weather to other minerals, particularly to vermiculites and smectites, and the K^+ ion released during weathering is an important source of K for plants. It is known that muscovite micas are more resistant to weathering than biotite and phlogopite and in the presence of latter two, muscovite tends to retain its K still more firmly and is a useless K-reserve (Pal, 2003). As a result, muscovite is more likely to persist than biotite or phlogopite in the highly weathered soils (Pal , 2003).

Vermiculite — Vermiculite consists of the 2:1 layer silicate structure described for mica, but instead of having a layer charge of ~1 per formula unit and K^+ ion in the interlayer positions, vermiculite has a layer charge of 0.9 to 0.6 and contains Ca^{2+} and Mg^{2+} ions as exchangeable cations in the interlayer (Figures 7d and 8d). The high charge per formula unit gives vermiculites a high CEC and causes them to have a high affinity for weakly hydrated cations such as K^+, NH_4^+, and Cs^+. Fixation of K^+ by vermiculites can be significant in soils high in vermiculite. Reported fixation of K^+ ions in black, alluvial and ferruginous soils of India is due only to the presence of vermiculite and not any other mineral like illite, hydrous micas and smectites (Pal, 2003).

Vermiculites in soils are believed to be formed almost exclusively from the weathering of micas and chlorites. It is often reported that dioctahedral vermiculites are most common in soils. However, trioctahedral vermiculite is very common in soils of arid and semi-arid regions of India and is the weathering product of biotite mica (Figure 7d).

Smectites — The smectite group contains several minerals, such as montmorillonite, beidellite, nontronite, and saponite. Of these, montmorillonite is the most dominant, although others also occur in certain soils. The flake-like crystals of montmorillonite (Figure 7e) are composed of crystal units. The smectite group consists of minerals with the 2:1 structure like mica and vermiculite, but with a still lower charge per formula weight (0.6-0.25). As in vermiculite, the interlayer contains exchangeable cations (Figure 8d).

Dioctahedral smectites are the most common in soils. Their compositions range between the three end members like montmorillonite, beidellite and nontronite. In montmorillonite, Mg^{2+} is substituted for Al^{3+} in the octahedral sheet to produce the layer charge. In beidellite and nontronite, the layer charge is generated in the tetrahedral sheet. Beidellite contains Al^{3+} in the octahedral sheet, while in the nontronite, the octahedral sheet contains Fe^{3+}. Smectites do not fix K^+ ions as readily as vermiculites do because their layer charge is lower.

Smectite dominates in the clays of Indian shrink-swell soils developed in alluvium of Deccan basalt and is nearer to montmorillonite of the montmorillonite-nontronite series and does not have any K-selectivity (Pal, 2003). Its layer charge ranges from 0.28 to 0.78 mol(-)/$(SiAl)_4O_{10}(OH)_2$ (Ray *et al.*, 2003). The observed K-adsorption by these soils is due to the occurrence of small amount of vermiculite mainly concentrated in the coarse clay (2-0.2 μm) fractions (Pal and Durge, 1987).

Smectite crystals range in diameter from 0.01 μm to 1.00 μm. They are thus much smaller than the average kaolinite particles (Table 4). Cations and water molecules are able to move in between the crystal units of smectites. The movement of water between crystal units hydrates the cations and the large hydration energy involved is able to overcome the attractive forces between the unit layers for the interlayer cations, causing smectite to swell more than other layer silicates (van Olphen, 1966).

Smectites are also noted for their high plasticity and cohesion, marked shrinkage on drying and ready dispersion of their fine, and flaky particles (Table 4). The shrink-swell behaviour is most pronounced in the Vertisol order and in Vertic subgroups. The shrink-swell properties lead to engineering problems when houses, roads, and other structures are built on smectitic soils.

Chlorites — Chlorites are a group of clay minerals structurally related to the three-layer minerals. In chlorites, the charge compensation between smectite-type unit layers is by a positively charged interlayer octahedral hydroxide sheet (Figure 8e). A possible formula for such a hydroxide sheet is $[Mg_2Al(OH)_6]^+$. Both octahedral sheets (the one that is part of the 2:1 layer or the interlayer hydroxide sheet) may be either dioctahedral or trioctahedral, and may contain Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+} ions, giving a large number of different mineral species.

Chlorite minerals in soils are generally primary mineral, inherited from the parent rock and are found only in small amounts in soils. Under suitable (possibly acidic) environments, chlorites weather to vermiculite and smectite minerals (Kapoor, 1972). Chlorites in soils of the Indo-Gangetic Plains are rich in iron, as is evident from the ease of dissolution in HCl.

Hydroxy-interlayered Vermiculite and Hydroxy-interlayered Smectite — Hydroxy-interlayered vermiculite (HIV) and hydroxy-interlayered smectite (HIS) can be considered to form a solid-solution series, with the "pure end-numbers" consisting of smectite or vermiculite at one and pedogenic or aluminous chlorite at the other. Hydroxy-interlayered minerals are formed as Al^{3+} ions are released during weathering, which hydrolyse and polymerize to form large polycations with a postulated formula $[Al_6(OH)_{15}]^{3+}$ (or similar) in the interlayers of vermiculite and smectite. These polycations balance some of the charge of the 2:1 layer. The combination of a 2:1 layer with hydroxy-Al in the interlayer gives a structure similar to that of chlorite (Figure 8f). Thus, these minerals are called secondary chlorites. The degree of infilling of the interlayer with hydroxy-Al can vary from zero to almost complete. The interlayer hydroxy-Al is not exchangeable and, therefore, it lowers the CEC of smectite or vermiculite.

The interlayer hydroxy-Al impairs the shrinking and swelling characteristic of smectite (Kalbande *et al.*, 1992). In vermiculite, it reduces K-adsorption capacity by lowering the exchange capacity and by preventing the layers from collapsing around the K^+ ions. The positively charged hydroxy-Al interlayers may also provide active sites for adsorption of anions (Schulze, 1989).

Both, HIV and HIS are most common in Alfisols and Ultisols of India (Pal and Deshpande, 1987; Bhattacharyya *et al.*, 1997).

Mixed-layer or Interstratified Minerals — Phyllosilicates in soils do not always occur as discrete particles of mica, vermiculite, smectite, chlorite or kaolinite. One physically discrete particle may consist of a mixture of both mica and vermiculite layers. Such minerals are referred to as mixed layer or interstratified minerals.

Different types of interstratified minerals have been identified. Two component systems include mica-vermiculite, mica-smectite, mica-chlorite, chlorite-vermiculite, chlorite-smectite, chlorite-swelling chlorite and kaolinite-smectite. Three component mixed-layer systems can also occur. The sequence of layers can be regular or random. The random interstratification of layer silicates is common in Indian soils (Kapoor *et al.*, 1981; Tomar, 1985; Bhattacharyya *et al.*, 1993; Chandran *et al.*, 2005).

Partial loss of interlayer K^+ ions from micas or of interlayer hydroxides from chlorite is one way for the formation of interstratified minerals in soils. Other possibilities include (i) fixation of adsorbed K^+ ions by some vermiculite layers to yield mica-like layers, and (ii) formation of hydroxide interlayers to provide chlorite-like layers.

Palygorskite and Sepiolite — Structurally important element in these minerals is the amphibole double silica chain oriented with its long direction parallel to the c axis. The apexes of the tetrahedrons in successive chains point in opposite directions. Thus, they are structurally distinct from the typical 1:1 and 2:1 layer structures. The linked chains form a kind of double-ribbed sheet, with two rows of tetrahedral apexes at alternate intervals in the top and bottom of the sheets. The ribbed sheets are arranged so that the apexes of successive sheets point together, and the sheets are held together by aluminium and/or magnesium in octahedral co-ordination between the apex oxygens of successive sheets (Figure 8g).

Palygorskite and sepiolite are often found in soils of arid and semi-arid environments and have fibrous morphology in contrast to the platy morphology of most other clay minerals. Palygorskite has been identified in some desert soils of Rajasthan (Sarma and Sidhu,1982) and

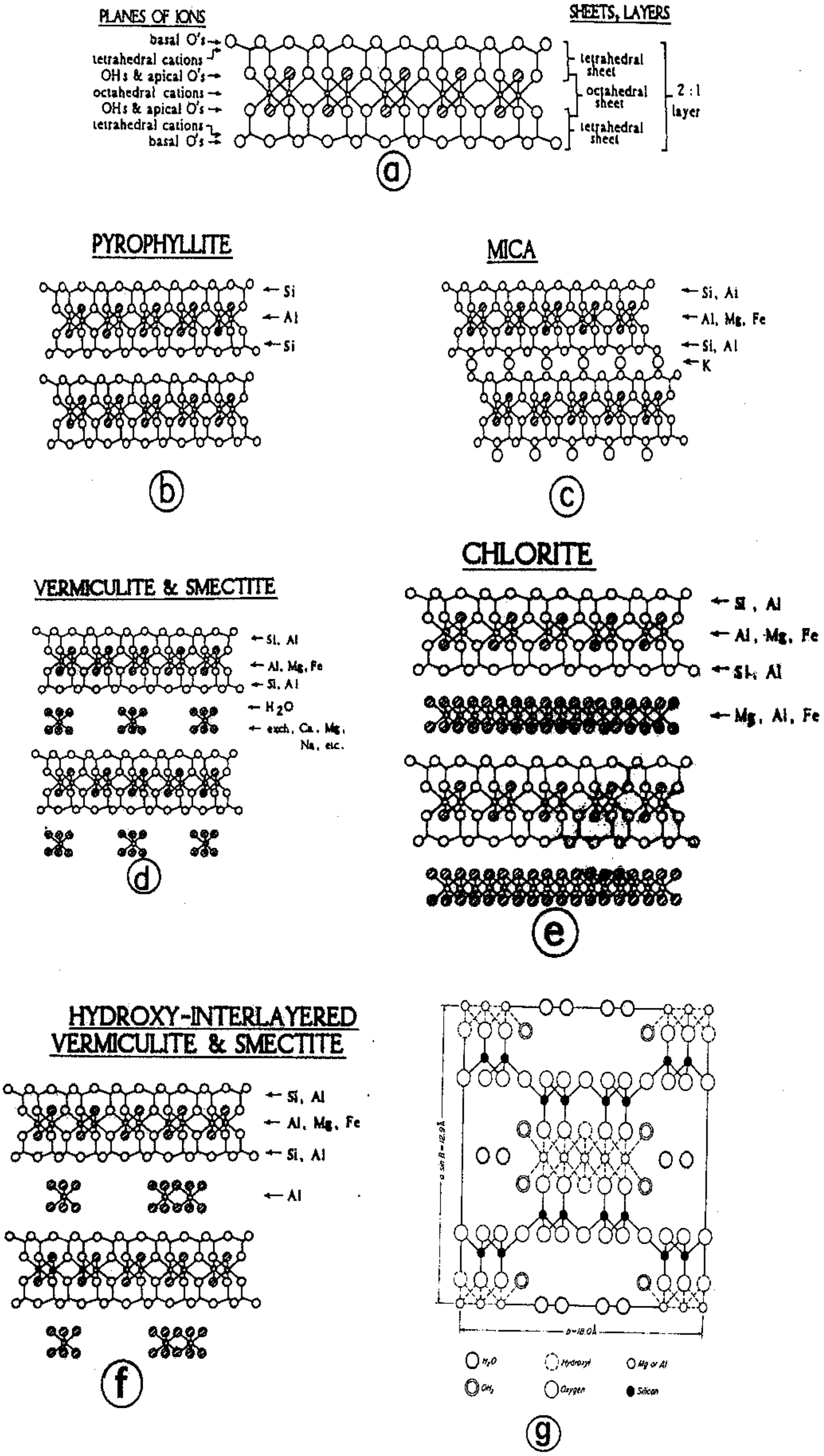


Figure 8. Structural scheme of soil minerals based on tetrahedral and octahedral sheets (a) 2:1 type minerals, (b) pyrophyllite, (c) mica, (d) vermiculite and smectite, (e) chlorite, (f) hydroxy-interlayered vermiculite and smectite, and (g) palygorskite

also in Vertisols of Gujarat (Pal *et al.*, 2003b). It releases Mg^{2+} ions when soils containing it are irrigated and high exchangeable Mg^{2+} ions cause dispersibility of clay particles, and in this way soils become poorly drained (Neaman and Singer, 2004).

Allophane and Imogolite — These two aluminosilicates exhibit short-range (or local) order, and are essentially poorly-crystalline or the structure is disordered. Structures with short-range order exhibit order over several nanometres, but on a larger scale, the structure is disordered.

Allophane is a mineral consisting chemically of variable amounts of O^{2-}, OH^{-}, Al^{3+}, and Si^{4+}, and is characterized by short-range order and a predominance of Si-O-Al bonds. It consists of small (dia: 3.5-5.0 nm) spheres, the structure of which has not been determined.

Imogolite consists of tubes several micrometres long with outer diameter of 2.3 nm to 2.7 nm and an inner diameter of ~1.0 nm. The tubes consist of a single dioctahedral sheet with the inner surface of OH^{-} replaced by O_3SiOH groups (Farmer *et al.*, 1983). The tubes are arranged in bundles 10-30 nm across and several micrometres long.

Soils containing large amounts of allophane and imogolite exhibit unique physical properties. These soils often have a low bulk density (0.25 - 0.3 Mg/m^3), high water-holding capacity (80-180% on oven dry basis), high liquid and plastic limits, and thixotropic tendency.

3.4. Oxide Minerals in Soils

In humid tropical climate, accumulation of soil colloids with compositions enriched in hydrous oxides of Al, Fe and Ti occurs because of de-silication. These inorganic colloidal substances range from amorphous to crystalline states in degree of organization.

3.4.1. Aluminium Oxides

A number of crystalline hydroxides, oxyhydroxides, and oxides of aluminium are found in nature. Gibbsite, one of the $Al(OH)_3$ polymorphs, is common in soils. It is one of the major minerals in Ultisols and Oxisols of tropical and subtropical regions. It is common in the silt and clay fractions of Ultisols of Meghalaya (Figure 7f). The gibbsite layer consists of a pair of hydroxyl sheets held together by octahedrally coordinated aluminium ions. The layers are held together by hydrogen bonding between hydroxyls of adjacent layers.

The oxyhydroxide of aluminium, boehmite (AlOOH), in which aluminium ions are octahedrally coordinated by oxygen and hydroxyl ions, occurs in the intensely leached, highly weathered soils, frequently in association with gibbsite. Geological materials that have undergone weathering for periods of several million years may contain appreciable amounts of boehmite along with large amounts of gibbsite.

3.4.2. Iron Oxides

Iron oxides, oxyhydroxides, and hydrated oxides are the most abundant among the metallic oxides in soils. These are present in most of the soils of different climatic regions as very fine particles in one or more of their mineral forms in varying concentrations. These different mineral phases have been referred to as "free iron oxides" previously in an attempt to differentiate between true oxides and the Fe bound in other minerals such as the silicates. This distinction is, however, unnecessary, because Fe in other minerals is not really present as an oxide. Therefore, it will be more meaningful to refer to these minerals collectively as "iron oxides" and subsequently distinguish between primary and secondary or pedogenic-forms (Schwertmann and Taylor, 1989).

The most common iron oxides in soils are haematite (Fe_2O_3), which imparts pink to bright red colour to soils, and goethite (α-FeOOH or α-$Fe_2O_3.H_2O$), which gives brown and dark reddish brown colours to soils. Iron oxides provide an extremely important reflection of the chemical properties of soils and the genetic processes that have governed soil formation.

Haematite, purple in colour, is of coarsely crystalline form, and may occur in silt and sand fractions of soils (Rengasamy *et al.*, 1978). Martite (Fe_2O_3) has a structure similar to that of haematite. Dark iron oxide coatings are often associated with coatings of pyrolusite (MnO_2).

Goethite is abundant in concretions in certain Oxisols and Podzols. Finely divided yellowish goethite is sometimes designated as limonite which absorbs much water. Thin films of goethite and haematite occur on the surfaces of grains in soils to give reddish and brownish tints. Lepidocrocite (FeOOH), an isomer of goethite, has often been reported in poorly-drained soils rich in organic matter (Jackson, 1964), particularly as bog ores. It imparts bright orange colour to soils.

The mineral magnetite (Fe_3O_4) is a magnetic iron oxide of spinel structure, inherited from the parent rock. It occurs in soils usually as a sand-size mineral of specific gravity 5.17. Oxidation of iron in Fe_3O_4 yields maghemite (Fe_2O_3), which is also magnetic.

3.4.3. Titanium Oxides

Rutile (TiO_2) and anatase (TiO_2) commonly occur in soils and clay sediments. Rutile in soils is usually inherited from the parent rocks, while anatase may be pedogenic (Jackson, 1964). These minerals are commonly found in soils developed from the metamorphic rocks and also from basalt. Leucoxene ($TiO_2.nH_2O$) is an amorphous hydrous titanium oxide.

3.4.4. Ilmenite

Ilmenite ($TiFeO_3$ or $TiO_2.FeO$) is generally found in soils developed from the gneissic rocks. The substitution of Ti for Fe in magnetite gives the titanomagnetite ($TiFe_2O_4$) to titanomaghemite ($TiFe_2O_5$) series which occurs in soils of Hawaii (Jackson, 1964).

4. Elemental Composition of Soils

Just as in the earth's crust (Table 5), a large proportion of the inorganic material of soils is composed of four elements: oxygen, silicon, aluminium and iron. Nearly 90% of the mineral matter of most of the soils consists of the combined oxides of silicon, aluminum and iron. During chemical weathering and leaching, the proportions of these and other constituents get changed largely. This is comprehended in the composition of the fine fractions of the subsoil, especially in the illuvial Bt horizons (Table 6).

In general, the oxides of calcium, magnesium, sodium and potassium each make up about 1-2%, and together constitute about 5-7% of many highly-weathered soils. However, in soils of arid and sub-humid climates, the percentages of these oxides are higher. The oxides of manganese, phosphorus, and sulphur generally constitute only a fraction of a per cent of the mineral soil components.

Table 5. Average chemical composition of the earth's crust

Element	Percentage	Oxide	Percentage
O	46.5	SiO_2	59.07
Si	27.6	Al_2O_3	15.22
Al	8.1	Fe_2O_3	3.10
Fe	5.1	FeO	3.71
Ca	3.6	CaO	5.10
Mg	2.1	MgO	3.45
Na	2.8	Na_2O	3.71
K	2.6	K_2O	3.11
Ti	0.6	TiO_2	1.03
P	0.12	P_2O_5	0.30
S	0.06	MnO	0.11
Cl	0.05	H_2O	1.30
C	0.04		

Source: Jackson (1964)

4.1. Silicon

The silicon content (as SiO_2) makes up a major portion of the mineral soils if not highly weathered. Due to de-silication in soils of humid tropical climates, silica is highly depleted. Therefore, laterites contain very small amount of SiO_2 (Table 6).

4.2. Aluminium

Next to oxygen and silicon, aluminium is the most abundant element in the earth's crust and in the majority of rocks and soils. As Al_2O_3, it ranges from 20 to 60% in highly-weathered soils and laterites (Jackson, 1964). The higher percentage of Al_2O_3 is generally associated with high percentage of gibbsite, as in bauxite ores. As SiO_2 decreases and Al_2O_3 is enriched, the molar ratio of SiO_2/Al_2O_3 in soil clays decreases from about 4 in crystalline clays rich in layer silicate minerals to less than 1 in clays high in allophane (amorphous).

4.3. Iron

The iron content (as Fe_2O_3) makes up 3-15% of soils in general. However, it can ex-

Table 6. Chemical composition of some major soils of India

Hori-zon	Depth (cm)	Chemical composition, %								
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO_2	Na_2O	K_2O
Alluvial soil of the Indo-Gangetic Plain in Sitapur district, Uttar Pradesh (Typic Haplustalf)[a]										
Ap	0-18	76.8	14.2	3.1	0.6	0.4	0.5	0.1	1.2	3.0
A/B	18-36	73.8	16.2	3.6	1.2	0.3	0.3	0.1	0.8	3.1
Bt1	36-88	70.1	19.7	3.9	1.5	0.3	0.3	0.1	0.7	3.1
Bt2	88-133	69.1	20.4	4.2	1.6	0.3	0.3	0.1	0.7	3.1
Bt3	133-175	67.4	20.6	4.9	1.4	0.3	0.7	0.1	0.8	3.2
B/C	175-200	68.9	19.3	4.3	1.3	0.5	0.8	0.1	1.0	3.6
Ferruginous soil on granite-gneiss in Bankura district, West Bengal (Typic Rhodustalf)[b]										
Ap	0-13	72.0	13.0	5.1	1.6	2.3	0.7	—	—	7.8
Bt1	13-32	63.0	27.2	6.9	1.7	2.0	0.7	—	—	7.1
Bt2	32-49	65.3	19.0	8.8	0.4	1.0	0.5	—	—	7.8
Bt3	49+	57.0	23.1	12.9	0.3	1.2	0.4	—	—	7.7
Laterite on serpentine rock in Kukusan mountains, S.E. Kalimantan, Indonesia (Oxisol)[c]										
A	0-100	7.6	10.9	65.1	0.3	—	0.3	0.3	—	—
B1	100-200	3.7	13.8	65.4	0.3	—	0.4	0.8	—	—
B2	200-500	2.5	12.1	68.7	0.2	—	0.9	0.8	—	—
B3	500-650	7.3	9.8	60.4	0.1	—	6.4	0.9	—	—
C1	650-700	19.0	8.4	50.0	0.1	—	7.6	0.7	—	—
C2	700-750	34.0	5.6	34.9	0.1	—	11.4	0.5	—	—
R	750+	39.4	2.5	8.4	Tr	—	33.2	0.1	—	—
Black soil of Deccan trap in Bijapur district, Karnataka (Calcic Pellustert)[d]										
Ap	0-20	44.2	14.8	12.9	1.2	7.6	4.6	—	0.8	1.1
A12	20-45	42.6	13.9	13.1	1.2	9.0	4.8	—	0.9	1.0
A13Ca	45-62	40.2	13.4	10.1	1.0	14.0	4.4	—	0.8	0.5
AC	62-95	42.1	13.3	11.6	1.2	11.8	5.3	—	0.7	0.7

Sources: [a]Srivastava *et al.* (1994); [b] Pal and Roy (1978); [c] Mohr *et al.* (1972); [d] Dasog and Hadimani (1980).

ceed 50% in laterites (Table 6). The higher content of iron in soils than in the earth's crust (Table 5), is due to soil development processes. Because of relatively higher iron oxide content, high degree of stability of soil aggregates and high porosity are usually associated with ferruginous soils.

The principal form of iron in soils is generally iron oxides, but iron is also an integral part of layer silicates of soil, like biotite, vermiculite and smectite. Smaller quantitites of iron occur in soils in pyroxenes and amphiboles.

4.4. *Titanium*

The titanium content (TiO_2) makes up not more than 2% in many soils of temperate, humid and arid climates. In soils, titanum occurs primarily as fine-grained crystals of free TiO_2 (anatase and rutile) and $FeTiO_3$ (ilmenite). Since these minerals are highly resistant to weathering, the titanium content of soils tends to increase as other elements are leached out. The TiO_2 content of soils other than laterites, is very low (< 2%, Table 6). In laterites, TiO_2 content ranges from less than 1% (Table 6) to 20% or more (Jackson, 1964).

4.5. *Calcium*

Except where calcium carbonate is present, the calcium content (CaO) is generally in the low range (<3%) in soils (Table 6). The CaO content of soils is lower than that of igneous and sedimentary rocks (Table 6), because of leaching of calcium from the upper horizons of well-drained soils, except under arid climates.

The calcium of igneous and metamorphic rocks occurs mainly in the plagioclase series of feldspars. Non-calcareous soils contain calcium in the form of plagioclase, augite, hornblende, and epidote. Because of the presence of these minerals, even the moderately-weathered ferruginous soils (Ustalfs) are dominated by exchangeable Ca^{2+} ions (Pal *et al.*, 1989). However, in black soils of semi-arid climates, the concentration of Mg^{2+} ions is higher than that of Ca^{2+} ions in the subsoil (Dasog and Hadimani, 1980; Balpande *et al.*, 1996).

Calcium carbonate occurs in many soils in lower horizons. However, $CaCO_3$ is found at increasingly lower depths as one proceeds from more humid to more arid regions. Calcareousness also increases in black soils of semi-arid climates from high rainfall (>900 mm) to low rainfall area (<900 mm) (Balpande *et al.*, 1996). Pedogenic $CaCO_3$ is mainly the mineral calcite, precipitated when the soil solution gets concentrated in the arid climatic conditions. This precipitation triggers the development of sodicity in the subsoils of black soils (Balpande *et al.*, 1996). Crystalline gypsum ($CaSO_4.2H_2O$) is also accumulated in soils of semi-arid and arid climates, as observed in black soils of southern India (Pal, 2003).

4.6. Magnesium

In soils with percolative moisture regime, magnesium is retained primarily in mafic minerals, such as biotite, augite, hornblende, and smectites. The magnesium content of soils (as MgO), is generally less than 1% (Table 6) in non-calcareous soils. Dolomite ($CaCO_3.MgCO_3$), which occurs in substantial quantities in some soils that are inherited from the parent rocks or are formed pedogenically (Jackson, 1964). In black soils of semi-arid parts of India, MgO content exceeds 2% (Table 6). As exchangeable cations, Mg^{2+} ions along with Ca^{2+} ions dominate the exchange complex of soils of non-percolative moisture regime, especially in the black soils of semi-arid climates.

4.7. Potassium

In the alluvial and ferruginous soils, the K_2O content is higher than 3%, whereas in black soils, it is lower (Table 6). The former two soils are rich in K-bearing minerals, whereas the latter are not.

The proportion of the total potassium of soils held in soluble and exchangeable forms is usually relatively small. The high potassium primary silicate minerals are: muscovite, biotite, orthoclase and microcline. The potassium availability of major soils of India is related to the K release from biotite mica contained in sand, silt and clay fractions (Pal *et al.*, 2001). Of the layer-silicates, only micas have a substantial potassium content. However, the K release from clay mica depends on the nature of mica, it being slow when the clay mica has more muscovitic character. Alluvial and ferruginous soils of the northwestern and southern parts of India are rich in K-bearing minerals, especially biotite mica and therefore, no crop response to chemical K-fertilizers is noticed even after long periods of cropping. Application of water-soluble forms of fertilizer, such KCl or K_2SO_4 is, however, necessary for intensive agriculture in soils of humid climates where biotite mica is fast depleted during weathering.

4.8. Sodium

The sodium-content (as Na_2O), in general, does not exceed 1% in most soils (Table 6). This is much less than the average of 3.7% in the earth's crust (Table 5). The lower Na_2O content in soils reflects weathering away of sodium-bearing minerals, primarily plagioclase feldspars. The high sodium content of ocean waters indicates the depletion of sodium through leaching from soil minerals. The release of Na^+ ions from plagioclase may be sufficient to cause the sodicity in soils of semi-arid climate (Pal *et al.*, 2003a).

Sodium in well-leached soils occurs in high-albite plagioclases and in small amounts in micas, pyroxenes, and amphiboles, primarily in the fine sand and silt fractions. Sodium occurs as NaCl, Na_2SO_4, $NaHCO_3$, and Na_2CO_3 in saline and saline-alkali soils.

4.9. Phosphorus

The P-content of most mineral soils is between 0.02% and 0.5%. About half of the soil phosphorus occurs in combination with organic matter of surface soils and the remainder resides in mineral or inorganic combination.

Phosphorus in inorganic form occurs mainly as calcium phosphate in alkaline and calcareous soils (Gupta and Abrol, 1990). The main calcium phosphate in soils is a variant of fluorapatite [$Ca_{10}(PO_4)_6F_2$]. With progressive weathering, soils develop acidity and phosphate becomes increasingly bonded to aluminium and iron. Calcium phosphate is insoluble at high soil pH conditions. However, on lowering the pH by amendment (through gypsum, for instance), it becomes available to the extent that application of phosphatic fertilizers may be avoided for the first few years of cropping. Iron and aluminium phosphates of acid soils become available only when pH of the soil is raised by amendments (lime, for example).

4.10. Molybdenum

The molybdenum-content of soils generally ranges from 1 to 10 ppm, but in certain soils it may be as high as 30 ppm or even more. Molybdenum occurs in soil mainly as MoO_4^{2-} ions and like phosphate, it undergoes fixation as basic iron and aluminum molybdates. With increase in soil pH by liming, the availability of soil molybdenum is enhanced.

4.11. Nitrogen

The amount of nitrogen in surface soils ranges from 0.02% to 0.25% in general, and is closely related to the amount of soil organic matter of which nitrogen makes up approximately 5%. Nitrates, nitrites, and exchangeable ammonium usually account for less than 1% of the total nitrogen content of mineral soils. When NH_4^+ ions substitute K^+ ions in micas of subsoil and rocks, these provide an additional amount of nitrogen. The mineral-humus complexes also account for much additional nitrogen of soils.

4.12. Sulphur

Sulphur is present in soils in both organic and inorganic forms. In well-leached soils much of the sulphur gets associated with organic matter. Soils of humid temperate region contain 50 to 500 ppm of water-soluble sulphate and 100 to 1500 ppm of total sulphate. Soils high in free iron oxides tend to contain sulphate ions substituting for hydroxyl ions in basic iron sulphate complexes. This form of sulphate, which is slowly extractable in alkali (NaOH) solutions, constitutes a reserve of slowly available sulphate.

Sulphur is added to soils through rain and snowfall. It is also added to soils through many commercial fertilizers and by irrigation waters used for crops and greenhouse culture.

4.13. Selenium

Like other trace elements, selenium is found in traces in most soils and rocks. Selenium-content from 2 to 10 ppm is considered very high in soils. High Se-content is likely to produce vegetation toxic to livestock. Certain native plants are "accumulators" of Se and their chemical analysis may be used as a guide in areas of excess selenium supply. During weathering, this element oxidizes to selenate which is subject to leaching, and combines with free iron oxides to form basic selenates.

4.14. Boron

The total boron-content of soils, in general, is in the range 4-98 ppm , compared to 10 ppm in igneous rocks and 4.5 ppm in sea water. The boron soluble in 85% phosphoric acid at 100 °C represents the amount that is present in organic matter and layer silicates. This acid extraction excludes boron present in the mineral tourmaline. Acid-soluble boron is associated with the mica of mature sediments and mica-derived clays of soils (Jackson, 1964).

Plant-available soil boron is well correlated with boiling water soluble boron, which frequently ranges from 0.2 ppm to 1.5 ppm in soils. Soils of semi-arid climates contain more boron (10-40 ppm) than soils of humid climates. Alkali soils carry excessive boron. Hence, leaching of undesirable boron to non-toxic levels before cropping should be an essential step in land management practices.

4.15. Zinc and Copper

The total content of zinc and copper of soils is generally lower (40-60 mg/kg for Zn and 20 mg/kg for Cu) than in the material from which the soils are formed (Hodgson, 1963). These cations are held in soils principally on organic or inorganic surfaces or substituted as accessory constituents in common soil minerals. They are strongly held by the soil surface. But, when these cations are present in bivalent states in highly insoluble oxides and phosphates, they become much less liable to leaching. This explains their low concentration during the formation of soils from rocks of the earth's crust. This also explains the lower concentration of Zn and Cu in soils of the Indo-Gangetic Plains.

These elements form a host of naturally occurring minerals, but only rarely these minerals represent an important source of zinc and copper from an agronomic point of view (Hodgson, 1963).

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Chapter 12

Soil Colloids and Ion Exchange in Soil

S.K. SANYAL, S.R. POONIA and T.C. BARUAH

1. Soil Colloids: Introduction

A colloidal system is a heterogeneous mixture of at least two phases* in which one phase is dispersed in a state of fine subdivision (particle size 1μm to 1nm) in another continuous medium. This continuous medium is termed as the dispersion medium. The size limits of 1μm to 1nm are not very rigid and there may be variations on either side of the range. When the dispersed phase is a solid (e.g., soil colloidal particles) and the dispersion medium is water (e.g., soil water), the colloidal system is referred to as a 'sol'. The properties peculiar to a colloidal system, which distinguish them from suspensions (particle size > 1μm), and true uni-phase solutions (particle size < 1nm), are primarily those arising from the large interfacial area, which is charged, characterizing the colloidal system. In other words, most of the important properties of colloidal systems in soils may be attributed to the large specific surface (or interface) charge density.

The soil colloidal fraction is the site of important processes in soil, governing ion-exchange, nutrient availability and fixation, soil physical properties, especially soil structure, hydraulic conductivity, infiltration, and also soil management. Soil colloids can be broadly classified into two types, depending on the nature of the linkages present and the types of compounds formed. These are:

(i) Inorganic colloids, and

(ii) Organic colloids.

The inorganic colloids cover aluminosilicate layer-lattice clay minerals; hydrous oxides and hydroxides of Fe, Al, Si and Mn in clay-size dimensions; amorphous silicates; and clay-sized primary minerals. The organic colloidal fraction in soil is constituted by soil humus.

2. Inorganic Soil Colloids

The aluminosilicate layer-lattice clays, the chief inorganic colloidal fraction in soil, are derived from the silicate minerals. Silicates are the most common minerals in the earth's crust, accounting for more than 90% of the latter. Most of the soils are also dominated by these silicates which occur as primary minerals, inherited from igneous or metamorphic rocks, and as secondary minerals formed from the weathering products of primary minerals. These silicates consist of the SiO_4^{4-}- tetrahedron (*see* later) as the basic structural unit, present as either a single, or in several joint combinations. Depending on the arrangement of SiO_4^{4-}- tetrahedron in the structure, the silicate minerals

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* In Physical Chemistry, a *phase* is defined as any homogeneous and physically distinct part of a system which is separated from other such parts of system by definite bounding surfaces.

are classified into different groups, as already discussed in the Chapter on 'Chemical Composition of Soils'.

2.1. *Basics of Phyllosilicate Minerals*

In common with colloids of diverse origin, the layer-lattice aluminosilicate clays (phyllosilicates) are characterized by large specific surface area and charge density. Because the crystal structure of phyllosilicates largely governs their properties, it is necessary to understand these structures. These structures have been extensively studied by employing various techniques, particularly since the discovery in the early-1920s that most of the clays are crystalline in nature, and subsequent application of the x-ray diffraction technique to elucidate the above referred crystal structures.

2.1.1. Structural Units in Phyllosilicates

The convenient way of treating the atoms in the aluminosilicate structures as rigid spheres is oversimplified, but it provides a useful starting point.

Closest Packing of Spheres — The central concept of stability of crystal structure involves packing of anions around a central cation in such a way that each of these ionic spheres touches six of its nearest surrounding neighbours. Such an arrangement is known as the hexagonal closest packing, as shown in Figure 1. This forms a sheet leaving two kinds of central voids (A-type and B-type) between the spheres (Figure 1). With another sheet of such hexagonal packing, when stacked on the top of the first sheet, then a central cation placed in A-type of voids will have four surrounding spheres (such as anions) arranged in a tetrahedral manner around the cation, while a cation occupying a B-type of void will have six such surrounding spheres, above and below the central cation, pointing towards the apices of a regular octahedron (Figure 2). A cation occupying a tetrahedral site (the A-site) is said to be in a four-fold or tetrahedral coordination state (*see* later), being bonded to four oxide ions (O^{2-} ions), which form the apices of a regular tetrahedron (Figure 2). A cation occupying an octahedral site (B-site) is in six-fold (or octahedral) coordination state, being bonded

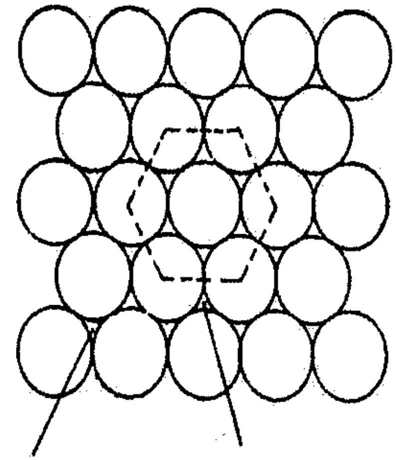


Figure 1. Hexagonal closest packing of spheres in a plane
Source: Schulze (1989)

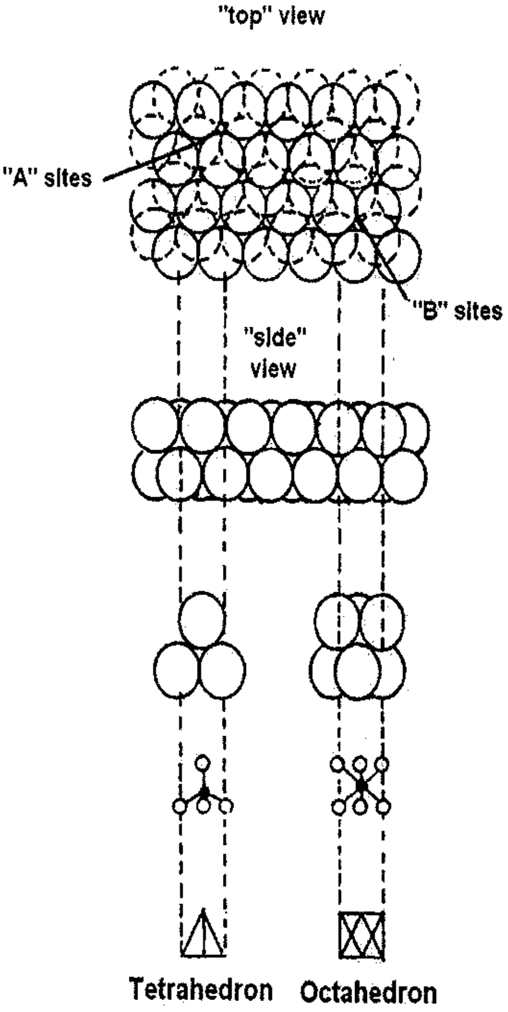


Figure 2. Tetrahedra and octahedra as a consequence of two planes of close-packed spheres
Source : Schulze (1989)

to six hydroxyl (OH^-) or oxide ions, arranged in the shape of an octahedron (Figure 2).

Silica Tetrahedral and Alumina Octahedral Sheets — A silica tetrahedron (SiO_4^{4-}) and an aluminium octahedron [$Al(OH)_6^{3-}$] are schematically depicted in Figure 2. A silica tetrahedral sheet is formed by sharing of three basal oxide ions of each (SiO_4^{4-})-tetrahedron with adjacent such tetrahedra in a and b directions (i.e., two dimensional) which will bring down the negative charge per unit tetrahedron (Figure 3). This leaves one unshared apical oxide ion in each tetrahedron, pointing upward from the basal plane accommodating the shared oxide ions. The apical oxide ion is free to form bond with other polyhedral atoms/ions. Indeed the term, 'Phyllosilicate' means "sheet silicates", which are thus minerals containing sheet-like arrangement of (SiO_4^{4-})-tetrahedra.

There are two ways of filling the octahedral sites with a central cation (e.g., Al^{3+} or Mg^{2+}), depending on the valency of the cation. A divalent cation (such as Mg^{2+}) can be placed into each adjacent octahedral site of the neighbouring octahedra which are joined together by sharing of octahedral hydroxyl ions of a [$Mg(OH)_6^{4-}$]-octahedron that reduces the negative charge per unit Mg-octahedron. The network of shared octahedra, $Mg_3(OH)_6$, is such that each Mg^{2+} ion shares one-third of the uni-negative charge of each of the six octahedrally arranged hydroxyl ions surrounding it, because each hydroxyl ion is shared equally by three Mg^{2+} ions. The resulting sheet is known as the trioctahedral sheet in which each octahedral site is occupied by a divalent cation (Figure 3).

For the dioctahedral sheet, however, only two out of each set of three octahedral positions are occupied by a trivalent cation (e.g., Al^{3+}) giving rise to the formula, $Al_2(OH)_6$ (Figure 3). It is thus evident that each of these tri- and di-octahedral sheets is electro-neutral.

Goldschmidt's Laws

The shape and size of a crystal structure is governed by the ratio of numbers of units (e.g., cations and anions), ratio of ionic sizes and properties of polarization of its structural units. Besides, allowance must be made for repulsive forces in ionic compounds, especially when the central cation is small, e.g., Li^+, and the surrounding anions have virtual contact with one another.

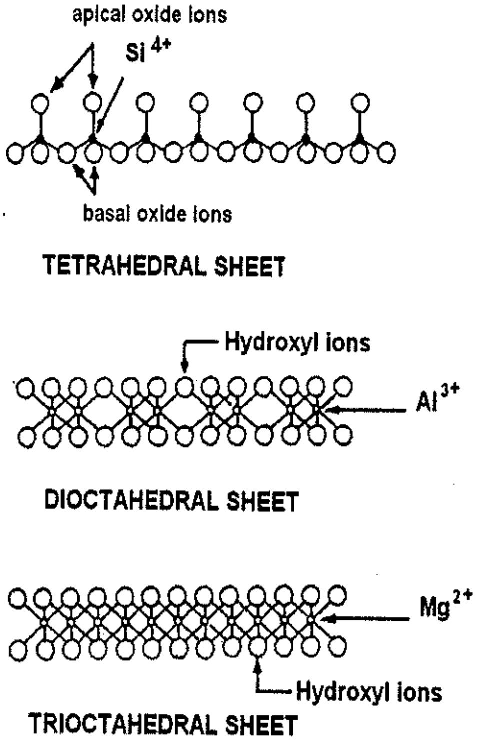


Figure 3. The tetrahedral, dioctahedral and trioctahedral sheets
Source: Schulze (1989)

The laws governing structural characteristics of the phyllosilicates are known as Goldschmidt's Laws – Law I and Law II.

(i) Goldschmidt's Law I — In an ionic crystalline compound, isomorphous replacement of one cation by another, without incurring any change in the order of the crystal pattern, is permitted provided that the radii of the cation replaced and the cation substituting it agree within 10-15%.

Such isomorphous substitutions may lead to a charge imbalance in the crystal structure since the charge (valency) of the two cations concerned may differ. Thus, substitution of Si^{4+} ion in a tetrahedral sheet (Figure 3) by Al^{3+} or that of Al^{3+} ion in dioctahedral sheet (Figure 3) by Mg^{2+} or Fe^{2+} ion will cause excess negative charge in sheet structures. This charge imbalance may be balanced by an appropriate and simultaneous substitution elsewhere, and/or by the retention of oppositely charged ions in the overall mineral structure (*see* later) so that the electroneutrality is maintained.

(ii) Goldschmidt's Law II: Radius Ratio Law — When the number of anions surround a central cation (with the closest packing of spheres) such that they satisfy the charge (of the cation) completely, the number of anions that can be so accommodated around the cation depends on the ratio of the radius of the central cation to that of the surrounding anions. Thus, this ratio of ionic radii governs what is known as the 'coordination number' of the central cation. The latter is thus basic to the shape of crystal forms. The ionic radii of a number of cations and anions pertaining to phyllosilicates, the cationic to anionic radius ratio ($r_+ : r_-$) [based on the radius of oxide ion, taken as the anionic radius (r_-) of relevance to phyllosilicates], the range of the values of these ratios ($r_+ : r_-$) corresponding to different coordination number of central cations, as well as the shape of the crystal structure or lattice are given in Table 1.

It can be shown by simple calculations that the tetrahedral site has a radius of 0.035 nm, while an octahedral site possesses a radius of 0.050 nm. By considering these sizes and data presented in Table 1, as well as by taking due cognizance of the Goldschmidt's laws, one arrives at the following important conclusions:

(i) A sphere of radius up to 0.41-times the radius of oxide ion can be accommodated in a tetrahedral site, while a sphere of radius up to 0.73-times the radius of oxide ion can be fitted into the octahedral site.

(ii) The Si^{4+} ion can remain in only four-fold coordination state in a tetrahedral sheet, while Al^{3+} ion can have both four- and six-fold coordination states in the tetrahedral and the octahedral sheets of phyllosilicates.

(iii) The cations such as Mg^{2+}, Fe^{3+} and Fe^{2+} ions can be accommodated only in the octahedral sites.

(iv) Potassium ion (K^+) can be accommodated in a dodecahedral arrangement of oxide ions, i.e. in between the two hexagonal arrays of oxide ions.

Table 1. Ionic radius, radius ratio, coordination number of central cations of phyllosilicate structures and shape of crystal lattice

Ion	Ionic radius (nm)	Radius ratio* (r^+ / r^-)	Range of radius (ratio for coordination number given in parentheses)	Coordination number of central cation in phyllosilicate structure	Shape of crystal lattice
O^{2-}	0.140	-	< 0.15 (2)	-	Linear
F^-	0.133	-	0.15 – 0.22 (3)	-	Equilateral triangle
Cl^-	0.181	-	-	-	-
Si^{4+}	0.039	0.278	0.22 – 0.41 (4)	4	Tetrahedral
Al^{3+}	0.051	0.364	0.41 – 0.73 (6)	4, 6	Tetrahedral Octahedral
Fe^{3+}	0.064	0.457	-	6	Octahedral
Mg^{2+}	0.066	0.471	-	6	-do-
Fe^{2+}	0.074	0.529	-	6	-do-
Mn^{2+}	0.080	0.571	-	6	-do-
Na^+	0.097	0.693	-	8	Cubic
Ca^{2+}	0.099	0.707	-	8	-do-
K^+	0.133	0.950	0.73 – 1.0 (8)	8, 12	Cubic Dodecahedral
Ba^{2+}	0.134	0.957	> 1.0 (12)	8, 12	- do-
Rb^+	0.149	1.050	-	8,12	-do-

*Ratio of cation radius (r^+) to O^{2-} ion radius (r^-)

2.2. Common Phyllosilicate Minerals in Soil

Among the common layer-lattice minerals, the important ones are the 1:1 and 2:1 type minerals. The details of the chemical composition and structure of these phyllosilicates have already been discussed in the Chapter on 'Chemical Composition of Soils'.

3. Organic Soil Colloids

These refer to the humic colloids, the main fraction of the soil organic matter, which are widely distributed all over the earth's surface. Nearly 70–80% of the soil organic matter consists of humic substances, viz. humic acid, fulvic acid and humin. These are believed to be produced by continuous decomposition of plant, animal and microbial bodies, encompassing alteration of carbohydrates, proteins, fats, resins, wax, and so on, followed by synthesis of complex humic products. The humic colloids are dark in colour, partly aromatic and amorphous with very high specific surface area and charge density and are essentially hydrophilic in nature. These substances are characterized by flexible polyelectrolyte behaviour, having polyfunctional groups, and very high molecular weights, ranging from a few hundreds to several thousands. A typical value of CEC (*see* later) of soil humic colloids (which is pH-dependent) may be of the order of 200–250 cmol(p^+)kg^{-1} or even higher. The typical functional groups of the organic colloids are carboxylic, phenolic hydroxyl, amino, amide, etc. and as a result, these act as proton donors or proton acceptors, depending on soil pH.

The humic colloids in soil often impregnate the soil mineral matter, e.g. the inorganic phyllosilicate clays (of soil) with which they remain in intimate association, forming clay-humic complexes.

4. Sources of Charges on Soil Colloids: Their Charge Characteristics

4.1. Isomorphous Substitution

Isomorphous substitution of cations by those of different charges (but having similar sizes within permissible limits) within the tetrahedral and the octahedral layer-lattice clay minerals leads to the development of net unbalanced charge within the lattice. Such a substitution takes place following the Goldschmidt's laws of crystal chemistry (*see* Section 2). Indeed an isomorphous substitution within Al-octahedral and Si-tetrahedral layers of higher-valent cations by lower-valent cations having similar sizes leads to permanent (pH-independent) negative charge. Examples are the substitution of Si^{4+} in tetrahedral layer by Al^{3+} in mica, vermiculite, illite, etc. and of Al^{3+} in the octahedral layer by Mg^{2+}/Fe^{2+} in montmorillonite. Positive charges on clay lattice may also arise through isomorphous substitution, e.g. by substitution of a lower-valent cation by a higher-valent one, such as occurs in the trioctahedral sheet forming substituted [$Mg_2AlO_2(OH)_2^+$] sheet. The latter is sometimes found in the trioctahedral sheet in some vermiculites and chlorites. The net permanent charge on the clay lattice obviously depends on the extent of these two types of isomorphous substitutions, although it is nearly always negative.

The charge of soil clays arising out of isomorphous substitution remains constant.

4.2. pH-dependent Charge

There is yet another source of charge of soil colloids, especially for kaolinite, the aluminosilicate clay, and also for the hydrous oxides and hydroxides of Fe and Al in clay-size dimensions, allophones and non-crystalline clays, as well as the organic humic colloids of soil. The negative charge here arises through the dissociation of proton from the exposed hydroxyl group or bound water of constitution at the edge and surfaces of the inorganic colloids, and is naturally pH-dependent. The carboxylic and phenolic (OH) groups of soil humic substances also behave as weak acids, dissociation of which (thereby contributing towards soil acidity) would depend on the dissociation constant of the acid, and the pH of the surrounding medium. The carboxylic group ionizes at relatively lower pH (close to pH 5.5-6.0) than the phenolic (OH) group (which ionizes at pH 9.0), and contributes to the pool of pH-dependent negative charges. However, the substituted phenols, such as nitrophenols, are stronger acids than phenols (due to electron-withdrawing character of nitro group) and ionize, contributing to negative charge of humic colloids, at intermediate pH between 6.0 and 9.0.

No soil organic fraction with a net positive charge has been reported so far at normal soil pH values. However, organic species (R, *see* later), bonded to (NH_2) functional groups, may protonate at low pH to yield positively charged ($R\text{-}NH_3^+$) units, that hold anions, capable of anion exchange.

From the above discussion on pH-dependent charge of soil colloids, e.g., Fe and Al hydroxides, it is clear that the exposed edge/surface hydroxyl groups can act as both an acid (donating a proton to the surrounding OH group) or a base (accepting a proton from the surrounding soil solution), depending on pH of the soil system, i.e., relative preponderance of H^+/OH^- ions in the vicinity of exposed edge and surface OH group of soil colloid. Such amphoteric nature of these soil colloids warrants that these exposed hydroxyls would behave as an "uncharged" group (neither a proton donor nor a proton acceptor) at an intermediate pH. The pH at which the net surface charge of the soil colloids is zero is known as the 'zero-point of charge' or ZPC. The latter is thus a characteristic of soil colloids (such as in acid soils) which are mixtures of permanent and variable-charge minerals. The concept of ZPC is illustrated in Scheme 1 with hydrous oxides of Fe and Al (in clay-size dimensions).

The ZPC of a soil component depends upon its relative acidity with respect to water. Thus, ZPC of silicic acid is 2.0, of goethite (α - $Fe^{III}OOH$) is 8.5 and of gibbsite [$Al(OH)_3$] is more than 9.0. However, even at ZPC, the permanent charge of soil colloid (such as the aluminosilicate clay) persists unchanged.

On the other hand, the modification of surface/edge charge characteristics of soil colloids (especially the inorganic colloids) leads to the modification of ZPC. Thus, phosphate-fixation by ligand-exchange (e.g., exchange of neutral OH_2 ligand to Fe or Al by the applied $H_2PO_4^-$ ion; *see* later) process raises the surface negative charge, and pushes the ZPC towards lower pH, i.e. a stronger H^+ ion concentration is required in the surrounding soil solution to render the surface of soil colloid neutral. Furthermore, intense weathering of a soil shifts its ZPC towards higher pH owing to greater accumulation of hydrous oxides/hydroxides of Fe and Al and also enrichment of soil layer-lattice clays with kaolinite (possessing mostly pH-dependent edge charge). Indeed, the ZPC of Ultisol or Alfisol is generally higher than that of an Inceptisol. Organic matter, on the other hand, pushes the ZPC towards lower pH.

The development of charges on soil components is schematically shown in Scheme 2.

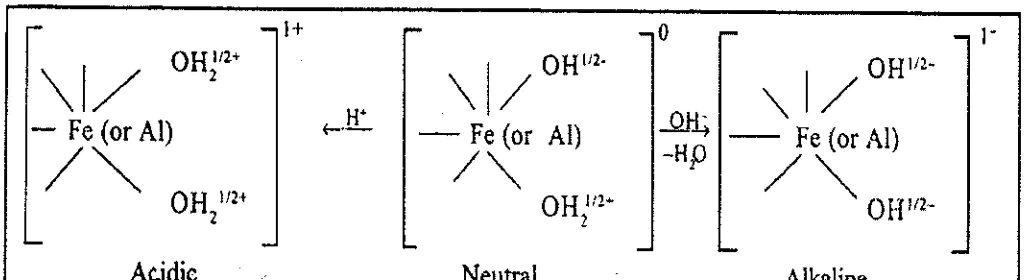
(i) On clay minerals (at edge/surface; pH-dependent negative charge)

(ii) On clay minerals (within lattice; permanent negative charge)

Mg^{2+}, Fe^{2+} replacing Al^{3+} in octahedral layer

Al^{3+} replacing Si^{4+} in tetrahedral layer

(iii) On hydrous oxides of Fe and Al (pH-dependent negative edge/ surface charge) Shown in Scheme 1.

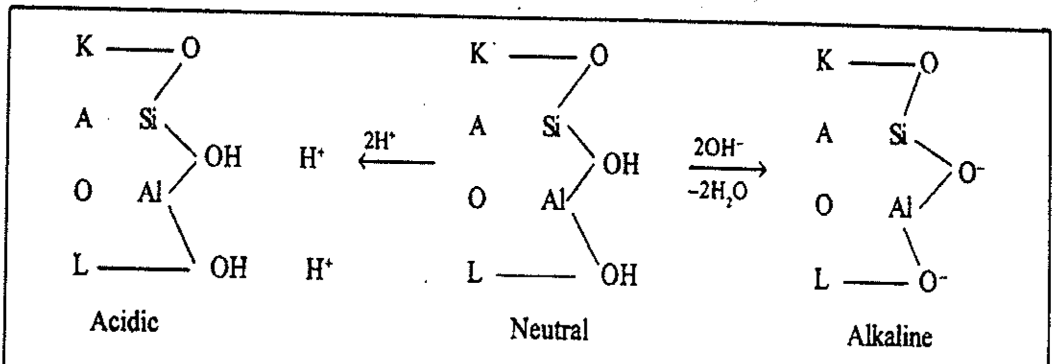


Acidic
(at pH less than ZPC,
contributes towards positive
charge and anion exchange)

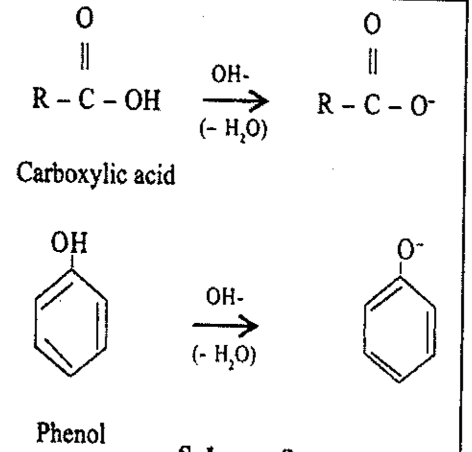
Neutral
(at the pH of ZPC)

Alkaline
(at pH greater than ZPC,
contributes towards negative
charge and cation exchange)

Scheme 1



Scheme 2



Scheme 3

(iv) On soil organic matter (pH-dependent negative charge)

Shown in Scheme 3.

4.3. *Electrical Double Layer of Soil Colloids*

The net charge on soil colloids is balanced by counter ions, such as interlayer cations of clay minerals, forming an electrical double layer. These counter ions, electrostatically attracted by the oppositely charged soil colloids, have a tendency (due to their thermal or kinetic energy) to diffuse away from the surface towards the bulk of soil solution where the counter ion concentration is lower. The equilibrium or balance between these two opposing (competitive) tendencies results in a distribution of the counter ions such that their concentration gradually decreases with increasing distance from the colloidal surface. In fact, it is postulated that the solution side of the aforesaid double layer consists of counter ions distributed into two broad regions, namely (i) a more or less fixed layer at a uni-molecular or uni-ionic (hydrated) distance from the colloidal particle surface (the so-called Helmholtz layer), trailed by (ii) a diffuse layer (the so-called Goüy-Chapman layer) of counter ions (in which some kinetic movement of the counter ions is possible), till the bulk solution is reached where the distribution of positive and negative ions (unaffected by the charge on the colloid which is far away) becomes uniform. Evidently, there is excess of cations and a deficit of anions in the diffuse double layer compared to their respective concentrations in the bulk solution. The above model or description of the electrical double layer at the colloid/solution interface is known as the 'Stern model'.

4.4. *Stability of Soil Colloids and their Coagulation/Flocculation*

The soil colloids are negatively charged, and as mentioned above, the counter ions (cations) are present in the fixed and the diffuse layer on the solution side of the electrical double layer at the soil colloid/soil solution interface. This causes a change of electrostatic potential from the solid surface (P) to the bulk soil solution (R) in such a manner that a sharp change in potential in the Helmholtz layer (PQ) is followed by a more gradual change in the Goüy-Chapman layer (QR). The potential difference, denoted by ξ (zeta), between the fixed part (Q) and the freely mobile portion (R) of the solution side of the double layer (Figure 4) governs the stability of the colloids. The higher the value of this potential (which is also known as the electrokinetic potential), the greater is the repulsion between two approaching soil col-

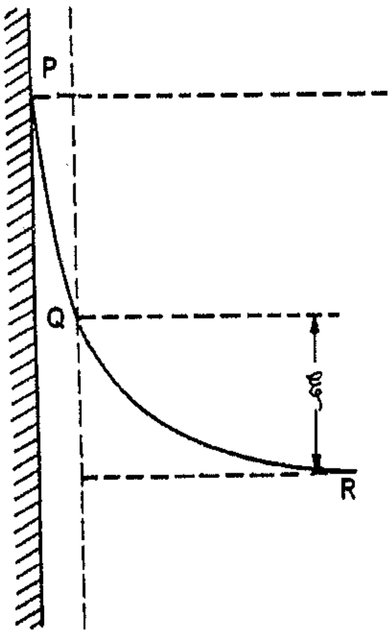


Figure 4. Electrokinetic (zeta) potential in an electrical double layer

loidal particles, swarmed by the respective counter ions of like charge in the neighbouring soil solution (e.g., the so-called 'clay micelles'), and hence less is the likelihood of these approaching particles to coalesce so that the larger will be the buoyancy force to keep these colloidal particles afloat and dispersed. This will lead to the stability of the soil colloidal sol.

By considering, as a first approximation, the electrical double layer at the soil colloid/soil solution interface to be equivalent to a parallel plate electrical condenser, with each plate carrying a charge of numerical value e per cm^2, the zeta potential (ξ) can be approximated by the potential difference between the plates, at a distance d apart [Equation (1)]:

$$\xi = \frac{4\pi ed}{D} \qquad ...(1)$$

where, D is the dielectric constant of the medium (water).

On addition of an electrolyte to the soil colloidal system, the cations of the added electrolyte tend to accumulate on the solution side of the electrical double layer, in the vicinity of the plane PQ (Figure 4). Upon gradual increase in the concentration of the added electrolyte, this cationic accumulation may reach such a proportion that there will be a virtual neutralization of some of the charge on the soil colloidal surface through a phenomenon which is termed as 'ion-pair' formation. It is facilitated by an increase in the cationic charge (i.e. valency) of the added electrolyte due to a higher bonding energy of the added cation for the given colloidal surface. This will bring down the value of 'e' [Equation (1)], and also of 'd', owing to release of some of the counter ions from the diffuse portion of the double layer to the bulk solution. The latter arises from the fall in the effective charge on the solid (colloid) surface, and hence its electrostatic attraction for the counter ions. In other words, the electrical double layer will be compressed with reduced charge density. Both these factors will bring down the ξ potential (Equation 1), enabling the approaching colloidal particles to coalesce with a concomitant reduction in buoyancy. The particles will thus settle under gravity, leading to coagulation or flocculation of the disperse phase (i.e. soil colloids) out of the dispersion medium, namely soil solution.

When the zeta potential attains the value of zero, the given colloidal system is said to correspond to the *isoelectric state* of the system concerned. It is apparent that for the aluminosilicate layer-lattice clay minerals (and soil, in general), possessing permanent (pH-independent) charge, the ξ potential is the combined function of the latter as well as the pH-dependent surface charge, while at the corresponding ZPC, only the net surface charge is zero, not necessarily the corresponding ξ potential. This underlines the difference between the ZPC and the *isoelectric point.* For the soil organic colloids and the hydrous oxides of iron and aluminium (possessing only pH-dependent charge), however, the two may be quite identical for obvious reasons. For instance, a polypeptide molecule (an amphoteric electrolyte), in its isoelectric state, is regarded as a neutral molecule even though it still has the ionized groups in a distribution of equal number of acidic and basic ionic groups.

The flocculation-dispersion behaviour of soil colloids has a strong bearing on the maintenance of favourable soil structure, thereby aiding soil aeration and drainage.

5. Electrometric Properties of Soil Colloids

5.1. Potentiometric and Conductometric Titrations

It is advantageous to study the electrometric (or electrochemical) properties of soil colloids such as soil clays when the latter are rendered homoionic with respect to a single cation that satisfies the entire cation-exchange capacity (*see* later) of the given clay. An acid clay, for instance, may be prepared by repeated leaching of the clay with a dilute mineral acid (e.g., 0.1 *N* HCl), followed by electrodialysis of the resulting acid clay to remove the excess electrolytes. A better way of obtaining the H-clay is to pass the clay suspension finally through a column of H^+ ion-exchange resin. The titration of such clay acids with alkalis provides important information regarding not only the exchange capacity, but also the nature and properties of the acid clay. Before proceeding further, let us refresh our knowledge of simple acid-base neutralization in aqueous solutions.

The gradual neutralization of an aqueous acid (e.g., acetic acid or HCl) by an alkali leads to a pH-metric (potentiometric) titration curve. An n-basic acid may show n-inflexions provided that the dissociation constants (K) of the (n-1)th and the nth stages of acidity are widely separated. Typically, the ratio (K_{n-1}/K_n) should be of the order of 10^4. In actual practice, however, the dissociation constants of a polybasic acid (such as orthophosphoric acid, H_3PO_4) are often closer together, and neutralization at one stage may overlap partially with the preceding or succeeding stages, giving rise to statistically monobasic acid behaviour with an average dissociation constant (Mukherjee, 1974). The total acidity of such an acid solution is independent of the alkali chosen to measure the former.

If, however, the anion of an acid is of colloidal dimension (such as the negatively charged clay lattice of an acid clay), the protons form altogether a different phase from the former, giving rise to a two-phase acid system. The H^+ ions (i.e., the exchangeable cations) cannot be separated out into the intermicellary solution, for instance, by ultrafiltration. The clay acid behaves like a weakly dissociating acid (like aqueous acetic acid) towards a glass electrode measuring pH.

On conducting titration with an aqueous alkali, the pH-metric titration curves not only show differences in their features, depending on the alkali used, but also register variations in total acidity. This is because the neutralization reaction here is a two-step process as shown below.

Step 1: Ion-exchange reaction between H^+ ion on the colloidal anion and cation of the added alkali [Equation (2)]:

$$\boxed{\begin{array}{l}\text{Colloidal antion}\\ \text{of acid clay}\end{array}}^{H+} + \underset{\text{Alkali}}{NA^+ + OH^-} \rightarrow$$

$$\boxed{\begin{array}{l}\text{Colloidal anion}\\ \text{of acid clay}\end{array}}^{Na+} + H^+ + OH^- \qquad ...(2)$$

Step 2: Neutralization of H^+ ion by OH^- ion in the solution phase [Equation (3)]:

$$H^+ + OH^- \rightarrow H_2O \qquad ...(3)$$

Some typical pH-metric titration curves of acid montmorillonite are shown in Figure 5.

The divalent Ca^{2+} ions, forming a stronger association with the colloidal anion of acid clay than the monovalent Na^+ ions, possess a greater H^+ ion replacing power (from the acid clay) than that of Na^+ ion. This leads to higher acidity (Figure 5) of the acid clay when titrated with $Ca(OH)_2$ than with NaOH. With $Ca(OH)_2$, the titrant, buffering (which amounts to flattening of the pH-metric titration curve; Figure 5) is observed at lower pH (Figure 5) which is the characteristic of a strong acid. With NaOH, such buffering is observed at relatively higher pH, a characteristic of weak acid.

Furthermore, the acidity of a colloidal acid increases (unlike a true acid) when titrated in the presence of neutral salts, so also the features of the titration curve change from those of a relatively weak acid to those of a stronger acid (Figure 5). This, again, results from an exchange of H^+ ion (also Al^{3+} ion, *see* later) for cations of the added salt preceding neutralization.

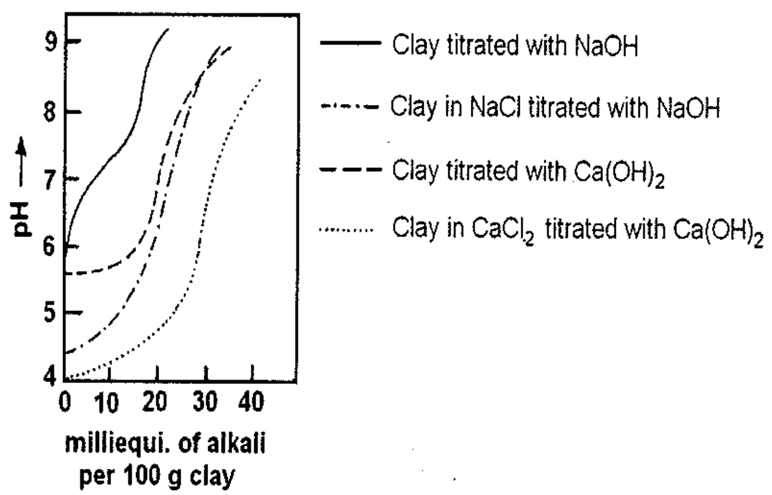


Figure 5. pH-metric titration curves of a clay separated from a Bengal soil showing the effect of alkali used and presence of salts

Source: Mitra and Kapoor (1969)

5.2. Exchangeable Aluminium Ions in Acid Soils

An acid soil is actually a mixed H-Al system, i.e. such a soil has both H^+ and Al^{3+} ions as exchangeable ions. As to the origin of exchangeable Al^{+3} ions, the H-soil or H-clay, when titrated immediately after preparation (on passage of the suspension through a column of H^+ ion-exchange resin), shows strong acid characteristics and a buffering at a low pH (Figure 6). The neutral salt extract contains little or no Al^{3+} ions. However, on aging (or on heating the suspension to, say, 95 °C), the titration curve changes markedly to those of weak acids, buffering occurring at higher pH with the total acidity remaining unchanged. The neutral salt extract, however, shows the presence of an increasing amount of Al^{3+} ions with the time of aging (or heating) (Figure 6). The number of inflexions in the titration curve also increases on aging. Such a conversion of H-soil or H-clay to mixed H-Al system can be arrested by keeping the suspension in a non-aqueous solvent such as acetone or methanol.

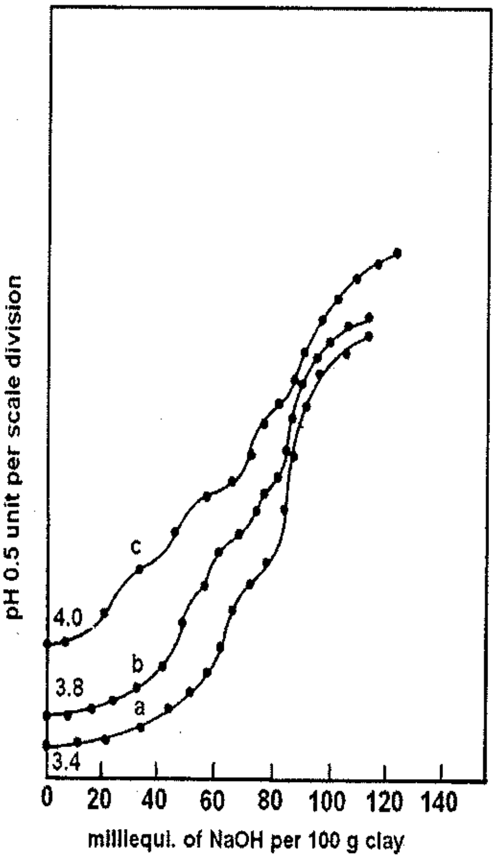


Figure 6. pH-metric titration curves of acid montmorillonite clay: (a) freshly prepared, (b) aged for one week, and (c) aged for nine weeks

Source: Mitra and Kapoor (1969)

The exchangeable Al^{3+} ions in H-clay or H-soil arise from the lateral mobilization of the octahedral Al^{3+} ions in the clay lattice (such as acid montmorillonite) by the exchangeable H^+ ions with which they exchange the position. This is a slow process, but it gets accelerated on heating. Such ionic migration is arrested in a non-aqueous solvent of relatively low dielectric constant (e.g., acetone/methanol). The exchangeable Al^{3+} ions being weaker acids (Lewis acid) than H^+ ions, it is no wonder that freshly prepared acid clays, showing strong acid behaviour, change over to weaker acid type on aging (Figure 6), exhibiting a greater number of inflexions (and hence greater types of acidic groups) compared to the freshly prepared acid (i.e. H-) clay. The total acidity, however, remains unaffected.

Homoionic acid clays (prepared in the usual way of acid leaching of the clay with dilute mineral acid, followed by electrodialysis), age considerably during preparation so as to contain appreciable amounts of mobilized Al^{3+} ions. If the aged clay is passed through a column of H^+ ion-exchange resin, the exchangeable Al^{3+} ions are replaced by H^+ ions of the resin. The resulting H-clay, on aging, would again mobilize octahedral Al^{3+} ions. Thus, if the processes of aging and recovering the H-clay are repeated, the resulting H-clay would reach a stage when the clay would show signs of degradation owing to continued depletion of Al^{3+} ions from the clay structure (Mukherjee, 1974). Indeed, such degradation has been confirmed by means of electrometric titrations, and X-ray and differential thermal analysis studies (Majumdar and Mukherjee, 1979).

The corresponding conductometric titration curves of acid montmorillonite also show stronger acid features for the freshly prepared H-clay, and a weaker (more polybasic) acid character on aging, the latter exhibiting a greater number of breaks in the conductometric titration curves. Figure 7 shows that the freshly prepared acid clay has fewer breaks (compared to aged acid clays), thereby signifying the appearance of new acidic species of weaker acidic strength in the aged acid clay. The total acidity of the clay remains unchanged on aging (Figure 7).

The electrometric titration curves of soil humic colloids (humic acid, fulvic acid and hymatomelanic acid) show features characteristic of weak polybasic acid with the cation-exchange capacity being variable and a function of the alkali used for titration.

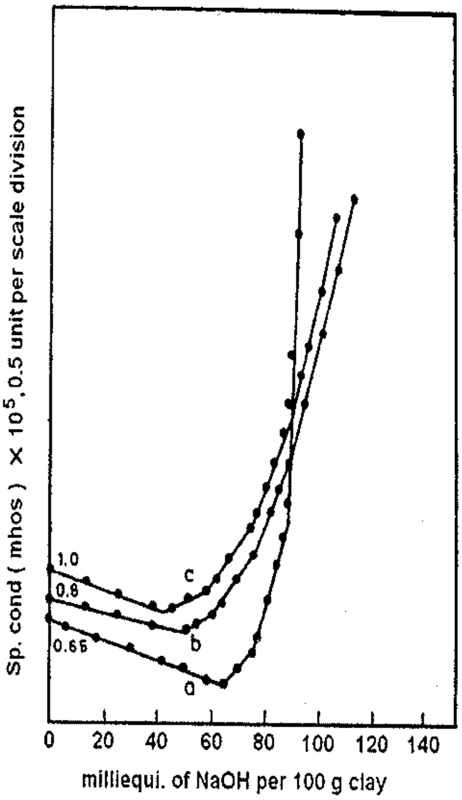


Figure 7. Conductometric titration curves of acid montmorillonite clay: (a) freshly prepared, (b) aged for one week, and (c) aged for four weeks
Source: Mitra and Kapoor (1969)

6. Electrokinetic Phenomena in Soil Colloids

It is well known that when an electric field is applied by sticking two water-filled glass tubes, encasing two platinum electrodes, into moist clay, and connecting these to an external source of electromotive force (E.M.F.) such as a battery, the liquid in the tube serving as a positive electrode (Figure 8a) becomes turbid while the water in the other tube remains clear. This indicates that clay particles move under the applied electric field towards the positive electrode. In another experiment, a clay plug is placed at the central part of a U-tube (Figure 8b) and is enclosed on both sides by sintered glass discs. On filling the U-tube with water, and applying an electric field through two electrodes inserted into water in the two arms of the U-tube, the water level in the arm having the negative electrode rises until the difference in water level between the two arms attains a constant value.

These two phenomena are known as electrophoresis and electro-osmosis, respectively, and are the direct consequences of the existence of electrical double layer at the clay/water interface, and slipping past of one layer of the said double layer over the other, the two layers possessing opposite (and equal) charges.

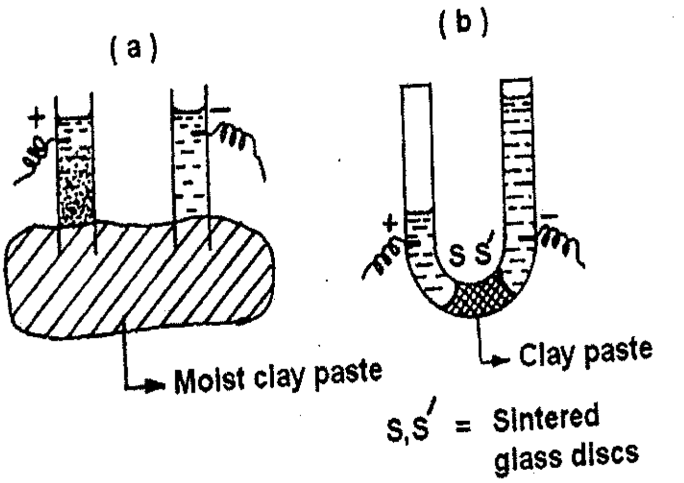


Figure 8. A schematic presentation of the phenomena of (a) electrophoresis of clay, and (b) electro-osmosis of clay

In electrophoresis, the negatively charged clay particles are free to move, and therefore migrate towards the positive electrode, while in electro-osmosis, the clay particles having been restricted from movement by the glass discs, the positively charged solution side of the double layer would move under an electric field towards the negative electrode.

A closer examination of electro-osmosis reveals that although the liquid flow is generally associated with the application of pressure difference (ΔP), the application of an electrical potential difference (i.e. an electric field) is doing this job in electro-osmosis. By analogy, one would then expect a pressure difference to induce an electric current which is generally the result of application of an electric field. Indeed, this is found to be so when the clay plug (Figure 8b) is subjected to a pressure difference. The ensuing current is termed as the streaming current, while the corresponding potential difference developed across the clay plug is known as the streaming potential. Here again, a mechanical separation of the solution side of the double layer (from the stationary clay particles) under the applied ΔP leads to development of streaming potential and the consequent current. It can be shown by Equation (4):

$$\left[\frac{v}{X}\right]_{\Delta P=0} = \left[\frac{i}{\Delta P}\right]_{X=0} \qquad \ldots(4)$$

where, X is the applied electric field across the clay plug (in electro-osmosis; Figure 8b), v is the corresponding velocity of electro-osmotic flow of water, ΔP is the pressure difference applied under zero (externally applied) electric field, and i is the corresponding streaming current. The term (v/X) represents the electro-osmotic mobility, while the term ($i/\Delta P$) represents the streaming current density generated by a unit pressure difference. Both these quantities are characteristics of the electrical double layer at the colloid/ solution interface.

In the year 1878, Dorn discovered a related phenomenon (Shaw, 1970) in which colloidal particles under sedimentation in water lead to the development of an E.M.F. between two electrodes inserted at different depths of the liquid column. This effect, opposite of electrophoresis, is known as Dorn effect, and the E.M.F. generated is known as sedimentation potential.

The above four phenomena are known as electrokinetic phenomena for reasons explained above as regards the mechanism responsible for these processes. Figure 9 demonstrates the streaming current as a function of hydraulic pressure difference applied across kaolinite/water system.

7. Visible and Infrared Spectroscopic Studies of Humic Colloids

7.1. Basic Principles

The electronic transitions in humic molecules lead to characteristic spectral absorption bands in the ultraviolet (UV) and visible

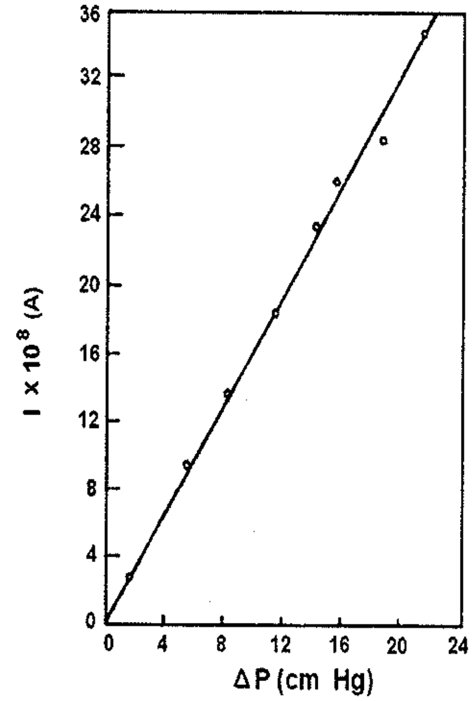


Figure 9. Relationship between streaming current (I) and hydraulic pressure difference (ΔP)
Source: Srivastava and Pal (1973)

region (together covering the wavelengths from about 200 nm to 800 nm) of the electromagnetic spectrum. The electrons involved are those in σ-bond (formed through face-to-face overlapping of atomic orbitals, as found in single bonds between C and H in CH_4), π-bond (formed through lateral partial overlapping of atomic orbitals such as found in olefinic bonds; the electrons are more mobile than those in σ-bonds), and the non-bonding (n) electrons (on oxygen, sulphur, nitrogen and halogens). The absorption of electromagnetic (e.g. light) energy (E) is quantized and is governed by the well known Planck's equation (Equation 5):

$$E = h\nu = h\frac{c}{\lambda} \qquad \ldots(5)$$

where, ν is the frequency; λ is the wavelength of the absorbed radiation; c, the velocity of light, and h is the Planck's constant.

The absorption of light energy in visible (and UV) regions by humic colloids is accompanied with promotion of the aforesaid electrons from the ground state to a higher energy state. It is frequently described as $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Here, σ^* and π^* denote the corresponding antibonding orbitals of higher energy than those of σ and π bonds, respectively. The $\pi \rightarrow \pi^*$ transitions are associated with much lower energy than the $\sigma \rightarrow \sigma^*$ transitions. Therefore, compounds having a large degree of unsaturation (π-bonds) will absorb energy at longer wavelength [Equation (5)], and hence the absorption bands will shift towards longer wavelengths. Extensive conjugation (i.e. C-C bonds and C=C bonds occurring alternately in a molecule) causes further lowering of $\pi \rightarrow \pi^*$ transition energy, owing to extensive delocalization of π-electrons. It leads to a greater shift of the absorption bands to longer wavelengths. This is particularly true in aromatic compounds, compared to their aliphatic analogues having the same number of C-atoms. Indeed, as the number of fused (co-planar) benzene rings increases, as in, say, anthracene, the extensive conjugative delocalization of π-electrons takes place, pushing the absorption band far in the visible spectrum of electromagnetic radiation. Such an absorption spectrum is given as a plot of absorbance (A) or optical density at various wavelengths (λ) of incident light as function of λ. The absorbance, following the Lambert-Beer's law, is given by Equation (6):

$$A = \log\frac{I_0}{I} = abc \qquad \ldots(6)$$

where, I_0 and I are the intensities of the incident and the transmitted radiations, respectively, at λ corresponding to maximum absorption by a given substance, 'a' is the molar extinction coefficient of the light-absorbing substance (e.g., humic colloid), 'c', its concentration and 'b' is the path length traversed by light through the given substance.

However, as compared to the absorption bands observed in the visible (and UV) regions (200-800 nm), the humic molecules (in common with organic molecules) show much larger number of peaks in the infrared (IR) spectrum (λ ranging from 2.5 to 15 μm, with the region 0.8 to 2.5 μm being known as near infrared and the one from 15 to 200 μm, known as far infrared region of electromagnetic spectrum).

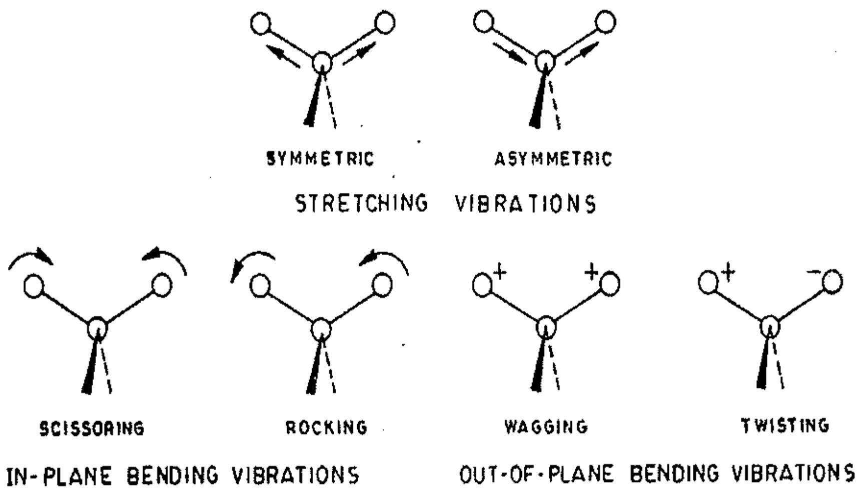


Figure 10. Vibrations of a group of atoms (+ and – signify vibrations perpendicular to the plane of the paper)
Source: Dyer (1971)

In the IR region, absorptions are often shown as a function of reciprocal wavelength or what is known as wave number. The wave number for instance for the near IR region, ranges from 12,500 to 4000 cm^{-1}. The energy (E) of absorption in the IR region is smaller than that in UV or visible region, the corresponding wavelength being longer (Equation 5), and is associated with the vibration of molecules, including stretching (in which the distance between two bonding atoms changes, but the atoms remain in the same position) and bending (or deformation in which the position of the atoms changes relative to the original bond axis). These modes of vibrations are illustrated in Figure 10.

As before, the energy of the various stretching and the bending vibrations of a bond is quantized, and the incidence of IR radiation of identical frequency causes absorption of energy by the organic molecule, leading to an increase in the amplitude of the given vibration. This, in turn, leads to an absorption peak in the IR spectrum. Perhaps the most significant application of the IR spectrum lies in the identification of the presence of a number of functional groups from the occurrence of the highly characteristic absorption peaks in the so-called "finger-print" region (7 to 11 μm).

7.2. Absorption of Energy in the Visible Region

The absorption of radiation energy in the visible region by soil humic and fulvic colloids often indicates the degree of aromatization and relative preponderance of aromatic and aliphatic nature of a colloid. Thus, the comparative absorption at 445 nm (denoted by E_4) and that at the longer wavelength of 665 nm (denoted by E_6) is taken to show the relative preponderance of aliphatic and aromatic groups, respectively, in the given humic molecule. The higher degree of aromatization of an organic molecule causes stronger absorption at longer λ for reasons explained earlier. More important parameter in this context is neither E_4 nor E_6, but rather the ratio, (E_4/E_6), which provides a better index of the above-mentioned preponderance. The fulvic colloids (the lower polymer and an earlier fraction than humic colloid of the soil organic matter, the humic colloid being of a higher polycondensate nature) possess typically higher E_4/E_6 ratio than their corresponding humic fraction. It is obviously linked with a lower extent of aromatization of the former, and the presence of a relatively larger proportion of aliphatic structures in the fulvic acids. Some representative values of the E_4/E_6 ratio for fulvic and humic colloids are given in Table 2.

7.3. Absorption of Energy in the Infrared Region

The functional group composition of humic colloids (e.g., humic acid and fulvic acid) can be inferred from their infrared (IR) spectrum. Thus, the presence of phenolic (OH), amide, methyl, free-NH-, carboxylic, carbonyl and

Table 2. E_4 / E_6 ratio for humic and fulvic acids

Soil location	Soil order	E_4/E_6 Ratio	
		Humic acid	Fulvic acid
Janji, Assam	Inceptisol	4.4	6.2
Kokrajan, Assam	Inceptisol	5.0	6.3
Raja Rammohanpur, West Bengal	Inceptisol	3.4	4.7
Golaghat, Assam	Alfisol	4.5	5.9
Deragaon, Assam	Alfisol	4.1	6.2
Synthetic humic acid (synthesized from glycine and hydroquinone)	–	2.9	–

Sources: Saha and Sanyal (1988); Sarmah and Bordoloi (1993); and Lahiri and Chakravarti (1995)

other important characteristics can be inferred from the finger-print region of the IR spectrum. In particular, the degree of aromatization can be ascertained from the presence of absorption bands/peaks in the region 1500-1600 cm^{-1} wave number. The different functional groups, present in the humic and fulvic acids of soil humic colloids, as revealed by a representative infrared spectral study of soil humic colloids, are summarized in Table 3.

Further, the IR spectrum of two synthetic humic acid samples (synthesized by alkaline oxidation of mixtures of the simple constituents of soil humic acids, namely the amino acids and phenolic compounds) is shown in Figure 11, in which per cent transmittance (bearing inverse relationship with absorption) is shown as a function of wave number.

To provide a comparison with soil humic colloids, the major IR bands of some representative clay minerals (the inorganic soil colloids) are listed in Table 4.

8. Coiling in Humic Substances: Hydrophobic Bond

The humic colloids exhibit hydrophobic and hydrophilic characters. While the various functional groups are generally hydrophilic, the (C-H) bonds are essentially hydrophobic. As a consequence, the humic colloids in aqueous medium (e.g., soil solution) remain in a coiled state. Such coiling is, in general, less marked in fulvic colloids than humic colloids; the latter possess a higher polycondensate nature and hence are more hydrophobic.

The interaction of the hydrophobic backbone of humic colloids with neighbouring water is (free) energetically (i.e. thermodynamically) unfavourable. As a consequence, the water molecules are drawn together, as by surface tension, and the non-polar groups tend to aggregate (much like oil droplets in water), leading to coiling, thereby minimizing their contact surface area with water, and hence the mutual interaction. The term, 'hydrophobic bond', has been coined to represent the association (aggregation as referred above) of the hydrophobic parts, excluding neighbouring water. But the term 'bond' may well be considered a misnomer here in that there exists no particular bond localized between two atoms of the hydrophobic residue, the association of which results under 'thermodynamic compulsion'.

9. Rheological Properties of Soil Clays

The science of flow of fluids, or in general, the science of deformation processes, developing with time, is known as rheology. The rheological or flow behaviour of clay suspensions is largely governed by the mode and the extent of interaction between the clay particles. These interactions may be of three types: edge-to-edge (EE), edge-to-face (EF), and face-to-face (FF) associations. This presumes that a well developed positively charged double layer exists at the edges of the clay particles, opposite in charge characteristics to that on the faces, which are predominantly negatively charged. As a result, there is an EF attraction causing "internal mutual flocculation", leading

Table 3. Relative intensity of major IR absorption bands of humic and fulvic acids of soils

Frequency (cm^{-1})	Assignment	Soils			
		Janji	Jorhat	Kakrajan	Golaghat
	Humic acids				
3450-3300	H-bonded OH, Free OH, Intermolecular bonded OH	B	B	B	B
2950 – 2850	Aliphatic C-H, C-H_2, C-H_3 stretching	S	S	S	S
1725 – 1640	C = O stretching of carboxylic acids, cyclic and acyclic aldehydes and ketones, quinones	Sh	W	M	W
1640 – 1585	C=C stretching vibration of double bonds of cyclic and acyclic compounds, benzene ring substitution	S	S	S	S
1540	NO_2 vibration of nitro groups	W	W	W	W
1515	C=C stretching vibration of benezene, pyridine, etc., benezene ring substitution, secondary amines	A	M	W	W
1470 – 1420	Aliphatic C-H deformation	W	W	S	S
1025	Si – O – Si vibration of silicates	S	S	S	S
	Fulvic Acids				
3450-3300	H-bonded OH, Free OH, Intermolecular bonded OH	SB	SB	SB	SB
2950 – 2850	Aliphatic C-H, C-H_2, C-H_3 stretching	W	A	W	W
2850 – 2500	Carboxylate ion	Sh	Sh	A	A
1725 – 1640	C = O stretching of carboxylic acids, cyclic and acyclic aldehydes and ketones, quinones	M	M	M	M
1640 – 1585	C=C stretching vibration of double bonds of cyclic and acyclic compounds, benzene ring substitution	S	S	S	S
1515	C=C stretching vibration of benzene, pyridine, etc., benzene ring substitution, secondary amines	W	W	W	W

A= Absent, B = Broad, M = Medium, S = Strong, Sh = Shoulder, W = Weak

Source: Sarmah and Bordoloi (1993)

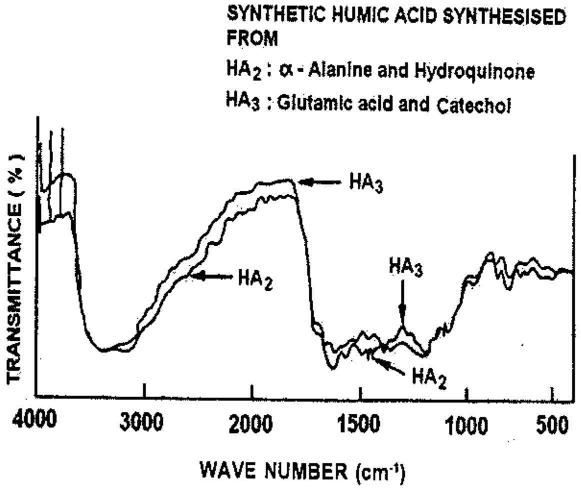


Figure 11. Infrared spectra of two samples of synthetic humic acids

Source : Saha and Sanyal (1988)

Table 4. The major IR absorption bands of some clay minerals

Major IR absorption bands (cm^{-1})		
Montmorillonite	Illite	Kaolinite
3620	3620	3700
3440	3460	3625
1650	2320	3490
1640 - 1630	1630	1430
1560	1460	1110
1505	1030 - 990	1025
1115	910	1000
1050	830	930
925	795	905
890	750	785
855	445	745
805	400	685
630	370	565
530		455
470		400
380		370
350		305

Source: Mondal *et al.* (1997)

to high viscosity (i.e., high resistance to flow). In fact, EF (and to an extent EE) association causes formation of card-house structure throughout the clay suspension. This imparts high viscosity to the system. On the other hand, FF association (through van der Waal's interaction, for instance) causes thickening of clay particles and an effective reduction of EF linkages. This leads to lowering of viscosity.

In the presence of electrolytes, when both the edge and face double layers are compressed, the nature of viscosity variations of clay suspensions is determined by two factors: (i) the balance between the residual EF attraction and FF repulsion, and (ii) the enhanced van der Waal's FF and EE attractions. The viscosity of montmorillonite (in sodium form, for instance) suspension exhibits a high degree of sensitivity towards the presence of extraneous electrolytes. The illite and kaolinite suspensions show progressively less dependence of their viscosity on the concentration of added electrolytes. This provides a relatively simple method (employing the viscosity determinations) for identifying the presence of montmorillonite as the dominating clay in a soil clay fraction. It has been observed experimentally that the viscosity-buffer curves of montmorillonite in particular, and of clay mixtures, in general, in which montmorillonite is dominant, show a distinct peak/hump. This hump gradually becomes less marked and shifts towards lower degree of per cent base saturation as the proportion of montmorillonite in the clay mixtures decreases. This is illustrated by the viscosity-buffer curves of clays and clay mixtures in Figure 12.

The distinct behaviour of montmorillonite, as against that of kaolinite or mica, may be attributed to the nature of its clay lattice to expand in the polar liquids. It causes easy accommodation of the hydrated cation (e.g., Na$^+$)

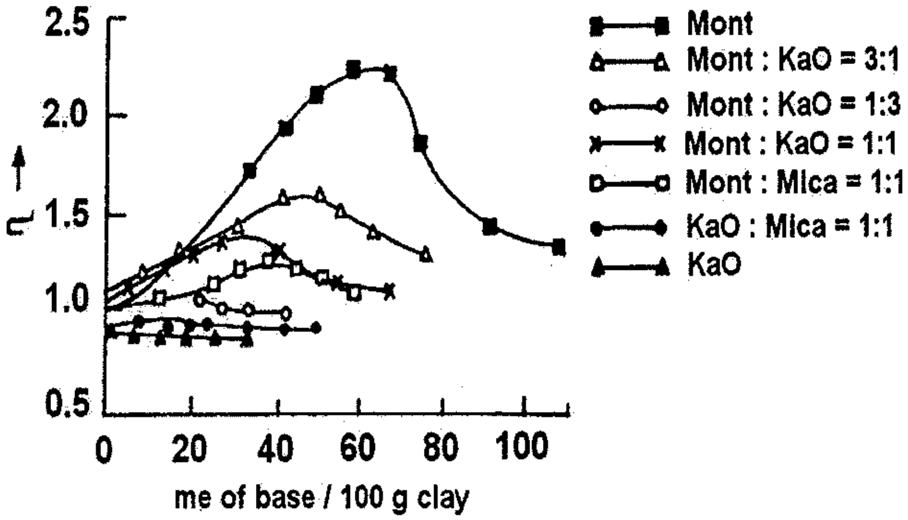


Figure 12. Viscocity buffer-curves of clays and of their mixtures
Source: Sahu and Das (1974)

of the added base largely in the expanding interlayer space up to about 75-80% base saturation, leading to a high value of the volume fraction (ϕ) of the dispersed clay particles (i.e., fraction of total volume occupied by the clay particles). This imparts high viscosity according to the Einstein's equation [Equation (7)].

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \qquad ...(7)$$

where, η and η_0 are the viscosity coefficients of clay suspension and pure water, respectively, at the same temperature. The numerical factor 2.5 has been assigned to spherical suspended particles, and for other shapes, different values have been assigned. Hence, the value of η increases, relative to the value of η_0, with concomitant increase in the value of ϕ.

In mixtures of montmorillonite with non-expanding clays, e.g., kaolinite, mica, etc., the volume-fraction at the same per cent base saturation will obviously be less, leading to a lower value of η.

Furthermore, this nature of montmorillonite to expand favours EF linkages, leading to high viscosity. However, at sufficiently high pH (e.g., beyond 75-80% base saturation in Figure 12), the positively charged double layer at the edges is significantly reduced so that the viscosity of the clay suspension falls due to snapping of EF linkages.

10. Ion Exchange in Soil

Ion exchange in soil system refers to exchange of equivalent amounts of ions between two phases in equilibrium in contact in a reversible process. When cations are involved, the process is termed cation exchange, while for anions, it is referred to as anion exchange. Such exchanges may take place between the soil solid (soil colloid or exchange) phase and the soil solution phase, or less commonly though, between the soil solid phases in contact (e.g. the Inverse Ratio Law; *see* later in Section 13), or soil solid phase and growing plant in contact (contact exchange).

The experimental evidence of cation exchange was provided around 1850 when Thomson, followed by J. Thomas Way leached soil with ammonium sulphate solution, and upon filtration, calcium, and to a lesser extent magnesium, potassium ions were detected in the filtrate, while less of ammonium ions were recovered compared to what was used for leaching. Initially, this phenomenon was described as base exchange. But on recognition of the fact that hydrogen ions can also be so exchanged, the wider term, namely cation exchange was used.

The composition of soil solution is known to change as a result of (1) dilution of soil solution (e.g., during rain or application of irrigation), (2) ion uptake by plants and leaching, (3) fertilizer application, (4) use of brackish groundwater for irrigation, (5) reclamation of salt-affected soils by leaching or use of chemical amendments, (6) sewage and sludge farming and use of industrial effluents for irrigation, etc. This leads to migration of, for instance, cations from soil colloidal phase to soil solution, and/or *vice versa* (cation release/fixation). The process involved is obviously ion exchange.

10.1. Cation Exchange Capacity

As stated above, interchange of a cation in soil solution phase with another on the surface of any surface-active material such as soil clay or organic matter in equivalent proportions in a reversible process is generally termed as cation exchange.

The cation exchange capacity (CEC) is defined as the capacity of the solid (e.g., soil) to adsorb and exchange cations. In other words, it is the sum total of exchangeable cations that can be adsorbed by a soil colloidal surface. It is expressed in the unit of cmol(p^+)kg^{-1} (in S.I. system) or meq. per 100 g in the classical (CGS) unit. Here (p^+) denotes proton.

Similarly, the anion exchange capacity (AEC) of soil colloid can also be defined. It is expressed (in S.I. system) in the units of cmol(e^-)kg^{-1}, (e^-) representing electron.

10.2. Bonding Energy of Exchangeable Cations

Considering the electrical double layer theory as applied to soil colloid system (see Section 11.2 and Section 4.4), the solid surface

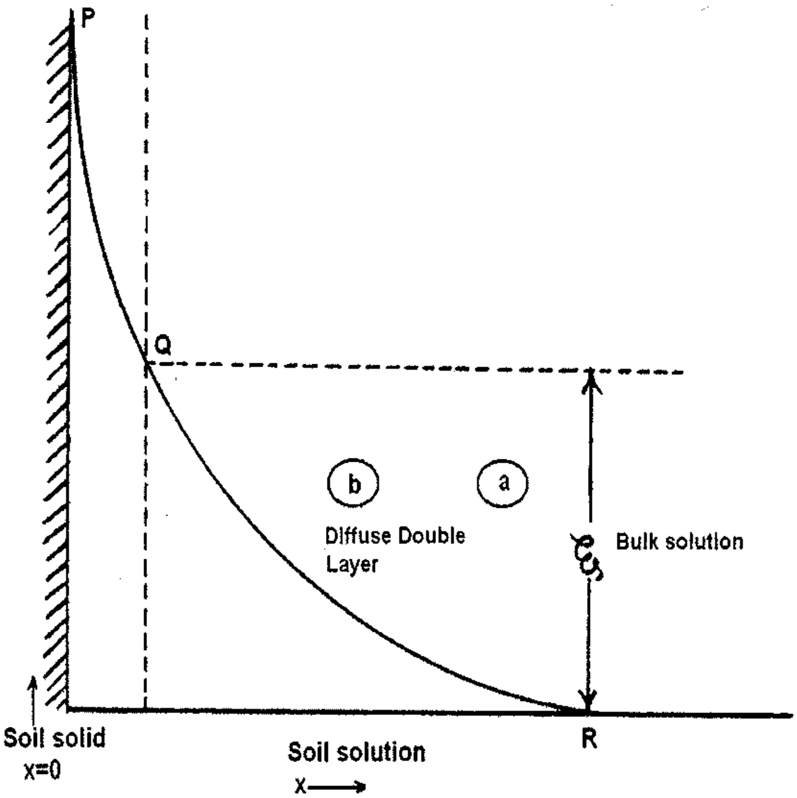


Figure 13. Electrical double layer at soil-soil solution interface

in soil, being predominantly negatively charged, the counter cations on the solution side of the double layer, especially those in the diffuse double layer (Goüy-Chapman layer; Region QR of Figure 4) are the exchangeable cations, amenable to exchange with the externally-added electrolytic cations (e.g., of the added fertilizer/amendments/irrigation water) (Figure 13).

The ionic strength (I) of a solution containing ions, which provides a measure of the intensity of the electric field due to such space change in the solution, is given by Equation (8):

$$I = \frac{1}{2}\sum_i m_i Z_i^2 \qquad \ldots(8)$$

where, m_i is the molality and Z_i is the valence (including sign) of the ion 'i' in the solution phase, with the summation (Σ_i) being extended to cover all the ionic species in the solution.

The activity (a_i) of an ion in a solution is related to its molality (m_i) by Equation (9):

$$a_i = \gamma_i m_i \qquad \ldots(9)$$

where γ_i is the activity coefficient of the ion 'i' in the solution phase while the activity, a_i, is its effective concentration. At infinite dilution, $\gamma_i \rightarrow 1$, and $a_i \rightarrow m_i$.

The activity coefficient (γ_i) of an ion in a solution is given by the Debye-Hückel Extended Law [Equation (10)]:

$$-\log \gamma_i = \frac{AZ_i^2\sqrt{I}}{1 + Bd\sqrt{I}} \qquad \ldots(10)$$

where, A and B are constants at a given temperature for the solvent (e.g., water for aqueous soil solution), d is the diameter of the hydrated ion, and I is the ionic strength of the solution.

For a soil solution, which is generally dilute (except for the salt-affected soil), the Debye-Hückel Extended Law is approximated by the Debye-Hückel Limiting Law, namely

$$-\log \gamma_i \approx AZ_i^2\sqrt{I} \qquad \ldots(11)$$

So that

$$-\log \gamma_i \propto \sqrt{I} \qquad \ldots(12)$$

for a given ion at a given temperature in aqueous solution.

Considering the position of the same exchangeable cation at either 'a' or 'b' in the diffuse double layer (Figure 13), the bonding energy (B.E.) of the given ion for the present colloidal surface will obviously increase with the fall of distance (i.e. x) of the ion from the colloidal surface (at x = 0 in Figure 13), according to the Coulomb's Inverse Square Law. That is, the B.E. at 'a' will be less than that at 'b'. However, the ionic strength (I) will increase as one moves closer to the surface (i.e., with fall in x) with the concomitant increase in the ionic charge density (i.e. Eq. 8). In other words, both B.E. and I would increase with the fall in x. That is, the bonding energy (B.E.) of the counter ions in the diffuse double layer is directly related to the corresponding ionic strength (I), i.e.

$$\text{B.E.} \propto \text{I} \qquad \ldots(13)$$

But, $-\log \gamma_i \propto \sqrt{\text{I}}$ (From Eq. 12)

Hence, $$(\text{B.E.})_i \propto -\log \gamma_i \qquad \ldots(14)$$

Thus, the negative magnitude of the logarithm of the activity coefficient of a counter (exchangeable) ion provides a measure of the corresponding bonding energy of the counter ion for the soil solid surface.

The adsorbability of cations to a charged surface (e.g. soil colloid) has been often discussed in terms of the *Hofmeister series* or *Lyotropic series*. Thus, the monovalent cations can be put in the following sequence according to their adsorbability:

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Bivalent cations follow the sequence given below:

$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$

For the cations of varying valencies, the *Lyotropic series* in respect of adsorbability is given as:

$Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$, and so on.

Obviously, the guiding factor for such orders of cation binding by a charged surface may be related to the concept of bonding energy that has been derived above [e.g., Eqs (10) and (14)] in that the net bonding energy (or adsorbability) of the counter ions on a colloidal surface is the reflection of the relative weightage of the valency and the size of the hydrated cations concerned.

11. Theories of Ion Exchange

11.1. Adsorption Isotherms

In this sub-section we are primarily concerned with the adsorption of molecules or ions from the soil solution on the surfaces of soil solids. The material adsorbed is called the adsorbate, and the material on which adsorption occurs is called the adsorbent. Indeed, phosphate adsorption by soils is a process which is mainly responsible for rendering the soluble phosphates (e.g., applied phosphatic fertilizer such as single superphosphate or diammonium phosphate) in soil solution unavailable to plants. Desorption of once-sorbed plant nutrients from soils and clays is often slow and irreversible, leading to a large hysteresis effect. Adsorbed ammonium ions are also less susceptible to nitrification in soil. The amount of material adsorbed per unit mass of the adsorbent depends largely on the nature of the adsorbate and the adsorbent; it also depends on the concentration of the adsorbate at equilibrium and temperature. Mathematically, it is expressed by Equation (15):

$$\frac{x}{m} = f(\text{Nature of adsorbate and adsorbent, C, T}) \qquad \ldots(15)$$

where, x is the amount of adsorbate adsorbed on mass m of the adsorbent, C is the equilibrium concentration of the adsorbate and T is the temperature.

For a given mass and surface area of the adsorbent, the amount adsorbed increases with increase in the concentration of the adsorbate. When an adsorbent is placed in contact with a solution, the amount adsorbed gradually increases, and the concentration of the surrounding ions or molecules (adsorbate) decreases. This leads to the release of adsorbate from the adsorbent towards solution. When the rates of such desorption becomes equal to the rate of adsorption, an equilibrium is established. When the concentration of adsorbate in solution increases (or decreases), the adsorbed substance also increases (or decreases) till a new equilibrium is established.

Adsorption data at equilibrium are reported in the form of adsorption isotherms. An adsorption isotherm is a plot between the amount adsorbed per unit mass of the adsorbent and the equilibrium concentration of the adsorbent, at a constant temperature.

Different equations have been developed to predict precisely the shapes of the experimental adsorption isotherms between different adsorbates and adsorbents. The most commonly used ones are due to Langmuir (1918), Freundlich (1926), and Brunauer *et al.* (1938), which are described below.

11.1.1. Langmuir Adsorption Theory

The basic theory of adsorption of gases on solids is due to Langmuir (1918) and it is based on the following assumptions:

(1) The surface of solid is made up of adsorption sites, each of which can adsorb one gas molecule. If another molecule hits the adsorbed molecule, it is deflected back into the gas.

(2) All the adsorption sites are identical in their affinity for that gas molecule.

(3) The presence of a gas molecule on one site does not affect the properties of the neighbouring sites.

(4) The rate of adsorption is proportional to the number of adsorption sites and the pressure of gas. The rate of desorption is proportional to the number of occupied sites.

The system is considered to be at equilibrium when the rate of evaporation of the adsorbed gas is equal to the rate of its condensation.

The linear form of the Langmuir adsorption is given as in Equation (16):

$$\frac{C}{x} = \frac{C}{x_m} + \frac{1}{x_m K} \quad \ldots(16)$$

where, C is the concentration of the adsorbate at equilibrium, x is the amount adsorbed per unit mass of adsorbent at any instant and x_m is the maximum amount adsorbed per unit mass of adsorbent as a monolayer, and K is the equilibrium constant related to bonding energy. Experimental adsorption data, when plotted as C/x versus C, should yield a straight line with the slope ($1/x_m$) and the intercept ($1/x_m K$) on the ordinate (Y-axis). It may, however, be remembered that a linear plot between C/x and C is not adequate to prove that adsorption data follow the Langmuir equation. A linear plot of the data is a necessary but not a sufficient condition of obeying the Langmuir equation.

Khasawnch and Copeland (1973) introduced the concept of Supply Parameter (SP) involving the coefficients and constants from the Langmuir equation (Eq. 16). Such SP is taken to provide the buffering capacity of the soil for the adsorbed nutrient due to change of concentration of the nutrient concerned. The SP is given by Equation (16a):

$$SP = \sqrt{(qC/x_m K)} \quad \ldots(16a)$$

where, q is identical with x (specific adsorption of the nutrient concerned) of Equation (16), while x_m and K are the Langmuir constants as given by Equation (16).

The adsorption maximum (x_m) of soils for various ions and molecules, such as phosphate, borate, sulphate, K, herbicides, etc., can be estimated from the slope of the linear plot between C/x and C. From such value of x_m, the surface area (A) of soils and/ or clays can be estimated using the relationship (17):

$$A = \frac{x_m\,(g)\,N\,(\text{number of molecules mol}^{-1})\,\pi r^2}{M\,(g\,\text{mol}^{-1})} \quad \ldots(17)$$

where, r is the radius of the adsorbate molecule, N is the Avogadro's number and M is the molecular weight expressed in grams of the substance. If the adsorbate happens to be a gas, then x_m and M in Equation (17) should, respectively, be replaced by the volume of the gas required to form a monolayer on the surface (v_m, cm^3), and volume occupied by a mole (molecular weight expressed in grams) of the gas, i.e., 22.4 litre at 273 K, so that Equation (17) becomes Equation (18):

$$A = \frac{v_m\,(\text{cm})^3\, N\,(\text{number of molecules mol}^{-1})\,\pi r^2}{22400\,(\text{cm}^3\,\text{mol}^{-1})} \qquad ...(18)$$

Normally, the Langmuir equation is not used to calculate the surface area of solids because it does not define total adsorption process but covers only a certain fraction of adsorption sites.

It is important to emphasize here that soils are mixtures of inorganic and organic substances, consisting of montmorillonite, kaolinite, oxides of iron and aluminium, and decomposed plant material, etc. with each substance reacting towards competing cations differently. In a sense, soil exchangers are essentially polyfunctional ion exchangers. The condition of identical exchange sites (assumption 2) (identical bonding energy) and no change of it during adsorption (assumption 3) thus becomes too restrictive for application of Langmuir equation in a soil system. The experimental exchange isotherm obtained for a soil system is a weighted sum of isotherms for different types/classes of exchange sites rather than for identical exchange sites.

Use of Langmuir equation becomes further restrictive for cation exchange equilibria, as it does not take into account the competition between the cationic species. According to this equation, the amount of a cation on the adsorbed phase is governed only by the concentration of that cation, independent of the concentration of the competing cation. Also, the Langmuir adsorption isotherm refers to gaseous adsorption on non-ionic solid, while adsorption in soil is essentially an ionic process.

11.1.2. Freundlich Isotherm

The Freundlich equation (1926), originally an empirical equation, but subsequently derived on a rigorous mathematical model, implies that the bonding energy of the adsorbate on a given adsorbent decreases with fractional coverage of surface area of the adsorbent. This is closer to reality than the assumption of a constant bonding energy inherent in the Langmuir equation. This is one of the most widely used adsorption equations to describe the experimental data on adsorption of ionic or molecular species in soil. However, the Freundlich isotherm does not predict any adsorption maximum. Mathematically, it is expressed by Equation (19):

$$x = K\,C^n \qquad (n < 1) \qquad ...(19)$$

where, x is the amount adsorbed per unit mass of adsorbent and C is the equilibrium concentration of the adsorbate. K and n are empirical constants, sensitive to the given adsorbent-adsorbate system and temperature. The linear form of this equation is obtained by taking logarithm of its both sides, when we get expression (20):

$$\log x = \log K + n \log C \qquad ...(20)$$

A plot of the experimental data of log x *versus* log C should give a straight line with a slope of n and an intercept of log K.

11.1.3. Brunauer, Emmett and Teller (BET) Adsorption Isotherm

The Langmuir equation represents the experimental adsorption data reasonably well in cases where adsorption becomes independent of pressure after the formation of monolayer. For many gases and vapours, however, it fails at higher pressures because more than a monolayer of adsorbed molecules is formed. The theory of Brunauer, Emmett and Teller (BET) extends Langmuir derivation to obtain an equation for multilayer adsorption.

The BET equation is based on the following assumptions (Brunauer *et al.*, 1938):

(i) Heat of adsorption in the second, third, ..., nth layers is the same as the heat of adsorption in the monolayer, i.e. heat of liquefaction or condensation of the gas, and

(ii) If the adsorption takes place on a free surface, then at p° (saturation pressure of the gas), an infinite number of layers can be built up on the adsorbent.

The BET equation used to define multilayer adsorption at any equilibrium pressure, p, is given in its linear form as Equation (21):

$$\frac{p}{v(p^0-p)} = \frac{(C'-1)p}{v_m C' p^0} + \frac{1}{v_m C'} \qquad ...(21)$$

where, v is the volume of gas adsorbed per unit mass of adsorbent, v_m is the volume of gas required to form a monolayer on the entire adsorbent surface of unit mass, C′ is a constant at a given temperature. According to this equation, a plot of the experimental data between $p/v(p^o-p)$ versus p/p^o should give a straight line with a slope of $(C'-1)/v_mC'$ and an intercept of $1/v_mC'$ on the Y-axis. The values of slope and intercept thus yield the values of constant, C′, and volume of gas adsorbed when the entire adsorbent surface is covered with a monolayer, v_m. The advantages of BET equation are:

(i) It describes the multilayer adsorption,

(ii) It yields the volume of gas required for the formation of a monolayer, and

(iii) It can be used to calculate the surface area of soils [e.g., by the use of Eq. (18)].

The BET equation is most useful between the relative pressures (p/p^o) of 0.05 and 0.45. The surface area can be calculated by multiplying v_m with the cross-sectional area of the adsorbate molecule. To determine surface area of soils and minerals, adsorbate molecules such as nitrogen, ethane, water, ammonia or other gases may be used. Weakly adsorbed molecules like nitrogen, however, may not penetrate into all the interlayer surfaces, resulting into an underestimate of total surface area. Use of strongly adsorbed molecules like ammonia, which penetrates into the internal surfaces also, leads to the measured surface area closer to the total surface area.

11.1.4. Hysteresis

It is generally observed that the ions which are adsorbed by a colloidal surface by ionic interactions, through non-specific retention mechanism, are desorbed during the desorption cycle by the expenditure of the same amount of energy as was released during the adsorption pathway. However, for the ligand exchange processes, such as those involved in the fixation of phosphate, sulphate, borate, etc., by soil colloids, and also the cation, namely K^+ (the latter being specifically sorbed in the interlayer space of illitic clay minerals), desorption generally requires much more energy in view of the fact that the retentive forces in such cases are primarily covalent in nature for the anions concerned, while ionic diffusion of K^+ occurs through a strongly negatively charged electric field in the illitic interlayer space. This leads to irreversibility of the adsorption-desorption processes involved, with the degree of such irreversibility depending on the nature of the soil colloids concerned (e.g., aluminosilicate clay minerals, hydrous oxide of Fe, Al, etc., in clay-size dimensions), and also the ions concerned. This effect is known as 'Hysteresis'. The hysteresis effect in K^+ ionic fixation-release processes depends not only on the amount of illitic minerals present in a given soil, but also on the state of weathering of such minerals. The more weathered the illitic minerals are (e.g., in Alfisols), the less will be the extent of hysteresis, as compared to that in the soils of more recent origin (e.g., Inceptisols, Entisols, etc.).

11.2. Electrical Diffuse Double Layer Theory

As stated earlier (Section 4.2), the layer-lattice silicate minerals have both the permanent and the pH-dependent charges. The oxides and humus components of such complexes, on the other hand, exhibit only the pH-dependent charge. In 2:1 layer-lattice silicate minerals, the pH-dependent charge is invariably less than the permanent negative charge. In majority of the cases, the soil colloidal complex at pH above 6 possesses a net negative charge. As a result, an electrical double layer is formed at the colloidal-solution interface which has already been explained earlier (Section 4.3).

The main assumptions of the theory of diffuse double layer are:

(i) The charged particle has flat surface without edge effect, i.e. the planar surface is effectively infinite in extent.

(ii) The exchange sites are uniformly distributed over the entire planar surface, i.e. the surface charge density is uniform.

(iii) The dielectric constant of water in the aqueous solution phase is constant.

(iv) The ions act as point charges.

(v) The interaction between ions is negligible and the charged surface and the ions interact only electrostatically.

(vi) The charge on the surface is neutralized by the excess of oppositely charged ions in the diffuse double layer, considering the Helmholtz's layer to be too small in extent as compared to the Goüy-Chapman layer.

For a mixture of monovalent and divalent symmetrical salt solutions, Goüy-Chapman's theory of the diffuse double layer has been used to obtain the relative amounts of the monovalent and divalent cations adsorbed on the clay surface. The fractional saturation of the exchange complex by the monovalent cation has been shown to be a function of surface charge density of the exchanger, cationic composition of the equilibrium solution and interaction between the diffuse double layers on the adjacent clay platelets. Such a relationship, based on the diffuse double layer theory, in its simplified form (Bolt, 1955), is given by Equation (22):

$$\frac{\Gamma^+}{\Gamma} = \frac{r}{T\sqrt{\beta}} \sinh^{-1} \frac{\Gamma\sqrt{\beta}}{r + 4V_d\sqrt{C_2}} \qquad \text{...(22)}$$

where,

Γ = The total surface charge density (mol/ m^2),

Γ^+/Γ = The fraction of the total surface charge neutralized by the monovalent cation,

C_1 = Equilibrium concentration of monovalent cation (mol/L)

C_2 = Equilibrium concentration of divalent cation (mol/L)

r = $C_1/\sqrt{C_2}$ ($\sqrt{mol}/\sqrt{L}$), is the reduced ratio of monovalent cation,

V_d = cosh Y_d ($Y_d = Ze\Psi_d/kT$), where Ψ_d is the electrical potential at the midway plane between two adjacent clay platelets

β = 1.08×10^{13} m mmol^{-1} at 298 K.

Because of the occurrence of surface charge density (Γ), reduced ratio of Na (r) and square root of the concentration of divalent cation (C_2) in the sine hyperbolic inverse function, the magnitude of their effect on the fractional saturation of the exchange complex by the monovalent cation is not easily discernible. The effect of soil and solution variables on the fractional saturation of the surface charge by the monovalent cation is thus illustrated by taking the following examples.

Example:

Given:

Equilibrium concentration of monovalent cation (C_1) = 0.1 mol/L

Equilibrium concentration of divalent cation (C_2) = 0.01 mol/L

Cation exchange capacity of soil (CEC) = 20 cmol(p$^+$)kg^{-1}

Specific surface area of soil (S) = 2×10^5 m^2/kg

r = $0.1 / (0.01)^{½} = 1$ mol^{½} L$^{-½}$

β = 1.08×10^{13} m mmol^{-1}

Γ = CEC/S = 0.1×10^{-5} mol m^{-2} = 10^{-6} mol m^{-2}

Taking the value of V_d as unity (i.e., non-interacting diffuse double layers) and substituting the values of r, Γ, C_2 and β in Equation (22), one gets Equation (23):

$$\frac{\Gamma^+}{\Gamma} = \frac{1}{10^{-6}(1.08 \times 10^{13})^{½}} \sinh^{-1} \frac{10^{-6}(1.08 \times 10^{13})^{12}}{1 + 4(0.01)^{½}} \qquad \text{...(23)}$$

$$= 0.304 \sinh^{-1} 2.347$$
$$= 0.304 \times 1.581$$
$$= 0.484$$

which is nearly equivalent to 50% saturation of the exchange capacity by the monovalent cation.

The **thickness of the diffuse double layer**, defined as δ, may be calculated by Equation (24):

$$\delta = \left[\frac{\varepsilon kT}{2n_o Z^2 e^2}\right]^{½} \qquad \text{...(24)}$$

where,

ε = Static permittivity of the medium,

k = Boltzmann constant,

T = Absolute temperature,

e = Electron charge,

n_0 = Number of ions per m^3 in the equilibrium solution, and

Z = Numerical value of the valency of the counter ion (cation in case of negatively charged surface).

The static permittivity of aqueous medium, ε, is equal to ε_0 D, with ε_0 being the permittivity in vacuum (8.85×10^{-12} C^2 J^{-1} mol^{-1}) and D is the dielectric constant of the medium (78.5 at 298 K for water).

Hence, on substituting the values of ε (= $694.7 \times 10^{-12} \times C^2\, J^{-1}\, mol^{-1}$), k (=$1.38 \times 10^{-23}$ J. K^{-1}), T (= 298 K), e (=1.602×10^{-19} C), and n_0 (= $C_0 \times 10^3 \times 6.02 \times 10^{23}$ ions m^{-3}) in Equation (22) at 25 °C (i.e. 298 K), one obtains Equation (25):

$$\delta = \frac{3.0\times10^{-10}}{Z}\left(\frac{1}{C_0}\right)^{1/2}.\text{m} \qquad ...(25)$$

or

$$\delta \approx \frac{3}{Z(C_0)^{1/2}} A^0 \qquad ...(26)$$

where, C_0 is the concentration of the equilibrium solution (mol/L).

For a 1:1 electrolyte (i.e., Z =1), and C_0 = 0.1 mol L^{-1}, δ is about 1nm, while at C_0 = 0.001 mol L^{-1}, δ is about 10 nm.

11.2.1. Factors Affecting the Thickness of Diffuse Double Layer (δ)

It is clear from Equations (25) and (26) that δ depends on the total electrolyte concentration, valence of the counter ion, dielectric constant of the medium and temperature.

(i) Total Electrolyte Concentration — The higher is the total electrolyte concentration, the smaller is the thickness of the diffuse double layer. On increasing the electrolyte concentration four-times, the thickness of the diffuse double layer reduces to half.

(ii) Valence of the Counter Ion — The higher is the valence of counter ion, the smaller is the thickness of diffuse double layer. At a fixed electrolyte concentration, the thickness of the diffuse double layer for divalent ions would be half that for monovalent ions.

(iii) Dielectric Constant of the Medium — An increase in the dielectric constant of a medium increases the thickness of the diffuse double layer. An increase in temperature decreases the dielectric constant of medium, causing a fall in the thickness of the diffuse double layer due, obviously, to a higher kinetic energy of the counter ions. These inferences were drawn earlier in a qualitative manner (Section 4.4).

11.3. Donnan Membrane Equilibrium

If an aqueous solution of an electrolyte consisting of two diffusible ions (a cation and an anion), is separated by a membrane from another solution containing a salt with a non-diffusible ion, then at equilibrium (when the flow across the membrane stops at a given temperature), the distribution of the diffusible ions will be unequal on the two sides of the membrane, even though the ionic activity (or concentration in a dilute system) product of equivalent amounts of the oppositely charged ions or ratio of equivalent amounts of the like-charged ions on the two sides of the membrane will be equal. This is known as the 'Donnan Membrane Equilibrium', and the membrane of selective permeability is known as a 'Donnan membrane'.

However, if an aqueous solution of NaCl of concentration C_1 is separated from another such solution of concentration C_2 ($C_1 > C_2$) by an ordinary ("open") membrane of equal permeability to Na^+ and Cl^- ions, there will be a flow from the first solution [say, the left-hand side (L) solution with respect to the membrane (M)] to the second one [say, the right-hand side solution (R)] till the NaCl concentrations on both sides of M become equal and an equilibrium is reached. Under such circumstances, at equilibrium

$$(C_{Na^+})_L = (C_{Na^+})_R \qquad ...27(a)$$

and

$$(C_{Cl^-})_L = (C_{Cl^-})_R \qquad ...27(b)$$

Obviously then,

$$(C_{Na^+})_L\,(C_{Cl^-})_L = (C_{Na^+})_R\,(C_{Cl^-})_R \qquad ...27(c)$$

However, if the left-hand side solution (L) with respect to the membrane (M) has a solution (of, say, NaCl) with a non-diffusible ion through the given membrane, i.e., a Donnan membrane, e.g., Na^+R^-, where R^- is a large (non-diffusible) resin anion (Figure 14), then diffusion of Na^+ and Cl^- ions will take place from L to R across M (Figure 14) until an equilibrium (no flow) is attained.

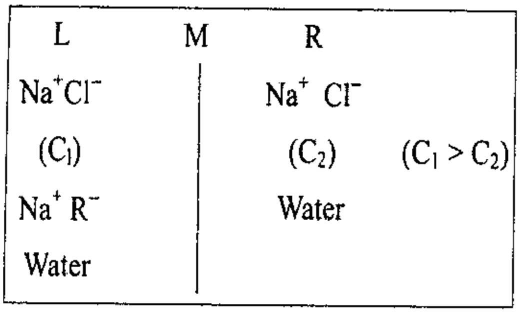


Figure 14. The Donnan membrane system

At equilibrium, for electrical neutrality on each side of the membrane (M):

$$(C_{Na^+})_R = (C_{Cl^-})_R \qquad \ldots(28)$$

And,

$$(C_{Na^+})_L = (C_{Cl^-})_L + (C_{R^-})_L \qquad \ldots(29)$$

where, the concentration terms refer to those at equilibrium.

According to the Donnan Membrane Equilibrium Theory, at equilibrium one obtains:

$$(C_{Na^+})_L\,(C_{Cl^-})_L = (C_{Na^+})_R\,(C_{Cl^-})_R \qquad \ldots(30)$$

Substitution of $(C_{Na^+})_R$ in Eq. (30) from Eq. (28) and $(C_{Na^+})_L$ from Eq. (29), one obtains from Eq. (30):

$$[(C_{Cl^-})_L + (C_{R^-})_L]\,(C_{Cl^-})_L = (C_{Cl^-})^2_R$$

or,

$$(C_{Cl^-})^2_L + (C_{Cl^-})_L\,(C_{R^-})_L = (C_{Cl^-})^2_R \qquad \ldots(31)$$

That is,

$$(C_{Cl^-})_L \neq (C_{Cl^-})_R \qquad \ldots(32)$$

And, in the same manner,

$$(C_{Na^+})_L \neq (C_{Na^+})_R \qquad \ldots(33)$$

Considering a soil colloidal system, the solid (charged) surface is swarmed by the oppositely charged counter ions on the solution side of the electrical double layer such that the counter ion concentration falls off as the distance from the solid surface increases in the diffuse double layer, while the concentration of the ions of the like charges (as on the soil solid or exchange surface) increases. Thus, there will be a region towards the terminal end of the solution side of the diffuse double layer (close to the bulk soil solution of even distribution of cations and anions) which will be dominated by the anions (for a soil colloid of net negative change). This region, intervening between the soil colloidal solid (i.e. exchange) phase and the soil solution phase, will act as if it were a Donnan membrane of selective permeability. Thus, considering the distribution of, say, K^+, Ca^{2+} and Cl^- ions between the soil colloidal (exchange) phase and the solution phase in such a Donnan system, one would have at equilibrium [from Eq. (30)]:

$$(C_{K^+})_{exch}\,(C_{Cl^-})_{exch} = (C_{K^+})_{soln.}\,(C_{Cl^-})_{soln.} \qquad \ldots(34)$$

and

$$(C_{Ca^{2+}})_{exch}\,(C_{Cl^-})^2_{exch} = (C_{Ca^{2+}})_{soln.}\,(C_{Cl^-})^2_{soln.} \qquad \ldots(35)$$

By combining Eqs (34) and (35), one obtains,

$$\frac{(C_{K^+})_{exch}}{(C_{K^+})_{soln.}} = \frac{(C_{Cl^-})_{soln.}}{(C_{Cl^-})_{exch}} = \sqrt{\frac{(C_{Ca^{2+}})_{exch}}{(C_{Ca^{2+}})_{soln.}}}$$

That is,

$$\left(\frac{C_{K^+}}{\sqrt{C_{Ca^{2+}}}}\right)_{exch} = \left(\frac{C_{K^+}}{\sqrt{C_{Ca^{2+}}}}\right)_{sol^n} \qquad \ldots(36)$$

This is the essential conclusion, in quantitative terms, in regard to ionic distributions between the exchange and solution phases at equilibrium in soil, behaving like a Donnan system for reasons explained earlier.

In order that the above equilibrium between the exchange and solution phase is maintained, any dilution of the solution phase, for instance, would, therefore, favour release of K^+ ions (monovalent) from the exchange phase to the diluted soil solution phase, and *vice versa* for the divalent Ca^{2+} ions. An increase in the concentration of the soil solution will have a reverse effect on the equilibrium distribution of monovalent and divalent cations between the exchange (or adsorbed) and the soil solution phases.

11.4. Cation Exchange Equations Based on Law of Mass Action

The formulations expressing the relationships between the cations in the solution and adsorbed phases of soil at equilibrium are termed as cation exchange equations. While describing some empirical relationships, it is assumed that (a) all the exchange sites are freely accessible to solution cations such that cation exchange takes place instantaneously, (b) the surface charge (i.e. cation exchange capacity) remains constant over the entire cationic composition of the exchange complex, (c) the adsorbed phase is homogeneous (i.e. the surface charge is distributed uniformly), (d) the anions are effectively excluded from the monolayer of cations, and finally (e) the surface does not form any chelate with cations. The surfaces of different layer-lattice silicate minerals with the net negative charge satisfy the above-stated conditions only to various degrees.

Such cation exchange formulations may involve homovalent ion exchange or heterovalent ion exchange systems.

For homovalent cation exchange equilibria, one has

$$A^{Z+}_{\text{soil}} + B^{Z+}_{\text{soln.}} \rightleftharpoons B^{Z+}_{\text{soil}} + A^{Z+}_{\text{soln.}} \quad \ldots(37)$$

For instance, one may consider the Na^+-K^+ ion exchange system in soil. Thus,

$$Na^+_{\text{soil}} + K^+_{\text{soln.}} \rightleftharpoons K^+_{\text{soil}} + Na^+_{\text{soln.}}$$

However, here K^+_{soil} on the product side does not imply that the entire amount of exchangeable Na^+ ion from the homoionic soil exchanger (rendered homoionic with Na^+ ions) will be replaced by K^+ ion at equilibrium so that the exchanger will become K^+ ion-saturated at equilibrium. The exchanger at equilibrium will have both Na^+ ion (the residual Na^+ ion) and K^+ ion (the substituting K^+ ion) as the exchangeable cations, but their proportion will vary, depending primarily on the initial concentration of the bathing electrolyte (e.g., KCl in this case).

The Law of Mass Action leads to the equilibrium constant as:

$$K_m = \frac{[B^{Z+}_{\text{soil}}]\,(A^{Z+}_{\text{soln.}})}{[A^{Z+}_{\text{soil}}]\,(B^{Z+}_{\text{soln.}})} \quad \ldots(38)$$

where, [ ] denote the activity of the exchangeable ion concerned on the absorbed phase (e.g., soil), while ( ) denote that in the solution phase at equilibrium.

These equations were derived by Kerr (1928) and Vanselow (1932) who made an assumption that the solid (exchange) phase is an ideal solid solution so that the activities of the adsorbed ions may be approximated by the corresponding concentrations [i.e., the activity coefficients of the adsorbed species in Eq. (38) are unity], for example, the respective mole fractions on the exchange phase at equilibrium.

The activity coefficients of the ions in the soil solution phase may be evaluated from the ionic strength of the solution phase, following the Debye-Hückel formulations [Eqs (10) and (11)], as explained in Section 10.2. For this reason, the Kerr-Vanselow formulations [Eq. (38)] do not lend themselves to the evaluation of the thermodynamic equilibrium constants, and K_m in Eq. (38) is termed as the "Selectivity Constant or Quotient". These formulations are mostly applicable to the homovalent ion exchange systems.

Gapon (1933) also considered the hypothesis of ideal solid solution as above, but dealt with the heterovalent systems which are of more practical value than the homovalent ion exchange systems. Gapon preferred to use the ionic concentrations on the adsorbed (exchange) phase in equivalent basis for taking care of the corresponding ionic activities (in practice, the ionic concentrations for reasons stated above).

For a heterovalent ion exchange equilibrium, namely

$${}_{Z_B}A^{Z_A^+}_{\text{Soil}} + {}_{Z_A}B^{Z_B^+}_{\text{soln}} \rightleftharpoons {}_{Z_A}B^{Z_B^+}_{\text{Soil}} + {}_{Z_B}A^{Z_A^+}_{\text{soln.}}$$

$$(Z_A^+ \neq Z_B^+) \quad \ldots(39)$$

Accordingly, the Kerr-Vanselow formulation (Eq. 38) should be modified to Equation (40):

$$K_m = \frac{[B^{Z_B^+}_{\text{soil}}]^{Z_A}\,(A^{Z_A^+}_{\text{soln.}})^{Z_B}}{[A^{Z_A^+}_{\text{soil}}]^{Z_B}\,(B^{Z_B^+}_{\text{soln}})^{Z_A}} \quad \ldots(40)$$

where, square brackets, [ ] and circular brackets, ( ), have the same significance as before. According to Gapon (1933), Eq. (40) reads as:

$$K_m\ (\text{or } K_G) = \frac{[CEC - A^{Z_A^+}_{\text{Soil}}]\,(A^{Z_A^+}_{\text{soln.}})^{1/Z_A}}{[A^{Z_A^+}_{\text{Soil}}]\,(B^{Z_B^+}_{\text{soln}})^{1/Z_B}} \quad \ldots(41)$$

An example will help to understand the transformation of Eq. (40) to Eq. (41). Thus,

$$2\,Na^+_{soil} + Ca^{2+}_{soln.} \rightleftharpoons Ca^{2+}_{soil} + 2\,Na^+_{soln.} \qquad ...(42)$$

By dividing both sides of Eq. (42) by 2, one obtains:

$$Na^+_{soil} + \tfrac{1}{2}\,Ca^{2+}_{soln.} \rightleftharpoons \tfrac{1}{2}\,Ca^{2+}_{soil} + Na^+_{soln.} \qquad ...(43)$$

In case one starts with a homoionic soil in respect of Na^+ ion as in Eq. (42), then at equilibrium, the soil exchange phase will have only Na^+ and Ca^{2+} ions as exchangeable ions. If the CEC is the cation exchange capacity of the given soil, while the degree of saturation of soil (exchange) phase at equilibrium with respect to Na^+ ion is given as Na^+_{soil}, then obviously, the Ca^{2+} ion saturation of the CEC at equilibrium will be given as:

$$Ca^{2+}_{soil} = CEC - Na^+_{soil}$$

provided that the CEC and the degrees of saturation with respect to the exchangeable cations at equilibrium are expressed on equivalent basis. Substitution of these facts in Eq. (41) in respect of the exchange equilibrium, as given in Eqs (42) and (43), would obviously lead to the form of K_m [Eq. (44)], which is identical with Eq. (41). Thus,

$$K_m\,(\text{or } K_G) = \frac{[Ca^{2+}_{soil}]^{1/2}\,(Na^+_{soln.})}{[Na^+_{soil}]\,(Ca^{2+}_{soln.})^{1/2}}$$

or,

$$K_m\,(\text{or } K_G) = \frac{[CEC - Na^+_{soil}]\,(Na^+_{soln.})}{[Na^+_{soil}]\,(Ca^{2+}_{soln.})^{1/2}} \qquad ...(44)$$

A large number of experimental data for homovalent and heterovalent cation exchange equilibria studies have been fitted to the Kerr-Vanselow and the Gapon equations to obtain the corresponding selectivity coefficients (K_m). These values of K_m for, say, a given homovalent ion exchange system (e.g., Na^+-K^+, Na^+-Rb^+, Na^+-Cs^+, Na^+-NH_4^+ exchange equilibria), obtained by equilibrating a given amount of a homovalent soil clay (e.g., Na^+-clay) with varying initial concentrations of a replacing cation (e.g., $K^+/Rb^+/Cs^+/NH_4^+$), when plotted against the corresponding position of equilibrium (e.g., the ionic composition of the solid phase at equilibrium), demonstrate wide variations as shown in Figure 15.

If K_m were a thermodynamic equilibrium constant, its values should have remained constant with the position of equilibrium, unlike what is apparent from Figure 15. When one examines a heterovalent ion exchange equilibrium, such variations of K_m are even wider, as is evident from an examination of the experimental data on K_m for K^+ - Ca^{2+} ion exchange (Figure 16).

Such variations stem from the assumption of ideal solid solution behaviour of the soil exchanger, thereby neglecting the activity coefficients of the adsorbed ions on the solid (exchange) phase, in the Kerr-Vanselow and the

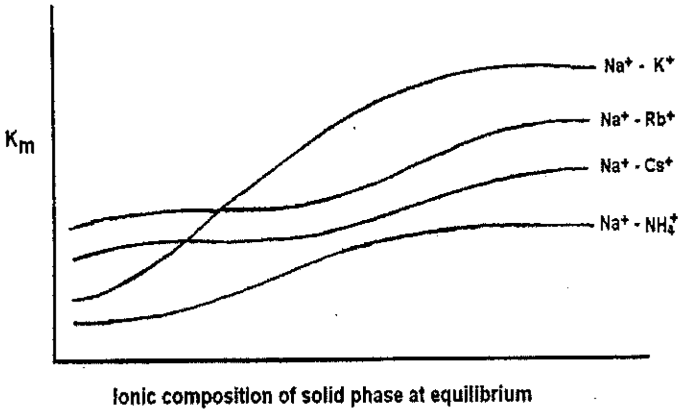


Figure 15. Plot of selectivity coefficient against position of equilibrium in a homovalent cation exchange equilibria

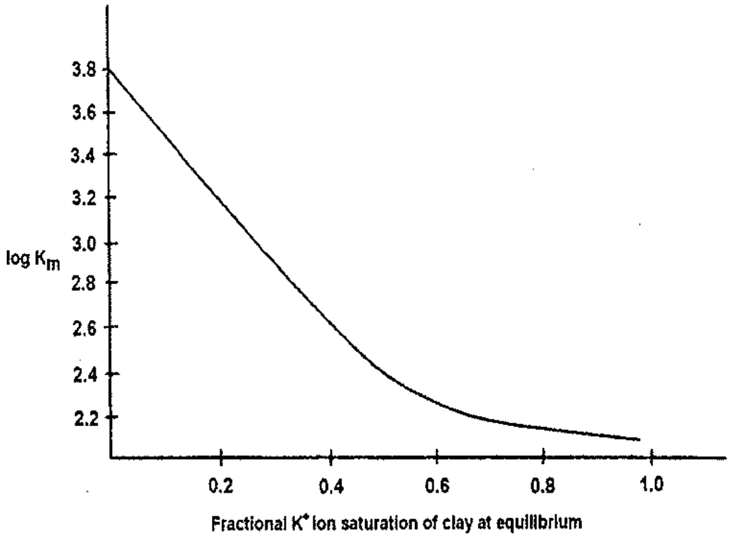


Figure 16. Plot of selectivity coefficient (log scale) against the position of equilibrium in heterovalent cation exchange equilibra

Source: Talibudeen (1972)

Gapon formulations. This is addressed by the thermodynamic theory of ion exchange which will follow.

11.5. Thermodynamic Theory (due to Gaines and Thomas, 1953)

Before proceeding further, it will be instructive to introduce, in brief, the concept of fugacity of a component (e.g., the solute) in a solution. The fugacity refers to the "escaping tendency", for instance, of a gas in a mixture. The fugacity (f) of a solute in a binary solution is related to its concentration (c) by the following equation:

$$f/c = 1$$

for all values of 'c' in an ideal solution, while

$$\lim_{c \to 0} \frac{f}{c} = 1$$

for a non-ideal solution.

The activity (a) of a solution in a binary solution is related to its fugacity (f) as,

$$a = f/f^0$$

where, f^0 is the fugacity in the standard state (of unit activity) of the solute. Obviously, in the standard state (a = 1), $f = f^0$.

The standard state of a solute (in which the solute has unit activity) in a binary solution is defined as that hypothetical solution which behaves ideally at a concentration (c) of 1 molar, 1 molal or 1 mole fraction, depending on the scale of concentration used.

However, such a concentration (1 molar, 1 molal, etc.) denotes too concentrated a solution to behave ideally as required in the above-stated definition of the standard state. Hence, the latter has got *no physical existence*, and it is *hypothetical*. In practice, ideal behaviour may be expected only in dilute solutions of concentration, 10^{-4}–10^{-5} *M*, and at further dilution.

For the above-noted standard state of the solute, we have:

$$a = f/f_0 = 1$$

And the solution being ideal, f = c = 1 *M* (say). Hence,

$$f = f^0 = 1M = c^0 \text{ (say)}$$

where, c^0 is the standard state concentration of the solute, namely 1 *M* (say) in this case.

11.6. Gaines and Thomas Theory of Cation Exchange in Soil

This theory refers to the general ion exchange equilibrium as given below [Eq. (39)]:

$$Z_B A^{Z_A +}_{\text{Soil}} + Z_A B^{Z_B +}_{\text{soln.}} \rightleftharpoons Z_A B^{Z_B +}_{\text{Soil}} + Z_B A^{Z_A +}_{\text{soln.}} \quad \text{...(39)}$$

The selectivity coefficient is given, following earlier arguments, by Eq. (45):

$$K_m \text{ (or } K_C) = \frac{(q_B/q_O)^{Z_A} (C_A/C_O)^{Z_B}}{(q_A/q_O)^{Z_B} (C_B/C_O)^{Z_A}} \cdot \frac{\gamma_A^{Z_B}}{\gamma_B^{Z_A}} \cdot C_O^{(Z_B - Z_A)} \quad \text{...(45)}$$

where,

q_0 = Total number of equivalent negative sites on the exchange phase,

q_A = Equivalent negative sites occupied by A^+ ions on exchange phase at equilibrium,

q_A/q_0 = Mole fraction on exchange phase at equilibrium as occupied by A^+ ions,

q_B = Equivalent negative sites occupied by B^+ ions on exchange phase at equilibrium,

γ_A = Activity coefficient of A^+ ions in solution phase at equilibrium,

γ_B = Activity coefficient of B^+ ions in solution phase at equilibrium,

C_0 = Total equivalent amount of positive sites in the exchange site (in the diffuse layer). It is equal to q_O, which is in the solid phase ($q_0 = C_0$),

C_A = Equivalent number of cationic sites in the solution at equilibrium occupied by A^+ ion,

C_A/C_0 = Mole fraction of A^+ ions in the solution phase at equilibrium, and

C_B/C_0 = Mole fraction of B^+ ions in the solution phase at equilibrium.

The selectivity quotient (K_m or K_C) is ***not*** a thermodynamic equilibrium constant in that the activity coefficient of the adsorbed ions in the exchange phase at equilibrium is ignored (is set equal to unity). The Gains and Thomas theory then proceeds to address this issue based on the following two assumptions:

(1) The adsorbed ionic layer is treated as a solid solution (***not*** ideal) so that the cationic concentrations are obtained from the fractions of the total ion 'sites' on the exchange phase, occupied by cations, A^+ and B^+ ions (q_A/q_0 and q_B/q_0), which are identical to the parameter, namely fractional saturation of the CEC.

(2) The standard state of unit activity of an adsorbed cation is taken to be that state when all the ionic sites on the exchange phase are fully saturated by the cation concerned and the system behaves ideally so that $a_+ = C_+ = 1$. That is, the activity coefficient, $f_+ = 1$. Hence, the bonding energy parameter in the standard state, namely, $-\log f_+$, is given as [Section 10.2, Eq. (14)]:

$$(\text{B.E.})_+ \, \alpha - \log f_+ = 0 \qquad \text{...(46)}$$

Thus, all the cations in their respective standard states will exchange with equal ease. Referring to Eq. (45), in the standard state for A^+ ions, one has,

$$a_{A^+} = f_{A^+} \frac{q_A}{q_0} = 1$$

But in this state, according to assumption 2, $q_A = q_0$ Hence, $f_{A+} = 1$

Thus, the value of the activity coefficient of the adsorbed A^+ ion, in its standard state of unit activity (i.e., f_{A+}), turns out to be unity, as shown above. Thus, the above relationships, based on assumption (2) of the Gains and Thomas theory, are self-consistent and also consistent with the definitions of fugacity, activity, activity coefficient and the standard state.

In general, the thermodynamic equilibrium constant (K) for the given ion exchange equilibrium (Eq. 39) is related to K_m (or K_C) by the relationship:

$$K = K_C \left(f_B^{ZA} / f_A^{ZB}\right) \qquad \text{...(47)}$$

where, f_A and f_B are the activity coefficients of the adsorbed cations, A^+ and B^+, on the exchange phase at equilibrium.

Because the activity coefficient of an ion varies with the ionic strength (I) of the medium [Eqs (10) and (11) of Section 10.2] for a heterovalent exchange of, say, K^+-Ca^{2+} ion exchange discussed earlier, I [$= {}^1/_2 \, \Sigma \, m_i Z_i^2$; Eq. (8)] will obviously change with the position of equilibrium, i.e., with more of K^+ ion, initially present on the exchange phase, being exchanged at equilibria for Ca^+ ions (with the initial concentration of $CaCl_2$ solution used for leaching being higher), I will increase, and hence the activity coefficient of both K^+ and Ca^{2+} ions on the exchange phase will be different compared to those obtained at a higher fractional saturation (at equilibrium) of the soil clay with K^+ ion.

This will render K_C (or K_m) change for f_A and f_B will change in order that the thermodynamic equilibrium constant (K) remains unaltered [Eq. (47)]. This explains the variations of K_C (or K_m) with the position of equilibrium in a heterovalent ion exchange reaction (Figure 16).

Even for the homovalent cation exchange (Figure 15), the activity coefficients of the monovalent cations involved need not be the same if one examines the Debye-Hückel extended Law [(Eq. (10), giving the activity coefficient of an ion. Further, the relative accessibility on the exchanger (e.g., the clay) of the original and the replacing cations (in a homovalent exchange) need not be the same for a series of replacing cations, depending on the preferential and specific adsorption. Hence, the ionic strength on the exchange (solid) phase will vary with the position of equilibrium for each pair of exchanging cations, so also the corresponding ionic activity coefficients, and hence the value of K_m (Figure 15). However, the variations in K_m have been found much more for the heterovalent ion exchange compared to the homovalent cases (Figures 15 and 16).

Such variations may also be traced to the heterogeneity of the exchange sites in the soil adsorbed phase. These exchange sites have been considered as homogeneous with respect to their specificity for a given cation in the derivation of the exchange equations. These exchange coefficients vary, though in different proportions, with the cationic saturation of the exchange complex. For instance, in Na-Ca exchange, the values of these coefficients increase with Na-saturation of the exchange complex. It has been found that the Gapon coefficient (K_G) can describe Na-Ca exchange isotherm with a fair degree of accuracy in 0-50 ESP range. Studies on illite, montmorillonite and soils indicate that the value of K_G remains fairly constant in the range, 0-50 ESP. Contrary to the increase in the values of selectivity coefficients with Na-saturation in Na-Ca or Na-Mg systems, their values decrease with the increase in K-saturation of the exchange complex in K-Ca or K-Mg systems. Indeed, the presence of K-specific exchange sites on aluminosilicate clay minerals in soils is the main reason for this opposing trend.

11.6. Clay-Membrane Electrode and Ionic Activity

A direct method for ionic activity measurement in suspension was developed by Marshall by way of using clay-membrane electrodes for determining the activities of Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+} ions with a saturated calomel electrode as a reference electrode. The clay membranes are reversible either to cations, in general, or to monovalent cations only. Because of lack of specificity, the measurement has been limited to homoionic systems and to systems containing monovalent and divalent cations. Marshall and his coworkers (1940) determined the ionic activity as a function of the degree of saturation (titration curves of H-clay, H-Ca and H-Mg clays), the degree of ionization of exchangeable ions, and the mean free bonding energy (ΔG_M). As per this approach, the bonding energy for a monovalent ion, in particular, a monovalent cation (e.g., M^+) is obtained from the formula (48):

$$\Delta G_M = RT \ln \frac{C_M}{a_M} \qquad \ldots(48)$$

where,

C_M = Concentration of total monovalent cation (sum of ionized and non-ionized portions), and

a_M = Measured activity of the given monovalent cation (MV).

Using the relationship introduced earlier [Eq. (9)], we have

$$a_M = f_M C_M \qquad \ldots(49)$$

where, f_M is the activity coefficient of the given MV (M^+), one obtains from Eq. (48),

$$\Delta G_M = RT \ln \frac{C_M}{f_M C_M} = - RT \ln f_M = RT \ln f_M^{-1} \qquad \ldots(50)$$

Marshall termed f_M as "fraction active" in that f_M (= a_M/C_M) is the fraction, accessible to the ionic activity measurement by the given clay membrane electrode, is capable of participating in the ion exchange equilibrium.

One may wish to examine Eqs (48) and (50) little more closely.

Thus, taking a clue from Marshall's idea that the exchangeable ions are only partly ionized, one would envisage the bonding process (and the reverse) of the MV (M^+) on an exchanger, S^- (e.g., soil colloid) as follows:

$$S^- + M^+ \xrightleftharpoons{\text{Bonding process}} \underset{(M^+ \text{ on the exchanger})}{S^- - M^+} \quad \ldots(51)$$

The reverse of the bonding process is given by expression (52):

$$S^- - M^+ (M^+ \text{ in bonded state}) \rightleftharpoons S^- + M^+ (M^+ \text{ in soil suspension}) \quad \ldots(52)$$

Therefore,

$$\Delta G_M \text{(bonding)} = RT \ln \frac{a_{M^+} \text{(bonded)}}{a_{M^+} \text{(free in soil suspension)}} \quad \ldots(53)$$

Assuming that the bonded MV (M^+ ion) is only partially ionized in the soil suspension, which is measured by the given clay membrane electrode (reversible to M^+ ions), one has

$$a_{M^+} \text{(free in soil suspension)} = a_M \text{(introduced earlier)}$$

and a_{M^+} (bonded) ≈ Total MV (M^+) concentration with the assumption that a_M is very small compared to total M^+ concentration = C_M

Hence, one has from Eq. (53),

$$\Delta G_M \text{(bonding)} = RT \ln \frac{C_M}{a_M} = -RT \ln f_M \quad \ldots(54)$$

Equations (50) and (54) are identical.

Indeed, it was shown qualitatively earlier (Section 10.2), that - log γ_i (where γ_i was the activity coefficient of a counter ion, 'i') provides a measure of the bonding energy of the given exchangeable ion ('i').

The same conclusion follows here [i.e. Eq. (54)] from an altogether different and a rigorous thermodynamic approach.

11.7. Krishnamoorthy-Davis-Overstreet Equation

Krishnamoorthy *et al.* (1948) introduced another approach, which is based on statistical thermodynamics. For mono-divalent exchange with $Z_A = 1$ and $Z_B = 2$, the general form of the Krishnamoorthy-Davis- Overstreet equation is given by Eq. (55):

$$K_{KDO} = \frac{a_B}{a_A^2} \frac{m_A^2}{m_B\left[\{m_A + 2 - (2/Y)\}m_B\right]} \quad \ldots(55)$$

where, m_A and m_B are the number of their moles in the adsorbed phase, respectively. Equation (55) can also be written as Eq. (56):

$$K_{KDO} = \frac{a_B}{a_A^2} \frac{M_A^2}{M_B \; \{M_A + 2 - (2/Y)\}M_B} \quad \ldots.(56)$$

where, M_A and M_B denote the mole fractions of cations A and B in the adsorbed phase, respectively.

12. Schofield's Ratio Law

This law states that if a negatively charged surface is in equilibrium with a solution containing certain activities (or concentrations) of monovalent, divalent and trivalent cations, the equilibrium will not be disturbed if the activities of the monovalent cations in the solution phase are altered by a certain factor, of the divalent cations by the square of that factor and of the trivalent cations by the cube of that factor. In other words, in a binary (two cations) system, the ratio of the cations held by a soil depends upon the ratio of the activities of the two cations in the equilibrium solution, in the case of homovalent cations (Na^+ and K^+ or Ca^{2+} and Mg^{2+}); the ratio of the activity of monovalent and square root of the activity of divalent cations, in the case of mono-divalent cations (Na^+ and Ca^{2+} or Na^+ and Mg^{2+}); and the ratio of the activity of monovalent and cube root of the activity of trivalent cations, in the case of mono-trivalent cations (Na^+ and Al^{3+}), and so on. The law thus requires that there is no exchange of cations between the adsorbed and solution phases of the soil so long as a_{Na}/a_K, $a_{Na}/(a_{Ca})^{½}$ and $a_{Na}/(a_{Al})^{1/3}$ do not alter with changes in the composition, dilution or concentration of the soil solution for Na^+-K^+, Na^+-Ca^{2+} and Na^+-Al^{3+} binary systems, respectively.

Indeed, for equilibrium in a binary exchange of cations between an adsorbed (e.g., soil colloidal or exchange) phase and a solution (e.g., soil solution) phase, such as one encounters in Eq. (43), namely,

$$K^+_{soil} + \tfrac{1}{2}\,Ca^{2+}_{soln.} \rightleftharpoons \tfrac{1}{2}\,Ca^{2+}_{soil} + K^+_{soln.} \quad \text{...(43a)}$$

One would have the corresponding selectivity coefficient [Eq. (44)]:

$$\frac{[Ca^{2+}_{soil}]^{1/2}\,(K^+_{soln.})}{[K^+_{soil}]\,(Ca^{2+}_{soln.})^{1/2}} = \text{Constant (say, K)} \quad \text{...(44a)}$$

where, [ ] denote the activity (or concentration) in the adsorbed phase, and ( ) indicate the activity (or concentration) in the soil solution phase. A rearrangement of Eq. (44a) leads to Eq. (44b):

$$\frac{[K^+_{soil}]}{[Ca^{2+}_{soil}]^{1/2}} = \frac{(K^+_{soln.})}{(Ca^{2+}_{soln.})^{1/2}} = K = \tfrac{1}{2}\ \text{(say)} \quad \text{...(44b)}$$

On irrigation, let us assume that the concentrations in the solution phase decrease 4-fold so that one obtains from Eq. (44b),

$$\frac{[K^+_{soil}]}{[Ca^{2+}_{soil}]^{1/2}} = \frac{(K^+_{soln.}/4)}{(Ca^{2+}_{soln.}/4)^{1/2}} = \tfrac{1}{2} \times \tfrac{1}{2} = \tfrac{1}{4} \quad \text{...(57)}$$

Because equilibrium demands that the value of K (= ½) remains constant, as long as the temperature does not change, it implies that to keep K (= ½), there will be re-distribution of ions and change of position of equilibrium between the adsorbed and the solution phases. Indeed, there will be release of K^+ ions from the adsorbed phase to the solution phase and fresh adsorption of Ca^{2+} ions present in the solution phase so that the value of K (= ½), as in Eq. (44b), is restored. In other words, when such equilibrium between the above-noted two phases is disturbed (e.g., on drying/fertilizer application/plant uptake/irrigation/rainfall, etc.), there will be always a shift of the monovalent cations (MV) from the concentrated to the diluted phase (e.g., K^+ ion moving in the above mentioned example from the adsorbed to the diluted solution phase), while the reverse would occur for the divalent cations (DV).

If, however, with the above-stated dilution of the solution phase on applying irrigation, appropriate steps had been taken to increase the K^+ concentration in the solution phase (e.g., by addition of MOP), in such a way that while Ca^{2+} ion concentration in the solution phase is diluted four times, that of K^+ ions is diluted only two times (i.e., √4 times), then Eq. (44b) would take the form of Eq. (58):

$$\frac{[K^+_{soil}]}{[Ca^{2+}_{soil}]^{1/2}} = \frac{(K^+_{soln.}/2)}{(Ca^{2+}_{soln.}/4)^{1/2}} = \frac{(K^+_{soln.})}{(Ca^{2+}_{soln.})^{1/2}} = \tfrac{1}{2}\ \text{(Constant)} \quad \text{...(58)}$$

That is, the constant of Eq. (44b) would have remained unaltered and the position of equilibrium between the exchange and the solution phases will not be disturbed as required by the Ratio Law.

Similar conclusions may be derived from the Donnan Membrane Equilibrium Theory, as applied to ion exchange processes occurring in soil. Indeed, Eq. (44b) is identical with Eq. (36) describing the Donnan membrane equilibrium between the exchange and the solution phases of the soil.

Thus, an important consequence of the Ratio Law is the applicability of the Donnan Membrane Equilibrium to the description of the distribution of ions between the exchange phase and the soil solution phase in equilibrium with each other. Thus, for a K^+-Ca^{2+} system, as stated earlier, one has the relationship (59):

$$\left(\frac{a_{K^+}}{\sqrt{a_{Ca^{2+}}}}\right)_{\text{Exchange or adsorbed phase}} = \left(\frac{a_{K^+}}{\sqrt{a_{Ca^{2+}}}}\right)_{\text{Soil solution phase}} \quad \text{...(59)}$$

While irrigating a soil with sodic/saline water (brackish water, for instance) having relatively high loading of Na^+ ion concentration, compared to the divalent Ca^{2+} and Mg^{2+} ions, the soil solution phase gets concentrated in respect of Na^+ ions, which, following the above-stated argument, tends to move to the relatively dilute phase (i.e., the exchange phase in this case), while the divalent cations move in the opposite direction. This tends to raise the ESP of the soil, and there is the possibility of dispersion of the exchange phase on continued use of such brackish water. This would cause a poor soil physical tilth.

To counter the above-noted alarming trend, pre-treatment of the irrigation source with gypsum (a standard package of practice) is often recommended. This would obviously ensure an increase of Ca^{2+} ion concentration in the irrigation water so as to prevent such rise of ESP of the exchange phase. That is, if the rise in Ca^{2+} ion concentration in the soil solution phase, upon such irrigation, is such that it is the square of the above-stated increase in Na^+ ion concentration, then according to the Ratio Law, there will be no shift in position of equilibrium between the exchange and the solution phases, and hence, the above-mentioned risk of sodification of the exchange phase is avoided.

13. Inverse Ratio Law

The Ratio Law considers the disturbance of the position of equilibrium between the exchange and the solution phases due to change in concentrations of the monovalent, divalent ions, etc., in the solution phase due to extraneous factors. However, such position may also be disturbed by the changes in concentrations (or activities) of the ions in the exchange phase. The consequences of the latter are dealt with by the Inverse Ratio Law (due to Matson).

Thus, given the possibility of occupying the exchangeable positions on the colloid (exchange) phase of a low or high charge density (i.e., with low or high CEC) clays in a mixture of colloidal dispersions, the monovalent cations are likely to be found in more number on the low charge density (i.e., "dilute" phase in respect of charge density) exchange phase of a colloid (e.g., clay), while the reverse will be true for the divalent cations. This ensues from the fact that the ionic fields of the monovalent cations are more compatible with the similar (but oppositely charged) ionic fields of the low CEC clays, while for the divalent cations, such compatibility is in respect of the ionic fields of high CEC clays. This bears similarity to what has been stated above in regard to consequences of the applicability of the Ratio Law or the Donnan membrane distribution in case of soil exchange phase - soil solution phase equilibrium.

Thus, when aqueous dispersions of kaolinite and montmorillonite clays are mixed and allowed to stand to reach a new equilibrium distribution of the corresponding exchangeable ions, the monovalent cations will be found in more numbers on the exchange phase of the kaolinite clay, while the divalent cations will populate mostly the exchange phase of the montmorillonite clay.

14. Plant Root Exchange in Soil

Plant roots behave as feeble ion exchangers in soil by virtue of possessing feeble net negative charge. Plant roots uptake cations from soil solution in exchange for secretion of equivalent quantity of H^+ ions (and as a result, the rhizosphere pH is generally lower than the bulk soil pH), while the anion uptake occurs in exchange for equivalent amounts of OH^- or HCO_3^- ions. However, because of imbalance in the cation/anion uptake by the plant, the corresponding root system develops a net negative charge, and hence an electrical double layer at the root-soil solution interfaces is formed.

Among the plants, the monocotyledons (e.g., cereals) have a lower root CEC than do the dicotyledons (e.g., legumes). Thus, the former root ion exchangers behave more like kaolinite clay, while the dicotyledons behave like montmorillonite clay. The monocotyledons, therefore, generally exhibit a preference for the monovalent cations over the divalent cations, while the reverse is true for the dicotyledons.

For instance, if rice and maize (cereals) are grown in the absence of extraneous potash application in a plot of land, marginal in potash supplying capacity, while berseem and rice are grown in an adjacent plot with suitable cultural and management practices (with no potash application), then it is more likely that both the crops of rice and maize would almost simultaneously show potash deficiency symptoms in the first plot, while there will be much delayed appearance of the deficiency symptoms in the crops of the second plot. This obviously follows from the preference of both rice and

Table 5. Cation exchange capacity (CEC), surface charge density (SCD) and specific surface area (SSA) of some clay minerals

Property	Kaolinite	Clay mineral fine mica	Smectite
Cation exchange capacity (CEC) [cmol(p$^+$) kg^{-1}]	3 - 15	15-40	80-120
Specific surface area (SSA) (m^2 g^{-1})	5 - 20	100-120	700-800
Surface charge density (SCD) (mol m^{-2})*	6.7 × 10^{-6}	1.65 × 10^{-6}	1.25 × 10^{-6}

* SCD = CEC/SSA

Table 6. Effect of organic carbon (O.C.) and surface charge density (SCD) on ΔG^0_r and K_G for Na-Ca exchange at 25 °C

Soil source	O.C. (%)	CEC [cmol(p$^+$)kg^{-1}]	SCD x 10^{-6} (mol m^{-2})	ΔG^0_r (kJ eq^{-1})	K_G (mol$^{-1/2}$ L$^{1/2}$)
1. India	0.19	11.2	1.01	0.25	0.460
2. India	0.85	11.7	1.41	0.97	0.300
3. U.K.	1.20	46.8	0.89	1.48	0.328
4. U.K.	2.30	20.8	1.72	3.19	0.260
5. U.K.	1.10	30.7	1.10	0.15	0.445
6. U.K.	5.20	30.0	2.28	5.00	0.260

Source: Poonia and Talibudeen (1977)

maize for potash uptake as compared to that of berseem, as explained above.

15. Factor Affecting Cation Exchange Capacity

The cation exchange equilibria in soils are affected by two types of factors: (i) soil factors, and (ii) solution factors.

15.1 Soil Factors

15.1.1. Effect of Clay Minerals

Some of the relevant properties of important clay minerals (Table 5) show that CEC and specific surface area (SSA) are in the order: smectite > fine mica > kaolinite. Nevertheless, the trend of the ratio of CEC to specific surface area (i.e. SCD) of these clay minerals is just the reverse. It is important to mention that as per the Diffuse Double Layer (DDL) equation, the main emphasis should be given to SCD rather than to CEC of clay minerals while describing the mono-divalent cation exchange equilibria data.

15.1.2. Effect of Organic Matter

Organic matter in a soil affects the cation selectivity in two opposing directions. Closely spaced carboxyl and phenolic groups present in organic compounds cause an increase in SCD of soil and thus selectivity towards multivalent cations. Contrary to this, an increase in organic matter in the soil results in the increase of internal : external surface area / exchange sites. This increases the preference of the exchanger for those monovalent cations like K^+ and NH_4^+, which are mainly influenced by the geometry of adsorption sites (Poonia and Niederbudde, 1990). The overall effect of organic matter on cation specificity is thus a result of these opposing phenomena (Table 6).

15.1.3. Surface Charge Density

The diffuse double layer (DDL) equation predicts that the higher the SCD of soil, the smaller would be the fractional saturation of the soil-exchange complex by the monovalent cation in a mono-divalent cation system. The SCD of soil, however, fails to predict the exchange behaviour of soils when the monovalent cations involved in the exchange process are strongly affected by the geometry of exchange sites. It is assumed in the DDL equation that charge density on soil surfaces is uniform. This assumption, however, does not hold true in most soils consisting of several types of

Table 7. Effect of total electrolyte concentration (TEC) on ΔG_r° and K_G for Na-Ca exchange

Soil	CEC [cmol(p^+) kg^{-1}]	SCD x 10^{-6} (mol m^{-2})	TEC (milliequi L^{-1})			
			25	50	75	100
			ΔG^0_r (kJ eq^{-1})			
1.	5.5	1.39	1.91	2.51	2.35	3.24
2.	17.0	4.91	3.88	4.64	5.94	7.70
			K_G($mol^{-1/2}$ $L^{1/2}$)			
1.	5.5	1.39	0.48	0.44	0.33	0.24
2.	17.0	4.91	0.66	0.54	0.52	0.50

Source: Poonia *et al.* (1984)

Table 8. Effect of Ca : Mg ratio on ΔG^0_r and K_G for Na-(Ca + Mg) system

Soil	CEC [cmol(p^+)kg^{-1}]	Organic carbon (%)	Ca : Mg ratio	ΔG^0_r (kJ eq^{-1})	K_G ($mol^{-1/2}$ $L^{1/2}$)
1.	13.32	1.37	3:1	0.69	0.512
			1:3	0.60	0.528
2.	20.27	0.60	3:1	1.07	0.477
			1:3	0.87	0.498
3.	11.19	0.27	3:1	1.97	0.387
			1:3	0.96	0.447

Source: Poonia *et al.* (1980)

clay minerals, organic matter and oxides. To describe the experimental data on mono-divalent cation exchange equilibria, the SCD thus needs to be multiplied by an empirical factor assuming no interaction between the adjacent clay platelets or by invoking interaction between the clay platelets without using an empirical factor.

15.2. Solution Factors

15.2.1. Effect of Total Electrolyte Concentration

The relative preference of soil for a divalent cation increases with the increase in total electrolyte concentration (TEC) of the equilibrium solution (Poonia *et al.*, 1984). The results shown in Table 7 indicate an increase in the relative preference for divalent cation over monovalent cation with the increase in TEC of the equilibrium solution.

15.2.2. Effect of Type of Cations

Cations of the same valency but of different hydrated size may have considerable difference in their specificity for exchange sites. To illustrate this, some results on Na-(Ca and Mg) exchange equilibria for soils having different physicochemical properties, are given in Table 8 (Poonia and Pal, 1979; Poonia *et al.*, 1980). The relatively larger values of ΔG_r and smaller values of K_G in Ca-dominated as compared to Mg-dominated system show higher preference of the soils for Ca over Mg.

15.2.3. Effect of Type of Anions

The cation exchange equations do not take into account the nature of anions. The formation of more extensive and stronger undissociated ion-pairs by divalent anions with divalent cations (e.g., $CaSO_4^0$ and $MgSO_4^0$) as compared to monovalent (e.g., $NaSO_4^-$) cations influence mono-divalent cation exchange equilibria in soils (Babcock and Schulz, 1963; Rao *et al.*, 1968). To illustrate this, some pertinent experimental results on the role of chloride and sulphate ions in water on Na-saturation of some soils are given in Table 9 (Mehta *et al.*, 1983).

16. Negative Adsorption

The interaction between anions and clay minerals, in principle, comprises two different

Table 9. Effect of anionic composition on ΔG^0_r and K_G for Na-Ca and Na-Mg systems

Soil No.	Na-Ca			Na-Mg		
	Cl	SO_4	SO_4^*	Cl	SO_4	SO_4^*
			ΔG^0_r (kJ eq^{-1})			
1.	3.87	2.57	3.52	3.62	2.04	3.57
2.	1.91	1.07	1.92	1.81	0.36	1.48
3.	2.91	1.83	2.87	1.90	0.73	1.73
			K_G ($mol^{-1/2}$ $L^{1/2}$)			
1.	0.49	0.61	0.50	0.54	0.67	0.55
2.	0.66	0.79	0.58	0.67	0.79	0.62
3.	0.54	0.62	0.54	0.62	0.78	0.62

*After considering ion pairs of $CaSO_4^0$, $MgSO_4^0$ and $NaSO_4^-$

Source: Mehta *et al.* (1983)

phenomena, viz. the bonding of the anions by positive charges presumably located on the broken edges of the clay, and the repulsion between the anions and the negative charges mainly on the planar surfaces of the clay particles. Both the electrostatic attraction between the anions and positively charged sites, and the chemical bonding may contribute to adsorption of anions. The repulsion of anions by the negatively charged sites leads to a local deficit of anions near a clay particle in comparison with the equilibrium solution. This deficit has been termed as 'negative adsorption'. As almost all the soils found in nature possess net negative charge, negative adsorption or 'anion exclusion' is exhibited to a certain extent by all soils.

17. Volume of Exclusion and Estimation of Specific Surface Area of Soil

The product of the equivalent distance of exclusion and the specific surface area of colloids yields equivalent volume of exclusion. The volume of exclusion is the volume that appears to be completely free of anions. For a soil of a given specific surface area, the volume of exclusion increases with the decrease of total electrolyte concentration, and conversely for a given electrolyte concentration, the higher the specific surface area of soil, the higher would be the volume of exclusion. The experimental estimation of volume of exclusion in combination with the calculated value of the equivalent distance of exclusion yields the specific surface area of colloids or soils. The determination of anion exclusion is an important method for the estimation of the specific surface area of soil.

When the volume of exclusion is multiplied by the equilibrium concentration of the anion (milliequi mL^{-1}), one gets the amount of anion excluded per unit mass of soil. The fraction of the liquid layer that is free of anions or salts increases with the decrease of moisture content in soil. When the equivalent distance of exclusion (δdl, cm) is a non-negligible fraction of the liquid layer (dl, cm), the following practical aspects are involved:

(1) Anions move faster than the mean flow velocity in soils. When a salt solution flows through soil pores, two phenomena, viz. anion exclusion near the walls (soil colloid surfaces) of the pores and the increase in velocity of liquid with the increase in distance from the colloid surface take pace. Both these phenomena result in faster movement of anions through soil than the mean interstitial flow velocity of the liquid calculated as the Darcy velocity divided by the water-filled porosity.

(2) Because of anion exclusion, i.e., repulsion of anions from the vicinity of the negatively charged surface, the concentration of anions in the easily extractable soil solution becomes higher than that in soil solution obtained by means of high-pressure filtration.

18. Anion Exchange

As has been discussed above, positively charged sites exist on the edges of layer-lattice silicate minerals (1:1 type in particular) and surfaces of oxides (with low specific surface area), mainly under acidic conditions. The total amount of anions held exchangeably by a unit mass of soil, termed as its anion exchange capacity (AEC), is therefore much less than the cation exchange capacity (CEC) of the soil. Further, contrary to cation exchange, the capacity of soil to adsorb anions increases as pH decreases or acidity increases, which increases the pH-dependent positive charge of soil colloids. In addition to pH, the adsorption of anions depends on the concentration of anions. Higher is the concentration of an anion, the greater is its adsorption. As the ratio of cation exchange capacity to anion exchange capacity of layer-lattice silicate mineral increases, the adsorption of anions decreases. Soils containing montmorillonite (CEC mainly due to isomorphous substitution) generally exhibit low AEC than those dominant in kaolinite and hydrous oxides of Al and Fe. Similarly, acid soils in the tropical and sub-tropical regions containing hydrous oxides of Al and Fe exhibit much higher AEC than alkaline and calcareous young soils of arid and semi-arid regions. Because humic colloids always carry negative charge, they can compete with other anions for the adsorption sites. Also, the selectivity of the positive sites with respect to different anions, as a rule, is much larger than that of the negative sites for cations. On the basis of experimental data, the preference of different anions for the positive sites has been found to follow the order:

$$SiO_4^{4-} > PO_4^{3-} >> SO_4^{2-} > NO_3^- = Cl^-$$

Consequently, SO_4^{2-}, NO_3^- and Cl^- ions are not adsorbed even if PO_4^{3-} ions are present at very low concentration in comparison to concentrations of other anions. At low pH values (< 6) and in the absence of PO_4^{3-} from a system, adsorption of SO_4^{2-} and Cl^- may also occur.

So far the adsorption of anions on layer-lattice silicates and oxides has been considered as being due to electrostatic force only. But some anions are bound in natural soils by mechanisms other than electrostatic. These mechanisms pertain to isomorphous displacement or substitution of hydroxyl ions from the lattice of clay minerals or hydrous oxides and the formation of chemical bonds with edge Al-groups of layer silicates. Fluoride ion (F^-), for example, has the same size as OH^- ion and may therefore substitute OH^- ion in an isomorphous manner, as shown below:

$$R\text{-}OH + F^- = R\text{-}F + OH^-$$

There is also evidence that the phosphate ion, despite having a different size from that of OH^- ion, is also bound as a structural non-diffusible unit by displacement of lattice OH, as the so-called 'ligand-exchanged' anion (see later).

The relatively strong preference for phosphate ions by clay minerals and hydrous oxides as compared to other anions of lower valency indicates the existence of chemical bonds between the solid phase and phosphate. This is supported by the fact that at high concentration of phosphate ions, the edges of the solids become negatively charged. This, evidently, would not occur if the binding mechanism between phosphate ions and layer-lattice silicate minerals or oxides was electrostatic in nature. The presence of chemical bonds between phosphate ions and edge Al groups of layer-lattice silicates is also supported by the low solubility of aluminium phosphates. More about ligand exchange will follow in the next section.

During decomposition, soil organic matter liberates organic compounds, which acquire negative charges due to the dissociation of protons from the carboxylic acids and phenolic hydroxyl groups. These negatively charged compounds displace phosphate ions from the adsorption sites and thus increase phosphate ions in soil solution. This phenomenon generally enhances phosphate availability to plants, even though organic matter in acid soils, rich in sesquioxides and amorphous Fe and Al oxides, sometimes reduces the plant availability of phosphate in soil. The humic colloids also chelate Al, Fe, Mn ions into soluble chelates which are thereby deactivated in immobilizing the phosphate ions in the soil solution.

19. Ligand Exchange

Let us first introduce as to what one understands by a ligand. A ligand, which may be an anion or a neutral molecule, satisfies the secondary valency or coordination number (Table 1) of a central cation in a crystal lattice. If it is an anion, then it simultaneously satisfies the primary valency as well. Thus, Fe^{3+} ion has got a primary valency of +3 and a secondary valency of 6 (Table 1). In $FeCl_3$, three Cl^- ions satisfy the primary valency (+3), while in $[Fe^{III}(CN)_6]^{3-}$, six CN^- ions satisfy the primary valency (+3) and the secondary valency (6) of Fe^{3+} ion. However, in $[Fe(H_2O)_6]^{3+}$ ion, six water molecules (neutral species) satisfy the secondary valency (6) of Fe^{3+} cation, while the primary valency (+3) remains yet to be satisfied. In the complex ion, $[Fe^{III}(H_2O)_4(OH)_2]^+$, two OH^- ions simultaneously (and partly) satisfy both the primary valency and the secondary valency of Fe^{3+} ion, while the four neutral water molecules satisfy the remaining (4 of 6) secondary valency of Fe^{3+} cation. In this case, OH^- ions and water molecules are both ligand to Fe^{3+} cation, and are liable to undergo exchange with the extraneous anions which would form covalent bonds with Fe^{III} ion.

The conjugate base of strong mineral acids (e.g., HCl, HNO_3, HBr, $HClO_4$, etc.), namely the monovalent anions derived from these acids, e.g., Cl^-, NO_3^-, Br^-, ClO_4^-, etc., undergo anion exchange and are held at the positively charged soil colloidal sites by virtue of electrostatic forces. Such retention of anions is also referred to as the non-specific anion retention. This may possibly be described as the physical adsorption in that no chemical bond is formed between the soil solid surface and the anions in the same sense that the exchangeable cations (e.g., in the diffuse double layer) swarm around a mica-type surface which has been discussed earlier (Section 4.4).

Several other anions, including the organic anions, are generally specifically adsorbed to the surface of clays or clay-sized primary minerals. These anions may be derived from both strong and weak acids, and are of mono- and polyvalent type. In this case, the anions, held at the specific sites, form a chemical bond with the surface group. This phenomenon is also known as ligand exchange in that the extraneous anion, acting as a ligand to the centrally located cation (in the clay lattice), substitutes an existing surface ligand (e.g., an OH^- ion or a H_2O molecule).

While anion exchange takes place only at the positively charged colloid surface, e.g., for a variable-charge surface, namely hydrous oxides of Fe^{III}, such as goethite [α - $Fe^{III}OOH$], at a pH below the corresponding ZPC (pH 8.5, vide. Section 4.2), such oxides, having only the pH-dependent charge, undergo ligand exchange at pH values below, above and even at the ZPC pH of the given variable-charge colloid surface. The same would be true for other types of soil colloid surfaces of variable-charge as well.

The ligand exchange is distinct from the simple anion exchange in that the phosphate, for example, in acid soil readily gets immobilized and removed from the soil solution, following a generous application of soluble phosphatic fertilizer, even in the presence of a strong (say 1*M*) solution of NaCl. This tends to suggest that phosphate and chloride anions compete for different types of adsorption sites. The former is chemisorbed in soil, while the latter undergoes electrostatic (physical) retention.

19.1. Adsorption Envelope

Recalling the Langmuir adsorption isotherm (Eq. 16), one obtains

$$\frac{C}{x} = \frac{C}{x_m} + \frac{1}{x_m K} = \frac{KC + 1}{x_m K} \qquad \ldots(60)$$

or,

$$\frac{x}{x_m} = \frac{KC}{1 + KC} \qquad \ldots(61)$$

where,

K = Langmuir constant related to bonding energy,

x_m = Adsorption maximum,

C = Equilibrium concentration in soil solution, and

x = Amount adsorbed per unit mass of the adsorbent.

On studying the adsorption in 0.1*M* NaCl solution of a series of anions such as phosphate, fluoride, silicate, etc., on goethite at pH range from 2.5 to 12.5 and a given temperature, followed by plotting of the corresponding x_m against the pH of the study for each adsorbate, the adsorption envelopes obtained are depicted in Figure 17.

The adsorption maximum (x_m) value for F^- is the highest at pH ~ 3.0, and for silicate at pH ~9.6 (a broad maximum), while for phosphate, two inflexion points are obtained, at pH ~6.7 and pH ~11.3 where the phosphate curve changes its slope.

Incidentally, the pK_a of HF is 3.2 (at 25 °C), that of silicic acid is 9.7, while the pK_2 and pK_3 of phosphoric acid are very close to (and little higher than) 6.7 and 11.3, respec-

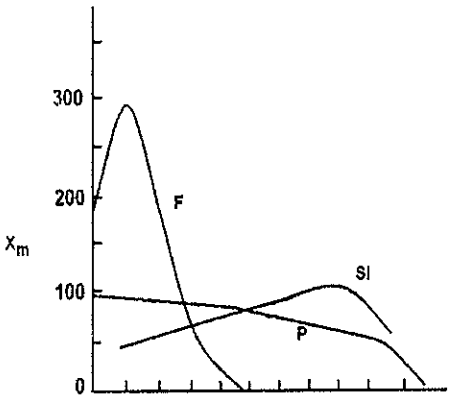


Figure 17. Adsorption envelope of specifically adsorbed anions
Source: Mott (1981)

tively. Presumably, if the experiment could have been continued below pH 2.0 (where goethite starts dissolving and losing its form), the phosphate curve would show a decreasing trend at a pH close to its pK_1, namely 2.1.

One would recall from the Henderson equation, giving the pH of a buffer mixture of a weak acid and its salt, namely Eq. (62):

$$pH = pK_a + \log (C_{salt} / C_{acid}) \quad \ldots(62)$$

Thus, at a pH ≈ pKa,

$$C_{salt} = C_{acid}$$

$$\text{i.e., } C_{anion} = C_{acid} \quad \ldots(63)$$

Keeping in view the nature of the adsorption envelopes presented in Figure 17, this tends to suggest that to cause maximum ligand exchange retention on goethite surface, not only the given anion, but the corresponding undissociated acid molecule also has an equally important role to play.

Let us take a look at the possible pathway of such ligand exchange reaction on goethite surface (which can be extended to cover other soil colloidal surfaces as well):

At a pH below the ZPC of goethite (pH < 8.5):

$$[\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{OH}_2]^{x+} + \text{O.PO.(OH)}_2^- \longrightarrow [\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{O.PO.(OH)}_2]^{-(1-x)} + \text{H}_2\text{O} \quad \ldots(64)$$

At the ZPC (pH = 8.5):

$$[\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{OH}_2]^{x_0} + \text{O.PO.(OH)}_2^- \longrightarrow [\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{O.PO.(OH)}_2]^{-(1-x_0)} + \text{H}_2\text{O} \quad \ldots(65)$$

At a pH above the ZPC (pH > 8.5):

$$[\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{OH}]^{-(1-x)} + \underset{\text{Undissociated acid}}{\text{HO.PO.(OH)}_2} \longrightarrow$$
$$[\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{OH}]^{-(1-x)} \ldots\text{H} \ldots\text{.} [\text{O.PO. (OH)}_2] \rightleftharpoons$$
$$[\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\underset{\text{H}}{\ddot{\text{O}}}\text{H}]^{x+} + \text{O.PO.(OH)}_2^- \longrightarrow$$
$$[\text{Oxide}-\underset{(\text{Fe}^{\text{III}})}{\text{M}}-\text{O.PO. (OH)}_2]^{-(1-x)} + \text{H}_2\text{O} \quad \ldots(66)$$

Thus, at a pH > ZPC, the undissociated phosphoric acid molecule plays a key role in supplying the proton from one of its dissociable (OH) groups to protonate the OH^- ligand of Fe^{III} in goethite, thereby converting it to a neutral (H_2O) ligand which is then replaced by the negatively charged $H_2PO_4^-$ ion, causing ligand exchange.

It is also apparent that at pH equal to or less than the ZPC, the net negative charge of the soil colloid would increase as a result of ligand exchange, involving, say, phosphate. This will raise the CEC of the soil. Indeed, in the volcanic ash soils of the East Indies, for instance, allophanic clay minerals, being amorphous with high specific surface charge density, have very high phosphate fixation capacity. To these soils, often a massive dose of phosphatic fertilizer (e.g., 1000 kg P_2O_5/ha) is added to satisfy the phosphate hunger of the soil, and in the subsequent crop seasons, moderate dose of such fertilizer is added, which is supplemented by a slow release of small amounts of phosphate from the (earlier) immobilized phosphate in soil. Furthermore, such massive application of phosphatic fertilizer causes a rise in the CEC of the soil due to ligand exchange process as explained above. In such instances, phosphate plays the role of not only a fertilizer, but also that of a soil amendment.

20. Quantity-Intensity Relations

Recalling the Gapon equilibrium [Eq. (39)],

$$\left[\text{Soil}\right]^{-}\begin{matrix}\text{Ca}^{2+}/_2\\ \text{Mg}^{2+}/_2\end{matrix} + \text{K}^{+}_{\text{soln.}} \rightleftharpoons \left[\text{Soil}\right]^{-}\text{K}^{+} + \tfrac{1}{2}(\text{Ca}^{2+}+\text{Mg}^{2+})_{\text{soln.}} \quad \ldots(39)$$

One has the corresponding selectivity coefficient, or the Gapon exchange constant, K_G (or K_m), given [vide Eqs (39) and (44)] as Eq. (67):

$$K_G \text{ (or } K_m) = \frac{[K^{+}_{\text{soil}}]\,(Ca^{2+}+Mg^{2+})^{1/2}_{\text{soln.}}}{[CEC - K^{+}_{\text{soil}}]\,(K^{+}_{\text{soln.}})} \quad \ldots(67)$$

where, square brackets [ ], denote the activity (or concentration) of the exchangeable ions concerned on the adsorbed phase and circular brackets ( ), denote the activity in the soil solution phase at equilibrium.

Rewriting Eq. (67), one obtains

$$K_G = \frac{[\text{Exch. } K^{+}]\,(Ca^{2+}+Mg^{2+})^{1/2}_{\text{soln.}}}{[\text{Exch. } Ca^{2+}+Mg^{2+}]\,(K^{+}_{\text{soln.}})} \quad \ldots(68)$$

Or,

$$[\text{Exch. } K^{+}] = K_G . [\text{Exch. } Ca^{2+}+Mg^{2+}] . AR^{K} \quad \ldots(69)$$

where, AR^K is the ionic activity ratio in the equilibrium soil solution, and is given by Eq. (70) in the equilibrium soil solution.

$$AR^{K} = \frac{a_{K^{+}}}{\sqrt{a_{Ca^{2+}+Mg^{2+}}}} \quad \ldots(70)$$

Assuming that the change in activity of the exchangeable $[Ca^{2+} + Mg^{2+}]$ in the exchange phase is small due to such ion exchange process, the ionic activity (or concentration) of these ions on the exchange phase may be assumed to remain virtually constant during the process so that it follows from Eq. (69):

$$[\text{Exch. } K^{+}] \approx \text{Constant} \times AR^{K} \quad \ldots(71)$$

Hence,

$$\Delta\,[\text{Exch. } K^{+}] = \text{Constant}\;\Delta\,AR^{K} \quad \ldots(72)$$

so that a plot of Δ [Exch. K^+] or ΔExch. K^+ against the corresponding AR^K at equilibrium for various initial ratios of K^+ to $(Ca^{2+} + Mg^{2+})$ ionic activities in the equilibrating solutions should yield a straight line, passing through the origin. In actual practice, however, deviation is noted from the expected linearity, as demonstrated in the plot in Figure 18.

Such deviation from linearity is generally exhibited by a soil at the lower ranges of the AR^K values. This arises from the release of K^+ ions from the non-exchangeable pool of K^+ ions in the soil when the solution level (and hence the exchangeable K level) is low, causing thereby a small value of AR^K in the soil solution. Such release, in turn, leads to a new position of equilibrium between the exchange and the soil solution phases.

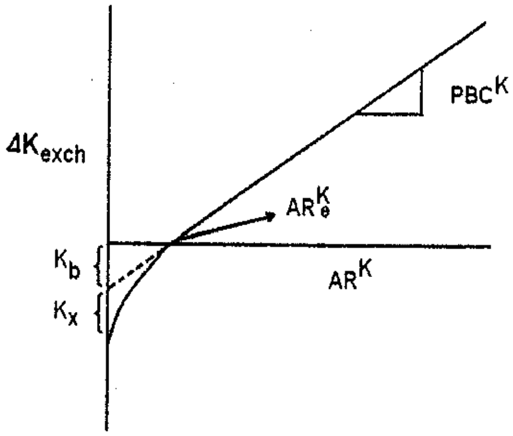


Figure 18. Quantity-Intensity plot of soil potassium

Because the Gapon equation [Eqs (39) and (41)] considers the equilibrium distribution of cations only between the exchange and the soil solution phases, the intervention by the non-exchangeable pool of K^+ ions, thereby disturbing the above noted equilibrium, would cause deviation from the linearity (as observed), demanded by the validity of the Gapon equation.

The plot in Figure 18 is referred to as the Quantity-Intensity (Q/I) relationship (Beckett, 1964), and brings out the changes in the quantity of, for instance, adsorbed potassium, in relation to the corresponding value of the activity ratio, $AR^{K}\left(= a_{K^{+}}/\sqrt{a_{Ca^{2+}+Mg^{2+}}}\right)$ in the equilibrium soil solution.

The Q/I curves may be obtained by equilibrating a number of soil sub-samples with a series of solutions containing increasing amounts of K in $CaCl_2$ solution of fixed concentration (say 0.01 mol L^{-1}). For each suspension, the difference between the potassium concentrations in the initial and equilibrated solution gives the amount by which the soil gains or loses potassium (ΔK) in reaching the equilibrium. The activity ratios, AR^K, are calculated from the cationic composition of the resultant equilibrium solution.

Several (Q/I) parameters are defined from Figure 18. These include the equilibrium activity ratio (AR^K_e) which refers to that value of the activity ratio in the equilibrium soil solution where the exchange phase neither gains nor releases exchangeable K^+ ions from or to the soil solution phase in contact. This value (AR_e^K) provides a measure of the inherent equilibrium soil solution activity ratio of the soil, and hence the inherent K^+ availability (to plants) compared to Ca^{2+} and Mg^{2+} availability.

The parameter, K_x, is related to the number of sites (on the adsorbed phase in soil) contributing towards specifically held K^+ ions. It was estimated from the difference between the intercept made by the interpolated linear portion of the (Q/I) plot and the intercept actually made by the (Q/I) plot on the Y-axis of the curve. Such K_x value is generally much higher for the illitic soil (with interlayer K^+ reserve as the non-exchangeable K pool of soil) as compared to the kaolinitic or the montmorillonitic soils.

The parameter K_b is defined as a measure of the labile K that the soil holds. The linear potential buffering capacity for soil K (PBC^K) is obtained from the slope of the linear portion of the (Q/I) plot (Figure 18). This refers to the inherent buffer capacity of a soil to maintain a given value of AR^K, i.e. the greater is its value [i.e. the steeper is the (Q/I) plot], the more will be the ability/tendency of the given soil to release K^+ from the exchange phase to the soil solution when K^+ is lost (through plant uptake and/or leaching), and *vice-versa* for K^+ gain by the soil solution (e.g., on fertilizer application and/or irrigation). All these (Q/I) parameters are therefore related to the chemistry and the fertility relationships of soil potassium.

21. Methodologies to Study Ion Exchange Equilibria

21.1.1. Flowchart Representation

The flowchart representation giving the procedural framework for cation exchange studies in binary cation systems is given in Figure 19. For non-equilibrium, time-dependent slow type of reactions, the Kinetic approach is a viable option for evaluation of thermodynamic parameters of cation exchange in soils with well-defined experimental methodology and theoretical considerations.

21.1.2. Equilibrium Procedure

The determination of cations on the exchange complex is generally carried out by two methods, viz. stripping technique and isotopic dilution technique.

Stripping Technique —In this technique, two approaches are adopted: (a) the soil in equilibrium with the solution is washed free of soluble salts with alcohol and then it is extracted in a salt solution (≈1*N*) (free from the cations on the exchanger); or (b) the soil with the equilibrium solution is centrifuged, the supernatant liquid is collected for analysis and the equilibrium solution left in the soil is measured. The total cations extracted in the salt solution minus the cations in the left-over equilibrium solution are designated as the exchangeable cations.

Isotopic Dilution Technique — A given amount of soil (say 1 g) with a known volume of untagged equilibrium solution (say 5 mL) is mixed with an equal volume of tagged solution of the same composition. The contents are fully dispersed and equilibrated for 48 h on a shaker. The equilibrated soil suspension is centrifuged and the radioactivity is measured in the supernatant liquid, using a suitable radiation-measuring device. The amount of adsorbed cation (A_X) is calculated using Eq. (73):

$$A_X = \left(\frac{CPM_{control}}{CPM_{test}} - 1\right)[A] \qquad ...(73)$$

where,

CPM = Counts per minute, and

[A] = Total amount of species x in solution.

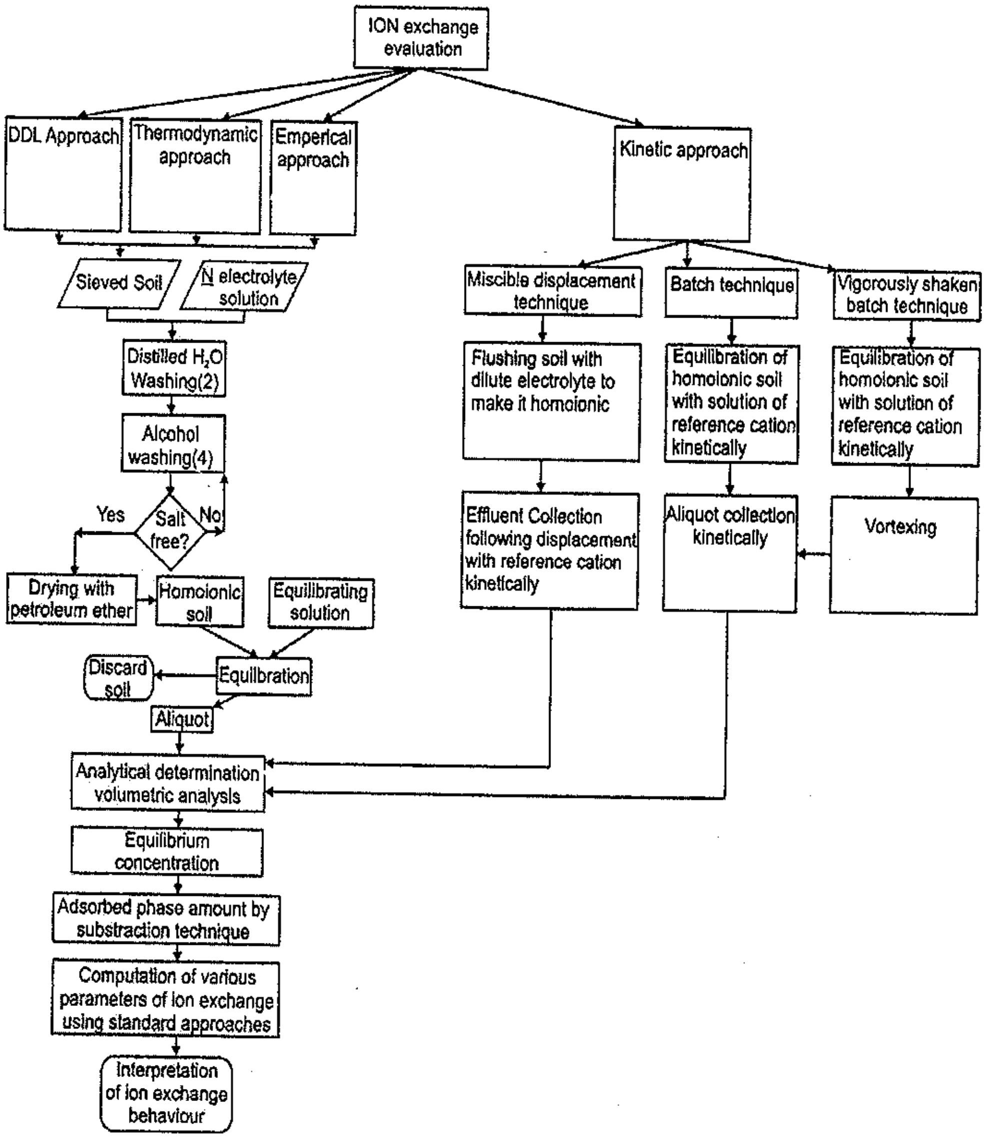


Figure 19. Flowchart representation of cation exchange equilibria studies in binary system

N.B.: Figures within the parentheses are number of washings usually needed

Source: Baruah and Patgiri (1996)

2.1.3. Kinetics of Ion Exchange

Notwithstanding the thermodynamic principles used to characterize exchange equilibria on clay and on soil surfaces, the use of a chemical kinetic approach to determine thermodynamic parameters has received increasing attention recently. It is particularly true for potassium exchange in clays and in soils. Although most studies on the kinetics of cation exchange in soils have been concerned with potassium release, the general principles for cation release are similar.

Techniques of common use for the study of kinetic reaction in clays and soils include Batch, Vigorously shaken batch and Miscible displacement or flow techniques.

For the kinetic model, the reaction written in exact stoichiometric expression is given by Eq. (74):

$$\text{Soil}^{-1}\text{Ca}^{2+}_{½} + \text{K}^{+}_{\text{sol}^{n}} \rightleftharpoons \text{Soil}^{-1}\,\text{K}^{+} + ½\,\text{Ca}^{2+}_{\text{sol}^{n}} \quad ...(74)$$

Equilibrium reactions between solution and adsorbed phases of soil profoundly influence K chemistry. The rate and direction of these reactions determine whether applied K will be leached into lower soil horizons or absorbed by plants or converted into unavailable forms, or else released into available forms. Knowledge about rates of reaction between solution and adsorbed phases of soil K is essential in order to predict the fate of the added K fertilizer in soils and make appropriate K fertilizer recommendations.

Miscible Displacement Technique

Miscible displacement technique refers to the mixing of soil solution initially present in both macro (non-capillary) and micro (capillary) pores in mobile and immobile regions with the invading solution, and consequently the displacement of the original solution from the system on the basis of equivalent pore volume. The miscible displacement technique simulates solute movement in soils under field conditions.

Prior to kinetic measurements on adsorption and desorption processes, soil samples should be passed through a 60-mesh stainless steel sieve and saturated with Ca using 1 *N* $CaCl_2$. Excess electrolyte should be removed with distilled water and with a 1:1 acetone-to-water mixture, until a negative test for Cl^- is obtained using $AgNO_3$.

For kinetics of K adsorption, 1 g of Ca-saturated soil is used and mixed with 50 mL of deionized water. The suspension is transferred into a 47-mm nucleopore filter column which is attached to a fraction collector on the terminal side and to a peristalatic pump on the delivery side. The pump is ideally required to deliver the K solution through the soil at a uniform flow rate of 1.0 mL per min. The aliquots are collected, preferably at 10-minute intervals until the concentration of the leachate equals that of the initial K concentration.

For kinetics of K desorption, the tubes, connected to the column, are rinsed thoroughly with distilled water and then the K desorption is initiated using 0.01*M* $CaCl_2$. This solution is passed through the soil until no K appears in the leachate. The quantity of K in solution for both the adsorption and desorption studies is measured. The kinetic experiments should also be carried out ideally at 25±1°C. The apparent adsorption and desorption rate constants are determined using the first-order kinetics as elucidated below.

Batch Technique

The miscible displacement technique suffers from the fact that the diffusion-controlled ion exchange is prominent, due to the prevalence of steady-state condition during the course of fluid dynamics and ion interaction. Thus, ion exchange may be over-estimated under such situations. Batch technique is an alternative to overcome this problem.

Similar to the miscible displacement technique, the soil samples are saturated with Ca using 1 *N* $CaCl_2$ solution; the excess salts are washed out with distilled water first and then with 1:1 acetone-to-water mixture, as long as chloride is present.

The 1-g samples of Ca-saturated soils are equilibrated with 50 mL of 50 µg K/mL of solution in centrifuge tubes at 25±1 °C on a reciprocating shaker. After sampling at 10-minute intervals, the suspension from each tube is centrifuged for 3 minutes at 2,000 rpm; then the supernatant solution is analyzed for K flame-photometrically. From the solution phase measurements of K as a function of time, the adsorption and desorption rate constants are worked out using the equations outlined below.

Vigorously Shaken Batch Technique

This technique is similar to the batch technique except that vortexing is done instead of shaking to achieve a better equilibration, especially in case of slow reactions, and to achieve quicker results. The theoretical consideration and experimental procedure are similar to the batch technique already described.

22. Theoretical Approach for Kinetic Studies

Referring to the $K^+ - Ca^{2+}$ exchange reaction in soil [(Eq. (74)], let us deal with the kinetic frame-work for the first-order K release and fixation reactions in soil (Sanyal and Majumdar, 2001). For K release, this equation assumes that the K concentration at the exchange sites of the soil colloid is the determining factor for the release rate of K into soil solution. In the batch technique, the rate is given by Eq. (75):

$$dK_t/dt = k_d (K_0 - K_t) \qquad ...(75)$$

where, K_t is the amount of K^+ ion released in time t, K_0, the amount of K^+ ion that could be released at equilibrium, while k_d is the desorption rate coefficient.

For a miscible displacement or flow technique, the rate is given by Eq. (76):

$$d(K_t/K_0)/dt = -k_d K_t/K_0 \quad \text{...(76)}$$

where, K_t and K_0 denote, respectively, the amount of K^+ ion on the exchange sites of the soil colloid at time t and time zero of desorption.

On suitably integrating Eqs (75) and (76) and utilizing the initial and boundary conditions, one arrives at the following integrated forms, namely

For batch equation:

$$\ln(K_0 - K_t) = \ln K_0 - k_d t \quad \text{...(77)}$$

or,

$$\log(K_0 - K_t) = \log K_0 - (k_d/2.303).t \quad \text{...(78)}$$

For miscible displacement or flow technique:

$$\ln(K_t/K_0) = -k_d t. \quad \text{...(79)}$$

or,

$$\log(K_t/K_0) = -(k_d/2.303).t \quad \text{...(80)}$$

A plot of log $(K_0 - K_t)$ against t leads to a linear plot from the slope of which the specific release reaction rate (k_d) is obtained in a batch technique. For flow technique, a plot of log (K_t/K_0) against t is used.

The first-order kinetics for K-fixation by soil/clays may also be described, e.g., for batch technique, we have:

$$d(K_0 - K_t)/dt = k_a K_t \quad \text{...(81)}$$

where, K_t and K_0 are the concentrations of K in solution at time t and time zero, while k_a is the adsorption rate coefficient.

For miscible displacement or flow technique, one has

$$d(K_t/K_\infty)/dt = k_a(K_\infty - K_t)/K_\infty = k_a(1 - K_t/K_\infty) \quad \text{...(82)}$$

where, K_t and K_∞ are the amounts of K at the exchange sites of the colloid at time t and at equilibrium.

The integrated forms are:

$$\ln K_t = \ln K_0 - k_a t \quad \text{...(83)}$$

or,

$$\log K_t = \log K_0 - (k_a/2.303).t \quad \text{...(84)}$$

For miscible displacement or flow technique:

$$\ln(1 - K_t/K_\infty) = -k_a t \quad \text{...(85)}$$

or,

$$\log(1 - K_t/K_\infty) = -(k_a/2.303).t \quad \text{...(86)}$$

Thus, a plot of log K_t against t leads to k_a from the slope of the resulting linear graph in a batch technique. The adsorption rate coefficient (k_a), in miscible displacement technique, is obtained from the slope of the linear plot of log $(1 - K_t/K_\infty)$ vs. time.

The first-order kinetics have been used by a number of workers to describe the exchange-kinetics and K-release from clay minerals, as well as surface and subsurface horizons of a number of soils (reviewed by Sanyal and Majumdar, 2001).

The equilibrium constant (K) for adsorption-desorption reactions in soil may also be derived from the corresponding adsorption-desorption rate coefficients, namely k_a and k_d, introduced above. Thus, it can be shown that for adsorption (fixation) process in soil, the corresponding equilibrium constant (K_a) is given by Eq. (87):

$$K_a = k_a/k_d \quad \text{...(87)}$$

While for the desorption (release) process in soil, the equilibrium constant (K_d) is obtained as per Eq. (88):

$$K_d = k_d/k_a \quad \text{...(88)}$$

Many reactions in soil are multi-step ones, each step (elementary reaction) being characterized by the corresponding equilibrium (K) as well as the kinetic (k) constants. In such case, for instance, in a two-step process of adsorption, the overall equilibrium constant (K_a) is given by Eq. (89):

$$K_a = K K' = k_a k'_a / k_d k'_d \quad \text{...(89)}$$

where, K and K′ are the equilibrium constants for the two elementary reactions, leading to the overall adsorption process, while k_a and k'_a are the corresponding adsorption rate coefficients and k_d and k'_d, the corresponding desorption rate coefficients.

23. Usefulness of Adsorption-Desorption Kinetic Data

The two salient reasons for studying the rate of soil chemical processes are:

- To predict how quickly reactions approach equilibrium or quasi-state equilibrium, and
- To investigate reaction mechanism.

Many reactions in soils are slow, yet they proceed at a measurable rate. Kinetic data on slow reactions may be of importance with regard to plant nutrition. Also, information about the reaction mechanism and processes occurring may be obtained from the kinetic data.

The analysis of adsorption isotherm data allows some prediction to be made on the field dosages of a chemical (e.g., fertilizer) to obtain a particular biological effect. The adsorption-desorption characteristics of a chemical, evaluated under laboratory conditions, and / or even in pot-culture experiments under greenhouse conditions (Hance *et al.*, 1968), merely provide an indication of how that chemical will perform *in situ*. The shift of the field performance from laboratory results is due to the use of excess water to soil ratio, extensive mixing in laboratory studies on one hand, and the effects of climatic variations, biological activity as well as agricultural practices followed (in the field) on the continued changes in the properties of soils, on the other.

In transferring results to field situations, it remains to be understood whether the kinetics of adsorption are comparable and whether the same surfaces are available in natural soils. Generally, the soils in the field are aggregated and the water content seldom exceeds the field capacity during the crop growing season.

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Chapter 13

Soil Acidity

N. PANDA, A.K. SARKAR and G.C. CHAMUAH

1. Introduction

Soils differ considerably in their acidity or pH. In aqueous systems, an acid is a substance that donates H^+ to some other substance. Conversely, a base is any substance that accepts H^+ or donates OH^-. Pure water undergoes slight self-ionization [Equation (1)]:

$$H_2O \rightleftharpoons H^+ + OH \qquad ...(1)$$

The H^+ ion actually attaches to another H_2O molecule to give H_3O^+:

$$H_2O + H^+ \rightleftharpoons H_3O^+ \qquad ...(2)$$

Since both H^+ and OH^- are produced by dissociation of a water molecule, H_2O is both a weak acid and a weak base. The product of H^+ and OH^- concentrations, is the dissociation constant of water or Kw:

$$Kw = [H^+][OH^-] = [10^{-7}][10^{-7}] = 10^{-14} \qquad \text{(at 25 °C)} \qquad ...(3)$$

Adding of an acid to H_2O will increase $[H^+]$, but $[OH^-]$ would decrease because Kw is a constant, viz. 10^{-14}. For example, in a 0.1 *M* HCl solution, the $[H^+]$ is 10^{-1} *M*; thus the $[OH^-]$ is:

$$\begin{aligned} Kw &= [H^+][OH^-] = 10^{-14} \\ & [10^{-1}][OH^-] = 10^{-14} \\ \therefore \quad & [OH^-] = 10^{-13} M \end{aligned}$$

The $[H^+]$ in solution can be conveniently expressed using pH which is defined as :

$$pH = \log 1/[H^+] = -\log [H^+]$$

Soil pH measures H^+ activity (Activity = Concentration × Activity coefficient) and is expressed in logarithmic terms. The practical significance of the logarithmic relationship is that each unit change in soil pH means a ten-fold change in the amount of acidity and basicity, as proposed by the Danish Chemist Sorensen in 1909.

Solutions having $pH < 7.0$ are acidic, while those with $pH > 7.0$ are basic or alkaline, and those with pH 7.0 are neutral. Soil pH represents the H^+ activity in soil solution (Active acidity) and does not measure the undissociated or potential acidity.

2. Sources of Soil Acidity

The important sources of soil acidity are: Exchangeable H^+ and Al^{3+}, Fe and Al oxides, soil organic matter and clay minerals.

Two adsorbed cations – Hydrogen and Aluminium — are mainly responsible for the soil acidity. Most of the hydrogen ions are held on the surfaces of clay particles and organic matter.

Active acidity is due to hydrogen ions in the soil solution. The potential acidity is due to hydrogen ions held in various chemical combinations and those adsorbed on the surface of solid particles. The exchangeable hydrogen ions present in soil neutralize the negative charge arising from the isomorphous substitution of cations. The hydrogen ions are thus due to the

Table 1. Relationship between pH and [H^+] concentration

Conc. of H_3O^+ (mol/L)	pH	Conc. of H_3O^+ (mol/L)	pH
10^{-1}	1	10^{-8}	8
10^{-2}	2	10^{-9}	9
10^{-3}	3	10^{-10}	10
10^{-4}	4	10^{-11}	11
10^{-5}	5	10^{-12}	12
10^{-6}	6	10^{-13}	13
10^{-7}	7	10^{-14}	14

permanent charge on the mineral surfaces. The pH-dependent charge may arise from the structural OH^- groups at the corners and edges of soil clay minerals, which dissociate into H^+ ions.

At low pH (< 5.0) aluminium becomes soluble and is adsorbed by silicate clays or is tightly bound by organic matter. The Al^{3+} ions are then hydrolysed in the soil solution releasing H^+ ions which contribute to soil acidity [Equation (5)]:

$$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+ \qquad ...(5)$$

Thus, in strongly acidic soils, H^+ ion activity in soil solution is very high. The influence of adsorbed hydrogen ions is of a lesser magnitude in strongly acidic soils.

In moderately acidic soils, bulk of the aluminium is converted to aluminium hydroxy ions [Equations (6) and (7)]:

$$Al^{3+} + OH^- \longrightarrow Al(OH)^{2+} \qquad ...(6)$$

$$Al(OH)^{2+} + OH^- \longrightarrow Al(OH)_2^+ \qquad ...(7)$$

Some of the aluminium hydroxy ions are adsorbed and act as exchangeable ions. They remain in equilibrium in soil solution. In the soil solution, they hydrolyse and produce hydrogen ions and thus contribute to soil acidity [Equation (8) and (9):

$$Al(OH)^{2+} + H_2O \longrightarrow Al(OH)_2^+ + H^+ \qquad ...(8)$$

$$Al(OH)_2^+ + H_2O \longrightarrow Al(OH)_3 + H^+ \qquad ...(9)$$

At pH below 5.0, iron also behaves like aluminium, but acidity generated by iron is much less than that of aluminium. In acid sulphate soils found in Kuttanad area of Kerala and Sunderbans of West Bengal, dissolved or free acidic substances like H_2SO_4, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ cause acidity. At higher pH (>5.0), amorphous aluminum and iron hydroxyl complexes may undergo hydrolysis and contribute hydrogen ions to the system.

Fine-textured soils containing high amounts of organic matter have more hydrogen ions than lighter soils with lower amounts of clay and organic matter. Moreover, different kinds of clay in soils hold variable amounts of hydrogen.

High aluminium ion concentration at the root surface may prevent the root from taking up phosphate, and the aluminium inside the living cell may interfere with sugar phosphorylation.

Soil organic matter or humus contains reactive carboxylic and phenolic groups that behave as weak acids. They dissociate, releasing H^+ ions. In organic soils and in mineral soils with high organic matter content, organic acids contribute significantly to soil acidity.

3. Classification of Soil Acidity

Soil acidity is of three kinds, namely (a) active acidity, (b) exchangeable acidity, and (c) reserve acidity. The hydrogen ions in the soil solution contribute to active acidity. It may be defined as the acidity developed due to concentration of hydrogen (H^+) and aluminium (Al^{3+}) ions in the soil solution. The concentration of hydrogen ion in soil solution due to active acidity is very small, implying that only a meager amount of lime would be required to neutralize active acidity. Inspite of smaller concentration, active acidity is important since the plant root and the microbes around the rhizosphere are influenced by it and because a dynamic equilibrium exists among active, exchangeable and reserve acidities in the soil.

In strongly acidic soils, the concentrations of exchangeable aluminium and hydrogen ions contribute to exchangeable acidity. It may be defined as 'the acidity developed due to adsorbed hydrogen (H^+) and aluminium (Al^{3+}) ions on soil colloids'. However, this exchangeable aluminium and hydrogen ions concentration is meagre in moderately acidic soils.

Aluminium hydroxy ions, and hydrogen and aluminium ions present in non-exchangeable form with organic matter and clays account for the reserve acidity. It is measured by titrating a soil suspension up to a certain pH, normally about 8.0, the amount of acidity in the soil being equivalent to the amount of NaOH used. When an acid soil is limed, gibbsite is formed from aluminium hydroxy ions with increase in pH. The potential acidity is much higher as compared to active or exchangeable acidity requiring much larger doses of lime to neutralize than what is required for neutralization of active acidity. Therefore, no attempt is made to neutralize reserve acidity. Liming is always limited to neutralize active acidy and part of the exchangeable acidity.

3.1. Active and Potential Acidity

The hydrogen ions in soil solution contribute to active acidity which is measured in terms of pH of the soil. Another part of the total acidity of the soil is called potential acidity. This refers to the acidity caused by hydrogen ions held in different chemical combinations and those adsorbed on the surfaces of solid clay particles and organic colloids. These hydrogen ions are in chemical equilibrium with the active hydrogen ions of the soil solution. When active acidity is neutralised progressively, the hydrogen ions from the potential sources are released into soil solution. When hydrogen ions change from the potential to active form, their places on the clay and organic surface are occupied by cations like Ca^{2+}, Mg^{2+}, K^+ and Na^+. Thus, total acidity is the summation of active and exchangeable acidity.

The role of mineral and organic colloids of soil in controlling soil pH has already been discussed. Out of the four factors, the most important is the proportion of cation exchange capacity of the exchange complex satisfied by bases. The other factors are: (a) nature of the clay and organic colloids, (b) kind of adsorbed bases, and (c) concentration of soluble salts in the soil solution.

The per cent base saturation is the ratio of the exchangeable bases and the cation exchange capacity of the soil [Equation (10)] :

$$\text{Percentage base saturation} = \frac{\text{Exchangeable bases } [\text{cmol}(p^+)\text{kg}^{-1}]}{\text{Cation exchange capacity } [\text{cmol}(p^+)\text{kg}^{-1}]} \times 100 \quad \text{...(10)}$$

Broadly, low per cent base saturation, i.e. below 50%, and a pH around 5.5, indicates acidity. On the other hand, when the base saturation touches 80%, and the pH is around 6.5, then an almost neutral soil exists.

3.2. Buffering of Soils : 2:1 clay minerals

Buffering is defined as the tolerance to changes in pH of a solution. With such tolerance, the rise in soil pH is minimal until enough liming material is applied to effect appreciable depletion of hydrogen and aluminium ions responsible for potential acidity. On the other hand, rapid lowering of pH of soils is prevented by the buffering action, which is ordinarily expected, as organic acids are formed due to organic matter decomposition, leading to the temporary increase in the H^+ concentration. Hydrogen and aluminium ions along with the adsorbed bases largely control buffering of soils. Soils having more of clay and organic matter exhibit higher buffer capacity, resisting the change in soil pH. The higher is the cation exchange capacity (CEC) of a soil, the greater is its buffer capacity, other influencing factors remaining the same.

The degree of buffering is highest between pH 4.5 and 6.0 and drops off below pH 4.5 and above pH 6.0. Soils having equal per cent base saturation will have the highest pH associated with hydrous oxide clay minerals and lowest pH in 2:1 type aluminosilicate clay minerals. However, the pH is intermediate in soils dominant in kaolinite and humus. Soils high in organic matter and clay, particularly montmorillonite or vermienlite, have high buffering capacity. Organic soils and clays have higher CEC values and are more strongly buffered than are sandy soils of similar agroclimatic region. The type of clay affects the pH-per cent base saturation relationship. At low pH, Al^{3+} and hydroxy aluminium ions react and block exchange sites in silicate clays and humus, which reduces the cation exchange capacity.

Net

On liming, obviously the CEC increases and more of Ca^{2+}, Mg^{2+}, etc. are adsorbed. Therefore, to raise the soil pH, additional lime is needed.

The buffering action is due to the influence of weak acids and their salts. Carbonates, bicarbonates and phosphates act as buffering agents. Organic acids are formed continually as a result of microbial activity. These organic acids are weak acids and serve as excellent buffering agents. Both organic and inorganic colloidal complexes present in the soil add to buffering process. The colloidal complex is similar to a mixture of weak acid and its salt and it functions like the acetic acid–sodium acetate buffer. Buffer capacity in soil is caused due to potential hydrogen of the exchange complex and its associated basic cations. Although pH gives some idea regarding the active acidity and to quite an extent base saturation, it hardly gives any idea about the buffering capacity of a soil.

4. Soil Reaction Correlations

The soil chemical properties and microbiological activities are highly influenced by the pH of soil. The concentrations of cations such as Ca^{2+}, Mg^{2+}, K^+, Na^+ as well as Al^{3+} in soil have a direct relationship with soil pH. At low pH, Fe, Mn and Al are highly soluble and attain toxic levels, whereas at high pH, these ions become deficient. Nitrification is slow below pH 5.5. Under acid conditions, the pH-dependent NH_4^+ fixation between lattices of expanding layer silicates decreases with decreasing pH. The availability of phosphorus, primarily $H_2PO_4^-$ and HPO_4^{2-} ions, is highly pH-dependent. Its availability in many soils is highest when the pH is neutral or slightly acidic and it declines as the soil becomes strongly acidic or strongly alkaline. In general, with increase in soil acidity, the availability of micronutrients present in cationic forms such as Fe, Mn, Cu and Zn, increases, whereas the availability of micronutrients present as anions, namely molybdenum and boron, decreases.

Occasionally, the harmful effect of soil acidity on leguminous plants seems to be caused by Mo-deficiency rather than Al-toxicity. In organic soils, the relationship of pH with nutrient availability is different from that in mineral soil. In acid organic soils, Cu may be deficient, whereas it is not so in acid mineral soils.

Generally, bacteria and actinomycetes are active in mild acidic, neutral and high pH soils. Fungi function well in a wide range of pH, predominating in acid soils than in soils of intermediate pH or higher pH. The bacteria such as Rhizobia in legumes, involved in atmospheric nitrogen fixation, are less effective in acid soils. Bacteria responsible for conversion of nitrogen, sulphur, etc. from organic to simple inorganic forms are less active in acid soils.

Degree of tolerance of plants to soil acidity is quite variable. The pH range of 6.0 to 7.2 is suitable for most crop plants. Many leguminous crops are sensitive to soil acidity. Iron requirement of rhododendrons is high, which is sufficiently available at low pH. Advantage is taken to grow many forest trees tolerant to acidity. Many species, particularly conifers, can tolerate soil acidity.

5. Acid Forming Factors

Acid soils are formed mainly due to acidic parent materials and leaching of bases caused by heavy precipitation. Use of acid forming fertilizers also contributes to soil acidity. Acid granite rocks as parent material, in the process of soil formation, render the soil acidic. Nitrogenous fertilizers like ammonium sulphate and ammonium nitrate are responsible for creating soil acidity as calcium and other bases are displaced by ammonium ions, leading to the formation of calcium sulphate which is leachable. Microorganisms are responsible for the decomposition of organic residues and nitrification. Acids formed in the process are neutralized by a base from either free calcium carbonate or an exchange complex. If the base saturation is low, acids generated are not neutralized. Carbonic acid is formed by the reaction of carbon dioxide with water. The solvent action of carbonic acid removes base-forming cations like calcium and magnesium. Stronger organic acids are formed due to microbial decay.

Inorganic acids such as sulphuric and nitric, are the suppliers of hydrogen ions. These acids along with strong organic acids create high acid conditions. Large quantities of sulphuric and nitric acids are formed in the atmosphere from oxides of nitrogen and sulphur emitted from the combustion of coal, gasolene and other fossil fuels in the cities and around large industrial complexes. Rainwater has a pH of about 5.6 due to the presence of carbonic acid. But under the influence of burning fossil fuels or smelting of sulphide ores, the pH of rainwater may be as low as 4.0. However, soils, being highly buffered, tolerate acid rain to a large extent.

6. Determination of Soil pH

The hydrogen ion activity or pH of a soil solution is measured by a standard equipment called the 'pH meter'. It has two electrodes, which are placed in a soil suspension in water. One of these electrodes is the glass electrode which measures the activity of hydrogen ions. A glass electrode consists of a thin bulb of glass separating the soil suspension or paste from an acid solution (HCl) of known H^+ ion activity in which is immersed an internal reference electrode of $AgCl/Cl^-$ (or Hg_2Cl_2/Cl^-). An electrometric potential, proportional to the hydrogen ion activity of the solution into which the electrode is dipped, develops across the glass membrane. The second electrode, which is known as the external reference electrode, is usually a calomel electrode. It is used as a reference electrode for measuring the potential of the glass electrode. Earlier, a hydrogen electrode was being used which has been replaced by a glass electrode (Jackson, 1973).

Net

The description of the electrochemical cell used for the measurement of soil pH is given below:

$$Hg, Hg_2Cl_2, KCl \parallel H^+(a_1) \vdots H^+(a_2) \parallel KCl, Hg_2Cl_2, Hg$$

E (emf) is given by

$$E = E_{ref} - \frac{RT}{F} \ln a_{H^+} \qquad \ldots(11)$$

$$= E_{ref} + \frac{2.303RT}{F} pH \qquad \ldots(12)$$

or,

$$pH = \frac{E - E_{ref}}{2.303RT} = \frac{E - E_{ref}}{0.059} \text{ at } 25°C \qquad \ldots(13)$$

where, E_{ref} is the emf of the external reference electrode.

The pH of a soil suspension varies considerably with its water content and it is always lower than the pH of the supernatant liquid. For acid and neutral soils, pH is generally low for a large soil : water ratio. In the system of clay lattice-exchangeable cations-solution a complex diffused double layer is formed. This electrical double layer is known as Helmholtz double layer. The surface of the clay lattice (inner layer) carries a negative charge. The outer layer has two parts — a positive layer created due to H-cations held on the clay lattice surface (Stern layer) and a positive layer diffused in the solution close to the lattice surface known as Guoy diffused layer. The pH value of the soil solution decreases through the diffused layer close to the negatively charged surface. The significance of the exchangeable H^+ ions can be appreciated when a soil suspension is allowed to settle and the pH is measured in the supernatant solution and the settled paste; the pH of the paste is generally about 0.2-0.5 pH unit lower.

The pH of a soil having a 0.01 *M* $CaCl_2$ remains unaffected over a wide range of soil : solution ratio. It is based on the relation called Ratio Law. Calcium is the most abundant basic metal cation in most soils and the addition of $CaCl_2$ solution does not usually change the proportions of the exchangeable cations and thus measurement of pH in 0.01 *M* $CaCl_2$ solution is advantageous. It compresses the diffuse double layer and supresses the hydrolysis. A 1 : 1 soil/ water paste may have pH one unit or more lower than a 1 : 5 soil/water suspension, which is a manifestation of the suspension effect. Apart from soil:water ratio, the electrolyte content and the carbon dioxide level also affect the soil pH value. Soils having high pH of more than 8.5 and containing free sodium carbonate and other soluble salts, show increase in pH when soil:water ratio is high. Dilution increases the hydrolysis of sodium clay with the formation of sodium hydroxide, leading to a large hydroxyl ion concentration. For this, 1 : 2.5 soil:water ratio is chosen. Since soil reaction varies with salt content, pH is often measured by making a soil suspension in salt solution of definite concentration. Soil suspension made in dilute calcium chloride solution for measurement of pH is somewhat beneficial. The activity of hydrogen ions divided by the square root of the activity of calcium ions is constant, according to the Ratio Law [Equation (14)]:

$$[H+] / \sqrt{[Ca2+]} = pH - \tfrac{1}{2}\,pCa = \text{Constant} \qquad \ldots(14)$$

The expression, pH – ½pCa, is known as the lime potential (LP) of a soil.

Since the value of lime potential does not depend on soil:water ratio or salt content, measurement of such pH in dilute aqueous $CaCl_2$ is more dependable. Since pH and pCa are measured in a clear solution, suspension effect is avoided. In a neutral soil, salt concentration affects the pH value due to increase in the apparent strength of acidic groups. By increasing salt concentration in an alkaline soil, the pH value is lowered due to reduction in the hydrolysis of the exchangeable cations like sodium. The bicarbonate concentration in the soil solution due to free calcium carbonate and magnesium carbonate influences the pH value.

7. Genesis, Occurrence and Characteristics of Acid Soils

The leaching of bases is the main cause of formation of acid soils, though parent acidic rock is also a contributing factor. In humid tropics, heavy precipitation accelerates the process of acidity. The soil-forming factors like mean annual temperature, vegetation, parent rock and hydrological conditions determine the degree of soil acidity. Acid soils in India have been formed due to drastic weathering associated with hot humid climate and heavy rainfall. Laterization, podzolization and accumulation of undecomposed organic matter under marshy conditions contribute to soil acidity. Estimates (NBSS & LUP, ICAR) show that about 35% of the acid soils of India are strong to moderately acidic (pH < 5.5), while 65% are slightly acidic (pH 5.5 to 6.5) (Table 2).

The acid soils are found in the Himalayan region, the eastern and north-eastern plains,

Table 2. Extent of acid soils in different states of India

(million ha)

States	Strongly acidic (pH < 4.5)	Moderately acidic (pH 4.5-5.5)	Slightly acidic (pH 5.5-6.5)	Total
Anurachal Pradesh	4.78	1.74	0.27	6.79
Assam	0.02	2.31	2.33	4.66
Bihar	—	0.04	2.32	2.36
Chhatisgarh	0.15	6.30	4.39	10.84
Goa	—	0.11	0.19	0.30
Himachal Pradesh	—	0.16	1.62	1.78
Jammu & Kashmir	—	0.09	1.48	1.57
Jharkhand	—	1.00	5.77	6.77
Karnataka	—	0.06	3.25	3.31
Kerala	0.14	2.87	0.75	3.76
Madhya Pradesh	—	1.12	10.60	11.72
Maharashtra	—	0.21	4.33	0.54
Manipur	0.43	1.44	0.32	2.19
Meghalaya	—	1.19	1.05	2.24
Mizoram	—	1.27	0.78	2.05
Nagaland	0.12	1.48	0.05	1.65
Orissa	—	0.26	8.41	8.67
Sikkim	0.28	0.32	—	0.60
Tamil Nadu	0.21	0.35	4.29	4.85
Tripura	0.06	0.75	0.24	1.05
Uttarakhand	—	1.18	2.30	3.48
West Bangal	—	0.56	4.20	4.76
All states	6.19	24.81	58.94	89.94

Source: NPSSLUP, Nagpur

peninsular India and the coastal plains under different agro-climatic situations. The soils occupy about 90 million hectares, constituting over one-fourth of total geographical area of the country (Table 2). About half of the area is under cultivation and rest is under forestry and other uses. About 25 million hectares of cultivated lands with pH value less than 5.5, are critically degraded with very poor physical, chemical and biological characteristics. The states having large areas under degraded acidic soils are: Arunachal Pradesh, Chhatisgarh, Kerala, Assam, Manipur, Nagaland, Mizoram, Meghalaya, Uttrakhand, Madhya Pradesh and Jharkhand. The degraded area in Chhatisgarh and Arunachal Pradesh is predominantly under forests. The alluvial acid soils are found in West Bengal, Bihar, Assam and parts of Orissa. The marshy acid soils are distributed across Assam, Kerala, West Bengal, coastal Orissa, South-east coast of Tamil Nadu and tarai regions of Uttrakhand, Bihar and West Bengal. The acid sulphate soils are unique to the Kuttanad area of Kerala.The classification of acid soils into broad soil groups, types and their distribution is given in Table 3.

Acid soils are base-unsaturated. The extent of base-unsaturation within pH range 5.0-6.0 generally varies from 16% to 67%. The active H^+ and Al^{3+} are bound to the clay. The $Al(OH)^{2+}$ is of minor significance and exists over a narrow pH range. The Al^{3+} is predominant below pH 4.7, $Al(OH)^{2+}$ between pH 4.7 and 6.5, $Al(OH)_3$ between 6.5 and 8.0 and $Al(OH)_4^-$ above pH 8.0. The iron also contributes towards acidity in several acid soils of Himachal Pradesh. Acid sulphate soils of Kerala are influenced by dissolved substances such as H_2SO_4, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$. A good correlation between extractable Al and organic carbon content of soil has been found in acid soils of Orissa. A higher amount of exchangeable H^+, compared to Al^{3+}, has been found in the surface layer of Alfisol, which is reversed in the lower layer. The acidity in the soils of north-eastern region is attributed to the presence of exchangeable Al^{3+}, its content [$cmol(p^+)kg^{-1}$] varying from 0.1 to 4.1 in Sikkim, 0.13 to 0.63 in Nagaland, 0.15 to 0.55 in Tripura, 0.04 to 3.53 in Meghalaya and 0.75 to 3.0 in the Brahmaputra valley of Assam.

8. Naturally Occurring Liming Materials including Industrial Wastes

Carbonates, oxides and hydroxides of calcium and magnesium are referred to as agricultural lime. Among the naturally occurring lime sources, calcitic, dolomitic and stromatolitic limestones are important carbonates. The other liming sources are marl, oyster shells and industrial wastes like steel mill slag, blast furnace slag, lime sludge from paper mills, precipitated calcium carbonate, etc. Burnt lime is ordinarily the oxide of lime or quick lime. Quick lime is produced in large kilns. Its reaction in soil is much faster compared to those of carbonates.

$$CaCO_3 + Heat \rightarrow CaO + CO_2\uparrow \quad ...(15)$$

$$[CaMg(CO_3)_2] + Heat \rightarrow CaO + MgO + 2CO_2\uparrow \quad ...(16)$$

Addition of water to burnt lime makes hydroxide or hydrated lime (slaked lime), which is more caustic than burnt lime [Equations (17) and (18)]:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad ...(17)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad ...(18)$$

The availability of cheap and effective liming materials is crucial for the success of acid soil amelioration programme. The agricultural grade limestone powder and marketable lime are effective, but may not be economical and available in plenty at all the places. A number of industrial by-products like basic slag, lime sludges, phosphogypsum and press mud, etc. are rich sources of calcium and could serve as cheap liming materials in some areas. The availability of basic slag with different steel industries is around 3 million tonnes (Table 4).

8.1. Reactions of Lime with Carbon Dioxide and Soil Colloids

Lime when applied to acidic soils in the form of either oxide, hydroxide or carbonate reacts with carbon dioxide and water to form bicarbonate [Equations (19)-(21)]:

$$CaO + H_2O + 2CO_2 \rightarrow Ca(HCO_3)_2 \quad ...(19)$$

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2 \quad ...(20)$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \quad ...(21)$$

Table 3. Classification of acid soils of India and their distribution

Broad soil group	Type	pH range	Distribution
Laterites	Plinthaquits, Plinthustults and Plinthudults	4.8-7.0	Karnataka, Madhya Pradesh, Orissa, West Bengal, Kerala, Assam, Jharkhand
Lateritic soils	Paleudalfs, Hapludalfs, Hapludults,Trophumults, Dystropepts,Ustropepts, Oxic intergrades	5.0-7.0	Kerala, Orissa, West Bengal, Assam, North-Eastern States, Jharkhand
Mixed red and yellow soils	Dystrochrepts, Udifluvents, Hapludalfs	5.5-6.5	Karnataka, MP, erstwhile UP, Orissa, Chotanagpur and Santhal Praganas of Jharkhand
Ferruginous red soils	Paleudalfs, Udifluvents, Udorthents, Plinthaquepts, Tropaquepts, Ultic intergrades	5.0-6.8	Tamil Nadu, parts of Karnataka, Maharashtra, Andhra Pradesh, Orissa, Jharkhand, Goa
Ferruginous red and gravely soils	Haplustalfs, Rhodustalfs	5.2-6.7	Assam, North-Eastern States, WB, Orissa, erstwhile UP, Andaman Islands
(i) Brown forest soils of Western Himalayas	Hapludolls,Udifluvents, Udorthents, Dystrochrepts, Haplumbrepts	5.5-6.0	Upper regions of Western Himalayas, Jammu and Kashmir, Himachal Pradesh
(ii) Brown forest podzolic soils	Hapludolls, Udorthents, Haplumbrepts, Dystrochrepts	5.1-5.4	Upper regions of Western Himalayas, Jammu and Kashmir and Himachal Pradesh
(iii) Brown forest soils of central Himalayas	Hapludalts, Udorthents, Udifluvents, Dystrochrepts	5.2-5.7	Lower regions of Central Himalayas, erstwhile UP
(iv) Brown forest podzolic soils of central Himalayas	Mollic Hapludalfs, Ultic-Hapludalfs, Haplumbrepts	4.7-6.0	Eastern Himalayas, North-Eastern States of Himalayan region, Arunachal Pradesh
Foot hill soils	Haplaquolls	4.5-6.5	Jammu and Kashmir, West Bengal, erstwhile UP
Peat soils	Histosols	3.5-4.5	Kerala, Assam
Alluvial soils	Haplumbrepts, Udifluvents	4.2-5.8	Assam, West Bengal, Bihar
Coastal alluvial soils	Tropofluvents, Sulfaquepts, Haplaquents, Udifluvents	3.5-5.8	West Bengal (Sunderbans), Kerala, some pockets of Tamil Nadu
Degraded saline and acid saline soils	Acid Fluvaquents	5.2-6.6	West Bengal, Orissa, parts of Tamil Nadu and Kerala

Source: Murthy *et al.* (1976)

These liming materials, on reaction with soil colloid, replace hydrogen and aluminium ions from the colloidal phase to soil solution:

$$\left.\begin{matrix}H^+\\ H^+\end{matrix}\right\rangle(\text{Clay}) + Ca(OH)_2 = Ca^{2+}\text{- (Clay)} + 2H_2O \quad \ldots(22)$$

$$\left.\begin{matrix}H^+\\ H^+\end{matrix}\right\rangle(\text{Clay}) + Ca(HCO_3)_2 = Ca^{2+}\text{- (Clay)} + 2H_2O + 2CO_2 \quad \ldots(23)$$

8.2. Lime Requirement

There are four important factors that govern the lime requirement, viz. (a) required change in pH, (b) buffer capacity of the soil to be limed, (c) chemical composition of the liming materials used, and (d) fineness of the liming materials. A fine-textured acid soil requires much larger quantity of lime than does a sandy soil or a loamy soil having the same pH value. Calcitic or dolomitic limestone reacts slowly with soil colloids, whereas burnt lime and hy-

Table 4. Availability of some liming materials in India

Acid soil region/State	Liming material	Estimated quantity available (million tonnes)	Approx. Cost/tonne (Rs)
Assam	Lime stone	15.0	4,000
Himachal Pradesh	Marketable lime	—	4,000
Jharkhand	Lime stone/Basic Slag	1.0	1,000
Kerala	Lime shells	4.0	6,000
Maharashtra	Marketable lime	0.2	2,000
North-Eastern Hill Region	Limestone	14.0	1,000
Orissa	Paper mill sludge	0.2	500
West Bengal	Basic slag	0.3	1,000
Others	Basic Slag*	3.0	1,000

Source: Participatory Resource Appraisal (PRA), ICAR Net Work Project on Acid Soils
*Available with different steel industries in the country.

drated lime react faster and bring about changes in soil pH within a few days.

8.2.1. *Chemical Equivalence of Liming Materials*

One molecule of calcium oxide, magnesium oxide or calcium hydroxide neutralizes the same amount of acidity as does one molecule of calcium carbonate. The $CaCO_3$ equivalent of burnt lime (CaO) can be calculated by the ratio of molecular weights of $CaCO_3$ and CaO [Equation (24)] :

$$\frac{CaCO_3}{CaO} = \frac{100}{56} = 1.786 \qquad \ldots(24)$$

This molecular weight ratio, when multiplied by the weight of pure $CaCO_3$ gives the $CaCO_3$ equivalent; i.e. 100 × 1.786 = 178.6. If the burnt lime has 90% purity, then 100 kg of it will have a $CaCO_3$ equivalent of 90 × 1.786 = 160.7. Likewise, the CaO equivalence of $MgCO_3$ is CaO/ $MgCO_3$ = 56/84 = 0.67, and Mg equivalence of MgO is Mg/MgO = 24/40 = 0.60.

8.2.2. *Fineness of Liming Materials*

Standard sieves having openings of designated size are used to measure fineness of liming materials. A 10-mesh sieve has 10 wires per inch and opening sizes of 2 mm. Similarly, a 60-mesh screen opening is 0.25 mm and 200-mesh screen opening is 0.075 mm. The designated screen size indicates the maximum diameter of particles that can pass along with smaller particles. The coarse particles of liming materials react somewhat slower compared to finer particles in neutralising the soil acidity.

Liming not only causes reduction in soil acidity, it also supplies calcium and magnesium for plant uptake. Frequency of liming varies with climate, soil, and cropping to be undertaken. Soils containing considerable amounts of clay and organic matter need more lime than do sandy and highly-weathered soils of the same pH level. Type of clay is also an important consideration to decide about the dose of lime. A soil having smectitic clay with higher exchange capacity would require more lime than a soil having kaolinite for an equal rise in pH. More lime is needed for a strong acid soil than for weakly acid soils. Liming factor may be defined as the factor by which the actual amount of lime required is calculated from the estimated amount of lime. The former would vary depending on the rate of limestone solubility, plant uptake and leaching during the reaction period. A liming factor of 1.5 to 2.0 is generally used.

8.2.3. *Measurement of Lime Requirement*

Exchangeable Aluminium as Lime Requirement Index — Generally, Al-toxicity is observed in highly-weathered soils of pH below 5.0. Under such condition, plant growth is frequently limited. To manage this, lime application based on the exchangeable Al extracted by neutral unbuffered 1*N* KCl solution is used as an index of lime requirement. Such an index is adopted mostly in soils of low cation-exchange capacity where exchangeable Al equals, and often exceeds the total exchangeable bases. From the values obtained for exchangeable Al, the lime requirement (LR) may be computed by the Equations (25) to (27):

For high Al-tolerant plants:

$$\text{LR} = 1 \times \text{Exchangeable Al} \quad \ldots(25)$$

For medium Al-tolerant plants:

$$\text{LR} = 1.5 \times \text{Exchangeable Al} \quad \ldots(26)$$

For low Al-tolerant plants:

$$\text{LR} = 2.0 \times \text{Exchangeable Al} \quad \ldots(27)$$

where, units for LR in terms of exchangeable Ca and exchangeable Al are cmol(p^+)kg^{-1}.

For determination of lime requirement, the buffer method of Schoemaker, Mclean and Pratt (SMP) is widely used in India. In this method, 5 mL of distilled water and 10 mL of extractant buffer (1.8 g nitrophenol, 2.5 mL triethanolamine, 3 g potassium chromate, 2 g calcium acetate and 53.2 g calcium chloride dihydrate, are dissolved in one litre of water and the pH of this solution is adjusted to 7.5 with dilute NaOH solution) are added to 5 g of soil. It is then stirred continuously for 10 minutes or intermittently for 20 minutes and the pH of the suspension is determined by a pH meter. The SMP buffer method is based on a generalized relationship between the buffer indicated lime requirement and $CaCO_3$ incubation–measured LR of a group of soils. Complications in the interpretation of the changes in buffer pH, brought about by mixing soil and buffer, arise from the facts that much of the acidity is pH-dependent and only a fraction of the total soil acidity reacts with the buffer. The SMP method has been designed for soils having considerable exchangeable Al and high LR.

$BaCl_2$–Triethanolamine (TEA) Method for Lime Requirement (Mehlich) — In this method, $BaCl_2$–TEA buffer of pH 8.0 is shaken with the soil and the amount of acidity reacting with the buffer is determined by titrating a fresh sample of buffer with acid down to the measured pH of the soil plus buffer. The difference between the two titrations gives a measure from which lime requirement is calculated.

9. Management of Acid Soils

The management of acid soils should aim at improving the production potential of the soil by either addition of amendments or manipulation of agricultural practices to obtain optimum yield under acidic conditions. One of the practices is to grow acid-tolerant plant species and varieties. Application of lime as an amendment to neutralize the exchangeable Al^{3+} to a certain extent is quite effective. Rice has good tolerance to acidity since flooding of rice fields raises the pH to almost neutrality. Short-duration rice grown in the uplands tolerate acidity. Minor millet (*Panicum miliare*) and finger millet (*Eleusine coracana*) are quite tolerant to acidity, showing meagre response to liming. Bengal gram, lentil, groundnut, maize, sorghum and field peas show medium response to liming. Pigeonpea, soyabean and cotton are sensitive to soil acidity and respond well to liming.

Amending acid soil with one time application of full dose lime as per lime requirement should be replaced by small doses of lime application to each crop. Application of 10-20% L.R. dose, mixing with farm yard manure in rows below the seeds or behind the plough at the time of sowing the crop, is quite beneficial. When the soil is moderately acidic, it can be managed with sufficient quantity of organic manure. The leaching loss of basic cations can be minimized by improving the physical conditions of soils through application of organic wastes and lime. Humified organic matter can bind tightly to aluminium ions and prevent them from building toxicity in the soil solution. Microbial decomposition produces low molecular weight organic acids and such materials also come through root exudation. These acids form soluble complexes and can save the plant from toxicity. Organic matter incorporated into soil contains a substantial amount of calcium that leaches and moves down the soil profile and checks aluminium toxicity. By this, calcium and pH levels are raised in both surface and subsoils. Since acid soils have high P-fixing capacity, its inherent acidity and acidity created in the root rhizosphere can dissolve the insoluble rock phosphates and release P. When the pH of soil is less than 5.5, ground rock phosphate as such can be applied. But at pH 5.6 to 6.5, a mixture of rock phosphate and super phosphate in 50:50 ratio is used for economy, since superphosphate will function as a starter.

For a soil with sub-soil acidity, gypsum ($CaSO_4.2H_2O$) or phosphogypsum (a byproduct from phosphate factory) is useful. Calcium from surface applied gypsum moves down the profile much faster than lime. Lime applied to the surface, on dissolution, raises pH and pH-dependent charge on the soil colloids, which hold calcium. Consequently, any anion released (OH^- or CO_3^{2-}) is removed. Gypsum, on the other hand, does not raise the soil pH and CEC. The SO_4^{2-} anion released by the dissolution of gypsum, accompanies calcium in the process of leaching. So gypsum raises the level of calcium and reduces the level of aluminium in both soil solution and exchange complex. Gypsum can be a source of sulphur for surface soil, but it cannot amend the surface acidity.

A large number of experiments on farmers fields (871) have been conducted under ICAR Net Work Project involving different crops and liming materials to evaluate the effect of liming and fertilizer addition on crop yields. Lime @ 2-4 q/ha was applied in furrows along with fertilizers at the time of sowing of crops. Liming alone increased the yields of different crops by about 14-52% over farmers' practice. The increase has been marked on wheat (52%) and mustard (35%) in West Bengal, on groundnut (45%) and pigeonpea (43%) in Orissa, on pigeonpea (34%) and maize (26%) in Jharkhand and on blackgram (26%) in Kerala. The response to the combined application of NPK and lime has been found better than the simple additive effects of fertilizer and lime, indicating a synergy or complementarity between fertilizer-use and liming. The yield of crops with 50% recommended NPK + lime @ 2-4 q/ha has been found equal or slightly higher than the yields obtained with 100% recommended NPK. The liming enhances nutrient-use efficiency, therefore, effects 50% saving of chemical fertilizers (Table 5).

Liming and fertilization have proved to be economical to different crops in acid regions of the country. The benefit – cost ratio increases with (i) liming alone (farmers' practice + lime), (ii) addition of fertilizers (100% NPK), and (iii) conjunctive use of fertilizers and lime (100% NPK + lime). The benefit–

Table 5. Yield of crops in acid soils with recommended fertilizer and half the recommended fertilizer + lime

(q/ha)

State	Crop	100% NPK	50% NPK + lime	Yield change (%)
Assam	Rapessed	9.7	10.1	+4.1
	Summer green gram	4.4	5.2	+18.2
Himachal Pradesh	Maize	34.0	33.1	-2.6
	Wheat	27.9	23.7	-15.0
Jharkhand	Maize + Pigeonpea (Maize equiv. yield)	69.0	65.0	-5.8
	Pea	38.4	50.8	+32.3
Kerala	Cowpea	8.6	10.6	+23.2
	Blackgram	6.4	8.1	+26.6
Meghalaya	Maize	30.5	30.3	-0.7
	Groundnut	14.2	21.3	+50.0
Orissa	Groundnut	22.5	23.6	+4.9
	Pigeonpea	12.0	12.2	+1.7
West Bengal	Mustard	8.2	8.4	+2.4
	Wheat	16.7	17.1	+2.4
All states		21.6	22.8	5.5

cost ratio has been found to vary from 1.4 to 4.3 with conjunctive use of lime and fertilizers. The net returns are, therefore, Rs 0.4 to Rs 3.3 per rupee invested, depending on the region and crop grown. The application of 50% NPK + lime is more economical than 100% NPK, as has been revealed by higher benefit: cost ratios in the former than the latter.

10. Industrial Wastes as Amendments for Acid Soils

The choice of amendment for acid soils depends highly on the availability of lime source and its cost. Industrial wastes such as steel mill slag, blast furnace slag, lime sludge from paper mills, cement kiln wastes, precipitated calcium carbonate, etc. have been used as amendments. Lime sludge from paper mills contains 65-85% $CaCO_3$, 2% R_2O_3 (sesquioxides), 1% free CaO and 1.5% free alkali. When exposed to rains, the sludge gets freed from alkali. The paper mills located in the acid soil regions of Assam, Nagaland, West Bengal, Orissa, Madhya Pradesh and Andhra Pradesh, produce around 1,87,000 tonnes of lime sludge annually which could be used for amending acid soils. Basic slag is a double silicate and phosphate of lime. It is estimated that for every tonne of hot metal about 500 kg of blast furnace slag is produced. For every tonne of steel, 200-250 kg of steel mill slag is produced. On an average, Indian slag contains 1-7% P_2O_5, 24-50% CaO and 2-10% MgO. Slag being hard is not reactive unless powered to optimum particle size of 60 mesh. Grinding in a ball mill being expensive, ultimate cost becomes high and therefore, slag has not gained popularity among farmers. Moreover, black cement is a potent competitor.

Good grade limestone suitable for industrial use cannot possibly be recommended as agricultural lime. Poor grade lime with comparatively high silica content could be used as an amendment. But, the poor grade limestone quarries are not operative and hence such materials are not marketed. Thus, the only choice is to utilize on the industrial wastes. Since most acid soils are less productive due to low fertility, low water retentivity and poor physico-chemical conditions, the resource-poor farmers of acid soil region are not able to afford commercial limestone. Therefore, it is often said that 'soil acidity and poverty are synonymous'.

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Chapter 14

Soil Salinity and Alkalinity

M.S. BAJWA and ANAND SWARUP

1. Introduction

Some amounts of salts are always present in soil. When the concentration of these salts is low, they are not harmful for the growth of plants. But, with the increase in salt content of the soil to high levels, plant growth is adversely affected, which, in turn, decreases the productivity of agricultural crops. The extent of reduction in growth and decrement in productivity, however, depends upon many factors such as kind and content of salt constituents, soil texture, distribution of salts in the soil profile, species of crop plants grown, level of soil-water-crop management and climatic conditions. Soils in which concentration of salts is so high as to adversely affect plant growth and crop productivity, are called salt-affected soils from agriculture point of view.

In arid and semi-arid regions, the annual rainfall is not sufficient to leach down salts to the deeper layers of soil. High evaporation in these areas, therefore, results in the accumulation of large amounts of salts in the root zone soil. The intensity of soil salinisation increases with increase in dryness of the climate. Maximum soil salinity, therefore, exists in complete desert conditions [e.g. in Chile, the Sahara, China, India (Thar desert) and other countries]. Salt-affected soils in humid regions (where leaching of salts is possible) exist only in the areas subjected to sea water intrusions in deltaic regions and other low-lying areas along the sea coast which get inundated by the sea water.

The major salts which lead to the formation of salt-affected soils include chlorides, sulphates, carbonates and bicarbonates of calcium, magnesium and sodium. The contents of potassium salts are generally low. Under dry arid conditions, large amounts of salts of boron, nitrates and fluorides can also accumulate. The role of these salts in soil salinization depends upon the kind of salts, their relative amounts in the soil, degree of their solubility and toxicity to plants. The solubility of carbonates of Ca (0.013 g/L) and Mg (2.5 g/L) is low which increases with increase in partial pressure of CO_2 and decline in pH of the soil. The solubilities of chlorides, sulphates and carbonates of Na are high (NaCl - 264 g/L, Na_2SO_4 - 161 g/L, Na_2CO_3 - 178 g/L, at 20 °C), while that of sulphate of Ca is low (1.9 g/L), and that of Mg is high (262 g/L). The chlorides of Ca and Mg are highly soluble (more than 400 g/L at 20 °C) in water.

2. Extent of the Problem

Salt-affected soils exist in all the continents of the world. Based on the FAO/UNESCO soil map, about 952 million hectares of land in the world is under varying degrees of deterioration due to excessive accumulation of salts in the soil profile (Table 1). Widely differing estimates about the area of salt-affected soils in different states of India are found in various reports, and hence accurate data are yet to be generated. However, approximation about these areas, made by the Central Soil Salinity

Table 1. Area under soil salinity and alkalinity in the world

(in million ha)

Continent	Salinity	Alkalinity	Total
North America	6.2	9.6	15.8
Mexico and Central America	1.9	–	1.9
South America	69.4	59.6	129.0
Europe	–	50.8	50.8
Africa	53.5	26.9	80.4
South Asia	83.3	1.8	85.1
North & Central Asia	91.6	120.1	211.7
South-East Asia	19.9	–	19.9
Australia	17.4	340.0	357.4
Total	**343.2**	**608.8**	**952.0**

Source : FAO/UNESCO, 1974. Soil Map of the World

Table 2. Area of salt-affected soils (soil salinity plus alkalinity) in India

State	Area (thousand ha)
Andhra Pradesh	394
Bihar (Erstwhile)	85
Goa	17
Gujarat	1649
Haryana	555
Punjab	480
Jammu & Kashmir	80
Karnataka	179
Kerala	45
Madhya Pradesh	242
Maharashtra	127
Orissa	135
Rajasthan	1183
Tamil Nadu	470
Uttar Pradesh (Erstwhile)	958
Andaman & Nicobar Islands	1
Delhi	0.6
Pondicherry	0.3
Total	**7421**

Source : Sharma (1998)

Research Institute, Karnal, is given in Table 2. These soils have different degrees of salinity and/or alkalinity in the soil profile. These are usually found in association with normal soils. Some salt-affected areas may exist even in humid and sub-humid zones.

Table 3. Contents of common elements in the earth's crust

Element	Content (%)	Element	Content (%)
Oxygen	49.13	Aluminium	7.45
Silicon	26.00	Hydrogen	1.00
Calcium	3.25	Carbon	0.35
Sodium	2.40	Chlorine	0.20
Magnesium	2.35	Sulphur	0.10
Potassium	2.35		

Source : Kovda *et al.* (1973)

3. Common Sources of Salts

3.1. Rocks and Minerals

Gradual release of salts due to geochemical and geohydrological processes at the exposed rocks and minerals in the surface of earth's crust is the direct source of salts in the soil. The elemental composition of the earth's crust which contributes to the soil salinity is given in Table 3.

The salts primarily originate as a result of hydrolysis, hydration, carbonation and oxidation-reduction of the following easily weatherable minerals inherited from the parent materials of the soils :

- Halite ($NaCl$)
- Gypsum ($CaSO_4.2H_2O$)
- Sulphides (Pyrites, FeS_2)
- Calcite ($CaCO_3$)
- Dolomite [$CaMg(CO_3)_2$]
- Apatite [$Ca_{10}(PO_4)_6F_2$]

- Feldspathoids (amphiboles)
- Olivine [$(Mg,Fe)SiO_4$]
- Feldspars:
  - Albite ($NaAlSi_3O_8$)
  - Anorthite ($CaAl_2Si_2O_8$)
  - Orthoclase ($KAlSi_3O_8$)
- Primary layer silicates:
  - Biotite [$K(Mg,Fe,Mn)_3Si_3AlO_{10}(OH)_2$]
  - Glauconite[$K(Fe,Mg,Al)_2Si_3AlO_{10}(OH)_2$]

The kind of primary minerals and the extent of their weathering determine the types of salts present in the soil. The salt solutions resulting from acid magmatic rocks (e.g. granite, gneiss) contain carbonates, chlorides, silicates and sulphates of sodium, whereas those resulting from alkaline magmatic rocks (basalt, diabase) contain mainly carbonates, sulphates and silicates of Ca and Mg. Each molecular unit of Na-feldspar produces one molecular unit of $NaHCO_3$ and that of Ca-feldspar produces one molecular unit of $Ca(HCO_3)_2$. The distribution and accumulation of salts released from minerals in the soil depend upon the physico-geographical and geohydrological conditions.

3.2. Ocean Water

The ocean water, containing about 42×10^{15} tonnes of dissolved salts (of which 85.6% is NaCl), can be a significant direct source of salts in the soils of the low-lying coastal areas and where marine deposits have become the parent material during the geological periods. Salts from the ocean can also be transported to the inland areas with rain water and by wind. Near the sea coast, the rain water may contain salts up to 200 mg/L, which rapidly decrease to only a few mg/L in the inland areas. The rain water near the sea coast contains high concentrations of chlorides of Na and Mg, but inland rain water is dominated by sulphates and bicarbonates of Ca and Mg.

3.3. Atmospheric Accession of Salts

Atmospheric accession of salts in the soil of inland areas can occur as a result of falling dried droplets of ocean water from the atmosphere (aerosol) along with the rain water or as dry salt-dust.

3.4. Marine Rocks and Evaporites

Marine rocks and evaporites developed with the upliftment of many parts of the continents from the sea/ocean are also important sources of salts in the soil. A typical example is the localised high concentration of salts along the lower Himalayas and the Shiwaliks, and a large part of the present Indo-Gangetic Plains, western Rajasthan up to the Aravallis and Kutch in India, which may be traced back to the upliftment of these ranges during the geological periods from under the sea. Some of the sea salts get precipitated during the process of deposition, while others remain entrapped in the alluvium. In the soils reclaimed from the sea, dominant soluble salts include halides (NaCl), gypsum ($CaSO_4.2H_2O$), and sulphides (FeS_2, Pyrites).

3.5. Salt Springs

Salt springs emerging from many regions can also add considerable quantities of salts to the soil, because volcanic gases and waters from the interior of the earth contain large quantities of chlorides. Such sources of salts can be important locally.

3.6. Economic Activities

In many regions, present-day salt-affected soils have resulted from the erroneous economic activities of man. Introduction of irrigation without provision of adequate drainage results in the disturbance of salt-water balance in the soil, which leads to the accumulation of salts. In the canal command areas, restriction of drainage due to improper planning of development works (roads, canals, railway-lines, etc.) results in the rise of water-table and hence salts from the lower layers of soil profile to the surface. In many arid and semi-arid regions, saline groundwaters used for irrigation can become direct sources of salts in the soil. Salts can also accumulate due to flooding by waters from mining shafts or by industrial effluents.

4. Origin of Salt-Affected Soils

The salt-affected soils have originated as a result of following factors:

(i) **Continental Cycles** (related with the movement, redistribution and accumulation of carbonates, sulphates and chlorides in the inland regions).

(ii) **Marine Cycles** (accumulation of NaCl from the ocean/sea in lowlands of coastal regions).

(iii) **Deltaic Cycles** (movement and accumulation of salts carried by rivers from the continents or delta valley ground streams or from the sea).

(iv) **Artesian Cycles** (salt accumulation due to evaporation of deep groundwaters wedged up to the surface through tectonic features or other processes), and

(v) **Anthropogenic Cycles** (salt accumulation due to erroneous human activities).

There are definite zones with respect to the accumulation and distribution of salts in the soil. This depends upon the mobilities of different salts. Highly leachable salts (NaCl, Na_2SO_4, Na_2CO_3, $NaHCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$) mainly contribute towards soil salinization. Consistent precipitation and dissolution reactions under varying geochemical and hydrological processes sustain and replenish the reserves of salts in the soil.

4.1.Salt and Water Balance Relationships

Since salts migrate mainly through soil solution, the salt and water balance (input - output relationship) in a region mainly controls the salt accumulation processes. The following inputs and outputs in the salt and water balance equations, determine the extent of salt build-up in the irrigated soils :

4.1.1. For High Land Internally Well-Drained Soils

Where water is getting drained from a given depth of soil and no water is rising due to capillary action, the relation is expressed by Equation (1):

$$\underbrace{D_{rw}.C_{rw}+D_{iw}.C_{iw}}_{\text{(Inputs)}} = \underbrace{D_{ew}.C_{ew}+D_{dw}.C_{dw}}_{\text{(Outputs)}} \pm S \qquad ...(1)$$

where, 'D' is depth of water and 'C' is salt concentration, 'rw' is rain water, 'iw' is irrigation water, 'ew' is water evapotranspired, 'dw' is drainage or percolating water and 'S' is change in salt content.

4.1.2. For Low Lying Areas

Where water is percolating downwards as drainage water (dw) from a given depth of soil and at the same time some water is rising through capillary action (cw), the relation is expressed by Equation (2):

$$\underbrace{D_{rw}.C_{rw}+D_{iw}.C_{iw}+D_{cw}.C_{cw}}_{\text{(Inputs)}} = \underbrace{D_{dw}.C_{dw}+D_{ew}.C_{ew}}_{\text{(Outputs)}} \pm S \qquad ...(2)$$

Since C_{rw} and C_{ew} are negligible, their values for practical purposes are considered as equal to zero. When inputs are more than outputs, salt accumulation takes place. The preponderance of evaporation over rainfall increases salt input over output and hence, results in salt accumulation in the soil. Therefore, the climatic, geomorphological, topographical, hydrological and biological conditions, which favour excessive evaporation of water, facilitate the processes of soil salinization. Climatically, salt-affected soils mostly occur in hot and dry arid regions where evaporation of the groundwater is high. Salinization does not occur when water-table is very deep (more than 10 m) and the soils are well drained despite the dryness of climate. Geomorphologically salt-affected soils are associated with low lands, i.e. flood plains, deltas, troughs, low river terraces, lakes and coastal regions. Even small differences in relief can result in a total change in the extent of salt accumulation.

Hydrologically, development of inland salinity is related to regions of high or rising water-table conditions in the soils, where the groundwater containing dissolved salts is under the direct influence of excessive evaporation and transpiration. In many canal command (irrigated) areas, the rise in water-table and salts to the surface has resulted in the disturbance of salt and water balance and hence, development of salt-affected soils.

5. Characterization of Salt-Affected Soils

For a detailed chemical characterization, salt-affected soils are analysed for pH [of 1:2 soil : water suspension (pH_2) and of saturation phase (pH_s)], electrical conductivity [of 1:2 soil : water suspension (EC) and of saturation extract (EC_e)], soluble cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), anions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-), and boron (in the saturation extract), exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), cation exchange capacity (CEC), exchangeable sodium percentage (ESP) and $CaCO_3$ content. Gypsum content of saline soils and gypsum requirement (for using it as an amendment) of alkali soils are also determined. The sum of all major soluble cations [mmol (+)/L] is approximately equal to the sum of all major anions [mmol (-)/L].

For physical characterization, determinations are carried out for saturation percentage, infiltration rate, hydraulic conductivity, particle size (clay, silt, sand) distribution, aggregation and stability of structure, particle density, bulk density and crust formation.

The total salt concentration in the soils can be easily determined and expressed as EC or EC_e, because electrical conductance is directly related to salt concentration in the solution. The electrical conductivity is expressed as millimhos/cm at 25 °C or deci-Siemens/metre at 25 °C. In SI units, the unit of conductivity is Siemens, 1S (Siemen) = 1 mho, so that 1dS/m = 1 mmho/cm. The EC values and other soluble salt relationships in the soil solution are given by Equations (3)-(5):

(i) For soil solutions having EC ranging from 0.1 to 5 dS/m :

- Total dissolved solids (mg/L) ≈

$$\text{EC (dS/m)} \times 640 \qquad \ldots(3)$$

- Sum of soluble cations or anions [mmol (+ or -)/L) ≈ EC (dS/m) × 10] ...(4)

(ii) For soil solutions with EC ranging from 3 to 30 dS/m :

- $\text{OP (bars)} \approx \text{EC (dS/m)} \times (-0.36)$ ...(5)

where, OP is the osmotic potential or the negative of osmotic pressure of solution which directly measures the effect of salinity on plant growth.

Expression of salinity as EC_e has special significance because saturation percentage (SP) of the soil is directly related to the plant available-moisture range, i.e. moisture content from Permanent Wilting Point (PWP) to Field Capacity (FC). Over a considerable textural range, the moisture content of the soil at PWP is approximately equal to one-half of that at FC and one-fourth of that at SP. Therefore, soluble salt-content in saturation extract will be about one-half of the concentration of the soil solution at the FC and about one-fourth of that at PWP. For this reason, the EC_e can be used directly for appraising the effects of soil salinity on plant growth (US Salinity Laboratory Staff, 1954).

Sodium saturation in the soil is expressed as exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR) in the soil solution (US Salinity Laboratory Staff, 1954), because of their significance in deteriorating physicochemical properties of the soil and adversely affecting the growth of plants. The ESP is calculated using Equation (6):

$$\text{ESP} = 100\,[(\text{Exchangeable } Na^+ \text{ ions})/(\text{CEC})] \qquad \ldots(6)$$

[all cations and CEC in mmol (+) / kg soil]

The value of SAR, i.e. the relative proportion of Na^+ ions with respect to $Ca^{2+} + Mg^{2+}$ ions in the soil solution is calculated by Equation (7):

$$\text{SAR} = [Na^+] / \sqrt{[Ca^{2+} + Mg^{2+}]/2} \qquad \ldots(7)$$

(all concentrations in mmol (+) / L)

The ESP of the soil can be predicted quite well from the SAR values and a Gapon-type exchange equation of the form of expression (8):

$$\begin{aligned} \text{ESR} &= \frac{X_{Na}}{X_{Ca} + X_{Mg}} \\ &= K_G \cdot \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+} + Mg^{2+}]}{2}}} \qquad \ldots(8) \\ &= K_G \cdot \text{SAR} \end{aligned}$$

where, ESR is the exchangeable sodium ratio, exchangeable (X) cations are expressed in mmol (+)/kg soil [1 mmol (+)/kg soil = 0.1 milliequivalent/100 g soil], and K_G is the Gapon constant whose values commonly range from 0.010 to 0.015. The values of ESR and

ESP/100 are approximately equal for many irrigated soils having ESP less than 25-30. The relationship between ESR and ESP is given by Equation (9):

$$\text{ESP} = 100\,(\text{ESR}) / (1+\text{ESR}) \qquad \ldots(9)$$

assuming CEC $\approx X_{Na^+} + X_{Ca^{2+}} + X_{Mg^{2+}}$.

For soils having higher SAR and ESP, the values of K_G and the ESP-ESR relationship have to be specifically determined for each soil.

6. Classification of Salt-Affected Soils

The salt-affected soils need to be classified into various groups for developing special systems of management for specific types of problems and constraints in the production of crops. In 1954, the US Salinity Laboratory Staff grouped salt-affected soils into three distinct classes, viz. (i) saline soils, (ii) alkali soils, and (iii) saline-alkali soils. But keeping in view the experiences about the effects of two common kinds of salts (neutral salts and alkali salts) on the properties of these soils and plant growth in India and other countries, salt-affected soils have been grouped into two categories only, viz. (i) saline soils, and (ii) alkali soils, in the soil map of the world (Szabolcs, 1974). The characteristics of these soils are described below.

6.1. Saline Soils

These soils contain sufficient concentration of soluble salts in the root zone soil to adversely affect plant growth and productivity. The soluble salts in these soils are predominantly the chlorides and sulphates of sodium, calcium and magnesium. The concentration of potassium is generally low. The concentrations of neutral salts (Cl^- and SO_4^{2-}) are much higher than those of alkali salts, namely carbonates ($CO_3^{2-} + HCO_3^-$). Excessive concentrations of boron, fluoride and nitrates may also be present in these soils under arid conditions. Many saline soils may also contain small to appreciable quantities of sparingly soluble gypsum ($CaSO_4.2H_2O$). These soils are characterized by saline efflorescence or white encrustation of salts at the surface. In India, these soils are known at some places as '*reh*' and in others as '*thur*'. When water-table is deep, grey patches often appear in the capillary fringe zone.

As per the US Salinity Laboratory Staff (1954), these soils have pH of saturation paste (pH_s) less than 8.5, ESP less than 15, and EC_e more than 4 dS/m at 25 °C. However, based on the Indian experience (Gupta and Abrol 1990), saline soils have been defined as those having pH_s less than 8.2, the EC_e more than 4 dS/m and preponderance of chlorides and sulphates of Na, Ca and Mg. The ratio of $[Na^+] / ([Cl^-] + [SO_4^{2-}])$ in soil solution is less than 1.0.

The physicochemical characteristics of saline soils are determined by the kind of salts present and their total concentration. Since the relative proportion of Na^+ ions with respect to Ca^{2+} and Mg^{2+} ions is low (ESP less than 15) in saline soils, the exchange complex does not have high amounts of adsorbed Na^+ ions. The dominance of Ca^{2+} and Mg^{2+} ions in soil solution and on the exchange sites and high total soluble salt/ electrolyte concentration results in flocculation of clay particles. The tightly adsorbed divalent (Ca^{2+} and Mg^{2+}) ions decrease the zeta potential (ξ) of the soil exchange complex, which, in turn, results in attraction of clay particles towards each other, causing flocculation. The relative difficulty with which common cations can be replaced or removed from the exchange complex, leading to increased flocculation of the clay particles, is in the following order: $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$. In the reverse order, these cations will cause dispersion of clay particles, which is a typical property of alkali soils. As a consequence of flocculation of clay particles, the saline soils are aggregated and highly permeable. When irrigated, water does not stagnate on the surface in the field.

6.2. Alkali Soils

These soils have sufficient sodium saturation and alkalinity to adversely affect plant growth and crop productivity. Carbonates ($CO_3^{2-} + HCO_3^-$) of sodium are the dominant salts. The concentration of neutral salts (Cl^- and SO_4^{2-}) is much lower. Sparingly soluble gypsum, which may be present in many saline soils, is nearly absent in alkali soils. In some parts of India, they are called '*Usar*' and in others '*Kallar*'. As per the US Salinity Laboratory Staff (1954), alkali soils are characterized by pH_S more than 8.5, ESP more than 15 and EC_e lower than 4 dS/m at 25 °C. However, experiences about Indian alkali or sodic soils show that the EC_e is limitless if originating from high concentration of carbonates and bicarbonates of sodium. Otherwise, EC_e is less than 4 dS/m at 25 °C. The pH values of more than 8.2 and the ratio of $[Na^+] / ([Cl^-] + [SO_4^{2-}])$ in soil solution more than 1.0 are more realistic criteria for distinguishing sodic soils of the Indo-Gangetic Plains from the non-sodic soils. When dispersed and dissolved organic matter is deposited on the surface, alkali soils give dark brown-black appearance (black alkali soils). In India, these soils are mainly distributed in arid and semi-arid regions of Punjab, Haryana, Uttar Pradesh, Bihar and Rajasthan states.

6.2.1. *Alkalinity of Alkali Soils*

The alkalinity in the alkali soils depends upon the relative concentration of Na_2CO_3 and $NaHCO_3$ and partial pressure of CO_2 (P_{CO_2}) in the soil solution. The relationship of P_{CO_2} and alkalinity in aqueous systems can be described through the reactions (10)-(12):

$$CO_2(g) + H_2O = H_2CO_3$$
$$K = (H_2CO_3) / P_{CO_2} \qquad ...(10)$$

$$H_2CO_3 = H^+ + HCO_3^-$$
$$K_1 = (H^+)(HCO_3^-) / (H_2CO_3) \qquad ...(11)$$

$$HCO_3^- = H^+ + CO_3^{2-}$$
$$K_2 = (H^+)(CO_3^{2-}) / (HCO_3^-) \qquad ...(12)$$

The values of log K, log K_1 and log K_2 are: –1.46, –6.36 and –10.33, respectively. The alkalinity (Alk) of aqueous solutions in equilibrium with CO_2 can be defined (Stumm and Morgan, 1970) by Equation (13):

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad ...(13)$$

Since the alkalinity of the aqueous solutions in equilibrium with CO_2 of the atmosphere is not appreciably affected by $[H^+]$ and $[OH^-]$ in the pH range 6-10, we may write it as Equation (14) or (15):

$$Alk = [HCO_3^-] + 2[CO_3^{2-}], \text{ in concentration terms} \qquad ...(14)$$

$$\text{or} \quad Alk = (HCO_3^-) + 2(CO_3^{2-}), \text{ in activity terms} \qquad ...(15)$$

Therefore, the alkalinity (CO_3^{2-} + HCO_3^-) in these solutions can also be considered to be equal to the total concentration of cations minus the total concentration of the anions, other than carbonates (Equation 16):

$$Alk = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] - [Cl^-] - 2[SO_4^{2-}] \qquad ...(16)$$

Substituting values of (CO_3^{2-}) from Equation (12) in Equation (15), we get Equation (17):

$$Alk\,(H^+) - (H^+)(HCO_3^-) = 2K_2\,(HCO_3^-) \qquad ...(17)$$

Combining Equation (17) with Equations (10) and (11) and rearranging results the relationship between H^+, Alk and P_{CO_2} can be written as Equation (18):

$$Alk\,(H^+)^2 - KK_1P_{CO_2}(H^+) - 2KK_1K_2P_{CO_2} = 0 \qquad ...(18)$$

Substituting the values of the equilibrium constants, Equation (18) (at 25 °C) becomes Equation (19):

$$Alk\,(H^+)^2 - 1.51 \times 10^{-8} \times P_{CO_2}(H^+) - 1.41 \times 10^{-18} \times P_{CO_2} = 0 \qquad ...(19)$$

Equation (19) reduces to Equation (20) or (21):

$$\log Alk - pH = \log P_{CO_2} - 7.82 \qquad ...(20)$$

or

$$pH = \log Alk - \log P_{CO_2} + 7.82 \qquad ...(21)$$

This shows that a 10-fold change in alkalinity (CO_3^{2-} + HCO_3^-) or 10-time change in P_{CO_2} results in a unit change in pH. These relationships suggest that the alkalinity of an aqueous carbonate system is its acid neutralizing capacity, and can be measured as the quantity of strong acid per litre required to attain a pH equal to that of the concentration of molar solution of Na_2CO_3 (Stumm and Morgan, 1970).

6.2.2. *Formation of Carbonates of Sodium and Alkalisation in the Soil*

Formation of carbonates of Na and alkalisation in the soil take place as a result of carbonation of alumino-silicate minerals in the presence of water [Equations (22)-(25)]:

$$\underset{\text{Albite}}{NaAlSi_3O_8} + HOH + CO_2 \rightarrow HAlSi_3O_8 + NaHCO_3 \quad ...(22)$$

$$HAlSi_3O_8 + 7HOH \rightarrow \underset{\text{Gibbsite}}{Al(OH)_3} + \underset{\text{Soluble silica}}{3Si(OH)_4} \quad ...(23)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \quad ...(24)$$

Na_2CO_3 is highly soluble (178 g/L at 20 °C) and its hydrolysis results in high alkalinity (pH up to 12).

$$Na_2CO_3 + 2HOH \rightarrow 2Na^+ + 2OH^- + H_2CO_3 \quad ...(25)$$

In the presence of CO_2, the pH is lowered because of the formation of bicarbonate of Na, according to the reaction (26):

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3 \quad ...(26)$$

The release of CO_2 with decomposition of organic matter in the soil accentuates the process of $NaHCO_3$ formation in soil. In arid regions, these reactions go on indefinitely, resulting in excessive accumulation of $Na_2CO_3.10H_2O$, $Na_2CO_3.H_2O$ and $NaHCO_3$ in the soil. With excessive evaporation under extreme arid conditions, carbonates and bicarbonates of sodium may accumulate in the soil as double salt crystals (Na_2CO_3. $NaHCO_3$. $2H_2O$) or pure $NaHCO_3$.

With increase in the concentration of soil solution due to evapotranspiration, the solubility limits of calcium sulphate, calcium carbonate and magnesium carbonate are exceeded and hence they get precipitated. Therefore, the relative proportion of Na^+ ions with respect to Ca^{2+} and Mg^{2+} ions (i.e. SAR) becomes high in soil solution, resulting in the increase of Na^+ ions on the exchange complex as per equilibrium (27):

$$Ca-X + 2Na^+_s \rightleftharpoons 2Na-X + Ca_s^{2+} \quad ...(27)$$

where, 'X' refers to soil exchange sites, and 's' to soil solution

Under the conditions which favour reaction (27) to proceed to the right hand side, soil Na saturation (ESP) increases to produce alkali soils.

Most alkali soils, particularly in the arid and semi-arid regions, contain $CaCO_3$ in the profile in some form, and constant hydrolysis of $CaCO_3$ sustains the release of OH^- ions in soil solution [Equation (28)]:

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^- \quad ...(28)$$

The OH^- ions so released result in the maintenance of higher pH in calcareous alkali soils than that in non-calcareous alkali soils.

The increase in ESP can markedly affect the physicochemical properties of the soil. High Na^+ saturation in the soil results in the dispersion of clay particles, i.e. they tend to repel each other and remain independent of others. Highly hydrated Na^+ ions increase the zeta potential of the exchange sites, resulting in the repulsion of clay particles from each other. These soils, therefore, have very poor structure.

The dispersed clay particles move downwards through soil pores and produce a dense or compact layer of very low permeability at some depth. Due to the decrease in hydraulic conductivity of alkali soils with increase in ESP, irrigation water stagnates at the surface in the field. Clogging of pores in the surface soil followed by drying, results in the development of crust, which hinders seedling emergence and deteriorates air-water relations in the root zone. Alkali soils become very hard when dry and sticky when wet. Due to wide spatial variability in the build-up of ESP in the soil, it becomes difficult to achieve optimum soil-moisture conditions in the entire field.

6.3. Saline-Alkali Soils

The US Salinity Laboratory Staff (1954) have defined saline-alkali soils as the soils which have EC_e more than 4 dS/m at 25 °C and ESP more than 15. These soils have been formed as a result of both salinization and alkalization processes. When high EC_e is due to high concentration of chlorides and sulphates of sodium, the pH of these soils seldom exceeds 8.5. Clay particles in theses soils remain flocculated. But, when EC_e is high because of soluble carbonates of sodium, the pH of these soils can be much higher than 8.5. With leaching of soluble salts of chlorides and sulphates of sodium, these soils behave like alkali soils.

6.4. Taxonomic Classification of Salt-Affected Soils

According to the Taxonomic Soil Classification System (Soil Survey Staff, 1975), the salt-affected soils of the arid zone are classified under the order Aridisol (characterized by dryness up to 1.5 m depth; having calcic, gypsic, salic and/or natric horizons; high EC, absence of oxic, mollic and spodic horizons; sometimes may have argillic horizon). In some regions, salt-affected soils have also been classified under the orders Alfisol, Mollisol, Inceptisol and Vertisol. Under this soil taxonomic system, the most common diagnostic horizon (epipedon) is Ochric, and subsurface horizons are argillic, natric, cambic, calcic, gypsic, and salic. As per available literature, different Orders, Sub-orders and Great Groups for the salt-affected soils in accordance with this classification are given in Table 4.

In the Order Entisol, the suborders Psamments, Fluvents and Orthents may also have salt-affected soils.

Table 4. Different orders, sub-orders and great groups for salt-affected soils

Orders	Sub-orders	Great Soil Groups
Aridisols	Argids	Natrargids,
	Durids	Natridurids
	Gypsids	Natrigypsids
	Orthids	Salorthids Calciorthids, Camborthids
Alfisols	Aqualfs	Natraqualfs
	Udalfs	Natrudalfs
	Ustalfs	Natrustalfs
	Xeralfs	Natrixeralfs
Mollisols	Albolls	Natrialbolls
	Aquolls	Natraquolls
	Cryolls	Natricryolls
	Udolls	Natrudolls
	Ustolls	Natrustolls
	Xerolls	Natrixerolls
Inceptisols	Aquepts	Halaquepts
	Ochrepts	Ustochrepts
Vertisols	Aquerts	Natraquerts, Salaquerts
	Usterts	Salusterts, Pellusterts, Chromusterts

6.5. Different Types of Salt-Affected Soils of India

Different types of salt-affected soils existing under different climatic regions of India and their main characteristics (Sharma, 1998) are given below:

6.5.1. Inland Saline Soils of Arid and Semi-arid Regions (Rainfall < 500 mm)

These soils are characterized by neutral to alkaline pH, high EC and low ESP; sulphates and chlorides are invariably much higher than carbonates; shallow saline groundwater-table; and remain waterlogged for some part of the year. These are distributed in parts of Haryana, Punjab, Rajasthan, Uttar Pardesh and Jammu & Kashmir.

6.5.2. Inland Saline Soils of Sub-humid Regions (Rainfall 1000-1400 mm)

These soils are characterized by neutral to alkaline pH, high EC, preponderance of chlorides and sulphates, developed on dolomitic alluvium. These may also contain sizable quantities of carbonates of sodium, and are distributed mainly in Bihar.

6.5.3. Inland Salt-affected Medium to Deep Black Soils (Rainfall 700-1000 mm)

These soils are characterized by neutral to highly alkaline pH, high EC, preponderance of chlorides and sulphates with or without bicarbonates, salinization and alkalization processes associated with rising water-table, montmorillonitic clay mineralogy, and high clay content (up to 80%). These are distributed in Madhya Pradesh, Maharashtra, Rajasthan, Andhra Pradesh, Gujarat and Karnataka.

6.5.4. Medium to Deep Black Soils of Deltaic and Coastal Semi-arid Regions (Rainfall 700- 900 mm)

These soils are characterized by neutral pH, high EC, preponderance of chlorides and sulphates with traces of bicarbonates, alkaline Vertisols with shallow water-table, high clay content, and montmorillonitic mineralogy. These are distributed in Saurashtra coast in

Gujarat and deltas of the Godavari and Krishna rivers in Andhra Pradesh.

6.5.5. Saline Micaceous Deltaic Alluvium of Humid Regions
(Rainfall 1400-1600 mm)

These soils are characterized by deep micaceous fine texture, neutral to slightly acid pH, high EC, preponderance of chlorides and sulphates over bicarbonates; absence of $CaCO_3$; and perpetual shallow saline groundwater-table. These are distributed in Sunderban delta in West Bengal and parts of Mahanadi delta in Orissa.

6.5.6. Saline-humic and Acid Sulphate Soils of Humid Tropical Region
(Rainfall 2000-3000 mm)

Developed under marine cycles, these soils are characterized by low pH, high EC, presence of humic (organic) horizon, preponderance of chlorides and sulphates, have ochric epipedon, shallow saline water-table, and variable amounts of pyritous clay. These are distributed in Malabar coast of Kerala.

6.5.7.Saline Marsh of Rann of Kutch
(Rainfall < 300 mm)

These soils are characterized by neutral to slightly alkaline pH, high EC, and preponderance of chlorides and sulphates. Their textural stratification is interspersed with gypsum, $CaCO_3$ and hydrated iron oxide accumulation. These are distributed in Rann of Kutch in Gujarat.

6.5.8. Saline and Alkali Soils of Indo-Gangetic Alluvium (Rainfall around 550 mm)

Characterized by sandy to loam in texture, these soils have slightly alkaline to high pH, variable EC, high ESP, preponderance of carbonates of sodium, with some quantities of neutral salts, calcareous having a calcic or a petrocalcic horizon, and poor permeability. These are distributed in parts of the states existing in the Indo-Gangetic alluvial region.

7. Effect of Salts on Plant Growth

The growth of plants is suppressed when the salt concentration is low, but may be entirely prevented if it is too high. In high salt soils, seeds usually fail to germinate, plants die at early seedling development and growth stages, plants show stunted growth and foliage becomes characteristically bluish-green. Under high levels of salinity and alkalinity, barren spots (patchy growth or slick-spots) appear or even the entire field may look barren. The harmful effects of increased accumulation of salts in the soil on plant growth can be ascribed to changes in the proportion of exchangeable cations, soil reaction, ionic balance in plants, physical properties of the soil and osmotic and specific ion toxicity effects. These changes adversely affect the activity of plant roots. The extent of soil salinity effects, however, depends upon the nature of the crop, level of salts and ESP, and agronomic management.

7.1. Osmotic Stress

The main effect of high concentration of soluble salts in soil on plants is osmotic stress. The semi-permeable membrane of plant roots permits the water to pass but rejects most of the salts. Therefore, osmotically it becomes difficult for the roots to extract water from saline solutions. Under osmotic stress, plant cells continue to divide but do not elongate, resulting in an increase in the number of cells per unit area which accounts for the typically dark bluish green colour of the foliage. Because plant growth is a function of total soil-moisture stress (sum of soil-moisture tension and osmotic pressure of the soil solution), efficient irrigation management is a crucial factor in these soils. The ability of plants to increase their internal osmotic pressure by production of organic acids or uptake of salts, also helps them to osmotically adjust in the soils having high salt concentration.

7.2. Toxic Effect of Some Ions

Many plants are sensitive to the toxic effect of some ions in soil solution. The ions which cause specific toxicities in the plants include chloride, sulphate, bicarbonate, sodium, magnesium, and boron. However, excessive intrusion of these ions in the roots and their movement in the plants through transpiration stream may lead to necrosis, burning of leaf tips and margins, and eventual death. Some plants can screen out toxic ions through the mechanism of selective absorption. Excessive Na^+ ions in the soil may exert harmful effect on plant growth through deterioration of soil structure and poor air-water relations caused by dispersion of clay particles in the root zone. In alkali soils having high ESP, calcium gets precipitated and its soil-solution concentration declines below the limiting value of 0.2 mmol (+)/L needed for plant growth. Excessive alkalinity can also have direct caustic effect on the roots of plants grown in sodic soils.

7.3. Nutritional Imbalances

Injury to plants can also occur due to the salinity induced cationic and nutritional imbalances within the plants. Some examples are : excessive absorption of Na^+ ions can lead to a decrease in the absorption of Ca^{2+}, Mg^{2+} and K^+ ions; high concentration of bicarbonates in soil solution can induce iron chlorosis, and high pH in alkali soils might accentuate deficiencies of micronutrient cations. Increase in salinity and alkalinity in the soil can also adversely affect soil biology, mineralization of organic matter and transformations of applied fertilizer nutrients.

7.4. Relative Salt Tolerance of Plants

The relative tolerance of plants to salts depends upon physiological constitution of the plant; its stage of growth, its rooting habit, its ability to regulate the ionic balance within the plant, the nature of salts, their relative proportions, their total concentration and distribution in the profile and climatic conditions in which they are grown.

Crop yields generally do not significantly decrease until the salt concentration in the soil solution exceeds specific levels, i.e. the threshold level, which can differ for different crops and their varieties. Above these threshold values, the yields of most agricultural crops tend to decline linearly (food and fibre crops) or asymptomatically (beans, onions, gram, lentil, etc.) with increase in salinity. The relative growth at soil salinity levels, exceeding threshold levels of a crop, are estimated using response functions (Mass and Hoffman, 1977) consisting of the following two linear lines : (i) One with zero slope representing yield/ growth stability under increasing levels of salinity in the growth medium, and the other (ii) where yield/ growth decreases as a function of increasing salinity of the growth medium, with the Equation (29):

$$Yr = 100\,b\,(EC_e - a) \qquad \ldots(29)$$

where, Yr is relative yield at a given EC_e, 'a' is the threshold salinity expressed as dS/m, and 'b' is the slope expressed in per cent per dS/m. The relative salt tolerance of different crops, important under Indian conditions, are presented in Table 5. The crops in this table have been arranged with respect to salinity threshold levels in the descending order.

The sodicity tolerance ratings of different crops also differ largely (Table 6). Besides these sodicity-tolerant crops, karnal grass, rhoades grass and para grass also have high degree of tolerance to alkali environment. The rating of relative salinity and alkalinity tolerance has a great agricultural significance because proper choice of crops to be grown during the process of reclamation of these soils can ensure better economic returns.

The tolerance or sensitivity of most crops to salt and Na^+ saturation is different at different stages of their growth. These differences can be efficiently exploited to minimize the harmful effects. Germination and early seedling establishment are the most sensitive stages for most of the crops. The other critical period is when a change from vegetative to reproductive phase occurs.

8. Management of Soil Salinity and Alkalinity Problems

Keeping in view the fact that plant growth can be restricted or entirely prevented by increased levels of salinity and alkalinity in the soil, these soils have to be reclaimed so that they become productive. The processes of accumulation of salts and build-up of ESP have to be reversed. To achieve these objectives, provision of adequate drainage, replacement of Na^+ ions from the soil-exchange complex and leaching out of soluble salts below root zone have to be ensured. Without adequate drain-

Table 5. Relative salt tolerance of important plant species under Indian conditions

Plant species	Threshold salinity (dS/m)	EC_e (dS/m) for relative yield		
		90%	75%	50%
Field Crops				
Cluster bean	8.8	9.4	10.3	11.7
Barley	8.0	0.0	13.0	18.0
Cotton	7.7	9.6	12.5	17.4
Sugarbeet	7.0	8.7	11.2	15.4
'Dub' grass	6.9	8.5	10.3	14.2
Sorghum	6.8	7.4	8.4	9.9
Wheat	6.0	7.4	9.5	13.0
Rye grass	5.6	6.9	8.2	10.8
Soybean	5.0	5.5	6.2	7.5
Cowpea	4.9	5.7	7.0	9.1
Date palm	4.0	6.8	10.9	17.9
Groundnut	3.2	3.6	4.1	4.9
Rice	3.0	3.8	5.1	7.2
Sudan grass	2.8	5.1	8.6	14.4
Alfalfa	2.0	3.4	5.4	8.8
Maize	1.7	2.5	4.0	5.9
Sugarcane	1.7	3.4	5.9	10.1
Berseem	1.5	3.2	5.9	10.2
Orchard grass	1.5	3.2	5.9	10.2
Mung bean	1.0	1.5	2.3	3.6
Vegetables				
Tomato	2.5	3.5	5.0	7.5
Cucumber	2.5	3.3	4.4	6.3
Spinach	2.0	3.3	5.3	8.6
Celery	1.8	3.8	5.8	9.8
Cabbage	1.8	2.8	4.4	7.6
Potato	1.7	2.5	3.8	5.9
Broad bean	1.6	2.6	4.2	6.8
Onion	1.2	1.8	2.7	4.3
Carrot	1.0	1.7	2.8	4.6
Turnip	0.9	1.9	3.7	6.4
Fruits				
Grape fruit	1.8	2.4	3.3	4.9
Citrus	1.7	2.3	3.2	4.8
Peach	1.7	2.2	2.9	4.1
Almond	1.5	2.0	2.8	4.1
Plum	1.5	2.1	2.9	4.3
Red pepper	1.5	2.2	3.3	5.1

Source : Singh (1998)

age and leaching of salts, proper reclamation cannot be achieved on a long-term basis. In addition to decreasing the salts and ESP levels in the root zone and maintaining them below the permissible limits (which depend upon salt and Na^+ ions tolerance of crops), soil management practices must ensure prevention from reverting the salinity and ESP to the original conditions. Following general principles have to be considered for properly understanding and implementing the reclamation measures :

(i) The total soluble salt concentration in the root zone has to be decreased to control osmotic effects on plant growth. Maintenance of total soil moisture tension (omotic pressure plus soil moisture tension) must be

Table 6. Relative tolerance of crops to alkalinity or sodicity

ESP (range*)	Crop
2-10	Deciduous fruits, nuts, citrus, avocado
10-15	Safflower, blackgram, peas, lentil, pigeonpea
16-20	Chickpea, soybean
20-25	Clover, groundnut, cowpea, onion, pearl millet
25-30	Linseed, garlic, clusterbean
30-50	Oats, mustard, cotton, wheat, tomatoes
50-60	Beets, barley, *Sesbania*
60-70	Rice

*Relative yields are only 50% of the potential in respective sodicity ranges

Source : Gupta and Abrol (1990)

ensured at optimum level so that plant roots can absorb adequate amount of water.

(ii) Water flows through the soil in the direction of maximum decrease of hydraulic head and the flow velocity is proportional to the hydraulic gradient. The design and layout of drainage system is controlled by this principle.

(iii) Since soluble salts in the soil are transported by water, the quality of water used for dissolving the salts, determines the efficiency of leaching and drainage processes. Therefore, availability of good quality water is of paramount importance for the success of reclamation work.

(iv) Salt concentration in soil solution, upward movement of salts and their accumulation increase with increase in the evaporation and transpiration from the surface of the soil and the vegetation, especially when groundwater-table is shallow.

(v) Increase or decrease of salts in the root zone depends upon whether the salt inputs are higher or lower than the salt outputs.

(vi) The cations in the soil solution and those adsorbed on the exchange complex are in equilibrium with each other. The dispersion and flocculation of clay particles and the effectiveness of amendments are controlled by this principle.

Systematic planning for reclamation work requires characterization of the problem (e.g. extent and kind of salinity or alkalinity/sodicity) as the first step. Thereafter, for each specific problem, specific systems of management have to be followed. The physical, hydrotechnical, chemical and biological methods (Kovda *et al.*, 1973) used for the amelioration of salt-affected soils are discussed below.

8.1. Physical Amelioration

The commonly followed physical methods for amelioration of salt-affected soils include deep ploughing, sub-soiling, sanding, profile inversion and scrapping. The first two methods break the impermeable layer, hard pan or cemented sub-soil layer existing at various depths in the soil profile to improve the internal drainage of the soil and facilitate the transportation of salts dissolved in water to deeper layers. Incorporation of sand in salt-affected soil is done to bring about permanent changes in texture, increase soil permeability and improve air-water relations in the root zone. In sodic soils having large amounts of clay, application of inadequate quantity of sand may, however, create problems because of the cementing effect. Therefore, large quantities of sand have to be applied to check this cementing effect.

Profile inversion can be adopted only under conditions where surface soil is good but the soil below some depth is sodic, saline or has undesirable characteristics. The objective is to retain the good soil of the surface, while inverting the saline/sodic sub-soil down. Since this is a very cumbersome method, it is generally not followed by the farmers.

Many farmers often resort to scrapping of surface by a few centimetres of salt/salty soil and dump it at some other place. This is only a temporary measure for improving the plant growth. Reclamation by this method cannot be achieved on a permanent basis, particularly under shallow water-table conditions where salts can again rise and accumulate at the surface due to evapotranspiration.

8.2. Hydro-technical Amelioration

The reclamation of salt-affected soils by this method involves basically the removal of salts from the saline soil or displacement of sodium ions from the exchange complex of alkali soils through the processes of leaching with water and drainage. This requires that sufficient water must pass through the soil to decrease salt concentration in the soil below the permissible limits and, in turn, maintain proper salt and water balance in the soil to be reclaimed. The leaching of the salt-affected soils leads to highly saline drainage water. Therefore, suitable measures for its disposal should be taken before initiating the leaching processes, particularly in areas having high water-table. The success of leaching of salts and reclamation, therefore, depends upon the efficiency with which salts can be removed from the soil. It is important to check the re-salinization or re-alkalization of the soils. Therefore, provision of adequate drainage system is a pre-requisite for any reclamation process.

The extent of leaching required depends upon:

(a) soil properties (soil texture, soil structure, soil pore geometry, cracking phenomenon and clay mineralogy),

(b) initial salinity and chemical composition of soluble salts,

(c) quality of the water (in terms of amount and composition of salts) used for leaching,

(d) leaching methods,

(e) water-table depth,

(f) efficiency of the drainage system, and

(g) salt tolerance of crops to be grown.

The amount of water of known salt concentration (C_{iw}), required for leaching of salts from the initial level of soil salinity (C_o) to the pre-determined level of soil salinity after leaching (C_f) can be worked out from the relationship of $(C_f - C_{iw})/(C_o - C_{iw})$ with D_w/D_s, i.e. the depth of water (D_w) displaced from a given depth of soil (D_s). The quantity of salts removed per unit depth of water applied determines the efficiency of the leaching process.

8.2.1. Leaching Requirement

In the soils irrigated with waters having different concentrations of salts (C_{iw}), the control on the building of salts at a given depth of the soil will depend upon the concept that the outputs of salts leaving an area should be more than, or equal to, the inputs, i.e. the quantity of salts entering the area. Keeping this in view, the first salt and water balance equation for internally well drained upland soils can be re-written as expression (30):

$$D_{iw}.C_{iw} - D_{dw}.C_{dw} + D_{rw}.C_{rw} = S \qquad \ldots(30)$$

and the second equation for low land soils as Equation (31):

$$D_{iw}.C_{iw} + D_{cw}.C_{cw} + D_{rw}.C_{rw} - D_{dw}.C_{dw} - D_{ew}.C_{ew} = S \qquad \ldots(31)$$

Assuming the concentrations of salts in rain water (rw) and evapotransired water (ew) as negligible, the salt content of a given soil volume at any time, 'S_T' for upland areas is given by Equation (32):

$$S_T = D_{iw}.C_{iw} - D_{dw}.C_{dw} \qquad \ldots(32)$$

and for low lying areas, by Equation (33):

$$S_T = D_{iw}.C_{iw} - D_{dw}.C_{dw} + D_{cw}.C_{cw} \qquad \ldots(33)$$

When S_T is zero at steady state condition, Equation (32) for upland soils reduces to the following relationships:

$$D_{iw}.C_{iw} = D_{dw}.C_{dw} \qquad \ldots(34)$$

or,

$$\frac{D_{dw}}{D_{iw}} = \frac{C_{iw}}{C_{dw}} = \text{Leaching Fraction (LF)} \qquad \ldots(35)$$

$$D_{dw} = D_{iw}.C_{iw} / C_{dw} = \text{Leaching Requirement (LR)} \qquad \ldots(36)$$

And Equation (33) for low-lying soils reduces to Equation (37):

$$D_{dw} = (D_{iw}.C_{iw} + D_{cw}.C_{cw}) / C_{dw} = \text{LR} \qquad \ldots(37)$$

The above equation indicates that with increase in salinity of irrigation water, more water (D_{iw}) will have to be applied to control salt build-up below the desired level. These LR calculations are sufficiently accurate for most of the crops. Leaching Fraction (LF) refers to the fraction of the depth of applied irrigation water that leaves the root zone as drainage water. These equations can be further modified by including the leaching efficiency factor.

8.2.2. *Leaching Methods*

Ponding continuously or intermittently with sufficient depth of good quality water on the surface of the soil and ensuring downward movement of water is traditionally the most commonly used method for leaching of salts. The effectiveness of this method depends upon how uniformly the water is applied and how much of it passes through the root zone soil. Land levelling is, therefore, an extremely important step before initiation of the leaching process. Variations in micro-relief within the field often lead to rise in salinity in the raised areas and leaching in the depressions. The permeability and initial salinity of the soil largely control the rate of leaching. As a general rule, leaching should be done with the depth of water equivalent to the depth of soil to be reclaimed. The passage of 1m leaching water per metre of soil depth under continuous ponded conditions normally removes approximately 80% of soluble salts from the soil.

The basin furrow method of leaching is considered to be more efficient. Under this method, water is allowed to meander back and forth across the field through adjacent sets of furrows. The quantity of water required is much less than that needed for ponding method of leaching.

8.2.3. *Drainage System*

Drainage system in saline soils should be designed to regulate the water and salt balance of both the surface soil and sub-soil. The sub-soil drainage is not very effective in highly impervious sodic soils. In areas where water-table remains shallow for most part of the year and the quality of groundwater is poor, installation of sub-soil drainage system will be more useful. The need for the development of either surface of sub-surface drains has to be worked out on the basis of the nature of soil, groundwater conditions, climate, cropping pattern, economic considerations, etc. Installation of sub-surface drains is much more costly than installation of surface drains.

8.3. *Chemical Amelioration*

Alkali/sodic soils contain Na_2CO_3 and $NaHCO_3$ which upon hydrolysis produce alkalinity:

$$NaHCO_3 + H_2O = Na^+ + OH^- + H_2CO_3$$

and

$$Na_2CO_3 + 2H_2O = 2Na^+ + 2OH^- + H_2CO_3$$

This leads to high pH and ESP and also to reduction in the availability of several essential plant nutrients. Crops grown on these soils invariably suffer nutritional disorders, resulting in low yields (Swarup, 1994). Reclamation of these soils basically requires replacement of exchangeable sodium ions from the soil-exchange complex by the more favourable calcium ions, as given by the expression (38) and the sodium thus exchanged is leached out of the root zone.

$$2Na\text{-}X + Ca^{2+}\ (\text{solution}) \rightleftharpoons Ca\text{-}X + 2Na^+\ (\text{solution}) \quad \ldots(38)$$

where, 'X' is the soil-exchange complex.

It can be accomplished by the application of chemical or organic amendments. Amendments are the materials that directly or indirectly through chemical or microbial action furnish or mobilize divalent cations, usually Ca^{2+} for the replacement of sodium from the exchange complex of the soil, followed by leaching to remove soluble salts and other reaction products. The type of chemical compounds and their quantities required for reclamation of alkali/ sodic soils depend upon the physico-chemical properties of the soil, desired rate of replacement of sodium ions, and economic considerations. The chemical amendments used for amelioration of these soils can be broadly grouped as follows:

(i) *Soluble Sources of Calcium:* Gypsum ($CaSO_4.2H_2O$), calcium chloride ($CaCl_2$) and phospho-gypsum (an industrial by-product)

(ii) *Sparingly Soluble Calcium Salts:* Calcite, $CaCO_3$, and

(iii) *Acids or Acid-formers:* Sulphur, sulphuric acid, sulphates of iron and aluminium, pyrites, lime-sulphur.

The effectiveness of each of these amendments mainly depends upon the presence or absence of alkaline-earth carbonates (particularly $CaCO_3$) in the soil. When soils contain $CaCO_3$, any soluble source of calcium and acids or acid-formers may be used. When the soils are non-calcareous, application of acids and acid-formers is not recommended and only soluble sources of calcium should be used. Application of sparingly soluble $CaCO_3$ for the reclamation of sodic soils is not recommended because its solubility decreases with increase in pH of the soil.

The reactions of these amendments in the soils containing $CaCO_3$ can be illustrated by Equations (39)-(47):

Gypsum :

$$2Na-X + CaSO_4 \rightleftharpoons Ca\text{-}X + Na_2SO_4 \qquad \ldots(39)$$

Calcium Chloride :

$$2Na-X + CaCl_2 \rightleftharpoons Ca\text{-}X + 2NaCl \qquad \ldots(40)$$

Sulphur : Microbial oxidation :

$$2S + 3O_2 = 2SO_3 \qquad \ldots(41)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad \ldots(42)$$

$$H_2SO_4 + 2CaCO_3 \rightarrow CaSO_4 + Ca(HCO_3)_2 \qquad \ldots(43)$$

$$2Na\text{-}X + CaSO_4 \rightleftharpoons Ca\text{-}X + Na_2SO_4 \qquad \ldots(44)$$

The microbial oxidation of sulphur is mediated by aerobic *Thiobacilli* group of chemoautotrophs.

Pyrites — Oxidation of pyrites, like sulphur leads to the formation of sulphuric acid. The overall reactions are given by Equations (45)-(47):

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \qquad \ldots(45)$$

$$2CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + Ca(HCO_3)_2 \qquad \ldots(46)$$

$$2Na-X + CaSO_4 \rightleftharpoons Ca-X + Na_2SO_4 \qquad \ldots(47)$$

The rate of oxidation of pyrites is, however, slow and depends upon the moisture content, oxygen availability, temperature, and particle size. When applied on the basis of water soluble sulphur-content, its efficiency in reclamation is quite high. Wide variations in water-soluble sulphur-content of pyrites (4 to 11%) supplied at different periods have been noticed (Sharma and Swarup, 1997).

Lime-sulphur and sulphates of iron and aluminium produce sulphuric acid, which further acts like the reactions given above. Calcium chloride is highly soluble in water but its high cost and hygroscopicity prohibit its use on a large scale. Acids are not generally recommended because of the high cost involved and difficulty in handling them at the field level.

Gypsum is, by far, the most economical and commonly-used chemical amendment. In India, the resources of gypsum are estimated to be more than 1000 million tonnes. The gypsum requirement (GR) for amelioration of alkali/sodic soil depends upon exchangeable sodium content to be replaced, exchange efficiency and the depth of soil to be reclaimed. The laboratory estimation of GR (US Salinity Laboratory Staff, 1954) is carried out by equilibrating a sodic soil with gypsum solution of known calcium concentration and then estimating the calcium deficit (as a result of exchange of sodium with calcium) in the extracted solution. This determination includes Ca^{2+} required to replace the exchangeable Na^+ ions plus that required to neutralize alkalinity.

The quantity of gypsum required to replace an initial level of exchangeable sodium (E_{Na_i}) and achieve its reduction to a desired level of exchangeable sodium (E_{Na_f}) per unit area and per unit depth of the soil, can also be calculated using Equation (48):

$$\text{GR (in cmol/kg soil)} = (E_{Na_i} - E_{Na_f})\,\text{CEC} \qquad \ldots(48)$$

where, ENa and CEC are in $cmol(p^+)kg^{-1}$ soil.

Since one cmol gypsum/kg soil is equal to 860 kg gypsum/10^6 kg soil, for one hectare to a depth of 0-15 cm (2×10^6 kg soil), the GR can be calculated by Equation (49):

$$\text{GR (kg/ha)} = 1720 \times (E_{Na_i} - E_{Na_f})\,\text{CEC} \qquad \ldots(49)$$

The GR worked out by these methods is based on 100% replacement of Na^+ by Ca^{2+} ions. Under actual conditions, the efficiency is always much lower. To compensate for the lack of a quantitative replacement, the GR worked out by these methods should be multiplied by 1.25. The quantities of different amendments to be applied in comparison with gypsum are given in Table 7.

Gypsum should be broadcast and incorporated in the surface 0-10 cm soil by discing or by using a cultivar. Mixing of gypsum in deeper soil decreases its effectiveness, as a fraction of the applied gypsum can react with soluble carbonates to precipitate Ca as $CaCO_3$. The optimum size of gypsum particles is determined on the basis of the required efficiency of

Table 7. Relative quantities of different amendments compared with gypsum

Amendment	Tonnes equivalent to 1 tonne of gypsum
Gypsum ($CaSO_4.2H_2O$)	1.00
Sulphur	0.18
Lime-sulphur	0.75
Sulphuric acid	0.57
Iron sulphate ($FeSO_4.7H_2O$)	1.62
Aluminium sulphate [$Al_2(SO_4)_3.18H_2O$)]	1.27
Limestone ($CaCO_3$)	0.58

reclamation, cost of grinding and ease of application. Mined gypsum ground to pass through 2-mm sieve has been found to be cost-effective and also efficient. Since the finer particles react faster, gypsum ground to pass through a 2-mm sieve can efficiently reclaim alkali soil. Experiments have shown that gypsum applied at a rate of 12-15 Mg/ha (50% GR of 0-15 cm soil) is sufficient to initiate reclamation process in rice-based cropping systems. Field studies have also shown that gypsum dose could be reduced from 50% to 25% GR when FYM @ 20 Mg/ha was also applied (Table 8).

8.4. Biological Amelioration

Organic materials and the action of plant roots improve biological activity in the soil. The decomposition of materials increases the concentration of CO_2 and organic acids in the soil which help in mobilizing calcium by dissolving calcium compounds. This can be accomplished by green manuring, incorporation of crop residues, application of FYM, pressmud and other organic materials.

The effectiveness of an organic material in reclaiming alkali soils depends on the amount of CO_2 produced and the reduced conditions through drop in redox potential under submerged conditions. Under field conditions, it has been observed that gypsum (50% GR), pyrite equivalent to gypsum on sulphur basis and FYM @ 30 Mg/ha were equally effective in increasing rice yields when a period of 30 days submergence prior to planting of rice was allowed (Swarup, 1981). The reduction in pH and ESP was, however, largest in gypsum-treated soil, followed by pyrites. Enhanced availability of nutrients in pre-submerged FYM-treated plots was chiefly responsible for the better rice growth. The magnitude of yield increase due to pre-submergence, FYM and rice husk application was less in wheat than in rice. It was because even though FYM and rice husk brought about a marginal improvement in the alkali soil, it was sufficient to improve rice yields as it could tolerate high ESP. But this extent of improvement in soil conditions was not adequate to obtain good yields of wheat because it is only moderately tolerant to sodicity.

Rice is preferred to be grown during reclamation of alkali soils owing to its high tolerance to soil sodicity. The ponding of water for optimum rice growth promotes build-up of partial pressure of CO_2 and leaching of salts,

Table 8. Effect of soil amendments on the grain yield of rice and wheat in a sodic soil

Treatment	Grain yield (Mg/ha)							
	Rice				Wheat			
	1989	1990	1991	Pooled	1989-90	1990-91	1991-92	Pooled
Amendments								
Control	2.98	4.55	5.23	4.25	0.20	1.00	1.18	0.79
Gypsum 25% GR	5.10	5.23	5.32	5.22	1.67	2.22	2.33	2.07
Gypsum 50% GR	5.44	5.46	5.34	5.41	1.99	2.31	2.42	2.24
Farmyard manure (FYM) (20 Mg/ha)	4.05	5.20	5.30	4.85	1.42	2.00	2.16	1.86
Gypsum 25% GR+ (FYM) (20 Mg/ha)	5.78	5.76	5.83	5.79	2.14	2.78	2.82	2.58
Gypsum 50% GR+ (FYM) (20 Mg/ha)	6.13	6.01	5.90	6.01	2.36	2.82	2.91	2.70
LSD (P = 0.05)	0.33	0.41	0.40	0.36	0.35	0.36	0.34	0.35

Source: Swarup (1994)

GR = Gypsum requirement; FYM = Farm yard manure resulting from the exchange of sodium by calcium.

The first change that occurs on flooding a soil is the depletion of oxygen supply. Consequently, its reduction is intensified, which leads to accumulation of gases, predominantly carbon dioxide. The partial pressure of CO_2 is an important entity because it determines the changes in pH, and other oxidation-reduction reaction in the soil. The results with sodic soils have shown that the pCO_2 increases rapidly and reaches a peak value at about 30 days after flooding, and the increase is more pronounced in the presence of organic material (Figure 1). Combined use of green manure and rice husk creates higher pCO_2, than rice husk or green manure alone (Figures 1 and 2). The increased pCO_2 of sodic soils helps in the reclamation processes by solubilizing native $CaCO_3$ and the released Ca removes Na from the exchange complex. The higher the pCO_2 build-up in the soil under rice culture, more is the reduction in pH and ESP of the soil (Swarup, 1998; 1992).

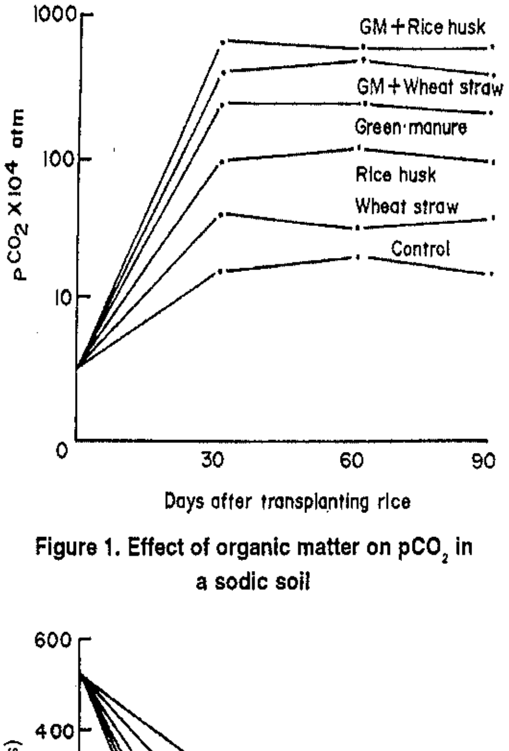

Figure 1. Effect of organic matter on pCO_2 in a sodic soil

The pace of reclamation of alkali soils, as evident from the increased permeability and reduction in sodicity, is considerably increased under rice culture. Increased hydraulic conductivity resulting from rice culture has been attributed to either the physical action of plant roots in facilitating water movement or the removal of entrapped air from the larger conducting pores. The electro-chemical property that differentiates a submerged soil from upland soil is its reduction potential (E_h) value. The aerobic soils have high positive potential, in the range of + 500 to +700 millivolts. Flooded soils are usually characterized by low potential and within a few weeks (2 to 4) negative potential as low as –300 to –400 millivolts is observed. (Swarup *et al.,* 1990). The E_h drops sharply during the first and second weeks of flooding the sodic soils and is lowest at 30 days rice growth (Swarup, 1988). Addition of organic matter leads to a steep fall in E_h in early stages (Figure 2) because of the accumulation of reducing substances as a result of O_2 depletion. Green manure with rice husk intensifies the reducing conditions and decreases the E_h value to as low as –250 millivolts. Redox potential decreases with increasing pH and ESP of soils, the effect being more pronounced in the presence of organic matter (Figure 3). It

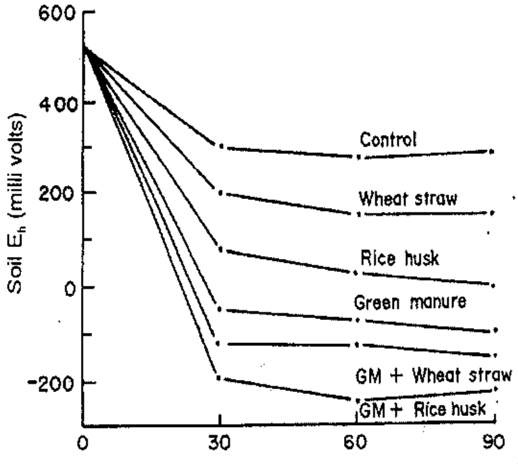

Figure 2. Effect of organic matter on the redox potential (E_h) in a sodic soil

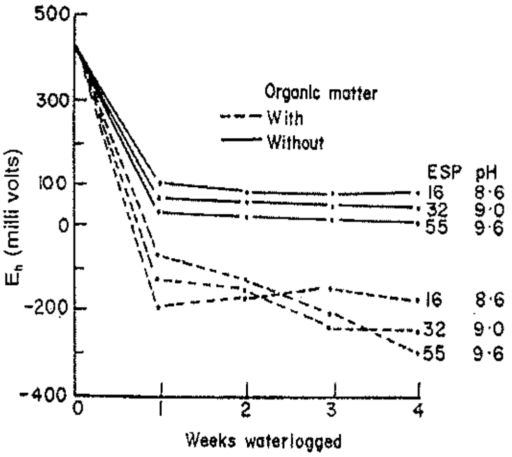

Figure 3. Influence of organic matter and waterlogging on redox potential (E_h) at varying levels of soil sodicity/ pH

shows that excess Na on the soil-exchange complex of sodic soils causes dispersion of soil particles and intensifies soil reduction, resulting in low E_h values. Since iron and manganese availability are controlled largely by pH and redox equilibria, drop in E_h of sodic soils upon flooding is extremely beneficial during rice-cultivation (Swarup, 1985; 1988; 1992).

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Chapter 15

Mineral Nutrition of Plants

R.K. RATTAN and N.N. GOSWAMI

1. Introduction

One hundred and nine elements have been identified and included in the periodic table so far. Most of these exist in the earth's mantle, earth's crust and soil, though the magnitude of their occurrence varies. To a certain extent, plant composition reflects the chemical composition of the soil. Since plant is an active entity, it exercises selectivity and discriminates in absorbing the soil-borne elements. Plants accumulate elements differentially, take up some elements in large quantities, and some others in relatively smaller quantities and completely reject most others.

Before moving further, let us understand some of the key terms used in this chapter.

Nutrient — A nutrient element is one that is required to complete the life-cycle of the organism and its relative deficiency produces specific deficiency symptoms. The adverse effects are relieved by the supply of that specific element only. Elements essential for the plants may not be essential for the other organisms and *vice versa*. Depending upon availability, the nutrient content in a plant could be deficient, sufficient or toxic. Nutrient content is considered deficient when it is so low that it severely limits growth and produces characteristic deficiency symptoms. Nutrient contents associated with only growth reductions and not accompanied by appearance of deficiency symptoms are termed insufficient. Range of nutrient content in plants associated with optimum crop yields is called sufficient. When the concentration of a nutrient element rises too high to cause significant growth reductions, it is termed toxic.

Available Nutrient — In the soil a nutrient element is distributed in different discrete chemical forms, which often exist in a state of dynamic equilibrium and constitute the pool from which plants draw it. Soil available form of a nutrient is that fraction whose variation in amount is responsible for significant changes in yield and response (Bray, 1948). The availability of these soil forms, however, involves not only their chemical and physical nature but also the ability of the plant to "forage" them with its root system. The nutrient available to the biological organisms is termed as bioavailable nutrient. In plant nutrition it is that portion of the nutrient in the soil that can be readily absorbed and assimilated by the plants. Available nutrient constitutes only a small portion of the total nutrient present in the soil.

Beneficial Elements — Beneficial elements are the mineral elements which stimulate plant growth, but are not essential or which are essential only for certain plant species, or under specific conditions. Some of the elements found to be beneficial are: silicon, sodium, aluminium, cobalt, selenium and vanadium.

Functional Nutrient — This term introduced by Nicholas (1961) is defined as an element that plays a role in plant metabolism, whether or not that role is specific or indispensable.

Trace Element — Trace element is an element found in low concentrations, perhaps less than one ppm or still less in soil, plant and water, etc.

Tracer Element — Radioisotope or a stable isotope of an element used for tracing its path in a system to study the mechanism of its interaction with the system, is called a tracer element.

Heavy Metal — A metal having specific gravity of more than 5.0 or having atomic number higher than 20 is termed as a heavy metal. As a corollary, any metal heavier than calcium is a heavy metal.

Nutrient Content — Concentration of a nutrient or its amount per unit weight of a plant tissue is termed as nutrient content. Nutrient content is expressed in terms of percentage (kg/100 kg or g/100 g) or ppm (parts per million), which is equivalent to mg of nutrient per kg of dry matter (mg/kg) or μg of nutrient per g of dry matter (μg/g). The per cent (%) of a nutrient is converted to parts per million (ppm) by multiplying with a factor of 10,000 or 10^4.

Nutrient Accumulation — Storage of a nutrient in a particular part or portion of the plant is called nutrient accumulation. Different plant parts store nutrients differentially.

Nutrient Uptake — Amount of nutrient taken up by the growing crops from either the soil or other sources, is called nutrient uptake. It is a product of plantmatter produced and nutrient concentration in plant. Suppose roots, straw and grain of a wheat crop producing dry matter of 2.5 t/ha, 6 t/ha and 4 t/ha contain 0.2%, 0.5% and 1.5% N, respectively, then the uptake of N will be as follows:

N uptake by roots = 2.5 (t/ha) × 0.2 (kg/100 kg)
= 0.005 t/ha = 5.0 kg/ha

N uptake by straw = 6 (t/ha) × 0.5 (kg/100 kg)
= 0.03 t/ha = 30kg/ha

N uptake by grain = 4 (t/ha) × 1.5 (kg/100kg)
= 0.06 t/ha = 60 kg/ha

Total N uptake by wheat
= 5 + 30 + 60 = 95 kg/ha

Total N uptake by the above ground portion
= 30 + 60 = 90 kg/ha

Nutrient Removal — The nutrient contained in the harvested portion of the crop is termed as the nutrient removed.

Let us now come to the main topic and find what are the essential nutrients.

2. Essential Nutrients

Elements needed by the plant without which it will not be able to survive are called essential nutrients. For an element to be regarded as an essential nutrient, it must satisfy the following criteria, as propounded by Arnon and Stout (1939):

(i) A deficiency of an essential nutrient element makes it impossible for the plant to complete the vegetative or reproductive stage of its life-cycle.

(ii) The deficiency is specific to the element and can be prevented or corrected only by supplying that element.

(iii) The element is involved directly in the nutrition of the plant, quite apart from its possible effects in correcting some microbiological or chemical conditions of the soil or other culture medium.

The seventeen nutrients recognized essential for plant growth are : carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo), chlorine (Cl) and nickel (Ni). Nickel is the latest addition to the list of essential nutrients, done in 1987. A detailed information on these essential nutrients as regard to the year of their discovery, name of the discoverer, average concentration in plant, etc. is given in Table 1. Depending upon the quantity required by the plant, nutrients are classified into macronutrients and micronutrients.

2.1. Macronutrients

Macronutrients or major nutrients are so-called because these are required in large quantities, more than that of iron. These in-

Table 1. Critical information on nutrients in relation to plants

Nutrient	Essentiality discovered authors (Discoverer)	Year of discovery	Plant usable form	Average conc. in plant tissue	Relative No. of atoms compared to Mo as one
H	Since time immemorial		H_2O	6%	60,000,000
O	Since time immemorial		H_2O and O_2	45.0%	30,000,000
C	Priestley *et al.*	1800	CO_2	45%	30,000,000
N	Theodore de Saussure	1804	NO_3^-, NH_4^+	1.5%	1,000,000
K	C. Sprengel	1839	K^+	1.0%	400,000
Ca	C. Sprengel	1839	Ca^{2+}	0.5%	200,000
Mg	C. Sprengel	1839	Mg^{2+}	0.2%	100,000
P	C. Sprengel	1839	$H_2PO_4^-$, HPO_4^{2-}	0.2%	30,000
S	Sachs and Knop	1860	SO_4^{2-}	0.1%	30,000
Cl	T.C. Broyer, A.B. Carlton, C.M. Johnson and P.R. Stout	1954	Cl^-	100 mg/ kg	3,000
Fe	E Gris	1843	Fe^{2+}	100 mg/ kg	2,000
B	K. Warington	1923	H_3BO_3, $H_2BO_3^-$, HBO_3^{2-}, BO_3^{3-}	20 mg/ kg	2,000
Mn	J.S. McHargue	1922	Mn^{2+}	20 mg/ kg	2,000
Zn	A.L. Sommer and C.P. Lipman	1926	Zn^{2+}	20 mg/kg	300
Cu	A.L. Sommer, C.P. Lipman and G. McKinney	1931	Cu^{2+}	6 mg / kg	100
Mo	D.I. Arnon and P.R. Stout	1939	MoO_4^{2-}	0.1 mg / kg	1
Ni	P.H. Brown, R.M. Welch and E.E. Cary	1987	Ni^{2+}	0.1 mg/ kg	1-2

Source: Tisdale *et al.* (1997)

clude C, H, O, N, P, K, Ca, Mg and S. Carbon, H and O constitute 90 to 95% of the plant drymatter weight and are supplied through carbon dioxide (CO_2) and water. Remaining six major nutrients, viz. N, P, K, Ca, Mg and S, are further subdivided into primary and secondary nutrients.

Primary Nutrients — Nitrogen, P and K are termed as primary nutrients because of their larger requirement by the plants and correction of their wide-spread deficiencies is often necessary through application of commercial fertilizers of which these are the major constituents.

Secondary Nutrients — Calcium, Mg and S are termed as secondary nutrients because of their moderate requirements by plants, localized deficiencies and their inadvertent alleviation by incidental accretions through carriers of the primary nutrients. For example, the phosphatic fertilizer, single superphosphate (SSP) contains both Ca and S. Likewise, ammonium sulphate, a nitrogenous fertilizer, also supplements S.

Micronutrients — Nutrients that are required in relatively smaller quantities but are as essential as macronutrients are termed micronutrients. These include iron, manganese, zinc, copper, boron, molybdenum, chlorine and nickel. Their importance can be judged from the fact that in the absence of one atom of Mo, 60,000,000 atoms of H, 30,000,000 atoms of C, 30,000,000 atoms of O and 1,000,000 atoms of N, may become ineffective from the point of view of plant nutrition. Micronutrients are subdivided into micronutrient cations (Fe, Mn, Zn, Cu, Ni) and micronutrient anions (B, Mo and Cl), depending upon the form in which plants absorb them.

Let us now learn about the functions and deficiency symptoms of individual nutrients.

Table 2. Approximate concentration of nutrients in mature leaf tissue of various crop plants

Nutrient	Deficient	Sufficient or normal	Toxic
N (%)		1-5	
P (%)		0.1-0.4	
K (%)		1-5	
Ca (%)		0.2-1	
Mg (%)		0.1-0.4	
S (%)		0.1-0.4	
Fe (mg/kg)	< 50	100-500	> 500
Mn (mg/kg)	15-25	20-300	300-500
Zn (mg/kg)	10-20	27-150	100-400
Cu (mg/kg)	2-5	5-30	200-100
B (mg/kg)	5-30	10-20	50-200
Mo (mg/kg)	0.03-0.15	0.1-2.0	> 100
Cl (mg/kg)	< 100	100-500	500 (?) -1000
Ni (mg/kg)	< 0.1		

Sources: Jones (1991); Tisdale *et al.* (1997)

3. Functions and Deficiency Symptoms of Nutrients

3.1. Macronutrients

We shall discuss macronutrients one by one.

3.1.1. Nitrogen

Nitrogen is absorbed by plant roots as NO_3^- and in the case of rice, as NH_4^+ also. In the N-sufficient plants, its concentration varies from 1 to 5% (10,000 to 50,000 ppm or mg/kg) (Table 2). This nutrient is most often deficient in soil and is the one which frequently creates serious nutritional problems. Nitrogen is a major component of plant cell and cell wall, the latter containing as much as 5% N. Cell cytoplasm and organelles contain different amounts of N in combination with C, H, O, P and S.

Functions — The major functions of nitrogen are :

- It is an essential component of amino acids, proteins, nucleic acids, porphyrins, flavins, purines and pyrimidine nucleotides, flavin nucleotides, enzymes, co-enzymes and alkaloids. Nitrogen-containing chlorophyll in the presence of solar energy fixes atmospheric CO_2 as carbohydrates. Being a constituent of nucleic acids viz. Ribo Nucleic Acid (RNA) and Deoxyribo Nucleic Acid (DNA), nitrogen is responsible for the transfer of genetic code to the off-springs. The proteins are constituents of structural units and participate in catalysis of biochemical reactions.
- Nitrogen improves the quality of leafy vegetables and fodders.
- Nitrogen fertilization improves protein quality of the foodgrain by enhancing the proportion of glutamic acid, proline, phenylalanine, cystine, methionine and tyrosin and decreasing the amounts of lysine, histidine, arginine, aspartic acid, threonine, glycine, valine and leucine in the grain.

Deficiency Symptoms — Plants having less than 1% N-content are usually regarded deficient in N. Stunted growth is the manifestation of N-deficiency. Due to high mobility of N in plants, its deficiency symptoms first appear on the older leaves in the form of light green to pale yellow colouration (through proteolysis) whose intensity depends on the severity of N-deficiency. Reduction in flowering and crop yields and lower protein content are associated with N-deficiency.

Excessive Consumption — Under conditions of large N-availability, succulence of the plants increases; taller plants and heavier heads cause lodging. A nitrogen-rich, luxuriant succulent crop is more susceptible to insect, pest and disease attacks.

3.1.2. Phosphorus

Phosphorus is the second most abundant mineral element in the human body, making up for more than 20% of the body's minerals. Plant roots mostly absorb phosphorus as the dihydrogen orthophosphate ion ($H_2PO_4^-$), but under neutral to alkaline environments, it is also taken up as monohydrogen orthophosphate (HPO_4^{2-}) ion. There are reports of P getting absorbed in organic forms such as nucleic acids and phytins. In normal P-sufficient plants, P-content varies from 0.1% to 0.4% by weight, which is 1/5th to 1/10th of N or K content (Table 2).

Functions — Once inside a plant, P gets incorporated into nucleic acids (RNA and DNA), phosphoproteins, phospholipids, sugar phosphates, enzymes and energy-rich adenosine triphosphate (ATP) and adenosine diphosphate (ADP). The ATP and ADP are the energy currency of the plants as ATP stores 12 kcal energy per mole contained in two pyrophosphate bonds between three P molecules. Major processes involving ATP are generation of membrane electrical potentials, respiration, biosynthesis of cellulose, hemicellulose, pectins, lignins, proteins, lipids, phospholipids and nucleic acids. Because of these processes, P is involved in energy transfer, photosynthesis, transformation of sugars and starch, nutrient movement within the plant and transfer of genetic characteristics from one generation to the next.

Deficiency Symptoms — In general, plants having less than 0.1% or 1000 ppm P are designated as P-deficient (Table 2). Because of its faster mobility in plants, P gets easily translocated from older tissues to the meristematic tissues. Therefore, deficiency symptoms of P appear first on the older leaves. Phosphorus deficiency, being associated with the accumulation of carbohydrates, results in the production of dark-green colour leaves. Under P-deficiency, severe restriction occurs in the growth of plant tops and roots. In general, P-deficient plants are thin, erect and spindly with sparse and restricted foliage. Also, the development of lateral buds is suppressed, leaves become narrow, making an acute angle with the stem-axis and the foliage turns bluish-green. Under conditions of continued deficiency, older leaves become bronzed or develop reddish-purple tips and leaf margins.

3.1.3. Potassium

Plant roots absorb potassium as potassium ions (K^+). Its concentration in healthy plant tissues varies from 1% to 5%, which is more or less equal to that of N (Table 2). Potassium is a unique element in the sense that plants can accumulate it in abundant amounts without exhibiting any toxicity symptoms. This behaviour has been described as the luxury consumption. Also, potassium plays a regulatory role in plant metabolism and development but is not a structural component of the plant.

Functions — Following are the functions attributed to K in plant nutrition:

- It regulates the opening and closing of the stomata, which are essential for photosynthesis, water and nutrient transport, and plant cooling.
- It plays a major role in transport of water and nutrients throughout the plant in xylem. Under reduced K supply, translocation of NO_3^-, PO_4^{3-}, Ca^{2+}, Mg^{2+} and amino acids is hampered.
- It increases root growth and improves drought tolerance.
- It neutralizes organic anions and other compounds within the plant and helps in maintaining cytoplasmic pH within the range of 7 to 8, ideal for many enzyme reactions.
- It activates a large number of enzymes (numbering more than 60), by way of exposing the active reaction sites. This includes starch synthetase enzyme responsible for starch synthesis. Under high K-levels, starch moves efficiently from sites of production to storage. Potassium is responsible for the activation and synthesis of protein-forming nitrate reductase enzyme.

- It enhances the crop quality. High concentrations of available K improve physical qualities and shelf-life of fruits and vegetables.
- It reduces lodging of crops and enhances their winter-hardiness.
- It imparts disease resistance to crops.

Deficiency Symptoms — Deficiency symptoms of potassium develop first on the older leaves. Chlorosis along the leaf margins is followed by scorching and browning of tips of older leaves which gradually progresses inwards. In addition, under K-deficiency, slow and stunted growth of plants occurs and plants lodge rather easily. Potassium-deficient seeds and fruits are shrivelled.

3.1.4. Calcium

Calcium is a secondary nutrient element absorbed by the plant roots as calcium ions (Ca^{2+}). Calcium in Ca-sufficient plants ranges between 0.2% and 1.0%. Among all the nutrients, Ca is most abundant in plant-available forms in the soil. However, its deficiencies are more common in acid soils of the tropics.

Functions — The functions of calcium are:

- It is a constituent of calcium pectate in the cell wall and maintains the integrity of the membranes. In seeds, Ca is present as calcium phytate.
- It is important for the growth of meristems and functioning of the root tips.
- It protects the root cells against ion imbalance, low pH and toxic ions like Al.
- It neutralises the charges on the acidic molecules of phosphoric acid and organic acids, viz. citric acid, malic acid, oxalic acid, etc., which are injurious to plant growth.
- It plays a role in mitosis (cell division) and helps maintain the chromosome structure.
- It activates phospholipase, arginine kinase, amylase and adenosine triphosphatase (ATPase) enzymes.

Deficiency Symptoms — Usually plants having Ca-content less than 0.1% (or 1000 ppm) are regarded as calcium-deficient. Field scale occurrence of Ca-deficiency is seldom encountered because of its abundance in soil. Calcium is immobile in the plant and cannot be readily translocated from the older to the new leaves and hence, deficiency symptoms appear on the younger structures. Under Ca-deficiency, root system is stunted. Young leaves are often distorted, small and abnormally green. The Ca-deficient leaves become cup-shaped and crinkled and the terminal buds deteriorate with some break-down of petioles. Other symptoms include desiccation of terminal buds and weakening of the stem structure. *Blossom end rot* in tomatoes and *Bitter pit* in apples are the Ca-deficiency symptoms.

3.1.5. Magnesium

Magnesium is absorbed by plants as magnesium ions (Mg^{2+}). Its concentration in Mg-sufficient plants varies from 0.1% to 0.4%. A large part of Mg is associated with organic anions like malate. Magnesium is a constituent of chlorophyll as Mg-porphyrin with one atom of Mg bound to four pyrrole rings.

Functions — The functions of magnesium are:

- Magnesium, being a constituent of chlorophyll, is indispensable in the following reaction of photosynthesis:

$$6CO_2 + 6H_2O \xrightarrow[\text{Phosphate energy}]{\text{Chlorophyll, light}} C_6H_{12}O_6 + 6O_2 \qquad \ldots(1)$$

- It is an activator of many enzyme systems involved in carbohydrate metabolism and synthesis of nucleic acids.
- It promotes uptake and translocation of phosphorus and movement of sugars within the plants.

Deficiency Symptoms — Magnesium is mobile within the plants with its symptoms of deficiency appearing on the older leaves. The Mg-deficient plants usually have less than 0.1% Mg. Magnesium-deficiency symptoms manifest themselves in terms of interveinal chlorosis and streaked or patchy effects on older leaves. Affected leaves usually turn small in final stages and curve upwards at margin. Under acute deficiency, the affected leaf tissues dry up and may even die. Interveinal chlorosis with tints of red, orange and purple colours is observed in some of the vegetable crops. 'Grass tetany' is a nutritional disorder common in cattle grazing on Mg-deficient pastures well fertilized with potassium.

3.1.6. Sulphur

Sulphur is absorbed by plants as the sulphate ions (SO_4^{2-}). There are some reports that S is absorbed by the foliage as SO_2. Like P and Mg, the concentration of S in healthy plants ranges from 0.1% to 0.4%. In view of large field scale occurrences of deficiencies in India, sulphur has been described as the fourth major nutrient after N, P and K.

Functions — The functions of sulphur are:

- Sulphur is an essential constituent of S-containing amino acids, viz. cysteine, cystine and methionine.
- Sulphur is a constituent of ferrodoxin-containing nitrogenase, which takes part in the biological nitrogen fixation (BNF) and other electron transfer reactions.
- It is involved in the metabolic activities of vitamins, biotin, thiamine and coenzyme A.
- It is involved in the synthesis of glucosides in mustard oil.
- It plays a major role in increasing the oil quality in oilseed crops.

Deficiency Symptoms — Depending upon the crop, plants having less than 0.1 to 0.2% S-content suffer from S-deficiency. Crop plants having N:S ratios more than 16:1 also can be suspected to be deficient in S. Sulphur deficiencies first appear on the younger growths as S is immobile in the plants. The fading of the normal green colour of the young leaves, followed by chlorosis is the most common deficiency symptom. In *Brassicas*, which are more susceptible to S-deficiency, the lamina is restricted, leaves show cupping owing to the curling of the leaf margins and arresting of the growing points. The older leaves become puckered with inward raised areas between the veins. The older foliage develops orange or reddish tints and may shed prematurely.

3.2. Micronutrients

Let us now get some idea about micronutrients, their functions and deficiency symptoms.

3.2.1. Iron

Iron is taken up as ferrous ions (Fe^{2+}) by plants. Its concentration in the range of 100-500 mg/kg in mature leaf tissues is regarded sufficient for optimum crop production. Iron is a transition metal, exhibits two oxidation states— Fe(II) and Fe(III) — in plants and forms complexes with organic ligands. Variable valency of iron assigns it a role in biological redox systems.

Functions — The functions of iron are:

- Iron is a constituent of two groups of proteins, viz. (a) Heme proteins containing Fe porphyrin complex as a prosthetic group: Cytochrome oxidase, catalase, peroxidase, leghemoglobin, and (b) Fe-S proteins in which Fe is coordinated to the thiol group of cysteine or to inorganic S: Ferrodoxin
- It activates a number of enzymes, including aminolevolinic acid synthetase and coproporphyrinogen oxidase.
- It plays an essential role in the nucleic acid metabolism.
- It is necessary for synthesis and maintenance of chlorophyll in plants.

Deficiency Symptoms — Plants having less than 50 ppm of Fe are usually classified as iron-deficient. It has been established that Fe^{2+}-content of the plant rather than the total Fe-content resolves Fe-deficiency better with 30 ppm Fe^{2+} being critical level of Fe-deficiency. Deficiency of iron results in interveinal chlorosis appearing first on the younger leaves with leaf margins and veins remaining green (Figure 1). Under conditions of severe Fe-deficiency, growth cessation occurs with the whole plant turning necrotic.

3.2.2. Manganese

Manganese is absorbed by the plants as manganous ions (Mn^{2+}). Healthy Mn-sufficient mature plants contain 20 to 300 ppm of Mn. Manganese, a transition metal, is present in plants

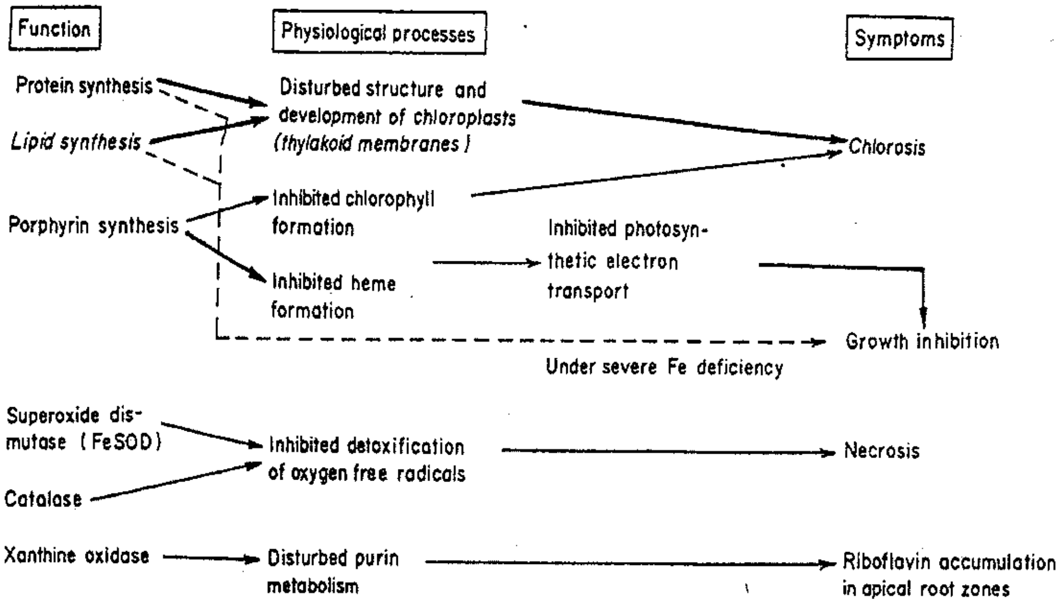

Figure 1. Possible relationship between physiological functions of Fe and visual symptoms of Fe-deficiency

Source: Romheld and Marschner (1991)

in Mn(II) form but is easily oxidizable to Mn(III) and Mn(IV) forms. Because of its variable redox status, Mn plays an important role in the photosynthesis and detoxification of superoxide free radicals.

Functions — The functions of manganese are:

- Manganese is an integral component of the water-splitting enzyme associated with photosystem II. Because of this role, Mn-deficiency is associated with adverse effects on photosynthesis and O_2 evolution.
- It is a constituent of superoxide dismutase (Mn-SOD). Role of Mn assumes criticality because Mn-SOD (present in mitochondria, peroxisomes, and glyoxysomes) protects cells against the deleterious effects of superoxide free radicals.
- Manganese has a role in tricarboxylic acid cycle (TCA) in oxidative and non-oxidative decarboxylation reactions with nicotine adenine diamide (NAD) malic enzyme catalyzing the reaction:

  $$\text{Malate} + \text{NADP}^+ \rightarrow \text{Pyruvate} + \text{NADPH} + \text{H}^+ + \text{CO}_2 \quad \ldots(2)$$

  and isocitrate dehydrohgenase catalyzing the reaction:

  $$\text{Isocitrate} + \text{NADP}^+ \rightarrow \text{Oxalosuccinate} + \text{NADPH} \quad \ldots(3)$$

Deficiency Symptoms — Manganese-deficient plants contain less than 25 ppm Mn. Deficiency symptoms of Mn are more severe on middle leaves than on the younger ones because Mn is preferentially translocated to the younger tissues. Interveinal chlorosis in dicotyledonous plants is characterized by the appearance of chlorotic and necrotic spots in the interveinal areas. In the monocotyledonous plants like cereals, manganese-deficiency symptoms appear as greenish grey spots, flecks and stripes on the more basal leaves (Grey speck). Chlorotic leaf areas soon become necrotic and turn red, reddish-brown or brown. Symptoms of Mn-deficiency are popularly known as: grey speck of oats, speckled yellow of sugarbeet, marsh spot of peas, *pahala* blight of sugarcane and frenching of tung trees.

3.2.3. Zinc

Plants absorb Zn as zinc ions (Zn^{2+}). Zinc-sufficient plants contain 27 to 150 ppm Zn in mature tissues. Since it does not have variable valency, it has no role in influencing redox processes directly.

Functions — The functions of zinc are:

- Zinc is a constituent of three enzymes. These are listed along with their biological role in the Table 3.

Table 3. Zinc-containing enzymes and their biological role

Zinc-containing enzyme	Biological role
Carbonic anhydrase (CA)	Localized in the cytoplasm and chloroplasts; facilitates transfer of the CO_2/HCO_3^- for photosynthetic CO_2 fixation. Under acute Zn-deficiency, photosynthesis is inhibited. Carbonic anhydrase is used in many cases for diagnosing Zn-deficiency.
Alcoholic dehydrogenase	Plays an important role in anaerobic root respiration and catalyses the conversion of acetaldehyde to ethanol. Thus, under waterlogged conditions, anaerobic root metabolism is impaired in the case of Zn-deficiency.
Superoxide dismutase (SOD)	Zinc-Cu-SOD detoxifies superoxide radicals and protects the lipids and proteins of the membranes against oxidation. Zn-deficiency characterized by reduced activity of SOD enzyme enhances the oxidation processes, viz. lipid and oxidative IAA degradation

- Zinc is involved in the synthesis of indole acetic acid, metabolism of gibberellic acid and synthesis of RNA .
- Because of its preferential binding to sulphydryl group, Zn plays an important role in the stabilization and structural orientation of the membrane proteins.
- Zinc influences translocation and transport of P in plants. Under Zn-deficiency, excessive translocation of P occurs, resulting in P-toxicity.

Deficiency Symptoms — Plants containing less than 15 ppm Zn are regarded deficient in Zn. Common deficiency symptoms of Zn are interveinal chlorosis, first appearing on the young leaves, reduction in the size of young leaves, which are often clustered or borne very closely, bronzing, and purple, violet reddish brown or brown coloration of the foliage.

In dicotyledonous plants, symptoms include short internodes (rossetting) and decrease in leaf expansion (little leaf). Names given to Zn-deficiency symptoms include: *Khaira* disease of rice reported from India (also called *Hadda* disease in Pakistan, *Akagare type II* in Japan, *Taya-taya* and *Apaya-pula* in Philippines), *white bud* of maize, *mottle leaf* (*little leaf*) or *frenching* of citrus and *little leaf* of cotton. *Khaira* disease-inflicted rice fields give a coppery brownish appearance and are characterized by the missing hills.

The first symptoms of Zn-deficiency appear in 3 to 4 weeks old seedlings when the young leaves develop reddish-brown pigmentation. This pigmentation which first appears in the middle of the leaf intensifies and covers the entire lamina. Tissues become papery, necrotic and under conditions of acute deficiency, whole mass collapses with arresting of the plant growth.

3.2.4. Copper

Like other micronutrient cations, copper is absorbed by plant roots as cupric ions (Cu^{2+}). The concentration of Cu in Cu-sufficient plants varies from 5 to 30 ppm and its toxicity occurs when Cu concentration is between 20 and 100 ppm (Table 2). Copper is a transition element existing in the plants as a component of a large number of proteins and enzymes as Cu(II) and can change its valency as per equilibrium:

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \qquad \ldots(4)$$

Functions — Copper is a constituent of a number of enzymes. These are listed along with their biochemical roles in Table 4.

- Copper is important in imparting disease resistance to the plants.
- It enhances the fertility of male flowers.

Deficiency Symptoms — Plants having less than 5 ppm Cu are regarded as Cu-deficient. Male flowers' sterility, delayed flowering and

Table 4. Copper-containing enzymes and their boichemical role

Copper-containing enzyme	Biochemical role
Plastocyanin	Located in chloroplasts, it is a component of electron system of photosystem II, and therefore influences phtosynthesis
Superoxide dismutase (Cu-Zn-SOD)	Located in cytoplasm, mitochondria and chloroplasts, it is involved in detoxification of superoxide radicals generated during photosynthesis. In glyoxysomes, Cu-Zn-SOD is thought to be involved in the control of peroxidation of lipids and hence, senescence.
Diamine oxidase	Located in apoplasts of epidermis and xylem tissues, it functions as the H_2O_2-delivery system for peroxidase activity in lignification.
Polyphenol oxidase	Involved in lignin biosynthesis. A decrease in polyphenol oxidase activity associated with Cu-deficiency results in delayed flowering and late maturity.
Ascorbate oxidase	Occurring in cell walls and cytoplasm, it catalyses the oxidation of ascorbic acid to dehydroascorbic acid. Cu^{2+} component of the enzyme reduces molecular oxygen to H_2O. Reduction in the activity of ascorbate oxidase with reduction in Cu supply presents it as a sensitive indicator for diagnosing Cu-deficiency.

senescence are the most important effects of Cu-deficiency. Chlorosis of the younger shoot tissues, white tips, reclamation disease, necrosis, leaf distortion, and die-back are the characteristic Cu-deficiency symptoms. Necrosis of the apical meristems results in elongation of the shoots in cereals and auxilliary shoots in dicotyledonous plants.

3.2.5. Molybdenum

Molybdenum is the only heavy transition metal taken up by the plants as molybdate ions (MoO_4^{2-}). A healthy Mo-sufficient plant contains 0.1 to 2 ppm of Mo. In the plant system under oxidative environments, it exists as Mo(VI) and undergoes reduction to Mo(V) and Mo(IV) forms. Ability of Mo to exist in variable valence states imparts it a biochemical role.

Functions — Molybdenum is a component of nitrate reductase, nitrogenase, xanthine oxidase/ dehydrogenase and sulphite oxidase. Because of these enzymes, Mo has the following functions:

- Biological nitrogen fixation (BNF) is catalysed by the Mo-containing enzyme, nitrogenase (essentially comprising of Mo-Fe-S protein and a Fe-S cluster protein) which directly transfers electrons to N_2. Because of its involvement in BNF, Mo requirement of nodulated legumes is particularly high.
- Nitrate is reduced by the nitrate reductase (NR) enzyme in cytoplasm by transfer of electrons from Mo to NO_3^-. Owing to close relationship between Mo supply, nitrate reductase activity (NRA) and plant growth, NRA has been used as an indicator of the status of Mo in plants.
- Molybdenum is involved in protein biosynthesis through its effect on ribonuclease and alanine aminotransferase activity.
- Molybdenum affects the formation and viability of pollens and development of anthers.

Deficiency Symptoms — The critical concentration of Mo-deficiency in plants is usually less than 0.1 ppm. Molybdenum deficiencies resemble the N-deficiencies. In plants with reticulate venation, the earlier effects of Mo-deficiency appear as chlorotic mottlings between the veins on old or middle leaves all over the surface. In *Brassica* spp, symptoms appear on 3 to 4 week-old plants. The Mo-deficient cauliflower plants exhibit chlorotic mottling and cupping of the middle leaves. Severely affected leaves show scorching and withering starting from the margins and extending to the entire lamina, leaving behind only petioles. Molybdenum deficiency in cauliflower is termed as whip-tail.

3.2.6. Boron

Boron is absorbed by the plants mainly as boric acid (H_3BO_3). However, it can also be absorbed in some of its anionic forms, viz. dihydrogen borate ($H_2BO_3^-$), monohydrogen borate (HBO_3^{2-}), and borate (BO_3^{3-}), under high pH conditions. Normal boron–sufficient plants have B-contents ranging from 10 to 200 ppm. Boron is neither a constituent of enzymes nor it activates any of the enzymes. Most important property of boron (boric acid) is to form stable complexes with organic compounds with cis-diol configuration. Boron performs the following functions:

- It is responsible for the cell wall formation and stabilization, lignification and xylem differentiation. As a consequence, B-deficiency causes changes in chemical composition and ultrastructure of cell wall, accumulation of toxic phenols, inhibition of lignin synthesis and a decrease in the production of indole acetic acid (IAA)(Figure 2). Decrease in IAA is responsible for the induction of Ca-deficiency.
- It imparts drought tolerance to the crops. Regular boric acid sprays help in mitigating harmful effects of drought.
- Boron plays a role in pollen germination and pollen tube growth.
- It facilitates ion uptake by way of increasing the activities of plasma-membrane bound H^+-ATPase (H^+-adenosine triphosphatase).
- It facilitates transport of K in guard cells as well as stomatal opening.

Deficiency Symptoms — Plants having B-concentrations of the order of 5 to 30 ppm are suspected to be B-deficient. Critical deficiency range of B varies from 5 to 10 ppm in graminaceous plants to 20 to 70 ppm in most of the dicotyledonous plants. Boron-deficiency symptoms become conspicuous on the terminal buds or youngest leaves, which become discoloured and may die under acute conditions of B-deficiency. Internodes become shorter and give a bushy or rosette appearance. Increased diameter of the stem and the petioles gives rise to the typical cracked stem of celery. Typical names given to B-deficiency in different crops are:

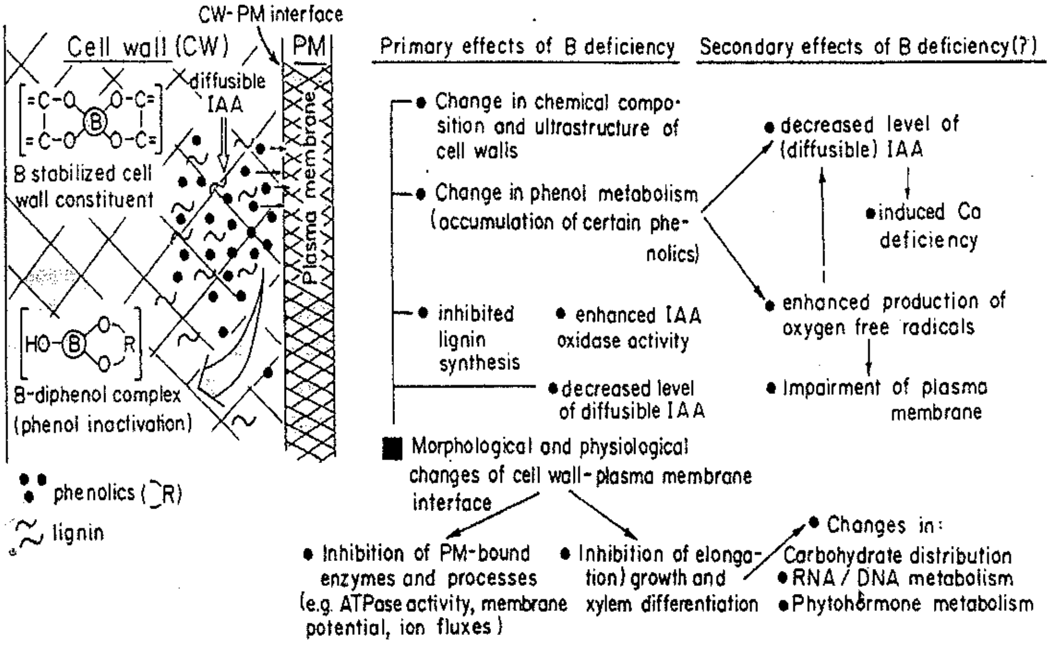

Figure 2. Role of boron in cell metabolism, and primary and secondary effects of B-deficiency

Source: Romheld and Marschner (1991)

- Heart rot of sugarbeet and mangold
- Browning or hollow stem of cauliflower
- Top sickness of tobacco
- Internal cork of apple.

3.2.7. Nickel

Nickel is absorbed by plants as nickel ions (Ni^{2+}). Its concentration in Ni-sufficient plants varies from 0.1 to 10 ppm. It exists in Ni(II) state but can also assume Ni(I) and Ni(III) states.

Functions — The various functions of nickel are :

- Nickel is associated with nitrogen metabolism by way of influencing urease activity. In systems where urea is used as the sole N fertilizer for foliar spray and Ni-supply is poor, lower urease activity causes urea toxicity to the foliage and leads to severe necrosis of the root tips.
- In free-living *Rhizobia*, adequate Ni-supply ensures optimum hydrogenase activity.
- It facilitates transport of nutrients to the seeds or grains.

Deficiency Symptoms — Critical level of Ni-deficiency in barley shoots is 0.1 ppm, as concentrations below this are accompanied by reduction in drymatter weight, decrease in amino acid content and accumulation of nitrates. Characteristic deficiency symptoms of Ni have not yet been defined adequately.

3.2.8. Chlorine

Chlorine is ubiquitous in nature. It is absorbed as chloride ions (Cl^-) by the plants. Normal healthy plants have Cl-content ranging from 100 to 500 ppm. It has often been neglected because it is present in abundance and is also supplemented through a large number of fertilizer carriers like muriate of potash, etc. and its deficiencies have not been reported from any where in India.

Functions — The various functions of chlorine are :

- It plays a major role in osmoregulation (cell elongation, stomatal opening) and charge compensation in higher plants.
- It acts as a cofactor in Mn-containing water splitting enzyme of photosystem II.
- Chlorine in abundance suppresses the plant diseases, viz. grey leaf spot in coconut palms, take-all and common root rot in wheat, common root rot and *Fusarium* root rot in barley, stalk rot in corn, stem rot and sheath blight in rice, hollow heart and brown centre in potatoes, *Fusarium* yellows in celery, and downy mildew in millet.
- Chlorine supply improves the nutritional quality of vegetables by preferentially lowering the NO_3^- -N concentration in tissues.

Deficiency Symptoms — Plants having less than 100 ppm Cl are usually designated as deficient. Deficiency symptoms of chlorine (that include wilting of leaves, curling of leaflets and chlorosis) are similar to that of Mn-deficiency.

3.3. Identification of Deficiency

A brief key to deficiency symptoms developed by Finck (1992) is given in Table 5. However, a correct interpretation of deficiency symptoms requires a great deal of field experience and should always be corroborated by the soil and plant analyses. It is also desirable to understand the roles of such factors that might produce symptoms similar to those of the other nutrients.

4. Beneficial Elements

4.1. Sodium

Sodium accumulates preferentially in the vacuoles and plays a role in maintaining the solute potential of the cell. Sodium can replace some of the essential functions of potassium in plants like sugar beet, table beet, turnip, etc. It improves the water balance of plants under limited water supply or under arid climate.

4.2. Silicon

Silicon has the beneficial role in rice and sugarcane crops. It contributes to rigidity and strengthening of the cell wall. It enhances the physiological availability of zinc in plants and counteracts zinc-deficiency-induced phosphorus toxicity. Silicon stimulates growth and yield

Table 5. A brief key to nutrient deficiency symptoms

Nutrient	Deficiency symptoms
	Symptoms appearing first on older leaves
Nitrogen	Chlorosis starting from leaf tips
Potassium	Necrosis on leaf margins
Magnesium	Chlorosis mainly between veins (which remain green)
Manganese	Brownish, greyish, whitish spots (e.g. on cereals)
Phosphorus	Reddish colour on green leaves or stem
	Symptoms appearing first on younger leaves
Sulphur	Mottled yellow-green leaves with yellowish veins
Iron	Mottled yellow-green leaves with green veins
Manganese	Brownish black spots (e.g. on legumes, potatoes)
Copper	Youngest leaf has white tip
Boron	Youngest leaf is brownish or dead (e.g. on beet)

Source: Finck (1992)

of cereals by indirect actions such as decreasing susceptibility to lodging, decreasing the incidence of infections with root parasites and pathogens, and preventing toxicity of iron and manganese.

4.3. Cobalt

Cobalt (Co) enhances N_2 fixation in legumes and improves the nutritional quality of the forage crops for ruminants. It is the metal component of coenzyme cobalamin; in *Rhizobium* and *Bradyrhizobium* spp, activity of methionine synthetase, ribonucleotide reductase and methylmalonyl-coenzyme A mutase are dependent on cobalamine.

4.4. Selenium

The chemistry of selenium (Se) is similar to that of S with Se exisiting in Se^{2-}, Se^{4+} and Se^{6+} states. Sulphate and selenate compete for the common uptake sites in the roots; resultantly higher SO_4^{2-} supply can strongly reduce uptake of Se. Unlike plants, Se is an essential element for animals. To avoid Se–deficiency in animals, the concentration of Se in diets should be 0.1 to 0.3 mg/kg dry matter. In livestock, symptoms of Se–deficiency include white muscle disease or nutritional muscular dystrophy.

4.5. Aluminium

In plant species having high tolerance and capacity for aluminium (Al), the beneficial effects of Al on growth accrue from its ability to alleviate toxicity of P, Zn and Cu.

4.6. Vanadium

Vanadium (V) favours nitrogen fixation in leguminous plants. The chemical behaviour of V and Mo is similar. It is thought that V might partly substitute the functions of Mo in nitrogenase system of *Azotobacter*.

Other elements being investigated for the beneficial effects on plants include bromine, iodine, lead, cadmium, chromium, fluorine, etc. but no conclusive evidence has been found so far.

5. Concepts of Nutrient Availability

Before dealing with the concepts of nutrient availability it is pertinent to describe /define the Liebig's law of minimum, the Mitscherlich's sufficiency concept, and the law of maximum by Wallace and Wallace.

5.1. Liebig's Law of Minimum

This law states that "the nutrient present in the least relative amount is the limiting nutrient". In its extreme form, it implies that "even if all but one of the essential elements be present, the absence of that one constituent renders the crop barren". Significance of this law can be visualized by imaging a barrel having staves of different heights (Figure 3). As hypothesized by Tandon and Kimmo (1993), such a barrel can only hold water up to the

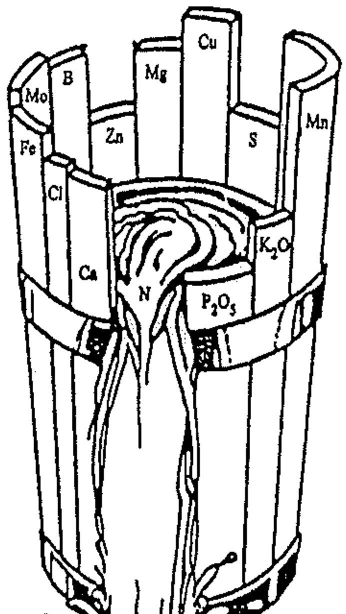

Figure 3. Liebig's Law of Minimum – A pictorial depiction

height of its smallest stave. Another way to visualize this is to imagine a bucket with holes at different levels. The lower level of water in the bucket will be controlled by the lower-most hole. If this hole is closed, then the water level will be controlled by the hole above it. For the barrel or bucket to hold water to its full capacity, all the staves should be of full height with no holes. Similarly, for a crop to produce to its full potential, all the nutrients and other factors of production should be at the sufficiency (optimum) level, meaning thereby that the nutrients should be neither at the deficient nor toxic level. In the case depicted in Figure 3, N is the most limiting nutrient, followed by P, K, Zn and S in that sequence. If N-deficiency is removed, then P will limit the yields. Removal of N and P constraints makes K limiting and so on till all are supplied in optimum combination. Following example further illustrates the law of minimum.

Quantitatively, say if a soil contains enough N for 5 t wheat drymatter (DM)/ha, enough P for 8 t and enough K for 10 t/ha, then 5 t/ha of wheat DM will be all that could be produced and N will be the "limiting" nutrient.

5.2. Mitscherlich's Law

Mitscherlich's law of physiological relationships states that the "yield can be increased by each single growth factor even when it is not present in the minimum as long as it is not present in the optimum". As per Mitscherlich's growth law "increase in yield of a crop as a result of increasing a single growth factor is proportional to the decrement from the maximum yield obtainable by increasing that particular growth factor". It implies that plant growth follows a diminishing increment type of curve, known as the "yield curves" (Figure 4).

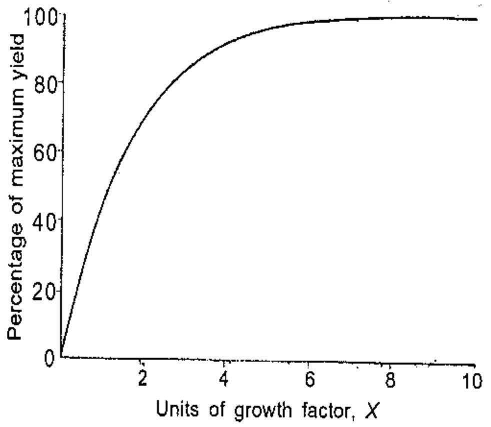

Figure 4. Percentage of maximum yield as a function of increasing additions of a growth factor, *x*

Mitscherlich related the potential yield of a crop to the amount of a given nutrient with the following equation:

$$\log (A - y) = \log A - Cb \quad \ldots(5)$$

where, A is the potential yield of the crop when the nutrient is not deficient, y is the yield when b amount of a given form of nutrient is present and C is the proportionality constant. Mitscherlich asserted that the value of 'C' was constant for widely-varying conditions. Assertion of constancy of 'C' represents a major concept of the nature of soil fertility, which *inter alia* reads "One deficient amount of a nutrient always produces the same proportion (same percentage) of that yield otherwise obtainable when the nutrient is adequate".

According to the Percentage Yield Concept of Baule (1918), when more than one nutrient is deficient, the final percentage sufficiency is the product of the individual sufficiency. For example, if phosphorus is adequate for 80% of the yield and potassium is adequate for 70% of the yield, then the final yield is 70% of the 80% yield, that is 56% of the yield obtainable when both the nutrients are adequate.

5.3. *Law of Maximum of Wallace and Wallace*

This law states that "when the need is fully satisfied for every factor required in the process, the rate of the process can be at its maximum potential, which is greater than the sum of the individual parts because of the sequentially additive interactions".

These basic laws have been used while developing the concepts of nutrient availability.

5.4. *Bray's Concept of Nutrient Availability*

According to Bray (1938), available forms of nutrients are those forms whose variations in amounts in soil are responsible for significant variations in yield and yield response. Bray postulated that the availability of these forms involves not only their chemical and physical nature, but also the ability of a plant to "forage" for them with its root system. This definition is comprehensive in the sense that it laid the foundation for characterization of the reservoir of available nutrients in soil under the influence of varying physical and biological environment.

5.5. *Bray's Concept of Nutrient Mobility*

Bray (1954) defined mobility as the "overall process whereby nutrients reach the sorbing root surfaces, thereby making possible their sorption into the plant". Thus, mobility involves the solution or exchange of the nutrient as well as the movement to the root surface. In a contemporary knowledge on plant nutrient, Bray recognized and categorized the nutrients into two categories. Anions like nitrate, chloride or bicarbonate, which are not adsorbed by the solid phase, remain in solution and are carried away to longer distances in response to their adsorption by the plant roots. Such nutrients were classified as "mobile" nutrients. Cations like K, Mg and Ca are held on the negatively charged surface of the colloidal clays and organic matter in the soil as exchangeable cations. These can be replaced by, and are in equilibrium with, the cations in soil solution. Concentration of these cations in soil solution is controlled by (i) kind and amount of the electrolytes in soil solution, (ii) the amount of the different exchangeable cations present, and (iii) their relative ease of release (Bray 1942). Phosphate ions are held in the soil by either anion exchange or ligand exchange or adsorbed or precipitated as sparingly soluble phosphates of Fe, Al, Ca, etc. Chemical equilibrium, dictated by different competing chemical reactions, determines the concentration of P in soil solution. Amounts associated with the solid phases, earlier in the exchangeable or labile forms, which are positionally closer to the soil surfaces, are readily available for absorption by the plant roots. Larger the distance of these ions from the absorbing root surfaces, more the time they take to reach the plant roots because of the restrictions imposed by the colloidal solid phases. Such nutrients are termed as the "immobile" nutrients. Classification of nutrients as mobile and immobile forms is given in Table 6.

Nutrient alone *per se* cannot be classified as either mobile or immobile. It is its form which is either mobile or immobile. For example, NO_3^- is mobile while NH_4^+ is immobile in the soil in spite of both being the forms of N.

Bray (1954) distinguished between the 'root system sorption zone' and 'root surface sorption zone' (Figure 5). He postulated that the mobile nutrients depend on the total amount available in the soil (root system sorption zone). For example, if on a relative scale, the total amount of available nutrient is enough to produce 2 t wheat/ha, and under the best management practices, the potential yield which can be realized is 5 t/ha, then the soil will

Table 6. Mobile and immobile nutrients in soils and plants

Plant		Soil	
Mobile	Immobile	Mobile	Immobile
Cl	B	H_3BO_3, $H_2BO_3^-$	NH_4^+
Mg	Ca	Cl^-	Ca^{2+}
Mo	Cu	NO_3^-	Cu^{2+}
N	Fe	SO_4^{2-}	Fe^{2+}/Fe^{3+}
P	Mn		MoO_4^{2-}
K	Zn		$H_2PO_4^-$,
	S		HPO_4^{2-}
			Mg^{2+}
			Ni^{2+}
			K^+

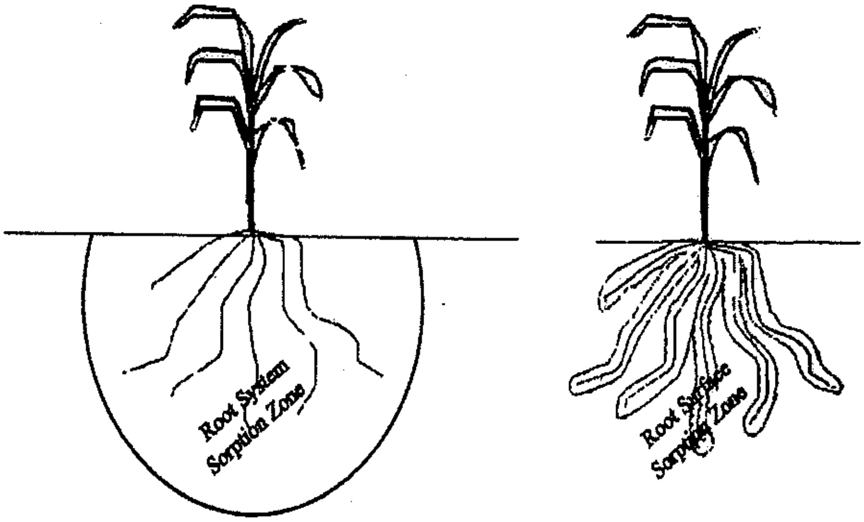

Figure 5. The root system(mobile nutrients) and root surface sorption zones (immobile nutrients) as proposed by Bray (1954) for nutrient management depending on mobility

produce only 2 t/ha, until the externally added amount is supplied optimally. Thus by implication, the mobile nutrients obey the Liebig's law of minimum.

On the other hand, Bray demonstrated that for the immobile nutrients, the total available amount *per se* is not important; what really is significant is the amount present in the root surface sorption zone and its possibility of transfer to plant root surface as a consequence of absorption by the plant root.

Integrating the concept of nutrient availability with mobility, Barber (1995) defined the available or bio-available nutrient as the "one that is present in a pool of ions in the soil and can move to the plant root during plant growth if the root is close enough". Operationally available nutrient is the one that is present (a) in a form that can be absorbed by the plants, and (b) in a pool of nutrients having an effective diffusion coefficient larger than 10^{-12} cm^2/s. Nielsen (1995) described bio-available nutrient as the one that is present in a pool of available nutrients and is close enough to arrive at a nutrient and water absorbing root surfaces during the period of (say) ten days.

Following illustrative example demonstrates the existence of root sorption zone for mobile NO_3^- and root surface sorption zone for $H_2PO_4^-$. Average diffusion distance (ΔX) is given by the Equation (6):

$$\Delta X = \sqrt{2D_e t} \qquad \ldots(6)$$

where, D_e is the effective diffusion coefficient (cm^2/s) and t is the time (s) for which diffusion occurs. Using Equation (6), the diffusion distances moved by different nutrient ions are given in Table 7.

According to Barber (1995), the available pool of the nutrient is the one having $D_e > 10^{-12}$ cm^2/s. For a nutrient to be bio-available, it will have to move a distance of 0.0013 cm in 10 days $(\Delta X = \sqrt{2\times10^{-12}\times10\times24\times60\times60} = 0.0013\,\text{cm})$.

This diffusion distance can be used for quantification of the soil volume capable of feeding the root having a known density [length of the root per unit of soil volume (Lv), cm/cm^3)] and root radius for both mobile nitrate (NO_3^-) and immobile phosphate ($H_2PO_4^-$) nutrients.

As shown in Table 7, distance moved by NO_3^- and $H_2PO_4^-$ ions in 10 days is 1.3 cm and 0.04 cm, respectively. Let the density of roots in soil (L_V) be 5 cm per cm^3 of the soil and the average root radius be 0.01 cm. In the case of phosphate, radial distance from the centre of root axis which could be explored by root for P will be 0.05 cm [0.04 cm (diffusion distance) + 0.01 cm (root radius) = 0.05 cm]

Volume of soil explored for P by the root

$$= Lv.\pi.\ r^2 = 5\,{cm}/{cm^3} \times \pi \times (0.05\ \ cm)^2$$

$$= 5\times3.14\times\left(5\times10^{-2}\right)^2 = 0.04\,{cm^3}/{cm^3}$$

$$= 4\%$$

Table 7. Distance moved by the ions through diffusion in 10 days

Diffusing ion	Diffusion coefficient (D_e) at field capacity (cm^2/s)	Diffusion time in 10 days (10x24x60x60 s)	Distance moved by diffusion (cm)
Nitrate	1×10^{-6}	8.64×10^5	1.30
Potassium	1×10^{-7}	8.64×10^5	0.40
Borate	1×10^{-7}	8.64×10^5	0.40
Calcium	1×10^{-8}	8.64×10^5	0.13
Magnesium	1×10^{-8}	8.64×10^5	0.13
Phosphate	1×10^{-9}	8.64×10^5	0.04
Manganese	1×10^{-9}	8.64×10^5	0.04
Zinc	1×10^{-9}	8.64×10^5	0.04
Molybdate	1×10^{-9}	8.64×10^5	0.04
Iron	1×10^{-10}	8.64×10^5	0.013
For any ion to be available	Needed D_e is 1×10^{-12}	8.64×10^5	0.0013

It implies that only 4% of the soil volume is explored for P or in other words 4% of the available-P is bioavailable over a period of 10 days. Suppose plant root has profuse root hairs and extends the radial distance around the root by 0.05 cm, then the total radial distance from the centre of the root will be 0.10 cm (0.01+0.04+0.05 = 0.10 cm). Volume of the soil explored by such a root with root hairs for P will be = $5 \times 3.14 \times (1 \times 10^{-1})^2 = 0.16\ cm^3/cm^3$ or 16% of available-P will be bio-available over a period of 10 days. This 4-16% of the soil volume is root surface absorption zone.

The case for nitrate ions could be treated as follows:

Distance moved in 10 days = 1.3 cm
Root density = 5 cm/cm^3
Radial distance from the axis of the root =
1.3 cm + 0.01 cm = 1.31 cm
Volume of soil explored for NO_3^- by root =
$5\ cm/cm^3 \times 3.14 \times (1.31\ cm)^2$
$= 26.9\ cm^3/cm^3$

It means that the root is able to explore 26.9 times the volume of the soil, which implies that whole of nitrate is bio-available in 10 days. Or in other words, mobile nutrient can be fed from the entire soil.

We can find out how much of the root density is sufficient to explore whole of the soil volume for NO_3^-. If root density capable of exploring the entire soil is taken as y, then the entire relationship assumes the form:

$$y\ (cm/cm^3) \times 3.14 \times (1.31\ cm)^2 = 1$$

or

$$y = 1 \times \frac{1}{3.14} \times \frac{1}{(1.31\,cm)^2}$$
$$= 0.19\ cm/cm^3$$

Thus, for obtaining all the available NO_3^-, root density needed is only 0.19 cm/cm^3. In reality, root density is much higher under field conditions. It shows that the mobile nutrient explores the whole soil.

6. Nutrient Movement in Soil

Transpiration of water by plants induces the movement of water from soil to plant. Nutrients which are dissolved in soil solution move to the plant roots with water in response to the hydraulic gradient created by the roots as a result of continuous absorption of water. However, differential requirements of nutrients *vis-a-vis* water by plants result in either accumulation or depletion of nutrients in the vicinity of root surface, thereby creating concentration gradients which induce the additional flow of nutrients either away from the root surface or towards it.

There are two separate processes involved in the movement of nutrients to plant roots. The movement of soluble nutrients with the soil solution can occur over much larger distances per unit of time than movement of nutrients through the soil solution. Movement of the nutrients with water is known as 'mass flow' and the movement through water as 'diffusion'. In addition, growing plant roots move

Table 8. Relative significance of root interception, mass flow, and diffusion in supplying corn with its nutrient requirement from a fertile Alfisol silt loam

Nutrient	Amount needed for 9500 kg grain/ha	Approximate amount supplied by		
		Root interception (%)	Mass flow (%)	Diffusion (%)
Nitrogen	190	2	150	38
Phosphorus	40	1	2	37
Potassium	195	4	35	156
Calcium	40	60	150	0
Magnesium	45	15	100	0
Sulphur	22	1	65	0

Source: Barber (1995)

into the soil and displace it. In the process, roots come in contact with the soil and intercept the nutrients from the soils through contact exchange. Thus, three mechanisms recognized for nutrient movement are: (i) mass flow, (ii) diffusion, and (iii) root interception; their relative significance is given in Table 8.

6.1. Mass Flow

Mass flow is the movement of nutrients through the soil to the root in the convective flow of water caused by the plant water absorption. The rate of nutrient transfer by mass flow (J) is given by the rate of water flux into the root (v) and the concentration of the ion in solution (C_i):

$$J = v \times C_i \qquad ...(7)$$

The average concentrations of Ca, K and P in soil solution of agricultural soils are: Ca, 10^{-2}; K, 10^{-3} to 10^{-4}; and P, 10^{-5} to 10^{-6} moles per litre. If a crop, producing a drymatter of 10 t/ha uses 300 litres of water to produce one kilogram of drymatter during crop growth, this amount of water would carry about 1200 kg Ca, 12-120 kg K and 0.9-9 kg P. The computation of these figures is shown for Ca as an example.

Total dry matter produced = 10 t/ha
= 10×10^3 kg/ha
= 10^4 kg/ha

Amount of water used for producing one kg of dry matter = 300 L

Amount of water used for producing 10^4 kg of dry matter = $10^4 \times 300$ L
= 3×10^6 L

Concentration of Ca in soil solution = 10^{-2} M/L
= $10^{-2} \times 40$ g/L
= 4×10^{-1} g/L

Amount of Ca moved along with water to plant root = 3×10^6 L $\times 4 \times 10^{-1}$ g/L
= 12×10^5 g
= 12×10^2 kg
= 1200 kg

Since amount of water transpired is for one hectare, hence Ca moved by mass flow is 1200 kg/ha. Similarly, mass flow contributions for other nutrients can be computed.

Actually, crop would take up and translocate about 10 to 30 kg Ca/ha, 50 to 250 kg K/ha and 20 to 30 kg P/ha. It clearly signifies the importance of mass flow in supplying Ca to plant roots. As a generalization, mass flow provides an over-abundance of Ca and Mg to plants in most of the soils. The same holds true for most of the mobile nutrients such as NO_3^- and SO_4^{2-}. Depending upon the soil solution concentration, relative importance of mass flow varies. Amount not supplied by mass flow is contributed by either diffusion or root interception.

6.1.1. Factors Affecting Mass Flow

Mass flow involves nutrient movement with water. Both, the amount of water and the volume of soil it comes from, affect the mass flow. In the dry soil, no mass flow of nutrients occurs because there is no water to carry them to the plant roots. Low temperature reduces transpiration and evaporation; resultantly reduced water flux occurs across the roots. Size of the root system affects the water uptake and consequential mass flow. Root density, however, is much less critical for nutrient supply by mass flow than for root interception and diffusion

6.2. *Diffusion*

When mass flow is unable to supply sufficient quantities of a nutrient and a continued uptake occurs, the concentration of the nutrient at the root surface is reduced and a concentration gradient is established. Ions move by thermal motion (Brownian movement) from points of higher concentration to lower concentration, when a concentration gradient exists. Movement of a nutrient ion in response to the concentration gradient is termed as 'diffusion'.

The amount of a nutrient ion diffusing across a unit area in unit time (F) with a concentration gradient (dC/dx) is given for steady-state diffusion by Fick's first law of diffusion:

$$F = -D.\,(dC/dx) \qquad \ldots(8)$$

Here, the minus (–) sign indicates movement from higher to lower concentration, i.e. opposite to the direction of the concentration gradient, dC/dx; D is the diffusion coefficient in the soil having units of cm^2/s.

The D is related to different soil parameters as:

$$D = D_w.\theta.f \qquad \ldots(9)$$

where,

D_w = Diffusion coefficient in bulk water (cm^2/s)

θ = Volumetric moisture content (cm^3/cm^3)

f = Impedance factor related to continuity of diffusion path (Dimensionless)

Equation (9) applies to a linear gradient with minus sign signifying that the movement occurs from higher concentration to the lower one. For transient state diffusion, change in concentration with time at a fixed distance x is given by Fick's second law:

$$(dC/dt) = D_e\,(d^2C/dx^2) \qquad \ldots(10)$$

where, D_e is the effective diffusion coefficient (cm^2/s).

Equation 10 is for linear diffusion. For cylindrical coordinates, describing the field conditions more realistically, Fick's second law assumes the form of Equation (11):

$$(dC/dt) = (1/r).\,(d/dr).\,[r.D_e.(dC/dr)] \qquad \ldots(11)$$

where, r is the radial distance from the centre of the root axis.

6.2.1 Factors Affecting the Diffusion

Effective diffusion coefficient (D_e) of a nutrient ion in soil is given by Equation (12):

$$D_e = D_w \cdot \theta \cdot f \cdot \frac{1}{b} \quad \left(\because\ b = \frac{dC}{dC_l} \right) \qquad \ldots(12)$$

where, b = Buffer power (dimensionless) is the slope of the curve depicting change in concentration of an ion in soil (C) per unit change in concentration of the same ion in soil solution.

D_w is related to the mobility of an ion and other parameters as:

$$D_w = \mu KT = \frac{KT}{6\pi r\eta} \qquad \ldots(13)$$

where,

μ is the chemical mobility (cm/s),

K is Boltzman's constant,

T is temperature in Kelvin,

η is viscosity, and

r is radius of the ion.

Substitution of the value of D_w in Equation (12) yields Equation (14):

$$D_e = \mu TK\theta f\,\frac{1}{b} = \frac{KT\theta f}{6\pi r\eta b} \qquad \ldots(14)$$

Distance travelled by the nutrient ion (ΔX) in cm in time t (seconds) is given by Einstein-Stokes' Equation (15):

$$\Delta X = \sqrt{2D_e t} \qquad \ldots(15)$$

Thus, the diffusion distance moved by diffusion is given by Equation (16):

$$\Delta X = \sqrt{2\mu KT\theta f(1/b)t} = \sqrt{(KT\theta ft)/3\pi r\eta b} \qquad \ldots(16)$$

All the parameters which affect volumetric moisture content, tortuosity of path length and buffer power do modify the diffusion coefficients and the consequential diffusive supply. Some of the key factors are as follow:

6.2.1.1. Soil Water

Liquid phase is critical as the water is a medium through which diffusion of nutrients in the soil occurs. The higher the moisture content, higher will be the diffusion coefficient, until the moisture content reaches saturation. In soil with low initial moisture content, water is adsorbed on the soil particles as a film around them. For diffusion to occur, continuity of moisture films is a must. If there is no continuity, diffusive movement will cease to occur. Incremental rise in water content makes soil water less and less viscous; water films grow in size and reach a level where most of water is bulk water, not influenced by the electrostatic attractions/ repulsions of the solid phase, including colloidal organic and inorganic particles. This causes a corresponding rise in the D_e values.

6.2.1.2. Soil Compaction

Soil solid, liquid and gaseous phases constitute 50%, 15-35% and 15-35% of the soil on volume basis. Liquid phase can occupy to a maximum of 50% of the volume; all of which could be available for diffusion. Incremental increase in the soil compaction at the same moisture content leads to the exclusion of air; soil particles come closer, the continuity of moisture flows increases, path to be traversed by the ion by diffusion becomes less tortuous and resultantly, the diffusion coefficient (D_e) exhibits an increase. The D_e value increases to a maximum at a specific level of soil compaction, which could be termed as the 'critical bulk density' (ρ_c). At this ρ_c value, whole of air space is excluded and it is only solid and liquid phase. Above this ρ_c, the D_e exhibits a decreasing trend with increasing ρ_c. Increase in compaction beyond ρ_c makes solid particles come closer at the expense of exclusion of the water and the physical hindrance created progressively reduces the D_e value.

Moisture and bulk density interact in influencing the D_e values through creating a variation in the path length, whose measure is the tortuosity or impedance (f). Based on the large volume of data, Barraclough and Tinker (1981) developed the following equations connecting f with θ for two texturally different soils:

Light- and Medium-textured Soils:

$$f = 1.58\theta - 0.17 \quad \text{...(17)}$$

Heavy and Organic Soils:

$$f = 0.99\theta - 0.17 \quad \text{...(18)}$$

Putting these values in equation yields for *Light and Medium-textured Soils:*

$$D_e = D_w(1.58\theta - 0.17)\theta\frac{dC_l}{dC} \quad \text{...(19)}$$

Heavy and Organic Soils:

$$D_e = D_w(0.99\theta - 0.17)\theta\frac{dC_l}{dC} \quad \text{...(20)}$$

For ions completely dissolved in solution, increase in soil moisture content decreases the C_l in such a way that the product of $\theta \times dC_l$ remains the same. Thus, relationship between D_e and θ is linear and positive for these ions. For interacting ions like P, Zn, Fe and K, where dC_l does not change due to buffering action, $D_e - \theta$ relationship is curvilinear.

6.2.1.3. Temperature

As a general rule, rate of chemical reaction doubles for every 10 °C rise in temperature. The rise in temperature increases the effective diffusion coefficient of a nutrient ion according to the Equation 13.

At very low temperatures, diffusion virtually ceases because ions need some minimum activation energy for enabling them to participate in the reaction. Rise in temperature in addition to overcoming this activation energy step, increases fluidity or reduces viscosity of water. This in turn facilitates diffusion of the ions.

6.2.1.4. Chemical Amendments

In Equation (12), buffer power (b) describes the quantitative relationship between concentration (C) of a nutrient ion in soil + solution phase per cm^3 of soil to concentration of the same ion in solution (C_l) per cm^3 of solution. It is given by the slope of the curve (C *vs* C_l). Chemical treatments like application of amendments (lime in acid soils and gypsum in sodic soils), manures and/or fertilizers, chelating agents, etc. modify the concentration of the nutrient ions in soil solution; the 'b' values undergo changes as a result of modifications in C_l and C values.

Amelioration of soil acidity through liming raises the pH of the acid soils. Resultantly, the concentration of cations exhibits a decrease and that of anions an increase in soil solution as per the following relationships

$$(Zn^{2+}) = 10^{5.8}\,(H^+)^2 \qquad \ldots(21)$$

$$(Cu^{2+}) = 10^{2.8}\,(H^+)^2 \qquad \ldots(22)$$

$$(Fe^{3+}) = 10^{2.7}\,(H^+)^3 \qquad \ldots(23)$$

$$(MoO_4^{2-}) = 10^{-20.4}\,(H^+)^{2-} \qquad \ldots(24)$$

Thus, diffusion coefficient of cations should decrease and that of anions should increase as a result of liming. Added calcium carbonate also progressively removes the cations from soil solution through adsorption, thus inducing their buffer power to rise and effective diffusion coefficient to fall. Application of gypsum in sodic soils reduces the pH of the soil, as a result of which, D_e rises.

Organic manures act as the store house of nutrients. In addition, they release low molecular weight organic substances which have the ability to form complexes with the cations, including the heavy metals. Complexation-induced rise in concentration of these metals in soil solution creates a reduction in buffer power and a hike in the diffusion coefficients.

6.3. Root Interception

Jenny and Overstreet (1939) propounded the 'theory of cation exchange'. This theory describes a mechanism for the reactions between adsorbents, or solids in general, without the participation of free electrolytes. Theory of contact exchange rests on the concept of overlapping oscillation spaces of adsorbed ions, or redistribution withtin intermingling electric double layers. This was propounded to embrace all the colloidal systems including soil colloids and plant roots. In simplicity, contact exchange as a mechanism for nutrient movement could be pictured as:

$$\boxed{\text{Clay}} - M^+ + H^+\boxed{\text{Root}} \rightarrow \boxed{\text{Clay}} - H^+ + M^+\boxed{\text{Root}}$$

and modelled as:

Cation exchange theory on further refining gave rise the concept of 'root interception', a term coined by Stanley A. Barber of Purdue State University, USA. It is used to describe the soil nutrients at the root surface that do not have to move to the interface to be positionally available for absorption, but are approached by the root itself in the soil. The quantity of the nutrients supplied by root-interception is taken as the quantity present in a volume of soil equal to the root volume. It is generalized that root volume for several crop species growing in soil is less than one per cent of the soil volume in 0-20 cm depth; hence calculations are based on the amount of the available nutrient in 1% of soil volume. Conceptually, as a root system develops and exploits more soil, soil solution and soil surfaces retaining adsorbed ions are exposed to the root mass, and absorption of these ions occurs by a contact exchange mechanism of Jenny and Overstreet (1939). Root interception of the nutrients in infertile soils can be enhanced by the mycorrhiza, a symbiotic association between certain fungi and plant roots.

6.4. Relative Importance of Mass Flow and Diffusion

Roots extract their nutrients from their immediate surroundings. If mass flow is not able to meet the demand set by the plant for a given nutrient, diffusion sets in and a concentration gradient is developed at the root surface. With increasing plant demand, cylindrical root explores more soil volume for the nutrient. A drop in the concentration of the nutrient which is maximum at the root surface, tends to increase as one moves away up to a certain critical distance, where it equals the concentration in bulk soil solution. This volume of soil where the concentration of the nutrient as a consequence of its absorption by plant root is lower than the bulk soil solution is termed as the 'diffusion volume'. Diffusion volume from which the plant derives the nutrient is determined by the diffusion characteristics. Diffusion volume of 1 gram fresh weight of roots depletion zone around the root is given by Equation (25):

$$\text{Diffusion volume} = \{[D/b\,\Delta C\,t/Q(Ar + Rr)]^2 - (Rr)^2\} \cdot 1/(Rr)^2 \quad \ldots(25)$$

where, D is the diffusion coefficient, b is buffer power ΔC is the concentration gradient, Q is the amount of nutrient taken up in time t, t is the time for which diffusion occurs, Ar is surface area of 1 g of root and Rr is the radius of the root.

As given in Equation (25), the diffusion volume is the volume which if continuously supplied with nutrient ions, will be capable of delivering these ions to the plant by diffusion.

Diffusion moves the nutrients rather slowly. As illustrated in Table 7, NO_3^- the most mobile ion could move 1.3 cm in 10 days, whereas Fe^{3+} will move only 0.013 cm. For a nutrient to traverse larger distances, movement will have to be only with water (i.e. by mass flow or convective flow). Once mass flow delivers the nutrient in the diffusion volume, then water carrying the nutrient need not reach the root surface for supplying the same to the root. Mass flow assumes special significance in charging the diffusion volume with the nutrient ions. Diffusion assumes greater significance in the root rhizosphere. Thus both these processes are complimentary and both can be rate-limiting but not at the same time.

7. Nutrient Uptake by Plants

Nutrient elements are absorbed by plant roots, in amounts whose magnitude depends on the plant need for those nutrients and the soil's ability to supply them. Once inside the plant roots, the nutrients are translocated to different plant parts and get accumulated in different plant organs. In this text, plant uptake is covered in two parts. One is nutrient absorption by the plants, and the other is nutrient uptake by different crops. The latter is important from the point of view of nutrient management in crops and cropping systems.

7.1. Nutrient Absorption by Plants

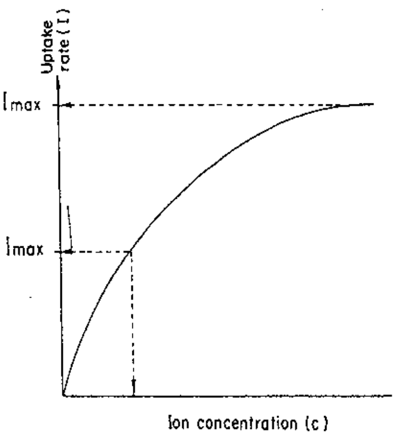

Figure 6. Relationship between ion concentration (C) and rate of uptake (I)
Source: Mengel and Kirkby (1982)

Nutrients are absorbed in their ionic form by plants and the nutrient ion uptake by plant roots is depicted in Figure 6. It Increases curvilinearly with rise in the concentration of ion in soil solution at the root surface, as per the relationship (26):

$$I_n = (I_{max} \times C_{la}) / (K_m + C_{la}) \quad \ldots(26)$$

where,

I_n = Rate of ion uptake,

I_{max} = Maximum rate of ion uptake when concentration C_{la} is not limiting,

C_{la} = Concentration of nutrient ion in soil solution at the root surface, and

K_m = Michaelis-Menten constant which represents a concentration of nutrient ion in soil solution when $I_n = I_{max}/2$.

The relationship depicted in Equation (26) reduces to the following linear forms [Equations (27) and (28)]:

$$(1/I_n) = (1/I_{max}) + (K_m/I_{max}) \times (1/C_{la}) \quad \ldots(27)$$

and

$$In = I_{max} - [K_m \times (I_n/C_{la})] \quad \ldots(28)$$

Equation (27) is termed as 'Linweaver-Burke plot' and Equation (28) as 'Eadie-Hofstee's plot'. Eadie-Hofstee's plot has been used extensively to characterize and compute the absorption parameters I_{max} and K_m.

Plant nutrition studies reveal that there is a minimum concentration of nutrient ion in soil solution (C_{min}) below which plant roots are unable to take up that ion and the Equation (26) is modified as Equation (29) to include C_{min}:

$$I_n = I_{max} \times [C_{la} - C_{min}] / [K_m + (C_{la} - C_{min})] \quad \ldots(29)$$

7.1.1. Nature of Ion Absorption

To determine the nature of ion absorption by plant roots, it is necessary to understand electrochemical potential (μ) of an ion. Electrochemical potential of an ion j is given by Equation (30):

$$\mu_j = \mu_j^0 + RT \ln a_j + z_j FE \qquad ...(30)$$

where,

μ_j = Electrochemical potential of the ion j,
μ_j^0 = Standard chemical potential of the ion j,
a_j = Activity of ion j in solution,
z_j = Valency of ion j,
F = Faraday constant,
R = Universal gas constant,
T = Temperature (K), and
E = Electrical potential

The driving force for the movement of an ion in direction x is obtained by differentiation of Equation (30) with respect to x [Equation (31)]:

$$d\mu_j / dx = (RT / a_j) \times (da_j / dx) + z_j F(dE / dx) \qquad ...(31)$$

Thus, ion j moves in response to concentration gradient (da_j /dx) and the electrical gradient (dE / dx).

Consider two solutions separated by a semi-permeable membrane with an equilibrium between both the solutions, i.e. there is no net flow of an ion. Under this condition of passive equilibrium, $d\mu_j$ / dx = 0, the Equation (31) changes to Equation (32):

$$z_j F(dE / dx) = -(RT / a_j)(da_j / dx)$$

or

$$dE / dx = -(RT / z_j F)(1 / a_j)(da_j / dx) \qquad ...(32)$$

If plant cell having a membrane is immersed into a solution, a portion of the solution enters through the membrane and the remainder stays outside, then electrical potentials of inside (E^i) and outside (E^o) solution can be calculated by integrating Equation (32).

$$E^i = -(RT / z_j F) \ln a_j^i \qquad ...(33)$$

$$E^o = -RT / z_j F \ln a_j^o \qquad ...(34)$$

Difference in electrical potential ($E^N = E^i - E^o$), termed as 'Nernst potential', is given by Equation (35) which can be obtained by subtracting Equation (34) from Equation (33):

$$E^N = E^i - E^o = (RT / z_j F)(\ln a_j^o - \ln a_j^i) = (RT / z_j F) \ln (a_j^o / a_j^i) \qquad ...(35)$$

If we consider a univalent cation like K^+ with its activity outside (external solution) and inside (cytoplasm) as 1.0 m*M*/L and 10.0 mM/L, and convert natural log (ln) to logarithm to the base 10, then E^N at which these two solutions will be in equilibrium at 25 °C can be given by Equation (36):

$$E^N = 2.303\ RT / (+1) F \log (1/10) = -59.2 \text{ mV} \qquad ...(36)$$

For a univalent anion like Cl^-, with its activity outside (external solution) and inside (cytoplasm) as 1.0 m*M*/L and 10 m*M*/L, and after converting natural log to logarithm to the base 10, then E^N at which these two solutions will be in equilibrium at 25 °C is given by Equation (37):

$$E^N = 2.303\ RT / (-1) F \log (1/10) = +59.2 \text{ mV} \qquad ...(37)$$

Root membranes have a typical −120 mV to −180 mV electrical potential difference. These membranes are able to hold higher concentrations of cations in the cytoplasm relative to outside concentration but anions cannot be held inside in similar proportions. Thus, at normal cation concentrations, cations are absorbed in response to the electrochemical potential gradient, whereas pumping of anions inside is against the existing electrochemical potential gradient. For example, a membrane with an electrical potential difference of −120 mV, can accumulate 100-times, 10,000-times and 1,000,000-times more univalent, divalent and trivalent cations inside the cell, respectively compared to their outside concentrations.

In a thermodynamic sense, absorption of ions by plant roots along the electrochemical potential gradient is termed as passive absorption. Conversely, ionic absorption against electrochemical potential gradient by expenditure of metabolic energy is called active absorption.

7.1.2. *Active/ Passive Absorption*

It is possible to predict whether a particular type of absorption is active or passive if the data are available or can be measured for the concentration of a given cation or anion in the outside solution (apoplasm) and inner solution (cytoplasm) separated by a semi-permeable membrane. Also, the electric potential (E_m) of this membrane is experimentally measured using microelectrodes. The Nernst's potential for this membrane can be computed employing Equation (35). If it is termed as E_{cal}, then the difference between the E_m and E_{cal} constitutes the driving force (E_d) as given by Equation (38):

$$E_d = E_m - E_{cal} \qquad \ldots(38)$$

For cations, a negative value of E_d indicates passive uptake and a positive value indicates active uptake across the root. Conversely, in the case of anions, negative value of E_d indicates active uptake and positive value, the passive uptake.

It is illustrated with the help of data depicted in Table 9.

7.1.3. *Nutrient Interaction in Plant*

The crop yield is the result of a large number of simultaneous growth factors. The effect of various factors has a part in common because all these effects are based on the same principle of nutrient uptake. This principle is called the 'General relation'. The effects partly differ because they are related to a special function. The general relation for the growth function has been based on the diffusion equation (39):

$$(1-q/\theta)\,[1-q/a\,(x-x_0)]\,[1-q/b\,(y-y_0)] = F \qquad \ldots(39)$$

in which the special function for each growth factor can be represented by relations (40) and (41):

$$q_x = a\,(x - x_0) \qquad \ldots(40)$$

and

$$q_y = b\,(y - y_0) \qquad \ldots(41)$$

Combining the above equations leads to :

$$(1 - q/q)\,(1 - q/q_x)\,(1 - q/q_y) = F \qquad \ldots(42)$$

where, q is the actual yield; q_x and q_y are the theoretical yields for x and y; θ is the maximum yield; a,b are the growth parameters, and F is the flexibility factor.

Table 9. Nature of uptake on the basis of data on E_m and E_{cal}

Ionic species	E_m (mV)	E_{cal} (mV)	E_d (mV)	Nature of uptake
Zn^{2+}	-120	-60	-60	Passive
Zn^{2+}	-120	-180	+60	Active
MoO_4^{2-}	-120	-60	-60	Active
MoO_4^{2-}	-120	-180	+60	Passive

The flexibility factor, F, expresses the range of ratios of absorbed nutrients wihout which unhampered growth is not possible. If the ratio between the nutrients is sticking fixed (say, for n parts of N, the plant would absolutely need p parts of P and k parts of K), then F would be zero. A healthy growth is possible only when these ratios vary within certain limits and there is a small positie value of F. The maximum effect of the particular nutrient can only be expected, if the supply of other plant nutrients is adequate.

7.2. *Theories and Mechanisms of Ion Uptake*

An early well-known theory for describing ion uptake mechanism is the 'electrochemical theory' of Lundegardh. Subsequently, the concepts of ion pumps and carrier hypothesis were added. These are described below.

7.2.1. *Electrochemical Theory*

Lundegardh (1945) proposed that an electrical potential gradient existing between the cell membrane and outside solution is responsible for the migration of electrons from inside solution (cytoplasm) to the outside membrane (apoplasm). This electron flow causes migration of anions from outside to inside. Schematic representation in Figure 7 depicts that oxygen deficit in cytoplasm induced by respiration is responsible for a drop in redox potential of the cytoplasm. Lundegardh believed that cytochromes (Fe-containing substances)

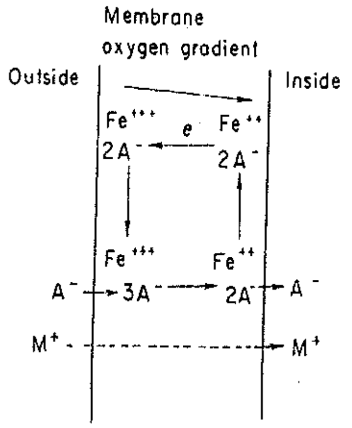

Figure 7. Hypothetical scheme relating anion uptake to electron flow in the membrane
Source: Lundegardh (1945)

present on the outer membrane (which proved to be wrong subsequently as these are housed in mitochondria) contained Fe in Fe(III) form because of higher redox potential. When these cytochromes move through thermal motion across the membrane inside, Fe(III) is reduced to Fe(II) by acquisition of electrons from the respiratory chain. On return to outside the membrane, Fe of cytochrome is oxidized by losing an electron, which combines with H^+ to form water. Outward flow of the electrons is balanced by the counter-flow of anions into the cell.

Lundegardh deduced that since cytoplasm of the cell is negatively charged compared to the outside, energy must be spent in pumping anions into cytoplasm and cations move along with anions just to maintain balance between anions and cations. This theory suffered from two major inaccuracies, viz. (i) Cytochromes are not located in the cell wall, and (ii) ideally, four anion molecules should move in response to the consumption of one molecule of O_2, but actually, this number is much higher. Nevertheless, this theory has some historical significance as for the first time it was pointed out that there is an electron flow in the membrane, efflux or outward flow of H^+, and the existence of an electrical potential gradient. These observations formed the basis for the subsequently-developed theories on ion uptake.

7.2.2. *Ion Pumps and ATPases*

Adenosine triphosphate (ATP) is the energy currency of plants. The ATPases are a group of enzymes located on the plant cell membranes, split ATP into ADP and inorganic phosphate (P_i) with energy release as per relationship (43):

$$ATP \rightarrow ADP + P_i + Energy \qquad \ldots(43)$$

Energy released is utilized for the operation of H^+ pumps and consequential ion transport. Plant cell membrane ATPases, located both on plasma membrane and tonoplast, are central component in the Mitchell's electro-osmotic theory based on the operation of the ion pumps. Functioning of ATPase-run H^+ pump is depicted in Figure 8. As pictured by Mengel and Kirkby (1982), membrane mobile anions X^- and JO^- combine with $2H^+$ ions of the cytoplasm to get protonated as XH and JOH. These XH and JOH induce breakdown of ATP to yield ADP, P_i and energy and in the process get condensed into X–J complex. The X–J complex undergoes hydrolysis to yield XH and JOH and these resultant compounds, utilizing energy of ATP breakdown, move to the outer side of the membrane where they get deprotonated to X^- and JO^-, thus ejecting two protons (H^+) out of the cell, and this cycle repeats continuously ejecting protons by using the energy of ATP breakdown. Operation of this ATPase-run H^+ pump is responsible for the negative charge of the cell and alkaline reaction of the cytoplasm.

The ATPase-H^+ pumps work on the potential (electrical and chemical potential) with the driving force given by Equation (44):

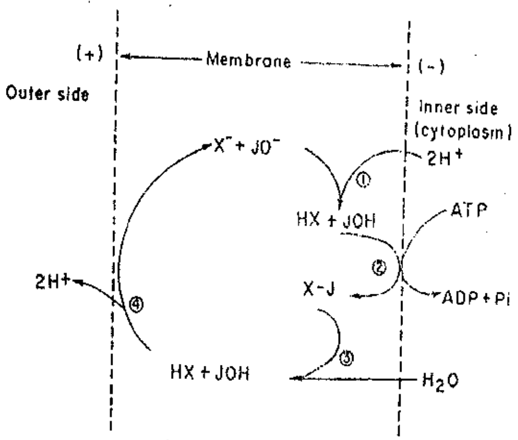

Figure 8. Hypothetical scheme of an H^+-pump (ATPase) pumping $2H^+$ per 1 ATP out of the cell
Source: Mengel and Kirkby (1982)

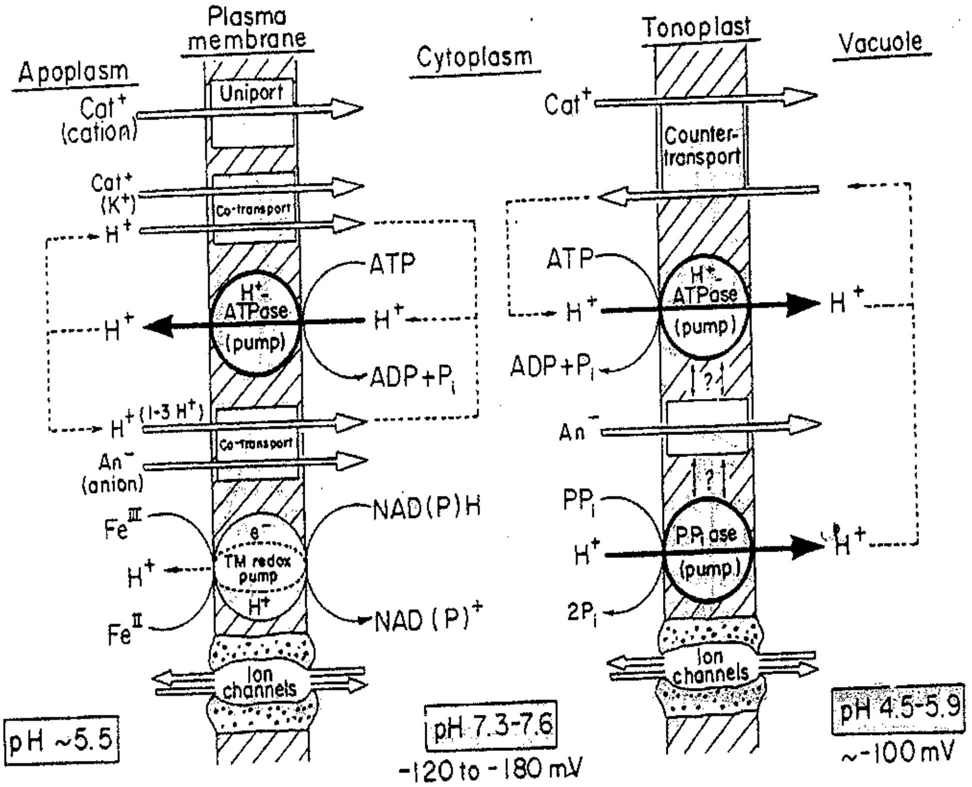

Figure 9. Model for the functioning and location of electrogenic proton pumps (H^+-ATPase, PPiase), trans-membrane redox pump [NAD(P)oxidase, ion channels, and transport of cations and anions across the plasma membrane and tonoplast]

Source: Marschner (1995)

$$\text{pmf} = \Delta\text{pH} + \psi \qquad \ldots(44)$$

where,

pmf = Proton motive force or electrochemical potential gradient of H^+ ions across the membrane,

ΔpH = Change in pH in the cytoplasm and apoplasm, and

ψ = Electrical potential difference across the membrane.

Proton motive force (pmf) is the force by which protons are transported against an electrochemical gradient across the membrane. Thus, efflux of the protons out of the cytoplasm is an energy-requiring process.

It has now been established that ATPase-H^+ pumps are located both on plasma-lemma and tonoplast and these play a major role in the control of pH of the cytoplasm, vacuole and apoplasm, whose values, in general, are 7.3-7.6, 4.5-5.9 and 5.5, respectively (Figure 9). Variations in pH and the electrical potential difference induce secondary reactions in terms of movement of cations and anions into the cytoplasm and vacuoles. Cations are transported passively or downhill across the plasmalemma into the cytoplasm along the electrical potential gradient of –120 mV to –180 mV. Such a transport is termed as '*uniport*'. At a membrane potential of –120 mV, the concentration of a univalent cation like K^+ in cytoplasm, which comes in equilibrium with outside apoplasm concentration of 1 m*M*/L is 100 m*M*L. If the concentration of K^+ in apoplasm is less than 1 m*M*/ L, then K^+ will still be taken but only by expenditure of energy. Such a transport is called '*counter-transport*'. It could also accompany H^+ when the latter is moving back to cytoplasm in response to the H^+ gradient, which is termed as '*co-transport*'. The co-transport of anions along with proton influx across the plasmalemma is also a distinct possibility and it is referred to as '*co-transport or symport*'. As per the model depicted in Figure 9, cations enter vacuole across tonoplast as '*counter-transport*' and anions as '*co-transport*'. In addition to operation of ATPase-H^+ pumps operating at plasmalemma and

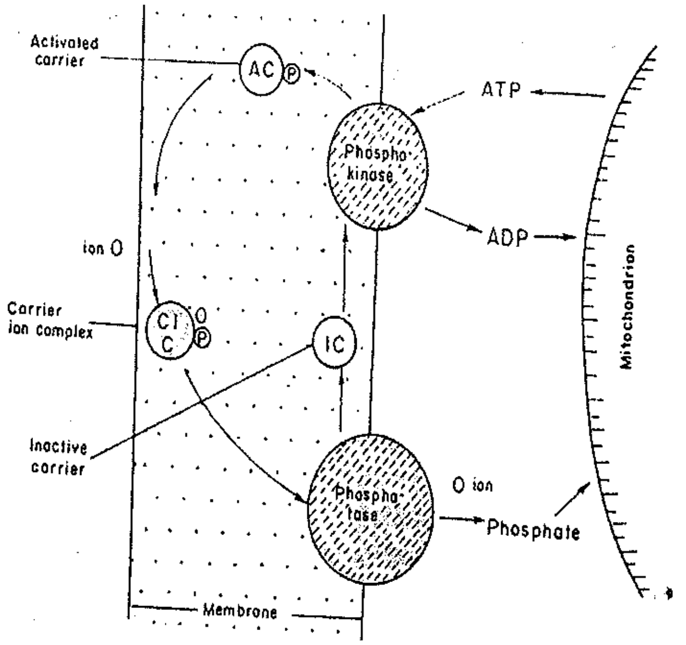

Figure 10. Carrier ion transport across a membrane involving energy expenditure
Source: Mengel and Kirkby (1982)

tonoplast, opeartion of the redox pumps involving NADPH as electron donor on plasmalemma and pyrophosphatase (PPiase) on tonoplast has also been confirmed.

7.2.3. Carrier Hypothesis

Carrier hypothesis was proposed by Epstein (1953) to describe basically the active accumulation of ions across the cell membrane. This theory recognizes the existence of carrier molecules on the semi-permeable cell membranes. These molecules are called 'carriers' because these possess the specific binding sites for particular ions. According to this theory, ions transported to the surface of the plant roots from the soil combine with the carrier molecules, forming an ion-carrier complex. Semipermeable membrane allows the selective diffusion of the ion-carrier complex into the cytoplasm. Ion uptake involving carrier molecule, as given by Mengel and Kirkby (1982), is presented in Figure 10. As per this schematic diagram, an ion combines with a carrier molecule, in this case a phosphorylated compound, forming an ion-carrier complex. This ion-carrier complex, preferentially diffusing across the membrane, encounters the phosphatase enzyme which splits off the phosphate of the complex and as a result, the carrier loses its affinity for the ion and the ion is released into the cytoplasm. This released carrier is regenerated and activated by phosphokinase enzyme located on the inner side of the boundary through utilization of energy released from the break-down of ATP. This activated carrier again traverses to the outer side of the plasma membrane, intercepts an ion, transports it across the plasma membrane, loses ion to the cytoplasm and loses its activity. It gets regenerated and the cycle goes on. Chemically, this cycle has been pictured by Mengel and Kirkby (1982), as depicted in Scheme 1.

Carrier hypothesis is described by the enzyme kinetics, well known as Michaelis-Menten kinetics and has been expressed in the form of Equation (26). Ion uptake is described by two constants, I_{max} and K_m, evaluated by using either Linweaver-Burke or Eadie-Hofstee's plots, as given in Equations (27) and (28), respectively.

7.3. Nutrient Uptake Models

A mathematical model is an equation or set of equations which represents the behaviour of a system. In modelling, the processes are described by different equations. In soil-plant system, processes related to nutrient uptake involve (a) release of adsorbed or exchangeable ions into solution (desorption), (b) transport of the ions dissolved in soil solution or

$$\text{Carrier} + \text{ATP} \xrightarrow{\text{Phosophokinase}} \text{Carrier(P)} + \text{ADP} \qquad \ldots(45)$$

$$\text{Carrier(P)} + \text{Ion} \longrightarrow \text{Carrier (P)-Ion} \qquad \ldots(46)$$

$$\text{Carrier(P)-Ion} \xrightarrow{\text{Phosphatase}} \text{Carrier} + P_i + \text{Ion} \qquad \ldots(47)$$

$$\textit{Net:}\ \text{Ion} + \text{ATP} \longrightarrow \text{Ion} + \text{ADP} + P_i \qquad \ldots(48)$$

Scheme 1

those released into it from the solid phase to the plant roots, (c) absorption of these ions by the plant roots, and (d) ultimate translocation and redistribution of these ions in the different plant parts. These processes have been simulated in the logical sequence and integrated in the form of different models for (i) identifying the processes which describe the nutrient uptake, and (ii) evaluating quantitatively the effects of different parameters on the nutrient uptake.

Models are essentially of two types, viz., empirical and mechanistic. Empirical models are those which describe facts by statistical means and regressions, also often called black-box models. These have not found wider applications in nutrient uptake studies because of the complexities involved in the latter. Mechanistic models, aimed at explaining a phenomenon by means of basic biophysical, biochemical and physiological mechanisms, have been used extensively because these are mainly built to determining the reliability or usefulness of the model.

Mechanistic models again are of two types, viz. steady state and transient models. For better understanding of these models, let us describe the steady state and transient state terms.

The flow of nutrients through a soil could be in a steady state if the flux to the plant root is constant, synchronizing with the influx of the same across the root. It implies that the soil acts simply as the volume element conducting the nutrient flow. It is neither a sink nor a source of the nutrients. In many systems, steady state is not achieved until some time has elapsed after the system is started or initiated. If the soil acts as either a sink or source of the nutrient influencing and/ or modifying its flux in relation to time, this is a transient state condition.

7.3.1. Steady State Models

Diffusion theory has been used in developing the steady state models. Assumption made is that diffusion is the only transport mechanism of nutrients to plant roots and the diffusive flux is driven by the concentration gradient, as given in the Equation (8). The higher the concentration difference in the soil solution between the soil and the plant root, the higher is the concentration gradient and it will lead to higher flux to the plant root. Steady state condition requires that the diffusive flux of the nutrient to plant root is equal to its influx (I_n) across the root. If the influx (I_n) is known, then the concentration difference between the soil and the root surface needed for getting a diffusive flux equal, can be computed from the equation developed by Barraclough (1986) from the model proposed by Baldwin *et al.* (1973):

$$\Delta C_L = \bar{C}_{li} - C_{la}$$

$$= \frac{\mathrm{In}}{4\pi D_l \theta f}\left(1 - \frac{1}{1-\pi a^2 L_v} \ln \frac{1}{\pi r a^2 L_v}\right) \qquad \ldots(49)$$

where, C_{li} is the solution concentration in bulk soil, C_{la} is the concentration at the root surface, a is the root radius (cm) and L_V is the root length density (cm/cm^3). For a known C_{li} and I_n, the C_{la} can be computed from the Equation (49). For several levels of a given nutrient, one can get the pairs of I_n and corresponding C_{la} values. Using this approach, Seeling and Claassen (1990) obtained the I_{max} and K_m values for corn as 52×10^{-14} mol/cm/s and 67 μM, respectively. These values compared satisfactorily with those obtained experimentally from the solution culture experiment.

7.3.2. *Transient Models*

With progressive absorption of nutrients by the plant roots, their concentration at the root surface changes continuously. Transient models try to describe this dynamic process of nutrient uptake and the concomitant changes in the ion concentration and distribution in the rhizosphere.

7.3.3. *Development of Model*

One such model used extensively has been developed by Barber and Cushman (1981) and described in detail by Barber (1995). This model was developed with the underlying assumption that mass flow and diffusion are the two nutrient supply mechanisms in soil to plant roots. Further, nutrient uptake by plants follows Michaelis-Menten kinetics, as given in the previous section. Previously, the description has been made on the radial diffusive flux. In this model, diffusion and mass flow acting simultaneously to supply nutrients to the root surface is considered. Nutrient flux (J_r) is given by Equation (50):

$$J_r = D_e \frac{\partial C_s}{\partial r} + v_0 C_l \qquad \text{...(50)}$$

where, D_e is the effective diffusion coefficient, r is the radial distance, C_s is the concentration of ions on the solid phase that readily equilibrates with C_l, the concentration of ions in the soil solution, and v_o is the rate of water flux into the root.

For conservation of solute and because the area at r becomes smaller as r decreases, we have:

$$\frac{\partial 2\pi r J_r}{\partial r} = \frac{2\pi r \partial C_s}{\partial t} \qquad \text{...(51)}$$

Substituting the value of J_r from Equation (50) into Equation (51), we may obtain Equation (52):

$$\frac{\partial(rD_e \partial C_s / \partial r + r v_0 C_l)}{\partial r} = \frac{r \partial C_s}{\partial t} \qquad \text{...(52)}$$

Using the relation $\partial C_s = \partial C_l b$ (i.e. $b = \partial C_s / \partial C_l$) to convert C_s to C_l and $av_o = rv$ at a, we get

$$\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{rD_e \partial C_l b}{\partial r} + a v_0 C_l\right) = \frac{\partial C_l b}{\partial t} \qquad \text{...(53)}$$

which can be further reduced to Equation (54):

$$\frac{\partial C_l}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_e \frac{\partial C_l}{\partial r} + \frac{a v_0 C_l}{b}\right) \qquad \text{...(54)}$$

where, a is the root radius.

When used with the appropriate boundary conditions, this equation of continuity can be used to calculate the concentration gradient radially from the root as it changes with time. From this we can calculate C_{la}, the concentration in soil solution at the root surface.

Following assumptions were made by Barber and Cushman (1981) while developing the model using the continuity equation:

- The soil is homogenous and isotropic. This assumption guarantees the independence of location with respect to soil characteristics involved in determining the nutrient influx. When soil volumes differ, nutrient uptake can be calculated for each volume.
- Soil water conditions are maintained essentially constant near field capacity. No appreciable soil water gradient perpendicular to the root is assumed in the calculations of nutrient flux. The soil water gradient at this water level is usually relatively flat. It simplifies the nutrient transport mechanism.
- Nutrient uptake occurs only from nutrients in solution at the root surface.
- Root exudates or microbial activity on the root surface do not influence nutrient flux.
- Nutrients are moved to the root by a combination of mass flow and diffusion.
- The relation between net influx and concentration can be described by Michaelis-Menten kinetics.
- The roots are assumed to be smooth cylinders with no root hairs or mycorrhizae (except as otherwise noted). This assumption is necessary to have radial geometry. Root hairs may be taken into account by calculating nutrient flux to the root hairs and as well as the root cylinders.

- D_e and b are assumed to be independent of concentration (Because this is not true for some ions, values averaged over the concentration range of interest are used in some cases). This is essential to linearize the nutrient-transport equation.
- Influx characteristics are not changed by root age or plant age (except as noted). This assumption is only used to simplify the calculations and can be modified wherever time-dependent changes are to be included.
- Influx is independent of the rate of water absorption.

Equation (54) requires an initial condition and two boundary conditions before it can be used to describe the concentration gradient perpendicular to the root. The initial condition is simply $C_{li} = C_{la}$ at t= 0, which describes a uniform nutrient distribution in the vicinity of the root.

The inner boundary condition at the root surface, where r = a, can be developed by assuming that uptake follows Michaelis-Menten kinetics, so

$$J_r = \frac{I_{max}\left(C_{la} - C_{min}\right)}{K_m + C_{la} - C_{min}}, \quad r = a, t > 0 \qquad \ldots(55)$$

If we now substitute, J_r from Equation (50) and use the relation $bC_l = C_s$, we get

$$D_e b \frac{\partial C_l}{\partial r} + v_0 C_l = \frac{I_{max}\left(C_l - C_{min}\right)}{K_m + C_l - C_{min}}, \quad r = a, t > 0 \qquad \ldots(56)$$

Equation (56) is the resultant expression for the inner boundary.

If we assume that roots do not compete for nutrients, the outer boundary, r_1, will remain constant, where r_1 is the half-distance between roots.

$$C_l = C_{li}, \quad r = r_1, \quad t > 0 \qquad \ldots(57)$$

If the concentration gradients extending from the adjacent roots do overlap, then the outer boundary becomes

$$J_r = 0 \quad \text{at } r = r_1, \quad t > 0 \qquad \ldots(58)$$

The technique for solving this equation is described by Barber and Cushman (1981). Numerical solution including the Crank-Nicholson method to solve a finite-difference form of Equation (54) is involved.

Solving Equation (56) gives the influx at the root surface with time. When diffusion supplies a part of the nutrient to plant root, concentration of that nutrient drops at the root surface with time as the uptake proceeds. Decreasing concentration at the root surface (a) in turn decreases influx with time. Total uptake can then be obtained by summing up influx over time; this is the approach for a root that is not growing. In the usual situation for annual plants, the plant starts from seed, and new roots are continually being produced. Uptake by each new root starts at progressively later times during plant growth.

Initial uptake by the plant roots can be expressed by Equation (59):

$$T = 2\pi a L_0 \int_0^{t_m} J_r(a,S)\,dS \qquad \ldots(59)$$

where, T is total uptake at time t_m, L_0 is the initial root length, and J_r (a, S) is the influx at the root surface S.

If we incorporate root growth into this relation, we get:

$$T = 2\pi a L_0 \int_0^{t_m} J_r(a,S)\,dS + 2\pi a \int_0^{t_m} \frac{df}{dt} \int_0^{t_{m-1}} J_r(a,S)\,dS\,dT \qquad \ldots(60)$$

where, df/dt is the rate of root growth.

Equation (60) has been solved to calculate nutrient uptake by plant roots growing in uniform soil systems by Barber and Cushman (1981).

This nutrient uptake Model has following 11 parameters:

1. I_{max}, maximum influx at higher concentrations (nmol/m^2.s),
2. K_m, nutrient concentration in solution – C_{min} where I_n is one-half of I_{max} (μmol/L),
3. C_{min}, concentration in solution where I_n ceases (μmol/L),
4. L_0, initial root length (cm),

5. k, rate of root growth (cm/s),
6. a, root radius (cm),
7. v_0, mean water flux (cm/s),
8. r_1, half distance between root axes (cm),
9. D_e, effective diffusion coefficient for the nutrient in soil (cm^2/s),
10. b, the buffer power of nutrient in soil (dimensionless), and
11. C_{li}, initial concentration of the nutrient in soil solution (μmol/L).

Parameters 1-3 are determined from the solution culture experiment by making a plot of I_n vs C_l. Parameters 4, 5 and 6 are computed from the root measurements, with 5 determined from a plot of root length vs time. Parameter v_0 is calculated with root suface area with time and total water use. Half distance between root axes (r_1) is computed from the root density (L_v) in the soil using relationship $r_1 = 1/(\pi L_v)^{1/2}$. The C_{li} is measured from the concentration of the nutrient in displaced solution and D_e and b are determined in the laboratory.

7.3.4. *Verification of the Model*

Once the model is developed, the next logical step is its verification by comparing the actual nutrient uptake (x) obtained experimentally with uptake predicted by the model (y) through linear equation (y = a + bx). In such studies, slope (b) of 1 and intercept zero (0) is an indicator of perfect agreement. Such verifications have been done for this model for K (Li and Barber, 1991), P (Cox, 1991) and Zn (Adhikari and Rattan, 2000). One relationship given in Figure 11 shows that the Zn-uptake by different rice cultivars could be predicted accurately ($r^2 = 0.99$) with intercept of 0.075 (tending to zero) and slope of 0.891, very close to 1.

7.3.5. *Sensitivity Analysis*

Sensitivity analysis provides a means to use the model to evaluate the degree of influence of the specified parameters by evaluating one parameter at a time and considering all parameters to be independent of one another. After accurate description of the nutrient uptake by the model, it is useful to carry out the sensitivity analysis. Silberbush and Barber (1983) carried out the sensitivity analysis for potassium uptake by soybeans grown in pots on Raub silt loam soil using initial values given in Table 10 by systematically changing the individual values from 0.5 to 2.0 times the initial value, keeping all other values at the initial levels. Model was used to predict the K-uptake for a period of 10 days. It is expected that parameter with the steepest slope of the curve of predicted uptake vs increasing ratio is the most sensitive. According to the results of Silberbush and Barber (1983), given in Figure 12, predicted K-uptake is the most sensitive to root growth rate (k), followed by root radius (r_a). Soil parameters, viz. concentration of K in soil solution, buffer power and diffusion coefficient of K (D_e) are the next most sensitive parameters. Since the changing I_{max}, K_m and C_{min} have little effect on the K-uptake, it implies that root geometry and soil supplies of K restrict K-uptake by soybean more than the kinetics of K-absorption.

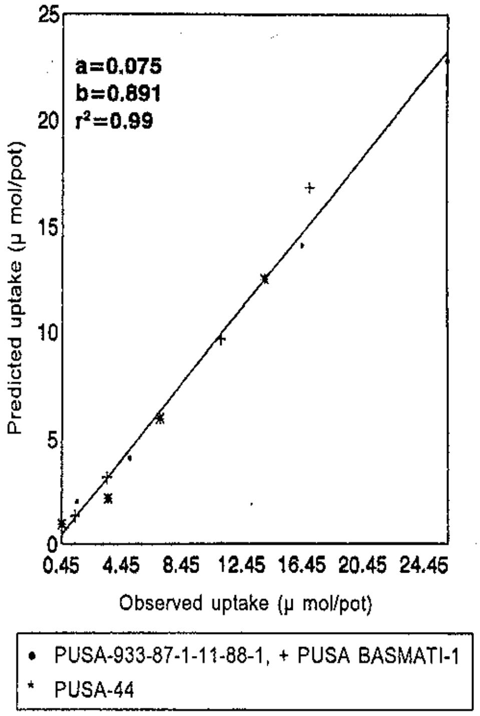

Figure 11. Predicted and observed uptake of zinc by different rice cultivars

7.4. *Uptake of Nutrients by Crops*

The crops draw nutrients from soil. Uptake of the nutrients need not be in the same ratio as these occur in soil. For example, Ca is

Table 10. Soil and plant parameters for the Barber-Cushman model, their symbols and values for potassium uptake by Williams soybeans growing on Raub silt loam

Symbol	Parameter	Initial value
D_e	Effective diffusion coefficient in bulk soil	3.47×10^{-8} cm^2s^{-1}
b	Soil buffer power	24.0
C_{li}	Initial concentration in soil solution	250 mmol L^{-1}
v_0	Water influx to root	5×10^{-7} cm s^{-1}
r_0	Root radius	0.015 cm
r_1	Half-distance between roots	0.2 cm
I_{max}	Maximal influx rate	70.5 nmol $m^{-2}s^{-1}$
C_{min}	Minimal concentration, where $I_n = 0$	1.4 mmol L^{-1}
Km	Concentration - C_{min} where $I_n{}^a = ½$. Imax	10.3 mmol L^{-1}
L_0	Initial root length	250 cm
k	Root growth rate	0.03 cm s^{-1}

$^a I_n$ is net influx rate at r_0.

Source: Silberbush and Barber (1983)

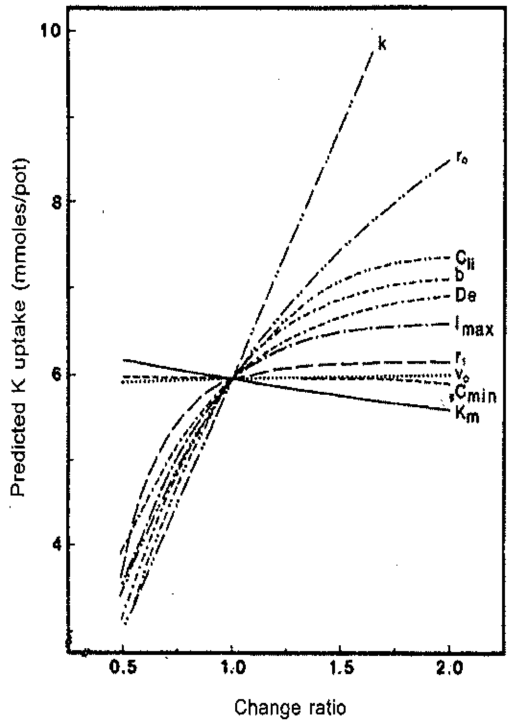

Figure 12. A sensitivity analysis of predicted potassium uptake using the Barber-Cushman model, showing the effect on predicted potassium uptake of varying each parameter while holding the remaining parameters constant at the level shown in Table 10

the most abundant ion in soil solution, yet its uptake by wheat is much less than those of N, K and P (Table 11). Survival of domesticated animals and human life requires that these crops are harvested and the produce is consumed. Consumption of the produce removes nutrients from the soil. Soil gets depleted of its finite nutrient reserves. Result of exploitative intensive agriculture has been the progressive appearance of nutrient deficiencies. For efficient nutrient management, complete knowledge of the nutrient uptake by crops is necessary.

Information compiled from a large number of sources on the total uptake of nutrients is summarized in Table 12.

In spite of variations in nutrient uptake in different soils and by crops grown on the same soil, following generalizations can be made:

- Uptake of N is equal to that of K.
- Calcium uptake is roughly half of N and K uptake.
- Uptake of P, Mg and S is either similar or about same and is normally one-fifth of N or K uptake.
- Iron uptake is usually one-hundredth of N or K uptake. Mn, Zn and B uptake is half that of Fe, two-hundredth that of N or K and one-fortieth of P, Mg or S uptake.
- Uptake of Cu is just half that of Zn, B or Mn, and uptake of Mo is one-tenth that of Zn.

Thus, if Mo uptake is taken as one unit, the uptake of other nutrients can be represented as: Cu = 5; Mn, Zn, B = 10; Fe = 20; P, Mg, S = 400; Ca = 1000; and N, K = 2000 units.

The total uptake of nutrients varies with the crop yield. Crops grown, and amounts of fertilizers and organic manures used also influence the uptake of nutrients.

Table 11. A comparison of concentrations of ions in soil solution with amounts taken up by a crop of winter wheat

Nutrient	Concentration in soil solution (*M*)	Concentration relative to Ca	Uptake by wheat (kg ha^{-1})	Uptake relative to Ca
N	2×10^{-3}	0.4	128	5.6
P	1×10^{-5}	0.002	27	1.2
K	1×10^{-3}	0.2	110	4.8
Ca	5×10^{-3}	1.0	23	1.0
Mg	2×10^{-3}	0.4	11	0.5
S	1×10^{-3}	0.2	9	0.4

Source: Gregory *et al.* (1979)

Table 12. Total uptake of nutrients

Major nutrients	Total uptake (kg/ha)	Micro-nutrients	Total uptake (g/ha)
N	30 - 180	Fe	600-4400
P	4 - 43	Mn	17 - 1857
K	30 - 200	Zn	28 - 725
Ca	15 - 114	Cu	12 - 639
Mg	4 - 55	B	65 - 347
S	5 - 33	Mo	11 - 45

7.4.1. Types of Crops and Cropping Systems

The nutrient uptake by crops grown in India is described below.

Cereal Crops — Data from long-term experiments (Swarup and Wanjari, 2000) have shown that amongst the cereals, finger millet mines the maximum amount of nutrients and maize the least (Table 13). Rice and wheat crops consume similar quantities of N. Uptake of K is almost equal to that of N in rice but is less in wheat. Uptake of P and micronutrients, with the exception of zinc, is more by the rice crop, compared to wheat, probably because of higher mobilization of these nutrients from their native soil reserves. Higher consumption of S and Zn by upland crops of wheat, maize and finger millet appears to be associated with their higher availability under oxidative environments. Boron uptake by different crops is given in Table 14.

In acid soils where wheat yields are low, the nutrient removal in general and that of K in particular, is quite low. Uptake of B and Mo by cereals and other crops is low in highly leached acid soils.

Pulses and Oilseed Crops — Legume-grain and oilseed crops are characterized by the production of lower economic yields than cereals. These crops shed their foliage which gets recycled into the soils. Upon maturity, their twigs, stems and branches are also harvested. The leafy portion remains in the soil. Uptake of N by leguminous crops is much higher, whereas uptake of K is more in the oilseed crops (Aulakh *et al.*, 1985). Much of N absorbed by the leguminous crops comes from the biological fixation of the atmospheric N. Sulphur and Ca removal is much more by the oilseed crops. In mustard and *raya*, the uptake of S is higher than that of P. On the basis of S-uptake, relative to N, the crops can be arranged in the following order:

> Yellow mustard = *taramira* > *raya* > sesamum. > soybean = sunflower > groundnut = mungbean = black gram = pigeonpea > linseed > gram = lentil.

Thus, with the exception of linseed, S-uptake is more by oilseed crops. Soybean, being both a leguminous and an oilseed crop, removes larger quantities of N, P, K, Ca, Mg and S. Generally, cereals, pulses and oilseed crops require 1-6, 5-13 and 5-20 kg S/t of economic produce with mean values of 4, 8 and 12 kg S/t, respectively (Kanwar and Mudahar, 1984).

Root, Fruit, Forage and Plantation Crops— The forage crops associated with very large production of the drymatter remove the maximum quantities of N, P and K, followed by

Table 13. Average grain yield and total nutrient uptake by crops in different soils

Crops	Location	Soil type	Grain yield (t / ha)	Total nutrient uptake									
				N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu
				kg / ha						g / ha			
Rice	Barrackpore	Entrochrept	3.9	70.6	12.8	71.8	23.0	17.0	–	1296	624	312	26
Rice	Pantnagar	Hapludoll	5.3	106.0	28.5	130	–	–	–	2212	710	182	203
Rice	Bhubaneswar	Haplaquept	3.0	61.0	12.6	70.0	–	–	6.3	–	–	–	–
Wheat	Ludhiana	Ustochrept	2.7	116.5	18.2	102.2	–	–	–	1541	329	188	52
Wheat	Jabalpur	Chromustert	4.2	110.0	16.7	101.2	37.0	13.0	12.9	–	–	–	–
Wheat	Pantnagar	Hapludoll	3.8	87.0	19.7	76.0	–	–	–	1955	253	218	148
Maize	Ludhiana	Ustochrept	2.6	61.9	11.8	72.6	–	–	–	932	231	108	32
Maize	Palampur	Hapludalf	3.2	79.0	12.0	66.0	45.0	23.0	11.0	–	–	—	
Finger millet	Coimbatore	Ustochrept	3.0	107.1	17.8	123.9	81.0	52.0	–	1481	1857	725	106
Finger millet	Bangalore	Haplustalf	4.3	132.4	30.9	118.2	114.7	55.2	33.0	–	–	–	–
Soybean	Ranchi	Haplustalf	1.6	130.0	6.4	50.0	–	–	–	–	–	–	—
Soybean	Jabalpur	Chromustert	2.6	176.0	17.2	92.3	54.0	16.0	11.8	708	219	120	85

Source: Swarup and Wanjari (2000)

Table 14. Boron uptake by different crops

Crop	Botanical name	Grain yield (t/ha)	Total B uptake (g/ha)
Maize	*Zea mays*	2.02-2.70	195-347
Chickpea	*Cicer arietinum*	1.43-2.48	87-142
Pigeonpea	*Cajanus cajan*	1.27-3.23	121-339
Sesame	*Sesamum indicum*	0.38-0.77	86-156
Mustard	*Brassica campestris*	1.22-1.44	188-259
Lentil	*Lens culinaris*	0.98-1.37	65-94

Source: Sakal *et al.* (1996)

root, fruit and plantation crops (Table 15). The fruit and root crops consume more K than N, whereas in forages, the order is just the reverse. Oilpalm, sugarcane, coffee and tobacco crops remove more K than N. The forages remove more P than other crops.

Cropping Systems — Nutrient removal by a cropping system is a function of the total drymatter production of the system, nature of the crops, and fertility of the soil. The system producing higher drymatter yield removes far larger quantities of nutrients (Table 16). The finger millet-based cropping system removes the maximum amount of nutrients. Among the rice-based cropping systems, rice-wheat exhausts nutrients much more than rice-rice system; by and large, Mollisols of *tarai* region support a more productive system and consequential, larger depletion of the nutrients. Phosphorus and K limit the productivity of soybean-wheat system more on Haplustalfs of Ranchi than on Chromusterts of Jabalpur. Phosphorus has become critical nutreint limiting productivity at Bangalore and Coimbatore.

Fertilizer Application Rates — Generally, more the nutrients added through the fertilizer, higher is their uptake by the crops. The uptake is a function of nutrient content in the plant and the drymatter production and since both usually increase with the amount of fertilizer application, uptake shows a rise. Fertilizer additions, enabling enhanced drymatter production, catalyze the removal of other nutrients. For example, on alluvial soils of Anand, Gujarat, a rise in the rate of fertilization was directly responsible for enhanced uptake of Fe, Zn, Mn, B and Mo (Takkar, 1996).

Table 15. Nitrogen, phosphorus and potassium uptake by root, forage, fruit and plantation crops

Crop	Yield (t / ha)	Content (kg / ha)		
		N	P	K
Root crops (Contents of tubers only)				
Cassava	30	120	40	187
Potatoes	36	115	18	161
Forage crops (Yield of dry crop)				
Lucerne	10	200	20	170
Napier grass	24	360	64	298
Plantation crops (Contents in harvested fraction)				
Oil palm (Yield of oil)	2.5	162	30	217
Sugarcane (Cane yield)	88.0	45	25	121
Rubber (Yield of dry rubber)	1.1	7	1	4
Coffee (Made coffee)	1.0	38	8	50
Tea (Dried leaves)	1.3	60	5	30
Tobacco (Cured leaves)	1.7	116	14	202

Source: Cooke (1985)

Table 16. Average uptake of nutrients by cropping systems in long-term experiments

Location	Cropping system	N	P	K	Ca	Mg	S	Zn	Fe	Mn	Cu
		kg/ ha/ year						g/ha/ year			
Barrackpore	Rice-wheat-jute	176	34	210	121	56	–	787	4559	972	54
Hyderabad	Rice (*kharif*)-rice (*rabi*)	145	39	172	88	436	–	189	2193	1949	672
Bhubaneswar	Rice (*kharif*)-rice (*rabi*)	120	25	139	–	–	18	–	–	–	–
Pantnagar	Rice-wheat-cowpea (fodder)	219	54	236	–	–	–	431	5422	1034	384
Ludhiana	Maize-wheat-cowpea	237	41	227	–	–	–	371	3439	908	111
Palampur	Maize-wheat	148	23	111	69	33	18	–	–	–	–
Coimbatore	Fingermillet-maize-cowpea	247	36	271	116	118	–	534	4196	3152	221
Bangalore	Fingermillet-maize-fodder cowpea	295	50	261	186	87	25	–	–	–	–
Jabalpur	Soybean-wheat	286	34	194	91	29	25	285	1953	615	147
Ranchi	Soybean-wheat	220	14	82	–	–	–	–	–	–	–

Source: Swarup and Wanjari (2000)

7.4.2. Conjunctive Application of Organic Manures and Inorganic Fertilizers

The application of farmyard manure along with adequate amount of fertilizers is a soil-fertility building practice. It increases the uptake of N, P, Ca, Mg, S, Fe, Mn, Zn, Cu, B and Mo and sustains productivity at either the current level or enhances it. Sustainable productivity as a result of conjunctive use of organic manures and inorganic fertilizers observed in this practice, is attributed to the ability of farmyard manure (FYM) to meet the external requirements of the secondary nutrients and micronutrients. The long-term fertilizer experiments on acid soils of Ranchi, for example, have shown that NPK application enhances the uptake of all the nutrients through higher production of biomass (Rajeev-Kumar *et al.*, 1993). Addition of FYM and lime enhances the nutrient uptake further. Their role in making these nutrients available in the soil is, however, markedly different. While FYM application improves availability of all the micronutrients, application of lime increases the same, in particular the Mo-availability.

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Chapter 16

2 /

Nitrogen

S.K. MOHANTY, T.A. SINGH and M.S. AULAKH

1. Nitrogen as an Element and its Cycle in Nature

Nitrogen (N) is the first member of Group V elements of Periodic Table, followed by phosphorus, arsenic, antinomy and bismuth. Collectively these elements are called "Pnicogens", and their compounds are called 'Pnictides'. The name comes from the Greek word "pnigomos" meaning "suffocation". The lighter members of this group, N and P are typically non-metals and form only acidic oxides. Nitrogen has atomic number (z), 7 and atomic weight 14.0067. Nitrogen occurs principally as diatomic (N_2) in the atmosphere, lithosphere, biosphere and hydrosphere. It is also found in chilesaltpeter ($NaNO_3$) and in plants and animals in the form of proteins. A bulk of N (98%) is present in the lithosphere (soils, sediments, silicate minerals, fossils and rocks). The atmosphere contains 50,000-times more N_2 than soils. The atmospheric air over each square foot of earth's surface contains about 2,700 kg of N_2. Biosphere also contains considerable amount of nitrogen. However, unlike many other elements, N is in a constant state of change and its distribution is not uniform. In the hydrosphere, it occurs as N_2, NH_4^+, NO_3^-, NO_2^- and particulate matter.

Elemental N is usually obtained by fractional distillation of liquid air. Since N has lower boiling point (77.4 °K) than O_2 (92.2 °K), it is more volatile and evaporates preferentially. Very pure N_2 gas can be obtained by thermal decomposition of ammonium nitrite [Equation (1)]. It is interesting to note that pure N_2 obtained from the decomposition of compounds was the key that led to the discovery of noble gases. A N_2 molecule contains a triple bond (N≡N) and therefore, remains very stable to dissociation into individual atoms. A reaction of N_2 with O_2 is thermodynamically inhibited under ambient conditions, though it takes place under certain extreme situations (e.g. during lightening) [Equation (2)].

$$NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g) \qquad ...(1)$$

$$2N_2(g) + 5O_2(g) + 2H_2O \rightarrow 4H^+ + 4NO_3^- \qquad ...(2)$$

[illegible]

It is fortunate that reaction (2) is rare, as otherwise, atmospheric N_2 and O_2 would combine and dissolve in the oceans to form solutions of dilute nitric acid (Sienko and Plane, 1985).

A principal compound of N is ammonia (NH_3). Commercially, it is important as the most economic pathway of N_2 fixation, i.e. conversion of atmospheric N_2 into useful compounds. In Haber's process, synthetic ammonia is manufactured by passing the nitrogen-hydrogen mixture through a bed of catalysts consisting of iron + metal oxides, such as aluminium oxide (Al_2O_3). Fertilizer industries mostly follow this pathway process to commercially manufacture nitrogen fertilizers for use in the agriculture.

The nitrogen cycle is depicted in Figure 1. In the nitrogen cycle, all the involved processes are dynamic and proceed simultaneously to maintain equilibrium in the nature.

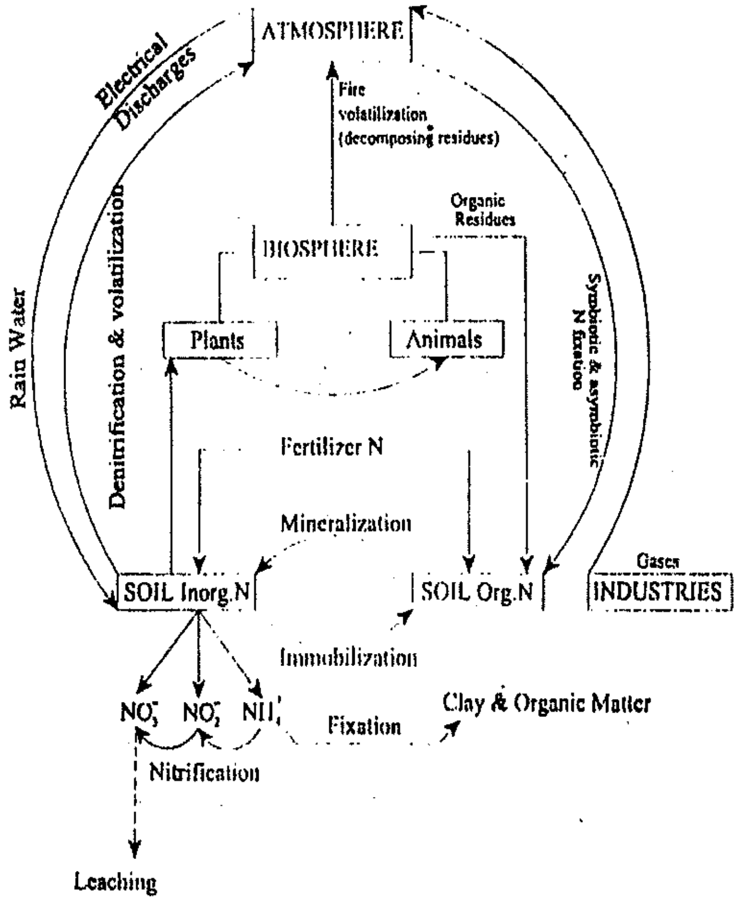


Figure 1. The nitrogen cycle in the environment
(*Source*: Srivastava and Singh, 1996)

2. Nitrogen as Plant Nutrient and Pollutant

కాలుష్యం

A dynamic equilibrium exists among the various forms and processes of nitrogen in the soil. Nitrogen additions and losses, and N transformations within the soil are important for agriculture (as essential plant nutrient) as well as environment (as pollutant) since the gaseous losses of N increase atmospheric pollution. Nitrogen plays an important role in increasing the agricultural production, and being a constituent of protein, it increases the food value. It also influences the quality of environment. Due to these reasons, N has been most extensively investigated, for studying its source, availability, transformation and cycle in soil-plant-water-atmosphere system, biological fixation of atmospheric N, as a pollutant and conservation of energy source.

A majority of soils in the world are mineral soils, and organic soils occupy only a small area. Nitrogen deficiency in mineral soils and crops is widespread, and N is the most extensively limiting plant nutrient in crop production. Now about 50% of human population relies on fertilizer N for food production and the world uses around 132 million tonnes of fertilizer N (FAO, 2008). The consumption of nitrogen fertilizer is steadily increasing in developing countries like India and China due to rising food demand of growing population. Contrary to this, consumption was more in the developed countries earlier.

A diverse pool of nitrogen compounds such as organic compounds (urea, amines, proteins, amides), and mineral forms of N (NO_3^- and NH_4^+) in soil as well as gases that are chemically active in the troposphere (NO, NH_3) determine N availability to crops, and pollution and greenhouse effect. Distribution of N on the landscape is not uniform across the world. Natural inputs like biological nitrogen fixation (BNF) and dry and wet depositions dominate N budgets in Africa (79%), Oceana (79%) and Latin America (72%). In contrast, anthropogenic chemical N sources dominate the overall

0.02
↑ Inc
T.N
O.C

budgets in Asia (74%), North America (61%), and Europe/former Soviet Union (59%) (Mosier *et al.*, 2004).

3. Nitrogen in Soil

3.1. Nitrogen Content of Indian and World Soils

The total N-content of soils generally varies from 0.02% to 0.44%. Due to tropical and subtropical climates, the Indian soils are generally poor in organic matter and consequently, have low N-content, with total N of surface mineral soils varying from 0.02% to 0.13%. Total N-content of some typical Indian and world soils is given in Tables 1 and 2, respectively. Organic carbon-content in different soil horizons of some typical soil series of India are given in Table 3, and it ranges from 0.310% to 0.825% in top soils. An examination of different horizons reveals that the organic carbon content is maximum in surface layer and progressively reduces at lower horizons.

The total N-content of soil depends on several factors like soil type, texture, soil pH, soil E_h (redox potential), climate, topography, vegetation, fertilizer management, etc. Among these factors, climate has the most striking effect on soil organic matter content which in turn determines the N-content of the soil. Under natural conditions, as the temperature increases, the N-content decreases at a given humidity level, whereas at a given temperature, it increases with increasing humidity. Due to hot and dry climate, tropical and subtropical soils have N-content lower than that of the soils in temperate and humid zones.

Whether under forest cover or field crops, soils contain 10-20 times as much N as does the standing vegetation, including roots. Virgin soils are rich in N. Cultivation leads to disintegration and decomposition of soil organic matter (SOM) and hence there is a decrease in the N-content of soils. The decrease may be as high as 25% during the first 20 years and 10% and 7% during the second and third 20-year periods, respectively. Equilibrium is generally established between 60 and 100 years in temperate climate and in a shorter period in tropical climate.

[illegible]

Usually, heavy- or fine-textured soils contain more N than light- or coarse-textured soils. Similarly, if the soil is heavily fertilized with N during crop cultivation, soil N-content will be substantially more over a short period than the unfertilized soils. The total N-content in the soil decreases with depth in the soil profile.

0.02 - 0.44%
India
T. N - 0.02 - 0.13%
O.C. → 0.31-0.825%

Table 1. Total N-content in some Indian soils

Location (State)	Soil class	Texture	N (%)
Nainital (Uttarakhand)	Aquic Hapludoll	Silty clay loam	0.128
Hisar (Haryana)	Typic Ustochrept	Clayey	0.083
Mohanpur (West Bengal)	Typic Ustifluvent	Sandy clay loam	0.088
Jorhat (Assam)	Typic Dystrochrept	Loam soil	0.118
Bangalore (Karnataka)	Paleustalf	Sandy loam	0.026
Mato (Orissa)	Vertic Halaquept	Sandy loam	0.066
Palampur (Himachal Pradesh)	Typic Hapludalf	Silty clay loam	0.076
Jalalpur (Gujarat)	Ustochrept	Clayey	0.083
Gurdaspur (Punjab)	Udic Hapludalf	Loam	0.031
Varanasi (Uttar Pradesh)	Udic Ustochrept	Sandy loam	0.031
Chidiatapu (Andamans and Nicobar Islands)	Umbric Fluventic Haplustalf	Sandy loam	0.114
Kanpur (Uttar Pradesh)	Typic Ustochrept	Sandy loam	0.040
Vallabh Nagar (Rajasthan)	Typic Natrustalf	Sandy clay loam	0.024
Rahuri (Maharashtra)	Vertic Ustopept	Clayey	0.045
Cuttack (Orissa)	Aeric Haplaquept	Loam	0.058
Port Canning (West Bengal)	Fluventic Halaquept	Silty clay loam	0.053
IARI (New Delhi)	Typic Ustochrept	Clayey	0.062

Table 2. Total N-content of soils of some countries of the world

Name of the country	Location	N (%)	References
Pakistan	Multan	0.39	Makhdum *et al.* (2007)
West Africa	Bondouky	0.36	Michali *et al.* (2007)
West Africa	Burkina	0.43	Michali *et al.* (2007)
West Africa	FSO	0.50	Michali *et al.* (2007)
Japan	Nagoya	0.51	Wada and Toyota (2007)
USA	South Florida	1.04	Liu *et al.* (2007)
USA	Michigan	0.47	Nyiraneza and Snapp (2007)
USA	California	0.38-0.70	Jackson (2000)
Spain	Navalcarnero, Madrid	0.10	Gonzalez *et al.* (2008)
Canada	Lethbridge	0.20	Zvomuya *et al.* (2008)
New Zealand	Hamilton	2.38	Zaman *et al.* (2008)
UK	East Loan	1.57	Griffiths *et al.* (2008)
Austria	Austria	0.48	Hoyle *et al.* (2008)
Argentina	Buenos Aires	0.20	Ciampitti *et al.* (2008)

3.2. Forms of Soil Nitrogen

Nitrogen in soil exists in two major forms: (i) organic N, and (ii) inorganic N (Figure 2). A bulk of total nitrogen is present in the organic form and only about 2% is present in inorganic form except where large quantities of inorganic N fertilizers have been added. Up to 8% of total N of the surface soils and up to 40% in subsoils may be present in the 'clay fixed' form (Brady and Weil, 2007).

3.2.1. Organic Nitrogen

The organic N, particularly the hydrolyzable form, is slowly mineralized and is transformed to mineral N through aminization, ammonification and nitrification processes and becomes available to crops. In contrast, non-hydrolyzable N is resistant to mineralization. The stability of some fractions of the organic N is due to the formation of complex organic molecules, which resist mineralization.

Nitrogen present in the organic manures, biofertilizers, green manures, crop residues and several organic wastes, besides the N fixed with the intervention of biofertilizers, is mostly in the form of organic N. Proteins, polypeptides and amino acids ($R\text{-}NH_2$) are the most common organic constituents of plant and animal materials. Unless these organic forms of N are mineralized to inorganic forms, plants cannot utilize N from them.

3.2.2. Inorganic N

The inorganic forms (NH_4^+-N, NO_3^--N and NO_2^--N) are very important from crop nutrition point of view, because plant roots take up N from the soil mostly as NO_3^--N and to some extent as NH_4^+-N. The NO_2^- form is unstable and is usually present in soil in lesser extent. However, heavy application of N fertilizers, anaerobic conditions of the soil, extreme pH values, salinity and low temperature favour its accumulation in soil. In aerobic soil, NO_3^--N is the dominant form, whereas in the anaerobic soils, NH_4^+-N is the dominant form of mineral N along with traces of NO_2^--N. The balance between these two dominant forms is governed by (a) microbial activity involved in the mineralization-immobilization turnover (MIT), (b) the factors affecting MIT, and (c) soil redox potential. Ammonium ions remain in the soil in exchangeable form on the colloidal particles, though some may also be present in soil solution. Nitrate ions, on the other hand, mostly remain in the soil solution, though some of them might be bound to the positive sites of the soil colloids. The mineral N-content (both NH_4^+ and NO_3^-) decreases with soil depth. The inorganic form is liable to be lost through different types of losses like run-off, ammonia volatilization, leaching, denitrification and fixation by clay minerals, as discussed later in Section 5.

Table 3. Organic carbon content of some representative soil series of India

Soil series and location	Horizon depth (cm)		Organic carbon content (per cent)
Katki (Typic Haplustalfs) Meerut (Uttar Pradesh)	Ap	0-12	0.600
	A3	12-28	0.225
	B1t	28-45	0.300
	B21t	45-78	0.240
	B22t	78-99	0.195
	B3t	99-140	
Jagdishpur Bagha (Typic Ustrifluvent) Pusa, Bihar		0-15	0.600
		15-42	0.285
		42-76	0.105
		76-105	0.100
		> 105	0.180
		> 126	0.075
Lukhi (Typic Ustrochrepts) Gurgaon, Haryana	Ap	0-8	0.360
	A	8-27	0.165
	BW1	27-55	0.105
	BW2	55-86	0.100
	BW3	86-125	0.100
	BW4	125-178	0.030
Lukhi (Typic Ustrochrepts) Gurgaon, Haryana	Ap	0-8	0.360
	A	8-27	0.165
	BW1	27-55	0.105
	BW2	55-86	0.100
	BW3	86-125	0.100
	BW4	125-178	0.030
Vijayapura (Typical Kandiustalfs) Kodihalli, Bengaluru Karnataka	Ap	0-7	0.255
	HP	7-21	0.270
	Bt1	21-46	0.270
	Bt2	46-87	0.285
	Bt3	87-104	0.150
Trivandrum (Ustic Dystropepts) Trivandrum, Kerala	AP	0-9	0.720
	A	9-25	0.150
	C	52-84	0.120
Zarifa Veeran (Typic Natrustalfs) Karnal, Haryana	AP	0-5	0.310
	AP	5-24	0.105
	Bt1	24-56	0.075
	Bt2	56-85	0.105
	BcK	86-118	0.075
	C1K	118-140	0.120
Matour (Dystric Eutrochrepts) Kangra, Himachal Pradesh		0-20	0.825
		20-42	0.315
		42-65	0.195
		65-90	0.195
Chomu (Typical Ustipfamments) Bikaner, Rajasthan		0-8	0.17
		8-17	0.15
		17-30	0.11
		30-50	0.09
		50-70	0.09
		70-90	0.08

Source: National Bureau of Soil Survey and Land Use Planning, Nagpur and Indian Institute of Soil Science, Bhopal (Personal Communication through T.A. Singh)

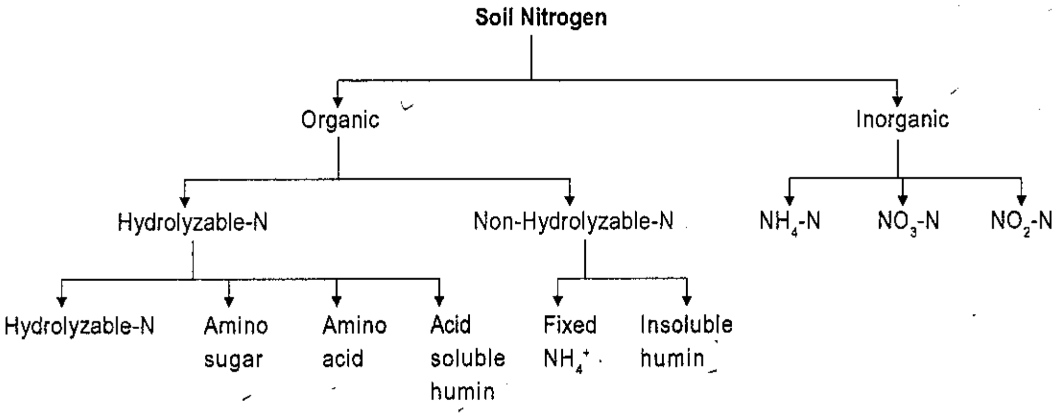


Figure 2. Flow diagram of different forms of soil-N
(*Source*: Tusneem and Patrick, 1971)

$$\xrightarrow{\hspace{3em}\text{Mineralization}\hspace{3em}}$$

$$R\text{—}NH_2 \underset{-2H_2O}{\overset{+2H_2O}{\rightleftharpoons}} OH^- + R\text{—}OH + NH_4^+ \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} 4H^+ + \text{energy} + NO_2^- \underset{-\frac{1}{2}O_2}{\overset{+\frac{1}{2}O_2}{\rightleftharpoons}} \text{energy} + NO_3^-$$

$$\xleftarrow{\hspace{3em}\text{Immobilization}\hspace{3em}}$$

...(3)

3.3. *Mineralization of Organic N in Soil*

Mineralization of organic nitrogen can be defined as the process by which N in organic compounds gets converted into the inorganic ammonium or nitrate ions. The organic N compounds present in SOM, organic manures and crop residues are attacked by a heterogeneous group of soil microorganisms, mineralizing it into inorganic form [Equation (3)]. Mineralization covers the whole series of reactions brought forward by soil microbes till the formation of NO_3^-. The mineralization is faster in the presence of fresh or easily decomposable organic material. However, mineralization is very slow in the case of organic N forms that are less or hardly oxidizable, including lignin and humus of complex nature and of high molecular weights.

Under natural soil conditions, mineralization and immobilization processes (converting mineral N to organic N) usually occur simultaneously. The process of mineralization includes several steps like aminization, ammonification and nitrification, which are discussed below.

3.3.1. Aminization

It is a process of enzymatic digestion by non-specific heterotrophic bacteria, actinomycetes and fungi by which protein and proteinous compounds are decomposed into amino acids or amines [Equation (4)]:

$$\text{Protein} \xrightarrow[\text{Heterogeneous soil microbes}]{\text{Enzymatic reaction}} \text{Polypeptides}$$

$$\xrightarrow[\text{hydrolysis}]{\text{Enzymatic}} \text{Amino acids, or Amines} + CO_2 + \text{Energy} \quad ...(4)$$

Amino acids or amines formed due to aminization are either utilized by microbes (immobilized) or mineralized further to NH_4^+ by the process of ammonification.

3.3.2. Ammonification

It is defined as the process of transformation of amines/amino acids to ammonia by microbial enzymes. These amino acids and amines are converted enzymetically by bacteria (aerobes and non-aerobes), fungi and actinomycetes to ammonium form, as shown by Equations (5) and (6):

$$R\text{-}NH_2 + HOH \xrightarrow[\text{hydrolysis}]{\text{Enzymatic}} NH_3 + R\text{-}OH + \text{Energy} \quad ...(5)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
$$\text{or } 2NH_3 + H_2CO_3 \rightarrow$$
$$(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{2-} \quad ...(6)$$

+250mV

Due to the production of OH^- and CO_3^{2-} ions, the pH of the soil increases, especially in flooded soil. Since many microbes are involved in the process of ammonification, it is efficiently carried out in well-drained soil with abundance of basic cations. The ammonium formed may then be oxidized to nitrite and nitrate through nitrification, fixed by clay lattice (ammonium fixation), immobilized by heterotrophic organisms or released to the atmosphere in gaseous form.

3.3.3. *Nitrification*

Nitrification is the process of enzymatic oxidation of NH_4^+ to NO_3^- brought about by certain nitrifying microorganisms. It is a two step oxidation process, the conversion of NH_4^+ to NO_2^-, and NO_2^- to NO_3^-, as shown by Equations (7) and (8):

$$\underset{\text{Ammonium}}{NH_4^+} \xrightarrow{[O]} \underset{\text{Hydroxylamine}}{HONH_2} \xrightarrow{-2H} \underset{\text{Hyponitrite}}{\tfrac{1}{2}HONNOH} \xrightarrow{[O]} \underset{\text{Nitrite}}{NO_2^-} + H^+ + \text{Energy} \qquad \ldots(7)$$

$$NO_2^- + \tfrac{1}{2}O_2 \xrightarrow[\text{(Nitrobacter)}]{\text{Bacterium}} NO_3^- + 20\ \text{kcal} \qquad \ldots(8)$$

The first step leading to the production of NO_2^- is carried out by *Nitrosomonas*, *Micrococcus*, *Nitrospira* and *Nitrogela* bacteria and the second leading to NO_3^- formation is carried out by *Nitrobacter* and *Nitrocystis*. The population of nitrobacteria is usually between 1×10^5 and 1×10^7 per gram of soil. The process of nitrification results in the release of ionic hydrogen which causes acidity. Nitrification is affected by several factors such as supply of ammonium ions, soil aeration, moisture, pH, temperature, and C:N ratio.

The presence of NH_4^+ is necessary for nitrification but excessive NH_3 is toxic to nitrobacteria and inhibits the growth, especially of *Nitrobacter* and may result in the accumulation of high levels of NO_2^-, which is toxic to plants. The nitrification rate in the soil where O_2 is not a limiting factor (aerobic soils), is quite high. Soil aeration is perhaps the most critical factor affecting nitrification. The oxygen concentration of around 20% is most favourable. Therefore, well-aerated soils are considered the best. The presence of adequate O_2 is necessitated because the nitrobacteria are obligate autotrophic aerobes and will not produce NO_3^- from NH_4^+ in the absence of molecular O_2. In fact, nitrification is determined by redox potential (E_h) of the soil. In soils having E_h more than +250 mV, nitrification takes place and in soils with E_h less than +250 mV, NO_3^- starts getting denitrified, which is common in submerged soils.

The nitrification progresses well when the water content is one-third to one-half of the water-holding capacity and would be less under dry to extremely dry conditions. Similarly, excess of soil moisture has a negative effect on nitrification. Although nitrification can occur in soils having pH 4.5 to 10.0, neutral to alkaline soils (pH 7-9) are more congenial, with the optimum pH around 8.5. Soil temperature in the range of 25-40 °C is optimum for nitrification. At freezing point and 50 °C, the nitrification ceases. The temperature co-efficient (Q_{10}) between 5 °C and 40 °C is 2.0, i.e. the nitrification rate doubles for each 10 °C rise in temperature between 5 and 40 °C.

Several pesticides and other agrochemicals, including nitrification inhibitors have deleterious effect on nitrification, as they may inhibit or retard it (discussed later in Section 4.3.2).

3.3.4. *Significance of C:N Ratio*

The carbon:nitrogen ratio of SOM, organic manures and crop residues assumes great significance in MIT as relative degree of mineralization of organic N, its availability in soil, and immobilization are governed by the C:N ratio. When an organic material of high C:N ratio (for example, straw of cereals having C:N ratio 30:1 or wider) is added to the soil, the microbes become active due to C substrate availability and multiply rapidly to decompose the material. As a result, their demand for N increases, which they meet from the mineral N present in the soil, as also the N applied through fertilizer, leading to a sharp reduction in mineral N (Figure 3). As the decomposition proceeds and the level of C substrate decreases, the demand for N by microbes also decreases, resulting in the mineralization of

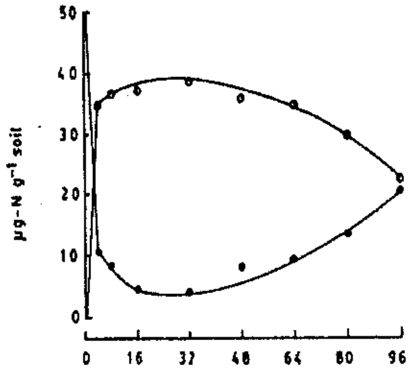


Figure 3. Immobilization of applied fertilizer ^{15}N (—○○○—), and mineralization of immobilized ^{15}N (●●●) in a soil amended with wheat residue
Source: Aulakh (1988)

organic N. In the case of organic material of narrow C:N ratio (for example, leguminous green manure containing 1.5-1.7% N and having C:N ratio < 30:1) is added, due to less C substrate, the multiplication of microbes is not so high and hence there is less demand for N, resulting in mineralization of added organic N. Consequently, there is more availability of N in soil for the crops. Therefore, the C:N ratio of the added residues is critical. Application of small amounts of fertilizer N in soils receiving organic material with wide C:N ratio would stimulate decomposition of nitrification.

With time after the addition of organic matter, the C:N ratio usually stabilizes almost to a constant value in the soil under cultivation. The C:N ratio of Indian soils ranges from 8.5:1 to 12:1, being wider in forest soils and narrower in cultivated soils, with an average of 9.45±0.63 (Jenny and Raychaudhuri, 1960). The ratio becomes wider with increase in annual precipitation, which enhances the leaching loss of mineral N from soils.

3.3.5. Calculation of Mineralization of Organic N in Soil

Studies have shown that only about 1.5-3.5% of organic N of a soil mineralizes annually. Even then this rate of mineralization of soil organic matter is able to take care of normal growth of plants, except under situations where soil is sandy, very poor in organic N or crop demand for N is more than the mineralization.

Amount of nitrogen mineralized in a year can be computed if the organic matter content is known. Using some hypothetical numbers, mineralization of organic N in soil can be computed as:

$$\frac{\text{kg of N mineralized}}{\text{ha in 15-cm deep layer}} = \left(\frac{\text{A kg SOM}}{\text{100 kg soil}}\right)\left(\frac{\text{B kg soil}}{\text{ha 15-cm deep}}\right)\left(\frac{\text{C kg N}}{\text{100 kg SOM}}\right)\left(\frac{\text{D kg SOM mineralized}}{\text{100 kg SOM}}\right) \quad \ldots\ldots (9)$$

where, SOM is soil organic matter, 'A' is the amount of SOM in soil (if suppose SOM is 2.0%, then 'A' is 2 kg in 100 kg soil), 'B' is the weight of soil/ha in 15-cm plough layer (this can be calculated using soil bulk density of 15-cm depth, e.g. 2×10^6 kg soil/ha), 'C' is the amount of N in soil (if suppose total N is 3% of SOM, then 'C 'is 3 kg N/ 100 kg SOM), and 'D' is the amount of SOM likely to be mineralized in one year in a given soil. This depends on soil texture, climate and management practices. Assuming that 2.5% or 2.5 kg SOM is mineralized per 100 kg soil, then the value of mineralized N will be:

$$\frac{\text{kg of N mineralized}}{\text{ha in 15-cm deep layer}} = \left(\frac{\text{2 kg SOM}}{\text{100 kg soil}}\right)\left(\frac{2 \times 10^6\ \text{kg soil}}{\text{ha 15-cm deep}}\right)\left(\frac{\text{3 kg N}}{\text{100 kg SOM}}\right)\left(\frac{\text{2.5 kg SOM mineralized}}{\text{100 kg SOM}}\right)$$

$$\frac{\text{kg N mineralized}}{\text{ha}} = \left(\frac{2}{100}\right)\left(\frac{2 \times 10^6}{1}\right)\left(\frac{3}{100}\right)\left(\frac{2.5}{100}\right)$$

$$= 30\ \text{kg N/ha/year}$$

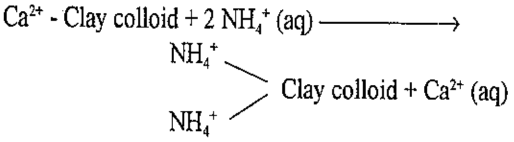
3.4. *Dynamics of Mineral N in Soil*

Mineral N (also referred to as plant available N) includes NH_4^+, NO_3^- and NO_2^- forms. Since NO_2^- is highly unstable in soil, it is either immediately oxidized to NO_3^- form or reduced to NO_x forms. The dynamics of other two forms (NH_4^+, NO_3^-) is influenced by the aeration status or Eh of the soil. Upland soils are usually aerobic or oxic, whereas lowland or flooded rice cultivation creates anaerobic or anoxic situations having low Eh value due to partial or total absence of O_2 and oxidative compounds like NO_3^-, Fe^{3+} and Mn^{4+}. Soil mineral N is used by plants, fixed in the clay lattice (ammonium fixation), immobilized by heterotrophic organisms or released to the atmosphere in gaseous forms.

3.4.1. *Transformations of Mineral N in Aerobic Soil*

In aerobic soil, the mineralization of native SOM or added organic materials into soil proceeds up to the nitrification stage, giving predominantly NO_3^-, though some NH_4^+ is also present. Similarly, any ammonium-containing fertilizers like ammonium sulphate, ammonium chloride, etc. when applied to soil, get dissociated into NH_4^+ ions [Equation (10)]. Ammonium ions so formed are either (a) readily oxidized to NO_3^- through nitrification [Equations (7) and (8)], (b) adsorbed on the clay complex [Equation (11)], thus entering into the exchange complex, (c) remain in soil solution, (d) fixed by clay lattice, or (e) immobilized by soil microbes, but very little leach down. Hence, there is always accumulation of NO_3^- ions, which are either (a) taken up by the crop, (b) adsorbed onto the anion exchange sites of soil colloid, (c) remain in the soil, (d) undergo leaching to the lower soil horizons as they are readily soluble in water, or (e) immobilized by soil microbes during MIT. Nitrate ions, being more mobile than NH_4^+ ions, are more prone to the leaching loss.

$$(NH_4)_2SO_4 \xrightarrow{\text{Dissociation}} 2NH_4^+ + SO_4^{2-} \qquad \text{...(10)}$$



$$Ca^{2+}\text{ - Clay colloid} + 2\,NH_4^+\,(aq) \longrightarrow \begin{matrix} NH_4^+ \\ NH_4^+ \end{matrix} > \text{Clay colloid} + Ca^{2+}\,(aq) \qquad \text{..... (11)}$$

3.4.2. *Transformation of Mineral N in Anaerobic Soils*

Due to the presence of water layer on the soil surface of flooded rice fields, O_2 is displaced from soil, besides its consumption by the soil microbes. In flooded soils, as the O_2 supply is virtually cut off due to 10,000-times less diffusion of atmospheric O_2 through floodwater than in air, a two-layered soil profile is developed (Figure 4). Redox potential (Eh) drops sharply, reaching even negative values because of reduction of the soil. The surface water and upper soil layer of a few millimetre thickness remains oxidized due to diffusion of atmospheric O_2 and is characterized by the presence of oxidative compounds like NO_3^-, Fe^{3+}, Mn^{4+}, whereas the lower soil layer is a reduced one, which is anaerobic, grayish in colour, containing reduced materials like NH_4^+, Fe^{2+}, Mn^{2+}, organic acids, H_2S, etc. This two-layered soil profile influences the transformation of mineral N to a great extent in anaerobic soils.

In the oxidized soil-water interface, mineralization of organic N continues up to the NO_3^- stage. When NH_4^+-N containing fertilizers are added to such soil, then NH_4^+ ions in this upper layer get oxidized to NH_3, which either (a) gets volatilized to the atmosphere because of higher partial pressure of CO_2 and higher floodwater pH developed due to alkalinity, (b) moves down to the reduced layer or (c) gets nitrified and NO_3^- thus formed moves down to the reduced layer. On the other hand, mineralization of organic N in the reduced layer stops at the NH_4^+ stage, since nitrification is inhibited due to lack of O_2. Therefore, there is either (a) an accumulation of NH_4^+ ions in the reduced layer, (b) due to mass flow, NH_4^+ ions move towards the plant roots for absorption, or (c) as the root rhizosphere is oxidized, some of the NH_4^+ ions get nitrified, and the resultant NO_3^- is either absorbed by root or diffuse away from the rhizosphere to the reduced soil. Nitrate in the reduced layer (both moved down from upper oxidized layer and from rhizosphere) is used as the terminal acceptor of electrons in the respiration of facultative anaerobes and is reduced to NO, N_2O and finally to N_2 via denitrification (discussed later in Section 5.3).

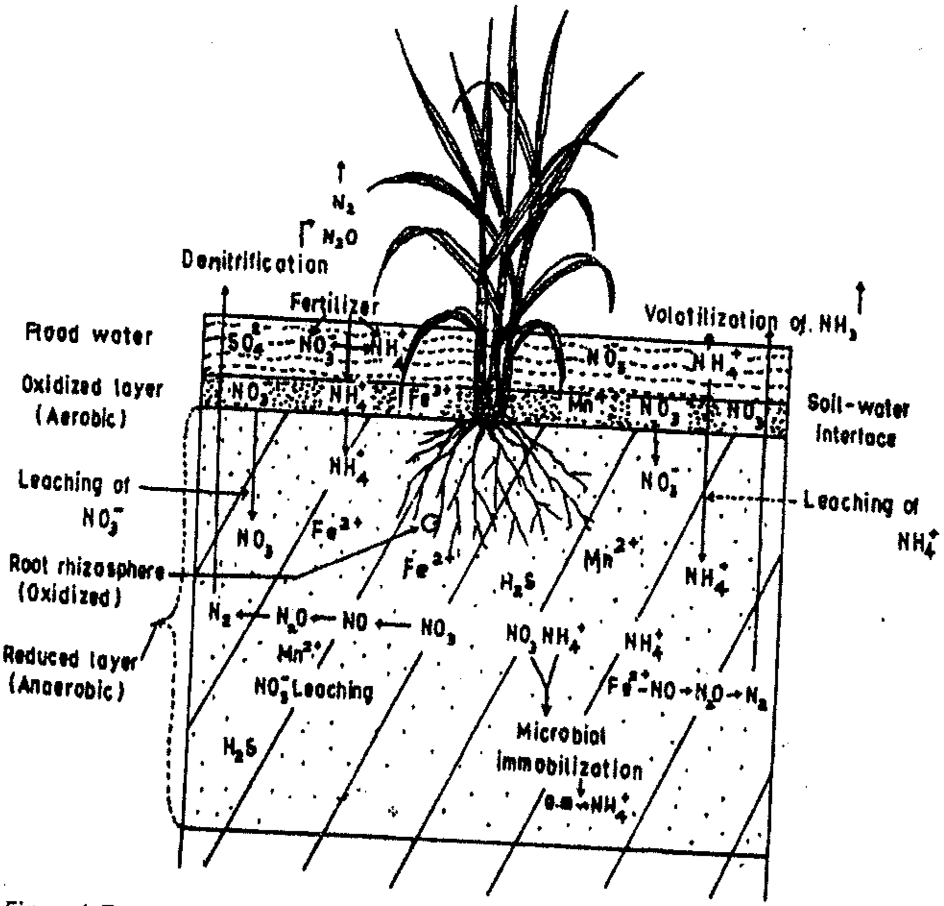


Figure 4. Two-layered soil profile of flooded rice field and nitrogen transformations – A schematic diagram

The dynamics of NH_4^+ in the reduced soil can be described by one of the reactions given below [Equations (12) to (14)] (Mohanty and Patnaik, 1975):

(i) $Y = a + bt + ct^2$ ...(12)
(For soils with high C and N, medium clay and CEC)

(ii) $Y = a + b \ln(t+1) + c[\ln(t+1)]^2$ ...(13)
(For soils with low C and N, high clay and CEC)

(iii) $\ln Y = a + b \ln(t+1) + c[\ln(t+1)]^2$ ...(14)
(For soils with medium C and N, medium clay and CEC)

where, Y is the content of available NH_4^+-N (in ppm) at time 't' (in days) after submergence, 'a' is a constant and 'b' and 'c' are regression coefficients.

4. Crop Needs and Responses to Applied N

In a majority of mineral soils, the content of total N, organic N, mineral N as well as rate of mineralization of organic N is generally low and therefore, response of crops to added N is very common. Optimum supply of N from extraneous sources increases crop production significantly.

In N-deficient plants, N being mobile in plant body, moves from older leaves to younger leaves, and therefore, N deficiency symptoms (pale yellow or yellow) are first observed in older leaves while young leaves are still green in colour. N-deficiency in plants leads to early senescence, loss of yield and less protein content.

Before the advent of green revolution (pre-1960s) mineralization of the SOM and low rates of N application (20-40 kg N/ha), besides the organic material returned to soil in the form of manure, crop residue, etc. were sufficient to get the low to medium yields of traditional (all) varieties. In the era of green revolution during 1960s and thereafter, use of high-yielding, short-statured, nutrient responsive crop varieties assumed importance for boosting production to feed the ever increasing population.

Table 4. Effect of different levels of fertilizer N application on grain yield of rice and wheat crops in India

Nitrogen level (kg/ha)	Yield of rice* (t/ha)	Yield of wheat** (t/ha)
0	3.32	1.82
40	5.09	2.61
80	5.54	3.60
120	4.93	4.25

Sources: *Rao and Moorthy (1995);
**Iswari Singh and Tiwari (1987)

Then the extraneous supply of N (besides P and K) application became essential and the optimum rate of application increased to about 120 kg N/ha or even more (Table 4). Major cereal crops like wheat, rice and maize use 1 kg N to produce 44, 68 and 49 kg grain, respectively (Ladha *et al.*, 2005). Magnitude of response, however, depends on several factors such as, inherent supply of soil N, SOM content, temperature, water management practices, N management practices (time, method, and source), crop management and magnitude of losses from the soil-plant environment.

An excessive use of N for crop production causes more succulent growth of crops, drooping of leaves, low sugar accumulation, more soluble N, less vitamins and minerals (Brady and Weil 2007). Further, the use of excessive N reduces fertilizer-use efficiency, lowers crop yields due to lodging from excessive vegetative growth, besides potential NO_3^- leaching below the rooting zone and thereby causing NO_3^- contamination of groundwater.

4.1. Sources of Nitrogen in Soil

Soil gains nitrogen from fertilizers, organic manures, crop residues, biofertilizers, green manures, organic wastes, rain water and bacterial nitrogen fixation.

4.1.1. Fertilizer N

Nitrogen is added to soil through inorganic and organic sources, which undergo several processes in the soil, as discussed above. The chemical fertilizers contain concentrated N and are widely used to meet the demand of high-yielding crop varieties. In these fertilizers, N is present as either NH_4^+, NO_3^- or both or as amide (NH_2^-). Some of the NH_4^+-N-containing fertilizers are ammonium sulphate (20.6% N), ammonium chloride (25% N), and diammonium phosphate (18% N). While potassium nitrate (16% N) is a NO_3^--N-containing fertilizer, others like calcium ammonium nitrate (25% N), ammonium nitrate (35% N), and ammonium sulphate nitrate (26% N) are the examples of fertilizers containing N in both NH_4^+ and NO_3^- forms. Urea, the amide form of nitrogenous fertilizer, containing 46% N, is the most commonly used fertilizer in India.

Ammonium-containing fertilizers get solublized in the water present in soil and are dissociated into acid and basic radicals, and the fate of NH_4^+ ions formed [Equation (10)] in aerobic and anaerobic soils is discussed in Section 3.4. Nitrate-containing fertilizers dissociate in soil to give NO_3^- ions, and the fate of which is also discussed in Section 3.4. A nitrate-containing fertilizer should not be used in the anaerobic soils as it will be lost from the soil due to denitrification.

4.1.1.1. Hydrolysis of Urea

As urea contains N in $-NH_2$ (amide) form, it is converted into ammonium carbonate in soil by the enzyme urease [Equation (15)]. Urea is readily soluble in water and also being nonpoplar in nature, it is liable to be subjected to leaching losses before its conversion to ammonium carbonate. Therefore, soil-fertilizer management should endeavour efforts to complete the process of hydrolysis in the shortest possible time. The hydrolysis of urea takes about 3-7 days in soil. Since the process is essentially a microbial enzymatic one, a soil having higher C-substrates will take less time for completion of hydrolysis. Urea hydrolysis is usually faster in high-pH soils.

$$\underset{\text{Urea}}{NH_2\text{-}CO\text{-}NH_2} \xrightarrow[+\,2H_2O]{\text{Urease}} \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3} \quad \ldots(15)$$

Under aerobic soil conditions, ammonium carbonate, being an unstable compound, is further hydrolyzed to ammonium hydroxide and carbonic acid as per Equation (16). Carbonic acid subsequently decomposes to yield water and CO_2 [Equation (17)]. Ammonium ion is oxidized to nitrate through nitrification [Equations (7) and (8)]. The fate of nitrate thus formed is discussed in Section 3.4.1.

$$(NH_4)_2\text{-}CO_3 \xrightarrow[\text{Hydrolysis}]{2H_2O} 2NH_4OH + H_2CO_3 \quad ...(16)$$

$$H_2CO_3 \xrightarrow{\text{Autolysis}} H_2O + CO_2 \quad ...(17)$$

In the anaerobic soil, the ammonium carbonate gets dissociated into NH_4^+ and CO_3^{2-} ions. Ammonium ions either enter into the exchange site of soil colloids or remain in soil solution, as discussed above in Section 3.4.2.

4.1.2. Organic Sources

The organic manures, besides containing N have other macro and micro-nutrients, mostly in complex organic molecules with little amounts of NH_4^+ and NO_3^- forms. The mineralization of organic N up to NH_4^+ or NO_3^- level has been discussed above in Section 3.3.

As these sources contain much less N as compared to chemical fertilizers, they are required to be applied in large amounts to meet the N requirement of high-yielding crop varieties, which may not be easily available, besides handling and transportation difficulties. However, organic sources are useful in maintaining the soil health and are eco-friendly also. Therefore, integrated use of chemical and organic sources of N is the best option for sustaining high levels of crop production and maintaining soil health. The benefits of integrated nutrient management (INM) are discussed later in Section 4.3.7.

4.1.2.1. Farmyard Manure, Compost and Other Organic Wastes

The commonly used organic sources are farmyard manure (0.5-1.5% N) and compost (0.5-2% N). Organic refuses of urban areas are composted without or with the introduction of earthworms (vermicompost). Water storage tank silt, sewage sludge, and pressmud from sugar mill are the other sources of N. However, the addition of N through these materials is not large. With upcoming of poultry and piggery farming, large quantities of poultry and piggery manures are also becoming available for use. As these manures contain more N (1-3%) than other manures, they release substantial amount of mineral N on mineralization, and their applications have shown increase in yield of horticultural crops, cereals and other crops.

4.1.2.2. Green Manures

Green manuring is a traditional practice being followed for a long time, particularly in rice. It has several advantages like faster mineralization, eco-friendliness, and multiple nutrient supply capability. It also helps in soil sustainability and in improving the efficiency of chemical fertilizers when applied along with it. Twenty tonnes of fresh green manure can supply as much as 40-90 kg N/ha. Among the green manure crops, *dhaincha* (*Sesbania aculeaae* and *Sesbania rostrata*) and sunnhemp (*Crotolaria juncea*) are commonly used. *Glyricidia maculata* is also used as a green leaf manure. These green manure crops belong to the leguminous group and are capable of fixing atmospheric N_2 by root nodules (discussed later in Section 4.1.3), which becomes available to the crop on their incorporation into the soil. For a better and quicker decomposition, 45-60 day-old succulent green manure crop should be incorporated into the soil.

4.1.2.3. Crop Residues

Nearly half of the dry matter produced annually in cereals, legumes, root and tuber crops is the inedible phytomass (aboveground plant parts). Agricultural crop residues are also good sources of N and other nutrients. After harvesting of crops like rice, wheat, pearl millet, sorghum, sugarcane, jute, etc., large amounts of straw and dried leaves remain on the soil surface. On decomposition, they supply some amount of N. The extent of addition of N through these materials is highly variable and may vary from 5 to 20 kg N/ha. Residues of leguminous crops, including roots are better sources of N than cereals. Numerous field studies conducted in different regions of India have illustrated considerable yield benefits due to incorporation of legume residues after maturity in different cropping systems. The benefits of legume residues are mainly due to their high N-contents sequestered through biological N_2 fixation.

4.1.3. *Biological Nitrogen Fixation and Biofertilizers*

Biological N_2 fixation (BNF) is an important biochemical process associated with plants kingdom. The BNF is carried out by certain bacteria, actinomycetes, blue green algae, fungi and yeast. The most important of these are the bacteria, which have the ability to fix the atmospheric N_2 in symbiosis with the plants or as free-living organisms (non-symbiotically). Symbiotic N fixation is of more importance and the amount of N fixed is quite appreciable.

Biofertilizers are microorganisms, which can bring about soil nutrient enrichment. Among these, symbiotic (*Rhizobia* species) and non-symbiotic fixers of N (*Azotobacter* and *Azospirillum*) are commonly used in agriculture. Free living blue-green algae in rice fields can provide 10-20 kg N/ha, while azolla, a fern, in association with blue-green algae, can supply 30-40 kg N/ha. However, these biofertilizers alone cannot meet the N requirement of crops and their use has to be integrated with fertilizer N to get a good yield. Biofertilizers are discussed later in Section in 4.1.3.2.

4.1.3.1. Symbiotic Nitrogen Fixation

Rhizobia species are bacteria and are capable of having symbiotic relationship with leguminous crops of vital agricultural importance. These *Rhizobia* have the ability to infect the plant roots and form nodules in them. It is in these nodules that atmospheric N_2 is reduced to NH_3 in the presence of the enzyme nitrogenase. A energy required to break the triple bond between nitrogen atoms in the N molecule is supplied by the host plant from photosynthesis. The ammonia is further converted to L-ketoglutamic acid and finally to glutamic acid. It is pertinent to note that there is a specific association between the *Rhizobia* species and the legume species, and there are 20 species of *Rhizobia*. The biochemical pathway of nitrogen fixation is illustrated by Equations (18) and (19):

$$\begin{array}{ccc} \text{16 Mg ATP} & & \text{16 Mg ADP + 16 Pi} \\ & \searrow \quad \nearrow & \\ N_2 + 8H^+ + 8e^- & \longrightarrow & 2NH_3 + H_2\uparrow \end{array} \qquad \ldots(18)$$

$$\text{1/2 Oxoglutarate} + NH_4^+ + \text{ATP} + \text{NAD(P)H} + H^+ \rightarrow \text{Glutamate} + \text{NAD(P)} + \text{ADP} + \text{Pi} \qquad \ldots(19)$$

Most of the N fixed in nodule is utilized by the plants themselves. However, during the process, some N is released in the form of amines and amino acids into the soil. Upon the death of the microorganisms and incorporation of the roots, the N remaining in the nodules is added to the soil. The symbiotic relationship requires that the plants, in turn, should provide carbohydrates needed by the microbes. Infection takes place when the C:N ratio in the soil is wide, whereas less infection occurs when the C:N ratio is narrow. During the initial stages, the nodules absorb some N from the soil. Therefore, a small starter dose of 15-20 kg N/ha is beneficial to stimulate the growth of young seedlings. Seed inoculation with *Rhizobium* proves effective. Excessive N application could cause considerable inhibition in the activity of glutamine synthetase and nitrogenase.

The amount of N fixed ranges from 40 kg/ha to more than 200 kg N/ha/year. Some representative figures are given in Table 5. The fixation depends on the type of legume; effectiveness of bacterial strain; inorganic or mineralizable N-content of soil; fertilizer N applied; adequate supply of phosphorus, potassium and secondary nutrients and favourable soil environmental conditions (mainly temperature,

Table 5. Biological nitrogen fixation by some legumes

Crop	Nitrogen fixed (kg/ha/annum)
Mungbean	70
Soybean	105
Beans	58
Peas	48
Horsegram	40
Groundnut	42
Cowpea	90
Lentil	130

moisture and pH). In soils where a particular legume crop is introduced, the native population of specific *Rhizobium* sp. may be absent or insufficient and inoculation of the right type may be very beneficial. After the native population builds up over a number of years, inoculation may be omitted.

The mere presence of nodules on legume roots does not necessarily mean that they would fix nitrogen. The occurrence of red colour leghaemoglobin in the nodules indicates the presence of effective N_2 fixers. Also, all legumes do not have nodules.

4.1.3.2. Non-Symbiotic Nitrogen Fixation

Blue-green Algae and Azolla — Autotrophic blue-green algae play an important role in N_2 fixation in waterlogged rice culture. More than 125 species accomplish this task under certain conditions. Some well known species are: *Nostoc*, *Calothrix*, *Anabaena*, *Aulosira*, *Tolypothrix*, *Scytonema*, *Chlorogea*, *Cylinderospermum* and *Mastigocladus*. They are aerobic and photosynthetic. They thrive best in waterlogged rice soils on the surface of water under neutral to alkaline pH conditions. The amount of BNF varies from 14 to 50 kg N/ha/year.

In water bodies, a close associationship has been observed between the blue green algae, *Anabaena* and an aquatic fern, *Azolla pinnata*. The algae live in cavities in the leaves of the fern. *Azolla* has been used for centuries in the South East Asia as a green manure under ideal conditions (humid and optimum 20-30 °C) as this association can meet 30 kg N ha^{-1} to 50% of the N requirements of rice. In India, however, this is not very prominent; due to the prevalence of hot and dry climate in most of the rice growing areas, except eastern India and to some extent in south India.

Free Living Bacteria and other Organisms — Certain bacteria, fungi, yeasts (heterotrophs) and actinomycetes (autotrophs) living in the soil system could fix N_2. The bacteria groups include both aerobes (*Azotobacter*, *Azospirillum*, *Beijerinckia*, *Enterobacter* and *Derxia*) and the anaerobes (*Clostrodium*, *Aerobacter*, *Methanobacterium*, *Rhodospirillum*, *Chromatum*, *Chlorobium* and *Rhodomicrobium*). These organisms live in rhizosphere or even at the surface of plant roots and in the intercellular spaces of epidermal root cells. However, the amount N fixed is low and is only 5-10 kg N/ha/year, though there are reports of N_2-fixation as high as 60-90 kg N/ha/year (Brady and Weil, 2007). The C_4 plants (maize, sorghum and tropical forages) are the specific host plants for *Azospirillum lipoferum*, while the C_3 plants (wheat, barley, oats, rye and rice) are specific hosts for *Azospirillum brasilense*.

Besides carbon energy sources, microorganisms need low levels of available soil N, adequate supply of other mineral nutrients, near neutral pH and suitable moisture for proper growth. After their death, the organic N present in their bodies mineralizes and becomes available to plants.

Fixation by Trees and Shrubs — In agroforestry systems, both leguminous and nonleguminous trees and shrubs fix considerable N_2. *Mimosa* and *Acacia* species are examples of such leguminous plants. Some non-legumes, belonging to genus *Alnus* (*Betulaceae*), *Myrica* and *Umptonia* (*Myricaceae*), *Casuarina* (Casuarinaceae), etc. have root nodules and fix N_2 in the same way as do legumes. Phyllospheric fixation of N_2 carried out by *Frankia*, an actinomycetes, has also been reported in these plants.

4.1.4. Nitrogen from Rain Water

The nitrogenous compounds present in the atmosphere are brought down with rain and snow to the earth's surface. The origin of many of these compounds is the earth's surface. Ammonia is lost to the atmosphere due to volatilization from soil and possibly from plant foliage; industrial activities (combustion of fossil fuel) and natural fires. The N_2O is from denitrification losses. The NO_3^- and NO_2^- ions result from the electrical discharges in the atmosphere due to oxidation of N_2 by O_2 (acid rain). The organic N is swept from the soil surface to the upper layers in the atmosphere by wind erosion. On an average, 7-9 kg N/ha/year is brought down by rain water and added to soil. Tropical areas receive 10-30% more N than temperature zones through this route.

4.2. Nitrogen Use Efficiency

Nitrogen-use efficiency (NUE) is a parameter which is indicative of the extent of utilization of applied N by the crop. Generally, not more than 50% of the applied N is utilized by crops; of the other 50%, a part is retained in soil, some is fixed by clay lattice and the remainder is lost to the atmosphere.

4.2.1. Parameters of Nitrogen Use Efficiency

Nitrogen-use efficiency could be measured by several ways like Apparent N Recovery (AR_N), Agronomic Efficiency of N (AE_N) and Production Efficiency of N (PE_N). These parameters are derived using formulae (20-22):

$$AR_N\ (\%) = \frac{TU_N - CU_N}{AF_N} \times 100 \qquad \ldots(20)$$

$$AE_N\ (\text{kg/ha}) = \frac{GY_F - GY_C}{AF_N} \qquad \ldots(21)$$

$$PE_N\ (\text{kg grain/kg N absorbed}) = \frac{GY_F - GY_c}{TU_N - CU_N} \qquad \ldots(22)$$

where, TU_N is the total N uptake from fertilized plot (kg/ha), CU_N is the total N uptake from unfertilized control plot (kg/ha), AF_N is the amount of applied fertilizer N (kg/ha), GY_F is the grain yield in fertilized plot (kg/ha), and GY_c is the grain yield in unfertilized control plot (kg/ha).

Using the plant N-uptake data given in Table 6, calculations for AR_N, AE_N and PE_N are illustrated below:

Apparent Recovery, AR_N at 60 kg N

$$= \frac{70.46\ \text{kg} - 31.34\ \text{kg} \times 100}{60\ \text{kg/ha}}$$

$$= 65.2\%$$

Agronomic Efficiency, AE_N at 60 kg N

$$= \frac{3790\ \text{kg} - 2500\ \text{kg}}{60\ \text{kg/ha}}$$

$$= 21.5\ \text{kg grain/kg N applied}$$

Production Efficiency, PE_N at 60 kg N

$$= \frac{3790\ \text{kg} - 2500\ \text{kg}}{70.40\ \text{kg} - 31.34\ \text{kg}}$$

$$= 32.58\ \text{kg grain/kg N absorbed}$$

'Physiological N efficiency' is yet another parameter of nitrogen-use efficiency and it is defined as the change in grain yield per unit change in accumulation of N in aboveground biomass controlled by the mode of photosynthesis (C_3 or C_4 photosynthetic pathway) and grain N concentration, which is also influenced by N supply.

4.2.2. Fertilizer N Recovery in Subsequent Crops (Residual Effect)

The amount of fertilizer N utilized by subsequent crops (residual effect) can be ascertained directly by using ^{15}N-labelled fertilizer. The International Atomic Energy Agency (IAEA, 2003) based on multilocational studies, has reported an average recovery of about 65% by aboveground plant portions (grain + straw) from single application of ^{15}N-fertilizer during the first direct crop and only 5.7-7.1% in the five subsequent crops. The average recovery of applied ^{15}N by different cropping systems has been found as 3.3%, 1.3%, 1%, 0.4% and 0.5% in 2nd, 3rd, 4th, 5th and 6th subsequent crops, respectively.

4.3. Strategies for Increasing Fertilizer N Use Efficiency

Since nitrogenous fertilizers are expensive and hardly 50% of the applied fertilizer N is utilized by the crop and the other half of unutilized N poses problems of environmental degradation, efforts should be made to increase its efficiency. For efficient N-use, it is important that there is a synchrony between crop demand and N supply. Plant-need based application of N is crucial for achieving high yields and N-use efficiency. NUE can be increased by focusing on two aspects:

(i) Increasing fertilizer-N efficiency during the growth period of crop, and
(ii) Reducing different N losses so that crop uptake may be more or if the crop does not utilize, more N could be retained in the soil for the use of subsequent crop.

Managing of plant growth limiting factors would increase N-demand of the crop, leading to more utilization of available N. Traditionally, the NUE centres on fertilizer, soil, water and crop management, as these along with location and climate are the major controlling factors for N-use.

4.3.1. Fertilizer Source

Plants absorb nitrogen mostly as NO_3^- and NH_4^+ ions. Any fertilizer that supplies either of these two ions is regarded as a good source. However, ammoniacal fertilizers (ammonium-containing and ammonium-forming) are preferred over nitrate form of fertilizers to minimize N losses and increase nitrogen-use efficiency.

4.3.2. Slow-release N fertilizers, Urease and Nitrification Inhibitors

Several products have been developed with the purpose of slowing the release and/or nitrification of applied N to synchronize the supply of N with the crop demand and consequently decrease N losses via leaching and/or denitrification. Slow-release fertilizers such as urea super granule (USG), sulphur-coated urea, neemcake-coated urea, neem-oil coated urea, nimin, and polymer-coated urea, nitrification inhibitors, and urease inhibitors (such as phenylphosphorodiamidate, PPD) have been evaluated for rice and wheat crops.

Several natural and synthetic products like *neem* (*Azadiracta indica*) cake, *karanj* (*Pongamia glabra*) cake, *neem* oil, nimin, and chemicals such as DCD (dicyandiamide), Nitropyrin/N-serve [2, chloro-6-(trichloromethyl) pyridine], AM (2-amino, 4-chloromethyl pyrimidine), ATC (4-amino 1,2,4-triazole), thiourea, hydroquinone, calcium carbide (CaC_2), etc. have been used to retard nitrification in different crops and cropping systems. These materials restrict the growth of *Nitrosomonas* and keep the nitrogen in the NH_4^+ form. While ammonium thioulphate and thiourea are produced and marketed in Japan and Germany, nitropyrin is licensed for use in the USA.

However, use of such materials is limited due to their non-availability in the market and being more expensive than normal fertilizers. Even in the developed countries such as USA, nitrification inhibitors are used only on a limited scale. In India, farmers do not use commercial nitrification inhibitors to regulate the rate of nitrification of applied fertilizer N because of the high costs involved.

4.3.3. Method and Time of Fertilizer Application

Method and time of fertilizer application are important components of an effective nutrient management program. Being soluble in water, nitrogenous fertilizers are usually applied through broadcast. In order to minimize leaching and denitrification losses, application of fertilizer N is usually recommended in two or three splits. The number of fertilizer N splits and the timing of application depend largely on the crop and soil texture.

To minimize losses of N through ammonia volatilization in calcareous/alkaline soils, the first split of the fertilizer N may be applied just before pre-sowing irrigation, as a large portion of the fertilizer N in that case moves to 20 to 60 cm soil layer after irrigation, which, remains in a moist zone for a longer period, and therefore this method enhances the absorption of N by the plant roots, supports root growth in deeper soil layers, besides minimizing NH_3 volatilization.

Several experiments conducted in the farmers' fields suggest that placement of USG in fine-textured soil is more advantageous and increases NUE over the surface application of prilled urea (Mohanty *et al.*, 1999). However, adoption of USG is limited due to lack of its ready availability, additional labour cost for its placement, being costlier than prilled urea (PU). Similarly, band placement of fertilizers by the side of seed row in the anaerobic soil layer (in rice culture) has been as effective as deep placement of USG, in reducing NH_3 volatilization losses and improving grain yield. Draining of the field 1-2 days before broadcasting fertilizer and incorporation of the fertilizer by a rotary weeder could be done, under good water management system. However, this may lead to more temporary immobilization of applied N, resulting in lowering of NUE. If draining is not possible, urea mud ball application is a better alternative.

In contrast to most fine-textured rice-growing soils, coarse-textured highly-percolating porous soils under flooded rice do not favour ammonia volatilization as fertilizer N is transported to a higher depth along with the percolating water. In such soils, USG dibbled in the reduced zone of soil has not proved to be of any advantage over the standard practice of prilled urea application. Leaching of N from USG is a major cause of low NUE of USG in flooded rice grown in highly percolating soils.

4.3.4. Site-specific N Management

Site-specific N management can be prescriptive, corrective or a combination of both (Dobermann and Cassman, 2004). In the prescriptive method of site-specific N management, N-supplying capacity of the soil, expected crop demand, targeted yield, efficiency of fertilizer, and risk from weather and pest infestation are taken into account. This method is employed before seeding of crop. In the corrective procedure, N-content status of the standing crop is measured by employing certain diagnostic tools such as chlorophyll meter and leaf colour chart (LCC). Since most of the plant N is found in chloroplasts and chlorophyll protein, the N-content of the plant could be ascertained by using chlorophyll meter or LCC.

The soil plant analysis development (SPAD), as a diagnostic tool, helps in deciding the most appropriate time of application of N during the crop growth period. However, LCC is inexpensive and easy to use. It depicts gradient of green hues that are based on the wavelength characteristics of plant leaves — from yellowish green to dark green. In several studies, LCC reduced the N requirement of rice and wheat up to 25%

4.3.5. Fertigation and Foliar Application

Application of fertilizers through irrigation water, including drip system, is termed as fertigation. It provides the most effective way of supplying nutrients to the plant roots. Drip irrigation system can be used to apply any water-soluble fertilizer or chemicals in precise amounts, as and when required to match the plant needs, which can save fertilizer N up to 40%. Results of several studies on vegetable and fruit crops have shown that fertilizer application through drip irrigation results in a saving of 20-25% of the fertilizer. Under drip fertigation, NO_3^--N is higher in the upper soil layers compared to broadcast application.

A limited quantity of urea can be supplied as a foliar spray on crop canopy. This method offers advantages of lower losses due to surface runoff, microbial immobilization, volatilization and denitrification, etc. However, it runs the risk of N being washed off if there is rainfall soon after application. Moreover, this is not a substitute but a supplement for fertilizer N application at certain critical stages of crop growth, and the cost of labour for foliar spray of N may exceed the cost of fertilizer N saved. However, foliar application can be beneficial (a) when there is waterlogging and top dressing is not possible, and (b) in highly-percolating coarse-textured sandy soils to avoid leaching losses.

4.3.6.Balanced Use and Interaction of Nitrogen with Other Nutrients

Complementary and antagonistic effects among nutrients are known. Interaction can be defined as the changes brought about by one factor on the effect of another factor, which may be either positive or negative. For example, application of N to crops encourages the uptake of other nutrients due to production of more root biomass, which comes in contact with more soil mass, resulting in enhanced exploitation of nutrients present in soil. The effect of incremental addition of N on the uptake of macro- and micro-nutrients by rice crop is shown in Table 6. Therefore, the crops should receive nutrients in adequate and balanced amounts for sustainable crop productivity, optimum nutrient-use efficiencies, and reduced

Table 6. Effect of graded level of N application on the uptake of nutrients by rice crop

Level of N application (kg/ha)	Rice yield (t/ha)	Uptake of nutrients								
		N	P	K	Ca	Mg	Fe	Mn	Cu	Zn
						(kg/ha)				
0	2.50	31.34	7.04	40.88	7.23	10.08	1.93	1.58	1.77	0.69
30	3.21	55.33	9.11	54.16	12.94	17.88	3.54	3.16	2.94	1.05
60	3.79	70.46	10.31	64.78	13.56	19.76	5.28	2.94	3.56	1.26

Source: Pande *et al.* (1985)

environmental risks. Long-term experiments carried out in different regions of India have proved that balanced application of N, P and K reduces NO_3^--N accumulation in the soil profile, which otherwise is susceptible to losses through leaching and denitrification. However, the improvement in nutrient use efficiency with balanced application of NPK depends on crop, soil type and soil's inherent capacity to supply nutrients.

4.3.7. Integrated Nutrient Management

Integrated nutrient management (INM) draws and pools together the opportunities offered by the different sources of a nutrient such as fertilizers, organics and biologicals to meet the requirements of a crop. Fertilizer remains as the fulcrum of INM, without degrading the soil and water resources. The INM helps in maintaining balanced nutrients supply, checking micronutrient deficiencies and sustaining crop yields at a higher level, besides improving physical and biological properties of soil. Recyclable organic resources as an important component of INM, include animal manures, press-mud, rural and urban wastes, crop residues and composts. Green manuring is another practice having a special relevance in rice cultivation. The leguminous green manures have greater N-substitution potential as compared to the organic manures, but have limited residual value.

Most of the other the organic manures that form part of INM, have considerable residual effect as well. In addition to the nutrient value, the application of organic sources to complement fertilizer N rates results in higher crop yields, reduced denitrification and leaching losses of N with co-benefit of improved soil health due to C-sequestration (Table 7).

Another important component of INM is the biological N fixation by both symbiotic and non-symbiotic routes (discussed in Section 4.1.3)

4.3.8. Genetic Manipulation of Crops for Efficient Nutrient Utilization

It is necessary to develop nutrient-efficient crop cultivars. A nutrient-efficient plant genotype is one that would grow better, produce more and develop fewer nutrient deficiency symptoms than other plants grown at low level of the nutrient. The research carried out on rice cultivars at CRRI, Cuttack, has indicated that some cultivars could harness more N from the soil with their better root proliferation. Though NUE is commonly measured by grain yield and nutrient uptake, the improvement in grain quality (protein, oil, amino acids, etc.) cannot be ignored. Genetic manipulation of crops for efficient nutrient utilization could be developed through traditional breeding and biotechnological manipulations. The productivity of maize, as an example, has been enhanced by

Table 7. Effect of integrated use of fertilizer urea N (FN), sesbania green manure (GM) and wheat crop residues (CR) on rice yields, nitrate leaching, denitrification losses, N_2O emission and soil organic

Treatment	[a]Rice yield (t/ha)	[b]Denitrification losses (kg/ha)	[b]N_2O emissions (kg/ha)	[c]Nitrate leaching (kg/ha)	[c]Soil organic C (g/kg)
Control	3.40	18	6.9	59	3.7
120 kg FN/ha	5.622	58	12.4	94	3.7
GM_{20} + 32 kg FN/ha	5.85	50	11.8	78	4.1
[d]CR_6 + GM_{20} + 32 kg FN/ha	5.92	52	11.8	-	4.9
LSD (0.05)	0.24	6	3.4	12	0.4

[a]Three-year (years two-four of the experiment) mean yields.

[b]Cumulative for rice-growing season.

[c]Measured at the end of four-year experiment.

[d]6 t ha^{-1} crop residue + 88 kg N ha^{-1} through 20 t ha^{-1} sesbania green manure + 32 kg N ha^{-1} through fertilizer N.

Source: Aulakh *et al.* (2000; 2001a; 2001b) developing genotypes which have the ability to accumulate nitrate in their leaves during vegetative growth and to efficiently remobilize this stored N during grain filling (Hirel *et al.*, 2001). Similarly, some cultivars are known to fix N by their roots, due to non-symbiotic fixation.

4.3.9. Simulation Modelling Technique for Cereals

Simulation models are being increasing developed and employed for optimum N management and prediction of crop yields. The soil-crop simulation models in combination with field information and actual weather data are used to make N prescriptions at the beginning of a growing season and in real time during the crop growth. This not only optimizes the crop yield but encourages increasing NUE. These models besides predicting crop yield also throw light on N-management strategies, biotic and abiotic factors on crop growth yield, losses of N and NUE (Ladha, 2005).

4.3.10. Remote-sensing and Geographic Information System Technologies

Remote sensing (RS) and geographic information system (GIS) are also employed for optimizing N management. A good relationship exists between plant N-status and normalized difference vegetation index (NDVI) obtained with ground-based radiation sensors (Ladha, 2005). Therefore, remote sensing can be used as a guide for N management during the growth period of a crop. During off-season, the radiation can indicate N distribution in the organic matter, which helps in formulating N-management practice for succeeding crops. Similarly, the use of GIS and global positioning system (GPS) helps in refining nutrient recommendations for individual fields in comparison to conventional method of nutrient management.

5. Nitrogen Losses from Soil-Plant System

Mineral-N is gained by soil through inorganic fertilizers, mineralization of SOM and organic manures, BNF or other sources, as discussed above in Section 4.1. It is partially utilized by the crops, and the remaining N rarely accumulates in the soil because of its susceptibility to several avenues of losses during crop growth or fallow period, thus reducing NUE. The various ways of N losses from soil-plant system are leaching to deeper soil layers beyond the active root zone, gaseous losses of N to atmosphere via NH_3 volatilization and as NO, N_2O and N_2 through denitrification, thereby causing environmental pollution. Losses ranging from 4 to 21% of ^{15}N-fertilizer applied to wheat crop from the soil-plant system have been seen by Aulakh *et al.* (1984), depending on the treatments of crop residue (0 and 3 t ha^{-1}) and tillage (conventional and zero-till). A substantial portion of applied N is lost from the soil during the year of application.

5.1. Leaching of Nitrogen

The magnitude of leaching loss of N, mostly as NO_3^- ion, depends upon soil texture, hydrological conditions, water holding capacity, permeability and hydraulic conductivity of soil, water table depth, rainfall, crop canopy and dose of applied N, and it may vary from 2% to 50% of applied N. Among these factors, the major ones controlling leaching losses of NO_3^- are concentration of NO_3^- in the soil profile and quantity of water passing through the soil profile. Under irrigated systems, application of high fertilizer rates on porous soils could lead to substantial leaching losses of NO_3^-.

Leaching loss of nitrogen has been found to vary from 5% to 7% at Cuttack to as high as 60% in the laterite soil of Kharagpur under rice cultivation (Table 8). Vegetation retards NO_3^--N leaching from the root zone by absorbing nitrate and water. Leaching losses of N can also be reduced by increasing water-holding capacity of soil through addition of organic materials, split application, controlled irrigation (light irrigation with higher frequency instead of heavy irrigation), using nitrification inhibitors, using slow-releasing fertilizers, following crop rotations that include shallow and deep-rooted crops, and integrated use of organic and inorganic nitrogen fertilizers.

The leaching of unhydrolyzed urea could also occur in flooded rice grown on porous soils, particularly when applied as USG. If the soil is porous, a large amount of NH_2^--N from

Table 8. Magnitude of N transformation and losses through different processes from soil-plant system in different soils and suggested measures for reducing the losses

Location	Soil type	Magnitude of N loss, %	Measures for reducing the losses
		Leaching Losses	
Kharagpur	Hapludoll	44	Fractional application of nitrogen, organic manuring, use of coated and slow-release of fertilizers, integrated use of organic and inorganic N
Kharagpur	Laterite	60	
Cuttack	Aeric Fluvaquept	5-17	
Palampur	Typic Hapludoll	36-70	
Coimbatore	Typic Hapludoll	6-12	
Coimbatore	Typic Hapludoll	9-13	
	Hapludoll	9-13	
		Ammonia Volatilization Losses	
Kalyani	Haplustalf	5-10	Deep placement, incorporation into soil, addition of organic matter, use of coated fertilizers, placement of urea super granule, placement of ammonium N containing fertilizers
Coimbatore		2-3	
Cuttack	Aeric Fluvaquept	4-7	
Kankanady	Aquio Tropepts	2-4	
Aduthurai		4-6	
Palampur		6-20	
Pantnagar	Hapludoll	8-26	
Pusa (Bihar)		21-31	
		5-12	
		Denitrification Losses	
Ludhiana		5-7	Placement of NH_4^+ N containing fertilizer in reduced zone of soil, sub-surface placement of urea super granule (USG), and use of coated fertilizers, use of nitrification inhibitors with N fertilizers
Pantnagar	Hapludoll	28-42	
New Delhi	Typic Ustochrept	3-11	
Cuttack	Aeric Fluvaquept	10-44	

Source: Pande and Mohanty (1988)

applied urea fertilizer may get leached during the process of hydrolysis.

5.2. Ammonia Volatilization

Losses of nitrogen through NH_3 can taken place from soil from both the mineralized organic N and added fertilizer N sources. Volatilization of NH_3 occurs whenever there is free NH_3 in soil near the surface, and the losses can range from 5% to 35%, depending on the soil, environment and fertilizer management practices. However, NH_3 loss is less in flooded soil due to dilution of NH_4^+ ion in floodwater. The rate of loss of NH_3 from the soil surface is related to the partial pressure difference between aqueous ammonia in soil-water system [$NH_3(aq)$] and ammonia in the atmosphere (pNH_3) immediately above the soil-water surface, as shown by Equation (23), where, K_H is Henry's constant:

$$[NH_3\,(aq)] = K_H\, p.NH_3 \quad \ldots(23)$$

Increase in the $[NH_3(aq)]$ concentration or an increase in pH results in a shift in the equilibrium between $[NH_3(aq)]$ and $[pNH_3]$, resulting in loss of NH_3 to the atmosphere. At pH 9.5, the NH_4^+ and $NH_3(aq)$ are almost in equal proportions (50% each). At pH 5.0, 7.0 and 9.0, $NH_3(aq)$ is 0.00316%, 0.316% and 31.6%, respectively, which shows that for each unit increase in pH up to 9.5, there is a 10-fold increase in $[NH_3\,(aq)]$ concentration of the total ammoniacal N in the system. Therefore, at low pH values, NH_3 volatilization losses are less but increase with increasing pH.

Volatilization losses also depend on the type of fertilizer used. Ammonium containing fertilizers, when applied to neutral or acid soils, result in negligible volatilization losses. But, when urea is added to the acid soils, the losses could be more because of the consumption of H^+ during hydrolysis of urea causing increase in the pH around the granules of urea [Equation (24)]. In alkaline soils, the prevailing high pH triggers more volatilization losses [Equations (25) to (27)]. Calcium sulphate so produced is sparingly soluble and so the reaction favours NH_3 losses. Conversely, NH_3 volatilization losses would be less when soluble Ca salts are produced during the reaction.

$$CO(NH_2)_2 + H^+ + 2H_2O \rightarrow 2NH_4^+ + HCO_3^- \quad \ldots(24)$$

$$(NH_4)_2SO_4 + 2CaCO_3 + 2H_2O \rightarrow 2NH_4^+ + 2HCO_3^- + Ca^{2+} + 2OH^- + CaSO_4 \quad \ldots(25)$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O \quad \ldots(26)$$

$$(NH_4)_2SO_4 + Ca^{2+} + 2OH^- \rightarrow 2NH_3 + 2H_2O + CaSO_4 \quad \ldots(27)$$

In soils under upland conditions, losses of applied ammoniacal fertilizers through NH_3 volatilization could be substantial. The timing of fertilization and irrigation influence the losses through NH_3 volatilization. If applied on the wet soil surface following irrigation, as much as 40% of the top-dressed urea could be lost, but its application before irrigation reduces losses due to the movement of urea to subsurface layers. NH_3 volatilization (Table 8) could be minimized through light irrigation after urea application, and incorporation or placement of the fertilizers in the lower layers, use of coated fertilizers and addition of organic matter. Sandy soils or soils with low CEC favour more NH_3 losses because such soils hold only small amounts of NH_4^+ on the soil exchange complex besides having low pH buffering capacity.

In the flooded rice soils, high NH_3 concentration, especially in the overlying floodwater, high temperature, and carbonate and bicarbonate contents of floodwater also influence the NH_3 volatilization from soil-water system. Ammonia produced in the aquatic systems from fertilizer additions or mineralization of SOM may be involved in reactions, as shown by Equations (28) to (30):

$$NH_4^+ + OH^- \rightarrow NH_3\,(aq) + H_2O \quad \ldots(28)$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3\,(aq) + H_2O + CO_2 \quad \ldots(29)$$

$$2NH_4^+ + CO_3^{2-} \rightarrow 2NH_3\,(aq) + H_2O + CO_2 \quad \ldots(30)$$

Liming and high velocity wind also increase NH_3 volatilization losses, while crop canopy and higher floodwater depth often reduce such losses.

5.3. Denitrification Loss

Denitrification is a process limited to anoxic soils in which bacterial reduction of NO_3^- and NO_2^- takes place leading to the release of NO, N_2O and N_2 gases. A most commonly accepted reductive pathway for denitrification is illustrated in Equation (31). However the relative proportions of the resultant gases could vary considerably and depend upon the prevailing soil and climatic factors.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O\uparrow \rightarrow N_2\uparrow \quad \ldots(31)$$

Some of the organisms involved in the denitrification process are: *Thiobacillus denitrificans*, *Thiobacillus thioparus* (autotrophic), *Pseudomonas*, *Micrococcus*, *Achromobacter* and *Bacillus*. Denitrification is influenced by several factors, such as supply of nitrate substrate, organic C supply, aeration and water status (Eh of soil), soil texture, pH, temperature, etc. Denitrifying organisms use organic C compounds as source of energy and for synthesis of cellular constituents. Therefore, denitrification is strongly dependent on the availability of organic C supply through SOM, crop residues, root exudates, and green and farmyard manures.

Soil water can directly and indirectly influence denitrification through (a) provision of suitable conditions for microbial growth and activity, (b) restricting supply of O_2 to microsites by filling soil pores, (c) release of available C and N substrates through wetting and drying cycles, and (d) providing a diffusion medium through which substrates and products are moved to and away from soil microorganisms. When there is a shortage of O_2, the Eh of flooded soil falls below +250 mV in soil, some of the microbes utilize the combined oxygen present in inorganic compounds. Soil texture influences the denitrification process in several ways such as physical variations in soil structure, pore size, aggregation and water infiltration rates that affect aeration, water-holding/absorption capacity, and microenvironment. Denitrification is often more during day time than night due to higher temperature.

In upland conditions, heavy irrigation, intensive rainfall events and incorporation of fresh organic material could lead the development of congenial anaerobic conditions for denitrification in short spells only and therefore, N losses through denitrification are usually very small. However, anaerobic situations often develop and prevail for longer periods in flooded and lowland rice soils where denitrification is a major pathway of loss of N. The losses due to denitrification may range from 10 to 40% of the applied N.

Denitrification can be reduced to certain level by the use of non-nitrate fertilizers and their split applications, deep placement of NH_4^+-N, proper management of water and organics. Magnitude of N losses through different path ways from Indian rice soils are indicated in Table 8.

5.4. *Chemodenitrification*

Denitrification is mostly biologically catalyzed and closely linked to bacterial respiratory mechanism. Some N-oxides are, however, produced by non-microbial processes known as chemodenitrification (Brady and Weil, 2007), which is catalyzed by abiotic agents. This process is of minor importance in acidic and frozen soils. Acidic soil conditions favour NO_2^- accumulation, and chemodenitrification occurs when NO_2^- comes in contact with ammonium salts, amino compounds such as urea, and with lignins, phenols and carbohydrates [Equations (32) to (34)]. Chemodenitrification is not a very important process of gaseous N loss from the soil system.

$$2HNO_2 + CO(NH_2)_2 \rightarrow CO_2 + 3H_2O + 2N_2\uparrow \quad ...(32)$$

$$\underset{\text{(Organic molecule)}}{R\text{-}NH_2} + HNO_2 \rightarrow R\text{-}OH + H_2O + N_2 \quad ...(33)$$

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO\uparrow \quad ...(34)$$

5.5. *Immobilization of Nitrogen*

The conversion of inorganic N (NH_4^+ and NO_3^-) to organic forms by soil microorganisms is called immobilization. It is the reverse process of mineralization. Immobilization of N can take place by both biological (through microorganisms) and non-biological (abiotic) processes, with the latter being more important in forest soils. Soil microorganisms have a C:N ratio of about 8:1. To build up body tissues, the added or native inorganic N is utilized by these microorganisms. When any organic material of wide C:N ratio is added to soil, microorganisms initiate its decomposition [Equation (35)]. The availability of large C substrate results in an elevated N demand because of increased microbial activity and this N has to be supplied by soil, and added fertilizer N, or organic material, as discussed in Section 3.3.4. The immobilized NH_4^+ or NO_3^- ion enters into the microbial cell where it is converted into protein. This process results in temporary immobilization of N. Also, a significant immobilization of fertilizer N could occur in the surface oxidized layer of rice soils due to excessive algal growth.

$$\underset{\text{(Glucose)}}{C_6H_{12}O_6} + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad ...(35)$$

As the two opposite processes — continuous mineralization of organic N, and conversion of mineral N into organic products —

occur concurrently in soil under natural conditions (Figure 3), "net mineralization" would take place if mineralization exceeds immobilization. Conversely, net immobilization would occur if immobilization exceeds mineralization. However, the immobilized N, though not available to plants for a certain period, is not a permanent loss to the soil system.

5.6. Ammonium Fixation by Clay Minerals

When an ammonium-containing or ammonium-forming fertilizer (urea) is added to a soil, most of ammonium gets adsorbed on the cation exchange sites, but a part of it is susceptible to strong adsorption in the interlayer spaces of some 2:1 layer silicate clay minerals. The clay minerals with this property are: vermiculite > fine-grained micas > smectites. The ammonium ion has an ionic diameter of 2.96 Å, which is close to the 2.8 Å diameter of interlattice spaces in the 2:1 layer silicate minerals. This ammonium fixation is similar to the fixation of K^+ ions (ionic diameter 2.68 Å) and therefore NH_4^+ and K^+ ions compete for fixation of these minerals by clay. Fixed ammonium is normally not easily available for plants and microbes, though, recently fixed NH_4^+-N has been found in dynamic equilibrium with other forms of soil mineral N and a portion of which could move out of clay and become available to the nitrifying microorganisms. Ammonium fixation is often higher in subsoil than surface soil.

5.7. Soil Erosion and Runoff

Water and wind erosion could take away not only fertile surface soil but also the productivity of the soil as well. The surface soil has more organic matter than the lower layers, and therefore, the loss of the surface soil layer results in N loss. This loss depends on the severity of the erosion. In case of water erosion, the duration and intensity of rainfall, slope of the land and vegetation cover are the main factors influencing the losses. Erosion losses are more under fallow conditions than under vegetation cover. Runoff losses may be as high as 70% if heavy rainfall occurs on the day of fertilizer application. The magnitude of loss sharply decreases with the delay in rainfall. The average loss of N through erosion is considerably reduced when proper soil conservation and conservation tillage methods are adopted. Therefore, proper soil conservation measures go a long way in conserving the precious soil resources.

6. Nitrogen Balance Sheet

An apparent nitrogen balance sheet can be prepared by deducting the crop N recovery and soil N in control plot from that of fertilizer plot [Equation (36)]. However, a precise balance sheet of applied N can be worked out by using ^{15}N-labelled fertilizers taking into consideration the amount of N added through fertilizer, crop removal, and N remaining in the soil.

Nitrogen balance = (Amount of fertilizer N added to the soil through different sources) – (Crop uptake of N + N losses through various process + N remaining in the soil) .... (36)

For constructing N balance, the amount of applied ^{15}N-labelled fertilizer N is measured in various soil N pools and plants, and the amount of unaccounted-for N is assumed to have escaped from the soil-plant system. Calculations for ^{15}N balance sheet are illustrated below using data from a study of Aulakh *et al.* (1984) where 100 kg ^{15}N-labelled fertilizer N/ha was applied to wheat. After harvesting wheat crop, ^{15}N-labelled fertilizer N was determined in grain, straw, roots plus crown, and in different layers of 0-60 soil profile:

(i) Amount of ^{15}N-labelled fertilizer N applied to the soil = 100 kg N/ha

(ii) Total crop uptake of ^{15}N-labelled fertilizer N = 49.90 kg N/ha (grain = 27.0 kg N/ha, straw = 16.5 kg N/ha, and roots + crown = 6.4 kg N/ha)

(iii) ^{15}N-labelled fertilizer N remaining in 0-60 cm soil profile (Residual fertilizer N) = 29.16 kg N/ha (organic N = 27.92 kg N/ha, mineral N = 0.75 kg N/ha and fixed ammonium N = 0.49 kg N ha^{-1}).

^{15}N-labelled fertilizer N balance = 100 kg – (49.90 kg + 29.16 kg) = 20.94 kg N/ha i.e. 20.94 kg N/ha applied is unaccounted for, which is lost from soil-plant system.

7. Environmental Implications of Nitrogen Fertilization

One of the most important challenges facing humanity today is to increase food production to meet the expanding needs of population without degrading natural resources (soil, water and air). As the world population grows, stress on natural resources increases, making it difficult to maintain food security. Undoubtedly, use of fertilizers and manures is essential for producing sufficient food; however, this should not be done at the cost of polluting the environment. Profitable food production and safe environment should go hand in hand. Excessive use and improper management of N fertilizer produces NH_3, NO, and N_2O and results in NO_3^- leaching to groundwater.

7.1. Soil-plant Pollution

On the basis of total cropped area, the N-fertilizer use in India is not high. However, there are certain crops like vine yards in western India; wherein fertilizer-use is very high and may pose pollution problems. Wherever shallow-rooted crops like potato and leafy vegetables are fertilized heavily, NO_3^- accumulation in soil and/or leaching beyond the root zone may occur. Faulty animal manure disposal practices and manure pits are other potential sources of nitrate contamination of soil and shallow groundwater.

Extent of NH_4^+ and NO_3^- ions accumulation in soil depends on fertilizer N management. If heavy dose of N is applied, then NH_4^+ and NO_3^- could accumulate in soil, depending on the Eh status of soil. But, these ions are absorbed by the plant and some of these may get lost as gaseous losses. If NO_3^- accumulates in soil, plants take up more nitrate, some of which remains in plants as soluble N (NO_3^-, NO_2^-) and enters the foodchain from soil to plant and then to animals, and human beings.

7.2. Water Pollution

When fertilizer N is applied in excess of required N rate, large amount of NO_3^- may accumulate in the soil profile, which is susceptible to leaching by rain and irrigation water. High rates of leaching and nitrification in porous soils, and relatively high fertilizer N rates combine to make nitrate-leaching a serious problem in many irrigated areas.

Animal wastes appear to be another major contributors to high NO_3^--N in groundwater under village inhabitations and feedlots. Wide variations in NO_3^--N concentration in groundwater are seen and the same are attributed to variations in land use and management practices and unscientific disposal of animal dung and urine around dairy sheds.

Runoff water from fields receiving moderate to heavy doses of N fertilizer may contain higher concentration of NH_4^+ and NO_3^- ions. However, water pollution due to surface runoff has not been studied extensively.

Nitrate pollution of water is of main concern as drinking water is drawn mainly from groundwater. The quality of groundwater has a direct effect on human and animal health. If the drinking water has more than the safe limit of 10 mg NO_3^--N/L, ingested nitrate is converted to nitrite that is absorbed in blood, causing methemoglobinemia (commonly known as Blue Baby Syndrome) and gastric cancer.

7.3. Air Pollution and Climate Change

Though air contains 78% N, any change occurring in it causes imbalance in air composition. Nitrogen gas which exists in the atmosphere, is an inert gas, but its oxides are very reactive and are the potential source of atmospheric pollution in at least four ways: (a) NO and N_2O that are released from soil to atmosphere due to denitrification contribute to the formation of HNO_3, which is one of the principal components of acid rain, (b) N-oxides can react with volatile organic pollutants to form ground level ozone, a major air pollutant in the photochemical smog in urban areas, (c) Though constituting only 6-7% of the total loss of ^{15}N (Mohanty, 1997), when N_2O moves to the upper atmosphere it contributes to the greenhouse effect, which is 300-times more potent than of CO_2, and (d) When N_2O moves to the stratosphere, it reacts with and causes the depletion of stratospheric ozone, which shields the earth from harmful ultraviolet solar radiation (Brady and Weil, 2007).

Since fertilizer-use is markedly less in India as compared to developed countries and N fertilizers are applied in splits, environmental impacts are also expected to be less. However, every possible care should always be taken to achieve higher NUE and minimize environmental pollution. Integrated- and balanced-nutrient managements through inorganic and organic sources have shown immense benefits in improving soil health and crop productivity, and protecting environment. Formulation and adoption of careful strategies for applying appropriate amount of fertilizers and manures at proper times, using correct methods, should help synchronize nutrient supply with crop need and avoid excessive use in crops for economically viable sustainable crop production, and, in turn, reducing nitrate pollution of groundwater and water bodies as well as pollution of soil, plant and air.

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Chapter 17

Phosphorus

K.N. TIWARI

1. Introduction

Phosphorus (P), an essential nutrient for all living organisms, is a vital component of the substances that are building blocks of genes and chromosomes. In plants, it plays a role in virtually all biochemical processes that involve energy transfer. It is a constituent of adenosine triphosphate (ATP) which is often termed as 'energy currency' of the plant cell. Conversion of a mole of ATP to adenosine diphosphate (ADP) results in release of 32 kJ of energy. Uridine triphosphate (UTP), cytidine triphosphate (CTP) and guanosine triphosphate (GTP) are analogous compounds to ATP, which are required for the synthesis of sucrose, synthesis of phospholipids, and formation of cellulose, respectively. These nucleotide triphosphates are also involved in the synthesis of RNA and DNA. An adequate supply of P encourages root growth and enhances maturity. In seeds and fruits, P is stored as phytin, whereas in vegetable tissues, it is found as inorganic phosphate in the vacuoles. The total P-content in agricultural crops generally ranges from 0.1% to 0.5%. Deficiency of P leads to severe growth retardation, lowering of shoot/root ratio, reduced tillering in cereals, poor seed/fruit setting, poor quality and low yields. Visual deficiency symptoms appear as unusual dark green pigmentation on older leaves.

As an element placed in Group VB of the Periodic Table, P has the average atomic mass of 30.97 and atomic number of 15. A phosphorus atom can accept 3 electrons or give away 5 electrons, thus exhibiting oxidation-reduction state of -3 to +5. The +5 valence is important for most reactions in the soil as also in P fertilizer production. Phosphorus is taken-up mostly as the primary orthophosphate ($H_2PO_4^-$), but by some plants, it is also absorbed in the secondary orthophosphate form (HPO_4^{2-}). The amount of latter form of P increases with an increase in soil pH.

2. Global Phosphate Reserves and Resources

Phosphorus ranks 11th in order of abundance in earth's crust, through its concentration in many rocks is very small. It is also present in all soils, waters, organisms. Its reserves (i.e. deposits currently exploitable in economically-viable way) are found mostly as sedimentary formations and unrefined ore is known as phosphate rocks (PR). Depending on co-preciptation of three molecules of tricalcium phosphate with one molecule of CaF_2, $CaCl_2$ or $Ca(OH)_2$, three distinct types of apatites are formed namely, fluorapatite $[Ca_5(PO_4)_3.F]$, chlorapatite $[Ca_5(PO_4)_3.Cl]$ and hydroxyapatite $[Ca_5(PO_4)_3.OH]$. However, in most of the sedimentary deposites, partial replacement of PO_4 by CO_3 in apatite matrix has resulted in the formation of a series of carbonate apatites or francolites. These PR deposits differing in the grade (P_2O_5-content) are non-renewable and inequitably distributed in different countries. The US Geological Survey, in

2006, estimated world PR reserves at about 18,000 million tonnes, whereas P resources (potentially extractable with advancement in technology, but not economically feasible with currently available techniques) at about 50,000 million tonnes. Thus, with the current level of P-usage (PR production), P reserves and resources could last for between 105 and 470 years. Hence, the global P-supply is finite and it is necessary to use it efficiently so as to maximize period of its availability.

Countries like China, Morocco, Jordan, Egypt and Western Sahara, South Africa and USA are the major PR reserve holders, whereas India with its small share of global PR reserves depends largely on imports to meet its needs. Except an estimated PR deposits of 13.5 million tonnes in Jhamarkotra (Rajasthan) which are of high grade (about 30% P_2O_5), most of the other Indian PRs are of low grade (15-20% P_2O_5) and thus, are not suitable for use in the fertilizer industry.

3. Soil Phosphorus Content

The total P in soil consists of inorganic P- and organic P-forms. It occurs as orthophosphates in the mineral suite. A variable amount of P is associated with organic matter moiety, but in non-ortho forms. The total P-content of soils ranges between 200 and 2000 kg/ha in the upper 15-cm soil layer, with an average of 1000 kg/ha (Brady and Weil, 2002). The total P in Indian soils ranges from 120 to 2166 mg/kg. The soils derived from the parent materials rich in P, contain higher amount of total P. The total P-content is generally highest in soils developed on granite gneiss, followed by shales with basic intrusion, limestones with intrusions of micaceous schist and quartzite and a major fraction of total-P is present in clay. The total-P is rather poorly correlated with 'available P' in soils and therefore, rarely used as an index of soil fertility.

3.1. Inorganic Phosphorus

The inorganic P constitutes a dominant part of total P, and is considered to be the major contributor of P to the growing plants. In Indian soils, the share of inorganic P in the total P-content varies from 54% to 84% (Table 1). Phosphorus bound to aluminium (Al-P), iron (Fe-P) and calcium (Ca-P) constitutes the major active forms of inorganic P. The relatively less active are the occluded and reductant-soluble forms of P. These forms exist in all soils, but generally Al-P and Fe-P are more abundant in acid soils, and Ca-P dominates the neutral to alkaline soils (Table 2). Highly mobile-P in sodic soils is thought to be associated with sodium ions (Na+). Various forms of P are interrelated and contribute to the pool of plant-available P according to their physico-

Table 1. Total, organic and inorganic P-content in surface layer of Indian soils

State	Total P (mg/kg)		Organic P (% of total P)	Inorganic P@ (% of total P)	Organic C: Organic P ratio	
	Range	Mean			Range	Mean
Himachal Pradesh	732-2166	1200	19.9	80.1	45-137	64.4
Punjab	475-575	526	15.7	84.3	40-46.4	44.0
Haryana	488-1268	830	31.2	68.8	69.5-105.4	84.6
Uttar Pradesh	336-969	684	36.2	63.8	14.8-63.6	38.99
Rajasthan	120-530	370	45.6	54.4	15.2-117.3	33.0
Maharashtra	310-800	565	24.1	75.9	28-450	143.2
Assam	496-728	562	40.6	59.4	36.7-69.9	55.0
Mizoram	203-342	259	26.8	73.2	226-553	342
Orissa	152-620	397	46.0	63.1	20.1-171.1	35.8
Tripura	432-563	488	36.9	54.0	50.6-71.4	64.0
Tamil Nadu	190-1200	507	42.6	57.4	-	-
India	44-3580	-	-	-	-	-

Source: Tomar (2000). @Obtained by subtracting organic P from total P.

Table 2. Distribution of different forms of P in some Indian soils

Place and state	Total P (ppm)	Saloid-P	Al-P	Fe-P	Ca-P	Org-P	Unextracted P (occluded)	P-fixing capacity
		(% of total P)						
Ludhiana, Punjab	435	1.26	3.68	4.57	33.77	8.74	47.98	11.20
Bangalore, Karnataka	322	2.39	10.50	15.78	3.29	7.14	60.93	11.67
Rajahmundry, Andhra Pradesh	609	0.15	3.78	3.10	45.16	6.90	40.91	70.00
Kanpur, Uttar Pradesh	539	0	1.52	1.13	37.93	13.54	45.88	60.00
Pusa, Bihar	583	0.50	0.70	0.31	59.81	21.44	17.24	30.90
Agartala, Tripura	299	0	7.19	7.85	3.47	33.11	48.38	47.84

Source: Khanna and Datta (1968)

chemical properties such as composition, solubility, surface area, age, etc. The Al-P and Fe-P can constitute 1-25% (generally 8-10%) of total P in soils. Their proportion is higher in fertilized than unfertilized soils. The Ca-P can constitute 40-50% or even more of total P in many neutral to alkaline, and calcareous soils. In acid soils from south India, up to 40% of all P may be reductant-soluble. The reductant-soluble and occluded forms in acidic red and laterite soils can be twice as dominant as in neutral to alkaline alluvial or black clay soils. In highly-weathered acid soils of Bihar, over 50% of the total P is found in the occluded forms. The P-spectrum shifts from a Ca-P dominated one in young, neutral to alkaline soils of high base status towards a scenario dominated by occluded and reductant-soluble P in old, highly-weathered acid soils. The latter forms perhaps represent the ultimate P-sink in many tropical and subtropical soils, and to the extent possible, fertilizer management practices should aim at reducing the conversion of added P into these forms.

Very little P is present in the soil solution, its concentration being less than 0.1 mg/L P (0.5 kg P_2O_5/ha of plough layer) in unfertilized soils. At any time P concentration in soil solution is governed mainly by the P release and fixation/adsorption processes that occur continuously in the soil. As the P is drawn from soil solution largely through diffusion, it is replenished by the solid phase pool of available P. Fertilizer P is added to charge this pool. The Al-P and Fe-P fractions are the major contributors to plant-available P under most situations, including those where Ca-P is much more abundant than Al-P or Fe-P.

3.2. *Organic Phosphorus*

The proportion of organic P in mineral soils may vary between 20% and 80% of total P, depending on the age of soil, organic matter content, climate, vegetation, soil texture, land use, etc. The share of organic P to total P on average, varies from 16% to 46% in different states (Table 1), although intra-state variations in soil organic P are much larger and vary from as low as 3.2% to as high as 73% of the total P-content of the soil. In extreme cases, it is almost nil in the desert dunes of Rajasthan to more than 90% of total P in the new alluvial highlands of Assam. The principal organic phosphorus compounds present in the soils are: (i) inositol phosphate, (ii) phospholipids, (iii) nucleic acids, and (iv) other unidentified esters and phosphoproteins. The contents of nucleic acid and inositol P range from 0 to 18 mg/kg and 7 to 140 mg/kg, respectively in the calcareous soils of Rajasthan. Inositol hexaphosphate and phospholipids constitute 16% and 0.7% of organic P, respectively in Tamil Nadu soils, whereas in Uttar Pradesh (including Uttarakhand) soils, phospholipids constitute 1.9% to 4.7% of total organic P, inositol penta- and hexaphosphates form 10% to 29%, and lower inositol P forms 2% to 9% of the total organic P.

Perhaps due to the low organic matter content of many Indian soils and inadequate knowledge about organic P in soils, this fraction has not been as intensively investigated as the inorganic P fraction. Hence, the contribu-

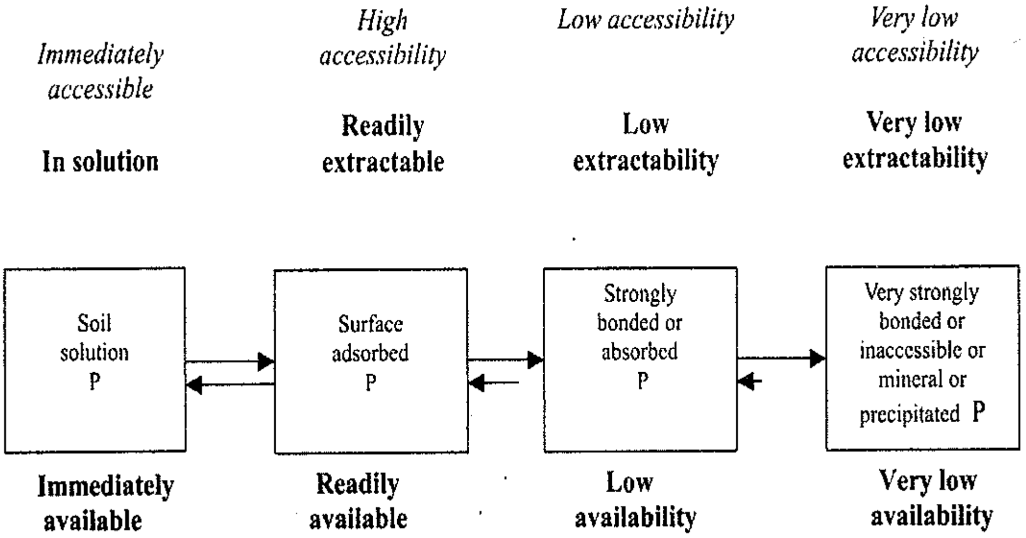


Figure 1. A conceptual illustration of different pools of inorganic P in soils
Source: Syers *et al.* (2008)

tion of organic P towards meeting the P needs of the crops is often underestimated. In fact, the major advantage of organic P is its slow release, which may not only be in synchrony with crop uptake, but also supply sizeable quantities of P during a crop season (Prasad, 2007).

3.3. *Influence of pH on the Forms of Inorganic Phosphate*

The type of phosphate ions present in the soil solution depends on the soil pH. In soils having neutral to slightly alkaline pH, the HPO_4^{2-} is the most common form. As the soil pH gets lowered and it becomes slightly to moderately acidic, both HPO_4^{2-} and $H_2PO_4^-$ ions prevail. At higher soil acidity, $H_2PO_4^-$ form tends to dominate (Figure 1). It can be represented by Equation (1):

$$\underset{\text{(Strong acidic solution)}}{H_2PO_4^-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_2O + HPO_4^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{(Strong alkaline solution)}}{H_2O + PO_4^{3-}} \qquad \ldots(1)$$

4. Phosphorus Transformation in Soil

4.1. *Soil Phosphorus Pools*

Inorganic P is more likely to be retained by soil components with a continuum of bonding energies, thus more strongly bound P is less available for uptake by plant roots and *vice versa*. Moreover, sorbed P has varying extractability or availability, related to the nature of its physical association with retaining components in the soil. Based on accessibility by the roots and extractability, and thus availability to the plants, P is considered to be in four different pools as conceptually shown in Figure 1. In the soil solution (first pool), P is immediately available for uptake by the plant. The readily-extractable P held on the soil surfaces represents the second pool, which is considered to be in equilibrium with soil solution P. The third pool represents less readily-extractable P that is more strongly bonded to soil components or is present within the matrices of soil components as absorbed P. This may become plant available with time. The P in the fourth pool has very low extractability and very slow availability because of one or more of the following reasons: (i) bonding very strongly with soil components; (ii) precipitation as partially-soluble P components; (iii) P becoming a part of soil mineral complex; or (iv) unavailability owing to its position within the soil matrix. The P in the second and third pools is considered labile, whereas P in the fourth pool is non-liable.

As mentioned earlier, the inorganic P-forms in soil are the compounds associated mainly with aluminium, iron and calcium (and also with other cations such as Zn, Cu, etc.). Their relative abundance and solubility is controlled by a number of factors including soil pH (Figure 2). The importance of inorganic forms of P in plant nutrition is strongly reflected in the soil test

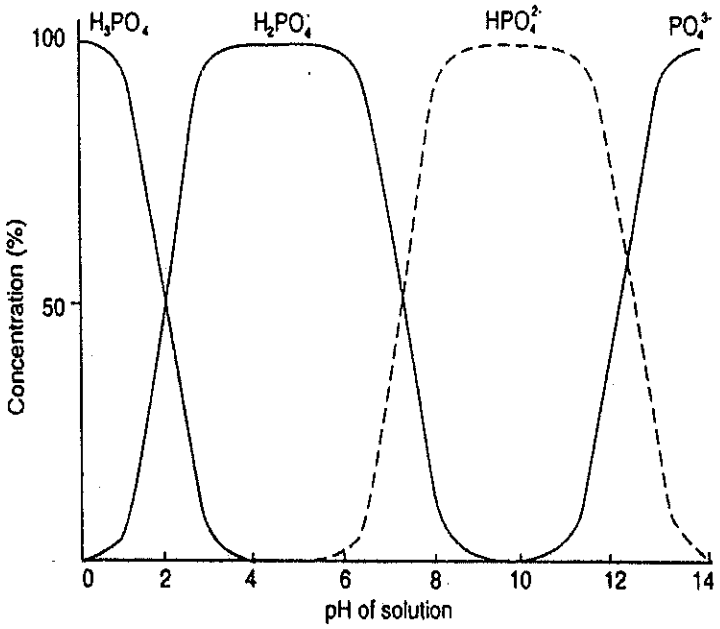


Figure 2. Relationship between solution pH and the relative concentrations of three soluble forms of phosphate. In the pH range common for soils, $H_2PO_4^-$ ions predominate

methods being used at present (Bray and Kurtz No. 1 and Olsen's sodium bicarbonate method). The estimates of plant-available P, which these methods provide, are based exclusively on the inorganic forms of P. However, it is to be noted that organic forms do contribute to plant nutrition through mineralization of soil organic matter.

Out of the three major groups of inorganic forms of P in soil, calcium phosphates are normally the dominant group in young soils in the initial stages of weathering, and for a given site in the sub-soil (all factors are related with basic soil reaction where calcium compounds are more stable). Often during the soil-weathering processes under adequate rainfall, bases (such as calcium, magnesium, sodium, etc.) are leached out of the soil leaving behind a material more acidic in character, and under such conditions, a part of the calcium phosphates may get converted to phosphates of aluminium and iron (Figure 3). The process may continue for years, but at no stage large quantities of P are left in the soil solution and the transfer is from one set of water-insoluble compounds to another set of water-insoluble compounds. The point of interest is that the soil P system contains a large number of compounds of differing reactivity which are sparingly soluble in water or soil solution, but nevertheless play an important role in crop nutrition.

4.2. Fertilizer Phosphorus

When a phosphate fertilizer, such as superphosphate, is applied to a soil, all its phosphorus being water-soluble immediately enters the soil solution and readily forms new compounds with calcium, aluminium, iron, manganese, etc. and gets out of the solution as soon as the newly-formed compounds are precipitated. These sparingly-soluble compounds are called initial reaction products. All these reactions take place in close proximity of the site of placement of a phosphatic fertilizer and are fairly rapid. The rate of reaction and the volume of soil affected are strongly influenced by the water-soluble component of P.

It is now well recognized that the value of phosphate fertilizers depends primarily upon the release of phosphorus from the initial reaction products rather than the fertilizer *per se*. The chemistry of soil phosphorus in cultivated soils, receiving soluble phosphate fertilizers is virtually the chemistry of these metastable phosphate compounds, their solubilities, and their interactions with other soil components. The major reaction product of monocalcium phosphate, $Ca(H_2PO_4)_2.2H_2O$ — the water-soluble

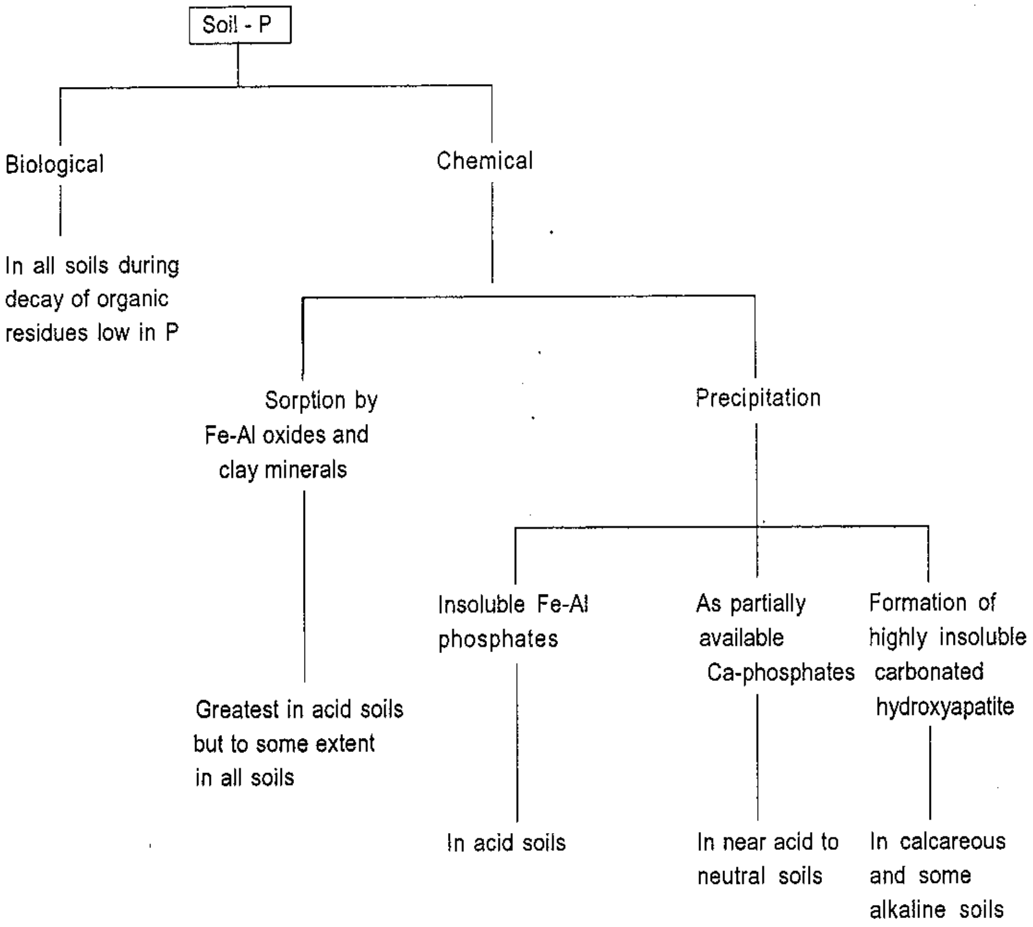


Figure 3. Schematic representation of phosphorus transformation in soils

constituent of superphosphates — with soil has been identified as brushite, $CaHPO_4.2H_2O$, which is often associated with monetite ($CaHPO_4$). The other product identified is octacalcium phosphate. The reaction products of monocalcium phosphate, mono-ammonium phosphate, and mono-potassium phosphate with some black, brown, and calcareous soils of India have been identified to be brushite, monetite, and taranakite in varying proportions. In some calcareous soils apparently containing magnesium, struvite ($MgNH_4PO_4.6H_2O$) and newberyte ($MgHPO_4.3H_2O$) have been detected. In addition, amorphous iron and aluminium phosphates are also formed. The reaction products vary in their ability to release phosphorus for utilization by crops.

It is thus clear that soil-fertilizer reaction products and not the fertilizers *per se* govern the supply of P to plants (Figure 4). The efficiency of a fertilizer may thus depend upon the degree and duration for which its reaction products can serve as sources of plant-available phosphorus.

4.2.1. Effect of Moisture Regime

The moisture regime during cropping also influences the transformations fertilizer P in the soil. Flooding and submergence of soils with a wide range of pH create reducing conditions which lead to reduction of ferric phosphate to ferrous phosphate, resulting in greater availability of P in the soil. Organic acids formed under submerged conditions also solubilize phosphates. For example, in a wheat-rice cropping sequence, added fertilizer P undergoes changes with increased formation of Al-P and Fe-P due to the initial wet conditions prevailing during wheat cultivation, and the availability is increased with flooding in the subsequent rice crop. However, in the rice-wheat sequence, initial flooding decreases Al-P and Fe-P, leading to relatively low availability of P to the subsequent wheat crop. Hence, the application of fertilizer P to wheat produces a better residual effect on the following rice crop. Generally, Al-P declines sharply after *kharif* rice and this decline is greater in high P soils. Fe-P gets depleted under rice but it improves after

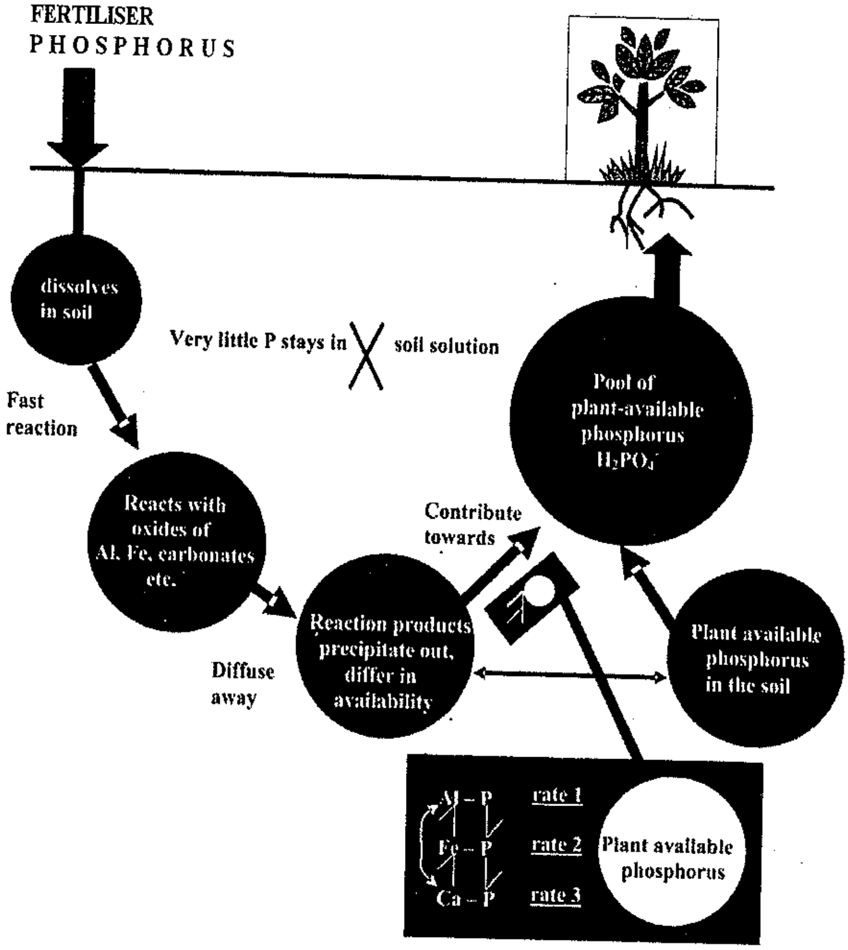


Figure 4. A generalized diagram of the reactions of applied phosphorus in soil and sources of plant available phosphorus

maize and millet, especially in low P soils. The reaction products containing iron assume special significance in rice nutrition as indicated by theoretical considerations and also confirmed by research reports. Ca-P continues to decrease due to cropping and the extent of decline is greater in rice-wheat rotation which is regarded as an exhaustive rotation compared with rice-maize or rice-millet rotation.

5. Phosphate Fixation

The fixation of P by soils has long been recognized. Thomas Way in 1850 demonstrated that the whole of phosphate was retained when solutions of sodium phosphate in water and guano in dilute H_2SO_4 were poured over a layer of calcareous soil. He suggested that an insoluble calcium phosphate was formed, resulting in a decrease in the solubility of the applied phosphate. Phosphate fixation or reversion can be viewed as the conversion of soil solution P to insoluble compounds by the soil components, causing reduction in the amount that plant roots can absorb. Mechanisms involving sorption and precipitation have been suggested to explain the P fixation in soils. In fact, P fixation is not an ideal adsorption on soil components, but a combination of adsorption, chemisorption and precipitation. Soil solution pH has a significant effect on phosphate fixation. In neutral to alkaline soils (pH 7 and above), phosphates get adsorbed on calcium carbonate and are then precipitated as tricalcium phosphate, and are slowly converted to insoluble apatites. In acid soils (pH below 7), iron and aluminum react with phosphate to form highly insoluble compounds. These reactions can be represented by the chemical Equations (2) and (3), respecitvely. In this way, some phosphate of the liable pool is continuously being transferred to the non-liable pool and thus becomes immobile.

1. In neutral to alkaline soils:

$$\underset{\text{Monocalcium phosphate (soluble)}}{Ca(H_2PO_4)_2} + \underset{\text{Calcium carbonate (lime)}}{2CaCO_3} \longrightarrow \underset{\text{Tricalcium phosphate (insoluble)}}{Ca_3(PO_4)_2} + 2CO_2 + 2H_2O \quad ...(2)$$

2. In acid soils:

$$\underset{\text{Aluminum ions}}{Al^{3+}} + \underset{\text{Dihydrogen phosphate (soluble)}}{H_2PO_4^-} + 2H_2O \longrightarrow 2H^+ + \underset{\text{Aluminum hydroxy phosphate (insoluble)}}{Al(OH)_2H_2PO_4} \quad ...(3)$$

In neutral to alkaline soils, reversion of soluble monocalcium phosphate (low basicity i.e. Ca/P ratio) to insoluble hydroxy apatite (high basicity) could be explained as under:

P-reaction products	Basicity (Ca/P ratio)
Monocalcium phosphate [$Ca(H_2PO_4)_2$]	0.5
⇓ *Soil solution Ca*	
Dicalcium phosphate [$CaHPO_4 . 2H_2O$]	1.0
⇓ *Soil solution Ca*	
Octacalcium phosphate [$Ca_8H_2(PO_4)_6 . H_2O$]	1.33
⇓ *Soil solution Ca*	
Tricalcium phosphate [$Ca_3(PO_4)_2$]	1.50
⇓ *Soil solution Ca*	
Hydroxy apatite $3[Ca_3(PO_4)_2].Ca(OH)_2$	1.67

On the other hand, variscite ($AlPO_4.2H_2O$) and strengite ($FePO_4.2H_2O$) are the final products in strongly acidic conditions where the pH is lower than 4. Since the products of phosphate fixation are sparingly soluble to insoluble, only minute amount of P is immediately available for uptake by the plants. As the soil solution is depleted of P by plant uptake, it must be replenished by dissolution of the solid-phase phosphates. If the solid phase of the compounds has a higher solubility, soil solution is replenished more readily. The initial products of fixation may revert to other products of even lower solubility.

Soil temperature also affects the solubility of chemical compounds. Phosphorus is available more in warm soils than in cold soils. Winter crops often respond to phosphate fertilizers even at relatively high soil P levels. This fact is important for P management in winter crops. Roots also grow faster in warm soils. Therefore, they explore more soil volume from which nutrients can be absorbed. The low solubility of P in soil further reduces its movement through diffusion. Therefore, the placement of phosphate fertilizers into the root zone is imperative for efficient utilization.

Three types of reactions could be considered important in relation to phosphate fixation in soils: (i) adsorption, (ii) isomorphous replacement, and (iii) double decomposition. The adsorption isotherms give an idea about the adsorption reactions. At low concentrations of phosphate in solution, the adsorption isotherm fits well either the Freundlich or the Langmuir equation. But, at high concentrations and on prolonged contact, other reactions take place. The isomorphous replacement of the hydroxyl ions with phosphate ions is a possibility.

The reactions of iron and aluminium hydroxides with the phosphate ions are probably most significant for phosphate fixation in soils. Studies on the hydroxides of iron and aluminium as well as a few minerals like goethite, haematitie, etc. have shown that one phosphate ion replaces two surface hydroxyl ions or water molecules and coordinates with two of the oxygen atoms of phosphate, each to a different Fe^{2+} ion. It has been noted that gibbsite forms a surface complex consisting of two adjacent phosphate ions and a central divalent cation of appropriate size, charge, and coordination properties. The other mechanism may be the formation of aluminium and iron phosphates of various solublities, depending upon pH of the system.

Based on the equilibrium constants and solubility product data of various soil phosphorus reactions, a phosphate cycle is depicted in Figure 5.

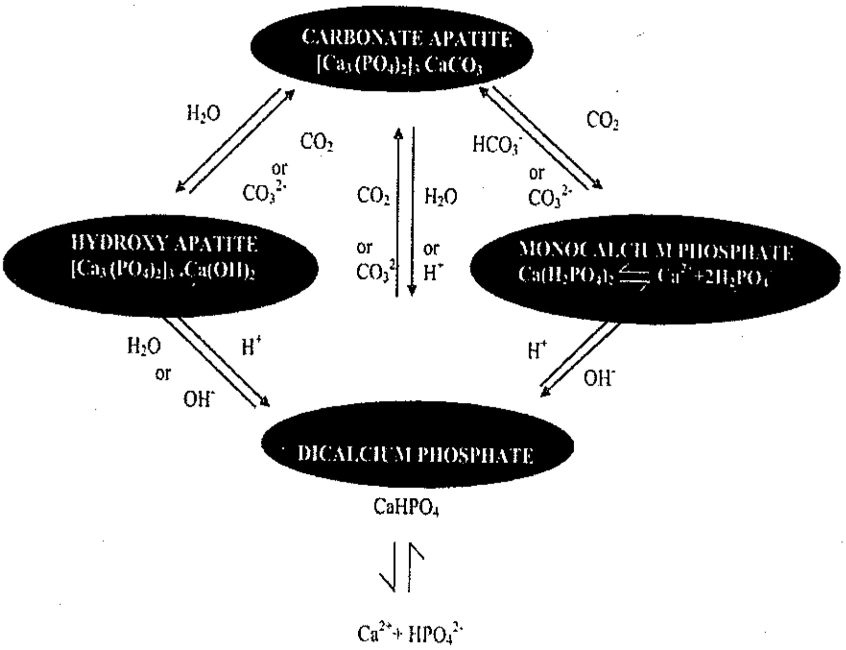


Figure 4. Phosphate cycle

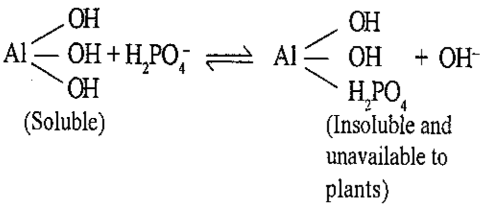
5.1. *Factors Affecting Phosphate Fixation*

There are various factors which affect phosphate fixation in soils like (i) nature and amount of soil components, (ii) pH, (iii) organic matter, (iv) temperature, and (v) overliming.

5.1.1. *Nature and Amount of Soil Components*

Adsorption and desorption reactions are affected by the type of surfaces contacted by P in the soil solution. However, various other soil components also affect phosphate fixation.

(i) Hydrous Oxides of Iron and Aluminium– Soils with significant contents of amorphous iron and aluminium oxides have larger P-fixing capacities than crystalline ones, because of their larger surface areas. About 78 to 89% variation in P-sorption in these soils has been assigned to oxalate-extractable Fe. Fixation of P by oxides of Fe and Al takes place over a wide pH range, as shown in reaction (4):



$$\mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{cases} + H_2PO_4^- \rightleftharpoons \mathrm{Al}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ H_2PO_4\end{cases} + OH^-$$

(Soluble) (Insoluble and unavailable to plants)

...(4)

(ii) Clays— Capacity of soil to adsorb P is related to the quantity and quality of clay. Soils containing large quantities of clay retain more P than those having small amounts of clay. Phosphorus is retained to a larger extent by 1:1 than 2:1 clays. There is more adsorption of phosphate in laterite soils (Nilgiris) because of the presence of kaolinite as the dominant clay mineral, and higher amounts of hydrous oxides of Fe and Al. The phosphate adsorption is minimum in black soils, being rich in smectite type of minerals which have practically no capacity for anion adsorption.

(iii) Soluble Silica— Capacity for P-sorption enhances with increased soil weathering (decreased Si solubility). The efficiency of utilization of phosphorus by rice has been found to increase with the addition of sodium silicate.

(iv) Amorphous Colloids— Amorphous aluminosilicates like allophane (Si–Al–Fe–O–OH–OH_2) have a large negative charge which is partly or entirely balanced by the complex aluminium cations. Phosphorus gets adsorbed by reacting with such aluminium ions.

(v) Calcium Carbonate— In calcareous soils, calcite acts as the adsorbent site for P. The amount and reactivity of calcium carbonate influence P-sorption. Impure calcites (with

hydrous ferric oxide as impurities) and those of high specific surface (clay-sized $CaCO_3$) result in more sorption of P and more rapid formation of Ca-phosphate precipitates. The suppression effect of $CaCO_3$ on the extractability of 0.5*M* $NaHCO_3$ (Olsen's reagent) may be due to (i) decreased dissolution of Ca-P or (ii) re-precipitation of dissolved P due to increased calcium activity in soil solution.

(vi) Cations— More P is sorbed with increasing valency of the exchangeable cations in the system. Acid soils retain more P than alkaline ones, whereas neutral soils adsorb more P than saline/sodic soils.

(vii) Anions— The effect of inorganic anions on P-sorption in alluvial, laterite and black soils indicates that anions are more effective in reducing P-sorption capacity in coarse-textured soils than in fine-textured ones. The effect is more pronounced in non-calcareous soils than in calcareous ones. Among inorganic anions, F^- is more effective than sulphate ions.

(viii) Supporting Electrolyte— Ionic nature and composition of the supporting medium is one of the principal variables that affect P-sorption. The P-retention enhances with increasing concentration of the supporting medium and decreases with monovalent cation in the electrolyte.

5.1.2. pH

In strongly acidic soils, phosphate is fixed largely through precipitation with iron and aluminum in solution, and by reactions with iron and aluminum hydrous oxides. In moderately acidic soils, P is fixed by hydrous oxides of aluminum and iron and by anion exchange on silicate clays. In slightly acidic soils, P is fixed by hydrous oxides of aluminum and iron, and by silicate clays, as insoluble calcium phosphates. In alkaline soils, the soluble P from fertilizer reacts initially with calcium to form dicalcium phosphate which later becomes octacalcium phosphate. Both of these compounds have limited water solubility, but they do provide P to plants. With time, these compounds revert to more insoluble forms of phosphate, such as tricalcium phosphate and hydroxyapatite. Even these insoluble compounds are slowly available to plants. Thus, the fixation of P does not result in a completely irreversible loss of available phosphate from the soil but continues to provide phosphorus to crop on a limited scale over an extended period of time. The fixation of phosphates in relation to different soil pH is presented in Figure 6.

5.1.3. Organic Matter

During decomposition of organic matter, various organic acids are produced which solubilize phosphates and other phosphate–bearing minerals and thereby lower phosphate fixation. The decrease in phosphate fixation due to the presence of sufficient organic matter in soils may be ascribed to the following reactions:

(a) By the formation of phosphohumic complexes that are easily assimilated by plants,

(b) Through the replacement of phosphate by the humate ion (anion exchange reaction), and

(c) By forming a coating on sesquioxide particles by humus as a protective cover and thus reducing the phosphate-fixing capacity of the soil.

5.1.4. Temperature

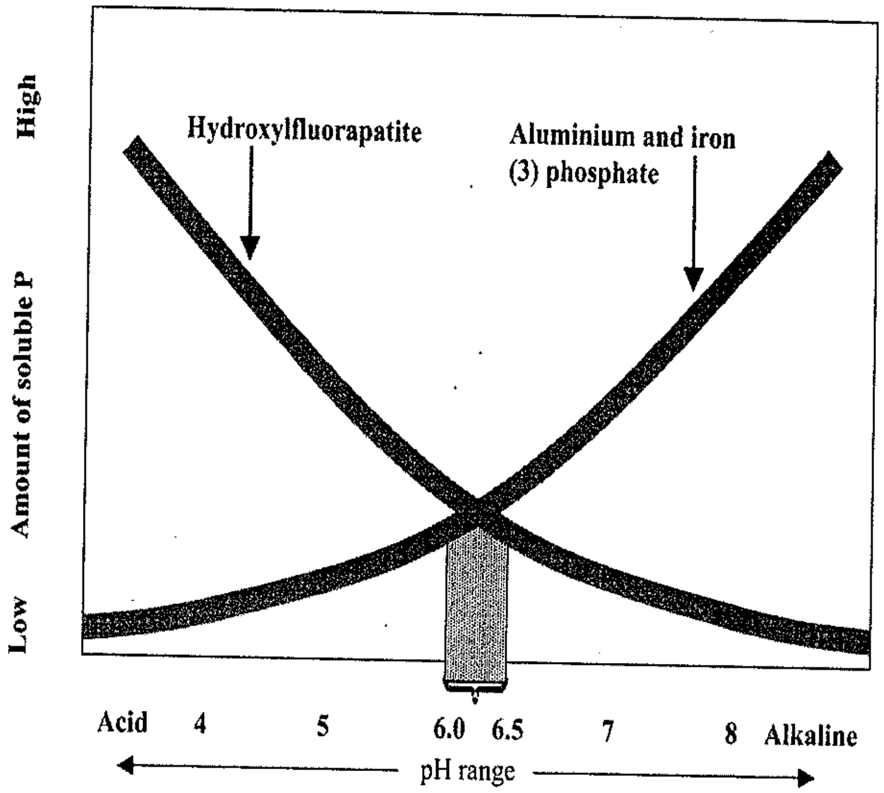
The rise in temperature generally enhances P-sorption in soils.

5.1.5. Overliming

Overliming increases the fixation of phosphorus by forming more insoluble Ca-P compounds in soil.

6. Organic Matter Addition *vis-à-vis* Sorption–Desorption

The incorporation of green manure or recycling of crop residues into soil influences the reactions of phosphate and consequently, its availability to plants. In calcareous soils, $CaCO_3$ immobilizes the added phosphate. Use of organic manures, however, partially offsets the effect of $CaCO_3$ by keeping the reaction products in metastable or poorly crystalline form for a longer period after the addition of a fertilizer. The incorporation of green manure also reduces P-sorption by soil. Amending soil



Solubility of calcium phosphates= Very good
Solubility of aluminium and iron phosphates= poor

Solubility of calcium, aluminium and iron phosphates= Equally good

Solubility of calcium phosphates=Poor
Solubility of aluminium and iron phosphates= Very good

Figure 6. A schematic diagram depicting the effect of soil pH on the solubility of different forms of phosphorus (*Source*: BASF, West Germany)

with organic residues/green manures helps in increasing the P-concentration in soil solution through mineralization of organic P and solubilization of native soil P compounds. This effect is more pronounced at a higher moisture level. The effect of green manure in regulating the release of P and enriching the labile pool is more pronounced in strongly acidic and alkaline soils than in normal soils.

7. Phosphorus Fixing Capacity of Soils

Amongst the soil groups, black, red, laterite, mixed red and black, red and yellow, and coastal alluvial soils exhibit higher P-fixation than the alluvial, grey brown, desert and other soils. The maximum phosphate-fixation in soils of Bihar and Jharkhand has been found to vary from 25% to 90%. In another study, more than half of the conversion of fertilizer-P has been found in the form of Al-phosphate, followed by Fe-phosphate. Similarly, 60-70% of the applied P has been found to remain fixed in the form of Al, Fe and Ca-P after the harvest of rice crop. The relationship of phosphate-fixing capacity of soils to added phosphate is depicted in Table 3, which reveals that the phosphate-fixing capacity is in the order: red soil > medium black > heavy black > grey brown > alluvial soils.

8. Phosphate Buffering Capacity

The phosphate buffering capacity (PBC) of soil characterizes the dynamic relation between labile solid phase (Quantity) and solution phase phosphate (Intensity) from which plants take up their supply. It is measured from the slope of the sorption isotherm or quantity-intensity isotherm, and it varies according to the solution concentration at which isotherm slope is measured. Various indices used to ex-

Table 3. Relationship of the P-fixation capacity with added phosphate in some Indian soils

Location	Type of soil	P fixed / P added
Delhi	Alluvial soil	0.26
Bikramganj (Bihar)	Old alluvium	0.36
Katihar (Bihar)	New alluvium	0.38
Kanke (Jharkhand)	Red loam	0.36
Aduthurai (Tamil Nadu)	Alluvial soil	0.56
Coimbatore (Tamil Nadu)	Black soil	0.48
Ludhiana (Punjab)	Grey brown	0.71
Pune (Maharashtra)	Medium black	0.75
Ranaghat (West Bengal)	Alluvium	0.80
Powarkheda (Madhya Pradesh)	Heavy black	0.81
Hyderabad (Andhra Pradesh)	Medium black	0.81
Naihati (West Bengal)	Red soil	0.85

press this parameter are: (i) slope at a standard equilibrium concentration of 0.2 µg/mL, (ii) slope at a standard equilibrium concentration of 0.3 µg/mL, (iii) maximum slope of the isotherm as solution concentration tends to zero, and (iv) ratio between the change in quantity factor and intensity factor designated as differential buffering capacity.

A close linear relationship exists between P- buffering capacity and ability of soil to sorb phosphate. The sandy soils have less PBC than the fine-textured soils. The PBC of acidic and neutral soils is a function of the amount and extent of crystallinity of hydrated oxides of Fe and Al. In calcareous soils, the amounts of exchangeable calcium and $CaCO_3$ determine the PBC. Differential PBC in soils from north-western India shows a significant relation with total Fe and Al, organic carbon and clay and in Sikkim soils with organic carbon-content. It is also reported that PBC per unit clay is more in red soils than in black and alluvial soils. Intensity is inversely related to PBC of soil; so soils with high PBC will have less P-concentration in soil solution for exploitation by plant roots, but sustain the concentration for a longer period.

8.1. Quantity-Intensity Relationships

In proposing the monocalcium phosphate potential as the best measure of available P in soil, Schofield (1955) divided measurements into 'intensity of supply' (as measured by phosphate potential) and quantity, indicating the total quantity of P in the soil. He has also emphasized the importance of the rate at which this function decreases as phosphate is taken up by plants from the 'pool' of phosphate in the soil which is at the same chemical potential. The 'capacity' of soil or, more aptly, the 'phosphate-buffering capacity' of the soil to resist depletion is determined by the nature of the relationship between intensity (I) and quantity (Q) factors. If Q and I are expressed in the same units, capacity 'C' is a dimensionless parameter. If Q and I are expressed as the weight of phosphate per unit volume of soil and solution, respectively, then capacity will depend on the bulk density of the soil, which also affects the volumetric soil-moisture content. In a limited range of P-concentration, where the Q/I relationship is linear, the capacity factor 'C' is constant. But, for the concentration ranges and the soil in which 'capacity' varies nonlinearly with intensity, a relationship of the type, Capacity = $\partial (RI_n)/\partial I$, where, R and n are constants, could be more appropriate.

The quantity-intensity relationships of P can be worked out using Equation (5):

$$Q = (K_1 c)(K_2 + c) \qquad \ldots(5)$$

where, c is concentration and K_1 and K_2 are constants.

For a given value of intensity, the quantity values for fine-textured soils are higher than for coarse-textured soils. Availability of P to plant is controlled by the mutual inter-play of factors such as quantity, intensity and phosphate-buffering capacity. These factors along with kinetic factors determine the diffusive flux of P to the growing roots. Attempts have, therefore, been made to predict the availability of applied P to crops through the combined use of all these factors in a dimensionless parameter known as 'supply parameter', $(Qc)^{1/2}/(K_1K_2)^{1/4}$. The supply parameter of P has been found to bear a close linear relationship with cumulative P desorbed, indicating thereby usefulness for predicting crop response to applied P.

9. Phosphorus Movement in Soil

Diffusion is the main process by which P moves from soil solution to the root surface. Thus, when plant roots remove phosphate ions from the soil solution and the concentration is lowered relative to the bulk solution, a concentration gradient develops and phosphate ions move down this gradient. The mobility of an ion is defined in terms of diffusion coefficient, which is usually smaller in soils than in a homogeneous media (like water). Marschner (1995) estimated the diffusion coefficients of $H_2PO_4^-$ (the most common form of orthophosphate) in water as 0.9×10^{-9} m²/s, but in soil the estimates ranged from 10^{-12} to 10^{-15} m²/s. At an average value of 1×10^{-13} m²/s, the movement of $H_2PO_4^-$ would be about 0.13 mm per day. This extremely slow movement of phosphate ions explains why it is necessary to have a sufficient supply of readily-available P through the volume of soil explored by roots during active growth periods. It also explains the observed superiority of placement of fertilizer P in the vicinity of roots compared with broadcasting.

10. Available Phosphorus Status

The P-fertility problems of the soils are three-fold: (i) total P-content of the soil is low, generally not more than one-tenth to one-fourth that of N, (ii) P compounds that occur in soil are sparingly soluble to insoluble, and (iii) fixation of soluble P-sources to unavailable forms. The total P-content is generally not directly related to plant-available P-content, whereas relative solubility of P compounds and fixation of phosphates govern to a large extent the availability of P in soil.

The P-fertility status of soils in India was first compiled by Ramamoorthy and Bajaj (1969), followed by Ghosh and Hasan (1979), Hasan (1996), and lately by Motsara (2002), using the data generated by soil testing laboratories (STLs) (Table 4). The recent scenario (Motsara, 2002) revealed that in India the soils of 42% of the districts are in low P-category, of 38% in the medium category and of 20% districts in the high P-category. When compared with the first summary published in 1969, districts falling in the low and medium P-fertility classes decreased by 5% and 11%, respectively, whereas those with high fertility increased by 16%. These comparisons though apparently indicate a build-up in available-P status over the years, such a conclusion should be drawn with caution, because not only the number of samples per district varied but also a variable number of samples were used for the preparation of soil fertility summaries in different years.

10.1. Available-P in Different Soil Types

An appraisal of available-P status in relation to the major soil groups or associations indicates that generally deep black, grey brown, desert and red loamy soils of semi-arid regions have medium fertility level. Similarly, foothill

Table 4. P-fertility status of Indian soils as compiled from the soil testing laboratories database

Year of compilation	No. of samples	Districts in P-fertility classes, %			Reference
		Low	Medium	High	
1969	1.3 million	47	49	4	Ramamoorthy and Bajaj (1969)
1979	9.2 million	46	52	2	Ghosh and Hasan (1979)
1996	9.6 million	49	49	2	Hasan (1996)
2002	3.65 million	42	38	20	Motsara (2002)

Table 5. Available-P content and some other related soil parameters in representative pedons of major soil types in India

Soil series	Horizon/ depth (cm)	pH (1:2.5)	Organic C (%)	Available P (kg/ha)
Katki (Typic Haplustalf)	AP/ 0-12	6.8	0.60	12.3
Jagdishpur Bagha	0-15	7.7	0.60	11.4
Lukhi (Typic Ustochrept)	AP/ 0-8	8.2	0.36	4.1
Modhpur (Typic Endoaqualf)	AP/ 0-13	6.0	0.47	9.7
Torkewali (Lithic Ustorthent)	0-17	7.4	0.66	25.9
Islamnagar	0-15	7.4	0.38	4.4
Coimbatore (Vertic Ustochrept)	0-15	8.1	0.20	5.2
Sukali (Typic Ustochrept)	AP/ 0-14	8.0	0.19	4.7
Patancheru (Udic Rhodustalf)	0-10	5.5	0.31	12.2
Vijaypura (Typic Kandiustalf)	AP1/ 0-7	5.6	0.25	56.5
Trivendrum (Ustoxic Dystropepts)	AP/ 0-9	5.6	0.72	4.8
Zarifa Veeran (Typic Natrustalf)	A1/ 0-5	10.3	0.31	18.8
Mataur (Dystric Eutrochrept)	0-20	6.5	0.82	14.5

soils, isolated alluvial strips of the northern region, and coastal alluvium that are not sandy in nature, largely depict medium available-P status. The few districts in which the soils are rich in this nutrient are part of arid tracts, foothills of high altitude, and cold and semi-dry regions where the intensity of cultivation has been low. The vast alluvial tracts of central, eastern and southern parts of the country, the latosols, medium black, mixed red and black soils, red (gravelly) loams of semi-humid or humid regions and sandy coastal alluvium are usually low in available-P. Notwithstanding these earlier reports, the available-P content of top soil in the representative pedons of major soil types differed inconsistently, irrespective of soil series and parameters like soil pH and organic C content (Table 5).

11. Soil Testing for Phosphorus

Routine soil tests measure P that is in the soil solution and in the readily-plant-available soil pool. Thus, the extractable P is not a definite quantity but will vary with the reagent used. However, provided that there is a strong relationship between the extracted P and the response of a crop to application of P fertilizer, the extracting reagent is considered reasonably good for soil testing. A number of soil test methods, including the ones using acids, salts, buffered solutions and alkalies, have been used by different workers for the determination of available phosphorus in soil. The most widely used methods by soil testing laboratories to measure available P in India are: 0.5 *M* $NaHCO_3$, pH 8.5 (Olsen *et al.*, 1954) and 0.03 *N* NH_4F + 0.025 *N* HCl (Bray and Kurtz, 1945). Yet, suitability of soil test methods for diverse soil-crop conditions is presented in Table 6.

Most of the STLs categorize soils as low, medium or high in available-P, according to the amount of P extracted and recommend fertilizer P doses accordingly. A soil analyzing less than 10 kg P/ha (Olsen-P) is categorized as low in available-P (deficient), between 10 and 25 kg P/ha as medium and over 25 kg P/ha as high in P for field crops. Some STLs have further expanded these ratings into 5 to 6 categories for more specificity in fertilizer recommendation purposes.

12. Phosphorus Removal by Intensive Cropping Systems

The nutrient removal under intensive cropping systems is of interest for developing fertilizer P management strategies. The estimates of nutrient uptake for a number of cropping systems are given in Table 7. The annual uptake of 75-100 kg P_2O_5/ha is quite common in 200-300% cropping intensity (2-3 crops/year), though in some cases, the amount of P removed can reach 150 kg P_2O_5/ha/year. The production of 8-12 t/ha of grain is associated with P uptake of 70-120 kg P_2O_5/ha.

Table 6. Soil test methods suitable under different situations

Method for available-P	Suitability
Olsen (0.5 *M* $NaHCO_3$, pH 8.5)	Neutral, alkaline, calcareous soils
Bray & Kurtz P-1 (0.03 *N* NH_4F + 0.025 *N* HCl)	Acidic and near-neutral soils
Bray & Kurtz P-2 (0.03 *N* NH_4F + 0.1 *N* HCl)	Tea, coffee, hilly rice soils
Nelson (0.05 *N* HCl + 0.025*N* H_2SO_4)	Groundnut*
Phosphorus desorption isotherm	Rice*
Electro-ultrafiltration (EUF)	Tea*

*Yet to be widely tested and adopted.

Source: Tandon (1987)

Table 7. Nutrient uptake by some high-intensity sequence-cropping and inter-cropping systems in India

Cropping system	Yield*(tonne/ha)	Nutrient uptake (kg/ha/year)			
		N	P_2O_5	K_2O	Total
Rice-wheat	8.8	235	92	336	663
Maize-wheat	7.7	220	87	247	554
Pigeonpea-wheat	4.8	219	71	339	629
Rice-rice	6.3	139	88	211	438
Soybean-wheat	7.7	260	85	204	549
Maize-wheat-greengram	8.2	306	62	28	646
Rice-wheat-greengram	11.2	328	69	336	763
Maize-potato-wheat	8.6+11.9(t)	268	96	358	722
Rice-wheat-cowpea(f_0)	9.6+3.9(f_0)	272	153	389	814
Rice-wheat-maize+cowpea	9.3+29(f_0)	305	123	306	734

* Under yield data: f_0 is fodder, t is tuber, and all others are grain.

Source: Tandon and Sekhon (1988)

13. Crop Responses to Phosphorus Application

The yield increases brought about by fertilizer P application in India are widespread, significant and economically attractive. For obtaining high yields in normal soils, P application is widely recommended, whether the crops are irrigated or grown under rainfed/dryland conditions. Responses to applied P depend on soil properties, initial available P, variety, level of N applied, and management practices. The high-yielding dwarf varieties of wheat have shown a 35% higher yield response to P than tall varieties. The application of 120 kg P_2O_5/ha in high P-fixing soil could produce similar responses as obtained from 60 kg P_2O_5/ha in low P-fixing soils. Response to P also increases with increasing level of N and by planting on the optimum sowing date prescribed for a variety.

14. Phosphorus Management in Cropping Systems

Phosphorus application, unlike N, is known to benefit the growth and productivity of more than one crop grown in succession. The residues of fertilizer P remain in the soil after a directly-fertilized crop has been harvested. Such residues reside in the soil in the form of an array of soil-fertilizer reaction products and their value can be expected to be in proportions to (i) their contribution to the 'labile' pool, and (ii) crop's ability to utilize it. The practical value of P-residues is the highest in intensive cropping systems with minimum gap between successive harvests. For how long the residual effect of a given application lasts in tropical and subtropical soils is not easy to judge. In India, the significance of residual P is maximum in systems which have been regularly receiving moderate-optimum level of fertilizer P. Some such systems are those which include wheat, rice, potato, groundnut, sugarcane, vegetables, plantation crops and intensively-fertilized fruit crops such as bananas and grapes. A complete picture of crop response to P is obtained when both the direct and the residual effects are taken into account. The amount and longevity of the residual effect of P depends primarily on the following factors:

(i) Rate, duration and frequency of P application,
(ii) Solubility of P fertilizer,
(iii) Soil properties, and
(iv) Type of crops, yield levels and extent of P removal.

In double cropping, on an average, the response to a single P application is in the ratio of 6:4 between direct and residual effect, respectively. The residual P contributes more to crop nutrition when the crop feeding on the P-residues is taken in the warm, wet *kharif* season as compared to the cooler *rabi* season. In alluvial soils, when 0.5 M $NaHCO_3$-extractable P was built up to about 73 kg P_2O_5/ha as a result of repeated P applications in a long-term maize-wheat system, the accumulated P-residues could adequately nourish two crops of maize and one crop of wheat, after which fresh P application became necessary to sustain high yield levels.

Among major grain crops grown in a sequence in the northern region, wheat is one of the most responsive crops to P application. Thus, while allocating fertilizer P among component crops in a system, the needs of wheat often receive priority. It also implies that in times of general or localized fertilizer shortages, wheat yields are most vulnerable to cuts in the fertilizer doses. This higher responsiveness of wheat to P as compared to *kharif* crops has been reported for a number of cropping systems in which wheat is rotated with cotton, groundnut or maize or pearl millet.

15. Proven Technologies for Increasing P-Use Efficiency

The technologies that have been found successful for increasing the efficiency of P-use are briefly discussed here under:

15.1. Time of Phosphorus Application

Phosphorus application as a basal dressing at seeding/planting or just prior to that, is the most widely recommended practice for seasonal crops. There have been some trials on the split/delayed application of P, but the results of such trials have remained inconsistent (Goswami and Kamath, 1981). The reasons for such inconsistancy may be related to initial level of available P in the soil, temperature regimes, and other factors such as incidence and timing of root rot diseases, etc. during the season. Although best results are obtained when all P is applied as a basal dressing to seasonal crops, a split/delayed application is better than not applying P at all and could be a suitable practice under the following situations: (i) if P-fertilizer is in short supply at planting, (ii) soils are medium in available P, and (iii) seasonal conditions favour the release of soil P during early periods of crop growth.

15.2. Methods of Phosphorus Application

For higher P-use efficiency in case of conventional water-soluble P fertilizers in upland crops, results are overwhelmingly in favour of drilling/ placement, whereas broadcast of P comes out as inefficient practice and is not advocated, except for flooded rice. The proper placement or drilling of P for upland crops is most important when dealing with P-deficient soils, lower rates of P application, water-soluble P-sources and in the crops with wider row spacing, as also in dry soil conditions in upper root zone during critical growth stages. Proper placement has the same significance in P management as split application has for N management. For fertilizers in which a part of P (nitrophosphates) or none (rock phosphate) is water-soluble, the common view is that the soil-fertilizer contact should be maximized and thus surface broadcast followed by mixing is more appropriate than their restrictive application (placement).

15.3. Liming of Acid Soils

About one-third of Indian soils are acidic in reaction. The beneficial effect of liming acidic soils on crop yields and improvement in the availability of P is well established.

15.4. Treatment of Planting Material with Phosphorus

Dipping the roots of rice seedlings in a slurry of single superphosphate and water prior to transplanting can be followed. It has been found that a root dip providing 10-30 kg P_2O_5/ha can increase rice yield significantly and compares favourably with higher rates of soil applied P. This technique of increasing P-use efficiency has not been widely tested under farmers' conditions. Similarly, some results are also available on the effect of soaking potato seed tubers in nutrient solutions before planting. The beneficial effect of soaking is maximum in low P-soils. The use of 0.4% solution of MAP, DAP or filtered SSP also increases P-uptake and potato yields.

15.5. Role of Mycorrhizal Fungi

Certain mycorrhizal fungi, known as VAM (Vesicular-Arbuscular Mycorrhizae) colonize plant roots and through this symbiotic association, help the plant to absorb more P in two ways: (i) VAM mycelia could act as an extension of the root system, enabling the plant to explore a larger soil volume resulting in a greater flow of P into the roots, and (ii) roots colonized by VAM are more efficient in absorbing P from low-P soils.

15.6. Role of P-solubilizing Microorganisms

The role of P-solubilizing microorganisms (PSM) in enhancing dissolution of insoluble and sparingly-soluble P was known as far back as 1960s. The interest in PSM has revived in recent years with a view to enhancing the availability of native soil-P and also to explore the possibilities of direct application of rock phosphate in neutral to mildly alkaline soils. Bacterial cultures namely *Bacillus megaterium* and *Pseudomonas striata*, or fungal species namely *Aspergillus awamori* is reported to add 30-35 kg P_2O_5/ha under ideal conditions. The performance of PSM is, however, constrained in semi-arid sub-tropical regions as those in north-west India, and at least two hypotheses could be given for the poor response. First, the organic-carbon content of the soils is very low, whereas the abundance of a carbon source is a pre-requisite for high efficiency of PSM. Reports on effectiveness of PSM under field conditions are scarce, yet the available information reveals a greater crop response to PSM inoculation on high organic matter soils (Chhonkar, 1994), or with the application of farmyard manure (a rich carbon source) on low organic matter soils (Wani and Lee, 1992). Second, average maximum temperatures higher than 35 °C in the months of July-August, and the average minimum temperatures lower than 10 °C in the month of January in most of these regions are certainly not congenial for PSM activity. Hence, the possibility of poor colonisation of PSM in rhizosphere at the high P-demanding vegetative growth stages of *kharif* and *rabi* crops cannot be denied. Nonetheless, it is an interesting area that needs to be explored.

15.7. Incubation of Insoluble Fertilizers with Organic Manures

The efficiency of rock phosphate can be increased in alkaline soils (pH 8.3) by pre-incubation with fresh cattle dung. However, its large-scale testing and evaluation on farmers' fields is yet to be undertaken. Some composts enriched with rock-P, or "phospho-composts" as these are called, have been developed and are effective in increasing the efficiency of P and crop yields. Use of farmyard manure also increases the efficiency of rock P. The reasons for this may be several, but the net result in terms of better P-availability, higher yields and more P-uptake have been demonstrated.

16. Relative Efficiency of Phosphatic Fertilizers

At low application rates (less than 60 kg P_2O_5/ha), the water-soluble or partially water-soluble P-forms with a large water-soluble component work better than do the citrate-soluble or partially water-soluble P-forms with a small water-soluble component. At higher P rates, the differences are small or the relationship is reversed. The parameters that influence the efficiency of P-forms of different solubilies are: (i) pH value of the soil, (ii) native supply of available P of the soil, (iii) level of the applied P, (iv) form of the concomitant fertilizers, (v) duration of plant growth, (vi) water supply, and (vii) P-fixing capacity of the soil.

The rock phosphates of India are of poor quality, hence their conversion to completely water-soluble forms entails high costs. It is possible to use the rock phosphates directly or by adding a small portion of water-soluble P to a large portion of rock phosphate, depending on the soil acidity and cropping system (Panda 1979).

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Chapter 18

Potassium

A. SUBBA RAO and M.S. BRAR

1. Introduction

The importance of potassium (K) in Indian agriculture has increased with intensification of agriculture. The consumption of K, which was 4.8% of the total world consumption in 1993-94, increased to 6.2% in 2003-04. The consumption of potassic fertilizers in India rose from 0.24 million tonnes in 1970-71 to 2.836 million tonnes in 2007-08. Despite that, it is estimated that there was a net negative balance of 5.82 million tonnes of K_2O in Indian soils during the year 2005-06, which comes out to be 30.5 kg K_2O/ha of gross cropped area. The gap between removal of K and its application to crops is widening. It is, therefore, imperative to understand dynamics of K in soil and then apply K fertilizer, matching with the K-needs of crops, to provide balanced nutrition, harvest good yields and maintain the potassium fertility status of Indian soils.

Potassium, among mineral cations essential for plants, is the biggest in non-hydrated size (0.1333 nm) with a large number (8 or 12) of oxygen atoms surrounding it in mineral structure, which suggests that the strengths of each K-O bond is relatively weak. Potassium has polarity equal to 0.088 nm^3, which is higher than that of Ca^{2+}, Mg^{2+}, Li^+ and Na^+, but lower than that of Ba^{2+}, Cs^+, NH_4^+ and Rb^+ ions. Ions with higher polarizability are preferred in ion exchange reactions. Potassium has hydration energy of 142.5 kJ g^{-1} ion^{-1}, which indicates little ability to cause swelling (Sparks, 2002).

2. Role of Potassium in Plant Nutrition

Potassium is an essential nutrient element required by all living organisms, including plants and animals. It is found in large concentrations (100-200 m*M*) in the plant cell sap. Potassium is not incorporated into the structure of organic compounds but remains in ionic (K^+) form in solution in the cell and is mobile in plants.

Potassium is required for the activation of over 80 enzymes. It plays vital roles in: (i) water relations (osmotic regulation, control of ionic balance, etc.), (ii) energy relations, (iii) translocation of assimilates, (iv) photosynthesis, (v) protein and starch synthesis, (vi) metabolic processes and grain/seed formation, (vii) improving quality of flowers, fruits, vegetables and other field crops in terms of size, shape, colour, taste, shelf-life, and fibre quality, etc., (viii) preventing lodging in crops, (ix) imparting resistance against environmental stresses such as drought, cold and frost, and (x) improving resistance to pests and diseases.

3. Deficiency Symptoms

Potassium deficiency does not manifest immediately in the form of visible symptoms. At first, the growth rate decreases and deficiency symptoms appear at later stages. Under restricted K supply, potassium deficiency symptoms generally appear on older leaves. In most plant species, tips and margins of older leaves turn yellow (chlorosis) and then die (necrosis), giving a burning look on edges. In several important forage and cover-crop legume species, potassium deficiency produces small white necrotic spots that form a unique pattern along the leaflet margins; this easily recognized symptom is often mistaken for insect damage/ disease infection (Brady and Well, 2007).

Potassium deficiency leads to (i) slow and stunted growth, (ii) weak stalks and susceptibility to lodging, pests, diseases, frost, etc., (iii) low yield, and (iv) poor quality of produce (Tandon and Sekhon, 1988).

Seeds from potassium-deficient plants are small, shrivelled, and are more susceptible to diseases. Fruit is lacking in normal coloration and is low in sugar content. Vegetables and fruits have a short shelf-life and deteriorate rapidly when shipped.

4. Potassium Uptake and Requirement

Time of potassium uptake and its translocation to reproductive part varies with different plants. However, plants generally absorb most of their potassium requirement during an earlier growth stage. Maize absorbs 70-80% K by silking time, and 100% is absorbed three to four weeks after silking. Cotton takes up about 30% of its potassium during the first twelve to fourteen days of blooming. During this period uptake of potassium is 3-4 kg/ha/ day. About 66% of the total potassium is rapidly translocated from the leaves and stem to the bur of the boll during boll fill (Thompson).

An estimate of potassium requirement of a crop can be obtained from its total uptake (K-content × yield). Potassium in normal healthy leaves varies between 1% and 4%. Potassium uptake is often equal to or more than that of nitrogen. Crop species differ in their K requirement (Table 1). Crops like banana, pineapple, papaya, alfalfa and sugarcane are among the heavy feeders of K. High crop yield and higher rates of application of N and P also accelerate K-uptake from the soil.

5. Potassium Minerals: Forms and Cycle

The main forms in which potassium is held in soils and the changes it undergoes as it is cycled through the soil-plant-animal system are depicted in Figure 1. Most of the potassium-containing minerals in soils are the dioctahedral micas, viz. muscovite $\{KAl_3Si_3O_{10}(OH)_2\}$, gluconite, illite (hydrous mica) and trioctahedral micas, viz. biotite $\{KAl(Mg, Fe)_3\ Si_3O_{10}(OH)_2\}$ and phlogopite; and the feldspars, viz. sanidine $\{KAlSi_3O_8\}$, orthoclase $\{(K, Na)AlSi_3O_8\}$ and microcline $\{(Na,K)AlSi_3O_8\}$. Transitional clay mineral (edge expanded illite, illite+ montmorillonite or illite+vermiculite) and allophanes ($SiO_2.Al_2O_3.2H_2O$ or $2SiO_2.Al_2O_3.3H_2O$) also

Table 1. Potassium uptake by different crops under field conditions

Crop	Botanical name	Yield (t/ha)	Total K-uptake (kg/ha)
Wheat	*Triticum aestivum* L.	3.90	137
Rice	*Oryza sativa* L.	5.14	180
Chickpea	*Cicer arietinum* L.	1.50	49
Pigeonpea	*Cajanus cajan*	1.20	16
Groundnut	*Arachis hypogaea*	2.54	95
Mustard	*Brassica juncea*	2.60	133
Soybean	*Glycine max* Merr.	2.50	101
Sunflower	*Helianthus annuus* L.	2.38	141
Sugarcane	*Saccharum officinarum* L.	87.60	270
Tea	*Camellia spp.*	1.00	37
Tobacco	*Nicotiana tabacum* L.	2.85	65
Alfalfa	*Medicago sativa* L.	91.90	669
Potato	*Solanum tuberosum* L.	29.50	119
Banana	*Musa paradisiaca* L.	38.00	1053
Pineapple	*Ananas sativa* Schutt.	84.00	440
Papaya	*Carica papaya* L.	150.00	415

Source : Tandon (1991)

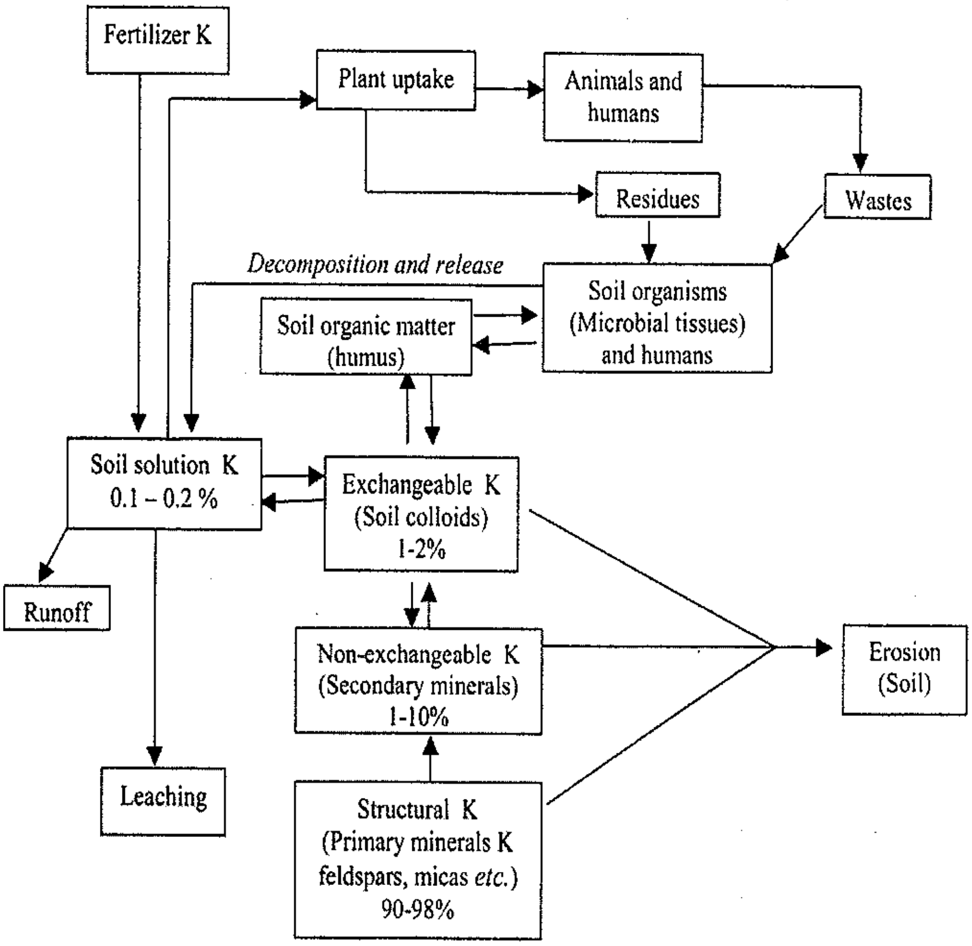

Figure 1. Major pathways in potassium cycle (adapted and modified from Brady and Well, 2007)

contain little amount of potassium (approx. 1%). Most of the potassium (90-98%) in soil is held in the primary minerals like micas (biotite and muscovite), potassic feldspars (orthoclase and microcline) and secondary minerals. Among these minerals, micas, especially biotite weather faster than feldspars and release potassium much more readily. Weathering of primary minerals makes their rigid lattice structure unstable.

With the passage of time, the potassium held in the interlayer spaces of 2:1 type minerals (micas) is made more mobile, firstly through non-exchangeable but slowly available form and finally through the readily exchangeable and the soil solution forms. Plants take up large quantities of potassium from soil. A portion of it is returned to the soil along with plant residues. Some of the potassium is lost with eroded soil particles and in runoff and some through leaching to groundwater. A portion of the K lost through leaching is again recovered on utilizing underground water for irrigation to crops.

6. Potassium Pools in Soils

A widely accepted concept divides the soil K into four compartments:

1. Soil solution K (K_{sl})
2. Exchangeable K (K_{ex})
3. Fixed or non-exchangeable K (K_f), and
4. K in the lattice of certain primary minerals (K_l).

The amount of K in each fraction varies with parent material, weathering stage, past cropping history, past fertilizer and manure use (i.e. the K balance), soil pH and soil water content. The content of soluble-K in the calcareous soils of Gujarat ranges from 0.003 to 0.21 c mol kg^{-1} soil, the exchangeable-K from 0.03 to 2.00 cmol kg^{-1} soil, non-exchangeable or fixed K from 0.32 to 21.70 cmol kg^{-1} soil and total K from 1.10 to 20.30 c mol kg^{-1} soil

(Golakiya *et al.*, 2001). In illite-dominant alluvial soils, water soluble K constitutes 17% to 30% of ammonium acetate extractable K. The ammonium acetate extractable (available) K constitutes about 6% to 16% of boiling nitric acid soluble (reserve) K (Brar *et al.*, 1986).

As indicated in Figure 1, the fractions such as solution K (K_{sl}), exchangeable K (K_{ex}) and fixed K (K_f) are related to each other through reversible exchange processes. Potassium released from both the K_{ex} and K_f pools replenishes the K removed by plants or leached into the subsoil. There are two mechanisms for the release of K to solution form. Firstly, a simultaneous release of K from both the pools to the soil solution. Secondly, a linear exchange process from the non-exchangeable to the exchangeable pool, and from the exchangeable pool to the soil solution. The soil solution K must be replenished quickly enough to meet the demand of a rapidly growing crop. After the addition of fertilizer or manures, when K is surplus in the soil solution, it is reverted back to both fractions through exchange and fixation processes.

The relative abundance of different forms of K in some selected soil series, representing alluvial, black-cotton and associated red and lateritic soils, is reported in Table 2. Exchangeable-K is generally more in black cotton and vertic type soils than in alluvial, red and lateritic soils. Illite-dominant alluvial soils contain the largest amounts of non-exchangeable K and total K. The kaolinite-dominant red and laterite soils contain the lowest amount of all forms of K.

6.1. Available Potassium Status

An assessment of the available potassium status of Indian soils has been carried out on the basis of 4.5 million samples analyzed during 1968-74 in the soil testing laboratories all over the country and district-wise classification of the soils has been made into low, medium and high categories. The coverage extends to nearly 88% of the districts, including the union territories from where adequate soil test information was available. The level of available potassium (ammonium acetate-extractable) has been found to be low (< 55 mg K/kg soil) in 20%, medium (55 to 135 mg K/kg soil) in 42% and high (> 135 mg K/kg soil) in 38% districts. The potassium status is low in Meghalaya, Mizoram, Pondicherry and Tripura. It is low in 67% districts of Assam, 58% districts of erstwhile Uttar Pradesh, 57% districts of Jammu and Kashmir, 44% districts of Kerala and 36% districts

Table 2. Forms of soil potassium (cmol kg^{-1}) in some benchmark soil series of alluvial, black, red and laterite soils of India

Soil series	Watersoluble K	Exchangeable K	Non-exchangeable K	Total K
Alluvial soils				
Nabha (Udic Ustochrept)	0.070	0.146	3.42	67.69
Rarha (Udic Ustochrept)	0.038	0.173	4.76	70.51
Average	0.054	0.159	4.09	69.10
Black soils				
Sarol (Typic Chromustert)	0.058	0.627	2.18	26.67
Shendvada (Typic Chromustert)	0.058	0.998	1.81	22.05
Average	0.058	0.812	1.99	24.36
Red soils				
Vijayapura (Oxic Haplustalf)	0.053	0.090	0.22	9.28
Tyamagondalu (Oxic Paleustalf)	0.033	0.107	1.38	56.41
Average	0.043	0.098	0.80	32.84
Laterite soils				
Kumbhave-5 (Fluventic Ostropept)	0.010	0.133	0.27	16.41
Nedumangad (Oxic Dystropept)	0.012	0.100	0.19	6.15
Average	0.011	0.116	0.23	11.28

Source: Sekhon *et al.* (1992)

of Himachal Pradesh. On the other hand, the whole of Gujarat state, 71-82% districts in Haryana, Madhya Pradesh and Rajasthan and 28-46% districts in Andhra Pradesh, Himachal Pradesh, Karnataka, Maharashtra, Punjab and Tamil Nadu are high in available potassium. The whole of Delhi, Chandigarh, Arunachal Pradesh, 80-85% districts in Orissa and West Bengal and most of the remaining districts fall in the medium category with respect to potassium availability (Ghosh and Hasan, 1976). A compilation of K-fertility status of soils made on the basis of 3.65 million samples during 1997-99 revealed that 21% districts were low, 51% districts were medium and 28% districts were high in available-K status (Tandon, 2004). This indicates a decrease in the K status of those districts, which earlier had high K status, possibly because of low K application. Although the critical level for evaluation of K deficiency in different soils differing in mineralogy are likely to differ; however, presently all the soils are being evaluated on uniform critical levels throughout the country.

6. Equilibrium among the Forms and Potassium Availability

At a given time, potassium in the solution and exchangeable forms constitutes the fraction readily available to plants. The exchangeable K tends to attain equilibrium rapidly with solution K but, only slowly with non-exchangeable K (Figure 2). The solution K concentration largely controls the K movement (diffusion) towards the plant roots and thereby, the K uptake by plants. On depletion of exchangeable K, the non-exchangeable K replenishes it and the supply of K to plants is maintained. When K is added to a soil through mineral fertilizers or organic manures in excess of its crop removal, it initially increases solution K and subsequently, increases the exchangeable and non-exchangeable K through the shifting of equilibrium from the right to the left (Figure 2). Except some saline soils, all the soils contain only small amounts of K in solution form. Potassium levels in solution depend much on the selectivity exercised by the adsorption sites. If these sites have specific affinity for K, the concentration of K in the soil solution tends to be rather low. If the binding sites are less specific for K, concentration in solution is generally high, as in kaolinite and smectite-rich soils.

7. Factors Affecting Availability of Potassium

Factors affecting the availability of potassium include soil texture, clay mineralogy, depth, soil pH and liming.

7.1. *Soil Texture*

It influences the status of both available and non-exchangeable potassium. Fine-textured soils generally possess larger amounts of both forms of K compared to coarse-textured soils. The effect of texture on K status is more conspicuous in alluvial (illite-dominant) than in black (smectite-dominant) or red (kaolinite-dominant) soils because of the presence of K-bearing minerals in the finer fraction of illite-dominant soil.

7.2. *Clay Mineralogy*

Potassium availability to plants is a function of quantitative mineralogical make-up, degree of weathering and nature of complementary cations on the exchange complex. The available (exchangeable) potassium is gener-

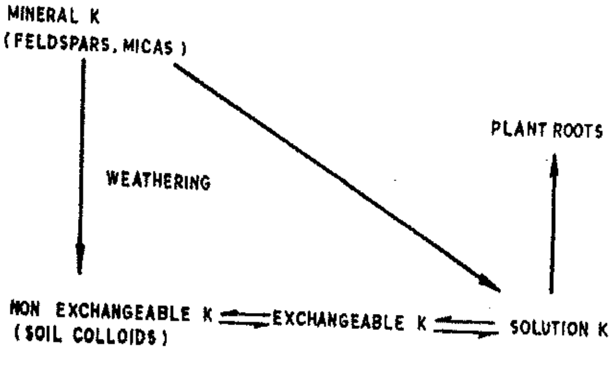

Figure 2. Potassium relationships in soils and plant roots

ally high in smectite-dominant vertisols, followed by mixed mineralogy, illite and kaolinite dominant soils. However, smectite-dominant soils may have low amounts of watersoluble K compared to illite-dominant soils. Both non-exchangeable-K and total K would be more in soils rich in micaceous minerals like illite. Kaolinite-dominant soils (laterite and red) are poor in available potassium.

7.3. Soil Depth

Indian soils depict characteristic differences in their K-content with depth. Calcareous alluvial soils show a decrease in both the available and non-exchangeable forms with depth. Alluvial soils from the Indo-Gangetic Plains show more available K in the surface soils, while non-exchangeable K is more in the sub-surface soils. In swell-shrink (Vertisols/deep black) soils, both available and reserve K decrease with depth.

7.4. Soil pH (reaction)

Soil pH plays a significant role in the availability of potassium in soil. In acid soils, H^+ ions and hydroxy-aluminum ions compete with K^+ ions for the exchange or adsorption sites and are able to keep more K^+ ions in the solution phase and reduce their susceptibility to fixation. As the pH increases, the H^+ and hydroxy-aluminum ions are neutralized or removed, making it easier for the K^+ ions to move closer to soil colloidal surfaces where they become susceptible to fixation. Hence, K-availability will be more in acid soils.

7.5. Liming

Liming of acid soils (with pH-dependent negative charge) increases the cation exchange capacity (CEC) of soil which results in increased K adsorption by the soil colloids and a decrease in the K level in the soil solution. Furthermore, high calcium concentration in the soil solution phase may reduce K uptake by plant, especially in soils containing high amount of $CaCO_3$.

7.6. Freezing & Thawing and Wetting and Drying

The freezing and thawing of moist soils may also be important in K release and fixation. With alternate freezing and thawing, soils release K, especially those having sufficient quantities of illite, whereas, no release may occur in soils containing low quantities of exchangeable K. During drying, K fixation or a decrease in K may occur, especially when exchangeable K is relatively high. However, a release of K from non-exchangeable K occurs when exchangeable K is low.

8. Quantity–Intensity Relations of Potassium

The concepts of intensity, quantity and buffering power proposed by Beckett (1964) are useful in describing and measuring the potassium supplying power of soils. The intensity factor is a measure of K in soil solution that is immediately available for absorption by plant root. Since this absorption of K is influenced by the activity of other cations like Ca^{2+} and Mg^{2+} in the soil solution, the potassium activity ratio (AR_K) [Equation (1)] is used, in place of K concentration alone, to indicate the intensity factor:

$$AR_k = \frac{[K^+]}{\sqrt{[Ca^{2+} + Mg^{2+}]}} \qquad \ldots(1)$$

The quantity factor (Q) is a measure of the capacity of the soil to maintain the level of K in soil solution (I) over a long period or the duration of crop growth. The capacity is mainly due to the exchangeable K, although some non-exchangeable K is released to meet a considerable portion of the crop needs. The buffering capacity indicates how potassium level in the soil solution (intensity) varies with the amount of labile form of this element (quantity). In quantitative terms, the buffering capacity is expressed as the ratio $\Delta Q/\Delta I$. The wider the ratio of $\Delta Q/\Delta I$, more buffered is the soil.

A typical $\Delta Q/\Delta I$ plot for a binary cation system as described by Beckett (1964), is shown in Figure 3 with the following components: Ex-K is the quantity factor (Q) that represents changes (gain or loss) in exchangeable K; AR_K is the intensity factor (I) or activity ratio for K; Ex-K_L is the labile K; Ex-K_S is specifically held K; E_x-K_0 is non-specifically held K; AR^0_K is the equilibrium activity ratio

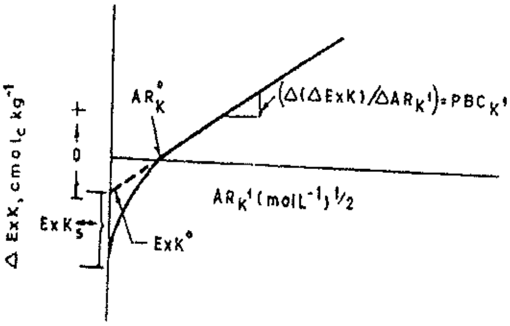

Figure 3. A typical quantity/intensity (Q/I) relations (adapted from Evangelou, 1994)

for K i.e. $[(a_K)/(a_{Ca})^{1/2}]$; and PBC_k is the linear potential buffering capacity for K^+. This relationship implies that the ability of soil system to maintain a certain concentration of a cation in solution is determined by the total amount of the cation present in readily available forms (exchangeable and solution) and the intensity by which it is released to the soil solution (Evangelou *et al.*, 1994).

For adequate crop nutrition, the concentration of plant nutrients in soil solution must be maintained at a satisfactory level throughout the growth period. Since total demand for K by crops is considerably higher than its presence in solution at a given time, the replenishment of soil solution K from the solid phase of the soil is a process of great practical significance. The data in Table 3 show that soils containing predominantly smectitic clay mineral have higher buffering capacity and lower activity ratio of potassium, whereas the reverse is true for kaolonite-dominant (red) soils. The smectitie-dominant (black) soils, therefore, can supply K over a longer period than kaolinite-dominant (red) soils. However, the immediate available K, as expressed by AR^0_k is more in kaolinite-dominant soils. Generally, with increase in clay content, the buffer capacity of a soil increases and activity ratio AR^0_k decreases (Figure 3).

10. Potassium Fixation

In the process of potassium fixation in soils, the added soluble K is converted into a form that cannot be extracted with a neutral salt solution, commonly employed to extract plant-available form of soil K. As a consequence of K fixation, availability of added K to plants decreases. The nature of clay fraction of the soil is an important factor in the fixation of K. The fixation is nearly absent in soils dominant in kaolinite, chlorite and unweathered micas; it is slight in montmorillonite, substantial in illite and large in vermiculite-dominant soils.

Potassium ions are adsorbed by clay minerals on the binding sites which differ in their

Table 3. Quantity-intensity relationship of potassium in some selected soils in India

Soil series	Texture	$AR^o_K x \cdot 10^{-3}$ $(M/L)^{1/2}$	PBC_K (c mol kg^{-1})/$(M/L)^{1/2}$	K (c mol kg^{-1})		
				$Ex\text{-}K_L$	$Ex\text{-}K_S$	$Ex\text{-}K_o$
Alluvial soils						
Nabha	Sand (6) *	8.0	7.5	0.25	0.19	0.06
	Loamy sand (10)	2.8	21.4	0.30	0.24	0.06
Rarha	Loamy sand (8)	3.4	20.6	0.24	0.17	0.07
	Loam (11)	1.4	57.1	0.21	0.13	0.08
Black soils						
Sarol	Silty clay (46)	1.8	333	1.00	0.49	0.51
(TypicChromustert)	Silty clay (50)	1.6	344	1.00	0.48	0.52
Shendvada	Clay (42)	2.8	232	1.10	0.45	0.65
(Typic Chromustert)	Clay (59)	2.7	259	0.95	0.25	0.70
Red soils						
Vijaypura	Sandy loam (14)	10.0	2.0	0.08	0.06	0.02
(Oxic Haplustalf)	Sandy clay loam (20)	4.0	3.0	0.08	0.07	0.01
Tyamagondalu	Loamy sand (4)	17.2	7.0	0.25	0.18	0.02
(OxicPaleustalf)	Sandy loam (14)	13.4	7.5	0.27	0.17	0.10

*Values in the parentheses indicate per cent clay;

Source : Sekhon *et al.* (1992)

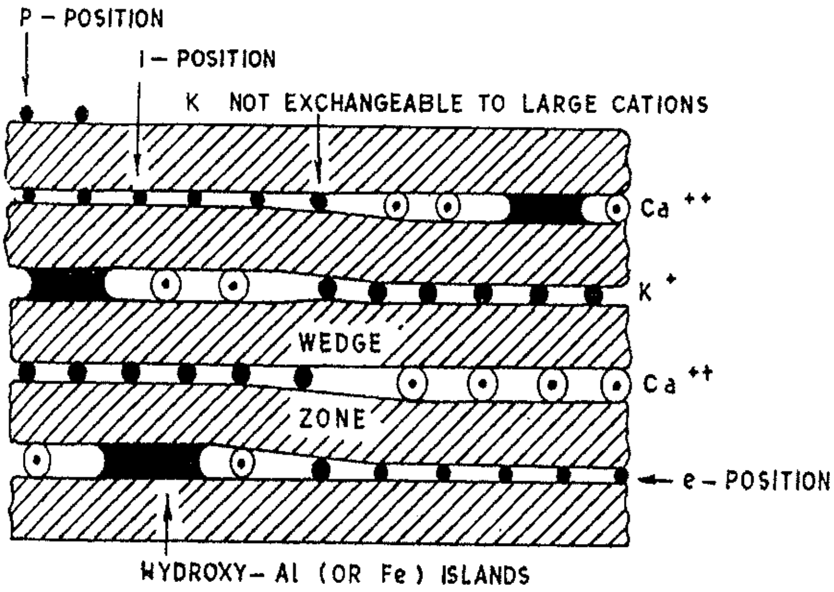

Figure 4. Model of an expandible layer silicate with interlayers, wedge zone, p-, e- and i- positions [after Rich (1968), *c.f.* Mengel and Kirkby (1987)]

selectivity (Figure 4). For the 2:1 clay minerals, such as illites, vermiculites and weathered micas, three different adsorption sites can be distinguished. These sites are at the planar surfaces (p-position), at the edges of the layers (e-position) and in interlayer space (i-position). The specificity of these three binding sites for K differs considerably. The binding selectivities for K by organic matter and clays of the kaolinite type are similar to the p-position sites. Here, the K–bond is relatively weak so that K adsorbed may easily be replaced by other cations, and particularly by Ca^{2+} and Mg^{2+} ions. The i-position has the maximum specificity for K^+. These binding sites largely account for K^+ fixation in soils.

The potassium added through manures and fertilizers initially increases the solution and exchangeable K contents. The saturation of the exchangeable complex with respect to K leads to the entry of K into wedge (partially opened) and interlayer spaces (Figure 4). This results in fixation of K in non-exchangeable form.

In smectitite-rich soils, K^+ ions are fixed at interlayer sites, which normally take part in exchange. When dehydration occurs, the lattice sheets come closer and the adsorbed cations loose their attendant water molecules. According to "Lattice Hole Theory" (Page and Baver, 1940), the exposed surface and surfaces between sheets of three layer (2:1) type minerals consist of oxygen ions, arranged hexagonally. The opening within the hexagon is equal to the diameter of an oxygen ion (approximately 2.8 Å). Ions having a diameter of this magnitude (e.g. K^+ 2.66 Å) will fit snugly into the lattice holes and such ions will be held very tightly as they come in contact with the negative electrical charges within the crystal. Owing to this, the layers are bound together, thus preventing dehydration and re-expansion of the lattice. Ions like NH_4^+ (2.86 Å) and Rb^+ (2.96 Å) whose diameters are close to 2.8 Å can also be fixed to a considerable extent. Relatively small hydration energies of K^+, NH_4^+ and Rb^+ result in easy dehydration of these ions and strong retention. Barium (Ba^{2+} 2.70 Å) ions with their higher energy of hydration, apparently cannot be readily dehydrated and fixed.

While larger ions cannot enter the cavities, the ions that are too small cannot sufficiently stabilize the resultant configuration. In vermiculite or illite, isomorphous substitution in tetrahedral position of their lattice creates negative charge close to the unit layer surface, which explains the strength of the bond between K^+ and the lattice sheet. Hence, in illite and vermiculite, K fixation can occur even under wet conditions. Potassium fixation is, therefore, a serious problem in soils containing illite and vermiculite clay minerals.

10.1. Factors Influencing Potassium Fixation

The degree of K fixation depends on a number of factors, such as (i) charge density (which means negative charge per unit silicate layer of the mineral), (ii) extent of the interlayer wedge zone that is depleted of K, (iii) moisture content, (iv) solution K concentration, and (v) the nature and concentration of competing cations in the surrounding medium. Fixation is high when charge density is high. Vermiculite and illite tend to fix K best under relatively wet conditions, while fixation by montmorillonite and the interstratified minerals occurs under drier conditions. Ions like NH_4^+ and H^+ can compete with K^+ for K fixing or binding sites. If the wedge zone is confined to the edge of the particle, then only small amounts of K can be fixed. On the other hand, if the zone penetrates deeply into the mineral, considerable amount of K can be fixed. Wetting and drying cycles lead to fixation of K in soils rich in available K. The fixing power of 2:1 type clay minerals usually follows the order: Vermiculite > Illite > Smectite (montmorillonite).

11. Potassium Release

The phenomena of both the fixation of exchangeable K and/or release of non-exchangeable K play an important role in the dynamics of soil potassium. The gradual release of K from the trapped positions in the mica lattice to form illite (hydrous mica) and eventually vermiculite with concomitant gain of water or H_2O^+ and swelling of K lattice is illustrated in Figure 5. The low hydration energy of K ion favours its entrapment. Low concentration of K in the solution due to leaching or crop removal favours release of K. In the absence of external additions of K, plants are capable of taking up a very large amount of potassium without bringing about substantial decrease in exchangeable-K. This means that K, which was not initially in exchangeable form, gets changed into exchangeable form and becomes available to plants. The 2:1 type of clay minerals are capable of both fixing and releasing potassium. Long-term field experiments provide more realistic estimates of K-supply from non-exchangeable sources. Data in Table 4 indicate the magnitude of the release of non-exchangeable K from representative soils of India using different resins. The capacity of different cation-saturated resins to replace non-exchangeable K from soils has been found in the order: H^+-resin > Ca^{2+}-resin > Na^+-resin > NH_4^+-resin. All these resins are more effective in desorbing K from smectitic black soils than from alluvial soils, having restrictive interlayer space, or red soils containing more K in the feldspars.

The exchange of K has been found to be diffusion controlled. The kinetics of release of K by sodium tetraphenyl boron has also shown that alluvial soils containing illite as a dominant clay mineral, release significantly larger amounts of K than smectitic black and kaolinite-dominant red soils (Dhillon and Dhillon, 1992).

The capacity of soils to supply K from exchangeable and non-exchangeable forms is not

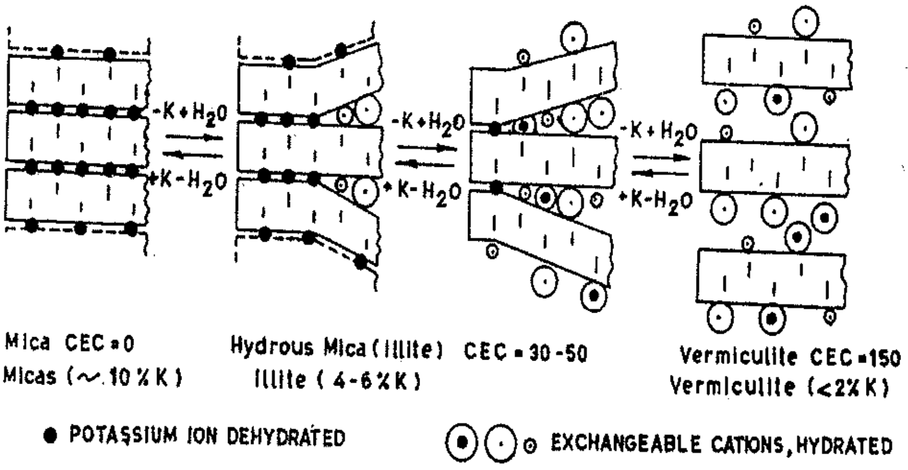

Figure 5. Interconversion of soil minerals : A mechanism of K release and fixation (after McLean, 1978)

Table 4. Cumulative amounts of K released (cmol kg^{-1} soil) in different cation-saturated resins from red, black and alluvial soils of India

Soils	Texture	H^+-resin	Ca^{2+}-resin	Na^+-resin	NH_4^+-resin
Red soils					
Tyamagondalu (Oxic Paleustalf)	Sandy	4.70	2.99	1.88	1.83
Patancheru (Udic Rhodustalf)	Sandy loam	5.58	2.73	2.31	1.92
Mean		5.14	2.86	2.10	1.88
Black soils					
Teligi (Typic Pellustert)	Clay	7.43	3.08	2.35	2.23
Kasireddipalli (Typic Pellustert)	Silty clay	7.98	2.89	2.60	2.25
Mean		7.71	2.99	2.48	2.24
Alluvial soil					
Nabha (Typic Ustochrept)	Loam	9.35	2.40	2.44	1.97
Kanjli (Typic Ustochrept)	Sandy	9.76	2.42	2.71	2.14
Mean		9.55	2.41	2.57	2.05

Source: Dhillon and Dhillon (1990)

easily determined because of the reversible transformation from one form to other that is assumed to occur in soil. Owing to the complexity that exists in the soil system, none of the methods is universally applicable for all the soils. Hence, Haylocks (1956) introduced the terms "Step-K", and "Constant Rate-K" as a measure of plant utilizable non-exchangeable potassium reserves in soil. Step-K is the release of potassium with repeated extractions with 1.0 *N* HNO_3 and the 'Constant Rate-K', which is the rate achieved when release of K with every extraction is equal to the previous one. The constant rate K which takes into account soil type and mineralogy may serve as a guide to the long-term K supplying power of soils.

12. Usefulness of Non-exchangeable K

Non-exchangeable K contributes substantially to potassium availability and uptake in soils rich in micaceous minerals, especially the illite-dominant alluvial soils and vermiculite-containing alluvial and black cotton soils. The assessment of non-exchangeable K status of soils is made using extractants like boiling 1*N* HNO_3, sodium tetraphenyl boron (NaTPB), H-resins, 6 *N* H_2SO_4, and exhaustive cropping (Srinivasa Rao *et al.*, 2001). Mica or illite followed by vermiculite with larger interlayer K are the major sources of non-exchangeable K. Illitic inceptisols and alfisols show larger amounts of non-exchangeable K as compared to vertisols. Smectitic vertisols and associated soils with high clay-content and with mica as an associated clay mineral have shown higher amounts of non-exchangeable K than kaolinite soils with low clay-content and low weatherable-micaceous minerals.

Under exhaustive cropping, non-exchangeable K contribution to total K uptake can be as high as 90% in alluvial soils. Highly-weathered red and lateritic soils are poor in K supply because of low non-exchangeable K reserves. Some perennial grasses like ryegrass (*Lolium perenne*) are very efficient in utilizing non-exchangeable K without yield reductions, whereas legumes like red clover (*Trifolium pretense*) is not an efficient user. Fertilizer K rates to be applied get reduced in proportion to the amount of non-exchangeable potassium. Subba Rao *et al.* (1993) have categorized the 21 surface soils of well-defined soil series of India developed on a variety of parent materials on the basis of non-exchangeable K resources (Table 5).

13. Losses of Potassium

Losses of potassium may take place in the form of luxury consumption, leaching, and soil erosion as described below:

13.1. Luxury Consumption

Some crops tend to absorb and accumulate potassium far in excess of their needs, if it

Table 5. Categorization of soils on the basis of non-exchangeable K resources

Category	Non-exchangeable K (mg/kg)	Soil series	Description
Very low	Up to 150	Balisahi, Kharbona, Vijayapura, Nedumangad, Kumbhav – 5	Kaolinite-dominant red, lateritic and acidic alluvial soils with coarse or fine texture
Low	151-300	Tyamagondalu,Bagru	Red soils and acidic alluvial soils with considerable amount of mica
Medium	301-600	Pithvajal, Kamliakheri, Sarol, Pemberty, Lukhi	Smectite-rich swell-shrink soils and coarse-textured alluvial soils
High	601-1200	Doddabhavi, Shendvada, Kalathur, Nabha, Masitawali	Smectite soils with appreciable amounts of illite and illitic-alluvial soils
Very high	>1200	Rarha, Khatki, Noyyal	Medium to fine illitic-alluvial soils and smectite soils with high mica or illite content

Source: Subba Rao *et al.* (1993)

is present in sufficiently large quantities in the soil. This tendency is termed 'luxury consumption' because the excess K absorbed does not increase crop yields to any appreciable extent. Wasteful luxury consumption occurs especially with forage crops. If plant residues are not returned to the soil, this excess potassium gets removed which is decidedly a wasteful loss. In addition, high levels of potassium may depress calcium uptake and cause nutritional imbalances in the plants as well as in animals who consume these plants (Brady and Well, 2007).

13.2. Leaching and Erosion Losses of K

Leaching losses can vary widely from traces to 4-5 kg/ha/yr, depending on soil, irrigation, fertilizer-usage and cropping. Leaching losses of the applied K are highest in light-textured soils (7-17 kg/ha/yr), organic soils and soils with kaolinite as the dominant clay mineral (Mengel and Kirkby, 1987). On fine-textured soils, the vertical movement of K in the profile is restricted and the extent of leaching losses is relatively small (3-8 kg/ha/yr). Since considerable amount of K is adsorbed by soil colloids, leaching losses of K normally do not result in yield loss, except on very sandy soils. Hence, for some crops, split application of K is recommended under high leaching conditions.

It has been estimated that about 5.37-8.40 million tonnes of soil nutrients are lost every year through water erosion in the country (Samra and Sharma, 2002). In this, the erosion loss of K is considerable and generally exceeds that of any other major nutrient element and it generally varies between 10 and 55 kg/ha/yr. Soil erosion also leads to considerable loss of total potassium from the soil.

14. Gain of Potassium through Groundwater Irrigation

Underground water is a very important source of irrigation in northern India, particularly in the states of Punjab, Haryana, Uttar Pradesh, Uttrakhand and parts of Rajasthan. In Punjab, out of the total irrigation water applied, 62% is taken from the underground sources. Potassium content of underground waters of Punjab varies from 0 to 7 milliequi/L (Brar, 1998). On an average, potassium added through one irrigation of 7.5 cm works out to be 7.5 kg/ha. In a rice-wheat cropping system where about 12 irrigations of underground water are normally applied, the addition of K is to the extent of 90 kg/ha. The mean values, however, may sometimes be misleading as large areas may be receiving a negligible amount of potassium from the underground waters. On the other hand, the negative balance sheet of potassium worked out without taking into consideration the contribution of underground water may be an over-estimation.

15. Crop Responses to Added Potassium

In India, crop responses to K have increased over time with intensification of agriculture in using high-yielding varieties, increased irrigation, adequate amounts of other nutrients like N and P, and improved management practices. Crop responses to K are large on laterites, red, red and yellow, and mixed red and black soils (Goswami *et al.*, 1976). The yield response in rice and wheat to the application of 60 kg K_2O/ha in the presence of 120 kg N/ha and 60 kg P_2O_5/ha, has been found to increase with the passage of time. Crops like rice, maize, wheat and finger millet respond to 60 kg K_2O/ha under irrigated and assured rainfall conditions. Under rainfed conditions, cereals and millets respond to 30 kg K_2O/ha, legumes (pulses) to 20 kg K_2O/ha (along with 20 kg N/ha and 40 kg P_2O_5/ha) and oilseeds to 40 kg K_2O/ha. A wide range of response to K-application across the country to major crops is presented in Table 6. It is now realized that crops grown on coarse-textured alluvial soils, some black soils, red and lateritic soils need K-fertilization, as these soils are poor suppliers of K for optimum crop production.

16. Potassium and Crop Quality

Potassium has long been referred to as the 'quality nutrient'. The quality effects are more closely linked to nutrient interactions such as N-K, than to absolute levels of K. Studies in India have shown that potassium increases the proportion of best quality grade tubers in potato; protein in cereals and pulses (Table 7); oil-content in oilseeds; total sugars, sucrose and vitamins, etc. in fruits; sucrose content and extraction, sucrose percentage in sugarcane and some other quality parameters in other crops.

17. Other Beneficial Effects of Potassium

Potassium improves the water-use efficiency and helps in maintaining yield under moisture stress and reduces the extent of crop losses under such conditions. Crop varieties which absorb potassium in preference to sodium, are relatively more tolerant to salinity and alkalinity. Potato plants well supplied with K, withstand frost better than low K plants. Potassium is also very effective in reducing fungal disease attack. Thicker cuticles and stronger epidermal cell walls prevent the entry of germinating spores in plant body. It has been found that the incidence of leaf roller, thrips, brown plant hopper and green leafhopper on rice decreases with potassium application.

18. Potassium Interactions with other Nutrients

Adequate supplies of other plant nutrients are required to obtain maximum responses to potassium fertilization; however, there are several unique relations between potassium and other nutrients due to the complementary ion effect (other cations held on the cation exchange positions of the clay) that are important in plant nutrition.

Potassium, calcium and magnesium perform one non-specific function of maintaining a level of ionic balance in the plant system. The "Viets Effect", named after F.G. Viets, states that higher Ca concentration in the outer solution either enhances the uptake of K or reduces the loss of K ions. Hence, the tissue K concentration increases. High potassium fertilization can decrease the availability of magnesium to the plant and may result in magnesium deficiency in crops grown on soils that are already low in magnesium. Negative K × Mg interaction has been reported in grapes (Bhargava, 1987), cassava (CTCRI, 1986), and coconuts leaf (Khan *et al.*, 1986). Low content of Mg and Ca in forages can affect animal by producing low blood serum (grass tetany disease). Generally, addition of K, results in a lower concentration of Ca or Mg, regardless of the crop grown (Figure 6).

High levels of potassium fertilization along with ammoniacal nitrogen (NH_4^+) also depress the magnesium-content of forage grasses and may result in grass tetany (hypomagnesaemia) in cattle. Sodium has been shown to substitute partially for potassium in some crops (Marschner, 1971).

Leaching of potassium in acid, sandy soils may be reduced by liming the soil to pH of 6.2-6.5; however, application of high rates of limestone to a soil low in potassium may induce potassium deficiency in crops growing on those soils. This problem occurs more on

Table 6. Yield response through potassium application in different crops

Location	Soil type	Crop	N	P_2O_5	K_2O	Response (kg grain/ kg K_2O)
Kota	Typic Chromustert	Soybean	60	120	0	
			60	120	30	4.0
			60	120	60	2.6
		Wheat	120	120	0	
			120	120	30	3.7
			120	120	60	3.7
Kanpur	Typic Ustochrept	Rice	150	30	0	
			150	30	40	2.1
		Wheat	150	30	0	
			150	30	40	1.8
			150	30	120	7.7
Faizabad	Inceptisol	Rice	150	60	0	
			150	60	40	7.8
		Wheat	150	60	0	
			150	60	40	12.8
			150	60	120	3.5
Varanasi	Typic Natraqualf	Rice	150	30	0	
			150	30	40	15.6
			150	30	120	2.7
		Wheat	150	30	0	
			150	30	40	8.5
Ludhiana	Typic Ustrochrept	Rice	150	60	0	
			150	60	50	8.6
			150	60	150	7.9
		Wheat	150	60	0	
			150	60	50	6.8
			150	60	150	1.9
Palampur	Typic Hapludalf	Rice	100	25	0	
			100	25	125	2.1
		Wheat	100	25	0	
			100	25	40	10.3
Coimbatore	Vertic Ustropept	*Kharif* Rice	150	120	0	
			150	120	30	10.1
			150	120	60	19.2
		Rabi rice	150	120	0	
			150	120	30	16.3
			150	120	60	5.4
Thanjavur	Udic Chromustert	*Kharif* Rice	150	30	0	
			150	30	100	10.4
		Rabi rice	150	30	0	
			150	30	100	3.2
			150	30	150	2.4
Pantnagar	Typic Hapludoll	Rice	170	30	0	
			170	30	40	7.5
		Wheat	170	30	0	
			170	30	40	23.4
Ranchi	Alluvial soil	Rice	150	60	0	
			150	60	50	17.2
			150	60	150	12.0
		Wheat	150	60	0	
			150	60	50	1.6
Jammu	Dystrochrept	Rice	150	100	0	
			150	100	40	1.4
			150	100	0	
			150	100	40	15.1

Source: Annual Report (2005-06), PDCSR, Modipuram.

Table 7. Effect of potassium application on crop quality

Crop	K levels (kg/ha)					LSD 0.05
	0	25	50	75	100	
			Protein (%)			
Chick pea	19.59	19.75	20.13	20.89	-	-
Lentil	26.12	26.40	27.00	27.12	-	-
Urdbean	24.30	24.40	24.70	24.30	-	-
Mungbean	23.40	24.00	24.12	24.05	-	-
Pigeonpea	20.60	21.40	21.79	21.68	-	-
Pea	21.00	21.70	22.05	21.84		
Pea (veg)	23.25	24.18	24.87	24.49	-	0.39
Potato tubers	0.96	-	1.02	-	0.99	0.02
			Total sugars (%)			
Pea (veg)	3.49	3.67	3.77	3.75	-	0.12
Potato tubers	0.57	-	0.59	-	0.67	0.02

Sources: Tiwari (1986) and Kanaujia *et al.* (1997)

$LSD_{0.05}$ = Least significant difference at 5%

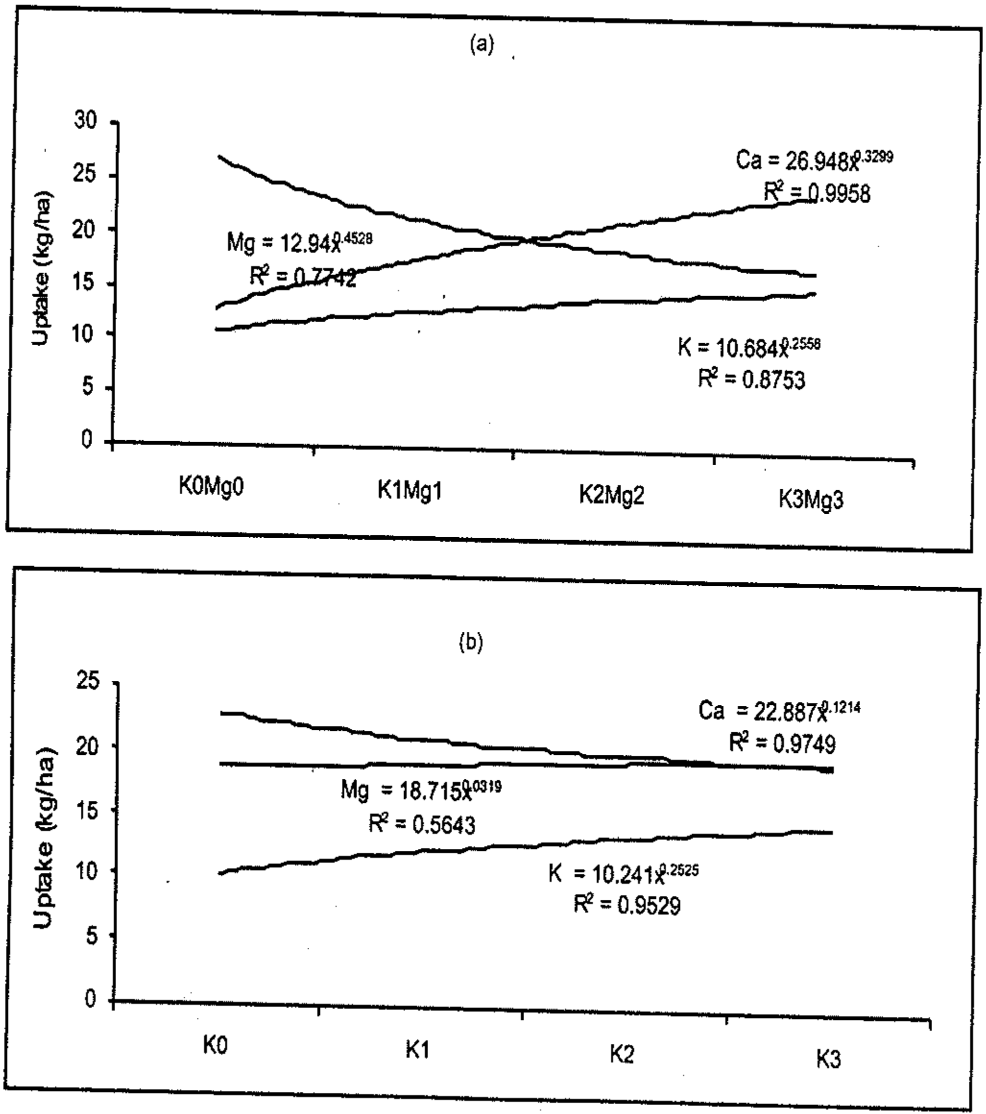

Figure 6. Effect of K and Mg fertilization on removal of K, Ca and Mg in Okra: (a) Balanced application of K and Mg, (b) Effect of K alone

(modified from Rani and Jose, 2009)

soils with predominantly 2:1 type clays (such as montmorillonite clays) rather than 1:1 type clays (such as kaolinitic clays).

19. Management of Potassium

19.1. Sources of Potassium and their Suitability

Potassium content of fertilizers is expressed as K_2O, although there is no such compound in fertilizers, nor it is absorbed by or found in the plant in that form. Soil and plant tissue analyses values are usually expressed in terms of per cent potassium (K) and fertilizer recommendations are expressed as K_2O.

India has no potash-rich soluble minerals and incrustations. Hence, all the fertilizer K used in Indian agriculture is imported. Potassium chloride or muriate of potash (MOP) constitutes 99% and sulphate of potash (SOP) one per cent of the total K fertilizer use. Muriate of potash (MOP) contains 60% K_2O (50% K) and SOP contains 50% K_2O (41.5% K). MOP is cheaper than SOP, since it is the raw material for the manufacturing of SOP. Some crops are sensitive to high amount of potassium chloride. These include tobacco, grapes, fruit trees, cotton, sugarcane, potatoes, tomatoes, straw berries, cucumber and onions. It is preferable to apply SOP to these crops. Oilpalm and coconut, on the contrary, appear to be chloride-loving crops and perform well with the application of MOP. Potassium nitrate, containing 44% K_2O (37% K) and 13% N, is a preferred fertilizer for spraying on fruit trees and horticultural crops. Recent studies in India have shown that schoenite (a double salt of potassium and magnesium) is as good a source of potassium as MOP for groundnut, banana, rice, wheat and maize.

Indigenous sources of potassium like wood ash, manure, crop residues, distillery and coir wastes, cement kiln dust, etc. can also be used wherever they are available, to minimize the use of costly fertilizers.

19.2. Methods of Potassium Application

Potassium fertilizers are generally broadcast or spread on the surface and mixed with surface soil. Only in soils with a low level of available K or with a high K-fixing capacity, band placement is recommended. In some soil-crop situations, split application is emerging as an alternative to basal application. These situations are: (i) rice grown in light-textured soils and acid soils in high rainfall areas in order to reduce leaching losses, (ii) low tillering and late maturing varieties, where the natural supply of K from soil plus irrigation water decreases in the later stages of crop growth, (iii) in highly reduced soils where conditions may hinder K uptake; and (iv) during the monsoon season.

Studies conducted in the states of Tamil Nadu, Uttar Pradesh, West Bengal and Tripura have indicated the beneficial effect of application of K in 2-3 splits in rice. Split application of both N and K in rice is recommended in Andhra Pradesh, Kerala, Orissa and Uttar Pradesh. Split application of K is also recommended in crops like sugarcane, banana, grapevines, papaya, pineapple and tea in different states (Tandon and Sekhon, 1988).

Potassic fertilizers and K-rich organic (poultry manure, 1.16%; biogas slurry, 0.08%; pulse residues, 1.6%; rice straw, 1.4%; vermicompost, 0.8%; etc.) and inorganic sources are being used in crops which remove large amount of K or in commercial crops for quality consideration. The beneficial role of K in crops grown under dryland conditions and in problem soils such as saline/sodic, poorly-drained, highly-leached and eroded soils remains to be fully harnessed. With further intensification of agriculture in the next 20 to 25 years, the requirement and use of potassium would increase to meet the expected enhanced K needs of crops and also to provide a balanced nutrition.

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Chapter 19

Secondary Nutrients

N.S. PASRICHA and A.K. SARKAR

1. Introduction

Calcium (Ca), magnesium (Mg) and sulphur (S) are conventionally classified as secondary nutrients. This does not mean that they have a secondary role in plant nutrition. It is only because their requirements by plants are quantitatively less than those of primary nutrients (NPK) that the term "secondary nutrient" is used. These three nutrients form a significant part of the earth's crust.

Calcium is the fifth most abundant element in the earth's crust, while Mg and S are ranked eighth and thirteenth, respectively. Some important information about these elements is given below.

Calcium and magnesium being small and strongly electrovalent, are the most abundant cations occupying the exchange sites of the soil colloids, both inorganic and organic. Thus, most soils, with the possible exception of highly weathered, leached acid soils, contain enough Ca and Mg for crop growth. Activity of Ca is related to its capacity for coordination, by which it provides stable but reversible intermolecular linkages, predominantly in the cell walls and at the plasma membrane. These Ca^{2+}-mediated linkages respond to local changes in environmental conditions and are part of the control mechanisms for growth and developmental process. Calcium is a non-toxic mineral nutrient, even in high concentrations, and is very effective in detoxifying high concentrations of other mineral elements in plants. The metalloenzyme, amylase, has calcium as the metal. Calcium is the major cation in the middle lamella of cell walls, of which calcium pectate is the principal constituent. Thus, calcium provides mechanical strength to tissues, enhancing cell division and plant growth, protein synthesis, carbohydrate movement and balancing cell acidity.

Characteristics	Nutrient element		
	Ca	Mg	S
Atomic weight	40.08	24.31	32.06
Atomic number	20	12	16
Specific gravity at 20 °C	1.52	1.74	2.07
Proportion of earth's crust (%)	3.20	2.50	0.10
Forms absorbed	Ca^{2+}	Mg^{2+}	SO_4^{2-}
Hydrated ionic radius (nm)	0.412	0.428	—
Hydration energy ($J\ mol^{-1}$)	1577	1908	—
Typical concentration in plant dry matter (%)	0.2-1.0	0.1-0.4	0.1-04

Magnesium is an essential constituent of chlorophyll in plants. Magnesium is also the most common activator of enzymes concerned with energy metabolism. The functions of Mg^{2+} in plants are related to its mobility within the cells, its capacity to interact with strongly nucleophilic ligands (e.g., phosphoryl groups) through ionic bonding, and to act as a bridging element and/or forming complexes of different stabilities. Although most bonds involving Mg^{2+} ions are ionic, some are partially covalent, as in the chlorophyll molecule. Magnesium forms ternary complexes with enzymes in which bridging cations are required for establishing a precise geometry between enzyme and substrate (Clarkson and Hanson, 1980). A high proportion of the total Mg^{2+} ions is involved in the regulation of cellular pH and the cation-anion balance. Calcium may sometimes inhibit the activating effect of magnesium by displacing it from the functional groups.

Sulphur occurs as sulphides in igneous and sedimentary rocks. Sulphur is also present in organic compounds in soil, in industrial wastes, sea-water and as gaseous emissions in atmosphere. Sulphur-deficiency normally occurs on old deeply-weathered land surfaces of strongly leached soils and soils away from sea and industrial areas. Sulphur absorbed as SO_4^{2-} ions is reduced in plants and incorporated in organic compounds. Sulphur is required for the synthesis of vitamins. It is essential for the production of three amino acids found in plants and animals. Proteins are the compounds in which most of the sulphur of plant tissues is incorporated. For every 15 parts of N in protein, there is 1 part of S, which implies that the N:S ratio is nearly constant within a very narrow range of 15:1. Sulphur requirements of crops are very similar to their phosphorus needs.

Deficiency Symptoms

Deficiency symptoms of Ca, Mg and S are different. Soils seldom become calcium-deficient, as long as soil pH is maintained towards neutral range. Deficiency of Ca is characterized by a reduction in meristematic tissue. Deficiency first appears in the growing tips and youngest leaves and subsequently in an advanced stage, necrosis of leaf margins occurs. One symptom of Ca-deficiency in apples is discoloration of the fruit meat. The condition is commonly called "bitter pit".

Magnesium-deficiency is common in plants growing on coarse-textured acid soils. Chlorotic interveinal pattern of leaves is common in many fruits and vegetables. Mg-deficiency first appears on lower leaves as a yellowish bronze or reddish colour, while leaf veins remain green. In strongly acidic soils (pH <4.5), there is reduced absorption of Ca and Mg by plants. Forages grown in acid soils have low Mg-content and cattle feeding on such forages may suffer from "Hypomagnesemia", called 'Grass Tetary' disease.

Sulphur-deficiency leads to inhibition of protein synthesis. In field crops, it is difficult to distinguish between the deficiencies of S and N. Yellowing of leaves in wheat is a common S-deficiency, but is often diagnosed as N-deficiency. In the case of leguminous crops, nodulation is often poor due to S-deficiency. In tomatoes, plants are smaller with stunted growth and lighter in colour. In general, mottled yellow-green leaves with yellowish veins in younger leaves is the characteristic symptom of S-deficiency.

2. Sources of Secondary Nutrients in Soil

Soil Ca and Mg other than those added through fertilizers or liming materials come from the weathering of rocks containing different minerals (Table 1).

The major sulphur source under natural conditions is the organic matter. More than 95% of total S in soil is present in the organic matter under temperate conditions. In tropics and subtropics, inorganic sulphates are also present, as these occur in appreciable amounts. Consequently, the total S in the organic form is relatively lower in these soils. It becomes available on decomposition of the organic matter in soils. Besides organic matter, the other sources are inorganic minerals present in the soil, atmospheric accretions of S through rainfall and S added through irrigation water.

Under tropical and subtropical conditions, the organic matter content of soil is generally less than that in the temperate regions of the

Table 1. Calcium and magnesium containing minerals

Minerals	Total CaO	Total MgO
	(%)	
Calcite	56.0	–
Apatite	50.0-53.2	–
Dolomite	33.2	12.2
Gypsum	32.2	–
Augite	18.7	15.7
Hornblende	4.6	17.3
Olivine	Traces	32.4
Serpentine	Traces	44.2
Magnesite	–	45.0
Kieserite	–	27.0
Schoenite	–	10.0-20.0
Epsom salt	–	16.0
Muscovite	–	0.0-3.0
Biotite	0.0-2.0	2.0-20.0
Anorthite	10.0-20.0	–
Tourmaline	0.0-6.0	0.0-12.0
Epidote	22.0-25.0	–
Talc (Soapstone)	–	19.0
Asbestos	–	31.0
Chlorite	–	35.0-38.0
Brucite	–	41.3
Illite	0.0-2.0	1.0-4.0
Montmorillonite	0.0-3.0	0.0-25.0

world. Whatever organic matter is added as crop stubbles or natural leaf fall, is immediately decomposed and its S is mineralized to SO_4^{2-}. The oxidation of S, which is present in organic matter in the form of proteins and amino acids, is mediated by a number of microorganisms. *Thiobacillus* bacteria act on S-substrates and bring about its oxidation. Thus, in the arid and semi-arid regions, much of the S in the soil may not be in the organic form. Due to obvious reasons, the inorganic forms of S are high under these conditions.

The total S in soil is present in organic combinations. Therefore, soils which are rich in organic matter will have high levels of S. In most of the cultivated lands, S ranges from 30 mg/kg to 50 mg/kg, but exceptionally high values can be encountered in soils that are salt-affected or are acid-sulphate in nature, as in some coastal regions.

Coarse-textured sandy soils generally have low total S-content as compared to fine-textured soils. This again is related to organic matter content in these soils. For the same reason, S-content is more in the surface soils than in the sub-soils. Generally, it decreases with depth. However, in some arid soils, the concentration of total sulphur may increase with depth because in these areas major portion of S is in inorganic form and exists as sulphate, which tends to move downward along with the limited rain water infiltrating the soil profile. Organic S may not be the dominant form in arid and semiarid soils of tropics and subtropics. Among Indian soils, only 30% of the total S in soil may be in the organic combination in alluvial soils (Entisols), but in Mollisols of *Tarai* region, it may be around 70%.

Microorganisms in soil play an important role in making S available to plants. Bulk of the inorganic sulphur in rocks is present as pyrites (FeS_2), but other minerals such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), gypsum ($CaSO_4.2H_2O$), cobaltite (COAsS), and epsomite ($MgSO_4.6H_2O$) may also supply sulphur to soils. In humid zones, organic sulphur is the major form of sulphur, while in arid zones, the sulphates of Ca, Mg, Na and K predominate. Atmosphere is another source of sulphur. Owing to industrial activity, through combustion of fossil fuels, SO_2 is produced and is brought down by rain. The annual gain of S from atmosphere has been estimated at 8-12 kg/ha in the western countries.

3. Removal of Secondary Nutrients from Soil

Secondary nutrients in soil may be lost due to crop removal, leaching, erosion and volatilization. The amount of secondary nutrients removed by crops depends on soil type, crop species, fertilizer sources and yield level (Table 2). Generally, legumes and root crops remove more Ca than do cereals and other grasses. While cereals may remove 10-20 kg Ca/ha, a good crop of *Brassica oleracea* may remove 150 kg Ca/ha (Kanwar, 1976). Continuous cropping of maize-wheat with NPK fertilizers in unlimed acid soils (Alfisols) of Ranchi, Jharkhand, resulted in the reduction of exchangeable-Ca^{2+} in soil from 2.9 to 1.0 cmol(p^+) kg^{-1} after 21 years and exchangeable-Mg^{2+} from 1.3 to 0.9 cmol(p^+) kg^{-1} after 10 years (Mathur *et al.,* 1989). Banana or pineapple

Table 2. Average removal of secondary nutrients by some crops

Crop	Economic yield (t/ha)	Total removal (kg/ha)		
		Ca	Mg	S
Rice	3.0	21	9	9
Wheat	3.0	16	14	14
Maize	5.0	27	39	19
Sorghum	2.5	16	12	7
Sugarcane	88.0	132	-	26
Cassava	45.0	131	108	15
Onion	37.0	16	18	34
Tomato	41.0	31	8	28
Coffee	2.0	143	33	27
Chickpea	1.5	28	11	13
Soyabean	2.5	35	19	22
Pigeonpea	1.2	23	15	9
Groundnut	2.0	39	20	15
Mustard	1.5	63	13	26
Sunflower	0.6	41	16	7

Source: Tandon (1989)

crops with yield levels of 40-50 t/ha remove 120-140 kg Mg/ha. Leaching losses of secondary nutrients are fairly high and these increase with rainfall and soil permeability. Appreciable loss of added lime [1.5 cmol(p^+) kg^{-1} exchangeable-Ca^{2+}] after rains was reported in Alfisols of Chotanagpur region of Jharkhand (Mandal *et al.*, 1975).

Common cropping sequences followed in different parts of the country annually remove 10-70 kg S/ha (Mehta and Raman, 1972), while intensive cropping system involving 3-4 crops/year can remove 30-72 kg S/ha (Mahapatra, 1997). As a thumb rule, sulphur removal per tonne grain production can be taken as 3-4 kg for cereals, 5-8 kg for millets, about 8 kg for pulses, about 12 kg for oilseeds and 16-18 kg for sugarcane. Among oilseeds, average figure for Crucifers is 18 kg S and for non-crucifer oilseeds it is 9 kg S (Aulakh and Pasricha, 1988). Among the families of crop plants, the requirement increases in the order: Gramineae < Leguminosae < Cruciferae. On the whole, S-requirement of oilseeds follow the order : Crucifers > Seasame = Sunflower > Legumes > Linseed.

For a good crop of wheat (say 4.5 t/ha yield) and rice (say 6 t/ha yield), grown in rotation, the removal of S is around 28 kg S/ha. An average crop of groundnut (2 t/ha), removes about 25 kg S/ha. In the mustard crop, the removal is maximum. A mustard crop yielding 2.0 tonnes of seed/ha can remove as much as 38 kg S/ha. Safflower is another oilseed crop that removes high amounts of S from soil; a crop of safflower yielding 2.5 t/ha removes as high as 27 kg S/ha. Table 3 shows the average sulphur removed by some of the commonly-grown crops in India under wide range of growing situations.

Table 3. Average removal of S by different crops in different states of India

Crop	Yield (tonne/ha)	S removal (kg/ha)
Wheat	4.5	8.1-27.0
Rice	6.0	5.4-14.5
Maize	4.0	8.8-18.4
Groundnut	2.0	6.6-42.0
Pigeonpea	1.5	11.2
Soybean	2.0	7.0-17.6
Chickpea	1.5	12.5
Rapeseed/mustard	2.0	22.2-54.0
Sunflower	2.5	15.5-29.3
Linseed	2.0	9.8-13.4

Source: Tandon (1991)

4. Forms of Secondary Nutrients in Soil

Indian soils are generally low in organic matter and have low cation exchange capacity. Deficiencies of Ca and Mg frequently occur in coarse-textured as well as acidic soils developed under high rainfall conditions. Being cations, both Ca^{2+} and Mg^{2+} ions are subject to cation exchange. These are found in soil solution and are adsorbed on the clay and organic matter surfaces. Soils usually contain less Mg than Ca because Mg^{2+} ions are not adsorbed as strongly by clay and organic matter as Ca^{2+} ions and further Mg^{2+} ions are more susceptible to leaching than Ca^{2+} ions. The importance of Ca and Mg as plant nutrients is more realized in acid and alkali soils than in neutral soils. In acid soils, lime-loving crops do not give high yields unless these are suitably fertilized with Ca and Mg. Similarly, in alkali soils, crops suffer due to lack of Ca and excess of Na. Though critical limits of exchangeable Ca

Table 4. Status of exchangeable Ca and Mg in soils of some states of India

Place	Ca	Mg
	$cmol(p^+)kg^{-1}$	
Ranchi (Bihar)	3.70	2.52
Palampur (Himachal Pradesh)	4.32	1.72
Jorhat (Assam)	8.96	1.60
Sikkim	0.50-0.75	2.60-9.40
East Khasi Hills (Meghalaya)	0.15-0.44	–
Darjeeling (West Bengal)	0.75-22.42	0.84-4.60
Madurai (Tamil Nadu)	4.80	2.60
Udool (Kashmir valley)	0.75-20.40	0.25-1.50

and Mg vary widely among soils, generally soil containing less than 25% of their CEC or less than 1.5 $cmol(p^+)\ kg^{-1}$ Ca have usually been considered as calcium deficient. Usually, soils containing 1.0 $cmol(p^+)\ kg^{-1}$ Mg or less than 4-15% of CEC occupied by Mg are considered deficient. The status of these nutrients in some Indian soils is summarized in Table 4.

Calcium is present in soils as mineral particles, $CaCO_3$, simple salts, Ca in soil solution and exchangeable Ca. The exchangeable and soluble forms of Ca are in dynamic equilibrium with each other. In sandy soils with low CEC, the amount of exchangeable Ca is very low. The nature of clay minerals influences the availability of Ca in soils. For example, 2:1 type clays require a higher degree of Ca-saturation for a given level of plant utilization compared to 1:1 type clays.

Magnesium is present in soils as water soluble, exchangeable and non-exchangeable forms. The non-exchangeable form is in equilibrium with water soluble and exchangeable Mg in a soil. The behaviour of Mg in soils, however, is similar to that of K^+ and Ca^{2+}. The availability of Mg in soils is affected by soil pH, texture, and clay content. Leaching of Mg from coarse-textured soils with low pH often results in its deficiency. Mg is also unavailable in soil rich in clay minerals such as chlorite and vermiculite due to fixation.

In soils, sulphur can be broadly grouped into four forms, viz. total S, organic S, non-sulphate S and available S. Among these forms, organic S (5 to 98% of available S in Indian soils) is most important. Sulphate ions, the plant available form of sulphur, are not adsorbed on clay or organic matter surfaces under neutral to alkaline conditions. Under such conditions, sulphur is present mainly in soil solution and is thus susceptible to leaching from the soil. In humid region soils, bulk of the sulphur is associated mainly with organic matter, which is mineralized by soil microorganisms into SO_4^{2-}-S form. The sulphur cycle (Figure 1) shows the relationships among atmospheric, fertilizer and soil sulphur sources. Sulphur-deficiency has become widespread in India especially in coarse-textured alluvial soils (Entisols, Inceptisols), red and lateritic soils (Alfisols) of Karnataka, Kerala, Jharkhand and West Bengal, black soils (Vertisols) of Madhya Pradesh, Maharashtra and Gujarat. Critical limit of $CaCl_2$ (0.15%)-extractable sulphur in soils is about 10 ppm. A rough estimate of the areas that are deficient in S in different states of the country is given in Table 5.

5. Mineralization of S-compounds in Soil

The sulphur in soil is being cycled continuously between inorganic and organic forms. The nature of compounds formed and their transformations are influenced by the biologically mediated processes, which, in turn, are affected by environmental conditions. As has been stated earlier in many cases, organic matter is the major source of soil S. Its oxidation to SO_4^{2-} ions is brought about by soil microorganisms and the process is called 'mineralization'. It is this mineralized form in which S can be taken up by plants and microorganisms. Rate of mineralization is affected by such factors as moisture, aeration, temperature and soil pH. The conversion of organic-S to SO_4^{2-} ions is

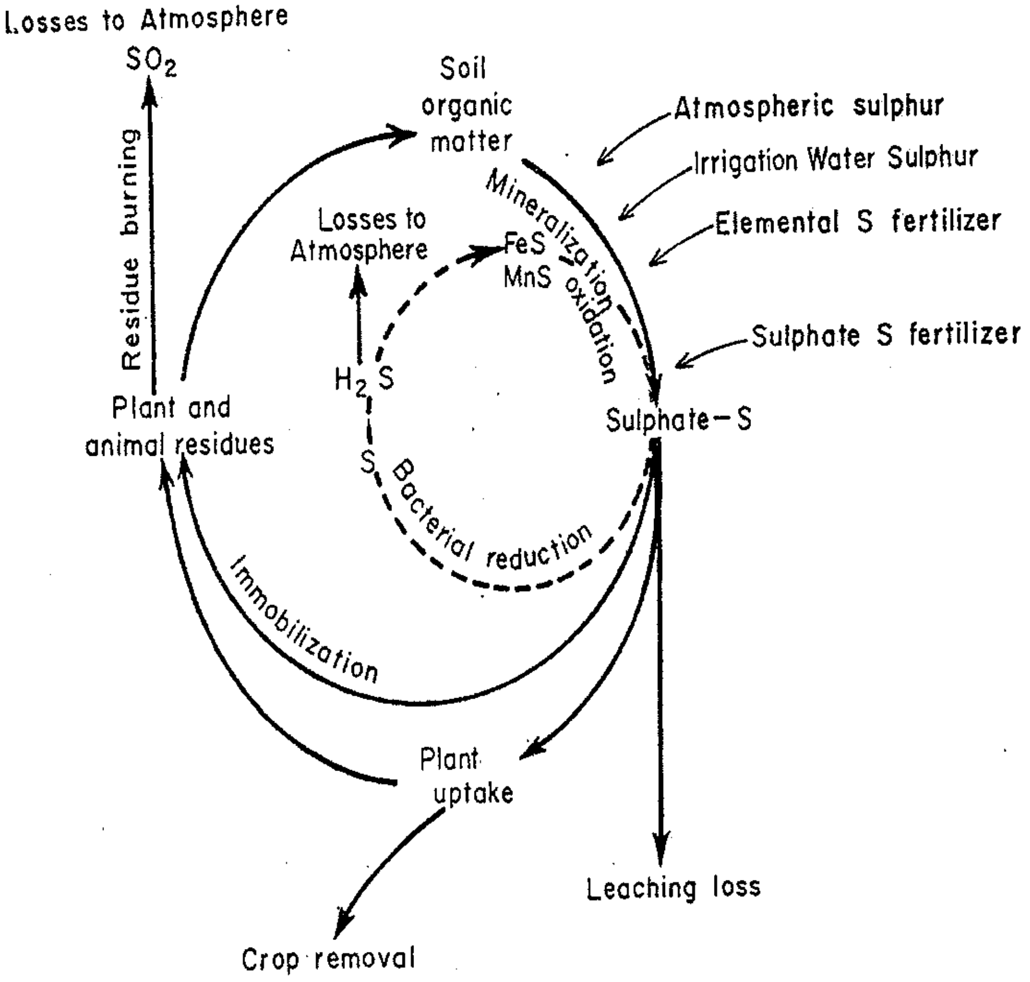

Figure 1. The sulphur cycle

an oxidation process, and cannot take place in the absence of oxygen. Proper aeration is, therefore, essential for this process to proceed. Also, this process cannot take place under submerged soil conditions, except in the aerated pockets of the soil. The mineralization process can be expressed by Equation (1):

$$\text{Organic S} \xrightarrow[O_2]{\text{Aeration}} SO_4^{2-} + H^+ \qquad ...(1)$$

The formation of end-product, SO_4^{2-} ions, is associated with the formation of H^+ ions. Hence, this process lowers the soil pH. This biological transformation in some cases requires very low pH in soil before the process can be initiated.

Under limited S-supply and in the presence of excess of carbonaceous materials, the mineralized-S can be readily used by microorganisms. Carbonaceous materials provide energy to the growing population of microorganisms, which consume the mineralized-S. Hence, crop plants may suffer from S-deficiency. This process is called "immobilization". Immobilization is a temporary phase, as on the death of the microbial population, the microbial S is mineralized to SO_4^{2-} which can be utilized by the growing plants. Sulphur in the soil is associated with organic carbon in a fixed C:S ratio of about 140:1. Thus, a favourable C:S ratio is more important than a large store of organic matter for S-response under tropical conditions. It is because the ratio influences microbial decomposition of organic matter.

A major transformation involving S is that of conversion/ oxidation of organic-S into sulphate. This process is similar to N-transformation in soil. Since this transformation is mediated biologically, extremes of temperature hamper this process. Optimum temperature for it is 35-40 °C. Soil moisture is another important factor. While moisture level of about 60%

Table 5. Extent of S-deficiency in soils of different states of India

State	Deficient areas (extent of deficiency)
Andhra Pradesh	Red soils of Telangana and Chittor districts (53-62%), Karimnagar (61%), Rangareddy, Mehboob Nagar, Nalagonda (>50%), Chittor (62%)
Bihar	Nawadah (60%), Patna (35%), Nalanda (30%), Bhojpur (15%), Gaya (12%) Samastipur, Saharsa and Darbhanga (26%)
Jharkhand	Lohardaga (77.9%), Latehar (70.9%), West Singhbhum (61.6%), Sahebganj (56.3%), East Singhbhum (46.6%), Pakur (42.2%), Dumka (42.2%), Saraikela (40.9%), Ranchi (36.7%), Godda (36.6%), Deoghar (35.3%), Gumla (34.8%), Hazaribagh (33.8%), Kodarma (33.1%), Garhwa (29.5%), Bokaro (28.3%), Chatra (28.1%), Simdega (25.8%), Jamtara (25.8%), Giridih (25.2%), Palamau (20.4%), Dhanbad (13.9%)
Gujarat	Bhavnagar (80%), Amreli (70%), Jamnagar (68%), Rajkot (35%), Bhruch (33%), Junagarh (30%), Surat (25%), Panchmalal and Dahod (37%)
Haryana	Sierozems of Hisar and Sirsa (40%), Ambala (80%) and Gurgaon (80%)
Karnataka	Dakshin Kannada, Uttari Kannada, Malnad area, Malaprabha command area, coffee-growing area and coastal soils of the state. The extent of deficiency ranges from 17% to 40%, Dharwad (47%), Kolar (20%)
Tamil Nadu	Coimbatore and Erode (27%)
Madhya Pradesh	Betul, Chindwara and Seoni (10-20%), Narsinghpur, Ratlam, Balaghat and Morena (21-40%), Rajnandgaon, Devas, Indore, Ujjain, Dhar, Mandsam, Jabalpur and Sagar (41-60%), Khandwa, Sehore, Sidhi and Bhind (61-80%), Gwalior and Morena (27-28%)
Chhattisgarh	Raipur (23%)
Maharashtra	Parbani (37%), Latur (14%), Ahmednagar (27%)
Orissa	Alluvial and black soils of Balasore, Cuttack, Ganjam, Kalahandi and Puri (45%), Khurda (35%), Dhenkenal (41%)
Punjab	Loamy sand and sandy loam of Ludhiana district (28-52%), Bhatinda (15-18%), Kapurthala (30-45%)
Rajasthan	Fine-textured calcareous soils of Udaipur area, Jaipur area (20%)
Uttar Pradesh and Uttrakhand	Mirzapur (80%), Gazipur (60-80%), Aligarh, Balia, Banda, Hardoi and Varanasi (40-60%), Agra, Allahabad, Fatehbad, Hamirpur, Kanpur and Mainpuri (20-40%), Farrukabad, Jalaun and Lalitpur (10-20%), Meerut and Jyotibaphule (28%), Jhansi (51%), Faizabad and Gorakhpur (64%)

of field capacity is good for oxidation of organic-S to sulphate, excessive moisture decreases the rate of oxidation due to low accessibility of oxygen or aeration.

6. Reduction-Oxidation Reactions of Sulphur

Sulphur exits like nitrogen, iron and manganese, in nature in more than one oxidation states. Hence, it is subjected to reduction-oxidation reactions in soil. These reactions are biochemical in nature and are mediated by autotrophic bacteria belonging to the genus *Thiobacilllus*. Under anaerobic conditions, when the availability of free air is completely cut off and all the soil pore-spaces are occupied by water, as in marshylands and lowland rice fields, partially oxidized chemicals such as NO_3^- and SO_4^{2-} are reduced and utilized by organisms like *Desulphovibrio* and *Desulphotomaculum*. In the process, these ions are reduced to nitrites, nitrous oxides, sulphites and sulphides. The end product may not always be the foul smelling H_2S because under the impeded drainage conditions, iron (Fe-III) and manganese (Mn-IV) are reduced to Fe^{2+} and Mn^{2+}, which react with sulphide to form relatively less-soluble sulphides of these elements [Equations (2)-(4)]:

$$R\text{-}C\text{-}SH + H_2O = R\text{-}C\text{-}OH + H_2S \qquad ...(2)$$

$$Fe^{2-} + S = FeS \qquad ...(3)$$

$$Mn^{2-} + S = MnS \qquad ...(4)$$

In the reduction-oxidation process, SO_4^{2-} is the last ion to undergo reduction after all the nitrate, Mn(IV) and Fe(III) ions have been reduced. This means intense reduction conditions are necessary before SO_4^{2-} is reduced. Under normal conditions of rice-wheat cropping system in light-textured soils low in organic matter, reduction conditions may not reach a stage where reduction of SO_4^{2-} sets in. However, in heavy-textured soils rich in organic matter and where rice-rice system is practised, there is a possibility of sulphide formation. The less-oxidised forms of S such as sulphite (SO_3^{2-}), thiosulphate $(S_2O_3)^{2-}$ and elemental sulphur (S) can undergo reduction relatively more rapidly. Sulphur-deficiency, observed in rice grown under submerged soils, sometimes results from rapid reduction of SO_4^{2-} to sulphide. Then crop shows a positive response to small applications of SO_4^{2-} at frequent intervals.

During decomposition of organic matter under normal arable soil conditions, organic sulphur compounds are transformed/oxidised to sulphates. The intermediate products of this transformation are: sulphides, thiosulphates and polythionates. This oxidation process is illustrated by Equation (5):

$$2S^{2-} + 2H_2O + 3O_2 \rightarrow 2H_2SO_4 \rightarrow 4H^+ + 2SO_4^{2-} \qquad ...(5)$$

In the presence of excess of aeration, oxidation of sulphides and sulphites can occur through purely chemical processes, while most of the oxidation reactions in soil are biochemical in nature. From Equation (5), it is clear that oxidation of organic-S to SO_4^{2-} through sulphides and elemental S results in the formation of sulphuric acid (H_2SO_4). This sulphuric acid on ionization, releases H^+ ions in the soil solution, which help in lowering the pH of the soil. Elemental S can be successfully used as an amendment in calcareous soils (Calciorthents) with high pH. Acid formed through oxidation of elemental S helps in dissolving $CaCO_3$ with the resultant decrease in soil pH [Equation (6)]:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad ...(6)$$

Some fertilisers may contain elemental S such as S-coated urea. Use of such materials may prove useful in alkali soils or alkaline calcareous soils. However, where the soils are acidic in nature, use of such sulphur-containing materials is not recommended, as these may increase soil acidity in the long-run.

The coastal areas where the soils undergo periodic flooding with sea water may experience extremes of acidity. When such soils are flooded, soil aeration is completely cut off and sulphur is reduced to sulphides by the autotrophic bacteria which use SO_4^{2-} for its oxygen requirement [Equation (7)]:

$$SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O \qquad ...(7)$$

In the process, soil acidity decreases which results in an increase in the pH to near neutrality. However, when sea water is drained and these coastal soils are prepared for cultivation, aeration occurs and sulphides are oxidised to sulphates again. With this oxidation, SO_4^{2-} and H^+ ions are released to the soil solution and pH of the soil may drop to as low as 2.0 to 1.4. These soils are so acidic that it is sometimes uneconomical to cultivate them. However, such soils can be utilized for growing wetland rice under flooded conditions. Some salt-tolerant rice varieties like *Pokali* can be grown under such situations. These soils, which are alternately flooded and drained, are generally fine textured. There are extremes of acid conditions in these soils. Such soils are also called acid-sulphate soils or cat clays. These soils, locally known as '*Kari*', occur in Ambalapuzha, Vaikom and Kottayam talukas in the Kuttanad region of the Kerala state. These soils are classified as Sulfaquepts and Sulphaquents.

Adsorption of sulphur in soils containing high amounts of hydrous-oxides of Fe and Al is common, especially in Ultisol, Oxisol and Alfisol. Adsorbed sulphate-sulphur can account

Table 6. Some materials containing secondary nutrients

Nutrient	Material	Content
Sulphur	Single superphosphate	9-12% S
	Ammonium sulphate	24% S
	Potassium sulphate	18% S
	Ammonium phosphate sulphate	15% S
	Gypsum	13-18% S
	Iron pyrites	22-24% S
Calcium		
$CaCO_3$	Agricultural limestone	80-95%
CaO	Dolomite	20-45%
CaO	Gypsum	40%
CaO	Single superphosphate	25-30%
CaO	Rock phosphate	39-48%
CaO	Calcium ammonium nitrate	10-20%
Magnesium	Magnesium sulphate	16% MgO
	Magnesite	40% MgO
	Dolomite	5-20% MgO
	Chelated Mg	2-10% Mg

Source : FAI (1994)

for up to one-third of the total sulphur in subsoils, while the same fraction represents less than 10% of the total sulphur in the surface soils. Sulphate-sulphur adsorption by soils is beneficial since if protects sulphur from leaching in high rainfall areas.

7. Materials Containing Secondary Nutrients

Some materials containing secondary nutrients, with their average nutrient contents, are listed in Table 6.

8. Importance of Secondary Nutrients in Indian Agriculture

8.1. Calcium and Magnesium

The amounts of Ca and Mg attain importance in areas where soils are either strongly alkaline or acidic. These soils are often deficient in Ca and Mg. Alkali soils occupy about 2 million hectares of land in India. These soils have high exchangeable Na, and Ca is a suitable ion to replace this Na from the exchange complex. Calcium is supplied through gypsum. The replaced sodium forms sodium sulphate which is leached down. Gypsum also reacts with sodium carbonate to form $CaCO_3$ and Na_2SO_4 which is leached down the profile. A thorough leaching of the soil with irrigation water should be done after application of gypsum to free it from sodium sulphate.

In acid soils, calcium saturation of exchange complex varies from 20% to 40%. In hilly areas of Mizoram (pH 4.5), in spite of acidic soil reaction, Ca is the dominant exchangeable-cation, followed by Mg. No regular distribution pattern of Ca^{2+} and Mg^{2+} ions is observed with respect to altitude. In India, acidic soils occupy about 25 million hectares of cultivated area, which require attention for improvement. Total CaO and MgO contents of these soils are low (0.1 to 1.0% and 0.24 to 1.2%, respectively); therefore, management of acid soils involves the use of liming materials. Significant increase in yields (45-545%) due to lime application has been reported in a number of crops under field conditions (Mandal *et al.*,

Table 7. Mean crop yields due to different sources of calcium in acidic soils of Jharkhand

Treatments	Soybean yield (q/ha)	Response (%)	Groundnut yield (q/ha)	Response (%)
No lime	23.1	—	17.5	—
1 LR (lime requirement) (28.5)*	37.2	30.2	24.7	41.0
Broadcast in the beginning $CaCO_3$ as furrow application (2.0)	27.5	18.7	25.8	47.6
$CaCO_3$ as furrow application (4.0)	30.5	31.6	27.2	21.0
Gypsum as furrow application (2.0)	27.7	19.4	24.2	38.2
Gypsum as furrow application (4.0)	28.2	21.6	22.2	26.7
CD (Pe = 0.05)	1.36	—	1.85	—

*(Lime, q/ha)

Table 8. Crop responses to magnesium application in different states of India

State	Crop (Soil)	Yield increase due to Mg application
Assam	Jute	300 kg/ha
Karnataka	Rice (red loam soil)	20%
Kerala	Rice (laterite soil)	15%
Kerala	Coconut	40%
Kerala	Groundnut (laterite soil)	13%
Tamil Nadu	Tea	8%
Tamil Nadu	Potato (Nilgiris)	84%
Uttar Pradesh	Maize (alluvial soil)	500 kg/ha
Uttar Pradesh	Maize (alluvial soil)	45%
West Bengal	Jute	Responses reported

Source : Tandon (1989)

1966). Lime ($CaCO_3$) or gypsum ($CaSO_4$) provide calcium to soil. Furrow application of 2-4 q/ha of $CaCO_3$ or $CaSO_4$ has been found to increase grain yield of soybean by 26.7% and pod yield of groundnut by 47.6%. The yield response due to $CaCO_3$ or $CaSO_4$ was mainly due to Ca which was deficient in acid uplands of Ranchi (Mathur, 1994) (Table 7).

It has been found that calcium as a plant nutrient is more important in Ca-deficient acid soils than as an amendment. The application of carbonate and sulphate salts of Ca @ 2-4 q/ha in furrows like a fertilizer nutrient at the time of sowing could increase the yield by about 48% (Mathur *et al.*, 1983). The improvement in crop yield due to gypsum, irrespective of fall in pH but owing to increase in exchangeable-Ca^{2+} status, indicates that calcium nutrition matters more than the change in soil pH.

Acid soils under high rainfall areas usually show excellent crop response to Mg-application. In red and lateritic soils of different parts of country, increases in yield to the tune of 20%, 42%, 26%, 28% and 23% have been observed in rice, groundnut, soybean, potato and wheat, respectively. A dose of 30-50 kg MgO/ha is recommended in soils having pH < 4.5 for growing tea. Magnesium-application improves quality of crops. It also increases oil content in mustard, starch in potato, and smoke quality of tobacco leaf. Levels of increase due to magnesium-application have been reported in a number of crops (Table 8) under field conditions.

8.2. Sulphur

The sulphurs-content in plants depends upon the growth stage and plant part, besides crop species. Its concentration is higher in the seeds/ grain than in straw at maturity. In *Brassica* oilseed crops, seeds contain appreciable S, as oil in these crops is rich in S-bearing compounds like non-volatile S-glucocides. Sulphur concentration in brassica seeds is around 1.19% and in straw, it is about 0.13%. In legumes, the concentration of S in seeds is around 0.25% and in straw, it is 0.2%. In cereals, S-content ranges from 0.16% to 0.20%. In most of the crop species, the critical limit of S in plants is 0.20- 0.25%, below which crops generally show S-deficiency and/or respond to applied fertilizer S.

In India, S-deficiencies are found in almost 40% of the cultivated area (Tandon, 1995). Different crop species have different S-requirements. Of all the crops, brassica species like rapeseed mustard, cabbage, turnips, etc. have highest S-requirement, followed by legumes such as berseem, clovers, groundnut and soybean. Cereals have the least requirement of this element. In general, oilseed crops have more S-requirement than other crops. Irrespective of total S-needs, this element is needed for making efficient use of other fertilizer-nutrients.

8.3. Optimum N:S Ratio

Sulphur metabolism in plants is closely linked with N, as both are constituents of proteins. A deficiency of S in plant retards its N-metabolism, resulting in increased concentration of N in amide and NO_3-forms. The desired N:S ratio for optimum growth and metabolism in plants has been found to be 15-16:1 in legumes and 11-12:1 in cereals. On an average, protein from legume contains less sulphur than protein from cereals, the N : S ratio being 40:1 and 30:1, respectively. Application of N to soils deficient in S may lead to reduction in yields. The optimum fertilizer N:S ratio varies among soils because of differences in the available soil N and S levels. However, one estimate of suitable available N:S ratio [(soil NO_3-N + fertilizer N)] / [(Soil SO_4-S + fertilizer S)] is approximately 7 under upland conditions. This probably exceeds the S-requirement in the tropics. It seems reasonable to suppose that a 10:1 N:S ratio in fertilizer, consistently applied, will adequately meet the S-requirement. In the absence of adequate S in soils, utilization of NO_3^- can be hampered. Leaching of under-utilized NO_3^- can create serious environmental problems. Nitrogen and sulphur are both involved in the protein synthesis. Thus, a shortage of S in relation to N leads to poor N fertilizer-use efficiency by crops.

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Chapter 20

Micronutrients

D.L. DEB, R. SAKAL AND S.P. DATTA

1. Introduction

The word 'micronutrients' represents some essential nutrients that are required in very small quantities for the growth of plants and microorganisms. Micronutrients, also called as 'trace elements', are: iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo), nickel (Ni) and chlorine (Cl). Amongst these eight micronutrients, the content of iron in soil as well as in plants is the highest and sometimes is higher than even P and S contents. Another element, namely cobalt (Co) is also regarded to be essential for the growth of certain higher plants, animals and microorganisms and is likely to be added to the list of these eight elements, as it is also required in small quantity. Of the eight micronutrients identified so far, Fe, Mn, Zn, Cu, and Ni behave like cations and B, Mo and Cl like anions in soils. Thus, the chemistry of micronutrient cations is different from that of micronutrient anions.

The importance of micronutrients has been realized during the past four decades when widespread micronutrient deficiencies were observed in most of the soils in our country, where intensive agriculture is practised. The micronutrient deficiency in soils has been attributed to the following changes in Indian agriculture: (i) continuous removal of micronutrients from soil by the recently introduced fertilizer responsive improved varieties of crops, particularly cereals which produce high biomass on fertilizer application; it reduces the concentration of micronutrients in soil solution below that required for the normal growth, (ii) use of micronutrient-free high analysis fertilizers in modern agriculture, and (iii) improved instrumentation techniques and increased knowledge about mineral nutrition of plants which has helped in the diagnosis of micronutrient deficiencies in soils and plants which escaped our attention earlier. The demand for increasing crop production will require a thorough knowledge of the soil factors that regulate the supply and availability of micronutrients in soils. Micronutrients are not only important for better crop productivity, but also essential for sustaining human and animal health. Inadequate consumption of any of essential micronutrients results in adverse metabolic disturbances, leading to sickness, poor health, impaired development in children and large economic costs to society. The deficiencies of micronutrient impart learning disabilities among children, enhance morbidity rates, lower work productivity, and increase healthcare costs.

2. Geochemistry of Micronutrients

Elemental characteristics of micronutrients in the context of general trends in the periodic table are depicted in Figure 1. The trace element content of soils depends on the parent rock type and weathering (geochemical and pedochemical) processes. Igneous rocks constitute 95% of the earth crust, while sedimentary rocks cover only 5%, of which 80% are shale, 15% are sandstone and 5% are lime-

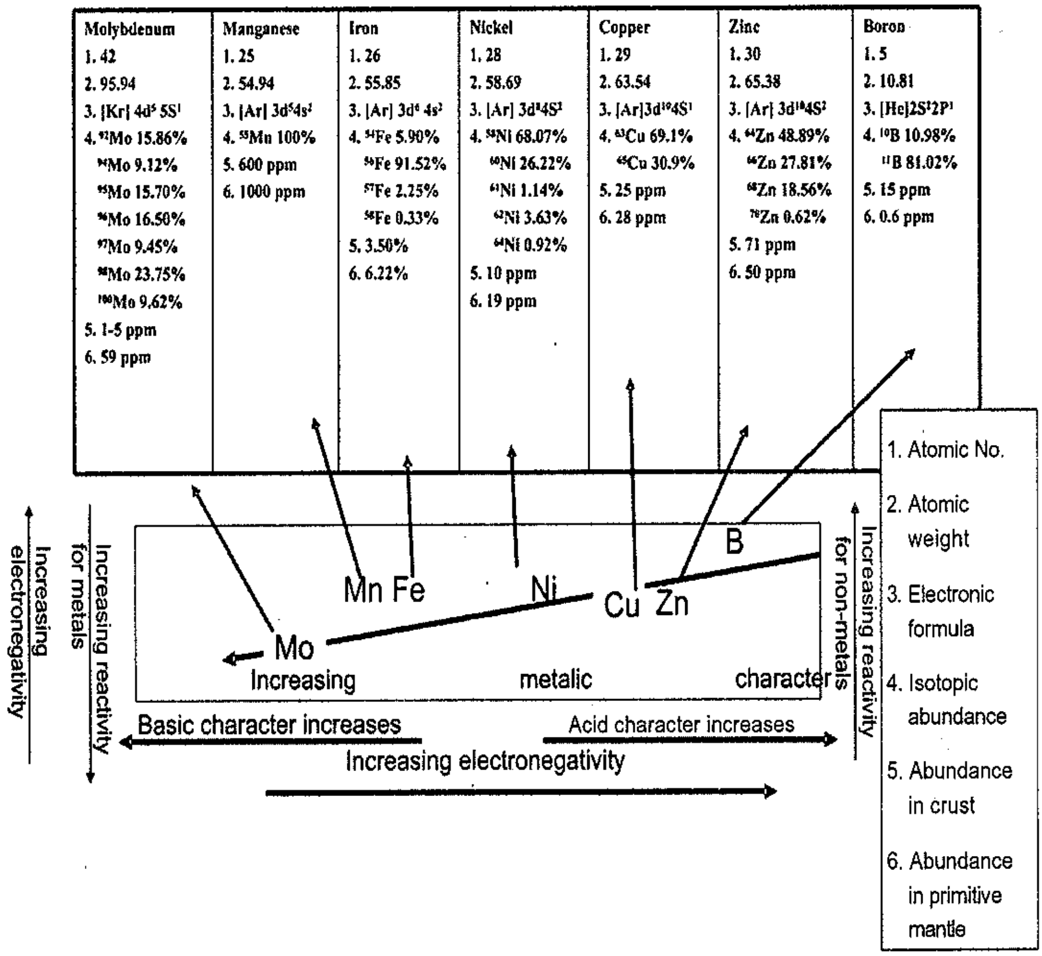


Figure 1. Elemental characteristics of six micronutrients in the context of general trends in periodic table

stone. Igneous rocks are formed as a result of fractional crystallization during cooling of basic magma. Early crystallization of igneous rocks is ultra-basic in nature, as they are low in SiO_2-content, whereas late crystallization of igneous rocks is acidic due to loss of bases and consequent increase in proportion of SiO_2-content. Basic igneous rocks are intermediate between these two categories. Basic rocks have higher content of Mn, Co, Ni, Cu and Zn, whereas sedimentary rocks are rich in B and Mo (Table 1). During the crystallization of minerals in rock formation, trace elements enter into the framework of minerals depending upon their charge and ionic radius. The position of a trace element in the mineral framework depends on its radius, whereas its abundance in mineral is decided by its chemical affinity. The smaller the electronegativity of a trace cation, the greater would be its tendency to enter in the ionic crystal lattice of minerals. Electronegativity is usually expressed on Pauling scale. The values of electronegativity on Pauling scale are 1.7, 1.9, 1.8 1.5, 1.8 and 2.0 for Zn^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Mo(VI) and B(III), respectively. The fate of released trace elements during weathering depends upon the ionic potential (ionic charge/ionic radius). Generally, trace elements with <2 of ionic potential (IP) are transported easily, whereas trace elements having IP between 2 and 12 are precipitated as hydroxides. Trace elements with IP of >12 form soluble oxyanions.

Trace elements can be divided into the following three groups based on the affinity of elements for different minerals (Table 2):

Lithophile: Trace elements that have affinity for silicate minerals are termed as lithophiles. Among micronutrients, B, Zn, (Fe), Mn and Ni are included in this group. The element listed within the parentheses shows secondary affinity.

Chalcophile: Trace elements that show affinity for sulphide minerals are called

Table 1. Micronutrient content in rocks and soils

(mg/kg)

Element	Earth crust (soil)	Igneous rock		Sedimentary rock
		Acidic	Basic	
Zn	50	50-60	70-130	80
Cu	100	10-20	100-200	30-40
Mn	900-1000	200-1200	1000-2000	200-1200
Ni	100	5-10	1500	20-100
Co	30	5-10	30-45	20-30
B	50	3-10	1-5	500
Mo	1-2	1.9	1.4	2

Source: Srivastava and Gupta (1996)

Table 2. Geochemical classification of micronutrient elements

Element	Lithophile	Chalcophile	Siderophile
B	x		
Mn	x		
Zn	x	x	
Fe	(x)	(x)	x
Ni	x	x	x
Mo		(x)	x
Cu		x	x

Note: (x) indicates secondary affinity

chalcophiles. This group includes Zn, (Fe), (Mo), Cu and Ni.

Siderophile: Trace elements that have affinity for iron minerals are called siderophile. This group includes Fe, Cu, Mo and Ni.

3. Source of Micronutrients in Soils

The micronutrients are present in soils mainly as their oxides, sulphides and silicates and are inherited from the soil-forming rocks and minerals through transformation during various stages of soil development. The micronutrient content of soil is determined by the chemical composition of its parent material. Both deficiency and toxicity of micronutrients in soil are related to the low or toxic content of the micronutrients in the parent rocks and minerals from which the soil has developed. The distribution of micronutrient minerals is not uniform in a soil and the spatial variation is very high. The natural sources of micronutrients in soil vary considerably from soil to soil and a generalized picture is given in Table 3 for the Indian soils. Besides inorganic minerals, organic matter also contributes substantially to the total content of micronutrients in surface soils. Soil amendments and fertilizer materials add frequently to the micronutrient pools in soils.

During the soil development process, lot of transformations take place in soil minerals and micronutrients are released in the reaction products. The micronutrient cations such as Fe, Zn, Mn and Cu released during these transformation reactions are either adsorbed on the soil colloids or may become a part of the secondary silicate minerals by the isomorphous substitution. The micronutrient anions such as molybdates and borates also combine chemically with soil constituents like phosphates and form new reaction products. Chloride is present in soil in considerable quantities and rain water too adds substantial amount of chloride to soils. Micronutrients are held tightly in various inorganic as well as organic combinations and become very slowly available to crops through chemical weathering and microbial decomposition reactions.

4. Status of Micronutrients in Indian Soils

Variability in the total micronutrient content of the soils is a mirror of the diversity in parent materials (rocks and minerals) from which these have originated (Rattan *et al.*, 2008). For example, green schist contains the highest concentrations of Zn, Cu, Mn and Fe, while sandstone is the poorest source of these micronutrients. Among sedimentary rocks, the

Table 3. Major natural sources of micronutrients, their chemical forms and range of content in surface soils

Sl No.	Micro-nutrient	Minerals	Major forms in nature	Total content in surface soil (ppm)	Available content in surface soil* (ppm)
1.	Zinc	Sphalerite (ZnS), Smithsonite ($ZnCO_3$), Hemimorphite [$Zn_4(OH)_2Si_2O_7.H_2O$]	Sulphides, Oxides, Carbonates and Silicates	7 to 1000	0.08-20.5
2.	Copper	Chalcocite (Cu_2S), Covellite (CuS), Cuprite (Cu_2O), Malachite [$Cu_2(OH)_2CO_3$] Chrysocolla ($CuSiO_3.2H_2O$), Azurite [$Cu_3(OH)_2(CO_3)_2$]	Sulphides, Oxides, Hydroxy carbonates, Silicates	1.8 to 960	Tr.-32.0
3.	Iron	Hematite (Fe_2O_3), Goethite ($FeOOH$), Magnetite (Fe_3O_4), Pyrite (FeS_2), Olivine [$(Mg,Fe)_2SiO_4$]	Oxides, Sulphides and Silicates	4000 to 2,73,000	0.36-174
4.	Manga-nese	Pyrolusite (MnO_2), Manganite ($MnOOH$), Rhodochrosite ($MnCO_3$), Rhodonite ($MnSiO_3$)	Oxides, Carbonates and Silicates	37 to 11,5000	0.60-164
5.	Boron	Borax ($Na_2B_4O_7.10H_2O$), Kernite ($Na_2B_4O_7.4H_2O$), Colemanite ($Ca_2B_6O_{11}.5H_2O$), Tourmaline[$Na(Mg,Fe)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$], Ulexite ($NaCaB_5O_9.8H_2O$), Kotoite [$Mg_3(BO_3)_2$]	Borates and Borosiliates	2.8 to 630	Tr.-24**
6.	Molyb-denum	Molybdenite (MoS_2), Ilsemannite ($Mo_3O_8.8H_2O$), Wulfenite ($PbMoO_4$), Ferrimolybdite [$Fe_2(MoO_4)_3.8H_2O$], Powellite ($CaMoO_4$)	Sulphides, Oxides and Molybdates	Trace to 12	Tr.-2.8***
7.	Chlorine	Muriate of potash (KCl), Sodium chloride, $NaCl$	Chlorides	20 to 1000	0.5-10.0****
8.	Nickel	Serpentine, Olivine	Silicates		

Note: *DTPA-$CaCl_2$ extractable; ** Hot water extractable; ***Ammonium oxalate (pH 3.3) extractable; ****Water extractable

Zn content was highest in the limestone. Shale, though comparable to limestone with respect to the Mn-content, contains considerably higher contents of Fe and Cu; sandstone is unusually low in all the micronutrient cations. Soils developed on flood plain alluvium (Fluvents) derived largely from silicious sandstone exhibit strikingly lower concentrations of Zn, Cu, Mn and Fe than Chromusterts developed on basaltic alluvium. In the case of B, sedimentary rocks contain more B than the igneous rocks. Soils developed on acid eruptic rocks, Ultisols and coarse-textured Entisols, are poor in the B content. Molybdenum is the least abundant among micronutrients in the lithosphere and its deficiency largely occurs in acid soils and also in the soils formed from parent materials low in Mo, such as sedimentary, basalt and granite. Peaty, alkaline and poorly-drained soils commonly have high Mo.

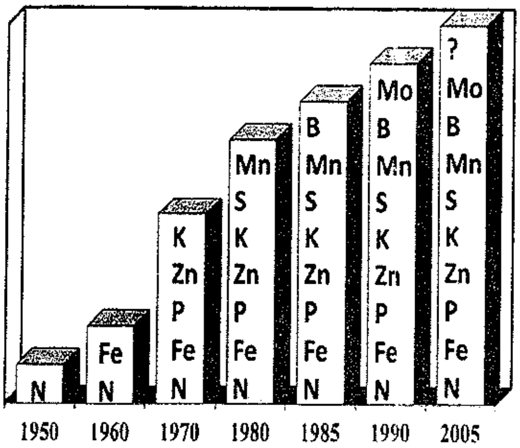


Figure 2. Progressive expansion in the occurrence of nutrient deficiencies in India
Source: Katyal and Rattan (1995)

The total content of micronutrients is a poor predictor of their supplying power to the plants. It is the soil-available micronutrient pool that represents the native level of plant-usable forms (Table 3). Due to introduction of high-yielding varieties, extension of areas under irrigation and use of high analysis NPK fertilizers, particularly under intensively cultivated lands, deficiencies of micronutrients have been on the rise in India over the past four decades (Figure 2). Out of about 250,000 soil samples analysed from 20 states of India under the aegis of the All India Coordinated Scheme on Micronutrients in Soils and Plants of the ICAR (now redesignated as All India Coordinated Research Project on Secondary, Micronutrients and Pollutant Elements in Soils and Plants), Zn-deficiency appeared to be widespread with 49% of the samples found deficient with less than 0.6 ppm DTPA-extractable content (Figure 3). Compared to Zn, deficiency of other micronutrients is less in proportion, although in extent, B-deficiency is next to Zn in order. Thirty-three per cent of the 36,825 soil samples analyzed were found to be deficient in available B (Figure 4). The per cent samples deficient in Fe, Mo and Mn reported are 13%, 7% and 4%, respectively. Coarse texture, high pH, calcareousness, declining organic carbon, and leaching aggravate Zn-deficiency. Irrespective of these soil properties, irrigated crops whose productivity is two-to-three times higher than of rainfed crops, suffered more often from Zn deficiency. Across soils and crops, lowland rice is invariably affected by Zn-deficiency. In general, Zn-deficiency is most widespread in red lateritic soils of Karnataka; leached and acid soils of West Bengal, Orissa and Maharashtra; and highly calcareous and old alluvium of Bihar.

Iron deficiency is most common in upland crops, particularly those grown on the calcareous/ alkaline soils of arid region. Adoption of rice-wheat cropping system in place of maize-wheat or groundnut-wheat in non-traditional

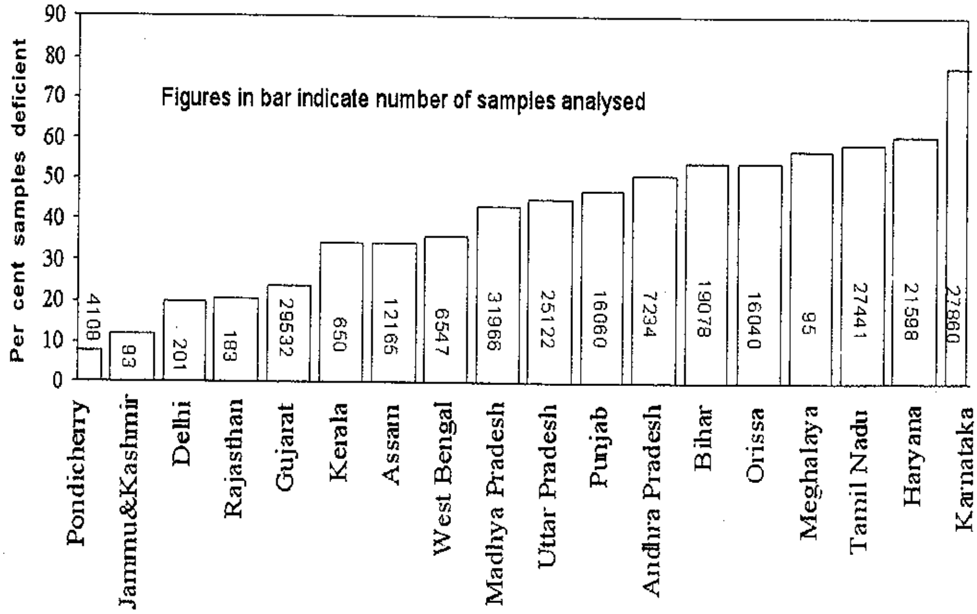


Figure 3. Extent of zinc deficiency in different agro-ecological zones of India
Source: Singh and Saha (1997)

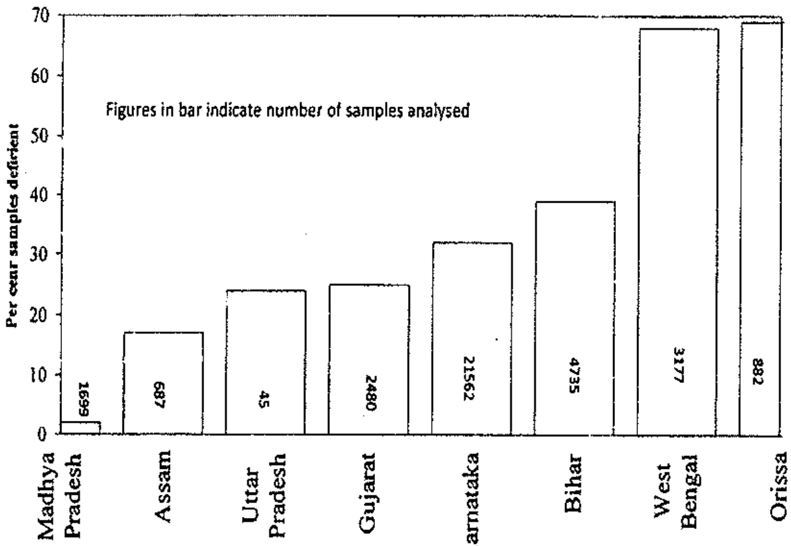


Figure 4. Extent of B-deficiency in different states of India

Source: Takkar (1996)

rice growing areas on highly permeable coarse-textured soils has been responsible for the occurrence of Mn deficiency. Copper deficiency is more prevalent on peaty soils of Kerala. The deficiency of Mo is common in acid soils of the humid region. Deficiency of Cl and Ni has not been reported in the Indian soils so far.

5. Physiological Functions of Micronutrients

The micronutrient cations are involved in enzyme systems as cofactors. With the exception of Zn, these are capable of acting as 'electron carriers' in the enzyme systems which are responsible for the oxidation-reduction reactions in plants. The physiological functions of micronutrients are described below:

- Zinc, copper and manganese are involved in carbohydrate and protein metabolism through several enzyme systems. Zinc is also involved in the synthesis of some growth promoting hormones and in the reproductive process of many plants which are very vital for grain formation. The most important metalloenzymes with which Zn is associated are: carbonic anhydrase, dehydrogenases, proteinases and peptidases.
- Iron-containing enzymes include cytochrome oxidase, catalase and peroxidase.
- Copper-containing enzymes include cytochrome oxidase, ascorbic acid oxidase and polyphenol oxidase.
- Manganese is a part of all dicarboxylases and dehydrogenases of TCA cycle. Manganese is an essential element in photosystem II where it participates in photolysis.
- Molybdenum is associated with nitrogenase and nitrate reductase enzymes and is essential for nitrogen fixing plants and microorganisms.
- Nickel is a component of the enzyme urease which is present in a wide range of plant species. Nickel participates in N metabolism of legumes during the reproductive phase of growth.
- Boron is associated with the rate of water absorption and translocation of sugars in plants.

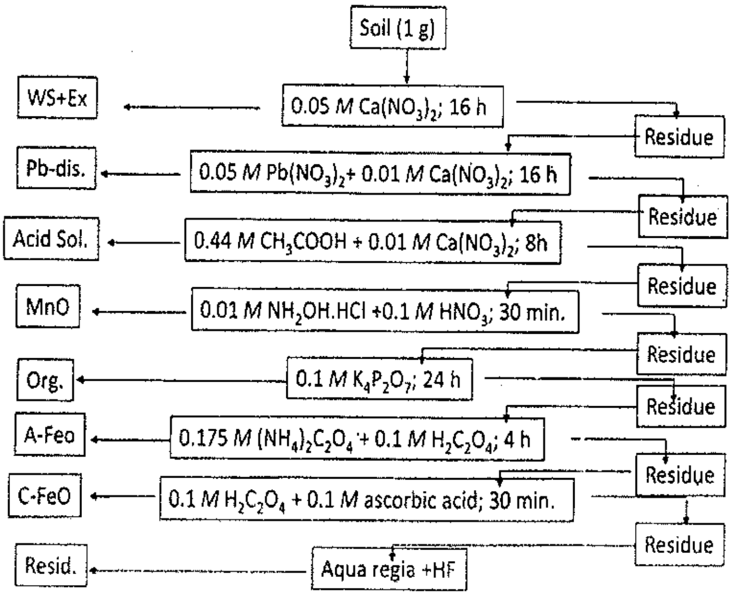
Thus, the micronutrients play very important physiological roles in the growth and development of plants and microorganisms.

6. Micronutrient Pools in Soil and their Significance in Plant Uptake

The total micronutrient content in soil is distributed into several organic and inorganic fractions of distinct characteristics. These fractions, however, do not represent discrete classical chemical compounds, but are the ones having similar response to a particular chemical reagent. There is no universally accepted method for the evaluation of the magnitude of different fractions. According to Viets (1962), micronutrient cations exist in the soils in five pools: (i) water soluble, (ii) exchangeable, (iii) complexed, adsorbed, chelated, (iv) occluded and bound in carbonates, sesquioxides and secondary minerals, and (v) primary minerals. Micronutrient cations distributed in the first three pools are in a state of dynamic equilibrium and contribute to their uptake by plants. With time, different fractionation schemes have been developed starting with the fractionation scheme of Smith and Shoukry (1968) for soil Zn. Fractionation scheme proposed by Miller *et al.* (1986) has received considerable attention as it can be used for all micronutrient cations (Figure 5). This sequential fractionation scheme partitions Zn into (i) water soluble, (ii) exchangeable, (iii) Pb-displaceable, (iv) acid soluble, (v) Mn-oxide occluded, (vi) organically bound, (vii) amorphous Fe-oxide occluded, (viii) crystalline Fe-oxide occluded, and (ix) residual. Sequential fractionation scheme for soil B, as proposed by Datta *et al.* (2002), partitions B into five pools, viz. (i) readily soluble, (ii) specifically adsorbed, (iii) oxide bound, (iv) organically bound, and (v) residual (Figure 6). This fractionation scheme is compatible with the subsequent colorimetric estimation of B in the extracts.

Attempts have also been made to determine the relative importance of various fractions of micronutrients to plant uptake. For example, Iyengar and Deb (1977) reported that more than 95% of soil zinc resides in mineral fraction and contributes very little to plant uptake; remaining less than 5% of soil Zn is present in water soluble, exchangeable and complexed fractions, but these fractions contribute maximum to the plant uptake. When the zinc fertilizer is applied to soil, depending on the soil characteristics, 12 to 34% of the applied Zn remains in these fractions and contributes to the residual effect of zinc fertilizer.

Soil solution B and B adsorbed weakly on the soil components can be considered as an intensity parameter; whereas B adsorbed specifically on clay surfaces or associated with organic matter represents the quantity factor of the B-supplying power of soils. Experimental evidences show that water soluble, exchangeable and Mn-oxide bound fractions are available to plants, whereas B associated with amorphous and crystalline Fe-oxides are unavailable. In organic soils, about half of the Mo is present in organically and sulphide bound fractions, while in mineral soils (B and C hori-



WS+Ex = Water-soluble + Exchangeable, Pb-dis = Pb-displaceable, Acid sol. = Acid soluble. MnO = MnO-occluded, Org. = Organically bound, A-Feo = Amorphous-FeO, C-FeO = Crystalline-FeO, Resid. = Residual

Figure 5. Flow diagram for fractionation of micronutrient cations in soils

Source: Miller *et al.*, 1986 as modified by Iwasaki and Yoshikawa, 1990

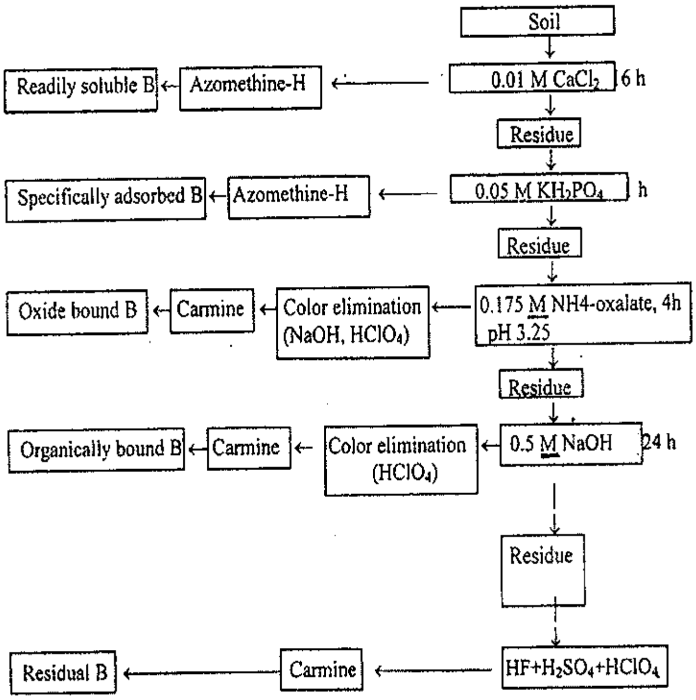


Figure 6. Flow diagram for the fractionation of B in soils

zons), very little of total Mo is present in the organic form. The carbonate and Mn-oxide bound fractions also contain lower amounts of Mo. Most of the Mo is associated with amorphous Fe-oxides.

6.1. *Soil Conditions Conducive for Micronutrient Deficiency and Toxicity*

Certain soil conditions induce micronutrient deficiency or toxicity to a growing crop. Micronutrient deficiencies occur on:

(i) Soils with very high pH,
(ii) Light-textured soils with low pH, developed under very high annual rainfall,
(iii) Intensively cultivated soils receiving high levels of high analysis NPK fertilizers for growing improved crop varieties, and
(iv) Organic soils.

The soils whose parent materials originally contain low amounts of micronutrients are most likely to show micronutrient deficiency under acid leaching as well as under intensive cropping. Acid soil conditions are most conducive for Mo-deficiency. Similarly, high pH soils such as sodic soils show Zn-, Fe-, Mn- and Cu-deficiency. Overliming of acid soils also causes deficiency of micronutrient cations. In acid sulphate soils, micronutrient toxicity limits the crop growth under upland soil conditions. But, under the waterlogged situation of rice cultivation such problems disappear mainly due to rise in soil pH. Iron toxicity in rice is observed in soils rich in Fe, under highly reducing submerged soil conditions due to the presence of easily decomposable organic matter. Under such soil conditions, Fe-induced Zn-deficiency is also expected. Soils surrounding copper and zinc mines that receive mine effluents show toxicity of these micronutrients to the growing crops. In organic soils, Cu-deficiency limits the crop growth. Micronutrient cations are usually held very strongly by the organic ligands.

7. Solid Phase-Solution Equilibria of Micronutrients in Soils

Plants absorb micronutrients from soil solution mainly in the ionic form (except B). Ions in the soil solution are buffered by those adsorbed onto soil surfaces or held by exchange sites. Besides, numerous minerals present in the soil impose limits on the chemical composition of soil solution. A mineral precipitates if soil solution is supersaturated, till the attainment of equilibrium. Similarly, a mineral dissolves if soil solution is under-saturated with respect to that mineral. The chemical equilibria between micronutrient ions present in soil solution and solid phases govern the solubility *vis-a-vis* availability of micronutrients in soils. The solubility of the native forms of micronutrient cations in soils is determined by simultaneous equilibria of several competing reactions such as their surface chemical bonding, precipitation of their solid phases, and solid solution phase chelation of metal cations (Sinha *et al.*, 1978).

Redox reactions are important in soils as they modify solubility relationships and affect mineral transformations. Lindsay (1979) introduced 'pe + pH' as a new redox parameter that simplifies the handling of many theoretical redox relationships (pe = –log electron activity; pH = –log H^+ activity). This parameter partitions the H^+ ions of an overall chemical reaction into those associated with the redox component of the reaction and those associated with the acid-base component. Redox potential can be expressed in terms of pe which is compatible with the unit of moles/litre on which pH is based. Hence, chemical and electrochemical equilibria can be expressed by a single equilibrium constant. The 'pe + pH' provides a convenient single-term expression for defining the redox status of an aqueous system. Dissociation of water into H_2 (g) or O_2 (g) imposes the limits of pe + pH on soils, which can be given by:

$H_2O + e^- = \frac{1}{2} H_2 (g) + OH^-$ ...(1)

$H^+ + OH^- = H_2O$ ...(2)

By combining Equations (1) and (2), we get:

$H^+ + e^- = \frac{1}{2} H_2(g)$ ...(3)

$K^\circ = [H_2(g)]^{\frac{1}{2}} / [(H^+)(e^-)]$ ...(4)

where, K° is the equilibrium constant in which both reactants and products have been expressed in activities.

or $\log K^\circ = \frac{1}{2} \log H_2 (g) - \log (H^+) - \log e^-$ ...(5)

For standard state conditions in which of (H^+) activity is 1 mole/litre and H_2 (g) is the partial pressure of H_2 gas at 1 atm, $\log K^0 = 0$

or $pe + pH = -\frac{1}{2} \log H_2 (g)$ ...(6)

Under the most reduced equilibrium conditions of natural aqueous environments, when H_2 (g) = 1 atm, pe + pH = 0.

Similarly, on the oxidized side, the redox limit of aqueous system can be expressed through following equations:

$H^+ + e^- + \frac{1}{4} O_2 (g) = \frac{1}{2} H_2O$ ...(7)

$K^\circ = H_2O^{\frac{1}{2}} / (H^+)(e^-)(O_2(g))^{\frac{1}{4}})$ ...(8)

or $\log K^\circ = -\log (H^+) - \log (e^-) - \frac{1}{4} \log O_2(g)$

(In dilute aqueous systems, the activity of water is very near to unity)

or

$pe + pH = 20.78$ [$\log K^\circ = 20.78$; $O_2(g) = 1$ atm] ...(9)

Equation (9) represents the most oxidized equilibrium conditions expected in natural aqueous environments.

In the following example, the applicability of pe + pH as a redox parameter in assessing the solubility of minerals in soils will be more clear. Whenever two oxide, hydroxide, carbonate, or silicate minerals contain a given element in more than one oxidation state, equilibrium between the two minerals fixes the redox at a constant pe + pH (Lindsay, 1981). For example, consider the Mn minerals MnO_2 (pyrolusite) and MnOOH (manganite) in which the oxidation states of Mn are Mn (IV) and Mn (III), respectively. The equilibrium between these two minerals can be expressed as follows:

$\beta\text{-}MnO_2$ (pyrolusite) $+ 4 H^+ + 2 e^- = Mn^{2+} + 2 H_2O$
$\log K^\circ = 41.89$ ...(10)

$Mn^{2+} + 2 H_2O = \gamma\text{-}MnOOH$ (manganite) $+ 3 H^+ + e^-$
$\log K^\circ = -25.27$ ...(11)

$\beta\text{-}MnO_2 + H^+ + e^- = \gamma\text{-}MnOOH$
$\log K^\circ = 16.62$ ...(12)

For Equation (12), the equilibrium expression is $1/[(H^+)(e^-)] = 10^{16.62}$

or

$pe + pH = 16.62$

These relationships show that as long as both pyrolusite and manganite are present and equilibrium is maintained, the pe + pH is fixed at 16.62. If additional electrons or protons are added, reaction (12) proceeds to the right with dissolution of pyrolusite and precipitation of manganite, but pe + pH remains at 16.62. The above example shows the practical implication of pe + pH in assessing the solubility of different minerals. This index of redox state of soil will be used to quantify the solid-solution equilibria of micronutrients in the following sections.

7.1. *Iron*

Iron is the fourth most abundant element in earth's lithosphere following O, Si and Al, which mostly occurs as ferromagnesian silicates. Most of the Fe released by weathering is precipitated as oxides or hydroxides; only a small part of Fe is incorporated into the secondary silicate minerals or complexed by soil organic matter. Being one of the major constituents of the lithosphere, various Fe-oxides not only govern the solubility of Fe in soil but these oxides are also capable of controlling the solubility of other major (e.g. P) and trace elements (e.g. Zn and Cu). The solubilities of Fe (III) oxides commonly found in soils can be expressed through following reactions:

$Fe(OH)_3$ (amorphous) + $3\ H^+ = Fe^{3+} + 3\ H_2O$ (log K° = 3.54) ...(13)

$Fe(OH)_3$ (soil) + $3\ H^+ = Fe^{3+} + 3\ H_2O$ (log K° = 2.70) ...(14)

$\frac{1}{2}\gamma\text{-}Fe_2O_3$ (maghemite) + $3\ H^+ = Fe^{3+} + 3/2\ H_2O$ (log K° = 1.59) ...(15)

$\gamma\text{-}FeOOH$ (lepidocrocite) + $3\ H^+ = Fe^{3+} + 2\ H_2O$ (log K° = 1.39) ...(16)

$\frac{1}{2}\alpha\text{-}Fe_2O_3$ (hematite) + $3\ H^+ = Fe^{3+} + 3/2\ H_2O$ (log K° = 0.09) ...(17)

$\alpha\text{-}FeOOH$ (goethite) + $3\ H^+ = Fe^{3+} + 2\ H_2O$ (log K° = -0.02) ...(18)

Using Equation (14), relationship of (Fe^{3+}) with soil pH can be developed as follows:

$[Fe^{3+}]/[H^+]^3 = 10^{2.70}$;

where [ ] indicates activity and activity of $Fe(OH)_3$ (soil) and H_2O are taken as unity.

or

$\log [Fe^{3+}] - 3 \log [H^+] = 2.70$

or

$\log [Fe^{3+}] + 3\ pH = 2.70$;

at pH value of 3 and 8, log [Fe^{3+}] will be -6.3 and -21.3, respectively.

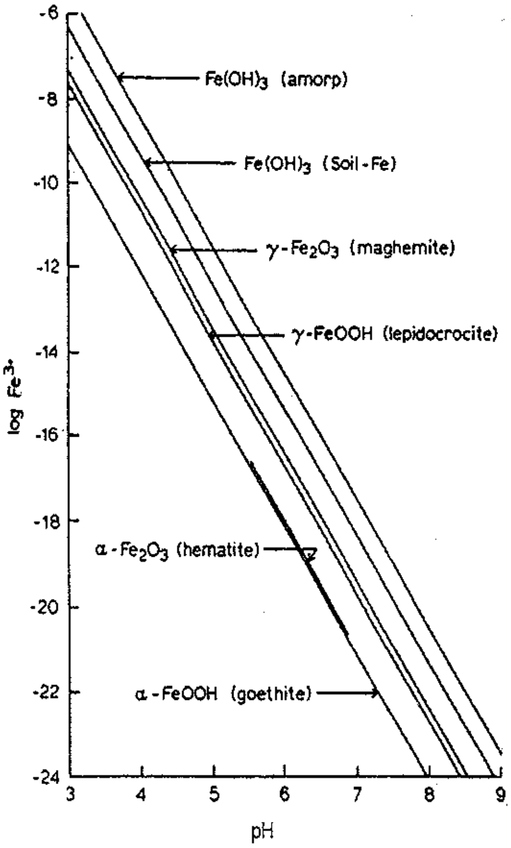


Figure 7. The activity of Fe^{3+} maintained by Fe(III) oxides and soil-Fe

Source: Lindsay (1979

Using the above-mentioned equations, similar solubility relationships can be developed for other oxides of Fe (Figure 7). Solubility of Fe (III) oxides decreases in the order: $Fe(OH)_3$ (amorphous)> $Fe(OH)_3$ (soil) > $\gamma\text{-}Fe_2O_3$ (maghemite) > $\gamma\text{-}FeOOH$ (lepidocrocite) > $\alpha\text{-}Fe_2O_3$ (hematite) > $\alpha\text{-}FeOOH$ (goethite). The activity of Fe^{3+} maintained by each of these oxides decreases 1000-fold for each unit increase in pH and vice versa. The solubility of Fe^{3+} maintained by $Fe(OH)_3$ (amorphous) is $10^{3.54}/10^{-0.02} = 10^{3.56}$ or 3631-times hihger than that maintained by $\alpha\text{-}FeOOH$ (goethite). Composition of various Fe-oxides has little bearing on the activity of Fe^{3+}, rather the solubility of Fe^{3+} is usually controlled by the most soluble oxides present. Chelation method is used to determine the activity of micronutrient cations in soils (Vlek *et al.*, 1974), where soil is equilibrated with solution containing variable mole-fractions of a given metal-chelate. At the end of the reaction period, pH and concentrations of micronutrient cations are measured.

From these measurements, it is possible to calculate the concentration of metal ions and corresponding solubility product of the solid phases, which are so-called as soil-Fe, soil-Zn and soil-Cu. Soils generally maintain the Fe^{3+} activity below that of $Fe(OH)_3$ (amorphous) as represented by $Fe(OH)_3$ (soil). Soil-Fe or

$Fe(OH)_3$ (soil) is used as a reference solid phase controlling the solubility of Fe^{3+} in soils. Soil-Fe may be an amorphous phase having greater degree of structural order than freshly precipitated $Fe(OH)_3$ (amorphous). In the case of crystalline Fe-oxides, transformations from one mineral to another and attainment of final equilibrium is an extremely slow process, particularly at higher pH. Hematite and goethite are expected to lower the solubility of Fe^{3+} towards their equilibrium levels in well-drained and highly-weathered soils not subject to frequent reductions.

Since Fe shows variable valency (+2 and +3), redox exerts profound impact on the solubility of Fe^{2+} in soil. The electron activity in soils controls the ratio of $[Fe^{3+}]$ to $[Fe^{2+}]$ in solution through the reaction (19):

$Fe^{3+} + e^- = Fe^{2+}$ $(\log K^0 = 13.04)$ ...(19)

Since, soil-Fe governs the $[Fe^{3+}]$ in soil, Equation (19) can be combined with Equation (14) as follows:

$Fe^{3+} + e^- = Fe^{2+}$ $\log K^0 = 13.04$ ...(19)
$Fe(OH)_3\ (soil) + 3\ H^+ = Fe^{3+} + 3\ H_2O$ $\log K^0 = 2.70$ ...(14)

$Fe(OH)_3\ (soil) + 3\ H^+ + e^- + = Fe^{2+} + 3\ H_2O$
$\log K^0 = 15.74$ ...(20)
or $[Fe^{2+}]/[(H^+)^3(e^-)] = 10^{15.74}$
or $\log Fe^{2+} = 15.74 - (pe + pH) - 2\ pH$

In the above reaction, one proton is associated with the reduction of Fe^{3+} to Fe^{2+}, whereas the other two protons are associated with 100-fold change in Fe^{2+} with pH. Thus, each unit change in redox and pH brings out 10-fold and 100-fold changes in the activity of Fe^{2+}, respectively. Activity of Fe^{2+} increases as soils undergo reduction, until the solubility of the more reduced Fe-mineral is exceeded. Let us consider the equilibrium relationships of soil-Fe and magnetite (Fe_3O_4):

$3\ Fe(OH)_3\ (soil) + 9\ H^+ + 3\ e^- = 3\ Fe^{2+} + 9\ H_2O$
$\log K^0 = 47.22$ ...(21)
$3\ Fe^{2+} + 4\ H_2O = Fe_3O_4\ (magnetite) + 8\ H^+ + 2\ e^-$
$\log K^0 = -35.69$ ...(22)

$3Fe(OH)_3 + H^+ + e^- = Fe_3O_4 + 5\ H_2O$
$\log K^0 = 11.53$ ...(23)

In Equation (23), one electron is required to reduce Fe^{3+} to Fe^{2+} because magnetite is a mixture of Fe_2O_3 and FeO. Equilibrium expression for Equation (23) is $1/[(H^+)(e^-)] = 10^{11.53}$
or $-\log (H^+) - \log (e^-) = 11.53$
or $pe + pH = 11.53$

It means that at pe + pH value of 11.53, soil-Fe and magnetite can coexist. In pe + pH range of 20.61 to 11.53, soil-Fe is stable and controls the solubility of Fe^{2+}. Below this pe + pH, magnetite is stable and controls the solubility of Fe^{2+}.

As pe+pH drops further, siderite ($FeCO_3$) is formed, depending on the partial pressure of CO_2 as follows:

$Fe_3O_4\ (magnetite) + 8\ H^+ + 2\ e^- = 3\ Fe^{2+} + 4\ H_2O$
$\log K^0 = 35.69$ ...(22)
$3Fe^{2+} + 3\ CO_2(g) + 3\ H_2O = 3\ FeCO_3\ (siderite) + 6\ H^+$
$\log K^0\ -23.76$ ...(24)

$Fe_3O_4 + 2\ H^+ + 2\ e^- + 3\ CO_2(g) = 3\ FeCO_3 + H_2O$
$\log K^0 = 11.93$
or
$1/[(CO_2\ (g)^3(H^+)^2(e^-)^2] = 10^{11.93}$
or
$-3 \log (CO_2) -2 \log (H^+) - 2 \log (e^-) = 11.93$
or
$2\ (pe + pH) = 11.93 + (3 \times -3.5)$
[at $10^{-3.5}$ atm of CO_2 (g)]
or
$pe + pH = 0.72$

At pe + pH value of 0.72 [if $CO_2 (g) = 10^{-3.5}$ atm], magnetite and siderite can coexist. In the pe + pH range of 11.53 to 0.72, magnetite is stable and controls the solubility of Fe^{2+}, and below this pe + pH, magnetite transforms to siderite, which controls the solubility of Fe^{2+}.

7.2. Zinc

Zinc minerals can be arranged in the decreasing order of solubility as follows: $Zn(OH)_2$ (amorphous) > α-$Zn(OH)_2$ > β-$Zn(OH)_2$ > γ-$Zn(OH)_2$ > ε-$Zn(OH)_2$ > $ZnCO_3$ (smithsonite) > ZnO (zincite) > Zn_2SiO_4 (willemite) > soil-Zn > $ZnFe_2O_4$ (franklinite; if soil-Fe controls the activity of Fe^{3+}).

Soil-Zn provides very useful reference solubility for Zn^{2+} in soils. The solubility of soil-Zn can be expressed through the following reactions:

$Soil\text{-}Zn + 2\ H^+ = Zn^{2+}$ $(\log K^\circ = 5.8)$ ...(25)

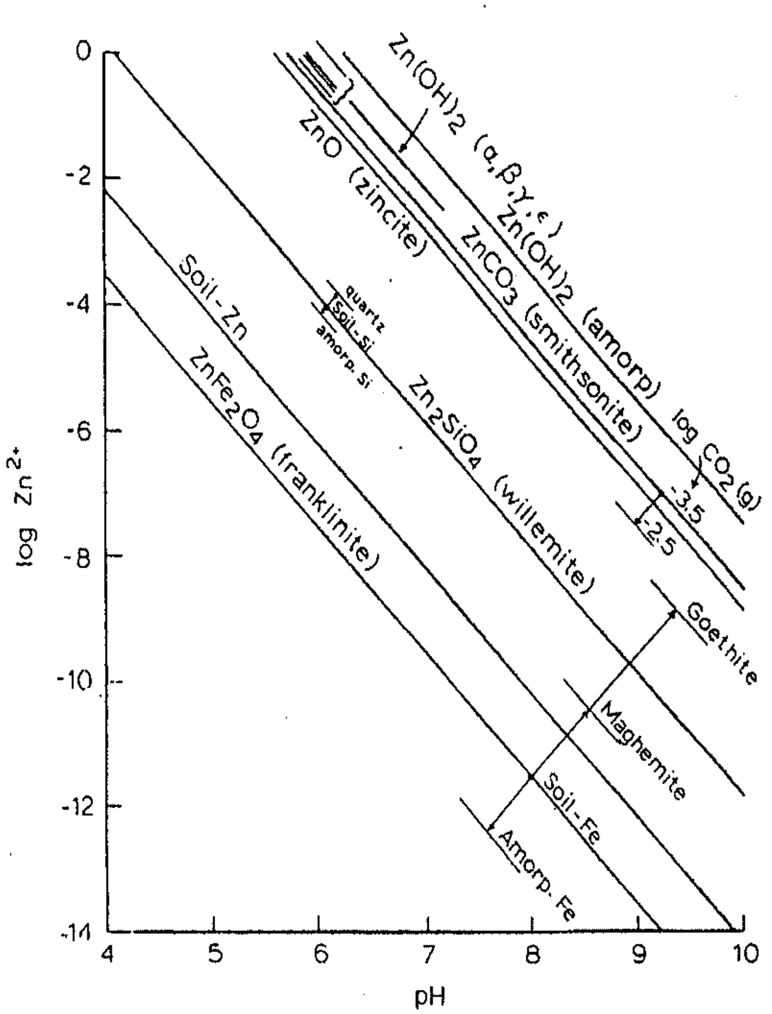


Figure 8. The solubility of zinc minerals compared to soil-Zn (*Source:* Lindsay, 1979)

or $(Zn^{2+})/(H^+)^2 = 10^{5.8}$
or $\log (Zn^{2+}) - 2 \log (H^+) = 5.8$
or $\log (Zn^{2+}) = 5.8 - 2$ pH

The log (Zn^{2+}) will be -2.2 and -10.2 at pH value of 4 and 8, respectively (Figure 8). All of the $Zn(OH)_2$ minerals, ZnO (zincite) and $ZnCO_3$ (smithsonite) are too soluble to persist in soils. Willemite (Zn_2SiO_4) is of intermediate solubility, but too soluble to account for the level of soil-Zn as occurring in most of the soils.

Let us now examine the solubility of franklinite ($ZnFe_2O_4$) in equilibrium with various Fe-containing minerals, because franklinite is a common mineral for both Zn and Fe.

$ZnFe_2O_4 + 8\,H^+ = Zn^{2+} + 2\,Fe^{3+} + 4\,H_2O$
($\log K^\circ = 9.85$) ...(26)
or
$[(Zn^{2+})(Fe^{3+})^3]/(H^+)^8 = 10^{9.85}$
or
$[(Zn^{2+})/(H^+)^2][(Fe^{3+})/(H^+)^3]^2 = 10^{9.85}$

Activity of Zn^{2+} as maintained by franklinite in equilibrium with soil-Fe, can be computed as follows:

$[(Zn^{2+})/(H^+)^2](10^{2.70})^2 = 10^{9.85}$
$[(Fe^{3+})/(H^+)^3 = 10^{2.70}$ as per equation]
or
$(Zn^{2+}) = 10^{4.45}(H^+)^2$ ...(27)

Similarly, franklinite in equilibrium with maghemite maintains the activity of (Zn^{2+}) as:

$[(Zn^{2+})/(H^+)^2](10^{1.59})^2 = 10^{9.85}$
$[(Fe^{3+})/(H^+)^3 = 10^{1.59}$ as per Equation (15)]
or
$(Zn^{2+}) = 10^{6.67}(H^+)^2$

Soil-Zn maintains the activity of (Zn^{2+}) at $10^{5.80}$ $(H^+)^2$ [as per Equation (25)], which is somewhere in between those maintained by franklinite in equilibrium with soil-Fe, and maghemite.

According to Equation (27), $\log [Zn^{2+}] = 4.45 - 2$ pH; log (Zn^{2+}) will be -3.55 and -11.55 at pH 4 and 8, respectively (Figure 8).

Since the solubility of soil-Zn is close to the solubility of franklinite in equilibrium with soil-Fe, this mineral appears to be responsible for governing the solubility of Zn in soils. However, solubility of franklinite shifts upwards and downwards depending on which Fe(III) oxide controls the activity of Fe in soils. For example, $Fe(OH)_3$ (amorphous) depresses and α-FeOOH (goethite; crystalline) enhances the solubility of franklinite, because of different levels of $[Fe^{3+}]$ maintained by these oxides.

7.3. Copper

The effect of pH on the solubility of soil-Cu can be quantified as follows:

$$\text{Soil-Cu} + 2\,H^+ = Cu^{2+} \qquad (\log K^\circ = 2.8) \qquad \ldots(27)$$

or

$$\log Cu^{2+} = 2.8 - 2\,\text{pH}$$

log $[Cu^{2+}]$ will be -5.2 and -13.2 at pH 4 and 8, respectively (Figure 9). Since cupric ferrite is a common mineral for both Fe and Cu, solubility of this mineral is influenced by soil-Fe as follows:

$$\alpha\text{-}CuFe_2O_4 \text{ (cupric ferrite)} + 8\,H^+ = Cu^{2+} + 2\,Fe^{3+} + 4\,H_2O \qquad (\log K^\circ = 10.13) \qquad \ldots(28)$$

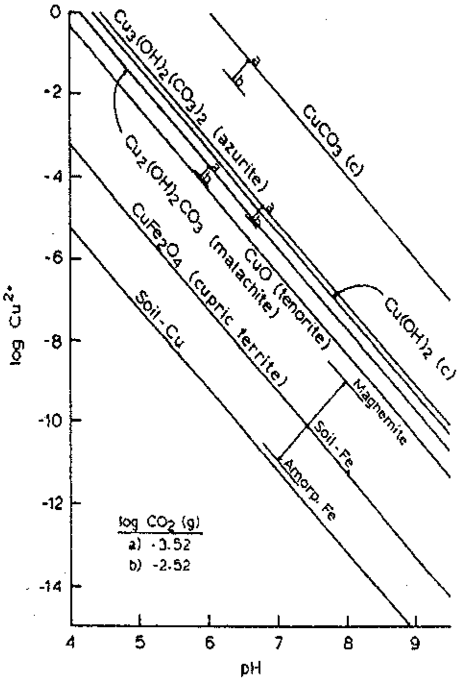


Figure 9. The solubility of copper minerals compared to soil-Cu

Source: Lindsay, 1979

Combining Equation (28) with Equation (14), we get,

$$\log Cu^{2+} = 4.73 - 2\,\text{pH} \qquad \ldots(29)$$

log (Cu^{2+}) will be -3.27 and -11.27 at pH 4 and 8, respectively (Figure 9).

In the similar way, solubility relationships can be developed for other Cu-minerals and important Cu-containing minerals can be arranged in the order of decreasing solubility as follows:

$CuCO_3$ (c) > $Cu_3(OH)_2(CO_3)_2$ (azurite) > $Cu(OH)_2$ (c) > $Cu_2(OH)_2CO_3$ (malachite) > CuO (tenorite) > $CuFe_2O_4$ (cupric ferrite) > soil-Cu.

All the Cu-minerals are more soluble than soil-Cu. The solubility of cupric ferrite in equilibrium with soil-Fe lies close to soil-Cu. Hence, it can be inferred that soil-Cu may indeed be cupric ferrite which possibly governs the solubility of Cu^{2+} in soils. Like franklinite, solubility line of cupric ferrite shifts up and down depending upon which Fe-mineral governs the solubility of Fe^{3+} in soils.

Since Cu exhibits variable valency, Cu equilibria in soils are greatly affected by redox as follows:

$$Cu^{2+} + e^- = Cu^+ \qquad (\log K^\circ = 2.62) \qquad \ldots(30)$$

or

$$\log (Cu^+/Cu^{2+}) = 2.62 - pe$$

Thus, activities of Cu^+ and Cu^{2+} are equal at pe value of 2.62 and their ratio changes by 10-fold for each unit change in pe. Now question arises, what are the stable minerals at different redox ranges? Combining Equations (27) and (30), we get:

$$\text{Soil-Cu} + 2H^+ + e^- = Cu^+ \qquad (\log K^\circ = 5.42) \qquad \ldots(31)$$

This equation can be combined with the solubility relationships of cuprous ferrite (α-$Cu_2Fe_2O_4$) and soil-Fe as follows:

$$2\,\text{Soil-Cu} + 4\,H^+ + 2\,e^- = 2\,Cu^+ \quad \log K^\circ = 10.84 \quad \ldots(31)$$

$$2\,Cu^+ + 2\,Fe^{3+} + 4\,H_2O = \alpha\text{-}Cu_2Fe_2O_4 \text{ (cuprous ferrite)} + 8\,H^+ \qquad \log K^\circ = 13.53 \qquad \ldots(32)$$

$$2\,\text{Soil-Cu} - 4\,H^+ + 2\,e^- + 2\,Fe^{3+} + 4\,H_2O = \alpha\text{-}Cu_2Fe_2O_4 \qquad \log K^\circ = 24.37 \qquad \ldots(33)$$

$2\ Fe(OH)_3\ (soil) + 6\ H^+ = 2\ Fe^{3+} + 6\ H_2O$
$\log K° = 5.40$ ...(14)
$2\ Soil\text{-}Cu + 2\ soil\text{-}Fe + 2\ H^+ + 2\ e^- =$
$\alpha\text{-}Cu_2Fe_2O_4 + 2\ H_2O$ $\log K^0 = 29.77$
or, $\log K^0 = 2(pe + pH) = 29.77$
or, $pe + pH = 14.89$

At pe+pH of 14.89, soil-Cu and cuprous ferrite can coexist. Soil-Cu is stable above pe+pH of 14.89 and below this redox, cuprous ferrite in equilibrium with soil-Fe becomes the stable minerals. Hence, soil-Cu controls the solubility of Cu^+ up to pe + pH of 14.89, while below this pe + pH, cuprous ferrite controls the solubility of Cu^+ in soils. As pe + pH drops below 11.53, magnetite becomes more stable than soil-Fe and therefore controls the Fe-solubility in soils. Hence, below this redox range, cuprous ferrite is to be equilibrated with magnetite instead of soil-Fe to get the quantitative relationship of activity of Cu^+ with redox and pH as follows:

$3\ \alpha\text{-}Cu_2Fe_2O_4\ (cuprous\ ferrite) + 24\ H^+ =$
$6\ Cu^+ + 6\ Fe^{3+} + 12\ H_2O$
$\log K° = -40.59$ ...(31)
$6\ Fe^{3+} + 2\ e^- + 8\ H_2O = 2\ Fe_3O_4\ (magnetite) + 16\ H^+$
$\log K° = 6.84$ ...(34)
$3\ \alpha\text{-}Cu_2Fe_2O_4 + 8\ H^+ + 2\ e^- = 2\ Fe_3O_4 + 6\ Cu^+ + 4\ H_2O$
$\log K° = -33.75$
or
$\log (Cu^+) = -5.63 - 1/3\ (pe + pH) - pH$

Now let us examine up to what pe + pH, cuprous ferrite is stable in equilibrium with magnetite:

$3\ \alpha\text{-}Cu_2Fe_2O_4 + 24\ H^+ = 6\ Cu^+ + 6\ Fe^{3+} + 12\ H_2O$
$\log K° = -40.59$ ...(31)
$6\ Fe^{3+} + 2\ e^- + 8\ H_2O = 2\ Fe_3O_4\ (magnetite) + 16\ H^+$
$\log K° = 6.84$ ...(34)
$6\ Cu^+ + 6\ e^- = 6\ Cu\ (c)$ $\log K° = 53.22$ ...(35)
$3\ \alpha\text{-}Cu_2Fe_2O_4 + 8\ e^- + 8\ H^+ =$
$2\ Fe_3O_4 + 6\ Cu\ (c) + 4\ H_2O$ $\log K° = 19.47$
or
$pe + pH = 2.43$

Here, c denotes crystalline form.
It is evident that cuprous ferrite and Cu (c) and magnetite can coexist at pe + pH of 2.43; cuprous ferrite is stable up to this pe + pH and below this pe + pH, Cu (c) is stable which controls the solubility of Cu^+.

7.4. Manganese

The chemistry of Mn in soils is complex because of its variable oxidation states, viz. Mn(II), Mn(III) and Mn(IV). Apart from these, Mn forms hydrated oxides with mixed valency states also. Under well oxidized condition, pyrolusite ($\beta\text{-}MnO_2$) is the most stable Mn-containing mineral. The solubility of $\beta\text{-}MnO_2$ can related with pH as follows:

$\beta\text{-}MnO_2\ (pyrolusite) + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O$
$(\log K° = 41.89)$ ...(10)
or,
$\log (Mn^{2+}) = 41.89 - 2\ (pe + pH) - 2\ pH$

At pe + pH of 20.61, log $[Mn^{2+}]$ will be -5.33 and -15.33 for pH 3 and pH 8, respectively (Figure 10). As pe + pH decreases, solubility of $\beta\text{-}MnO_2$ increases and solubility lines shift upwards. Let us examine at what redox range manganite (γ-MnOOH) can be formed. The solubility relationship of manganite with redox can be given through reaction (11):

$Mn^{2+} + 2\ H_2O = \gamma\text{-}MnOOH + 3\ H^+ + e^-$
$(\log K° = -25.27)$ ...(11)

On combining Equations (10) and (11), we get:

$pe + pH = 16.62$

It means that when pe + pH reaches this value, pyrolusite and manganite can coexist and below this pe + pH, pyrolusite dissolves, Mn^{4+} is reduced to Mn^{3+} and manganite gets precipitated. The activity of Mn is governed by manganite. As pe + pH decreases further, Mn^{3+} is reduced to Mn^{2+} as follows:

$\gamma\text{-}MnOOH\ (manganite) + 3\ H^+ + e^- = Mn^{2+} + 2\ H_2O$
$\log K° = 25.27$ ...(36)
$Mn^{2+} + CO_2\ (g) + H_2O =$
$MnCO_3\ (rhodochrosite) + 2\ H^+$
$\log K° = -8.08$ ...(37)
$\gamma\text{-}MnOOH + CO_2(g) + H^+ + e^- = MnCO_3 + 2\ H_2O$
$\log K° = 17.19$
or
$pe + pH = 17.19 + \log (CO_2)$

If CO_2 (g) is $10^{-3.5}$ atm, pe+pH reaches 13.65, manganite and rhodochrosite can coexist. If partial pressure of CO_2 (g) is fixed and pe+pH continues to drop, the solubility of Mn^{2+} will be governed by rhodochrosite, while manganite

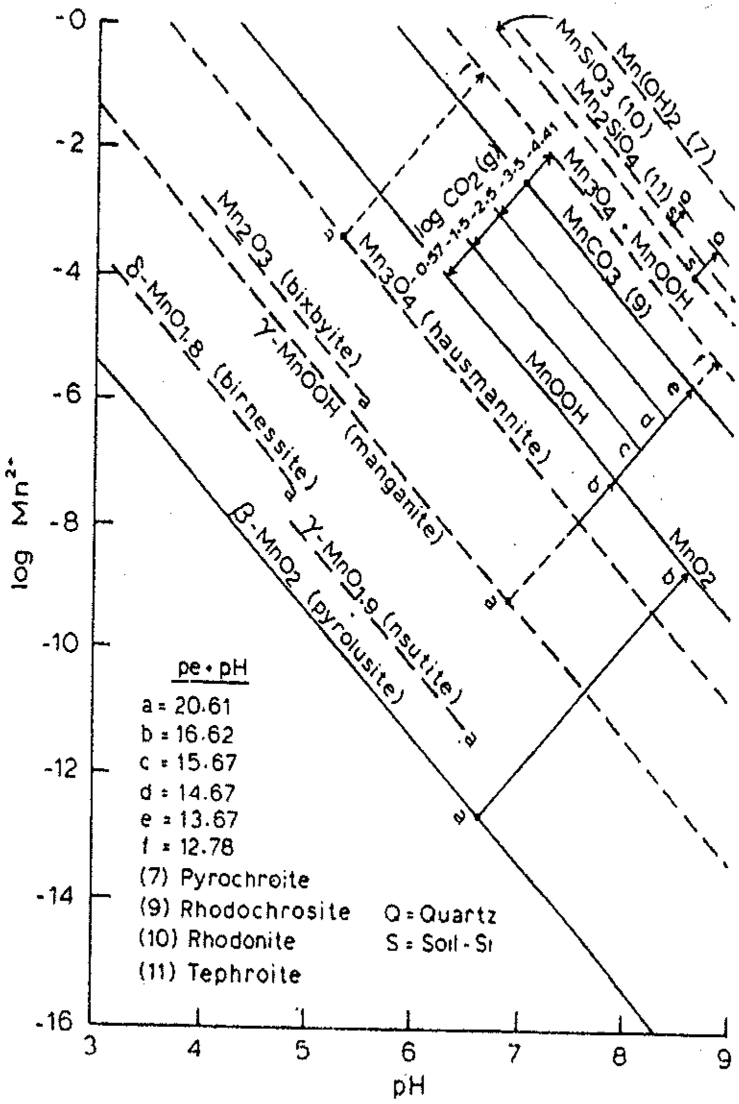


Figure 10. The effect of redox, $CO_2(g)$, and silica on the solubility and stability of manganese

Source: Lindsay (1979)

will dissolve. If partial pressure of CO_2 (g) is below $10^{-4.41}$ atm, rhodochrosite cannot be formed and manganite will control the solubility of Mn^{2+} until hausmannite (Mn_3O_4) forms at still lower pe+pH.

Let us examine, what is the critical value of pe+pH for the formation of Mn_3O_4 in equilibrium with values of γ-MnOOH.

$$3\ \gamma\text{-MnOOH (manganite)} + 9\ H^+ + 3\ e^- = 3\ Mn^{2+} + 6\ H_2O$$

$$\log K° = 75.81 \qquad \ldots(36)$$

$$3\ Mn^{2+} + 4\ H_2O = Mn_3O_4\ \text{(hausmannite)} + 8\ H^+ + 2\ e^-$$

$$\log K° = -63.03 \qquad \ldots(38)$$

$$3\ \gamma\text{-MnOOH} + H^+ + e^- = Mn_3O_4 + 2\ H_2O$$

$$\log K° = 12.78$$

or

$$pe + pH = 12.78$$

Hence, it is evident that γ-MnOOH and Mn_3O_4 can coexist at pe+pH of 12.78. Below this pe+pH, hausmanite governs the solubility of Mn^{2+}. The solubility of Mn^{2+} in soils appears to be governed by pyrolusite above pe + pH of 16.62, by manganite at slightly lower redox, and by rhodochrosite at still lower redox, depending upon the partial pressure of CO_2.

7.5. Boron, Molybdenum and Nickel

Most of studies have been focused on the adsorption rather than identification of solid phases which control the solubility of B and Mo. Tourmaline [$Na(Fe,Mg)_3Al_6(OH)_4(BO_3)_3.Si_6O_8$] is a stable mineral that might control B-solubility in soils. In soils with high pH, it is possible that $CaMoO_4$ (powellite) may provide some limit on the solubility of Mo. Usually, Mo-solubility increases rapidly with increase in pH, as Ca^{2+} activity is depressed due to formation of $CaCO_3$. Another mineral that could control the solubility of Mo in soils is $PbMoO_4$ (wulfenite). In the case of Ni, nickel ferrite ($NiFe_2O_4$) seems to be the most probable solid phase that can precipitate in soils (Sadiq and Enfield, 1984). Nickel aluminate ($NiAl_2O_4$) and nickel silicate (Ni_2SiO_4) are also metastable with respect to nickel ferrite. Nickel oxides and hydrous oxides are stable in soils with pH higher than 9. Below pe + pH of 5, the sulphides of Ni may control the concentration of Ni in soil solution.

8. Factors Affecting the Availability of Micronutrient Cations and Anions

Iron, manganese, copper, zinc and nickel are called micronutrient cations as these carry positive charges. Boron, molybdenum and chlorine occur as anions and carry negative charges. The effects of soil environment on micronutrient cations are different from those of micronutrient anions. So the effect of soil factors on the availability of micronutrient cations and anions will be discussed separately.

8.1. Effect on Cations

Certain soil factors tend to exert a similar effect on the availability of all the micronutrient cations. These factors are discussed in the next few paragraphs.

8.1.1. Soil pH

Soil pH is the most important factor which regulates the solubility and availability of micronutrient cations in soil. A very low pH indicates highly acidic soil reaction in which all the micronutrient cations occur in soil solution. Under such conditions, certain micronutrient cations may become toxic to common plants and one dominant ion in soil solution may hinder the absorption of other micronutrient cations, if the latter occur in low concentrations. On the other hand, if the pH of the soil is higher than 7.0, the micronutrient cations get precipitated as insoluble hydroxides. Under alkaline conditions, the micronutrient cations are changed largely to their oxides or hydroxides of comparatively lower solubility. Some examples are given below with each micronutrient cation:

$$Fe^{2+} + 3OH^- \rightarrow Fe(OH)_3$$
$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$$
$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$
$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$

(Soluble ion) (Insoluble compound)

All the hydroxides of micronutrient cations are sparingly soluble, but vary in degree of their solubility and availability. Each micronutrient cation differs from others with respect to its pH requirement for the formation of its hydroxide. The oxidation state of the micronutrient cation also affects the occurrence of the precipitate in relation to pH. The formation of insoluble hydroxides starts as soon as the pH of the soil solution is raised to 6.0 and above. The solubility and bioavailability of a micronutrient cations decreases above pH 6.0, thus necessitating the maintenance of soil pH around 6.0 for keeping the micronutrient cations in adequate amount in soil solution. One of the major objectives of liming is to keep the soil pH around 6.0 so as to reduce the concentration of micronutrient cations in soil solution below the toxic range. Overliming is harmful as it reduces the concentration of micronutrient cations in soil to such a level that a sensitive plant may suffer from the deficiency of micronutrient cations.

8.1.2. Oxidation State of Micronutrient Cations

Lower oxidation states of Fe, Mn and Cu (reduced states) are more soluble than higher oxidation states at the normal pH range of soils. The reduced states are encouraged by poor oxygen supply under submerged conditions. The presence of easily decomposable fresh organic matter in soil encourages anaerobic conditions at high moisture levels due to vigorous microbial activity which get energy (chemoautotrophs) directly from the oxidation of inorganic ions. The most common example is the oxidation of divalent Mn^{2+} to trivalent Mn^{3+} by certain fungi and bacteria. Certain organic compounds synthesized by the microorganisms or released by the plants as root exudates have oxidising or reducing power. It is observed that high pH of soil favours oxidation, whereas low pH conditions are favourable for the reduction of micronutrient cations in soil. At lower pH values, around pH 3.0, trivalent ferric iron gets precipitated as hydroxide, whereas divalent ferrous iron is not precipitated until the pH is raised to 6.0 or higher. The hydroxides of micronutrient cations at higher valence states are extremely insoluble and unavailable to plants.

In well-drained aerated calcareous soils, micronutrient cations exist in the oxidized state and their availability becomes very low, and therefore, plants suffer from micronutrient deficiency, although the total content of all the micronutrients may be very high. Under such conditions, the hydroxides and carbonates of high valent forms are too insoluble to meet the plant needs. Zinc is a divalent cation, but at high pH it forms zincate ions, $Zn(OH)_4^{2-}$. All these micronutrient cations can also exist in several complexed ionic forms such as $ZnCl_4^{2-}$, $Zn(OH)_4^{2-}$, $Fe(OH)_2^+$, $Cu(OH)_3^{2-}$, etc.

8.1.3. Interaction of Micronutrient Cations with Other Soil Constituents

The availability of micronutrient cations in soil is highly affected by inorganic ions in soil solution, soil solid constituents, especially free oxides of iron and aluminium, soil organic matter, fertilizers and amendments applied to soil. Silicate clays contain micronutrient cations, particularly Zn, Fe and Mn in the octahedral layer, especially in 2:1 type of clay minerals. These ions are released from the clay under certain soil conditions or fixed on the colloidal surfaces if their concentration in soil solution is increased by micronutrient fertilizer application. Such a fixation of micronutrients by soil clays may cause serious problems for Zn and Cu and is less significant for Fe and Mn because of their high total content in soils.

The presence of carbonate and bicarbonate ions in soil due to sodicity or overliming reduces the availability of micronutrient cations to field crops as well as orchard crops which suffer most from Fe deficiency.

Low temperatures also interfere with the availability of micronutrient cations in soil. It is the common experience of the wheat growers of north India that when the soil temperature goes down due to freezing, zinc deficiency appears in the crop. This deficiency of micronutrient cations in soil at low temperatures is mainly caused by the decreased solubility of native micronutrient cations. Wet soil conditions at low temperature further aggravate the situation in terms of decreased availability of micronutrient cations.

The ability of soil organic matter to hold micronutrient cations in stable combinations is well established. Numerous organic compounds are involved, including humic and fulvic acids and a number of organic acids in the formation of a large number of organo-metallic compounds having different solubilities. Some of the metal ions are held as insoluble complexes, such as the humic acid complexes and become unavailable to plants. But, some organic ligands can keep the micronutrient cations as soluble chelates and these are plant-available. Microorganisms also assimilate these micronutrient cations as they require these metal ions for many microbial transformation reactions and temporarily immobilize the micronutrients in their body, which however, are released after the death of the microorganisms through mineralisation process.

Microorganisms continuously produce chelating agents during the decay of plant and animal residues. These chelating agents have the ability to transform solid phase micronutrient cations into soluble metal complexes and thereby increase the availability of insoluble micronutrients to plants. Metal chelates are fairly stable and are protected against soil reactions. These chelates are readily assimilated by the growing plants. Natural chelating agents are found in the leachates of humus horizons of forest soils. Metal complexes of fulvic acids have high water solubilities and are available to plants. Organic soils retain large quantities of micronutrient cations in insoluble forms by complexation. Copper is retained very strongly in organic soils and such insoluble complexes are responsible for low availability of copper in organic soils. The zinc availability is also low in organic soils for similar reasons.

8.2. Effects on Anions

Chlorine, boron and molybdenum occur as anions in soils and these do not show any similarity in their behaviour in soils.

8.2.1. Chlorine

Among the three anions, chloride is absorbed in large quantities by plants and its availability in soil is not affected by any soil property as most of the chloride compounds are soluble in water. A substantial amount of chloride is added to soil through rain water. In humid regions, chloride is lost down the profile by leaching, as it is not adsorbed by soil colloids. In arid and semi-arid regions, chloride concentration is very high in surface soils, particularly in saline soils which may even become toxic to certain crops. Chlorine deficiency in soils is a rare phenomenon as chloride is also added to soil through impurities in different agrochemicals.

8.2.2. Boron

The availability of B in soil is affected considerably by soil pH. At low pH, most of the B compounds are soluble and thus B remains available to plants as boric acid. In sandy soils having low pH, B is lost down the profile by leaching if rainfall is high. In fine-textured soils, however, B leaching is not a major problem if the soil is not very low in pH.

Availability of B in acid soils is lower as compared to that in alkaline soils. Generally at higher pH values, availability of B increases. Liming of soil reduces B availability temporarily due to lime-induced B-fixation by freshly precipitated Al and Fe hydrous oxides. Overliming has been found to cause boron deficiency in crops. Occurrence of widespread B-deficiencies in calcareous soils of north Bihar bears the testimony.

Boron occurs mostly in organic matter in the surface soil and down the profile B content decreases. Mineralisation of soil organic matter releases B to be absorbed by plants. Under drought condition, B-deficiency in plants is observed due to lower availability of B in subsoils.

8.2.3. Molybdenum

Molybdenum chemistry largely resembles that of P in soils. All soil factors which increase availability of P in soils, enhance the availability of molybdenum as well. For example, Mo availability is very low in acid soils. Molybdenum gets fixed in iron and aluminium compounds as well as on silicates at low pH. The fixed molybdate can be made available to crops by phosphate application to soil which releases fixed molybdate ions by anion exchange, indicating that the fixation sites on soil colloids for phosphates and molybdates are the same.

Liming the acid soils increases the availability of native Mo. In Australia and New Zealand, liming of acid soils is a routine practice as Mo fertilizer application gives the same yield as obtained by liming in legumes without any Mo fertilizer application. Where liming is more expensive, fertilizer Mo application along with phosphatic fertilizers may give economic response, particularly in legumes and vegetable crops. Results of several field experiments have indicated the mutual beneficial effects of molybdate and phosphate on their uptake by plants in Mo-deficient soils. Sulphate, however, reduces the availability and uptake of Mo by crops, although the specific role played by sulphur in reducing molybdenum uptake by crops is not clearly understood.

9. Soil Management for Maintenance of Adequate Levels of Micronutrients

For a sound management of micronutrients in soil, adequate knowledge of the relationship that exists between different macro-nutrients and secondary nutrients and micronutrients and within different micronutrients is essential. Certain synergistic and antagonistic relationships between micronutrients have been established. The beneficial effects of Mo and P in legumes, Mn and Mo in field crops and Zn and P at normal levels of application in all field and orchard crops are well documented. Apart from these, proper levels of Ca in soil are essential for higher uptake of B. Between K and Cu, and K and Fe, a proper balance is essential for their normal uptake. Adequate level of Zn is essential for proper utilization of Cu and Mn. The antagonism between different nutrient ions has received more attention in recent years. It is, therefore, essential to understand the mechanisms of micronutrient interactions in soil and plant system.

9.1. Micronutrient Interactions

The presence of sufficient amount of available micronutrients in soil is not enough to provide adequate micronutrient nutrition to plants. Besides the soil factors, the plant growth factors also affect the uptake and assimilation of a micronutrient by plants. The uptake and assimilation of micronutrients are greatly affected by the micronutrient interactions that occur between the micronutrients and with some macronutrients and secondary nutrients. Such interactions may take place in soil, at the root surface, and within the plant or at all the three sites. These interactions modify the nutrition of plants and therefore should be adequately understood for adopting improved agronomic practices for getting good crop yield.

9.1.1.Mechanism of Interaction

Interaction is defined as the influence of one element on another in relation to the plant growth and crop yield. It is usually studied by applying two nutrients simultaneously at different levels and then measuring the differential response to one element in the presence of second element. As for example, the sum of yield response measured for individual applications of zinc or iron in rice may be higher or lower than the response obtained when both iron and zinc are applied together. When the combined effect of two elements gives a higher yield response than the sum of the individual responses of the two elements, the interaction is said to be positive. But when the combined effect on yield response is lower than the sum of the individual responses of two elements, the interaction is said to be negative.The positive interaction of micronutrients gives a higher yield and such interaction should be exploited in increasing the crop production. Conversely, all negative interactions will lead to a decline in crop yield and should be avoided in formulating agronomic packages for a crop.

One must understand how the negative or positive interaction takes place within or outside the plant. The mechanisms of negative interactions between P and Zn are discussed below, as this interaction has been studied quite extensively. The negative interaction between P and Zn in plant may occur due to any one of the following causes:

(i) Chemical Precipitation of Zinc in Soil— The formation of insoluble zinc phosphate, $Zn_3(PO_4)_2$, in soil is regarded as the cause of P-induced Zn-deficiency in soil as well as in plant. Studies on the solubility of Zn in $Zn_3(PO_4)_2$ and $Zn_3(PO_4)_2.4H_2O$ have shown that both these compounds can provide sufficient Zn in soil solution to support a good crop growth. Thus, it is now certain that P-induced Zn-deficiency in plant is not caused by chemical precipitation of Zn by P in soil.

(ii) *Interrelationships of Zinc and Phosphorus in Plant—* Several studies have revealed that P reduces translocation of Zn within the roots. This results in the low concentration of Zn in the above-ground portion of the plant and lowers the total uptake of Zn. It has been observed that applied P interferes in the uptake, translocation and assimilation of Zn by the plants. It has been further concluded that both P and Zn are mutually antagonistic whenever either of these elements exceeds some threshold value within the root. Usually, symptoms that appear on plant leaves heavily fertilized with P, are actually due to P-toxicity rather than Zn-deficiency. Zinc has the ability to control the rate of P-absorption by roots, possibly through some functional association in the cell membrane. Zinc-deficiency interferes with P-metabolism, enhancing the amounts of P absorbed by roots and transported to tops. Under condition of high P-supply, P accumulates to toxic levels in leaves, inducing or accentuating symptoms that resemble to Zn-deficiency. This effect of P and Zn-metabolism in roots seems to explain previously puzzling observations in which P treatments enhanced symptoms of Zn-deficiency without any reduction in Zn-content in plant top.

(iii) *Dilution Effect* — When the rate of drymatter production exceeds the rate of uptake of a nutrient, the concentration of that nutrient in the drymatter decreases. This is called *'dilution effect'*. The Zn-deficiency symptoms in plants may appear as a result of dilution effect at the maximum period of growth. Dilution effect appears when P fertilizer is applied in soil deficient with respect to P, but marginally deficient with respect to Zn.

In such soils, Zn fertilizer is not usually applied. The growth rate of plant increases with enhanced rates of applied P, but the uptake of Zn does not increase proportonately to maintain adequate concentration of Zn in plant tops. This may ultimately lead to the development of Zn-deficiency symptoms in the plant tops. The dilution effect depends on the magnitude of response obtained with P fertilization and on the rate of decrease of Zn concentration in the drymatter. If the response to P is low or nil and if the available Zn-content in soil is marginal, the dilution effect may not be observed on Zn-uptake even with high level of P fertilizer application.

(iv) *Disproportionate Distribution of Zinc in Roots and Tops* —Zinc is less mobile as compared to P within the plant and therefore, a large accumulation of Zn takes place in leaves, nodes and internodes. This effect is more pronounced in soils having deficient level of available-Zn. Application of P fertilizer in small doses results in higher uptake and concentration of Zn in the roots accompanied by large reduction in Zn concentration in the plant tops. It has been found that the site of P-Zn antagonistic interaction lies inside the root. But the exact mechanism of the negative interaction is not known. It is neither chemical nor biochemical, not even strictly physiological, as no direct proof has so far been obtained.

The negative interaction between P and Zn in which application of P fertilizer induces Zn-deficiency in plants with concomitant reduction in yield disappears with the application of Zn fertilizer along with P fertilizer. The negative interaction turns into a positive interaction with Zn fertilizer application as it maintains adequate level of Zn in the leaves and other plant tissues with concomitant increase in yield.

Apart from P and Zn interactions, there are several interactions between micronutrients and macronutrients and among micronutrients which may be attributed to any of the above mentioned causes.

The following antagonistic effects have been well established on the uptake of micronutrients by crops:

- Excess of P adversely affects utilization of Zn, Fe and Cu
- Excess of Fe adversely affects utilization of Zn and Mn
- Excess of Zn, Mn and Cu induces Fe-deficiency in crops
- Excess of S and Cu induces Mo-deficiency in crops
- Excess of lime induces deficiency of all micronutrients.

9.2. Micronutrient Management in Soil-Plant System

The examples of beneficial and antagonistic relationships between nutrients do caution about the difficulty in proper soil management for the maintenance of adequate levels of micronutrients in soil. Since production is to be increased per unit area of land, favourable balances are to be maintained between different nutrients so as to overcome the nutritional constraints limiting the crop production.

Since the micronutrient-need of a crop is specific, and the micronutrients are interrelated in their functional relationships, it is very difficult to generalise the soil management practices for maintaining adequate levels of micronutrients in soil. Since there is not much difference in the toxic and deficiency levels of a micronutrient, location-specific expertise and management is essential.

The knowledge about factors affecting the availability of micronutrients in soils provides a general guidance to the management practices to be followed for keeping them in available forms. Due consideration is to be given to soil texture, pH, soil water regimes, and $CaCO_3$-content before any management step is decided. The next consideration to be given is the intensity of cropping and the fertilizer consumption pattern. If consumption of NPK fertilizer is very high in an intensive cropping system, micronutrient deficieny is expected and micronutrient fertilizers should be recommended, if the soil tests show micronutrient deficieny. The incipient micronutrient deficiency in a soil can be overcome by selecting crop varieties which can efficiently absorb micronutrients from soil solid phases also. The simplest management of micronutrient deficiency in soils is to add micronutrient fertilizers along with NPK in alternate years, if soil test shows deficiency. Soil application of micronutrient fertilizers is more effective in field crops than spray application. In fruit trees, however, both are considered as effective methods of application. In spray application, micronutrients may be mixed with plant protection chemicals and macronutrients to reduce the cost of application.

Most of the micronutrients occur in acid soils in very high amounts which may become toxic to sensitive crops. It is very difficult to remove the micronutrients from the soil system once these have entered there. But, their solubility or availability can be changed by adding appropriate soil amendments. If lime is added to the acid soil, the micronutrient availability is decreased considerably. Similarly, in calcareous, alkaline and sodic soils, deficiencies of Fe, Zn, Cu and Mn are frequently observed. Use of gypsum, pressmud or sulphur as soil amemdments is beneficial in bringing down the high pH and increasing the availability of micronutrients in soils. Application of green manure is also beneficial in reclaiming such soils, if rice is grown under submerged soil conditions. It has been observed that maintaining soil pH around 6.0 is beneficial for the maintenance of adequate level of micronutrients in soils.

The micronutrient availability is regulated by the soil moisture regime. Since a good drainage condition of soil maintains aerobic environment, micronutrients occur in their oxidised states. The availability of micronutrients is comparatively less in the oxidised state even under acid soil conditions than in their reduced forms. Under submerged soil conditions, the reduced forms of Fe and Mn dominate the soil solution and Zn and Cu may become deficient to crop if the native content of these two micronutrients is low.

The most modern concept of micronutrient management in soil is to grow such varieties of crop which have the ability to extract the required micronutrients from insoluble sources. Such crop varieties are to be developed by genetic engineering by combining nutrient utilization efficient varieties with those having high-yield attributes by genetic manipulation and genetic engineering. A few such crop varieties are available now for cultivation in Australia and the USA without micronutrient fertilizer application. The response of cereals, pulses and oilseeds to micronutrient fertilizer application in India is given in Table 4.

9.3. Soil Tests for Micronutrients

The main objective of micronutrient soil tests is to identify the fields which are deficient or non-deficient with respect to a particular micronutrient. With this information, the corrective measures can be applied for overcoming micronutrient-deficiency problems of a particular field. Industry also needs this information for manufacturing a particular micronutrient fertilizer for a specific region. The government departments use this information for planning agricultural development programmes. Another important objective is to identify the fields where micronutrient fertilizer application will be profitable for getting higher crop yields.

Table 4. Micronutrient response in different crops of India

(kg/ha)

Micronutrient	Cereals	Pulses	Oilseeds
Zinc	< 200-7500	200-500	200-500
Molybdenum	200-900	Nil-190	Nil-220
Manganese	Traces-1070	20-200	110-550
Iron	300-1880	450-670	230-470
Copper	Nil-1780	–	Nil-800
Boron	10-1670	40-900	10-430

Source: Tandon (1995)

Table 5. Important soil test methods for micronutrients

Element (ppm)	Extractant	Soil:solution ratio	Shaking period (minutes)	Critical level of deficiency
Zinc	$0.005M$ DTPA + $0.1M$ TEA* + $0.01M$ $CaCl_2$ (pH 7.3)	1:2	120	0.5-1.0
	$0.1\ N$ HCl	1:5	30	1-5
	$1\ N$ NH_4OAc (pH 4.6)	1:10	60	0.2-0.5
	$0.05\ N$ HCl	1:2	5	1.0
Copper	$0.005\ M$ DTPA + $0.1\ M$ TEA + $0.01\ M$ $CaCl_2$ (pH 7.3)	1:2	120	0.2-0.5
	$0.1\ N$ HCl	1:5-10	30	1-3
	$1N$ NH_4OAc (pH 4.8)	1:2-4	60	0.2
Iron	$0.005\ M$ DTPA + $0.1\ M$ TEA + $0.01\ M$ $CaCl_2$	1:2	120	2.5-5.8
	$1\ N$ NH_4OAc (pH 4.8)	1:10-20	60	2
Manganese	$0.005\ M$ DTPA+$0.1\ M$ TEA + $0.01\ M$ $CaCl_2$	1:2	120	2-4
	$1\ N$ NH_4OAc (pH 7.0)	1:10	30	3-4
	$3\ N$ $NH_4H_2PO_4$ and $0.1\ N$ H_3PO_4	1:10	60	15-20
Boron	Boiling hot water	5:10	5	0.5-1.0
	$0.01\ M$ $CaCl_2$ + $0.05\ M$ Mannitol	1:2	60	0.25
	0.1 M Salicylic acid	1:2	60	0.45
Molybdenum	Ammonium oxalate (pH 3.3)	1:10	360	0.05-0.2

TEA = Triethanol amine

There are four important steps in soil testing:

(i) Collection of representative uncontaminated soil samples,

(ii) Selection of proper methods for the extraction and determination of content of available micronutrients,

(iii) Calibration of soil test data with crop response, and

(iv) Interpretation of soil test data and providing of recommendations.

Each of these steps is very important and requires expertise in micronutrient chemistry and in the behaviour of micronutrients in soil and plant systems. Thus, soil testing for micronutrients has become a subject of specialists.

Micronutrient soil tests are generally developed to measure the magnitude of micronutrient pools in soil that are related to plant availability. Attempts have also been made to develop soil tests for estimating the bioavailable micronutrients in a single extract. The chemicals that are used for extracting micronutrients from soil samples belong to different distinct groups, such as (i) water, (ii) dilute acids, (iii) chelating or complexing agents, and (iv) neutral buffered and unbuffered salts. These chemicals are used either singly or in combination for increasing their effectiveness in extractanting micronutrients from soil. The widely-used soil tests for micronutrients are described in Table 5.

One of the major advances in micronutrient soil testing has been the development of extracting solution that contains chelating agents, primarily DTPA (diethylenetriamine penta acetic acid) and EDTA (ethylenediamine tetra acetic acid). During extraction, chelates reduce the activity of free metal ions in solution through the formation of soluble metal-chelate complex. In response to this depletion of metal ions in solution, more metal ions come from the solid phases to replenish this depletion. Such depletion in the activity of metal ions in solution closely mimics the reduction in activity of metal ions in solution due to plant uptake (Figure 11). Thus, quantity of micronutrient cations extracted by a chelate reflects both initial concentration in the soil solution (intensity factor) and the ability of soil to maintain this concentration (capacity factor). Thus, chelating agents simulate removal of micronutrient cations by plant roots and subsequent replenishment from labile solid phases in the soil.

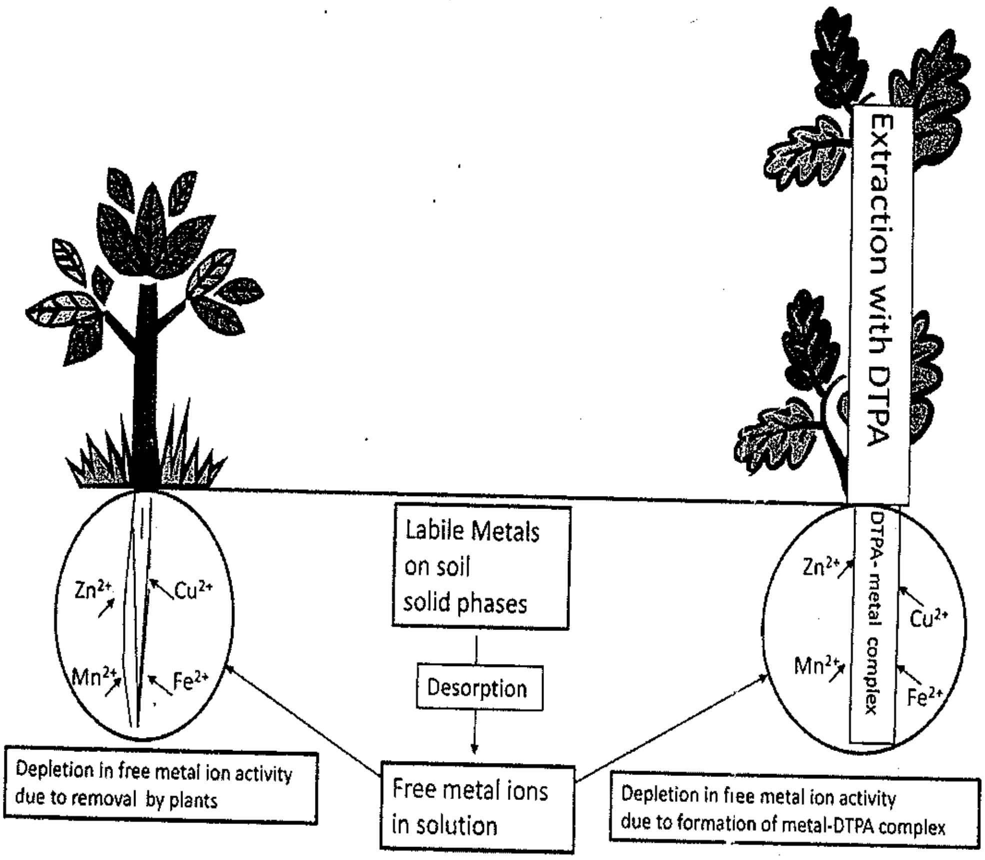


Figure 11. Extraction with DTPA simulates nutrient removal by plant roots and replenishment from labile solid phases in soil

The DTPA soil test of Lindsay and Norvell (1978) is widely used to assess the status of available micronutrient cations (Zn, Cu, Fe, Mn and Ni) in soil (Table 5). Selection of DTPA is based on its optimum combination of stability constants necessary to simultaneously extract Zn, Cu, Fe and Mn. Since, this extractant was developed for calcareous and alkaline soils, the extractant was designed to avoid excessive dissolution of $CaCO_3$ with release of occluded micronutrients, which are normally not available to plants. This objective was achieved partially by buffering the extractant in a slightly alkaline pH with triethanol amine (TEA) and partially by including soluble Ca^{2+} ions. Triethanol amine is selected as buffer because of its pKa = 7.8 and it clearly burns during flame atomization in atomic absorption spectrometry. Approximately two-thirds of the Ca is associated with DTPA. At the selected pH of 7.3, approximately 3/4th of TEA gets protonated and is present as $HTEA^+$. When TEA is added to soil, additional Ca^{2+} and Mg^{2+} ions enter into the solution, largely because of the $HTEA^+$ exchanging with Ca and Mg from soil exchange sites. This exchange generally raises the concentration of Ca^{2+} by 2 to 3 fold and aids in suppressing the dissolution of $CaCO_3$ in calcareous soils. At pH 7.3, about 70-80% of the buffering capacity provided by TEA is consumed in alkaline soils. Use of this extractant in acid soils is likely to result in neutralization of the remaining buffering capacity and pH of DTPA and soil extract becomes unpredictable. This leads to disruption of metal-chelate equilibria causing shifts in metal chelating tendencies.

The DTPA test is a good soil test that identifies near neutral and calcareous soils with insufficient available Zn, Cu, Fe and Mn for maximum yields of crops. Whenever one strays from the original design of the soil test or misuses it, one should be aware of the possible consequences and should pass that awareness to the others. If the test is applied to acid soils, the buffering capacity of the soil test solution may be exceeded (O'Connor, 1988). Metal-chelate equilibria disrupt and cause dra-

Table 6. Soil factors influencing the interpretation of soil test values for micronutrients

Element	Interacting soil factors	
	Essential	Probable
B	Texture, pH	Lime
Cu		Organic matter, Fe
Fe		pH, lime
Mn	pH	Organic matter
Mo	pH	Fe, P, S
Zn	pH, lime	P

Source : Cox and Kamprath (1972)

matic shift in individual metal chelating tendencies. Inclusion of pH in the regression equations for separating acid soils improves the relationship between DTPA-extractable metal and plant metal content.

Hot water extraction of B (Berger and Truog, 1939) is a commonly used method for obtaining an index of plant available B in soil. Extracting the soil with boiling water poses problems due to colour from organic matter and turbidity from suspended clay particles, in the colorimetric estimation of B. Apart from these problems, this method is difficult to adopt for the analysis of a large number of samples on routine basis. Mannitol-$CaCl_2$ (Cartwright *et al.*, 1983) for alkaline /calcareous soils and salicylic acid (Datta *et al.*, 1998) for acid soils hold promise as replacement for the tedious hot water method. Unlike other micronutrients, Mo-content in residual fraction is low and this element is predominantly associated with amorphous Fe-oxide fraction. Therefore, ammonium oxalate which was originally designed to extract amorphous Fe-oxides, has long been used for assessing the plant-available Mo. This is the most commonly used soil test extractant for Mo, not due to its unerring ability to predict Mo-deficiency, but because no better method is available.

Each soil test is different with respect to shaking time, soil : solution ratio, and critical limits. Critical limits for different extractants differ even for the same micronutrient under different soil conditions and type of crops. Climate also plays an important role in determining the critical limits of a micronutrient. It should be remembered that soil test values are empirical and may not be necessarily related to deficiency or sufficiency of a particular micronutrient under a given set of soil conditions, unless these are properly calibrated with crop response. It is, therefore, essential to take into consideration various soil factors while interpreting the soil test data. Soil conditions that influence the soil test data for micronutrients are given in Table 6. While interpreting the soil test data, these factors should be accorded due consideration. Once the influence of all these factors is critically assessed, the soil tests will be able to predict the amount of micronutrient fertilizer to be applied to a crop for getting the maximum economic response.

9.4. Transport of Micronutrients to Plant Root

Mass flow and diffusion are the are the two principal mechanisms of transport of micronutrients to plant roots (Barber, 1962). Details on the mechanisms of nutrient movement have been described in Chapter 15 (Mineral Nutrition of Plants). Diffusion contributes more than 80% of total micronutrients present in a plant, whereas mass flow seldom contributes more than 20% of the micronutrients absorbed by a plant. Zinc has received maximum attention all over the world. We shall restrict our discussion on the transport of Zn to plant root only. Diffusion coefficients of Zn (DaZn) in the illite-dominated Indian soils have been reported to vary from 1.00×10^{-11} to 2.07×10^{-8} cm^2/s (Deb *et al.*, 1983). Soils having DaZn values less than 10^{-10} cm^2/s are likely to suffer from Zn-deficiency unless proper soil management care is taken. Uptake of Zn by plant is closely correlated with its diffusion coefficient in soil (Rattan and Deb, 1981a;b). Any soil parameter be it physical or chemical, which is likely to influence the diffusion coefficient of Zn, certainly affects the uptake of Zn by plants. It is possible to increase the rate of zinc diffusion in soil by manipulation of the physical and chemical environment of soil (Deb *et al.*, 1983).

Comprehensive review by Deb *et al.* (1986) shows that the DaZn values show an exponential decrease with increase in soil pH, but the increase is logarithmic with increasing level of volumetric moisture content of soil. The DaZn values increase with increase in soil bulk density up to 1.5 g/cm^3 followed by a decrease above this value of compaction. Increase in ambient temperature from 5 to 30 °C increases the DaZn values by 4 to 20-times in certain soils. Application of higher levels of fertilizer Zn increases the DaZn values in soils. Application of chelating agents, both natural and synthetic, increases DaZn values in soils. by 100- to 1000-fold. Fulvic acid increases DaZn values by 10-fold, whereas humic acid does not show any increase in DaZn value in the same soils (Gupta and Deb, 1984). Application of organic manures in the form of FYM, poultry manure and piggery (5-10 t/ha) shows increase in DaZn values. Application of soil amendments such as gypsum and pressmud, increases the DaZn values in sodic soils without application of Zn fertilizers. The DaZn values of soils show an increase due to the application of increasing levels of P fertilizers, suggesting that P-Zn interaction site is extraneous

Table 7. Major micronutrient carriers with rates of their application

Micro-nutrient	Name of the salt	Formula	Micro-nutrient content (%)	Minimum micro-nutrient* (%)	Rate of soil application as nutrient (kg/ ha)
Zn	Zinc sulphate heptahydrate	$ZnSO_4.7H_2O$	21	21	2.5-10
	Zinc sulphate monohydrate	$ZnSO_4.H_2O$	33	33	
	Zinc oxysulphate	$ZnSO_4 + 4Zn(OH)_2$	55	–	
	Zinc oxide	ZnO	55-70	–	
	Zinc-EDTA	Zn-EDTA	12	12	
Cu	Copper sulphate pentahydrate	$CuSO_4.5H_2O$	24	24	1.0-5
	Copper sulphate monohydrate	$CuSO_4.H_2O$	35	–	
	Copper oxysulphate	$CuSO_4 + 3 Cu(OH)_2$	13-53	–	
		$CuCO_3 + Cu(OH)_2$	57	–	
	Copper-EDTA	Cu-EDTA	9-13	–	
Mn	Manganese sulphate trihydrate	$MnSO_4.3H_2O$	26-28	–	10-25
	Manganese sulphate monohydrate	$MnSO_4.H_2O$	30-32	30.5	
	Manganese oxysulphate	$MnSO_4.MnO$	40-49	–	
	Manganese dioxide	MnO_2	55-65		
	Manganese-EDTA	EDTA-Mn	5-12	–	
Fe	Ferrous sulphate	$FeSO_4.7H_2O$	19	19	5-20
	Ferric sulphate	$Fe_2(SO_4)_3$	17	–	
	Ferric chloride	$FeCl_3$	5-18	–	
	Iron-EDTA	Fe-EDTA	12	12	
B	Borax	$Na_2B_4O_7.10H_2O$	10.5	10.5	2-5
	Boric acid	H_3BO_3	17.5	–	
	Solubor	$Na_2B_4O_7.5H_2O +$ $Na_2B_{10}O_{16}.10H_2O$	19	19	
Mo	Sodium molybdate	$Na_2MoO_4.2H_2O$	37-39	–	0.05-0.10
	Ammonium molybdate	$(NH_4)_6Mo_7O_{24}.4H_2O$	54	52	
Cl	Potassium chloride*	KCl	48	–	**

Source: *As per FCO (1985), FAI (1998)

** Usually not applied as fertilizer supplier of chloride, except in coconut crops to soil. Liming of acid soils decreases the DaZn values in most of the soils, but the decrease is not appreciable at low levels of liming. Overliming reduces the DaZn values of soil due to a Zn-stress condition.

9.5. Common Micronutrient Carriers and their Rates of Application

Both soluble and insoluble micronutrient carriers are utilized in routine agricultural practices to supply adequate level of micronutrients in soil. A list of common micronutrient fertilizers is given in Table 7 along with their rates of application. For each micronutrient, there are one or two main fertilizer carriers which are commonly used as fertilizers. In India, the most common fertilizer for Zn is $ZnSO_4.7H_2O$, although in the USA and other countries, zinc sulphate monohydrate and zinc oxysulphate are more popular because these are more concentrated fertilizers than zinc sulphate heptahydrate. Zinc oxide (ZnO) is also another fertilizer source of Zn, but its Zn-content is variable due to impurities. For other micronutrient cations, their sulphate salts are used as fertilizer because these are water soluble. Manganese dioxide (MnO_2) is also used as fertilizer but its efficiency is much less as compared to $MnSO_4$. Micronutrient chelates are water soluble and these are now becoming popular for use in field and orchard crops. Boron is applied as sodium tetraborate and boric acid. Molybdenum is usually applied as ammonium molybdate and sodium molybdate, which are water soluble. For chlorine, sodium chloride and calcium chloride are used as fertilizers, depending on the crop, especially in the coconut crop.

It may be mentioned that the micronutrient management in soil requires expert knowledge. Many commercial preparations are available in the market for use as foliar spray. In micronutrient-deficient soils, such commercial preparations are not very useful. Proper soil management and soil application of adequate level of micronutrients is beneficial to the crops. Unlike N, P, K and S, excess application of micronutrients in soil adversely affects the plant growth and may lead to the deterioration of soil fertility and reduction in crop production. Scientific soil management needs a thorough understanding of the behaviour of micronutrients under different soil conditions.

9.6. Depletion of Micronutrients by Crops

Depletion of micronutrients from soil by crops is a century-old process. Since crop yields were not very high before the introduction of high-yielding varieties in Indian agriculture, such depletion was replenished by micronutrient addition to soil through organic manures and micronutrient bearing low analysis fertilizers, especially superphosphate before mid-1960s. High crop yield in agriculturally progressive districts of India removed substantial amounts of micronutrients from soil, especially Zn and B, causing yield reductions. Micronutrient depletion in soil depends on the soil fertility level and crop yields. Higher the crop yield, more is the micronutrient depletion from soil.

The extent of micronutrient removal in different cropping systems is presented in Table 8. The decline in DTPA-Zn content in soil due to cropping has also been studied. The effect of different fertility levels on the depletion of

Table 8. Average removal of micronutrients by major cropping systems

Cropping system	Yield level (tonne/ha)	Nutrient removal (g/ha)					
		Zn	Fe	Mn	Cu	B	Mo
Rice-rice	4+4 = 8	320	1224	2200	144	120	16
Rice-wheat	4+4 = 8	384	3108	2980	168	252	16
Maize-wheat	4+4 = 8	744	7296	1560	616	–	–
Soybean-wheat	2.4+4 = 6.5	416	3362	488	710	–	–
Pigeonpea-wheat	2.0+4=6.0	287	3456	493	148	–	–

Source : Takkar (1996)

Table 9. Effect of different fertility levels on DTPA-Zn content of a calcareous soil after 5 cycles under rice-wheat and rice-maize and after 18th crop in rice-wheat-jowar and rice-mustard-mungbean cropping sequences

Fertility level	DTPA-Zn in cropping sequences (ppm)			
	Rice-wheat	Rice-maize	Rice-wheat-jowar	Rice-mustard-mungbean
Control*	1.48	1.22	1.07	1.22
Low Fertility	1.41	1.18	1.03	1.09
Medium Fertility	1.30	1.14	1.06	1.10
High Fertility	1.25	1.07	0.99	0.94
Initial DTPA-Zn (ppm)		2.93	3.26	

Source : Sakal *et al.* (1996)

* Control means no fertilizer application, low fertility refers to 50% of recommended dose of NPK and medium fertility refers to 100% of recommended dose and high fertility refers to 150% of recommended dose

DTPA-Zn content of soil under different cropping sequences is presented in Table 9.

It is evident from the data presented in Tables 8 and 9 that the micronutrient depletion in soil depends on the cropping sequence as well as on the fertility level. It appears that the maize-based cropping sequence depletes the maximum micronutrients from soil, especially Zn and Fe. The DTPA-extractable Fe, Mn and Cu in soil show slight variations after intensive cropping. In order to maintain high crop productivity, periodic application of zinc fertilizer is necessary, based on the soil test data.

10. Micronutrients and Human Health

The human health status is to a large extent conditioned by the intake of mineral elements in the daily diet, through drinking water, and by inhalation of dust. Since about 98% of the human food is produced on the land, soil is a primary source of mineral elements, which get into human food chain via plants directly or indirectly as animal products (meat, milk, etc.). Intake of mineral elements from the soil environment varies according to species and function of forage behaviour. Wild animals for instance, usually forage over extensive areas and therefore stand a reasonable chance to ingest the necessary critical load of essential elements. On the other hand, domesticated animals, particularly ruminants, are more vulnerable to low levels of essential elements because of confined grazing areas. Human food supply usually originates from a wide area, either because human beings travel over large distances or because food is transported. The same applies to drinking water, the second most important source of micronutrients in human diet. As most people in the developed countries consume piped drinking water that is pumped over great distances, correlation between composition of local water sources and health status is poor. For similar reason, geographical correlations between mineral elements and human health status are mainly limited to isolated locations where people live on local agricultural produce and drink from local water resources.

Zinc is one of the most important essential trace elements in human nutrition. It is essential for the functioning of a large number of enzymes which are important (i) during pregnancy (pregnant women require much more Zn in their diet than otherwise), (ii) for brain growth of infants, (iii) in immune competence, and (iv) in playing possible role as anti-carcinogen. Its abnormal metabolism is related to certain disorders such as diabetic complications (Song *et al.*, 2005). Oxidative stress has been considered as the major causative factor for diabetic cardiomyopathy. Zinc has a critical antioxidant action in protecting the heart from various oxidative stresses. Whole grains, pulses and unpolished rice are good sources of Zn in the diet. Red meat is also a good source of Zn, and pork and chicken slightly less so. Copper is essential for human beings. It forms organic complexes and metallo-protein, specially haemoglobin. It regulates maturation of connective tissues, development of the bones, and participates in lipid metabolism.

Iron is an important element in all living organisms as a key component of haemoglobin and a number of enzymes. It is involved in developing resistance to infection. Anaemia is more common in growing children, subject to infections at school; it is more common in women because of blood losses during menstruation and childbirth. Manganese appears to be relatively neglected trace element in biogeochemistry and geo-medicine compared to the attention given to other elements like Zn, Fe and Cu. Yet, Mn appears to be very important in human health. Most attention is given to its possible role as an anti-carcinogen. In view of its redox capabilities, Mn could be seen as an anti-oxidant, which may explain its role in controlling certain types of cancer. It plays an important role in the synthesis of numerous enzymes helpful in utilizing fats. It is necessary for the bone growth, development, reproduction, lipid metabolism and moderation of nervous irritability.

Nickel is an important element for the heart muscle, liver and kidneys. It is involved in hormone, lipid and membrane metabolism. Moybdenum plays a biochemical role in enzymes such as aldehyde oxidase and xanthine oxidase. Legumes, grains and organ meats are good sources of Mo, while fruits, root, stem vegetables and muscle meat are poor ones. Chlorine in the form of chloride anion occurs widely in food stuffs. There is a wide variation in human intake of chloride in view of its variable intake of chloride through kitchen salt. In human, 88% of chloride is extracellular and contributes to the osmotic activity of body fluids. Electrolyte balance is maintained by adjusting total dietary intake and excretion via kidneys and gastrointestinal tract. Minimum daily requirement of chloride for a person between the age of 25 and 50 years is recommended as 750 mg (FAO/WHO, 2000). Toxicity of chloride depends on the associated cations present; that of chloride itself is unknown. Although micronutrients are required by humans for normal metabolism, most of them may also be toxic in levels above the very low body requirement. Available deficiency and toxicity limits of micronutrients along with their impact on human health are presented in Table 10.

Increasing the content of micronutrients, particularly of Zn and Fe in edible portion of crops for improving human health is a global challenge (Cakmak, 2008). Zinc deficiency ranks 11th among the 20 most important factors in the world and 5th among the 10 most important factors in developing countries. Similarly, deficiency of Fe stands 6th among ten leading causes of illness and disease in low-income countries. Food fortification and supplementation are being widely used in some countries to mitigate the Zn and Fe deficiencies in humans. However, these approaches appear to be expensive and not easily accessible in developing countries. Alternatively agricultural strategies (e.g., breeding and fertilization) appear to be cost-effective and useful in improving micronutrient concentrations in edible portion of crops. Although genetic biofortification appears to be most sustainable and cost effective, this approach is a long-term process requiring substantial effort and resources. A successful breeding programme for biofortifying cereals and other food crops with Zn and Fe is dependent on the size of plant-available Zn and Fe pools in soils. However, in many cereal-growing areas, soils have a variety of chemical and physical problems that significantly reduce solubility and impair root absorption of Zn and Fe. Hence, the genetic capacity of newly developed (biofortified) cultivars to absorb sufficient amount of Zn and Fe from soil and accumulate in the grain may not be expressed to the full extent. It is, therefore, essential to have a short-term approach to increase Zn and Fe concentrations in the cereal grain.

Application of Zn and Fe fertilizers (e.g. agronomic biofortification) offers a rapid solution to the problem, and represents useful complementary approach to genetic biofortification. There are increasing evidences showing that foliar or combined soil+foliar application of Zn fertilizers under field conditions are highly effective and practical to maximize uptake and accumulation of Zn in the grains of cereal crops.

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Chapter 21

Analysis of Soil, Plant and Fertilizer for Plant Nutrients

C.L. ARORA and H.L.S. TANDON

1. Introduction

Methods of chemical analysis of soil, plant and fertilizer are as numerous and varied as the field of chemistry itself. The methods employed for the analysis of soil, plant and fertilizer, have traditionally been based on the time consuming gravimetric or colorimetric techniques. But, over the past two decades, there have been tremendous advancements in the field of electronic- and computer-based rapid techniques which have facilitated the otherwise cumbersome job of analysis. The modern techniques of multi-element extractions and their simultaneous analysis have virtually revolutionized the analytical work. The elemental analysis consists of two distinct steps, namely extraction and quantitative determination. This chapter is not an all inclusive text on the subject, but it describes in some details the more commonly used analytical procedures for the analysis of soil, plant and fertilizer. The subject is dealt with in greater details in several publications (Anonymous, 1992; 2006, Chopra and Kanwar, 1991; Dhyan Singh *et al.*, 1999; FAO, 2000; Jackson, 1973; Tandon, 2005, among others), which may be referred to for more details.

2. Soil Analysis

2.1. pH

pH is a measure of the H^+ ion concentration and is measured on a 0-14 scale. Soil pH is usually measured in a soil-water suspension by using a glass electrode pH meter. The pH meter is an instrument which measures the voltage developed by the combination of a glass electrode and a reference calomel electrode. It is calibrated to measure the voltage in terms of pH units. Actual pH readings can be obtained by calibrating the instrument with buffer solutions of known pH values. There is also a provision for applying correction for variations in temperature.

The pH value is erratic and unreliable when measured on soils at the moisture equivalent, i.e. field capacity or below due to the poor contact between the soil and the glass electrode and high mechanical resistance of the soil. In general, the more dilute the suspension, the higher will be the pH in both the acidic as well as alkaline soils. The rise in soil pH from the sticky point to a soil-water ratio of 1:10 is usually of the order of 0.2 to 0.5 unit. However, a 1:2 soil:water suspension seems to give the most uniform results.

2.2. Electrical Conductivity

The electrical conductivity (EC) of the soil solution is an index of the amount of soluble salts present in the soil. It is measured by using a conductivity meter with a conductivity cell. The instrument is calibrated to measure the electrical conductivity in terms of dS/m (deci Siemens per metre). The electrical conductivity of normal soils is generally less than 0.8 dS/m.

The percentage of soluble salts in soils can be computed from the following relationship:

Percentage of soluble salts in soil =
[0.064 × Electrical conductivity × Saturation percentage] / 100

The electrical conductivity in the above relationship refers to that of the saturation extract of the soil. Since it is difficult to obtain saturation extracts of a large number of soil samples and the electrical conductivity varies with the soil:water ratio, it has been found most practical to use 1:2 soil:water ratio for routine testing. The suspension after thorough stirring with a glass rod, is allowed to settle and the conductivity cell is immersed in the upper supernatant solution for measuring the electrical conductivity.

2.3. Extraction Techniques for Elements

2.3.1. Total Elemental Analysis

2.3.1.1. Nitrogen

The nitrogen in soil is present mostly as organic compounds, viz. proteins, amino acids, amides, amines, etc. and partly as inorganic forms such as nitrates, nitrites (unstable), ammonium, etc. The total N is determined by digestion of the soil with concentrated sulphuric acid in the presence of selenium as an oxidising agent, converting all forms of N to NH_4^+, as described below:

Method — A known weight (1 g) of the soil is taken in a 150 mL conical flask and treated with 10 mL of digestion mixture containing sulphuric acid and selenium dioxide. Salicylic acid (about 1 g) is also added to include the nitrates and nitrites. The digestion is carried out by heating the flask on a hot plate till the soil colour changes to white. The contents of the flask are cooled and diluted to a desired volume, depending upon the procedure of estimation. The N in the digest is estimated by either steam distillation using micro-Kjeldahl apparatus or colorimetrically on an Auto Analyzer or a Flow Injection Analyzer.

2.3.1.2. Other Elements

For the extraction of total amounts of elements other than N, the soil is processed by any one of the following methods:

- Na_2CO_3 fusion
- $HClO_4$ digestion
- HF digestion

Na_2CO_3 Fusion Method — The soil (< 100 mesh) is thoroughly mixed with anhydrous sodium carbonate (1:3 to 1:10) and transferred to a platinum crucible. After fusion in a furnace, or on a Bunsen burner, the melt is cooled and dissolved in 100 mL of 1*N* HCl taken in a beaker, dried on a sand bath for dehydrating the silica, rewetted in 20 mL of 3*N* HCl and heated to dissolve the contents. After filtration, the desired volume is made up with deionized water. The extract can be used for the determination of total P, Ca, Mg, Zn, Cu, Mn, Fe, Al, Ti, etc.

$HClO_4$ Digestion Method — If total P is the only constituent to be determined in soils, it can be completely extracted by digestion with 70% perchloric acid in the ratio of 1:2. The soil (2g) is taken with 4 mL $HClO_4$ in a 50-mL beaker, covered with a watchglass and put on a hot plate. The digestion is continued till the soil changes its colour to white. *It should not be taken to dryness.* The contents are then cooled and diluted to the desired volume before filtration.

HF Digestion Method — For elements like Co and Mn, the digestion of soil in HF is preferred. The soil (1g) taken in a platinum crucible is treated with 2 mL water and 1 mL $HClO_4$ before 5 mL HF is added. The contents are evaporated to dryness. The residue is heated with 1 mL HCl and 5 mL water till it dissolves. After cooling, the desired volume is made up after filtration.

For Mn, 0.5 g soil is treated with 4 mL HF and 2 mL sulphuric acid. The digestion is conducted at low temperature till the soil colour changes to white.

The HF extract of the soil can be analysed on Atomic Absorption Spectrophotometer (AAS) or Inductively Coupled Argon Plasma–Atomic Emission Spectrophotometer (ICAP-AES) only if the sample is evaporated to complete dryness after digestion so that there is no free HF which would otherwise eat away the glass nebulizer as well as other quartz torch tubes. Some ICAP-AES instruments have the Teflon nebulizer which is resistant to HF. These instruments are described in a subsequent section.

2.3.2. Available Elemental Analysis

It has been established that there is a poor relationship between the total elemental content of a soil and plant response to their application. Some procedures have been developed to extract that portion of the specific element from the soil, which has some relationship to plant utilization. The available content of an element in the soils includes forms which contribute to the plant requirement. However, it must be understood that the amount of the element extracted is not the exact amount available for utilization, but is only a measure of that amount. Its value is determined by the significance of the correlation between the amount extracted and plant response to its application.

Although water extraction after equilibration would be a reasonably good measure of available nutrient status for most soils, it is not suitable for rapid soil testing application in view of the long time required for equilibration. In addition, the amount of elements extracted by water is quite low, which would require sensitive analytical procedures for their accurate determination.

Most of the extraction procedures used today were developed in the 1940s and 1950s by chemists who had a thorough knowledge and appreciation of the elemental forms existing in soils. There are extraction reagents and procedures specific for P, S, Ca, Mg, K and Na as well as the micronutrients B, Cu, Fe, Mn, Mo and Zn, either individually or in groups. Recently, newer extraction procedures have been introduced that can be used for more than one elements or a group of similar elements.

The available elemental analysis is used for soil testing. Any given test method is not universally applicable. In general, the procedures suitable for acid soils are not suitable for alkaline soils. Some procedures have been designed for use on acidic sandy soils having relatively low cation exchange capacity. Similarly, specific procedures have been designed for soils with high exchange capacity due to either a high clay and/or organic matter content. Even organic soils require an entirely different soil testing system. Therefore, it is important to know the suitability characteristics of the test procedure before it is chosen for soil analysis.

2.3.2.1. Nitrogen

The available N in a soil represents that fraction of the total N which is usable by the plants. The inorganic N in soil is predominantly in NH_4^+ and NO_3^- forms, while NO_2^- form is seldom present in detectable amounts. The inorganic form of nitrogen in soils is usually extracted by neutral solutions of potassium ($1N$ K_2SO_4 or $2N$ KCl) or calcium ($0.01M$ $CaCl_2$) salts. Nitrate is extracted by using one of the several extracting reagents; the more common being $2N$ KCl using 1:10 soil : solution ratio and 5 minute shaking time. In another procedure, a saturated CaO solution is used as the extracting reagent with 1 : 3 soil : solution ratio and 5 minute shaking time. The nitrate content in the extracts can then be determined by a number of techniques, viz. colorimetry, specific ion electrode, etc.

Although, most of these soil tests for N are of limited value, these could be extremely useful where applicable. Most soil testing laboratories are using organic carbon status of the soil as an index of the availability of nitrogen. The alkaline potassium permanganate ($KMnO_4$) method of Subbiah and Asija (1956) extracts relatively easily oxidizable fractions of organic nitrogen and has been found to have a better correlation with the utilization of nitrogen by most crop plants.

Method — A known weight of soil (5 g) is treated with excess of alkaline $KMnO_4$ solution (0.32%), (made alkaline with 2.5% NaOH solution) and heated to boiling. The ammonia evolved is absorbed in a known volume of a standard acid ($N/50$ H_2SO_4), the excess of acid is titrated against a standard alkali ($N/50$ NaOH). The volume of acid used for absorption is used to calculate the available N in the soil.

Calculations:

Weight of soil taken = 5g
Volume of $N/50$ H_2SO_4 taken = 10 mL
Volume of $N/50$ NaOH used = X mL
Volume of $N/50$ H_2SO_4 used for absorption of NH_3 = (10-X) mL
1 mL of $N/50$ H_2SO_4 = 0.00028 g of N
Available Nitrogen (%) = $[(10\text{-}X) \times 0.00028 \times 100]/5$
Available Nitrogen (ppm) = Percentage× 10,000
Available Nitrogen (kg/ha) = Percentage × 22,400

The soils are rated as low (< 272 kg/ha), medium (272-544 kg/ha) or high (> 544 kg/ha) in available N.

2.3.2.2. Phosphorus

Plants take up phosphorus in the form of soluble anions $H_2PO_4^-$ and HPO_4^{2-}, but the quantity of water-soluble phosphorus at any one time is very small and often not related to P-uptake by the plant. Among the inorganic fractions, calcium, iron and aluminium phosphates are in dynamic equilibrium with water-soluble phosphates. Therefore, a measure of these forms is a useful index of the available phosphorus in the soils.

A list of the most common availability indices for P is given in Table 1. On the sandy acid soils, Mehlich No. 1 is mostly used. The Morgan's extractant once in wide use, has been modified (Wolf, 1982) for application under a wide range of soil conditions. The most widely used extracting reagent for P determination in acid soils is Bray and Kurtz P_1 (Bray and Kurtz, 1945), which is $0.03N$ NH_4F in $0.25N$ HCl. The extraction of P by this reagent is based on the solubilization effect of H^+ on soil phosphorus and the ability of the F^- ion to lower the activity of Al^{3+} ion and to a lesser extent those of Ca^{2+} and Fe^{3+} ions in the extraction system. The method should normally be limited to soils with pH less than 6.8 because the high degree of base saturation in the alkaline soils lowers the solubilizing ability of the extractant.

Bray & Kurtz P1 Method — The soil (2 g) is shaken with 20 mL of the extracting reagent for 5 min. An aliquot of the filtrate is treated with sulphuric-molybdate reagent to produce blue colour, the intensity of which is measured on a spectrophotometer at 882 nm. The colour is stable for about 4 hours. The soils are categorized as low, medium and high in available P on the basis of critical values of < 34 kg/ha, 34-68 kg/ha and > 68 kg/ha, respectively.

None of the "acid" extractants mentioned above are well suited for use on alkaline soils, although the bicarbonate extractants work reasonably well over the wide range of soil pH. For the alkaline soils, the $0.5M$ sodium bicarbonate extracting reagent (Olsen *et al.*, 1954), or the modified ammonium bicarbonate-DTPA (diethylene-triammine penta acetic acid) extraction methods of Soltanpour and Schwab (1977) are the suitable procedures.

Olsen's Sodium Bicarbonate Method — A known weight of soil (1 g) is shaken with 20 mL of 0.5 M sodium bicarbonate solution (pH 8.5) in the presence of Darco-G 60 or activated charcoal for 30 minutes. The carbonate activity in the soil is raised resulting in decreased activities of calcium, iron and aluminium. Thus, some phosphorus from the surfaces of the soil phosphates of Ca, Fe and Al is brought into solution. The low activity of calcium also prevents the precipitation of the liberated phosphate as calcium phosphate. An aliquot (5 mL) of the filtered extract is then used for the estimation of available phosphorus colorimetrically (at 660 nm) using the molybdate blue colour method. The colour is stable for 24 hours. The soils are categorized as low, medium and high in available phosphorus on the basis of critical values of < 10 kg/ha, 10-25 kg/ha and > 25 kg P/ha, respectively. A multi-element method which includes

Table 1. Availability indices for phosphorus

Parameter	Mehlich No.1	Bray P1	Morgan (Wolf)	Olsen	AB-DTPA
Acceptability	Sandy acid soils, low in CEC	Acid soils moderate in CEC	All soils	Alkaline soils	Alkaline soils
Sample size	5 g	2 g	30 cm^3	1 g	10 g
Reagent	0.5*N* HCl + 0.025*M* H_2SO_4	0.03*N* NH_4F+ 0.025*M* HCl	0.73*M* NaOAC + 7.4*M* HOAC at pH 4.8	0.5*M* $NaHCO_3$ at pH 8.5	2*M* NH_4HCO_3+ 0.005*M* DTPA at pH 7.6
Volume (mL)	25	20	60	20	20
Shaking time (min)	5	5	5	30	15
Critical level (kg/ha)	34-67	34-68	–	12-24	8-14
Primary reference	North Carolina Soil Test Division Mimeo (1953)	Bray and Kurtz (1945)	Wolf (1982)	Olsen *et al.* (1954)	Soltanpour and Schwab (1977)

P, developed by Soltanpour and Schwab (1977), is described under micronutrients.

2.3.2.3. Major Cations (Ca, K, Mg and Na)

The extractants for major cations are either salt solutions such as the widely used neutral normal ammonium acetate (NH_4OAc) (Schollenberger and Simon, 1945) or the Morgan extractant as modified by Wolf (1982) or the Mehlich extractant, which uses the H-ion as the exchange cation. For the alkaline soils, water extraction is recommended. The AB-DTPA (Table 1) is suitable only for K and Na as Ca and Mg are partially precipitated by the bicarbonate anion. A two-step extraction procedure using neutral normal ammonium acetate has been suggested by McLean *et al.* (1982) for improving the interpretation of this extraction procedure for K.

The neutral normal ammonium acetate (NH_4OAc) extraction procedure is used mostly for determining the exchangeable cations in the soil testing laboratories in India. The advantages of this reagent include its effectiveness in wetting the soil, replacing exchangeable cations, ease of volatility during analysis and suitability for use with flame photometer. The cation concentrations determined by this procedure are referred to as "exchangeable" for non-calcareous soils. For calcareous soils, the cations are referred to as "exchangeable plus soluble".

Method — A known weight of soil (5 g) is shaken with 25 mL of neutral normal ammonium acetate (NH_4OAc) solution for 5 minutes and filtered through Whatman filter paper No. 42. The extracts are analysed for Ca, Mg, K and Na by emission spectrophotometry (flame photometer or ICAP-AES) or atomic absorption spectrophotometry. The soils are rated as low, medium and high in available K on the basis of critical levels of < 113 kg K/ha, 113-280 kg K/ha and > 280 kg K/ha. A multi-element extractant developed by Soltanpour and Schwab (1977), which also includes K is described under micronutrients. Generally, a soil is considered to be deficient in Ca if it contains less than 1.5 m.e. exchangeable Ca/100g soil or occupies < 25% of CEC. Corresponding limits for Mg are 1 m.e. and < 4% of CEC (Subba Rao and Sammi Reddy, 2005).

2.3.2.4. Sulphur

Plant available S exists in soils as sulphate (SO_4^{2-}) anion. The frequently used extracting reagents for available sulphur include calcium dihydrogen phosphate [$Ca(H_2PO_4)_2.2H_2O$] containing 500 ppm P, neutral normal ammonium acetate, 0.5*N* ammonium acetate plus 0.25 *N* acetic acid, 0.001*N* HCl, 0.5*M* sodium bicarbonate, Morgan's reagent (10% sodium acetate in 3% acetic acid) , 1% NaCl, 0.15% calcium chloride and 0.5 *N* ammonium chloride buffered with ammonium hydroxide to pH 7.0, etc. The amount of sulphur extracted by a particular reagent depends on the soil characteristics such as texture, organic matter content and electrical conductivity. The commonly used extractant for a wide variety of soils is 0.15% $CaCl_2$ solution (Williams and Steinbergs, 1959).

Method — A known weight of soil (5 g) is shaken with 50 mL of the extracting solution for 30 minutes. The extracts (generally 25 mL) are brought to near dryness and taken up in 5 mL of 0.01*N* HCl, which are then treated with 1 mL of 1% ferric chloride ($FeCl_3$) solution, followed by 1 mL of 40% NaOH to precipitate the interfering soil colloids (organic as well as inorganic). The precipitated material is removed by filtration. The filtrate is acidified with 1 mL of glacial acetic acid (Arora and Takkar, 1988). The sulphate in this extract is estimated turbidimetrically using barium chloride procedure of Chesnin and Yien (1951). The turbidity can be measured by either a spectrophotometer (at 420 nm) or nephelometer/turbiditymeter. The soils containing < 10 ppm sulphate-S are rated as deficient in available sulphur.

2.3.2.5. Micronutrient Cations

The micronutrient elements include zinc, copper, iron, manganese, nickel, boron, molybdenum and chlorine. The available forms of the first five elements are their cations (i.e. Zn^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+} and Ni^{2+}) while those of latter three are their anions (borate - $H_2BO_3^-$, molybdate – MoO_4^{2-} and chloride – Cl^-). Several extractants ranging from neutral salt solutions to acids of different strengths as well as many chelating and complexing reagents have been used for the determination of available micronutrients in soils. Most extraction procedures are for a particular nutrient or for those micronutrients which are similar in their chemical characteristics. Consideration of other soil properties like pH, organic matter content and texture, etc. is necessary to improve the interpretation of the actual laboratory results obtained by an extraction procedure. The effect of pH, shaking time and temperature on the DTPA-extractable micronutrient cations is shown in Table 2. Temperature variations can be a source of major error, particularly when extractions are carried out without temperature control facilities. The availability indices for micronutrients are given in Table 3.

Table 2. Effect of shaking time, temperature and pH on DTPA-extractable micronutrients

Parameters	Nutrient, mg/kg soil			
	Zn	Cu	Mn	Fe
Shaking time, Hours				
1.0	0.26	0.33	7.6	3.4
3.0	0.28	0.41	10.1	4.4
16.0	0.27	0.68	20.0	7.7
Temperature, °C				
15	0.32	0.35	12.1	3.67
25	0.34	0.45	18.7	5.52
35	0.53	0.66	28.4	7.01
pH of extractant				
7.0	0.28	0.35	9.8	4.3
7.3	0.28	0.35	9.0	4.1
7.9	0.28	0.35	7.0	2.3

Source: Lindsay and Norvell (1978)

The DTPA micronutrient soil test by Lindsay and Norvell (1969) is useful for the extraction of all the micronutrient cations including Zn, Cu, Fe and Mn, especially for their determination on atomic absorption spectrophotometer. The chemical composition of DTPA extractant is: 0.005*M* DTPA-0.01 *M* $CaCl_2 \cdot 2H_2O$-0.1 *M* triethanolamine. Its pH is adjusted to 7.3. The theoretical basis for the DTPA extraction is the equilibrium of elements in the soil with the chelating agent (DTPA). The pH 7.3 enables DTPA to extract Fe and other metal cations. For the triethanolamine, pH is kept close to 7.3.

Method — A known weight of soil is shaken with 20 mL of the reagent for 2 hours. The clear filtrate is used for the estimation of Zn, Cu, Fe and Mn by atomic absorption spectrophotometer. The soils, in general, are categorized as deficient in available Zn, Cu, Fe and Mn if their DTPA-extracable amounts in soils are below 0.8 ppm, 0.2 ppm, 4.5 ppm and 3.0 ppm, respectively.

2.3.5.6. Boron

Hot water extractable-B is the singular direct measure of available B in use at present (Berger and Truog, 1939). The extraction involves boiling the soil in water for a specified

Table 3. Availability indices for micronutrients

Micronutrient	Indices	Critical level (ppm)	
		Range	Mean
B	Hot water soluble	0.1-2.0	0.7
Cu	Mehlich No.1	0.1-10	3.0
	DTPA + $CaCl_2$ (pH 7.3)	0.12-2.5	0.8
	AB-DTPA (pH 7.6)		1.8
Fe	DTPA + $CaCl_2$ (pH 7.3)	2.4-5.0	4.0
	AB-DTPA (pH 7.6)		4.0
Mn	Mehlich No. 1	4-8	7.0
	DTPA+$CaCl_2$ (pH 7.3)	1.0-2.0	1.4
	0.03*M* H_3PO_4	0-20	10
	AB-DTPA (pH 7.6)		1.8
Mo	$(NH_4)_2C_2O_4$ (pH 3.3)	0.04-0.2	–
Zn	0.1*N* HCl	2.0-10.0	5
	Mehlich No.1	0.5-3.0	1.1
	DTPA+$CaCl_2$ (pH 7.3)	0.25-2.0	0.8
	AB-DTPA (pH 7.6)		1.5

time period. Obtaining a clear filtrate after boiling may be a problem. The use of double filter paper is helpful. Some workers have proposed boiling soil in a 0.1% solution of $CaCl_2.2H_2O$ to obtain a clear filtrate.

A comparison of the AB-DTPA (ammonium bicarbonate-DTPA) and hot water as extractants for B has shown that hot water soluble B has a better relation with the plant content. The quantities of B extracted by HCl and hot water correlate well. Generally, the plant concentration correlates slightly better with the dilute acid than with the hot water method. The dilute acid, however, extracts only about half as much B as hot water. At low concentrations in soils, this reduction would amplify the analytical problems.

Method — The hot water soluble boron is extracted by boiling 10 g soil with 20 mL deionized water for 10 minutes. Clear extracts are obtained by filtration and boron is either determined colorimetrically using Azomethine-H reagent or emission spectrophotometry using ICAP-AES. For most crops, the soils are rated as deficient, normal and high in available boron if the B content is <1.0 ppm, 1.0-2.0 ppm and > 2.0 ppm, respectively.

2.3.5.7 Molybdenum

The Grigg or Tamm reagent, acid ammonium oxalate solution buffered at pH 3.0 remains the primary extractant for available Mo (Grigg, 1953). Soil pH, however, is a more important factor than extractable Mo in determining Mo uptake or yield response. The Mo-content in soil extracts is determined by thiocyanate which forms an amber colour complex with Mo in the presence of a reducing agent. Molybdenum is determined colorimetrically at 470 nm. It can also be estimated by emission spectrophotometry using ICAP-AES. The sufficiency range of available Mo in most soils has been reported to be 0.04-0.20 ppm.

2.3.5.8. Multi-element Analysis

For simultaneous multi-element determination, Soltanpour and Schwab (1977) developed a solution of AB-DTPA (1*M* NH_4HCO_3-0.005*M* DTPA, pH=7.6), for simultaneous extraction of P, K, Zn, Cu, Fe and Mn from soils. It is more suitable for the alkaline soils, while the Morgan-Wolf reagent [a mixture of 10% sodium acetate (trihydrate) and 3% glacial acetic acid buffered at pH 4.8], is more suited for acidic soils (Table 1). The AB-DTPA procedure is described below.

The DTPA chelates the metals and ammonium ion exchanges with potassium ion and brings it into the solution. Upon shaking, the original pH (7.6) rises due to evolution of CO_2. As the pH rises, bicarbonate changes to carbonate. The carbonate ions precipitate calcium from calcium phosphates and thus increase the solubility of phosphorus. This method has been found to be highly correlated with ammonium acetate method for potassium, sodium bicarbonate method for phosphorus and DTPA method for Zn, Cu, Fe and Mn. The ranges and sensitivities are the same as those for DTPA, sodium bicarbonate and ammonium acetate methods for micronutrients, phosphorus and potassium, respectively.

Method — A known weight (10 g) of soil is shaken in a 125 mL conical flask with 20 mL of AB-DTPA solution on a reciprocating shaker for 15 min and is filtered through a Whatman No.42 filter paper or its equivalent. Concentrated HNO_3 @ 0.25 mL per 2 mL of the filtrate is added and shaken for about 10 min to get rid of carbonate-bicarbonate matrix which otherwise would clog the capillary tip in the nebulizer. This solution is used for the simultaneous multielement determination on ICAP-AES (Arora and Hundal, 1995). The available amounts of different nutrients extracted by AB-DTPA are interpreted on the basis of index values given in Table 4.

3. Plant Analysis

Plant analysis is complementary to soil testing. It can be carried out on the growing plants (leaf analysis or tissue testing) for diagnostic purpose as well as to study nutrient uptake and also on plants after harvest to estimate the total nutrient uptake and removal. In many situations, the total or even the available content of an element in soil fails to correlate with the plant tissue concentration or the growth and yield of crop. This can be due to many reasons including the physicochemical properties of the soils and the root growth patterns. On the other hand, the concentration of an element in the plant tissue is, generally, positively correlated with the status of plant nutrition. Therefore, the plant analysis is used as a diagnostic tool to determine the nutritional causes of plant disorders/diseases. The plant analysis constitutes:

(i) the collection of the representative plant parts at the specific growth stage,
(ii) washing, drying and grinding of the plant tissue,
(iii) oxidation of the powdered samples to solubilize the elements,
(iv) estimation of different elements, and
(v) interpretation of the status of nutrients with respect to deficiency/sufficiency/toxicity on the basis of known critical concentrations.

As a diagnostic tool, it is more commonly used for fruit trees or plantation crops than for field crops. It also has its own limitations which have been dealt in detail by Bhargava (2002).

Table 4. The available amounts of different nutrients extracted by AB-DTPA

Status	Nutrients (ppm)					
	P	K	Zn	Cu	Fe	Mn
Low	3-4	< 60	< 0.9	< 0.5	< 2.0	< 1.8
Medium	4-7	61-120	1.0-1.5	-	2.1-4.0	-
Adequate	8-11	>120	>1.5	>0.5	>4.0	>1.8

3.1. Collection and Preparation of Plant Samples

Plant scientists have standardized the procedures for collection of samples of plant tissue which reflect the nutrient concentrations corresponding to the health of the plant. For diagnostic purposes, there has to be a specific plant part at a specific stage of the growth, because the concentrations of different nutrients vary significantly over the life-cycle of a plant. Generally, the recently matured fully expanded leaves just before the onset of the reproductive stage are collected and put in perforated paper bags. Some available guidelines are provided in Table 5. Freshly collected plant samples are often contaminated with dust, dirt and residues of the sprays, etc. and need to be washed first under a running tap water, followed by rinsing with dilute HCl (0.001*N*), distilled water and finally with deionized water. The washed samples are dried in a hot air oven at 60±5 °C for 48 hours and ground in a stainless steel mill to pass through a sieve of 40/60 mesh.

3.2. Oxidation of Plant Material

The main objective of oxidation is to destroy the organic components in the plant material and convert the elements in mineral form.

Table 5. Plant tissue sampling guidelines for different crops

S.No.	Crop	Index tissue	Growth stage/time	Sample size (No.)
		Field/food crops		
1.	Rice	3rd leaf from apex	Tillering	50
2.	Wheat	Flag leaf	Before head emergence	50
3.	Sorghum	3rd leaf below inflorescence	Bloom	25
4.	Maize	Ear leaf	Before tasseling	15
5.	Barley	Flag leaf	At head emergence	25
6.	Pulses	Recently matured leaf	Bloom initiation	50
7.	Potato	Recent fully developed leaf	Half grown	15
8.	Cassava	4th leaf from apex	Juvenile phase	25
		Oil crops		
9.	Groundnut	Recently matured leaflets	Maximum tillering	25
10.	Sunflower	Youngest matured leaf blade	Initiation of flowering	20
11.	Mustard	Recently matured leaf	Bloom initiation	50
12.	Soybean	3rd leaf from top	2 months after planting	25
13.	Castor	Petiole, recently matured leaf	Bloom initiation	20
14.	Coconut	Pinnal leaf from each side of 4th leaf		2
15.	Oil palm	Middle 1/3rd minus midrib of 3 upper & 3 lower leaflets from 17 fronds of mature trees and 3 fronds of young trees		20
		Fibre crops		
16.	Cotton	Petiole, 4th leaf from apex	Initiation of flowering	50
17.	Jute	Recently matured leaf	60 days old	50
		Sugar crops		
18.	Sugarcane	3rd leaf from top	3-5 months after planning	15
19.	Sugarbeet	Petiole, youngest matured leaf	50-80 days old	25
		Stimulants		
20.	Tobacco	3rd leaf from top	45-60 days old	15
21.	Tea	3rd leaf from tip of young shoots		100
22.	Coffee	3rd or 4th pair of leaves from apex of lateral shoots	Bloom	25
		Temperate fruit crops		
23.	Almond	3rd leaf from top	Beginning of bloom	15
24.	Apple	Leaves from middle of terminal shoot growth	8-12 weeks after full bloom 2-4 weeks after formation of terminal buds in bearing tree	50
25.	Apricot	Fully expanded leaves, mid shoot current growth	Early-June to mid-July	50
26.	Cherry	Fully expanded leaves, mid shoot current growth	July - August	50
27.	Peach	Midshoot leaves, fruiting or non-fruiting spurs	Mid-summer	50
28.	Pear	Leaves from middle of terminal shoot growth	8-12 weeks after full bloom 2-4 weeks after formation of terminal buds in bearing tree	50
29.	Plum	Leaves from middle of current season's extension growth	January-February	100 leaves from 25 trees

Contd.

Table 5. Plant tissue sampling guidelines for different crops — *Contd.*

S.No.	Crop	Index tissue	Growth stage/time	Sample size (No.)
		Tropical fruit crops		
30.	Banana	Petiole, 3rd open leaf from apex	Bud differentiation 4 months after planting	15
31.	Cashew	4th leaf from tip of matured branches	Beginning of flowering	15
32.	Custard apple	5th petiole from apex	2 months after new growth	30
33.	Fig	Fully expanded leaves	July-August	25
34.	Grapes	5th petiole from base	Bud differentiation stage for yield forecast. Petiole opposite to bloom for quality	200
35.	Citrus fruits	3-5 months old leaves from new flush; Ist leaf of the shoot	June	30
36.	Guava	3rd pair of recently matured leaves	Bloom stage(Aug. or Dec.)	25
37.	Mango	Leaves + petiole	4-7 months old leaves from middle of shoot	15
38.	Papaya	6th petiole from apex	6 months after planting	20
39.	Pineapple	Middle 1/3rd portion of white basal portion of 4th leaf from apex	4-6 months	100
40.	Pomegranate	8th leaf from apex	Bud differentiation. In April for Feb. crop and Aug. for June crop	50
41.	Sapota	10th leaf from apex	September	30
42.	Ber	6th leaf from apex from secondary or tertiary shoot	2 months after pruning	40
43.	Muskmelon	5th leaf from tip (omit unfurled)	Flowers start to small fruit	12
44.	Water melon	5th leaf from tip (omit unfurled)	Flowers start to small fruit	12
		Vegetable crops		
45.	Beans	Upper most recent fully developed trifoliate leaves		10
46.	Beet root	Most recent fully developed leaf		20
47.	Cabbage	Wrapper leaf	2-3 months old	15
48.	Carrot	Most recent fully matured leaf	Mid grown	15
49.	Cauliflower	Most recent fully matured leaf	At heading	12
50.	Cluster bean	1st fully developed leaf		12
51.	Cucumber	5th leaf from tip (omit unfurled)	Flower bud start to small fruit	12
52.	Brinjal	Leaf blades with midribs minus petioles from most recent fully developed leaves		12
53.	Onion	Top , no white portions	1/3rd to 1/2 grown	12
54.	Peas	Leaflets from most recent fully developed leaflets	First bloom	50
55.	Spinach	Most recent fully developed leaf	30-50 days	15
56.	Radish	Most recent fully developed leaf	30 days	15
57.	Squash	Blades with midribs from most recent fully developed leaves		12
58.	Tomato	Leaves adjacent to inflorescence	Mid bloom	15
59.	Turnip	Most recent fully developed leaf		12

Contd.

Table 5. Plant tissue sampling guidelines for different crops — *Contd.*

S. No.	Crop	Index tissue	Growth stage/time	Sample size (No.)
		Ornamental and flowering plants		
60.	Bougainvillea	Most recent fully developed leaf		25
61.	Carnation	5th and 6th leaf pairs of non-flowering shoots		50
62.	Jasmine	Most recent fully developed leaf		50
63.	Chrysanthemum	Most recent fully developed leaf		25
64.	Gladiolus	Most recent fully developed leaf		12
65.	Hibiscus	Most recent fully developed whole leaf		15
66.	Rose	Most recent fully developed compound, 5th leaflet leaf	Flower bud pea size	10

Source: Several published sources compiled by Bhargava and Raghupathi (2005)

The plant materials can be oxidized by either dry-ashing at a controlled high temperature in a muffle furnace or wet digestion in an acid or a mixture of two or more acids.

3.2.1. Dry-ashing

The powdered plant materials are ashed in tall-form silica crucibles at 500 °C in a muffle furnace for 3-4 hours. Temperature is an important consideration in dry-ashing. High temperatures are likely to result in the loss of some volatile elements but with adjusting the time of muffling between 2-72 hours, any significant effect on the analytical results can be avoided. Nitrogen and sulphur, being highly volatile, are lost more or less completely during dry ashing even at 500 °C. At higher temperatures, elements like K are also reported to be lost. The ash is dissolved in 2 mL of 6*N* HCl, heated on a hot plate to near dryness and taken in 10 mL dilute HCl (0.01*N*) or 20% aqua regia before making up the final volume with deionized water. These extracts contain different amounts of insoluble materials, mainly silica, depending upon the plant species. These insoluble materials settle down on keeping for sometime or can be separated by filtration before estimation of different elements. All elements, except N and S, can be estimated in these extracts by any known technique. In general, the results obtained by this method, are quite satisfactory and are comparable with those obtained by wet digestion procedures (Table 6). Moreover, B can only be determined by dry-ashing since it is volatilized during wet digestion with di- or triple-acid mixtures.

3.2.2. Wet Digestion

The powdered plant samples can also be dissolved by digesting in acids, usually HNO_3, $HClO_4$ and H_2SO_4 . These acids are used either singly or in combinations of two or three acids, e.g. a di-acid combination is HNO_3 and $HClO_4$ (in 3:1 ratio) or a triple acid is a mixture of HNO_3, $HClO_4$ and H_2SO_4 (in 9:3:1 ratio). A triple acid combination destroys the organic matter in a shorter time without any hazard but is unsatisfactory for plant materials with high Ca and in cases where S is one of the test elements. The insoluble sulphate renders the method unsuitable because of adsorption of different element ions on the precipitate and exclusion of Ca from the analysis. The use of perchloric acid in the di- or triple-acid digestion mixtures results in the formation of sparingly soluble potassium perchlorate, resulting in lower estimates of K, especially when the plant material contains more than 1% K (Arora and Bajwa, 1994). The sparingly soluble potassium perchlorate may act as adsorption sites for other elements and thus may decrease their estimated values. As such, for multi-element analysis, the plant materials should be digested in nitric acid alone (Table 6).

For wet digestion, finely powdered plant sample (0.5 g) is kept overnight in a 25 cm long digestion tube with 5 mL conc. nitric acid. The digestion is carried out in the tube digestor at about 125 °C till about 2 mL of the digest is obtained. The digest has a pale yellow colour and a kind of insoluble scum in samples high in oil/fat which can be removed by further

Table 6. Effect of method of oxidation on the estimation of elemental composition of 11 different plant materials (Mean values)

(mg/kg)

Element	Method of oxidation				
	Dry ashing	HNO_3	Di-acid* (3:1)	Di-acid*(10:1)	C.D. (5%)
P	2807	2922	2679	3024	230
K	16083	16957	8662	15281	3192
Ca	10133	10320	9463	10203	308
Mg	3673	3862	3487	3789	168
S	2283	3058	2943	3083	218
Zn	46.5	48.4	46.1	49.0	2.4
Cu	7.65	8.04	7.34	7.87	0.42
Fe	307	318	286	297	N.S.
Mn	116	120	108	121	8.8
B	30.8	31.5	27.4	30.5	2.5
Na	631	635	553	638	59
Al	271	232	228	229	16.2
As	4.58	6.26	5.62	6.16	1.01
Pb	3.96	6.57	6.62	6.53	0.99
Cd	0.197	0.217	0.243	0.252	0.036
Co	1.283	1.336	1.328	1.373	N.S.
Ni	0.947	1.020	1.003	1.096	N.S.

Source: Arora and Bajwa (1994)

Note: *Di-acid is a mixture of nitric and perchloric acids

digesting with 2 mL of 30% hydrogen peroxide (H_2O_2) until again 2 mL of the digest is obtained. After cooling, the desired volume is made up with deionized water.

3.3. Analysis

The extracts obtained by digesting with nitric acid alone or in combination with hydrogen peroxide are suitable for analysis of all the elements including, B, except N, on a flame photometer, atomic absorption spectrophotometer as well as ICAP-AES.

3.4. Interpretation

The plant analysis results are interpreted as deficient, low, sufficient, high and very high or excess on the basis of the respective concentration ranges of various nutrients which vary significantly across different crops. Critical Nutrient Level is defined as the nutrient concentration below which the plants are expected to respond to the application of that nutrient. It is the lower value of the concentration range for sufficient category. Over about past 40 years, lot of data have accumulated and information is available in the bulletins/ books. One such publication is: *Plant Analysis – An Interpretation Manual*, edited by Reuter and Robinson (1997). Critical nutrient values for some crops are given in Table 7.

4. Analysis of Fertilizers

Generally, in fertilizer analysis the estimations are made for nitrogen, phosphorous, potassium, calcium, magnesium, sulphur and micronutrients. The methods are briefly described here and for more details, other publications may be referred (Anonymous, 2011; Tripathi, 2005).

4.1. Major Nutrients

4.1.1. Nitrogen

For the estimation of nitrogen in a fertilizer, its samples are solubilized by digesting in a digestion mixture consisting of H_2SO_4 and SeO_2 till a colourless digest is obtained. The

Table 7. Critical levels of nutrients for different crops

Crop	N	P	K	Ca	Mg	S	Zn	Cu	Fe	Mn	B
			(%)						(mg/kg)		
Wheat	2.00	0.11	1.00	0.10	0.10	0.15	10	3	10	10	5
Rice	1.96	0.10	1.00	0.15	0.10	0.09	10	3	70	20	6
Groundnut	2.50	0.25	0.60	1.25	0.30	0.20	20	6	50	50	25
E.Clover	X	0.15	1.30	0.20	0.15	0.20	15	5	30	15	10
Cotton	3.60	0.30	0.90	1.00	0.30	0.18	20	4	30	30	8
Chick pea	4.00	0.15	1.70	1.20	0.30	0.15	20	5	50	64	15
Sugarcane	1.80	0.18	1.30	0.14	0.09	0.13	15	1	5	15	1
Maize	3.00	0.16	1.25	0.10	0.10	0.20	11	3	10	15	5
Sunflower	3.20	0.20	1.80	1.40	0.31	0.43	20	3.7	60	41	29
Kinnow	2.40	0.07	0.40	2.00	0.15	0.21	15	4	40	20	15
Grapes	0.80	0.10	0.60	0.87	0.20	0.08	20	5	35	30	13
Guava	1.31	0.14	1.30	0.89	0.25	0.20	28	10	144	202	X
Peach	2.40	0.09	1.00	1.00	0.20	0.10	15	3	60	20	15
Pear	2.30	0.10	0.70	0.80	0.13	0.10	10	5	60	20	20
Litchi	1.30	0.80	0.80	0.50	0.40	0.10	15	5	50	50	25
Mango	1.00	0.08	0.30	1.00	0.20	0.15	20	10	70	60	50
Potato	2.50	0.15	2.25	0.30	0.15	0.30	15	2	11	10	2
Cauliflower	2.50	0.15	2.00	5.00	0.25	0.30	15	3	50	25	20
Tomato	3.00	0.30	2.00	0.60	0.50	0.50	25	5	100	50	30
Peas	2.70	0.30	1.80	1.10	0.35	0.20	40	10	50	40	15

Source: Collected from various sources in *Plant analysis — An Interpretation Manual*, edited by Reuter and Robinson (1997); *Soil & Plant Analysis – Agronomy Handbook*, edited by Don Ankarman and Richard Large.

nitrogen in different forms gets converted to ammonium form which can be estimated by either micro-Kjeldahl distillation apparatus or Auto-Analyzer. However, the water-soluble NH_4^+-containing fertilizer can be analysed without digestion.

4.1.2. *Phosphorus*

For the estimation of total phosphorus in fertilizers, the samples are digested as for nitrogen estimation (as above). Phosphorus in the diluted extracts is estimated colorimetrically using the vanado-molybdate yellow colour method. Alternatively, P can be estimated by emission spectroscopy technique using ICAP-AES.

4.1.3. *Potassium*

Fertilizers containing potassium (potassium chloride and potassium sulphate) are water soluble and have small insoluble impurities. Since the flame photometer is capable of measuring K up to 10 ppm only, the fertilizer will need a dilution of about 40,000 times. This can be obtained in two steps, first by dissolving 0.5 g of the fertilizer in a 500 mL measuring flask first and then diluting 2.5 mL of this solution to 100 mL.

4.1.4. *Calcium and Magnesium*

In fertilizers, the calcium and magnesium could be present as chloride, nitrate, sulphate or carbonate. While nitrate, chlorides and sulphates are water soluble, the carbonate is soluble in an acid only. Therefore, while preparing solutions, the materials containing calcium and magnesium are dissolved by boiling in 1:1 HCl, which is suitably diluted before estimation by versenate (EDTA) titration method, or by emission or absorption spectrophotometers

4.1.5. *Sulphur*

Sulphur-containing fertilizers are water soluble, except those containing elemental S or less soluble calcium sulphate. Solutions of nitrate-free fertilizers such as sulphates of ammonium, potassium, zinc, copper, ferrous and manganese, N-P and N-P-K complexes and mixtures, are prepared in dilute hydrochloric acid (about 3*N*). Samples of single superphosphate are dissolved by boiling in 1:1 HCl. The solutions are filtered through Whatman filter paper No. 40. Sulphate is determined by gravimetric method involving precipitation by barium chloride. The weight of the barium sulphate formed is then used to calculate the percentage of sulphate in the sample (Anonymous, 2006; Tripathi, 2005)

4.2. Micronutrients

Almost all the micronutrient carriers except their oxides are water soluble and are determined as follows.

Method — A known weight (0.250 g) of the micronutrient fertilizer is transferred into a 250 mL measuring flask and is dissolved in 100 mL of deionized water. About 5 mL of 6*N* HCl or 40% aqua regia are added to acidify the medium and the final volume is made up with deionized water. These solutions can be directly analysed on an ICAP-AES. For analysis on an atomic absorption spectrophotometer, the detection limits are much lower and further dilution of this solution would be needed. For a micronutrient fertilizer containing about 20% of the element, an aliquot (1 mL) of the solution prepared as above is transferred to a 100 mL measuring flask and volume is made up with deionized water. This solution will be around 2 ppm with respect to the element to be analysed.

5. Instrumental Analysis

The elemental concentration in the prepared extracts of soils as well as plants can be determined by a number of analytical procedures with some elements determined by more than one technique. All but a few analytical procedures involve some form of spectroscopy, the utilization of specific wavelengths of light and their intensity to determine elemental concentration. These basic procedures are absorptiometry, emission spectroscopy, atomic absorption spectroscopy, specific ion electrodes and ion chromatography, which are briefly described below:

5.1. Absorptiometry

The radiant energy may be absorbed, entirely or partly, by the molecules in a medium. The absorption involves the transfer of energy to the medium. The absorption process is a specific phenomenon which is related to the characteristic molecular structure of the medium. The absorption spectrophotometry refers to the measurement of radiation absorbed by or transmitted through a solid or solution in the visible, ultraviolet or infrared wavelength regions of the electromagnetic radiation. The absorption of light in the visible region, usually by a solution, is also called colorimetry. The fraction of the intensity of the incident light, which is transmitted through the medium/solution is termed as 'Transmittance', i.e.

$$T = P / P_0 \qquad \text{...(1a)}$$

where, P and P_0 are the intensities of the transmitted and incident lights, respectively. The percentage of light transmitted (%T) is correlated with the presence and concentration of a particular element or ion in solution. When the per cent transmittance is plotted against the concentration, a curve is obtained which shows that the %T is not proportional to the concentration. A quantitative insight into the relationship of light absorption to the concentration is defined by Beer-Lambert Law; according to which

$$\log_{10}(P_0 / P) = abc \qquad \text{...(1b)}$$

where, $\log_{10}(P_0/P)$ is called absorbance (A) or optical density. It is a function of the constant absorptivity, 'a', of the substance, the thickness, 'b', of the absorbing medium and concentration, 'c', of the coloured ions or molecules in the solution. The value of the constant 'a' depends upon the (i) wavelength of radiation, and (ii) nature of the absorbing material.

Therefore, the combined Beer-Lambert Law is expressed by Equation (2):

$$A = abc \qquad \text{...(2)}$$

Thus, absorbance of a light absorbing medium is defined as the product of absorptivity, the length of the optical path, i.e. the diameter of the test tube containing the solution and the analyte concentration.

Since $(P_0 / P) = 1 / T$ (T = Transmittance) ...(3)

$\log (1 / T) = abc$ ...(4)

Hence, $A = \log (1 / T)$ or $\log (100/ \%T)$ ...(5)

A spectrophotmeter is a relatively inexpensive instrument and easy to use. The main components in a spectrophotometer include a light source, a means of obtaining a monochromatic beam of light, a sample holder or cell and a detector. The more sophisticated spectrophotometers employ either a prism or grating in lieu of the interference filter to obtain a specific wavelength (monochromatic) of light, thereby improving their performance.

5.2. Atomic Emission Spectrophotometry (AES)

When a salt is introduced into a flame, a characteristic light is usually seen. For example, with a sodium salt, this light is yellow in colour, and with a copper salt, it is green in colour. Emission of such characteristic radiation by each element and the correlation of the emission intensity with the concentration of that element forms the basis of the emission spectroscopy. Therefore, 'emission spectroscopy is the measurement of the intensity of characteristic wavelengths emitted by different elements when excited by a source of energy'.

The Quantum Theory predicts that each atom or ion has definite energy states in which the various electrons can exist. In the normal or ground state, the electrons are in the lowest energy state. On addition of sufficient energy by thermal, electrical or plasma sources, one or more electrons may be excited to a higher energy state and they move farther from the nucleus. These excited electrons tend to return to the ground state and in doing so, emit the extra energy as a 'Photon' of radiant energy. Since there are definite energy states and only certain transitions are possible, there is a limited number of wavelengths possible in the emission spectrum. The greater is the energy in the source, the higher is the energy of the excited electron and therefore, more is the number of the lines that may appear. However, the wavelengths of the existing lines will not change.

The relation between the frequency 'v' of the radiation emitted to the energies E_1 and E_2 of the two states of the atom is given by the expression (6):

$$E_2 - E_1 = hv \quad ...(6)$$

or,

$$E_2 - E_1 = hc / \lambda \quad ...(7)$$

where, 'h' is the Planck's constant (6.6256×10^{-27} erg sec), 'c' is the velocity of light (2.9979×10^{10} cm/sec) and 'λ' is the wavelength of the emitted radiation

3.2.1. Sequence of Events in Emission of Radiation by Atoms

When an aerosol is uniformly delivered into a source of energy, the following sequence of events takes place:

(i) The water or other solvent is vaporized, leaving minute particles of dry salt [Equation (8)]:

$$NaCl\ (l) \rightarrow NaCl\ (s) \quad ...(8)$$

(ii) The dry salt is vaporized and a part or all of the gaseous molecules are progressively dissociated to give neutral atoms which are the potentially emitting species [Equations (9) and (10)]:

$$NaCl\ (s) \rightarrow NaCl\ (g) \quad ...(9)$$

$$NaCl\ (g) \rightarrow Na^{o}\ (g) + Cl^{o}\ (g) \quad ...(10)$$

(iii) The vapours of the neutral metal atoms or of molecules containing the metal atom are then excited by the thermal energy of the source. Ionization of the neutral atoms may also occur to some degree [Equation (11)]:

$$Na^{o}\ (g) + \text{Energy} \rightarrow Na^{ex} \rightarrow Na^{+} + e^{-} \quad ...(11)$$

(iv) Some of the free metal ions unite with other radicals or atoms present in the flame gases [Equation (12)]:

$$Na^{+} + OH^{-} \text{ or } O^{2-} \text{ (from flame gases)} \rightarrow NaOH \text{ or } Na_2O \quad ...(12)$$

(v) From the excited state of the atom or molecule or ion, a reversion takes place to the ground electronic state, (a) partly by impacts with other species, and (b) partly spontaneously by emission of light.

Subsequently, the neutral atoms, ionized atoms and the molecules of NaOH and Na_2O will be excited and their characteristic spectra will appear in emission.

Note: The spectrum of an ionized atom (ion) is quite different from that of a neutral atom. In fact, the spectrum of a singly ionized atom will bear a strong resemblance to that of the neutral atom of atomic number one less.

5.2.1. Common Instruments in AES

Common instruments based upon the technique of emission spectroscopy are:

- Flame Photometer
- Electric Spark/Arc Emission Spectrophotometer
- Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer (ICAP-AES)

5.2.1.1. Flame Photometer

The first development in emission spectrophotometry that had a significant impact on soil testing and plant analysis was the flame photometer which first appeared in 1950s, making potassium and sodium determinations easy. The gas flame as a source of excitation for atomic emission has been used extensively under the name of 'Flame Photometry'. It is used principally for the estimation of alkali and alkaline earth metals. The intensity of radiation from the flame at a wavelength of a given element is directly proportional to its concentration. A flame photometer consists of:

(i) Pressure regulators and flow meters for the fuel gases

(ii) Atomizer

(iii) Burner

(iv) Optical system

(v) Photosensitive detector, and

(vi) Instrument for indicating or recording the output of the detector.

Flames and Flame Temperatures — A flame is used for:

(i) transforming the sample to be analysed from the liquid or solid state into the gaseous state,

(ii) decomposing the molecular compounds of the test element into neutral atoms, and

(iii) exciting the neutral atoms to light emission.

Many combustible gases have been utilized for obtaining a range of temperatures (Table 8).

Table 8. Flame temperatures of different mixtures of gases

Fuel	Flame temperature (°C) In air	In oxygen
Illuminating gas	1700	2700
Propane	1925	2800
Butane	1900	2900
Hydrogen	2100	2780
Acetylene	2200	3050
Cyanogen	2330	4550

An ordinary air-gas flame, because of its low temperature (about 1700 °C) is only energetic enough to excite about a dozen elements, chiefly alkali and alkaline earth metals. Mixtures of hydrogen and acetylene with oxygen produce much hotter flames and correspondingly greater excitation.

Emission Intensity vs Concentration —When interferences are absent, the procedure for calibrating a flame photometer for a given metal is as follows: When the flame burns properly and the correct filter is in place, or the monochromator has been set at the correct wavelength, the deionized water is introduced into the atomizer and the background emission is recorded or zero suppression controls are adjusted to bring the instrument reading to zero. Next, the most concentrated standard is introduced and the sensitivity is adjusted so that the maximum scale reading or 100 is attained. The zero reading is rechecked and adjustments, if any, are made. These two steps are repeated until duplicate readings are within one scale division out of 100 total divisions. Then several standards of lower concentrations are introduced in turn and the respective readings are recorded. The instrument readings are plotted on the axis of ordinates versus concentrations on the axis of abscissa to produce the calibration curve.

5.2.2.Electric Spark/ Arc Atomic Emission Spectrophotometer

Due to lower temperature of gas flames, the flame photometers can be used for the estimation of alkali metals and alkaline earth metals only. For the estimation of heavy metals, high temperature sources like electric arc or spark (around 3000 °C) are used. As many elements can be excited simultaneously, such instruments are equipped with a better dispersing system like diffraction grating, photodetectors like photomultiplier tubes and recording devices like typewriters to measure the intensity of multi-elements at the same time. Such instruments are called atomic emission spectrophotometers.

5.2.3.Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer (ICAP-AES)

Another major excitation mechanism operates through a plasma produced electrically in a carrier inert gas such as nitrogen or argon. The energy levels of argon make it suitable for plasma production and it has the advantage of chemical inertness.

A 'Plasma' may be defined as a neutral gas, containing significant number of both positive and negative ions or free electrons. A plasma can only be created and maintained by the continued injection of enough energy to ensure that new ions are created fast enough to compensate for those that are continually recombining to form neutral atoms.

The ICAP source consists of three concentric quartz tubes through which argon flows and a two- or three-turn gold plated copper coil surrounding the tubes near the upper end. Alternating current at a frequency of 27.14 MHz and power levels up to several kilowatts is passed through the copper coil. Once some ions have been produced by means of an auxiliary spark circuit, a heavy current is caused to flow in a circular path in the ionized gas, powered by magnetic induction. This raises the temperature of the resulting plasma to some 10,000 K. This is far above the softening point of quartz. The plasma torch is protected from destroying itself by using the flow of argon as a coolant. The bulk of the argon enters the outer tube at a tangential angle, so that it swirls through the annular space at high speed, thus moderating the temperature. The hot plasma tends to stabilize in the form of a toroid at a little distance from the walls and this also serves to prevent overheating.

The sample is aspirated in a nebulizer and is carried by a slower stream of argon directed centrally towards the "hole in the doughnut". The sample gets heated by conduction and radiation and may reach 7000 K, at which it is completely atomized and excited. Loss of analyte atoms by ionization, a source of difficulty in flame and spark does not occur significantly in ICAP spectroscopy, presumably because of the presence of more easily ionized argon atoms.

The advantages of ICP-AES are:

- High quality multi-element simultaneous analysis
- Refractory elements like P, B, W, Zr and U can be determined
- High linear dynamic range
- Exceptional stability over long periods of operation
- Excellent detection limits – 0.1 to 10 ppb
- Reduced inter-element effects
- Background emission interference is nil
- Self-absorption of radiation is nil, and
- Loss of analyte atoms by ionization does not occur significantly because of the presence of more easily ionized argon atoms.

5.3. Atomic Absorption Spectrophotometry (AAS)

The atoms in the non-excited, non-ionized, ground states are capable of absorbing light at characteristic wavelengths which they otherwise emit when excited. That makes the underlying principle of atomic absorption spectrophotometry. A resonant line of some intensity is decreased when passed through the flame containing atoms of the same element as the cathode of the generating lamp. A monochromator is used to isolate that line or wavelength from the remainder of the emitted radiation. The intensity of the radiation is measured with and without the sample to obtain a reading in per cent absorption and the concentration of the element of interest is determined by comparing the reading to the one obtained for a standard or series of standards. The instrument can also be calibrated to read directly in concentration.

The instrumentation used for atomic absorption is similar to that used for flame emission, except for the source of radiation to be absorbed by the atoms in the flame. The narrow line emission radiation which is to be absorbed by the dissociated atoms is typically generated by a specific lamp called 'Hollow Cathode Lamp'. It consists of a glass or quartz envelope containing two electrodes, the cathode of which is cup-shaped and made of a specified element. The material of which anode is made is not critical. The lamp is filled with a noble gas such as neon or argon under low pressure. The front face of the lamp is made up of quartz or any of the several types of glass, depending on the wavelength it must emit. The application of 100 or 200 volts will produce, after a short warm-up period, a glow discharge with most of the emission coming from within the hollow cathode. Positive ions from the inert gas bombard the cathode, removing metal atoms by a process known as sputtering. These atoms can then accept energy of excitation and emit their characteristic radiations. The emissions consist of discrete lines of the metal plus those of the fill gas. Single element and multi-element lamps are available. It is possible to fabricate hollow cathode lamps with a mixture of several metals lining the cathode cup as long as they do not interfere spectrally with each other and provided that they require about the same amount of energy for vaporization. This makes it possible to determine several elements without the necessity of changing lamps. Some examples of multi-element hollow cathode lamps are:

Ca, Mg and Al;
Fe, Cu and Mn;
Cu, Zn, Pb and Sn; and
Cr, Co, Cu, Fe, Mn and Ni.

Compressed air and acetylene gas are most commonly chosen as oxidant and fuel, respectively. The maximum temperature attainable is about 2200 °C. When higher temperature is needed, nitrous oxide can be substituted for the air. This gas decomposes to give a 2:1 mixture of nitrogen and oxygen, compared to 4:1 ratio in air. The highest temperature it can reach on burning acetylene is almost 3000 °C. Pure oxygen cannot be used with acetylene because the flame propagates so rapidly that flashback cannot be avoided.

During the recent past, electrical heating as an alternative to the flame has become more popular. Several types of heaters have been proposed of which the most successful consists of a small tube of graphite. It is heated by passing through it a large current, up to 500 A, at low voltage. The tube, often called graphite furnace, must be surrounded with an atmosphere of an inert gas such as argon to prevent oxidation of both the sample and the hot carbon. The temperature of the graphite atomizer is generally programmed in three stages. It is first raised to about 300 °C for about a minute to evaporate the solvent. Any organic matter is then removed by charring at about 1700 °C for another minute or so. Only after this, the temperature is increased to the point needed to dissociate inorganic compounds into atoms; this may require a temperature as high as 3000 °C. Each of these time intervals and temperatures can be varied to meet the requirements of different samples.

The advantages of atomic absorption spectrophotometry are:

- Highly specific for the element of interest
- Spectral interferences are almost non-existent
- Two spectral lines would have to coincide within 0.5 nm. Only a few such coincidences occur, almost none with analytical significance. Molecular absorption can occur, but is usually overcome easily by the use of higher temperature flames, e.g. nitrous oxide-acetylene.
- Interferences are few and are easily removable.

- Detection limits are improved for a number of important elements compared with flame emission.
- Atomic absorption requires that an element be completely dissociated from its chemical bonds. It is easily achieved at temperatures below the air-acetylene flame temperature (2200 °C) for many elements. Therefore, small differences in temperatures or chemistry of the flame will have little effect on most elements.
- Instrumentation is extremely simple to operate, eliminating the need for highly trained personnel.

5.4. Ion Chromatography

Ion chromatography (IC) is used for the determination of a large number of anions and cations using the phenomenon of ion exchange for the separation and many detection techniques like conductivity, UV/visible absorbance detectors, etc. It is commonly employed for anions like fluoride, chloride, nitrite, bromide, nitrate, chlorate, phosphate, sulphate, etc.; and cations like lithium, sodium, ammonium, potassium, magnesium, calcium, etc. and also for heavy metals. Ion chromatography with conductivity detection compliments the traditional HPLC. It is specially useful when the analytes do not contain chromophores, or when it is desirable to determine chromophoric and non-chromophoric molecules in a single run.

5.5. Specific Ion Electrodes

Specific ion electrodes work on the same principle as that of the glass electrode used for measuring H-ion concentration. These electrodes employ liquid or solid ion exchange membranes, or solid membranes composed of single crystals, or precipitates compressed into a plug or dispersed in a matrix such as silicon rubber. The membrane separates sample from the electrode filling solution and is selective for the ion being determined. A potential develops across the membrane, depending on the ion concentration in the unknown solution and is measured against a constant reference potential with a specific solution as described by the Nernst equation [Equation (13)]:

$$E = E_0 - S \log (A) \qquad \ldots(13)$$

where,

E = Measured electrode potential,
E_0 = Reference potential (a constant),
A = Ion concentration in unknown solution, and
S = Electrode slope.

Specific ion electrodes are available for determining a number of elements. These are widely used for the determination of nitrate, chloride and fluoride anions in soil extracts and ammonium in soil and plant digests. The instrument components are: specific-ion electrode and reference electrode (these may be separate electrodes or as one combined electrode), and a recording meter. The advantages of the specific ion electrodes are speed of determination and simplicity of operation. However, these are not without limitations, which include lack of sensitivity when the analyte of interest is in low concentration and interferences.

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Chapter 22

Soil Fertility Evaluation

G.S. SEKHON, M. VELAYUTHAM and D.K. BENBI

1. Introduction

Crop production broadly depends on the fertility of the soil where a crop is raised. The kind and quality of seed, climate of the region, soil moisture regime and plant protection measures adopted by a farmer are some of the other factors which affect the quantum of production. But even if all these factors of crop production are in the optimum, the fertility of a soil largely determines the ultimate yield. The differences in crop production resulting from the manipulation of soil fertility are depicted in Figure 1.

During the early period of our civilization when population was sparse, and land was plentiful, people settled along riversides where annual flooding enriched the soil. At other places, shifting cultivation was adopted to give rest to the land and regain soil fertility. When settled agriculture came to be practised and farmers learnt the advantages of adding animal and vegetable manures, their use gradually picked up. In course of time, the value of green manure crops, particularly legumes was also recognized. The period from the middle of nineteenth century to the beginning of twentieth century marks an era during which much progress was made in the evaluation of soil fertility and its improvement with the addition of manures and fertilizers. Jean Baptiste Boussingault (1802-1882), a widely travelled French Chemist, established a farm in Alsace to carry out field plot experiments. He carefully added analyzed manures to his plots and properly weighed the harvested crops, to maintain a balance sheet, which showed inputs from rain, soil and air. At about the same time, Justus von Liebig (1803-1873), a German Chemist, made some remarkable statements, many of which hold the ground even today. He stated, for example, that carbon, hydrogen and oxygen contained in the plants are obtained from carbon dioxide and water; the alkaline metals are needed for neutralization of acids formed during the metabolic activities in the plants; phosphates are necessary for seed formation, and plants absorb everything indiscriminately from the soil, but excrete from their roots those materials that are non-essential. He also propounded the 'law of the minimum', which says that "Every field contains a maximum of one or more and a minimum of one or more nutrients. With this minimum, be it lime, potash, nitrogen, phosphoric acid, magnesia or any other nutrient, the yields stand in direct relation. It is this factor that governs and controls the yield. With this minimum, the yield will remain the same and not increase even though amounts of nutrients be increased a hundred fold."

In 1843, J.B. Lawes and J.H. Gilbert established an agricultural experiment station at Rothamsted, England. By 1855, they settled the following points:

(i) Crops require both phosphorus and potash, but plant composition is no guide to their requirements by the crop.

(ii) Non-leguminous crops require a supply of nitrogen for their growth and development.

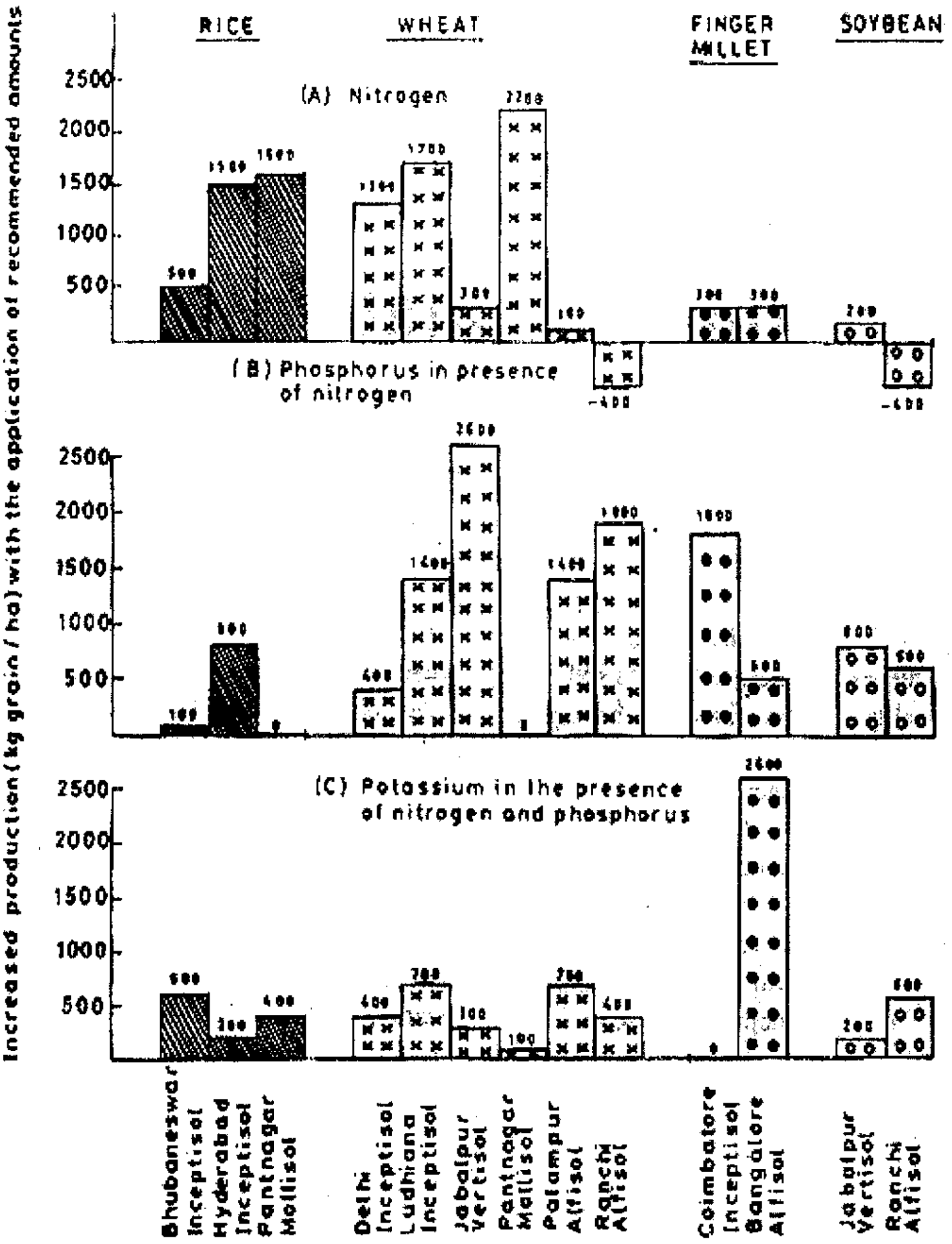

Figure 1. Increase in crop production from improvement in soil fertility

The contribution of ammonia nitrogen by the atmosphere is insufficient to meet the crop needs.

(iii) Soil fertility can be maintained by means of chemical fertilizers.

(iv) The beneficial effect of fallow lies in the increase in availability of nitrogenous compounds in the soil.

Later, many experiment stations around the world started long-term fertilizer experiments. These studies showed remarkable benefits from the use of animal manures and fertilizers, fallowing and green manuring and tremendous depletion of soil fertility with concomitant yield reductions as a consequence of continuous cropping without addition of manures or fertilizers.

2. Nutrient Deficiency Symptoms of Plants

As already mentioned (Chapter 15), the cultivated plants require nine macronutrient and eight micronutrient elements for their optimum growth and development. There are considerable differences amongst crops and cultivars of the same crop in the amounts of these elements absorbed by them from the soil, the differences being larger in case of micronutrients. The nutrients in a germinating seed usually meet the needs of the embryonic plant for the first few days of its life-cycle. Plant roots are the first to come out. Later, the emerging shoots with the help of stored nutrients and photosynthesis, make the plants grow. Plant growth involves a large number of enzymatic reactions and metabolic processes, which depend upon adequate supplies of nutrients. When a nutrient element is deficient in soil, certain deficiency symptoms, which are more or less characteristic for the plant and the nutrient, may appear. This abnormal appearance on a growing plant is a visual method of evaluating soil fertility and diagnosing the malady affecting the plant. The deficiency symptoms mostly express themselves in terms of stunted growth of plant, discolouration of the leaves and veins, pigmentation of various descriptions, shape and size of the fruit and delay in maturity.

The deficiency symptom of an element is not a direct expression of the deficiency of that nutrient. Apparently, a nutrient deficiency may disturb the plant metabolism, leading to the production of certain intermediate organic compounds in relative abundance and consequent shortage of some others. This abnormal situation expresses itself in the form of a deficiency symptom.

Nitrogen, for example, is one element that is deficient in many soils. When the quantity of nitrogen is less, the production of chlorophyll decreases and carotene and xanthophyll – the yellow pigments – show up. The leaves of cereals, suffering from phosphorus deficiency, on the other hand, develop a dull greyish-green colour, and a red pigment in the leaf bases due to anthocyanins. Some potassium-deficient plants accumulate diamine putrescine with characteristic symptoms. Another symptom of potassium-deficiency is the premature death of the older leaves because potassium is highly mobile and is transported rapidly to the younger leaves. Sulphur-deficient plants have increased levels of amines, amides and nitrates due to restricted synthesis of nitrogenous substrates as proteins and hence, reduced amounts of chlorophyll. For this reason, deficiency of both nitrogen and sulphur causes chlorosis with resultant yellowing of leaves. However, there is a subtle difference. Sulphur is relatively immobile within the plant. Hence, newer leaves of S-deficient plants usually show chlorosis earlier than the older leaves. On the other hand, nitrogen is highly mobile within the plant and therefore N-deficient plants show chlorosis first on the older leaves.

Zinc is known to be an essential constituent of three plant enzymes– carbonic anhydrase, alcohol dehydrogenase and superoxide dismutase. Zinc also appears to be required in the synthesis of auxin via intermediates in the metabolic pathway, through tryptophan to auxin. Owing to disturbed auxin metabolism, zinc-deficiency often shows itself in the failure of leaves to expand and stems to elongate, giving a terminal rosette effect. In the zinc-deficient trees of citrus, apple and peach, the mature leaves may show pale green to yellow interveinal mottling. In zinc-deficient maize crop, the older leaves may have purple fins, while younger leaves may develop yellow or white interveinal chlorotic stripes. The symptoms of deficiency of a few nutrients in some selected crops are depicted in colour at the end of this book.

Although deficiency symptoms are excellent diagnostic aids for detecting nutrient deficiencies in soils, they have the following limitations:

(i) It is not easy to relate a deficiency symptom to the deficiency of a particular nutrient. The yellowing of the leaf or chlorosis is shown with deficiency of more than one nutrient element. A trained eye and the history of the soil management can arrive at a reasonably good preliminary diagnosis of the malady, provided there is no other interfering factor at work.

(ii) A disease or insect damage may resemble certain minor element deficiencies.

(iii) A multiplicity of deficiencies or extenuating factors may further complicate the diagnosis. For example, accumulated sugar in maize may combine with flavines to form anthocyanins (purple, red, and yellow pigments). Sugar accumulation may result from an insufficient supply of phosphorus, cool nights and warm days, insect damage to the roots, nitrogen deficiency, etc. Of course, a careful analysis of the situation can help arrive at a very good guess of the causative factor.

(iv) Nutrient deficiency symptoms are observed only after the crop has already suffered an irretrievable loss. However, in cases where the deficiency symptoms are observed early, it may still be possible to correct the deficiency to some extent and harvest a modest crop.

However, a study of deficiency symptoms cannot be dismissed regarding it as of little use. A judicious utilization of deficiency symptoms together with other diagnostic techniques such as soil testing and plant analysis, certainly do a lot to promote efficient crop production through a wise use of manures and fertilizers.

3. Evaluation of Soil Fertility

Evaluation of soil fertility consists of estimating the nutrient–supplying power of a soil. A proper evaluation of the fertility of a soil before planting a crop helps in adopting appropriate measures to make up for the shortcomings and ensuring a good crop production. These methods for evaluating the soil fertility may be biological or chemical.

3.1. Biological Methods

The biological methods consist of raising a crop or a microbial culture in a field or in a sample of the soil, and estimating its fertility from the volume of crop or microbial count. Although these methods are direct estimates of soil fertility, they are time-consuming and, therefore, not well adapted to the practice of soil testing. On the other hand, chemical testing of a soil is reasonably rapid and is, therefore, more handy for advisory work on a mass scale.

3.2. Chemical Methods

The chemical methods for evaluating the soil fertility consist of analyzing a sample of the soil for its content of essential plant nutrients, which are expected to be in relatively short supply and whose deficiencies can be corrected by appropriate additions of suitable fertilizers. One of the approaches could be to analyze a soil for the total content of a nutrient by digesting the soil sample with strong acids or alkalis, but this technique was given up when it was found to have a poor relationship with plant-available quantities of the nutrient. So, the usual practice today is to obtain an extract from a sample of soil by adding to it a small volume of a solution containing mild chemical reagents. For this, soil is air-dried and ground to pass a 2-mm sieve. The nutrient concentration is measured in an aliquot of the extract and results are expressed in terms of the quantity of that nutrient on per unit mass of soil or on volume basis. For a detailed description of the methods usually followed in soil testing, readers may see Chapter 21.

The choice of a chemical method to estimate nutrient availability in soils involves a selection of the most appropriate extractant and definition of the extracting procedure which may together remove quantities of the nutrient that are highly correlated with the biological index of nutrient availability on a group of soils. There is always some theoretical basis for the choice of an extractant. Ranking of different chemical methods of soil testing depends upon the analysis of the selected group of soils by each of the methods, correlating the sets of estimates with the biological indices and listing them in the order of the coefficients of correlation. Sekhon and Velayutham (1978) have discussed the limitations of present soil test methods and their interpretation for estimating available potassium in soils of India.

3.2.1.Multinutrient Extractants

The analysis for more than one nutrient through a single extract simplifies soil testing. A combination of equilibrant and extractant was proposed by Baker and Amacher (1981). Their solution contains 2.5×10-4 molar potassium chloride, 10×10-4 molar magnesium chloride, 50×10-4 molar calcium chloride, and 4×10-4 molar diethylaminetriamine penta acetic acid (DTPA), and is buffered at pH 7.3, with triethanolamine. The proposed concentrations of potassium, magnesium, and calcium chosen for the test solution, represent optimum availability levels for the growth of most crops. The changes in the solution composition during equilibration with the soil provide information on the deviation of soil from the ideal but these do not affect the quantities of micronutrient and trace elements brought into solution by the chelating agent, DTPA. If the concentration of potassium, magnesium or calcium in the solution after equilibration is equal to or greater than the initial concentration, the availability of the ion in the soil is considered adequate. Molar activities of phosphate are also obtained from the same extract. The phosphorus extracted by the Bray and Kurtz ($0.025\ N$ HCl + $0.03\ N$ NH_4F) extractant is considered an index of the quantity factor of that element. In the Baker and Amacher programme, the quantities of nutrients recommended for addition are those needed to bring the soil up to the ideal level plus the amounts expected to be removed by the crops.

Electro-ultrafiltration of soil with water as the extractant was suggested by Nemeth (1979). A suspension of soil in water (1:10) is stirred in the central chamber of an assembly of three chambers, connected by membranes which permit the passage of solutes but not solids. A direct current is passed between electrodes in the outer chambers. It moves anions through the filter to the positive electrode, where they form acids. The cations move through the other membrane to negative electrode, to form hydroxides. Suction is applied to the outer cells to collect nutrient solutions at designated intervals for analysis.

As electro-ultrafiltration proceeds, the successive fractions are removed with the application of increasing voltage. The 50-volt potential is maintained for the first 5 minutes and it is expected to remove potassium ions in soil solution almost quantitatively. The exchangeable potassium is removed thereafter in another 25 minutes at 200 volts. When the electrical potential is raised to 400 volts and temperature to 80 °C, a measure of non-exchangeable potassium is obtained. One disadvantage from which the electro-ultrafiltration method suffers is the high cost of the ultrafiltration units and the limited number of samples, which can be processed per unit per day.

3.2.2. *Interpretation*

The interpretation of soil test results requires a lot of background information and much intuitive thinking. It is useful to know the variation in soils with respect to pH, organic matter and soil texture; and special problems like waterlogging or sodicity. Ordinarily, there is a greater probability of obtaining a profitable response from the applied fertilizer on soils testing low in a nutrient element than from soils testing high in that element. However, when difference in soil test estimate is accompanied by a variation in any one or more of the aforesaid soil attributes, interpretation of soil test results becomes increasingly complex.

One way of interpreting the soil test results is to classify them into low, medium and high categories. Such a classification is based on the observation, as already stated, that a low testing soil, in the absence of an applied nutrient, produces a very poor crop and when a small amount of that nutrient is added to it, the resultant increase in yield is much more in this soil than what would come about from applying an identical amount of that nutrient to a soil which is high or even medium in its native supply (Figure 2).

When adequate background information is available, it is possible to increase the number of soil test categories from three to five, viz. very low, low, medium, high and very high.

3.2.3. *Calibration*

In practice, the use of such a classification to interpret soil test results requires collection of background information. This requires conducting a sufficient number of field experiments covering as large as the range of soil test estimates, encountered in the soil testing laboratory area and developing suitable soil test crop response relationships to describe the situation. This work of determining the caliber of a soil test is known as calibration. The calibration of soil tests can be represented by a linear equation [Equation (1)]:

$$Y = a + bX \qquad \ldots(1)$$

where, Y is the yield of a nutrient X or a crop yield, X is the nutrient element whose deficiency is corrected by applying a fertilizer, and b is the yield increase per unit quantity of the deficient nutrient applied.

The implication of using Equation (1) is that unlimited yields can be obtained from a soil by simply increasing the amount of nutrient

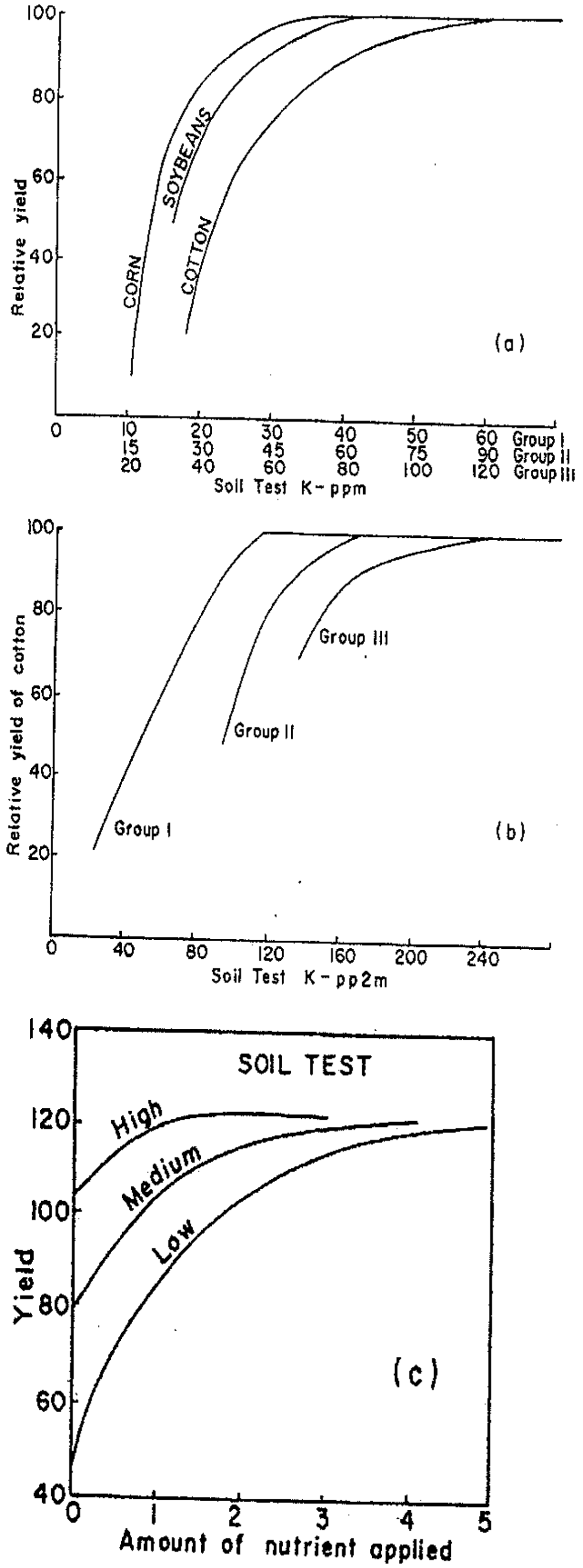

Figure 2. A schematic diagram showing the relationship between a soil test and probability of yield increase with the supply of deficient nutrien: (a) Relationship between soil-test K and relative yields of corn, cotton and soybeans (*Source*: Rouse, 1968); (b) Relationship between soil test K and response of cotton to K in three groups of soils (*Source*: Cope & Rouse, 1973); and (c) Yield response from nutrient additions at three soil test levels (*Source*: Barber, 1973)

X and yield increase with each successive application of deficient fertilizer nutrient is constant, which is an unrealistic proposition. Generally, the crop response to applied nutrient is curvilinear and the yields tend to plateau at higher rates or even decline at excessively high rates of nutrient application. Mitscherlich (1909) hypothesized that there exists a maximum yield for a crop grown on a given soil and the yield increment from fertilizer addition is proportional to the decrement from the maximum. The relationship may be expressed as [Equation (2)]:

$$Y = A(1-e^{-kX}) \qquad \ldots(2)$$

where, A is the maximum yield, X is the deficient nutrient and k is a curvature coefficient. The curvature coefficient, k, may be taken as a measure of efficiency of the applied nutrient in producing maximum yield. The greater is the response curvature, the smaller is the fertilizer requirement at a given soil test value. One of the problems with the Mitscherlich equation is that it is nonlinear in form and needs iterative fitting. Therefore, attempts have been made for more convenient models such as exponential, polynomial (e.g., quadratic), linear plateau, and quadratic plateau with some success. Not only the quadratic but also polynomials of the transformed input variable such as square-root quadratic have been used. The choice of a model depends on the shape of the nutrient-yield response relationship (Figure 3). In the exponential function type, absolute maximum is never reached but does not indicate a toxic level or decrease in yield from an excess of a nutrient. By contrast, the quadratic function provides for a maximum yield, with increasing levels of a nutrient, and then indicates a toxic level or decrease in yield, with further increase in the levels of the nutrient. However, quadratic function could indicate a toxic level or decrease in yield long before such toxicities actually occur under field conditions. Some workers have advocated the use of linear response plateau (LRP) and quadratic response plateau (QRP) models, which imply a response surface with plateau maximum. In the LRP model response range is considered linear as compared to curvilinear in QRP model.

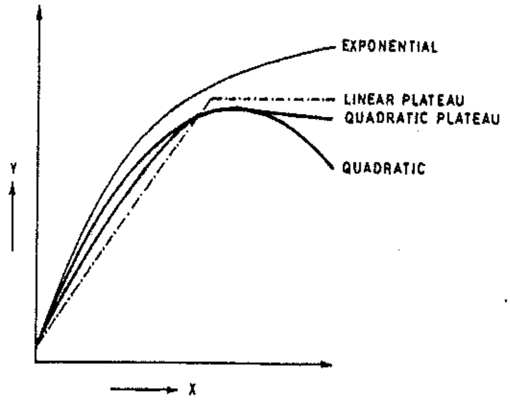

Figure 3. Diagrammatic representation of different nutrient-yield response models

Depending upon the size of the experiment, more than one nutrient and soil test estimates from more than one soil depth can be related with crop yield in a single multiple regression equation.

The crop response to an applied nutrient is not a function of the magnitude of a deficient plant nutrient only. If another nutrient element is simultaneously deficient in a soil, then correcting the deficiency of one of them in the presence of other's deficiency will influence the increase in yield differently than when the deficiencies of both the plant nutrients are corrected together. Often, there may be sizeable interaction effects. Field experiments carefully made can detect them and reflect in the resultant soil test crop response equations.

4. Targeting Crop Yields

Considering the crop yield to be a continuous function of plant nutrient supply in the growth medium, calibrations were obtained for different levels of soil fertility (created in adjacent field plots with addition of different amounts of fertilizers to the preceding crop, in the cropping sequence) with a given crop in a soil (Ramamoorthy *et al.*, 1967). The procedure of creating different levels of fertility artificially in adjacent plots was adopted to ensure homogeneity in soil management and weather, whose diversity in experiments performed at different locations and in different seasons usually leads to poor correlations. From such experiments, fertilizer dose to attain a specified yield target is obtained [Equation 6] by computing three basic parameters, namely (i) NR— nutrient requirement per unit of economic yield, [Equation (3)] (ii) CS— contribution from soil available pool [Equation (4)], and (iii) CF— fractional recovery of applied fertilizer nutrient [Equation (5)].

$$\text{NR (kg nutrient /Mg grain)} = X_f / GY \qquad ...(3)$$

$$CS = X_0 / STV_0 \qquad ...(4)$$

$$CF = [X_f - (STV_f \times CS)]/A_f \qquad ...(5)$$

$$\text{Fertilizer dose (kg/ha)} = \frac{(NR \times T) - (CS \times STV)}{CF} \qquad ...(6)$$

where, X_f and X_0 represent amounts (in kg) of nutrient in the grain plus straw of fertilized and unfertilized crops, respectively; GY is the grain yield (in megagram, Mg), STV represents soil test value (in kg/ha) with subscripts *f* and *0* indicating soil test value of fertilized and unfertilized plots, respectively; A_f is the amount of fertilizer nutrient applied (in kg/ha); T is the target grain yield (in Mg/ha). Soil test based fertilizer recommendations for targeted yield of rice (7 Mg/ha) and wheat (5.5 Mg/ha) grown in alluvial soils of Punjab are illustrated in Figure 4 (Benbi *et al.*, 2007). Subba Rao and Srivatsava (2001) have compiled the soil test based fertiliser recommendations for targeted yields of crops.Similar compilations covering 40 years of work, as Technical Bulletins for extension adoption by the soil testing laboratories have been prepared by the various cooperating centres of the All India Coordinated project on soil test crop response correlation of the ICAR.

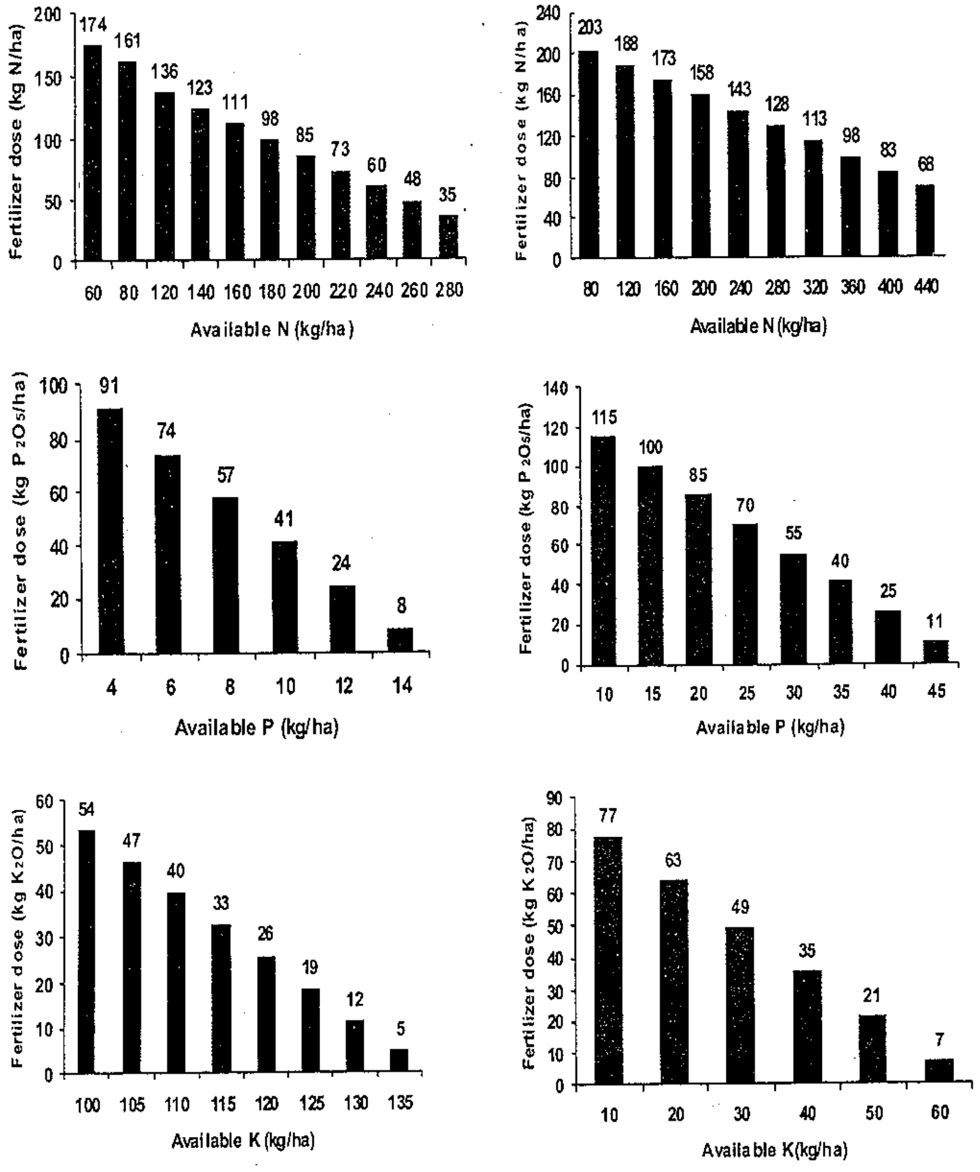

Figure 4. Soil test based fertilizer recommendations for targeted yield of rice (7 Mg/ha) and wheat (5.5 Mg/ha) grown in alluvial soils of Punjab (*Source:* Benbi *et al.*, 2007)

Under integrated nutrient management where inorganic fertilizers are applied together with organic sources, the fertilizer dose to attain a specified yield target is obtained by computing (i) CO-contribution of added organic material towards crop nutrient supply [Equation (7)], and (ii) CF*- fractional recovery of fertilizer nutrient in the presence of added organic source [Equation (8)].

$$CO = [X_{0m} - (STV_{0m} \times CS)]/A_m \quad \ldots(7)$$

where, X_{0m} is amount (in kg) of nutrient in the grain and straw of crop in the organic alone plots; STV_{0m} is the soil test value (kg/ha) of the organic alone plot; A_m represents amount of nutrient (in kg) added through organic source. The fractional recovery of fertilizer nutrient (CF*) in the presence of added organic source is computed using nutrient uptake and soil test data from plots receiving both inorganic fertilizer and organic source, that is integrated nutrient management (INM) plots.

$$CF^* = [X_{INM} - (STV_{INM} \times CS) - (A_m \times CO)]/A_f \quad \ldots(8)$$

The fertilizer nutrient dose for a specified yield target under INM is obtained by Equation (9), subtracting the contribution of organic source in Equation (6):

$$\text{Fertilizer dose (kg/ha) under INM} = \frac{(NR \times T) - (CS \times STV) - (CO \times A_m)}{CF^*} \quad \ldots(9)$$

Reddy *et al.* (1987) and Reddy *et al.* (1989) have reported the optimum C/N ratio and the fertiliser recommendation derived for some crops by using the above formula.

Generally, a precise estimate of contribution of nutrient from soil available pool (CS) is difficult to obtain and most often is the reason for erroneous estimates of fertilizer dose for a targeted yield. The per cent contribution from the soil is influenced by soil type, texture, rooting depth and nutrient release characteristics of the soil. Since the per cent nutrient contribution from soil is obtained by dividing the nutrient uptake in control plots by soil test value [Equation (4)], the approach is heavily biased towards high fertility of native and applied nutrients (Milap-Chand *et al.*, 2004). For example, the per cent P contribution from soil available pool decreases with an increase in soil test value of phosphorus (Figure 5). It could be explained on the basis of increased denominator (STV) without corresponding increase in numerator (P-uptake). Since soil-P status in such fertility gradient experiments is artificially raised by the application of inorganic P fertilizer, the P uptake in control plots does not show significant increase due to restricted supply of soil-available N and other nutrients in control plots. Low CS values, especially at high P soil tests, underestimate P supply and provide exaggerated fertilizer P requirements. Further, a large variation in soil test values of available phosphorus exists in fertility gradient experiments, while variation in soil-available N are encountered only within a narrow range. Subsequently, the uptake of nutrients in control plots depends on N availability. Therefore, in ascertaining fertilizer requirement for a nutrient, its interaction with other nutrients must be considered.

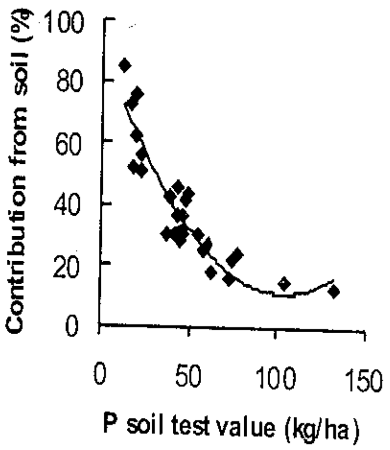

Figure 5. Relationship between soil test values of P and its contribution from soil in rice
Source: Milap-Chand *et al.* (2004)

The soil efficiency parameter for a nutrient should be estimated (i) separately for soils of low, medium and high fertility with respect to that nutrient, and (ii) from plots adequately fertilized with other nutrients to account for the interaction effects. For attaining high yield targets using soil test based fertilizer adjustment equations, the soil-test crop response field experiments from which these equations are derived, should have sufficient number of plots where such high yields have been obtained. A new method has been proposed (Maruthi Sankar *et al.*, 1983) for better estimation of soil and fertiliser nutrient efficiencies from the soil test-crop response field experimental data of the All-India Coordinated Soil Test-Crop Response Project. Ramamoorthy (1993) advocated selection of 16 out of 88 treated plots of the STCR field experiment, based on significant yield/ yield response observations,and regressing the uptake of nutrients from all the 16 plots with the soil test values,S,and fertiliser dose of the particular nutrient, F, of the 16 plots and identifying the two regression coefficients as Cs and Cf values respectively.

Suggestions for improvements in predictability and application of target yield equations have been made by Ramamoorthy (1994) by introducing a factor to accommodate curvilinearity in target yield equations and the use of factors for real (actual) soil nutrient supply and real (actual) fertilizer recovery instead of apparent soil nutrient supply and apparent fertilizer recovery so as to account for the priming effect. The real fertilizer recovery and the crop yield in the presence of nutrient priming effect could be estimated by regressing actual yields obtained along with the fertilizer doses applied on the basis of apparent soil nutrient supply and fertilizer recovery for several yield targets.

Some of the other factors leading to non-attainment of targeted yields are: (i) the variations which may occur in the amounts of plant nutrients required per unit of produce for different levels of crop yields and the estimates of fractional recovery of fertilizer nutrient; (ii) the empirical nature of soil tests, the soil depths from which the samples are collected, and (iii) the differences in productivity of the soil of the experimental area *vis-á-vis* soils where adjustment equations are used. Velayutham (1979), velayutham *et al.* (1985) and Velayutham (2011) advocated "The Law of Optimum" governing the targeted yield concept and the importance of soil test-crop response correlation studies for site and situation specific fertiliser recommendations for increasing agricultural productivity and production. Goswami and Biswas (1974) and Velayutham and Tandon (1995) have discussed various approaches for soil fertility evaluation and fertilizer recommendation for crops.

5. Critical Value Approach

As already stated, one way of interpreting soil test is to classify them as low, medium and high. A good classification takes care that one group of soils gives a statistically significant larger yield response to applied nutrients than the one immediately above. In practice, it requires sufficient labour in categorizing the soils in accordance with pH, texture and organic matter content, etc. and the crops according to rooting patterns and rates of dry matter accumulation.

Data collected systematically to calibrate soil tests with crop response to applied nutrients provide a suitable basis to define critical values. On an average, these will provide the best separation of soils that give little response, low response and high response to applied nutrients.

Critical values are specially useful when public administration has high concern for increasing crop production in areas producing generally low-to-moderate yields and adequate profitability of a costly input is vital to the propagation of technology for improved agriculture. A set of critical soil test values for use by the soil testing laboratories as calibrated during late 1950's for the tall varieties of cereals was given by Muhr *et al.* (1965).

The critical value approach is also useful for mapping soils over large areas where it is difficult for every farmer to get all his fields tested and the available physical facilities preclude such a course of action. Soil fertility maps provide useful guidance for an efficient fertilizer-use under such situations.

Visual inspection method has been used during the initial phase of developing the critical value approach. Accordingly, soil test values obtained from the entire area are plotted on the X-axis and the corresponding responses to an applied nutrient are plotted on the Y-axis, either as a point or as a bar. A mere look at the scatter diagram or the histogram will show a clear separation of the highly-respon-

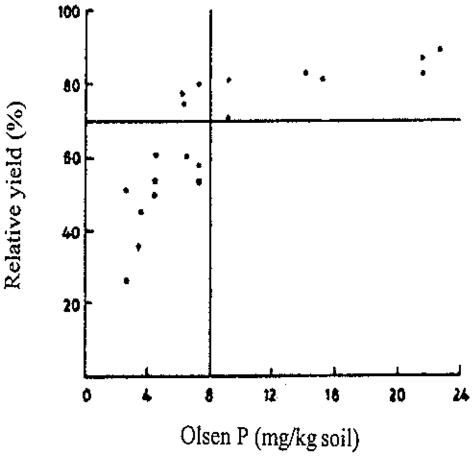

Figure 6. Critical limit of soil P for ryegrass as per the scatter diagram suggested by Cate and Nelson (1965)
Source: Singh and Bishnoi (1996)

sive soils from the moderately-responsive, and non-responsive soils. Some overlap of responding and non-responding soils, with similar soil test values is expected in such an exercise. However, a careful inspection of the data does point out a dividing line below which the probability of obtaining a larger yield response to applied nutrients is much more than in the soils above this line.

Two suggestions have been made by Cate and Nelson (1965; 1971) to help distinguish the dividing line with more facility and accuracy. In the graphical approach, the yields of the control as percentage of the maximum yield (per cent yield) for different soils are plotted on the Y-axis against the soil test values on the X-axis. Thereafter, a transparent overlay with a vertical line and an intersecting horizontal line is placed on the graph paper in such a manner that the number of points in the first and the third quadrants are the maximum and the numbers in the second and fourth quadrants are the minimum. This placement ensures that bulk of the points are concentrated in two quadrants: one in which low soil test values are associated with low relative yields and the other in which high soil test values are associated with high relative yields (Figure 6).

The statistical approach rests on the premises that responsive soils and non-responsive soils are two distinct populations in which relationship between soil test values and relative yields is described by two different straight lines. Hence, the critical value may be defined by a point of intersection between the two lines, which differ in the magnitude of slope. In statistical parlance, the best fitting straight line in a scatter diagram is the one in which the sum of squares of deviations of observed yields from their mean is the minimum. Hence, in an iterative procedure, a few most likely intersecting points are considered. For the two resulting straight lines, sums of the squares of deviations from the mean are calculated. The set that gives the least sum of squares defines the critical value.

Some information on critical limits of available P, K and S in well-known soil types of India for different crops is presented in Tables 1, 2, and 3, respectively. As is apparent from the tables, the critical value of available nutrient in soil varies with soil type, agro-climatic

Table 1. Critical limits of available P in soils for different crops and soils based on data from different regions of India

Crop	Soil type	Critical limit (mg P/kg soil)
Rice	Alluvial	10.6-11.8
	Red	2.9-3.5
	Coastal-Alluvial	13.0
	Black	5.8-6.5
	Laterite	13.6
	Mix red and yellow	6.3
	Submontane (Himachal Pradesh)	13.5*
Wheat	Alluvial	3.3-7.9
	Black	9.4-16.3
	Submontane (Himachal Pradesh)	15.4*
Pearlmillet	Alluvial	4.8
	Black	7.7
Maize	Alluvial	12.3
Sorghum	Alluvial	8.9
Chickpea	Alluvial	10.2
Groundnut	Black	6.5
	Alluvial	16.6
Raya	Alluvial	5.1-6.5
Cotton	Alluvial	11.9
Sugarcane	Alluvial	4.8
Potato	Alluvial	8.6-11.5
Jute	Alluvial	4.8
Berseem	Alluvial	7.0

*Bray and Kurtz method, and all others by Olsen method
Source: Adapted from Subba Rao and Reddy (2005)

Table 2. Critical limits of available K (NH$_4$OAc-extractable) in soils for different crops based on data from different regions of India

Crop	Soil and state	Critical limit (mg K/kg soil)
Rice	Medium black, Andhra Pradesh	100
	Red soils, Andhra Pradesh	75
	Light soils of Kodad, Andhra Pradesh	68
	Alluvial, Andhra Pradesh	190
	Calcareous, Bihar	58
	Laterite, Maharashtra	76-87
	Alluvial, Uttar Pradesh	117-120
Wheat	Calcareous, Bihar	60
	Alfisol Puto series, Bihar	48
	Alluvial, Uttar Pradesh	95-100
Maize	Calcareous, Bihar	81
	Haplustalfs, Rajasthan	47
	Valuthalakudi series, Tamil Nadu	71
Pearlmillet	Alluvial, Andhra Pradesh	160
	Medium black, Andhra Pradesh	95
	Black Calcareous, Gujarat	137
Sorghum	Islamnagar series 3 & 4, Madhaya Pradesh	240
	Typic Chromusterts, Maharashtra	335
Potato	Submontane, Himachal Pradesh	120
Cotton	Alluvial Tolewal and Samana series, Punjab	50
Chickpea	Alluvial Rarha and Uttari series, Uttar Pradesh	105-137
Groundnut	Black calcareous, Gujarat	65

Source: Adapted from Subba Rao and Reddy (2005)

Table 3. Critical limits of available S (CaCl$_2$-extractable) in soils for different crops in India

Crop	CaCl$_2$-S (mg/kg)
Rice	10
Wheat	13
Maize	13
Sorghum	8
Finger millet	7
Groundnut	10
Mustard	10
Sunflower	18
Soybean	14

Source: Adapted from Subba Rao (1995)

conditions, crop and crop variety. For example, the critical limit for available (NaHCO$_3$-extractable) P in soil for wheat ranges from 3.3 mg/kg in alluvial soils of Gujarat to 16.3 mg/kg in black soils of Madhya Pradesh (Table 1). Information compiled from different studies shows that the critical value of available (NH$_4$OAc-extractable) potassium ranges from 47 mg K/kg soil for maize in Haplustalfs of Rajasthan to 335 mg/kg soil for sorghum in vertisols of Maharashtra (Table 2). Obviously, the potassium-availability depends on the amount of exchangeable-K and soil mineralogy. The exchangeable-K is generally more in the vertisols and vertic type soils and in the fine-textured alluvial soils than in the red and latertic soils, acidic alluvial soils with kaolinite as dominant clay mineral, and coarse-textured alluvial soils. Most alluvial soils have illite as the dominant mineral in their clay fraction and quartz-feldsapr, quartz-mica or quartz alone as the dominant mineral in their silt fraction. All black soils have smectite as the dominant clay mineral, while quartz alone is the dominant mineral in the silt fraction in several soils and feldspar in others. All red, laterite and acid-sulphate soils have kaolinite as the dominant clay mineral and generally quartz as the dominant mineral in the silt fraction. Because of appre-

Table 4. Categorization of well-defined soil series of India on the basis of non-exchangeable K status of soils

Category	Non-exchangeable K (mg/kg)	Soil series	Description
Very low	<150	Balisahi, Khabona, Vijayapura, Nedumanagad, Khubhave-5	Kaolinite-dominant red, Lateritic and acidic alluvial soils with coarse or fine texture
Low	151-300	Tyamagondalu, Bagru	Red soils and acidic alluvial soils with considerable amount of mica
Medium	301-600	Prithvajal, Kamliakheri, Sarol, Pemberty, Lukhi	Smectite rich swell-shrink soils and coarse-textured alluvial soils
High	601-1200	Doddabhavi, Shendvada, Kalathur, Nabha, Masitawali	Smectite soils with appreciable amounts of illite and illitic-alluvial soils
Very high	>1200	Rarha, Khatki, Noyyal	Medium to fine illitic alluvial soils and smectite soils with high mica or illite

Source: Subba Rao *et al.* (1993)

ciable contribution of non-exchangeable K towards soil K supply, it is relatively difficult to establish critical limits for available potassium in soils. Studies on soil test calibration based on non-exchangeable (boiling nitric acid extractable) K are limited. Categorization of soils based on non-exchangeable K can be used as a measure of their relative K-supplying capacity to soil. Subba Rao *et al.* (1993) have categorized 21 surface soils of well-defined soil series of India developed on a variety of parent materials on the basis of non-exchangeable K (Table 4). Non-exchangeable K reserves are generally higher in illite-dominant alluvial soils, followed by smectite-dominant soils. Kaolinite- dominant soils contain less non-exchangeable K. The total K is generally more in illitic alluvial soils. With the exception of some illite/ mica-containing smectite- and kaolonite-dominant soils, all other vertisols and vertic type soils and red lateritic soils possess less total K.

6. Soil Test Summaries

Soil testing provides sound information about the fertility and productivity of the soils. This enables the farmer to make the most profitable use of some of the costly inputs (fertilizers and amendments) in farming. However, neither all farmers have the information or inclination to get all their soils tested nor is the soil testing service adequately equipped to perform this job on all the millions of fields across the length and breadth of the country. Hence, there is a need to compile soil-wise and crop-wise soil test summaries for all the important agro-eco-regions, where already, there is sufficient use of fertilizers or where higher demands are anticipated in the future. It is necessary to have sufficient number of soil samples as well as representative sampling, in order to ensure correct assessment of the prevalent situation.

Soil fertility maps such as of Ghosh and Hasan (1976, 1979, 1980) and Motsara (2002) incorporating the results of appropriate soil test summaries are very useful in informing the agricultural administrators and fertilizer industry to chalk out plans for a balanced fertilizer-use and fertiliser promotion programmes, as illustrated by Ramamoorthy et al (1969) at village level in Delhi Territory and by Velayutham and Ghosh (1981) for the different districts in the country. Naidu *et al.* (2008) have discussed with case studies how soil-test-based fertilizer recommendations can minimize fertilizer misapplication in different agro-climatic zones. For a convenient follow-up of the suggestions; district/block maps, showing soil details, should accompany the country maps. The soil fertility maps with district boundaries may be superimposed on the soil map of the state/district, so that nutrient management recommendations may go along with other soil management recommendations, thus improving soil quality and ultimately leading to the fertility capability classification of soil, as proposed by Sanchez *et al.* (1982).

The soil test results are depicted in either of the two ways:

- Categorizing areas having more than 50%, 25-50% or less than 25% nutrient-deficient soils (the percentage could be varied); and
- Nutrient index value (Parker, 1952) calculated from the proportion of soils under low, medium and high available nutrient categories, as represented by expression (10):

$$\mathrm{NIV} = \frac{N_l + 2N_m + 3N_h}{N_l + N_m + N_h} \qquad \ldots(10)$$

where, NIV is nutrient index value; N_l, N_m and N_h are the number of soil samples falling in the category of low, medium and high nutrient status and are given weightage of 1, 2 and 3, respectively. The same relationship assumes the form of expression (11):

Nutrient index value (NIV) =

[(Percentage of soils high in available estimates of a nutrient × 3) + (Percentage of soils medium in available quantities × 2) + (Percentage of soils low in available quantities × 1)] ÷ 100 ...(11)

when the number of soil samples in each category are expressed as percentage of total samples analysed or assessed.

Accordingly, areas with nutrient index value > 2.33 could be considered high, those with NIV between 1.34 and 2.33 or 1.51-2.50 could be considered medium, and those with values < 1.5 or <1.33 could be regarded low in the native supply of that nutrient.

For appropriate advisory work, soil fertility maps or soil test summary reports should be accompanied by appropriate fertilizer use recommendations for each fertility class. In the beginning, these recommendations are seldom available unless field experiments to develop fertilizer recommendations are conducted along with the start of soil testing programme. Where local research work is lacking, recommendations for similar soils and crops can be borrowed from outside. However, for optimum utilization of soil test information, some minimum work under local agro-ecological situations is necessary.

Fertilizer use in an agricultural area is seldom optimum over all fields. There are always differences among farmers in the level of adoption of improved agricultural technology. Hence, differences in soil fertility in an agricultural tract are bound to develop in an unpredictable manner. The effects of fertilizer use in an agricultural area over a period of time may either deplete or build-up fertility. Nutrients like nitrogen and potassium, which are subject to leaching losses, and over large areas are generally applied in amounts less than their removal, tend to deplete with time. On the other hand, nutrients like phosphorus and zinc which interact with the soil and are usually applied in amounts much larger than their removal, tend to build-up in the soil. Such changes contribute much to the variability in nutrient supplies in an agricultural area. A periodical updating of soil test summaries is, therefore, necessary.

7. A Good Soil Sample is Important

Soil sample is the basis on which advice is tendered to the farmer for a profitable manipulation of the soil. Hence, it is essential that the soil sample should be truly representative of the field. Usually, a composite sample of approximately 500 g of soil is taken from a field. If a field is too heterogeneous, as it may appear from the undulating nature or knowledge about the previous crop cover, several samples from the parts of soil which are apparently more homogenous, should be collected. It has been observed that the error in sampling a field is generally bigger than the error in laboratory analysis. Also, it is true that a soil test is no better than the sample on which it is performed.

For cultivated crops, soil samples are ordinarily taken up to a depth of 15 cm. Ideally, samples should be taken prior to seeding. Since this is not always possible, soil samples are collected any time when soil conditions permit. The recommendations for the use of fertilizers are generally valid for a few seasons. In order to make an intelligent use of periodical soil tests, careful recording of inputs and outputs is essential.

Table 5. Sufficiency ranges of macronutrients on the basis of leaf analysis for wheat, rice and cauliflower at two different stages of plant growth

Crop	Sampling stage	N	P	K	Ca	Mg	S
		(%)					
Wheat	Tillering	4.0-5.0	0.2-0.5	2.5-5.0	0.2-1.0	0.14-1.0	0.15-0.65
	Flag leaf maturity	4.0-5.0	0.2-0.5	2.0-4.0	0.2-1.0	0.14-1.0	0.15-0.65
Rice	Mid tillering	2.8-3.6	0.14-0.27	1.5-2.7	0.16-0.39	0.12-0.21	0.17
	Panicle initiation	3.0-3.4	0.18-0.29	1.5-2.7	0.19-0.39	0.15-0.39	0.15
Cauliflower	Buttoning	3.0-5.0	0.4-0.7	2.0-4.0	0.8-2.0	0.25-0.60	0.6-1.0
	Heading	2.2-4.0	0.3-0.7	1.5-3.0	1.0-2.0	0.25-0.60	

8. Plant Analysis

Although plant analysis is not the direct evaluation of soil, it is a valuable supplement to soil testing in the task of soil fertility evaluation. Plant analysis is useful in confirming nutrient deficiencies, toxicities or imbalances, identifying hidden hunger, evaluating fertilizer programmes, and determining the availability of elements. Protagonists of plant analysis consider that diagnosis of ailing plant is akin to the diagnosis of an ailing human being. For example, when a plant suffers from a hidden hunger, it should be analyzed for its nutrient content, just as an anaemic patient is tested for his or her blood haemoglobin. In any case, plant analysis helps to diagnose the hidden hunger when a crop has been raised with a certain amount of manures and fertilizers, shows no apparent deficiency symptoms and yet appears to be less than optimum crop. Detection of hidden hunger in crops is gaining increasing importance as yield goals rise and potential production needs to be obtained on dwindling acres to feed the yet increasing population. Plant analysis can be particularly advantageous in determining the availability of nutrients. Sometimes, adequate nutrient levels may be present in the soil, but because of other problems such as soil moisture conditions and inadequate amounts of some other nutrients, the plant availability of the nutrient in question may be constrained (Westerman, 1990).

Two types of plant analysis are generally carried out: (i) Tissue tests made on fresh tissue in the field, and (ii) A complete analysis conducted in the laboratory equipped with a flame absorption spectrophotometer and inductively coupled plasma optical emission spectrophotometer. Rapid tests, generally conducted, for the determination of nitrogen, phosphorus and potassium, on the sap from ruptured cells, are semi-quantitative and predict nutrient deficiencies on the spot. The plant diagnostician should be well acquainted with the physiology of the plant, soil management, and incidence of insect pests and diseases. An abnormal plant giving a high test for a nutrient element does not necessarily mean its adequacy in the soil, but that some other growth factor may be interfering in the expression of the results.

For most diagnostic purposes, plant analyses are interpreted on the basis of critical value approach, which uses tissue nutrient concentration calibrated to coincide with 90% or 95% of the maximum yield, below which the plants are considered deficient and above that value, sufficient (Munson and Nelson, 1990). The nutrient composition of a plant changes as the plant matures and with the part of the plant sampled; therefore, critical levels are defined for a specific plant part at a specified stage of maturity. For most crops, there is a 'Sufficiency Range' of nutrient composition over which yield will be maximized rather than a single value. Sufficiency ranges for nutrient elements established for wheat, rice and cauliflower (Mills and Jones, 1996; Hochmuth and Hanlon 1995) are listed in Tables 5 and 6. Sufficiency ranges for each nutrient in leaf samples remained constant at their two different stages of growth for wheat and rice crops. In cauliflower, sufficiency ranges for N, P, K, Ca, Mn and Cu varied at both buttoning and heading stages.

The major disadvantage of critical value and sufficiency range approaches is that they

Table 6. Sufficiency ranges of micronutrients on the basis of leaf analysis for wheat, rice and cauliflower at two different stages of plant growth

Crop	Sampling stage	Fe	Mn	Zn	Cu	B
				(mg/kg)		
Wheat	Tillering	30-200	20-150	18-70	4.5-15	1.5-4
	Flag leaf maturity	30-200	20-150	18-70	4.5-15	1.5-4.0
Rice	Mid tillering	90-190	40-740	20-160	6-25	5-25
	Panicle initiation	70-190	40-800	20-160	6-25	6-15
Cauliflower	Buttoning	30-60	30-80	30-50	5-10	30-50
	Heading	30-60	50-80	30-50	3-5	30-50

do not consider nutrient balances and interactions for diagnosis and require different critical values for different tissue ages. Sufficiency ranges are unable to rank, which nutrient element is most limiting if more than one nutrient is found to be deficient. Besides, sufficiency ranges are available only for specific stages of plant growth. If the growth stage of a crop is not between the established ones, interpretation is more difficult.

A new approach of Diagnosis and Recommendation Integrated System (DRIS) (Beaufils, 1973: Walworth and Sumner, 1987), which considers nutrient concentration ratios, rather than individual elemental concentration for interpreting plant tissues composition, has been proposed to overcome the above limitations. The DRIS approach measures the relative balance between nutrients by means of index values with negative values indicating insufficiencies and vice versa. In addition, DRIS reveals not only the most limiting nutrient but also the order in which other nutrients are likely to become limiting. The establishment of DRIS norms does not require fertilizer response trials, rather these can be established from a large data set of independent leaf tissue composition and their corresponding yield for a particular tissue. In Indian Punjab, DRIS has been used in diagnosing nutrient requirements for lychee (Hundal and Arora, 1995), kinnow (Hundal and Arora, 2001) and guava (Hundal *et al.*, 2007). The DRIS evaluation and sufficiency range approach have been found to be equally effective and in agreement for diagnosing deficiencies of N, P, K, Ca, S, Mn, Zn and Cu in guava trees at different locations in Punjab (Hundal *et al.*, 2007). Relative deficiencies for N, P, K, Ca, Mg, S, Mn, Zn, and Cu, corresponding to relative excesses for Fe, have been detected by DRIS evaluations (Table 7). The DRIS approach can also be employed to compute low, sufficient, high, and excessive/ toxic ranges for nutrients (Bhargava, 2002).

9. Soil Organic Matter: Key Indicator of Soil Fertility

Soil organic matter (SOM) is recognized as a key indicator of soil fertility and has long been regarded as a source of plant nutrients, principally N, and substantially P, S and micronutrients besides being promoting a range of soil physical characteristics. Most of soil organic carbon (SOC) is associated with organic matter, although charcoal may be an important constituent in ecosystems subject to frequent fires. The global pool of SOM is estimated to contain about 1500 Pg (1 Pg = 10^{15} g = 1 billion tonnes) C to 1 m depth (Batjes, 1997) and about 2456 Pg C to 2 m depth. This compares with estimates of 600-700 Pg C in aboveground biomass, 800 Pg C in atmosphere, and about 40,000 Pg C in the oceans (Schimel *et al.*, 1994). The geologic C pool comprises 5,000 Pg with 4,000 Pg C as coal, 500 Pg C as gas and 500 Pg C as oil. Reserves of inorganic carbon (as carbonate) stored in soils have been estimated to be about 720 Pg C (Sombroek *et al.*, 1993). For a detailed description of carbon stocks in soils and phytomass in various agroecosystems and fluxes between the atmosphere and the terrestrial biosphere, the reader may refer to Nieder and Benbi (2008).

Table 7. Leaf mineral compositions, DRIS indices and the most required nutrient elements of guava fruit tree recorded at different locations of Punjab, India

Location	Leaf mineral compositions and DRIS indices										Relative order of nutrient requirement
	N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	
	%						mg/kg				
Gudda	0.68	0.157	0.854	1.045	0.329	0.224	425	86	57	11	N>Ca>S>Mn>Cu>K>P>Zn>Fe
	(-1181)	(15)	(-29)	(-397)	(-257)	(-93)	(1309)	(-73)	(774)	(-67)	
Raikot	1.52	0.077	0.635	1.491	0.482	0.222	405	157	42	19	P>N>K>Ca> S >Mg>Cu>Mn>Zn>Fe
	(-260)	(-675)	(-251)	(-203)	(-46)	(-184)	(888)	(252)	(312)	(166)	
Kumrodha	1.64	0.121	0.295	1.725	0.353	0.217	416	72	21	9	K>Mg>Mn>P>N>Cu>S>Zn>Ca>Fe
	(-65)	(-81)	(-728)	(4)	(-156)	(-62)	(1255)	(-91)	(-12)	(-64)	
Chugwa	1.56	0.114	0.795	0.912	0.606	0.154	538	61	20	6	Ca>S>Cu>Mn>P>N>Zn>K>Mg>Fe
	(-164)	(-191)	(-29)	(-506)	(264)	(-432)	(1716)	(-250)	(-85)	(-322)	
Halwara	1.39	0.111	0.873	1.243	0.279	0.188	282	73	19	20	Mg>Ca>P>S>N>Zn>Mn>K>Cu> Fe
	(-128)	(-142)	(54)	(-153)	(-254)	(-136)	(639)	(-87)	(-88)	(294)	
Jagroan	1.46	0.126	0.893	1.105	0.359	0.161	386	83	44	10	S>Ca>N>P>Mg>Cu>Mn>K>Zn>Fe
	(-207)	(-137)	(4)	(-319)	(-166)	(-371)	(944)	(-84)	(432)	(-95)	
Chuklan	1.62	0.13	0.879	1.596	0.319	0.212	353	29	24	22	Mn>Mg>S>N>P>Ca>Zn>K>Cu> Fe
	(-64)	(-58)	(46)	(-50)	(-217)	(-94)	(929)	(-921)	(44)	(386)	
Chugwa	1.64	0.135	0.689	1.221	0.369	0.196	489	102	15	11	Zn>Ca>S>Mg>K>N>P>Cu>Mn>Fe
	(-138)	(-96)	(-141)	(-264)	(-175)	(-214)	(1336)	(33)	(-305)	(-36)	
Malakpur	1.56	0.121	0.513	2.079	0.443	0.225	394	65	19	5	Cu>K>Mn>N>P>Zn>S>Mg>Ca>Fe
	(-118)	(-108)	(-250)	(87)	(-20)	(-69)	(1081)	(-157)	(-75)	(-370)	

Note: Figures within the brackets indicate DRIS values

Table 8. Soil organic carbon stocks in different agro-ecoregions and soil types in India

Agro-ecoregion	Soil type	Area (Mha)	Organic C (Pg)	
			0-30 cm	0-150 cm
Cold arid	Shallow skeletal soils	15.2	5.96	10.47
Hot arid	Desert and saline	31.9	2.51	10.43
	Red and black	4.9	1.21	4.21
Hot semi-arid	Alluvial	32.2	3.88	15.24
	Black	48.6	1.30	2.58
	Red and black	16.5	0.55	1.72
	Red and loamy	19.1	0.46	1.41
Hot sub-humid	Alluvial	23.2	0.32	1.28
	Red and yellow	36.4	0.76	2.05
	Red and lateritic	26.8	0.67	1.70
Warm sub-humid to humid	Brown forest and podzolic	21.2	0.52	1.55
Hot sub-humid to humid	Alluvial	12.1	0.42	1.20
Warm perhumid	Brown and red hill	9.6	0.79	3.76
	Red and lateritic	10.6	0.45	1.49
Hot, sub-humid to semi-arid	Coastal alluvial	8.5	0.23	0.91
Hot, humid to perhumid	Red, lateritic, alluvial, loamy and sandy	11.9	0.96	3.19
Total (India)		328.7	20.99	63.19

Source: Adapted from Velayutham *et al.* (2000)

Soil organic C stocks in soils of India have been estimated to be 21Pg and 63Pg in the upper 30 cm and 150 cm, respectively (Velayutham *et al.*, 2000). These stocks constitute about 3% of the global C stocks and 10-12% of the total C stocks of the tropical regions. The distribution of SOC stocks in soils of different agro-ecoregions (Sehgal *et al.*, 1992) of the country shows (Table 8) that the maximum amount is in the surface soils of hot semiarid regions, followed by cold arid, hot arid and sub-humid zones.

9.1. Carbon Sequestration

Carbon cycles globally among the three distinct pools, namely, the atmosphere, the ocean and the terrestrial ecosystems. Soils carry the largest pool of actively cycling C in the terrestrial ecosystems. Fluxes between soil organic carbon and the atmosphere are important and can be positive (sequestration) or negative (emission of CO_2). Carbon sequestration refers to increasing the amount of C stored in vegetation and soil. It occurs through direct and indirect fixation of atmospheric CO_2. Direct soil C sequestration occurs by inorganic chemical reactions that convert CO_2 into soil inorganic carbon compounds such as calcium and magnesium carbonates. Direct plant C sequestration occurs as plants photosynthesize atmospheric CO_2 into plant biomass. Subsequently, some of the plant biomass is indirectly sequestrated as SOC during decomposition processes. The amount of C sequestrated at a site reflects the long-term balance between C uptake and release mechanisms. Better management of agricultural soils, restoration of degraded soils and ecosystems, restoration of former wetlands now being used for agriculture have a vast potential of C sequestration.

Management practices or technologies that increase carbon input to the soil and decrease output/losses of carbon lead to carbon sequestration in soils (Table 9). Enhanced biomass production, humification of organic materials returned to the soil, aggregation by formation of organo-mineral complexes, deep placement of organic carbon beneath the plough zone, deep rooting, and calcification result in greater C sequestration. Management practices, which favour or facilitate these processes include return of above-ground and below-ground biomass to the soil, exogenous application of organic materials (e.g. animal manure, compost, sludge, etc.), adoption of agroforestry systems, intensification of agriculture by adopting rec-

Table 9. Strategies for C sequestration in agricultural soils

Increase input	Decrease output
Increasing crop productivity	Erosion control
Diversified crop rotations	Reduced or no tillage
Higher return of crop residues	Mulch farming
Increasing use of organic manures	Reduced bare fallow
Green manuring	Input of low quality organic material
Intensive cropping	
Elimination of winter fallow	
Agroforestry systems	
Improved irrigation	
Greater root biomass	
Depth placement of carbon	
Switching from annual crops to perennial vegetation	

ommended management practices, reducing winter fallow or periods with no ground cover, changing from monoculture to rotation cropping, switching from annual crops to perennial vegetation, and increasing area under forests. Switching from annual crops to perennial vegetation increases residue production, plant roots and reduces soil disturbance, thus enhancing soil C sequestration.

Management options that result in reduced output through decomposition or soil respiration include reduced or no-tillage practices, mulch farming, reduced bare fallow or increased cropping intensity. No-till agriculture greatly reduces the degree of soil disturbance normally associated with annual cropping. Physical disturbance associated with intensive soil tillage increases the turnover of soil aggregates and accelerates the decomposition of aggregate associated SOM. No-till increases aggregate stability and promotes the formation of recalcitrant SOM fractions within stabilized micro- and macro- aggregate structures, and reduces soil erosion. Croplands under no-till systems show increase in soil C compared to more intensive tillage operations. Greater cropping intensity can increase water- and nutrient-use efficiency and biomass production by plants, thereby increasing C inputs to soil and reducing organic matter decomposition rates (Paustian *et al.*, 2000). Biotic C sequestration has co-benefits of increased soil fertility and crop productivity. Recently, Benbi and Chand (2007) have shown that the contribution of one megagram of C per hectare in the plough layer to wheat productivity ranged from 15-35 kg/ha and it has a fertilizer N equivalence of about 4.75 kg N/ha.

9.2. Potential for C Sequestration by Agriculture

Because of historic losses of C from soils, estimated to be between 41 Pg and 55 Pg, the soils have significant capacity to sequester C. The C sequestration potential of a soil depends on climate (temperature and precipitation), type of vegetation it supports, nature of parent geological material (texture and mineralogy), depth of solum, soil drainage, edaphic environment, SOM content and its ability to resist microbial decomposition, and land management practices (Swift, 2001).

Restoring wetlands has a large potential for C sequestration, because erosion of topsoil and organic matter from upland catchment areas is deposited in wetlands and the decomposition rate is slow. It has been estimated that in temperate and cool climates annually 0.5-1 Mg C/ha can be sequestered by restoring wetlands, 0.2-0.8 Mg C/ha by restoring severely degraded soils and 0.2-0.5 Mg C/ha by mine soil reclamation (Lal, 2004a).

Average global C sequestration rates, when changing from agriculture to forest or grassland have been estimated to be 33.8 g C/m^2/yr and 33.2 g C/m^2/yr, respectively (Post and Kwon, 2000). But, there is a large variation in the length of time for and the rate at which C may accumulate in the soil, related to the productivity of the recovering vegetation, physical and biological conditions in the soil, and the past history of SOC inputs and physical disturbance. Enhancing rotation complexity (i.e. changing from monoculture to continuous cropping, changing crop-fallow to continuous cropping, or increasing the number of crops in a rotation system) can sequester on an average 20±12 g C/m^2/yr, excluding a change from continuous corn to corn-soybean, which may not result in significant accumulation of C (West and Post, 2002). Analysis of results from a global database of 67 long-term experiments showed that a change from conventional till-

Table 10. The potential of carbon sequestration in soils of India

Region	Area (Mha)	C-sequestration potential (Tg/yr)
Arid	52.0	0.67-1.34
Semi-arid	116.4	2.33-4.66
Sub-humid	86.4	3.46-5.18
Sub-humid/humid	33.3	2.06-2.72
Perhumid	20.2	2.42-3.03
Sub-humid/semi-arid	8.5	0.34-0.51
Humid/Perhumid	11.9	1.43-1.79
Total	328.7	12.71-19.23
Secondary carbonates	328.7	21.78-25.6
Erosion control	-	4.80-7.20
Total	328.7	39.29-52.03

Source: Adapted from Lal (2004b)

age (CT) to no-till (NT) could sequester 57±14 g C/m^2/yr, excluding wheat-fallow system, which may not result in SOC accumulation with a change from CT to NT. Carbon sequestration rates, with a change from CT to NT, can be expected to peak in 5 to 10 years with SOC reaching a new equilibrium in 15-20 years. Since no single land-management strategy in isolation may be adequate to enhance carbon sequestration, it is important to evaluate the integrated combination of various land-management strategies.

Globally, potential for C sequestration in soil over 50-year period has been estimated to be 24-43 Pg C (0.4-0.9 Pg C/yr) through improved management of the existing agricultural soils, restoration of degraded lands, permanent set-asides of surplus agricultural lands in temperate developed countries and restoration of 10-20% of former wetlands now being used for agriculture. The potential of soil carbon sequestration in India is estimated at 39-52 Tg C/yr (1 Tg = 10^{12} g) (Table 10), which includes restoration of degraded soils (7.2-9.4 Tg C/yr), soil inorganic carbon sequestration (21.8-25.6 Tg C/yr) and reduction in erosion-induced emission of C (4.32-7.2 Tg C/yr) (Lal, 2004b). Technological options that have been found to be efficient for soil C sequestration in India include green manuring, mulch farming and/conservation tillage, afforestation, agroforestry systems, grazing management/and ley farming, integrated nutrient management and manuring and choice of cropping system. There is a considerable uncertainty in the estimates, concerning both C flux rates and soil C storage capacity. Since soils have a finite capacity to store additional C, the total amount of C sequestered and the estimates thereof depend on the time horizon considered. Further, permanence of C sequestered in soil depends on the continuation of the recommended management practices.

10. Problems and Prospects

The problems encountered in soil fertility evaluation pertain to soil sampling, handling, analysis, and interpretation of results. For sampling, it is necessary to make the field thoroughly homogeneous and then a reasonable amount of soil may be collected from 8-10 random sites within each sampling unit, from a uniform depth of soil, so as to make a composite sample.

Handling of the samples before analysis involves their air-drying and pulverizing so as to pass through a standard sieve. In some laboratories (such as at Iowa State, USA), the soil samples for potassium analysis are kept field-moist. Similarly, there are suggestions for grinding the soil sample to pass through a sieve as much as possible and then to mix both the coarse and the fine particles.

Chemical tests to analyze samples of soil for finding available amounts of plant nutrients have been adequately standardized. However, it is always useful to cross-check the accuracy of analysis through a system of internal and external checks. This helps the laboratory to correct the errors of the laboratory equipment and the technician, if any.

The problems of interpretation arise most often from the paucity of background data. Hence, it is essential for each laboratory to obtain a set of background data, relevant to the soils of the region where it is located and about the crops for which it usually makes the recommendations.

Provision of food and agricultural products in India for a population, which has already crossed the one billion mark in the year 2000 requires the development and a judicious utilization of land resources. The high crop yields obtainable with the advent of the 'Green Revolution' have placed heavy demands on soil nutrients, which must be replenished to maintain and if possible, to increase the yield levels. Vast areas of farmland in India suffer not only from inadequate amounts of manures and fertilizers but also from nutrient imbalances. A sound soil test information can serve a very useful purpose under such circumstances. The vast network of soil testing service (more than 500) in the country is able to offer this facility to only a fraction of the peasantry. Hence, there should be a well-defined scheme to first assess and then monitor changes in soil fertility in different soils, agro-eco-regions and cropping systems. Selection of representative sites and collection of stratified soil samples from well-defined soil classification units involve huge work. For efficient execution at a minimum cost, this activity should be an inalienable part of the work of the existing soil test laboratories, adequately strengthened by the Agricultural Universities, Agriculture Departments of the state governments and the fertilizer industry for providing site-specific nutrient management recommendations to the farmers and for periodically monitoring the "soil health" of the country. Special emphasis must be placed on uncovering the soil nutrient deficiencies in areas that are currently low-yielding in relation to their potential exhibited by the yields obtained in coordinated agronomic experiments in eastern Uttar Pradesh, Bihar and parts of Madhya Pradesh. Current high cost development of groundwater is withholding the yield improvement. However, national economy will require this development through rainwater harvesting, artificial recharging and catchment area protection to provide a sustainable basis of foodgrain increases in the future.

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Chapter 23

Soil Biology and Biochemistry

P.K. CHHONKAR, R.P. PAREEK, D.L.N. RAO and T.K. ADHYA

1. Introduction

The soil is teeming with millions of living organisms which make it a living as well as a dynamic system. Under a microscope, it reveals a complex arrangement of soil particles and pore spaces filled with air and water. It is in these pore-spaces that plant roots and millions of organisms develop, ranging from sub-microscopic to macroscopic in size (Figure 1). These organisms not only help in the development of soils but are also the primary driving agents of nutrient cycling, regulating the dynamics of soil organic matter, enhancing the amount of nutrient acquisition by vegetation; conferring stress tolerance, resisting pathogens and improving plant health. Their most important role in organic matter decomposition is to mineralize nutrients from the dead tissues to such forms as become available to plants for growth. But for the activities of these organisms in soil, life on the earth would have come to a halt, as all available plant nutrient elements would have ended-up locked in the organic debris, disrupting the nutrient cycles. Microoganisums are responsible for the soil self-cleansing that provides protection against many plant and animal pathogens introduced into this milieu by both natural and man-made means. They breakdown most of the 45,000 or so chemical compounds that humans use in daily life.

Microbes are the basis of the biosphere; a staggering 5×10^{31} cells exist, weighing 50 quadrillion tonnes, constituting about 60% of the total biomass. Bacteria produce about half of the oxygen on the planet. Of 41,000 Pg (1 Pg = 10^{15} g) of carbon in the globe, soils contain 1550 Pg and biota 550 Pg. While the total C, N and P in the plant biomass globally is 560 Pg, 12-20 Pg and 1-2 Pg, respectively, in procrayotes the C, N and P contents are 300-500 Pg, 70-120 Pg and 7-12 Pg, respectively. Thus, it is difficult to overstate the importance of microorganisms; the soil-microbe complex is vital because of the services it provides to agriculture, waste management, water industry, and the natural and semi-natural environments.

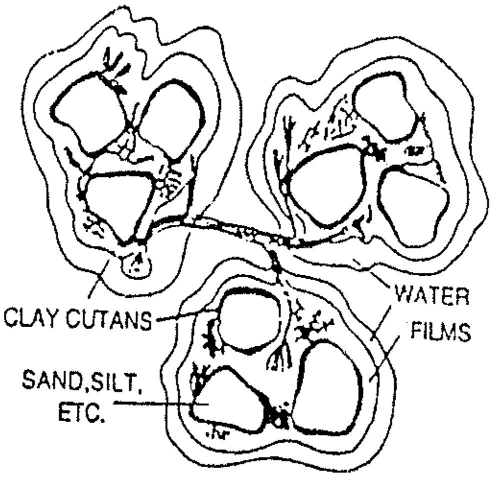

Figure 1. Schematiac representation of three microhabitats in soil

The pore space is filled with aqueous and gas phases. Note the hyphae growing through the pore space. The hyphae are surrounded by water which may contain bacteria, bacteriophages and dissolved substances. (Not to scale)

2. Soil as Habitat for Organisms

The requirements for sustaining life are being met adequately in the soil which is a congenial habitat for supporting organisms of a highly diverse nature. Oxygen of soil air, trapped in pore spaces and dissolved in soil water, is used for respiration by the aerobic organisms and the oxygen consumed during respiration is being constantly replenished. The energy (food) requirements of soil are provided by soil organic matter (SOM) and the reduced substances get continuously added to it. These substances when oxidised by the heterotrophic population of soil, yield energy for their growth. Soil also contains all major and minor nutrient elements needed for the protoplasmic synthesis and thus meets the requirements of growth and multiplication of soil organisms.

Water is essential for life and constitutes around 95 per cent of the protoplasm. The water holding capacity of soil which depends upon the soil organic matter content and the clay mineralogical composition of the soil, helps in sustaining growth and activities of soil organism. Organisms utilize soil water held in the pore spaces. Soil also offers protection to organisms, requiring different temperature and pH options for growth, resisting sudden changes in temperature and pH due to its thermal-insulation characteristic and buffering capacity.

3. Organisms in Soil

Organisms present in soil are classified into two main groups: (i) Soil flora, belonging to plant kingdom, and (ii) Soil fauna, the animal forms. These are further divided into two subgroups: (a) macroorganisms, i.e. those organisms which are big enough to be seen by an unaided eye, and (b) microorganisms which are so small that these can be seen only after magnification using a microscope. A comprehensive presentation classifying soil organisms into specific groups is given in Figure 2.

Soil organisms can also be classified on the basis of requirements of molecular oxygen, temperature and mode of nutrition, etc. Organisms that need O_2 for respiration and cannot survive without it are called 'obligate aerobes' and those which are aerobic but also adapt to grow under anaerobic environment using oxidized substances like NO_3, SO_4, CO_2, etc. as terminal electron acceptors in place of O_2 in respiration, are classified as 'facultative anaerobes'. An example of such organisms of great agricultural significance in soil is the denitrifying bacteria. The organisms which grow in the absence of O_2 are called 'obligate anaerobes', like Clostridia, Methanobacteria.

The organisms have specific optimum temperature requirements for their growth. Any change from the optimum temperature will not kill the organisms but will reduce their growth

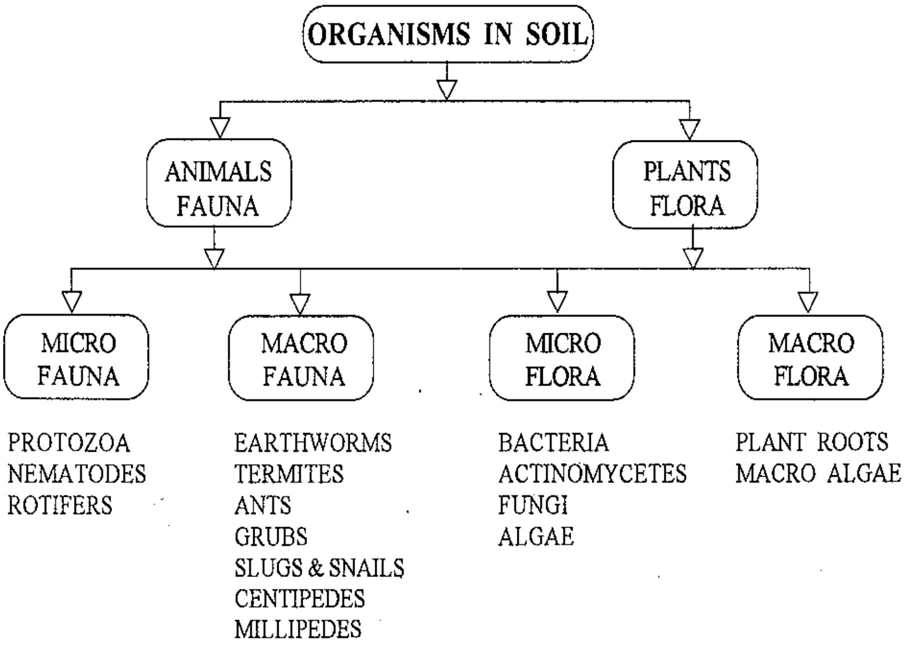

Figure 2. Important groups of organisms commonly present in soil

rate. Psychrophiles have optimum temperature for growth below 10 °C, while the group of organisms with optimum temperature between 20-35 °C are termed as 'mesophiles'. This group is highly dominant and numerous in most of the cultivated soils of India. A temperature higher than 45 °C favours development of thermophiles, commonly encountered in the compost pits.

Based on the mode of nutrition, soil organisms are classified into two groups— heterotrophs and autotrophs. Heterotrophs derive energy by oxidation of organic compounds, while autotrophs derive their carbon from CO_2 for cell synthesis. The group of autotrophs is further sub-divided into 'chemoautotrophs' which get energy from the oxidation of simple inorganic compounds, and 'photoautotrophs', which derive energy from sunlight.

Since most soil microorganisms require preformed organic carbon sources for growth, carbon requirement is used to classify microorganisms. Oligotrophy, which is used to describe organisms that can live in environments with very low nutrient concentrations is important within soil ecosystem, which is often nutrient-limited. Environments such as groundwater are even more C-limited. Copiotrophic bacteria, on the other hand, require higher concentrations of carbon in the environment.

More than 90% of the planet's genetic biodiversity is resident in soils. The current estimates for the numbers of procaryotes, which include the Bacteria and Archaea, range from 300,000 to 1 million species or more but only about 5000 species have been described. Current best estimates of the number of bacteria suggest that there may be as many as 10^9 bacteria per gram of soil comprising more than 20,000 species. It is generally recognized that most microoganisums in soil cannot be cultured on artificial media since such media lack in essential elements required for their growth. No universal medium presently exists that can support the growth of all soil bacteria. With the advent of molecular techniques, the incredible diversity of soil microorganisms is finally being unravelled. With less then 1 % of the microorganisms having been actually isolated and identified, soil biology is still considered to be in its infancy. We have no idea of the function or the potential importance of the unculturable fraction, which is a rich reservoir of genes that can be exploited as a valuable source of antibiotics, drugs and other industrially important products. As molecular techniques allow for a more complete assessment of soil microoganisums, our understanding of the significance of bacteria in soil will rapidly expand.

3.1. Macroorganisms in Soil

The macroorganisms in soils include Acari, Collembola, Enchytracidae, Isoptera, Isopoda, Amphipoda, Diplopoda, Earthworm, Coleoptera, Mollusca, etc. (Figure 3). A population or biomass estimation of these soil animals is highly difficult because they are not uniformly distributed in the soil and are highly mobile. Even though fewer in numbers than microorganisms, these organisms are very useful in soils as:

(i) They help in the decomposition of organic residues in soil by mixing, churning or fragmentation as they eat on plant material,

(ii) They form burrows and tunnels which increase soil aeration, drainage and turn in large amount of surface soil,

(iii) With organic material as their food, the ingested soil in the guts of earthworms gets converted into worm casts called 'mull humus', and

(iv) Some of these organisms like mites, termites and acrinemites feed on soil micro-organisms including plant pathogens.

Some of the soil macroorganisms which play important role in soil fertility are discussed below.

3.1.1. Earthworms

Earthworms belong to the class Annelida and their several genera are found in soil. There are about 1800 species of earthworms in the world. Some of the species in Indian soils are 10-25 cm long. Uncultivated lands and grasslands, having lot of plant litter, have more earthworms. The total biomass of earthworms in soil ranges from 110 to 1100 kg/ha (furrow slice). Their population decreases on cultivation due to reduction in organic matter, with

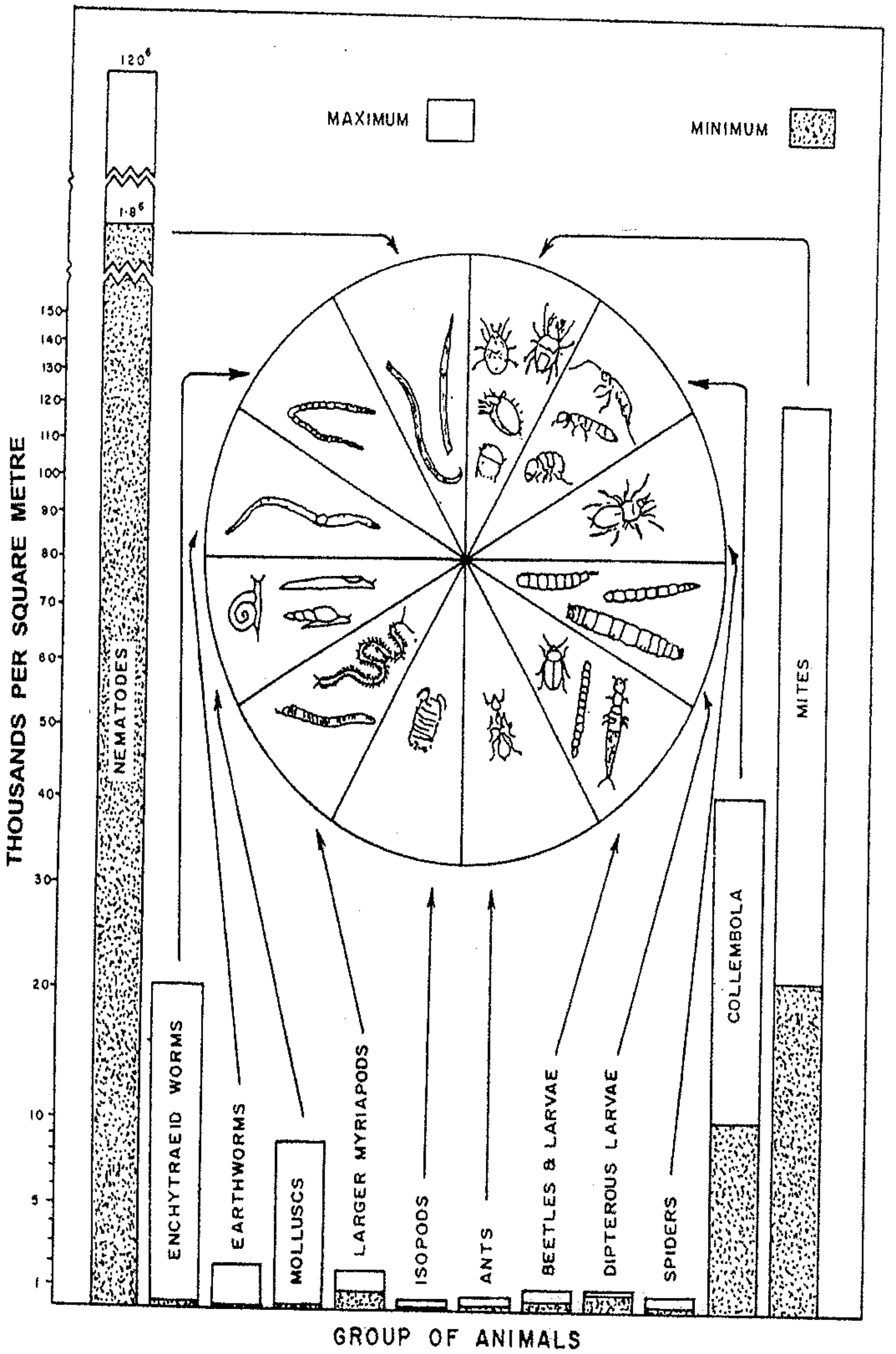

Figure 3. Number of animals per square metre in soil of a European grassland, based on the estimates of Stockli (1946) modified by Macfadyen (1957) and plotted on a logarithmic scale. Such figures are only indicative, since they are mostly calculated from small samples. Of the groups shown, spiders and centipedes are wholly carnivorous and ants predominantly so; beetles, fly maggots, mites, and nematodes range widely in their diet according to species; the remaining groups feed largely on decaying organic matter, many Collembola being also closely associated with fungi and other microorganisms

tillage which causes mechanical injuries, and on pesticide application which is toxic in nature. Dry, waterlogged, clay, sandy or gravelly soils having low organic matter are not suitable for the growth and activity of earthworms.

Earthworm cast is a rich source of nutrients, particularly N, P, Ca, etc. and contains more bacteria and organic matter. Dead tissues of earthworm decompose faster due to their high protein content. Geophagus species of earthworms ingest material per day which is 5-36 times of their body weight. Casting rates of tropical earthworms are reported to be as high as 2600 t/ha/year. Earthworms do intimate mixing of organic matter with mineral matter, which increases the stabilization of clay-bound carbon, depending on soil type. Earthworm-worked soils generally have high porosity, increased water holding capacity, higher water infiltration rate, more water-stable aggregates and increased availability of plant nutrients. These organisms may also affect microbial population as they ingest microbes along with soil and organic matter. Alternatively, they increase the surface area and availability of organic matter for microbial action by mixing it thoroughly with soil.

Vermicompost — In a recent development, earthworms are being used for hastening the decomposition of farm waste for composting. The product is called 'Vermicompost'. Many exotic as well as indigenous species being used for composting are: *Eisenia foetida*, *Eudrilus engeniae* and *Perionyx excavatus*. *E. foetida* is reported to be more efficient than others. Another term generally used in relation to vermicomposting is 'vermiculture', which is culturing of earthworms for composting and the place used for culturing earthworm is called 'wormiri'.

3.1.2. Termites

Termites also influence soil properties and processes through four types of activities:

(i) Physical modification of soil profiles by constructing mounds, sheeting and foraging runways;

(ii) Changes in soil texture emanating from the movement of clay fractions from subsoil for constructions they make;

(iii) Changes in the nature and distribution of organic matter and plant nutrients through litter brought into nests, which is digested by termites and decomposed by the microbes *in situ* (The termite-worked soil has higher CEC and exchangeable bases than the surrounding soil); and

(iv) The changes in soil drainage and moisture regimes on constructing subterranean galleries.

In intensively-cultivated soils, the population of termites is low. However, forest and pasture lands have mound-forming termites. Termites have cellulose decomposing microbes in their guts and thus their excreta has lower organic matter content than that of earthworms.

3.1.3. Plant Roots

Plant roots, which have immense role in the formation, fertility and productivity of soil, can also be considered as one of the soil macroorganisms. Plant roots exercise tremendous influence on soil properties. However, being the primary source of organic matter in soil, plants and their roots supply food and energy to saprophytic soil organisms and maintain the soil biological activity. In addition, by exerting physical pressure on soil particles, they form many channels and capillaries, press the soil making cracks changing bulk density in microsites. In the long-run, plant roots also influence soil texture but more often improve soil structure. By producing different chemicals as root exudates, roots influence the chemical and biological environment of soil around them. The term *Rhizosphere* was coined to encompass these influences. An environment under the influence of roots, the rhizosphere is chemically, biologically and probably physically also a different environment.

Roots produce (i) *exudates* – chemical compounds leaking from roots; (ii) *secretions* – chemical compounds released through plant metabolic processes; (iii) *mucilages* – complex compounds produced by roots or through bacterial degradation; (iv) *mucigels* – gelatinous layers composed of mixture of mucilages and soil particles; and (v) *lysates* – compounds released from root cells through bacterial degradation. These compounds at the soil root interfaces have a special kind of nich for the proliferation of microbes. Such niches are different from the root surface in contact with mucigel called *rhizoplane.*

3.2. Microorganisms in Soil

3.2.1. Bacteria

Bacteria are the smallest and most numerous of the organisms present in soil. They are single cell organisms and their size is approximately 1 micron in diameter and up to 10 microns in length. In spite of their small size, the bacterial biomass could be as high as 3500 kg/ha of surface soil due to their large population. The bacteria in soil are of different shapes. Those with spherical cells are called *cocci*, rod-shaped cells are called *bacilli*, and long spiral-shaped are termed as *spirilla*. The number of bacteria is highly variable, depending upon soil type, nature of crop cover and climatic conditions. Generally, soils with low organic matter and sandy texture have very low population. Some of the bacteria survive in soil under unfavourable conditions by forming spores which are resistant to prolonged dehydration and high temperatures. Direct examination of soil for bacteria shows that *cocci* and small rod-shaped bacteria are dominant in most of the soils. Some of the bacteria are surrounded by gummy capsules also.

The different bacterial genera commonly occurring in diverse soils are : *Pseudomonas, Arthrobacter, Clostridium, Bacillus, Achromobacter, Micrococcus* and *Agrobacterium*. The genus *Bacillus* has largest representation in soils in terms of species. Strictly anaerobic bacteria of the genus *Clostridium* occur in most soils, even under aerobic conditions. The occurrence of clostridia shows the presence of micro-anaerobic sites where these bacteria flourish. Aerobic soils receiving easily metabolizable organic matter also show anaerobiosis due to O_2 stress, created by rapidly developing aerobic bacteria which bring down partial pressure of O_2 and enrich the soil atmosphere with CO_2 conducive for anaerobic growth.

The presence of enterobacteria in soils, which strictly are not soil bacteria, is of great ecological significance, as it is indicative of fecal contamination. Their presence is a potential health hazard, particularly in growing crops whose edible plant parts come in direct contact with soil. Thus, enteric pathogens may get into food chain and cause human diseases.

There are many bacterial genera of significance for agricultural productivity, which do not appear on non-selective growth medium and require specialized techniques for their isolation. The autotrophic bacteria like nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*, and sulphur oxidizing bacteria, *Thiobacillus*, can be studied only using special growth medium. Also, there are soil bacteria which directly feed on other bacteria. Even though the number of such bacteria is small, they are significant for maintaining a biological equilibrium in soil by keeping a check on the growth of other bacteria. They belong to the genus *Bdellovibrio,* which are highly motile. Others are slime bacteria or myxobacteria which belong to the genera *Myxococcus* and *Polyandium.*

Bacteria due to their large number and very rapid rate of multiplication, play a very significant role in carrying out various biochemical reactions that control availability of plant nutrients. The processes of N_2 fixation, phosphate solubilization, organic matter decomposition and synthesis of humus, nitrification and denitrification, protein decomposition and ammonification, etc. lead to transformation of various macro- and micro-nutrients in soil and help in plant nutrition.

Certain free-living soil bacteria can reduce the atmospheric nitrogen to ammoniacal form, thus enriching soil with plant available nitrogen. These bacteria belong to the genus *Azotobacter, Azotomonas* and develop freely in soil, which are relatively high in organic matter. The genus *Beijerenckia* and *Derxia* are unique; they can fix nitrogen in soils which are highly acidic (pH 4.0). *Clostridium* fixes nitrogen under anaerobic conditions and can be of economic significance in flooded soils. Beside these free-living bacteria, there is another group belonging to the genus *Rhizobium* which fixes nitrogen in symbiosis with the legumes forming tiny out-growths on roots called legume root nodules, the sites of nitrogen fixation. *Azospirillum*, a spiral bacterium and others besides fixing nitrogen as free-living can also fix nitrogen in association with plants in rhizosphere entering into roots without forming nodule and the process is called "associative nitrogen fixation". The term 'plant growth promoting rhizobacteria' (PGPR) is now generally used to describe collectively all the beneficial microorganisms which promote plant growth by a variety of mechanisms like biological nitrogen fixation; phosphorus solubilization; production of plant growth hormones like indoles, gibberellins, cytokinins; production of antibiotics to inhibit pathogen; production of siderophores that bind iron and make it unavailable to pathogens (competetive antagonism); production of HCN, etc.

The soil bacteria responsible for transformation of nitrate to oxides of nitrogen and gaseous nitrogen resulting in the loss of fertilizer nitrogen are termed "denitrifying bacteria". These bacteria belong mainly to the genera *Bacillus, Pseudomonas,* and *Micrococcus*. These bacteria are essentially aerobic. However, under O_2-depleted conditions, these organisms use nitrates in place of oxygen as the terminal electon acceptor in the respiratory chain. Nitrate thus gets transformed to gaseous nitrogen or to nitrous oxide (N_2O) which escapes into the atmosphere. This process will take place under anaerobic or partially anaerobic conditions created due to the excessive soil moisture coupled with availability of easily-metabolizable organic compounds. However, even in well-drained soils, denitrification can take place on heavy application of easily-decomposable organic matter. The presence of a large population of denitrifying bacteria in soil is indicative of its potential to denitrify rather than the actual loss of nitrogen through denitirification.

The microbiological oxidation of ammonium to nitrate is one of the most important transformations taking place in soil, which helps plant nutrition since nitrogen is predominantly taken up as NO_3^- ion. This transformation is mediated by a group of bacteria called 'nitrifying bacteria'. It is a two-stage process wherein firstly ammonium is transformed into nitrite by bacteria belonging to the genus *Nitrosomonas* and in the second stage, bacteria of the genus *Nitrobacter* convert nitrite to nitrate. As the two processes take place simultaneously, there is no accumulation of nitrite as an intermediate. These bacteria are aerobic in nature. Hence, supply of oxygen is essential for this process. When oxygen supply is restricted, the activity of nitrifying bacteria goes down, lowering the nitrification rate. Any cultural practice which improves aeration results in enhancing nitrification. The optimum pH for these bacteria is between 6.5 and 7.5. Therefore, under acidic conditions nitrification is slow and is nearly negligible below pH 5.0.

3.2.2. Actinomycetes

Taxonomically actinomycetes are like bacteria which possess aerial hyphae like fungi. These organisms share characteristics of both bacteria (cell size, structure and mode of multiplication) and fungi (branching). They are in an evolutionary phase between the two. They are next to bacteria in numbers and are fairly widely distributed in soils. They are more common in dry soils and in undisturbed pastures and grasslands. Like bacteria, they are more common in neutral to slightly alkaline soils. They are aerobic organisms and therefore, their number is less in lowlands. As they can withstand drought conditions very well, they occur more frequently in soils undergoing dry spells. The species more commonly encountered in soils belong to the genera *Streptomyces, Micro-monospora, Nocardia* and *Thermo-actinomyces*. Many of the soil actinomycetes are known to produce antibiotics and have been commercially exploited to produce antibiotics of clinical importance. However, their role in biological equilibrium under natural soil conditions is doubtful as concentration of antibiotics produced by them seldom reaches concentration levels to inhibit the susceptible organisms.

Actinomycetes are nutritionally heterotrophic and are highly adaptive to degrade a wide range of organic substances, particularly those which are difficult to be decomposed by other soil organisms. They are also slow-growing organisms. Hence, they cannot compete with bacteria and fungi for the available nutrients and thus grow on substrates that are relatively more resistant to attack of bacteria and fungi. These organisms start functioning when easily decomposable fractions like sugars, starches, etc. are used up by bacteria and fungi and the more difficultly decomposable substances accumulate as they face less competition from other organisms. The role of actinomycetes in the synthesis of humus is well known. They are reported to produce a number of colour pigments contributing dark colour to soil humus. Actinomycetes population is also much larger in compost pits, as they can withstand high temperatures. Some of them are pathogens causing plant diseases such as potato scab, etc. The smell of a fresh soil wetted upon first rains is due to the production of volatile aromatic compounds by actinomycetes like geosmin, etc.

3.3.3. Fungi

Fungi are filamentous organisms with much larger cell width than actinomycetes. The filaments are called hyphae and the network of hyphae collectively is termed mycelium. The hyphae may be divided by cross walls called septa, while those without septa are called coenocytic and predominantly multiply by sporulation. They are heterotrophs devoid of chlorophyll and are primarily responsible for organic matter decomposition. Though their number in arable soils is less than that of bacteria, their biomass is equal or often more than bacteria owing to their size. Soil fungi can grow in a wide range of soil pH, but their population is more under acidic conditions because of severe competition with bacteria at neutral pH. A majority of fungi are aerobic and prefer to grow at optimum soil moisture. The contribution of these organisms in biochemical transformations under excessive moisture is negligible. Fungi are capable of sending hyphae into anaerobic zone in soil sustaining oxygen supply from the hyphae which develop in oxygen-rich environment and hence, the fungi growing in the surface soil, may send hyphae into deeper soil layers not sufficiently aerated.

Most of the soil fungi can be divided into three classes: (i) Phycomycetes, (ii) Ascomycetes, and (iii) Fungi Imperfecti. Phycomycetes are characterized by non-septate hyphae and spores are borne in sporangia. In Ascomycetes, the hyphae are divided by septa and a definite number of spores (usually eight), called ascospore, are borne in a sac like structure, ascus. Fungi Imperfecti, which are most frequent in soils, multiply by means of asexual spores called conidia. The genera most frequently encountered are: *Pythium, Rhizopous, Mucor, Cunninghamella* (Phyco-mycetes); *Chaetonium* (Ascomycetes); *Aspergillus, Penicillium, Verticillium, Alternaria, Fusarium* (Fungi Imperfecti). These fungi grow profusely in soils to which crop residues and organic manures have been added recently.

Fungi are heterotrophs and therefore derive nutrition from either living plant tissues as a parasite, causing plant diseases or dead tissues as a saprophyte. Saprophytic fungi perform a very important function in the decomposition of organic matter, particularly plant residues. Plants have rigid cell walls and low protein content, which make them resistant to the action of slowly diffusing hydrolytic enzymes. Being filamentous, fungi are able to penetrate the rigid plant tissues due to the pressure exerted by the hyphal tips. The hydrolytic enzymes produced inside tissues cause local softening of the tissues, resulting in increased diffusion of enzymes produced at the surface. Both bacteria and fungi then can act in tandem where bacteria move along with the fungal hyphae invading internal tissues, thus initiating decomposition of internal tissues by bacteria.

Some fungi form a symbiotic association with roots of higher plants, facilitating uptake of plant nutrients, particularly of those which are less mobile. This association is known as "mycorrhizal association". There are two types of mycorrhizal association:

(i) Ectotrophic mycorrhizae, where the fungus forms a mantle or sheath around the root surface (called Hartig net) and where the mycelium develops intercellularly. The fungi which form this type of association are species of *Boletus, Amenita,* etc.

(ii) Endomycorrhizae, where the fungus develops intracellularly in the root without forming Hartig net. In this association, the penetration of roots cells is characterized by the formation of terminal spherical structure called vescicles, which contain oil droplets and phosphorus. This type of mycorrhiza is called 'vesicular arbuscular mycorrhizae' (VAM) or simply arbuscular mycorrhizal fungi (AM fungi) and is of agricultural significance, particularly in the P-deficient soils, where the phosphorus in the vesicles diffuses out into the cytoplasm and is taken up by the plant. Fungi belonging to the genera *Glomus, Endogene* form this association.

The beneficial effect of these fungi on nutrient uptake has been attributed to three factors:

(a) Increased absorption of available nutrients from soil as the fungus changes root morphology, which results in the larger root surface available for nutrient absorption. Fungal filaments also act as the absorption surface,

(b) Increasing the nutrient availability by solubilizing insoluble nutrients like P, which thus become available to plant, and

(c) Increasing the nutrient mobility due to faster intracellular nutrient mobility and mobilizing nutrients from the soil mass not visited by the root system but traversed by the mycorrhizal hyphae.

3.2.4. Algae

Soil algae are chlorophyll-containing organisms. They are autotrophic, and therefore, their development is not restricted by organic carbon supply. They are abundant in habitats exposed to light and have sufficient moisture. They are unicellular, filamentous or form colonies from single cells.

Soil algae are classified on the basis of the colour (pigments) as: (i) Cyanophyta (blue green), (ii) Chlorophyta (grass green), (iii) Xanthophyta (yellow green), and Bacilliriophyta (golden brown). Blue green algae, also known as 'Cyanobacteria', are most important from the agricultural point of view because they fix atmospheric nitrogen and contribute towards the nitrogen economy of soils, particularly in rice cultures of tropics.

Blue green algae (BGA) have been reported to fix about 20 kg N per ha. Some of the important genera dominant in rice fields are *Anabaena, Nostoc, Phormidium, Scytonema, Aulosira, Tolypothrix,* etc. They fix nitrogen in specialized cellular structures called "heterocysts", which are thick walled and have low oxygen concentration that allows the enzyme nitrogenase to function optimally. The ability of BGA to fix N_2 was first demonstrated by P.K. De in the 1930s. The agricultural significance of blue green algae in the nitrogen economy of paddy soils was established by the R.N. Singh in early-1950s. Submerged soil conditions in the rice field provide an ideal environment for the growth of algae, as the soils seldom dry out. These organisms not only help in the N-nutrition of rice plants but are also reported to synthesize plant growth hormones and thereby help plant growth. As they have photosynthesizing capacity, they release O_2, which support aerobes in flood water. The beneficial effect of algal inoculation has been widely demonstrated in different types of soils and climatic conditions.

A. nitrogen fixing algae, *Anabaena azollae,* forms a symbiotic association with a fresh water fern, *Azolla* and fixes nitrogen. The azolla biofertilizer not only contributes towards soil nitrogen but also adds organic matter. Algae are also found in association with fungi called 'lichens'. In this association, the algae provide carbohydrates, produced through photosynthesis, to the fungi and the fungal symbiont provides mineral nutrition and regulates water supply. Lichens are distributed worldwide on rocks, soils, buildings, foliage, tree trunks, etc. Usually lichens are amongst the first colonizers of barren rocks and initiate soil formation.

3.2.5. Protozoa

Soil protozoa are single cell organisms belonging to animal kingdom and are larger in size than most microorganisms found in the soil. The life-cycle of protozoa consists of an actively growing phase when it multiplies, and a resting phase when under adverse environmental conditions like low moisture and high temperature, vegetative cell covers itself with a thick coating which is called 'cyst'. The protozoa are classified on the basis of mode of locomotion. Some move by long whip-like structures called flagella and others by short hair-like appendages called cilia; and still others by internal protoplasmic movement forming flexible temporary organ called pseudopodia or false foot.

In fertile soils, the number of protozoa may be up to 1 million per gram. Soils which are moist contain a large population of these organisms. As most of the soil protozoa are saprophytic, their population is high in soils with high organic matter. Some of the protozoa, however, directly feed on bacteria present in soil. Therefore, it was once thought that high protozoa population is detrimental to soil fertility because they reduce population of useful bacteria in soils. It is now considered that protozoa do not reduce bacterial population permanently, and moreover, soil organisms other than bacteria are also involved in plant nutrient availability. Protozoa mainly influence the organic cycle. Their predatory nature on bacteria contributes to the turnover of available nutrients and prevents immobilization of nutrients by keeping a check on bacterial population.

3.2.6. Nematodes

Amongst the microfauna, the nematodes are next in abundance to protozoa. Because of their narrow long bodies, they are also called thread worms. They may be either saprozoic, feeding on decaying organic matter or parasitic on living plants. Due to less number in soils, they are not of much significance in organic matter decomposition. However, parasitic nematodes cause plant diseases and thus gain significance in some localized pockets due to high population. By infesting plant roots, some nematodes form characteristics knots. In India, vegetable crops are particularly susceptible to nematode infestation. They are controlled by chemical fumigants. Amendment of soils with some non-edible cakes from *neem* and *karanj* and sawdust is also reported to control these parasites. Nematode trapping fungi parasitise on them in soil. These organisms otherwise have little role in soils.

3.2.7. Viruses

Viruses are ultramicroscopic organisms smaller than bacteria, which cannot be seen by an ordinary light microscope. They parasitise on animals, plants and microorganisms. Viruses parasitising bacteria are known as bacteriophages. When bacteriophages develop rapidly in a soil, they may kill useful soil bacteria and make the soil sick. A large-scale failure of nodulation in legumes is indicative of the presence of bacteriophages of the specific rhizobia.

(Necessary binding compounds

Sometimes a soil may act as a sink for viruses causing human diseases. For example, Hepatitis virus survives longer in soil than in any other habitat. Similarly, several enteric viruses can be traced to soil where they remain dormant for long periods and become active after they infect a suitable host. Soil viruses do not take part in nutrient transformations due to their parasitic nature. However, they may affect nutrient cycles indirectly by parasitising bacteria responsible for these cycles such as nitrifying bacteria, nitrogen fixing bacteria, cellulose hydrolysers, etc.

4. Interactions among Soil Organisms and their Role in Agriculture

Soil is the largest terrestrial ecosystem where a wide variety of relationships exist between different types of soil organisms. The interrelationships and interactions of various groups of a soil community are in a dynamic state and maintain a biological equilibrium in the community. Following interactions may occur between any two species:

(i) *Neutralism* — Here each organism behaves independently and this kind of interaction probably does not exist in the soil communities.

(ii) *Symbiosis* — This is an association between two organisms where both the partners derive mutual benefit. This association has been exploited usefully in agriculture. There could be many examples of symbioses. However, three symbioses have already been discussed. Of these, biological nitrogen fixation is of paramount importance for agricultural productivity, while another very important association called mycorrhiza is widespread in trees as well as in crop plants.

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(iii) *Protocooperation* — In this kind of association both partners are mutually benefited. Unlike symbiosis, protocooperation is not obligatory for their existence or performance of a particular activity. These associations abound in terrestrial ecosystem and are very useful in agriculture. A few of them are listed here:

(Necessary binding & compulsory)

(a) Synergism between VAM–Legume plant and *Rhizobium* — In this synergism, three organisms involved are vesicular arbuscular mycorrhizal (VAM) fungus, legume plant, and *Rhizobium.* The efficiency and benefit of mutualism among the three is much higher in terms of nitrogen fixation and phosphorus availability, resulting in higher yields of crop and improved fertility of soil.

(b) Synergism between phosphate solubilizers, legume plant and *Rhizobium.*

(c) Role of plant growth promoting rhizobacteria (PGPR) is also a good example of synergism where rhizobacteria help the plant by restricting the growth of pathogen in rhizosphere through different mechanisms, and provide some phytohormones or growth promoting substances. In legumes, they improve nodulation, nodule occupancy or strain competition and grain yield.

(iv) *Commensalism* — In this association, a partner derives the benefit of the company of the associate without affecting it. This type of relationship is found in organic matter decomposition. For example, true cellulose decomposers having enzyme called C_1 act on undegraded cellulose. Later, the partially-decomposed cellulose can be metabolised by many soil microorganisms.

The harmful associations are also many in soils, which sometime affect the crop production adversely:

(i) *Ammensalism* — It is a kind of relationship in which a partner supresses the growth of other partner by producing toxins like antibiotics, harmful gaseous compounds like NH_3, CO_2, ethylene, sulphur compounds, nitrite, H_2O_2, and HCN, etc. The antagonistic associations sometimes affect the useful process adversely. Sometimes, the growth of *Nitrobacter* and some fungi may be affected adversely by the large amount of NH_3 released during decomposition of leguminous green manures.

(ii) *Competition* — It is a universal phenomenon of co-existence in a community where one species is suppressed as the two species struggle for the limited supply of a nutrient or other common requirements. Such interaction in soil is harmful. Normally, a severe competition between soil microbes for limited availability of easily metabolizable carbon compound is a rule rather than exception, as it is readily used by almost all soil microbes. Therefore, the organisms having inherent capability to grow fast are better competitors.

(iii) *Parasitism* — It is an association where one partner lives in or on the body of the other (host) and feeds on the body fluid of the host. So this is a host-parasite relationship in which one is benefited while other is adversely affected. Parasitism is probably widespread in soil communities. Earthworms and other macroorganisms are also prone to parasitic attack by bacteria, fungi, viruses, etc. Commercial preparations are available in the market as biocontrol agents of root rot and wilt diseases.

(iv) *Predation* — It is the direct feeding of one organism on other. It is highly prevalent in protozoa. They feed on bacteria to strike a balance between the population of prey and predator. Myxobacteria and slime moulds also feed on soil bacteria.

5. Nitrogen Fixing Microbes and their Plant Association

Bacteria are capable of reducing nitrogen (N_2) to ammonia (NH_3) with the help of an enzyme called nitrogenase. The process is known as 'Biological Nitrogen Fixation' (BNF). Contribution by these nitrogen fixers is reported to be about 140 million tonnes N/year, whereas N-input through fertilizer is about 100 million tonnes N/year. The importance of these organisms in the nitrogen economy of soils thus becomes obvious.

5.1. Different Groups of N_2 Fixers

There are three main groups of N_2 fixers as given below:

(i) Symbiotic	–	*Rhizobia, Frankia, Anabaena*
(ii) Associative	–	*Azospirillum, Acetobacter, Herbaspirillum*
(iii) Free living	–	*Azotobacter, Derxia, Cyanobacteria, Rhodospirillum, Beijerinckia*

Symbiotic nitrogen fixers reduce nitrogen in association with plants by forming some specialized structures in plants. Some of the symbioses of agronomic importance are :

(i) Legume-*Rhizobium* symbiosis

(ii) Non-legume-*Frankia* symbiosis

(iii) *Azolla* -*Anabaena* symbiosis

Let us now learn a little more about these symbioses.

5.2. Legume-Rhizobium Symbiosis

Some plants of leguminosae family form a symbiotic association with bacteria of the genus *Rhizobium* which fix atmospheric nitrogen. Specific rhizobia for different legumes infect the root moving to the root cortex through an infection thread, which results in the formation of a tiny out-growth called legume root nodule. Few plants like *Sesbania rostrata* form such nodules on the stem as well. Nitrogen is fixed in these nodules. The association of legumes with rhizobia is host-specific. The presence of flavonoids and isoflavonoids in the legume root exudates is reported to be responsible for the host-specificity. The flavonoids are also implicated in triggering the process of nodulation. The nodules are of two types:

(a) Determinate: The growth of which stops after sometime as found in mungbean, and

(b) Indeterminate: In which nodule growth continues as in chickpea and clovers.

Once the rhizobia are delivered into cortical cells, they change their morphology and physiology to become bacteroid, the actual seat of N_2 -fixation. The bacteroids are separated from the plant cell contents by peribacteroid membrane synthesized by the plant. Bacteroids have nitrogenase enzyme and are embeded into leghaemoglobin, a hemeprotein. The role of leghaemoglobin is to regulate the supply of oxygen to bacteroids and to prevent the exposure of nitrogenase to O_2. The gaseous N_2 is converted to NH_4^+ which diffuses into cytosol to be carried to shoot for protein synthesis. Legumes are reported to fix a variable amount of N_2 (Table 1), depending on many factors like soil environment, air environment and host genotypes. The response of pulses to *Rhizobium* inoculation at farmers' fields at different locations is given in Table 2.

Table 1. Potential N contribution of N-fixing legumes in Indian soils

Crop	Fertilizer N equivalents (kg N/ha)	
	N fixed (kg N/ha/Year)	Residual effect in succeeding cereal crop
Alfalfa (*Medicago sativa*)	100-300	–
Clover (*Trifolium* spp.)	100-150	83
Chickpea (*Cicer arietinum*)	20-63	60-70
Cowpea (*Vigna sinensis*)	50-85	60
Greengram (*Vigna radiata*)	50-55	30
Groundnut (*Arachis hypogaea*)	112-152	60
Guar (*Cyamopsis tetragonoloba*)	37-196	-
Lentil (*Lens culinaris*)	35-100	18-30
Pea(*Pisum sativum*)	46	20-32
Pigeonpea (*Cajanus cajan*)	68-200	20-49
Soybean(*Glycine max*)	49-130	

Source: Subba Rao (1988)

Table 2. Response of pulses to *Rhizobium* inoculation at farmers' fields at different locations

Crop	Location	Number of trials	Increase in yield (kg/ha)	
			Range	Average (per cent)
Chickpea	Badnapur (Maharashtra)	5	140-160	10
	Durgapura (Rajasthan)	2	250-520	24
	Sehore (Madhya Pradesh)	3	120-140	20
Lentil	Dholi (Bihar)	3	50-110	15
	Ludhiana (Punjab)	5	40-60	20
Pigeonpea	Badnapur (Maharashtra)	4	20- 70	8
	Gulbarga (Karnataka)	1	80	9
Mungbean	Sehore (Madhya Pradesh)	5	140-180	7
	Badnapur (Maharashtra)	3	40-110	4
	Durgapura (Rajasthan)	2	30	15
Urdbean	Bhadnapur (Maharashtra)	2	50	13
	Dholi (Bihar)	5	70-80	17
	Pantnagar (Uttarakhand)	2	40-100	25

Source: Anonymous (1997)

5.3. Non-legume –Frankia Symbiosis

This symbiosis involves forest trees and shrubs, and a genus of actinomycetes called *Frankia*. There are about 264 species belonging to 25 genera, which take part in symbiosis with *Frankia*. Important actinorhizal plants are: *Alnus*, *Myrica*, *Elaeagnus*, *Dansea*, *Casuarina* and *Allocasuarina*. Families Casuariaceae and Myricaeae are found in tropics. *Casuarina* grows extensively in the coastal areas of Tamil Nadu, stabilizing sand at seashores. *Frankia* is a filamentous gram positive actinomycete. It is more like fungi having vesicles, a seat of N_2–fixation and sporangia bearing spores. The process of nodulation is similar to legume-rhizobia symbiosis and appears to be highly evolved. Amount of N_2 fixed by this symbiosis is almost equal to that of the legume–rhizobia symbiosis.

5.4. Azolla-Anabaena Symbiosis

Azolla is an aquatic fresh water heterosporous fern found floating free on the surface of the water worldover. All the species of *Azolla* have algal symbiont called *Anabaena azollae* in a specialized cavity in the upper leaf surface. The microsymbiont remains associated with *Azolla* throughout its life-cycle. The *Azolla* leaves are 1-3 cm in diameter and remain in tight clusters. *Azolla* is a fast growing plant having doubling time of 2-3 days under optimum conditions and supplies nitrogen to soil on its decomposition. The symbiosis is highly efficient N_2 –fixing system in rice fields and can fix up to 30-40 kg N/ha. Suitable growth temperature, 25-30 °C, and good availability of phosphorus are the two important requirements for the growth of *Azolla* and for harnessing about 120-150 kg N/ha.

It is most suitable for the region where temperature remains in the range 20-30 °C throughout the year. This has promise in coastal areas of Orissa, Andhra Pradesh and Tamil Nadu.

5.5. Non-specific Associative N_2 Fixers

Rhizosphere harbours a large number of rhizobacteria. Many of them promote plant growth by different mechanisms and one of them is biological nitrogen fixation (BNF). Rhizobacteria like *Azospirillum, Acetobacter, Azoarcus, Azotobacter, Flavobacterium, Pseudomonas, Herbaspirillum* are some of the nitrogen-fixing bacteria found in rhizosphere of different plants. These bacteria are capable of using exudates of roots as the source of energy. Some of these like *Azospirillum*, *Acetobacter* and *Herbaspirillum* are reported to be endophytes living in the cortical region of plant roots.

In the case of associative nitrogen fixers, *Azospirillum lipoferum* is reported to be associated with the roots of C_4 plants like maize, while *Azospirillum brasilense* is associated with C_3 plants like rice and wheat. Similarly, host-specificity is reported for *Azotobacter paspali* with *Paspalum notatum* cv. *batatis* but not with cv. *pensacola.*

Not only rhizosphere has associative nitrogen fixers, but phyllospheric association by epiphytes or leaf surface nitrogen fixers is also reported. It is observed that half of the Angiosperms, found in eastern India, have these organisms on the leaf surfaces. *Beijerinckia* is predominantly found on the leaf surface of rice, wheat, sugarcane and sorghum crops. Some of the plants have leaf nodule formed by *Beijerinckia.*

5.6. Free-Living Nitrogen Fixers

Many soil bacteria are capable of reducing molecular nitrogen to NH_4^+ without forming any association with plants. These organisms can be broadly placed into heterotrophic and phototrophic groups (*see* Box 1).

These organisms do not specifically form association with plants, though they may be encountered in the rhizosphere of many plants. Many of them are strictly aerobes, while others are strictly anaerobes. Similarly, some are purely heterotrophs, while others are photoautorophs, but all of them have nitrogenase enzyme. Interestingly, aerobes have protective mechanisms, like development of heterocysts in some cyanobacteria and respiratory protection, uptake of hydrogenases and switch on-off mechanisms in *Azotobacter*, for protection of nitrogenase from oxygen. Free living nitrogen fixers do not have high N_2–fixing capacity probably because of lack of sufficient food supply and unprotective niche. Unlike legume-rhizobia symbiosis, they supply about 10-15 kg N/ha; however, they also function as plant growth promoting rhizobacteria (PGPR) in promoting plant growth.

6. Effect of Different Agronomic Practices on Soil Organisms

Biological processes are central to the fertility and productivity of soil and sustainability of the agro-system. Agronomic management practices for crop production immensely affect the population and activity of soil organisms.

6.1. Tillage and Cultivation

Cultivation of virgin soil adversely affects the build-up of organic matter in soil because it exposes the enlarged soil surface to elements of nature. Different types of tillage operations like deep and excessive tillage, lead to rapid loss of organic matter while no-tillage conserves it. Churning and exposure of surface leads to higher microbial activity due to breaking of soil granulation and incorporation of air and surface crop residues. Puddling is another tillage operation bringing about many changes in the physical condition of soil and thereby affecting soil organisms. It is common knowledge that forest and virgin soils have more soil macroorganisms like earthworms, termites and arthropods than cultivated soils.

6.2. Cropping Practices

Monoculturing, mixed or interculturing have significant and different effects on population and activity of soil organisms. For example,

Box 1. Various heterotrophs and phototrophs

- Heterotrophs
    - Aerobes → *Azotobacter, Derxia, Beijerinckia*
    - Micro-aerobes → *Thiobacillus; Methylococcus, Xanthobacter*
    - Facultative anaerobes → *Klebsiella, Bacillus, Citrobacter*
    - Obligateanaerobes → *Clostridium, Desulfovibrio, Desulfotomaculum*
- Phototrophs
    - Aerobic → *Anabaena, Nostoc, Calothrix*
    - Micro-aerobes → *Plectonema, Gloeothece, Lyngbya*
    - Facultative anaerobes → *Rhodospirillum, Rhodopseudomonas*
    - Obligate anaerobes → *Chrotium, Thiocystis*

cereal–cereal rotation results in accumulation of toxic metabolites or root exudates which are not used. Changing crop sequences disturbs the unfavourable populations. Pulses and cereals in rotation have advantageous effects on soil organisms. Crop varieties may also have differential influence on rhizospheric population. Some rice varieties have more rhizospheric N_2-fixing capacity. Some soybean varieties have siderophore producing microbial population in rhizosphere and can meet the iron requirements of soils deficient in this element.

6.3. Manures and Fertilizers

Application of manures and fertilizers directly or indirectly increases the population of soil organisms. Manures when added to soil provide carbon source to soil organisms. These materials provide nutrients to soils, improve their physical condition and increase soil organic matter. All these improvements are interrelated, have direct and indirect beneficial effects on soil enzymes, population and activity of soil organisms; improving soil fertility and productivity. Green manuring is an age-old practice which adds lot of carbonaceous material of relatively narrow C/N ratio and supports tremendous activity and population of soil organisms. Any organic material like crop residues, sewage and sludge, etc. added in sufficient amounts to soil, improves the physical condition of soil, provides plant nutrients, and benefits soil organisms. Carbonaceous material having wide C/N ratio helps in the synthesis of more humus in soil.

Inorganic fertilizers also increase the soil microbial population. Continuous application of fertilizers may have harmful effect on soil macroorganisms; however, if carbon source is readily available in soil, the microbial population is increased. Indirect effect of fertilizer application is in producing more crop biomass, particularly through roots. Residues and root exudates benefit soil organisms and their activity. Application of phosphatic fertilizers increases N_2–fixation by free-living as well as symbiotic nitrogen fixers.

6.4. Soil Amendments — Liming and Gypsum Treatment

Soil amendments like liming or gypsum treatment of problem soils tremendously improve the activity and population of soil organisms. Liming of acidic soils has been reported to increase nodulation.

6.5. Pesticides

Sometimes application of pesticides has harmful effect on soil population. One reason of lower population of soil macroorganisms is continuous application of agricultural chemicals, particularly biocides. If these chemicals somehow accumulate in soil, they become toxic to soil population. Application of pesticides directly to soil reduces the microbial population temporarily and ultimately microbial balance in the soil population is restored.

7. Role of Organisms in Soil Fertility

Soils have various type of organisms, as described in the preceding sections. These organisms thrive in soils due to the presence of organic matter in soils, which serves as a source of energy for them. Soil organisms being largely saprophytic in nature derive carbon and energy from the organic matter and multiply. Upon death and decomposition, they release plant nutrient elements hooked with the organic matter. The soil microbial biomass constitutes about 2-4% of the soil organic matter content of soil and is a reservoir of plant nutrients that is readily available to plants owing to its rapid turnover. .

7.1. Decomposition of Organic Matter

Arable soils receive the supply of organic matter continuously through crop growth, while forest soils accumulate organic matter through tree litter. Plants take up inorganic nutrients from soil and convert them to organic forms. Soil organisms use the organic matter as a source of energy. In this process, carbon is released as CO_2 and nitrogen is converted to NH_4, which is further oxidized to NO_3 for use by plants. Similarly, other nutrients are also converted into plant-usable forms. This process of release of nutrients from organic matter is called 'mineralization' and is influenced by several factors. The C/N ratio, particle size, stage of decomposition of material finding entry into the soil, moisture, temperature, pH, aeration, availability of nutrients, clay-content of soil, tillage, loading rate and climate are some important factors which determine the rate of decomposition. The fate of released nutrients through soil microbial activity is schematically shown in Figure 4.

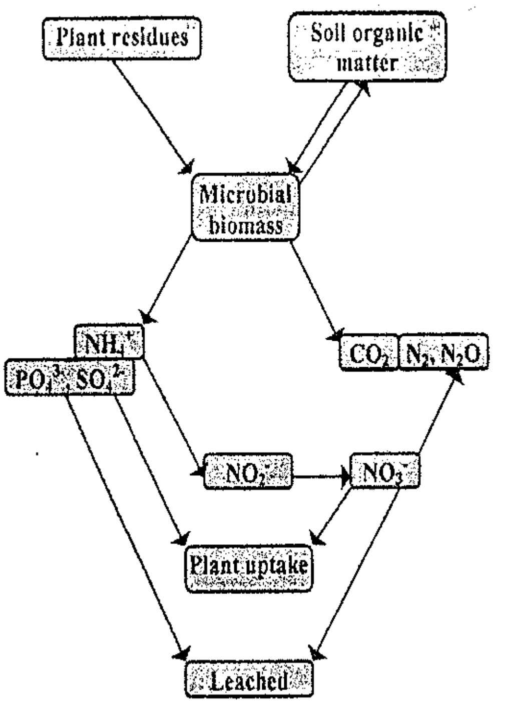


Figure 4. Fate of nutrients released through soil microbial activity

7.2. Plant Nutrient Transformations

An important function of microbes on this planet is to facilitate the recycling of elements. In the preceding paragraphs we have learnt how organically-bound nutrient elements are brought back to their mineral forms by soil organisms.

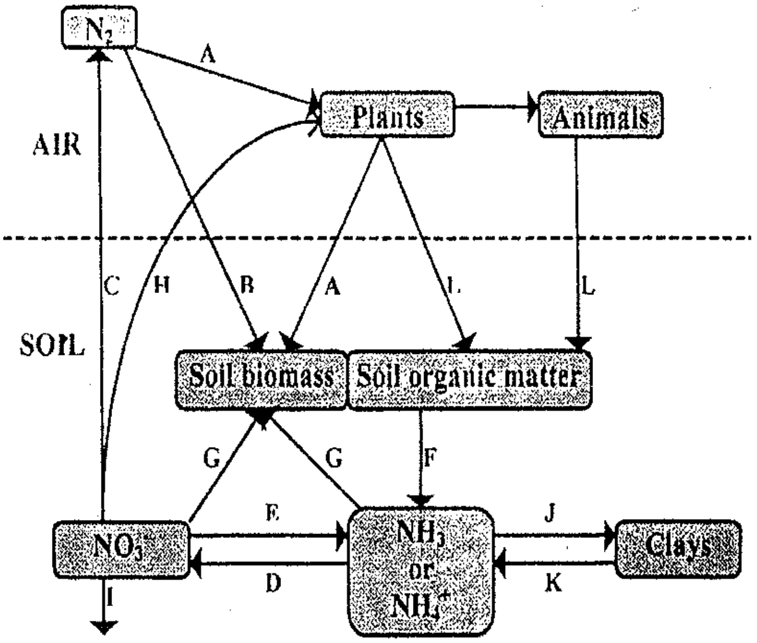
7.2.1. Nitrogen Cycle

Next to carbon, hydrogen and oxygen, nitrogen is by far the most important in plant productivity. Though nitrogen is abundant in atmosphere, it is found in different oxidation states. About 95 to 98% soil nitrogen is in organic form and is, therefore, decomposed by soil organisms. Soil mineral nitrogen is much susceptible to losses. Minimizing these losses assumes much importance in crop production. The nitrogen cycle in nature is represented in Figure 5.

Mineralization of Nitrogen — Organic forms of soil nitrogen are proteins, microbial cell wall, constituents like peptidoglycans and chitin, nucleic acids, free amino acids, and amino sugars, etc. A little amount of soil nitrogen may also be in the form of cholin and other phospholipids. All these compounds binding nitrogen are easily attacked by microbial hydrolytic enzymes. Proteins are hydrolysed by proteinases to peptones and by peptidases to peptides. These peptides are ultimately broken down to yield free amino acids. The amino acids or amino sugars, etc. are decomposed further to the level of ammonium ions (NH_4^+). The process of conversion of organic form of nutrient element to its mineral form (inorganic form) is called 'mineralization'. When organic nitrogeneous compounds are enzymatically hydrolysed to the level of NH_4^+, the process is called 'ammonification' (*see* Box 2).

A large segment of soil microorganisms is proteolytic, capable of growing under aerobic as well as anaerobic conditions. These organisms derive carbon, energy as well as reducing power from the organic substances and thus are heterotrophic in nature. Nitrogeneous compounds having narrow C/ N ratio are generally attacked by bacteria, followed by fungi. The ammonium ion released on mineralization of organic compounds is taken up by the crop, immobilized by soil microbes, oxidized to NO_3^-, fixed on exchangeable and non-exchangeable sites of clays and soil organic matter or lost through volatilization. Ammonium ion released in the process of mineralization is simultaneously immobilized by the soil microorganisms for their cell synthesis. Immobilization is the process of conversion of mineral form of element into organic form, a reverse process of mineralization. In the process of nitrogen immobilization, ammonium ion is incorporated into amino acids by the process called 'amination'.

The process of mineralization–immobilization goes on simultaneously in soil and it is difficult to estimate the amount of total NH_4^+ released or immobilized at a particular point. However, net mineralization or immobilization at a particular point of decomposition can be estimated by using specific techniques involving 15N. The rate of these processes is affected by many factors such as carbon : nitrogen (C/N) ratio of the material undergoing decomposition, lignification of the material, soil



A: N_2 fixation (symbiotic)
B: N_2 fixation (non symbiotic)
C: Nitrate reduction (dissimilatory)
D: Nitrification
E: Nitrate reduction (assimilatory)
F: Ammonification / Mineralization
G: Immoboization
H: Plant assimilation
I: Leaching
J: Ammonium fixation
K: Ammonium release
L: Residue degradation

Figure 5. The nitrogen cycle

Box 2. Various heterotrophs and phototrophs

Proteins
Peptides
Amino acids
Nucleic acids
Chitin

$$\xrightarrow[\text{Proteinases, Peptidases, Aminohydrolases Amidinohydrolases, Aminodehydrolases and Oxidases, Nucleases, Chitinases, etc.}]{\text{Ammonification}} \boxed{NH_4^+ + CO_2 + R}$$

pH and moisture, etc. The N_2-rich material having C/ N ratio as 25:1 or below shows net mineralization and thus the rate of mineralization will be faster and *vice-versa*. More the lignin content in the material, the slower is the rate of mineralization because microorganisms growing on such material do not have carbon substrate easily available for cell synthesis. The process of mineralization–immobilization occurs with N, P and S in the same manner and determines the amount of these nutrients available for plant uptake. However, other essential nutrient elements for plants are also released during the process of mineralization and soil organisms augment soil fertility by releasing nutrients from organic residues received by soils.

Nitrification — Ammoniacal nitrogen released through mineralization of proteinaceous substances is further oxidized to nitrates, a form readily available to plants. This process is called 'nitrification'. It is a two-stage process carried out by two different types of microbes. Organisms oxidizing NH_4^+ to NO_2^- are: *Nitrosomonas europaea, Nitrosospira briensis, Nitrosococcus nitrosus*, etc. and those oxidizing NO_2^- to NO_3^- are: *Nitrobacter winogradsky, Nitrospira gracilis, Nitrococcus mobilis*, etc. Nitrification is a useful process as a majority of crop plants take up nitrogen in the form of nitrates. However, if the rate of nitrification is faster than NO_3^- uptake by crop, nitrates may either be denitrified or lost by leaching, depending on conditions operating in the field. Generally, soil aeration, moisture, temperature and organic matter content influence the rate of nitrification in the soil.

Denitrification — The process of reduction of NO_3^- to N_2 or N_2O mediated by microorganisms is known as 'denitrification'. The process is wasteful as plant-available nitrogen is lost to atmosphere. This process is also called 'dissimilatory nitrate reduction'. Nitrates are also reduced to NH_4^+ and this is incorporated into proteins through formation of amino acids. This process is called 'assimilatory nitrate reduction'. This operates in all the green plants, bacteria, fungi, etc. Denitrification involves nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase enzymes. Two important factors encouraging rate of denitrification in soil are the presence of readily decomposable organic substrate for microbial growth and O_2 stress. Thus, rice soils are more prone to denitrification loss. Facultative anaerobes like *Alcaligenes, Bacillus, Flavobacterium, Paracoccus, Pseudomonas* are responsible for denitrification.

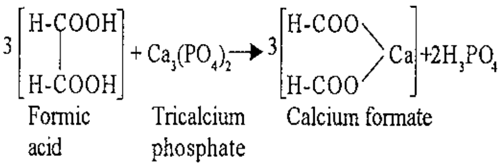
Biological N_2 Fixation — Substantial amount of atmospheric nitrogen which otherwise is not used by plants is added to soil through different types of nitrogen fixation processes, discussed earlier. This trait of procaryotic cell is being commercially exploited and will be discussed later.

7.2.2. Phosphorus Cycle

Phosphorus is a nutrient required by plants in large amounts. Approximately 30-50% of the total P in the soil is in organic combinations. Organic soil P is found in phytates (Ca or Mg salts of inositol hexaphosphate), nucleic acids, phospholipids, sugarphosphates, coenzymes, etc. Inorganic forms of soil P are iron phosphate, calcium phosphate, aluminium phosphate, etc. Most of the combinations of phosphates are either insoluble or poorly soluble, depending on the soil pH. Moreover, when soluble P is added to a soil, a large proportion of it becomes fixed on the soil colloids. A small proportion of this phosphorus is extractable with water, and even dilute acids and bicarbonates are not able to solubilize a major part of fixed phosphorus.

Interestingly, phosphorus increases the efficiency of carbon and nitrogen immobilization and thus, humus formation. Soil organisms play important role in soil P transformations. Besides mineralization–immobilization processes to release plant organic P through enzymes like phosphatases, microorganisms also attack inorganic form of P indirectly, the process is called phosphate solubilization. The mechanisms appear to be simple and involve the following steps:

(a) Heterotrophic microorganisms growing on organic substrates produce organic acids of different kinds, both aliphatic and aromatic. These acids reduce soil pH and hence increase availability of soil fixed P. Alternatively, these acids can also form weak ligands, chelating metal and liberating P in solution. Carboxylic and hydroxyl groups are known to chelate the metals.



$$3\begin{bmatrix}\text{H-COOH}\\ | \\ \text{H-COOH}\end{bmatrix} + Ca_3(PO_4)_2 \rightarrow 3\begin{bmatrix}\text{H-COO} \\ \text{H-COO}\end{bmatrix}Ca + 2H_3PO_4$$

...(1)

(b) The H_2S gas produced in the flooded soil may react with Fe-P, releasing the phosphorus in soil solution and forming Fe-S.

(c) Soil microorganisms are also known to produce compounds like siderophores and HCN, etc. which help in P solubilization.

(d) Mycorrhizal association improves P nutrition by solubilizing fixed P and also increasing its mobility.

7.2.3. Sulphur Cycle

Sulphur is an important plant nutrient element, transformation of which is affected by soil microorganisms. In soil, sulphur is found in both organic and inorganic forms. It is found in two types of compounds: (i) Organic sulphates, for example, sulphate esters (O-C-O-S), sulphamates (C-N-S) and sulphated thioglucosides (N-O-S); and (ii) Carbon bound sulphur (C-S), which includes amino acids, proteins, polypeptides, heterocyclic compounds

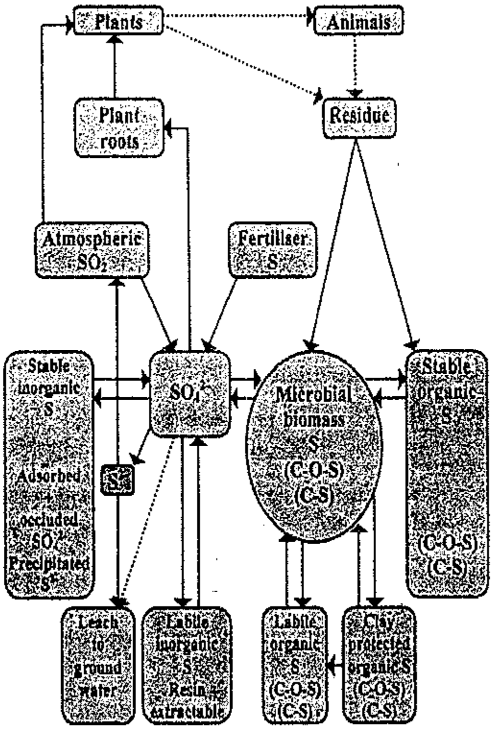


Figure 6. Main forms of sulphur and their transformation in soil-plant system

(biotin and thiamine), sulphonates, sulphones and sulphoxides. Inorganic sulphur is constituted by elemental sulphur (S^0), sulphide (S_2^-), sulphite (SO_3^{2-}), thiosulphate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$), and sulphate (SO_4^{2-}). Like nitrogen, sulphur also exists in a number of oxidation states, from +6 to –2 and in the biological system, most oxidized and most reduced forms of sulphur are important (Figure 6).

During mineralization, proteins are depolymerized to amino acids by the same process as that of nitrogen. The sulphur moiety of the sulphur containing amino acids is cleaved by enzymes like cysteine desulphydrase which cleaves the sulphur from cysteine amino acid and serine sulphydrase from serine amino acid. The sulphur released from amino acid is available to microorganisms for assimilation or for reduction. The microorganisms taking part in mineralization–immobilization of sulphur compounds are almost similar to the one mineralizing – immobilizing nitrogen.

Sulphur oxidising bacteria can be put into four categories:

(i) Obligate chemolithotrophs of genus *Thiobacillus*,

(ii) Facultative thread forming bacteria of genera *Beggiotoa*, *Thiothrix* and *Thioplana* which oxidize H_2S and deposit S,

(iii) Some heterotrophic bacteria and fungi like *Aspergillus*, *Penicillum*, *Arthrobacter*, *Bacillus*, *Pseudomonas* and some actinomycetes. These organisms do not get energy, unlike chemoautotrophs, in oxidizing inorgnic sulphur compounds. However, contribution of these organisms is more in oxidizing sulphur compounds when soil pH is not low, the range where *Thiobacillus* is more active; and

(iv) Photo-lithotrophs also called green and purple bacteria of the genera *Rhizospirillum*, *Rhodo-pseudomonas*, *Chlorobium* and *Chromatium*, are generally encountered in aquatic system.

Sulphur-reducing bacteria are quite specific in nature and are placed in about eight genera, important amongst which are *Desulfovibrio* and *Desulfomataculum*. They are obligate anaerobes and facultative chemolithotrophs using organic acids, alcohols and H_2 as electron acceptors. For example, lactic acid can receive electron from SO_4^{2-} in the presence of specific oxidase enzymes.

$$2CH_3CHOH\ COOH + SO_4^{2-} \longrightarrow 2CH_3COOH + HS^- + H_2CO_3 + HCO_3^- \quad \ldots(2)$$

They can also use H_2 to reduce inorganic sulphur compounds as given in Eq. (3):

$$S_2O_3^{2-} + 4H_2 \longrightarrow 2HS^- + 3H_2O \quad \ldots(3)$$

Some of the sulphur-reducing bacteria are nitrogen fixing and grow purely on inorganic compounds like CO_2 (carbon source), SO_4 (energy source), N_2 (nitrogen source) and H_2 (electron acceptor).

7.2.4. Other Mineral Elements

Some of the nutrient elements like iron and manganese are also oxidized–reduced by soil microorganisms in addition to being released from organic to inorganic form during mineralization of organic residues. Iron can exist in three oxidation states: Fe^0, Fe^{2+} and Fe^{3+}. Under acidic condition, Fe^0 is chemically oxidized to Fe^{2+} which up to pH 5 is stable, but at higher pH, it is further oxidized to Fe^{3+}. In soil, *Thiobacillus ferroxidans* is able to oxidize

Fe^{2+} to Fe^{3+} under acidic environment, as in case of sulphur oxidation. There are many other bacteria under aquatic environment that oxidize Fe^{2+}. These include *Leptothrix, Crenothrix* and *Gallionella* and render the iron unavailable to plants.

Some of the microorganisms produce siderophores, particularly under the environment of iron-deficiency. These siderophores act like organic ligands and chelate iron, thus increasing its availability to the bacteria-producing siderophore as well as to plant in rhizosphere. Some of the siderophore-producing microbes like *Pseudomonas* have also been reported to control plant diseases. Under anaerobic conditions, Fe^{3+} can serve as an electron acceptor for some facultative anaerobes like *Bacillus, Fusarium* and *Alternaria.* Recently, it has been shown that 'Vesicular-Arbuscular Mycorrhizae' (VAM) increases uptake of iron (Table 3).

Manganese oxidation at neutral or acidic pH is through enzymatic oxidation by soil bacteria like *Arthrobacter* and some of the fungi. The filamentous sheathed iron bacteria *Leptothrix* can also oxidize Mn^{2+} to Mn^{4+}. The manganese oxidizing bacteria may lead to Mn-deficiency symptoms in plants.

Indirect effect of soil organisms by modifying root environment and thereby improving or deteriorating the availability of nutrient elements to plant is also important. The availability of almost all the nutrients is indirectly affected by microbial metabolites accumulated in microhabitats by way of changing the soil pH or with some other mechanism.

Table 3. Influence of vesicular–arbuscular mycorrhizae (VAM) on DTPA– extractable Fe-content of soil (mg/kg) after harvest of Broccoli

Treatment	+VAM	-VAM	Mean
NPK	3.15	3.71	3.43
FYM + NPK	3.50	3.89	3.69
PYT + NPK	2.99	3.97	3.48
FYM + PYT + NPK	3.30	4.07	
Mean	3.23	3.91	
	Inoculation(I)	Source(S)	I × S
C.D. at 5%	0.18	0.15	0.28

Source: Purakayastha *et al.* (1998)

8. Soil Enzymes

Biochemical reactions are catalyzed by enzymes (protein molecules) which markedly increase the reaction rate and act in a precise and specific way. Some enzymes are activated only when they interact with an additional chemical component called co-factor or co-enzyme. Co-factors like Mg, Fe, Mn, Zn, Cu, Ni, Co, etc. or co-enzymes (complex organic molecules like vitamins) are thus essential for the functioning of various enzymes. The activity of any particular enzyme in soil is the result of activities associated with various biotic and abiotic components. Enzymes may be intracellularly located in proliferating and non-proliferating cells or with dead cells and debris. They may have leaked from cells or lysed cells and may exist temporarily in enzyme-substrate complexes or adsorbed onto clay minerals or associated with humic colloids. Oxidoreductases (catalyzing electron transfer reactions), transferases (catalyzing reactions with transfer of molecular groups, such as $-NH_2$, R-, CO-, etc.) and hydrolases (catalyzing bond hydrolysis) have been the most widely studied enzymes in soil because of their role in the oxidation and release of inorganic nutrients from soil organic matter.

Enzymes in soil may be synthesized by microbial, vegetal and animal cells, but probably microorganisms are the most important source. The term 'soil enzyme' is strictly applied to activity in soil when microbial proliferation is suppressed by either irradiation or chemical inhibitors, i.e., extracellular enzyme activity. Enzyme activity in soil was demonstrated 100 years ago and about 50-60 soil enzymes, representing all major groups, have been identified in various soils. Highest overall enzyme activity is observed in clay sized particles ($< 50\ \mu$) and clay-enzyme interaction is a highly complex process. Enzymatically-active organic matter fractions have been extracted from soil and the co-polymerization of enzymes with the humic molecules during organic matter synthesis stabilizes the enzyme activity in soil. Terminal amino groups as well as sulphydryl, phenolic and imidazole groups of the enzymes bind to carboxyl and carbonyl groups associated with the reactive quinones formed from phenols through both enzymatic (monophenol oxygenases, peroxidases, laccases) and abiotic catalysis.

Since 1960s there have been numerous attempts to correlate soil biology / fertility with the activity of soil enzymes. They have been most extensively studied in respect of their role in nutrient cycling, e.g.,

C-cycle : Amylase, cellulase, lipase, glucosidases and invertase
N-cycle : Proteases, amidases, urease and deaminases
P-cycle : Phosphatases
S-cycle : Arylsulphatases

Several attempts have been made to show soil enzyme activity-fertility-crop productivity relationships, but strong correlations can be expected only in unmanaged ecosystems or low input agricultural systems because in the managed systems, other factors may confound or override the relationship between soil biological activity and plant productivity. Urease activity is responsible for the breakdown of added urea in fertilized agriculture. Roots, fungi as well as bacteria produce acid phosphatase. Only bacteria produce alkaline phosphatases.

Soil enzymes are routinely used for soil quality measures as well as ecological indicators. With respect to soil quality, strong negative relationships have been found between enzyme activity and soil bulk density and a positive relation with water infiltration. Some alternative systems involving legume green manures have improved soil structure and enzyme activity as compared to conventional systems. Increased activities of several enzymes have been shown with organic amendments, green manure / crop residues, and municipal refuse. Cultivation depresses enzyme activity and conservation tillage practices produce less soil disturbance and have higher levels of enzymes in surface soil. Rao and Pathak (1996) (Table 4) have shown improved enzymatic activity in alkali and saline soils on restoration of carbon to the soils by organic matter amendment. The manipulation of soil enzyme activity has been exploited for practical applications. For example, urease inhibitors reduce ammonia volatilization and improve plant recovery of fertilizer nitrogen.

9. Soil Biological Quality

Soil organic matter (SOM) is central to soil quality assessments as it influences several soil properties, including infiltration rate, bulk density, aggregate stability, cation exchange capacity (CEC) and biological activity, all of which are related to a number of key soil functions. The effects of physical and chemical degradations of soils are quite obvious, but biological degradation due to the loss of specific soil organic matter fractions and the autochthonous microbial communities dependent upon them, are insidious. Physical and chemical properties of soil are shaped by its biological activity while biological activity is enhanced or limited by chemical and physical conditions. There is an increasing realization of the crucial links between microbial diversity, soil health and the sustainability of production systems (Rao, 2007).

A large, diverse, and active population of soil organisms may be the most important indicator of a healthy soil. But, a poor understanding of microbial diversity-function relationships has meant that there is very little progress in identifying such indicators. So for a working definition of soil biological quality and ease of analysis, biologically active fractions of SOM and biochemical attributes of soil have proven more useful. Soil respiration and nitrogen mineralization are widely used as indices of biological activity.

Particulate organic matter (POM > 53μm) represents a significant proportion of the slow pool of SOM and is important in maintaining the stability of macroaggregates (>250μm). Microbial biomass constitutes about 2-4% of the soil organic matter and represents the fraction of soil that is responsible for the energy and nutrient cycling and regulation of organic matter transformations. POM and microbial biomass are considered as biologically active fractions of SOM and are sensitive indicators of management-induced changes in the fate of crop residues and the turnover of SOM constituents. They predict the direction and rate of change of soil quality earlier and better than

Table 4. Effect of organic matter (*Sesbania* green manure) addition on microbial biomass and soil enzyme activity in salt-affected soils

Parameters	Carbon added (1% GM)	pH 8.1	pH 10.0	EC_e 1.0	EC_e 97.0
C_{min} (mg/kg)	-C	454	290	427	163
	+C	2070	1937	2103	895
Microbial biomass C (mg C/kg)	-C	196	151	182	67
qCO_2	-C	2.32	1.92	2.35	2.43
Dehydrogenase (µg TPF/g/24h)	-C	68.7	25.8	67.5	4.0
	+C	155.5	113.5	155.5	68.9
Urease*	-C	1.9	0.7	2.3	0.6
	+C	4.0	1.3	4.3	1.3
Protease**	-C	0.075	0.036	0.055	0.022
	+C	0.290	0.183	0.100	0.129
Asparaginase**	-C	8.18	0.92	8.07	0.46
	+C	15.57	4.73	14.65	1.38
Glutaminase**	-C	50.8	11.5	51.9	8.0
	+C	54.2	21.9	53.1	18.5
Deaminase#	-C	1.03	0.23	0.92	1.15
	+C	3.00	1.49	2.77	1.61

*µmol NH_3/g/h; **µmol substrate hydrolyzed/g/h; # µmol sub.hyd./g/48h; adapted from Rao and Pathak (1996).

other indicators. A decrease in microbial biomass carbon as a fraction of total organic carbon implies a reduction in microbial transformation and intensity. The metabolic quotient or qCO_2 is a more sensitive indicator of soil microbial reaction to cropping systems; lower values implying more stable and mature systems where carbon utilization efficiency of the microbial population is higher due to shift from zymogenous (r-strategists) to autochthonous microflora (K-strategists). Dehydrogenase activity has been widely used as a generalized comparative index of microbial activity, but it has not been consistently correlated with microbial activity.

Soil faunal activities are good indicators of soil biological condition. Soil microfauna (protozoa and nematodes) may reduce or increase microbial numbers and speed the turnover of microbial biomass and thus enhance nutrient availability. Mesofauna (mites, Collembola) increase substrate surface by fragmentation. Soil macrofauna (ants, termites, centipedes, millipedes, earthworms) communite and redistribute organic residues in the soil profile to increase the surface area, substantially modify soil structure through formation of macropores and aggregates through burrowing activities and faecal pellets. Although soil fauna are present in many highly productive soils, it is difficult to make broad generalizations about earthworms or soil fauna, in general, as indicators of high quality soils. Enumeration and identification of at least the burrowing soil fauna, and measurements of faecal deposits have been recommended to be a part of minimum data set for assessing soil quality.

Additions of organic residues, balanced fertilization, integrated nutrient management, conservation tillage have all been shown to improve soil biological condition. Most of the pesticides in common use in agriculture have been widely tested and there is a plethora of literature which conclusively proves that at recommended doses of application, they have no adverse influence on microbial activity. There is increasing concern about land application of bio-solid/municipal wastes laden with heavy metals. None of the heavy metals have any adverse effect on soil microbial biomass at the currently permitted levels of regulatory bodies like European Union.

9.1. Allelopathic Effects in Soils

Soil can get degraded biologically also by the exudation of specific chemicals by plants, which affect other plants, soil microorganisms and processes mediated by them. 'Allelopathy' refers to the influence of one plant on another by means of chemical exudates. Plant phenolic substances, tannins in particular, are the most responsible allelo-chemicals. Specific chemicals excreted by plants can influence the microflora through proliferation or inhibition of select microbial groups. For example, in an acid sulphate soil under eucalyptus plantation, actinomycetes comprised 90% of the total microbial counts. Nitrification is a particularly sensitive process. Rates of nitrogen fixation are reported to be much lower beneath the canopies of some shrubs like *Atriplex.*

10. Composting and Organic Farming

The preparation and use of good quality compost is integral to sustainable farming. In the aerobic process or 'heap method', the base material placed on a hard ground consists of hardwood materials like pigeonpea or cotton stalks, followed by layering with hard residues such as leaves, straw, urine soaked from animal shed, and garbage consisting of a mixture of vegetable and animal wastes with a base for neutralizing acidity. The heap can be rectangular in shape. After wetting with water, the heap is mud plastered and allowed to sit. The ideal condition for the moisture to be maintained is at about half saturation during the early stages, as near as possible to the condition of a pressed-out sponge. After the preliminary fungus stage (thermophilic) is completed and the vegetable wastes have been broken down sufficiently to be dealt with by bacteria, the synthesis of humus proceeds under anaerobic conditions when no special measures for aeration of the dense mass are either possible or necessary. To ensure uniform mixing and decay and to provide the necessary amount of water and air for the completion of the aerobic phase, two turnings, first at the end of 2-3 weeks and the second in a reverse direction at the end of 5 weeks are given. Soon after the second turn, the processing of ripening begins and under favourable conditions as much as 25% of additional free nitrogen is secured from the atmosphere through biological nitrogen fixation. A very high temperature of about 65 °C established at the outset continues with a moderate downward gradient to 30 °C at the end of 90 days, by which humus synthesis is completed and compost is ready.

The 'pit method' of composting is carried out in an elevated place to avoid waterlogging and is often protected by a shed. The layering at the bottom is usually urine-soaked bed from cattle shed. The bed is made of farm materials such as vegetables wastes, fodder remnants, green matter, etc. The bed layer is sprinkled with a slurry of cowdung and mixed with well-decomposed manure from the previous batch. This sort of layering and sprinkling with cowdung slurry is repeated until the pit is filled. The pit is filled till the raw material stands 15 to 18 inches above its edge and is then plastered with one inch of a mixture of mud and cowdung. Under such conditions, decomposition is anaerobic and high temperatures do not develop. Insoluble nitrogen compounds gradually become soluble and carbonaceous matter is broken down into carbon dioxide and water. Loss of ammonia is negligible because in high concentrations of carbon dioxide, ammonium carbonate is stable. The plastered pit also prevents fly nuisance. The compacted, moist material becomes composted in about four to five months without any further attention. The anaerobic process is particularly well suited for gardeners in or near cities and towns. Composts are comparatively less effective than fertilizers as they contain less than 2 % NPK, half of which is mineralized during the growing season. Rural compost generally contains 0.5 to 1.0 % nitrogen, 0.2% phosphorus (P_2O_5) and 0.5% potassium (K_2O), whereas urban compost can have higher nutrient content.

The microbial inoculum in the cow dung mixture used in composting is sufficient to complete the decomposition of all substrates, but compost accelerators containing inoculum of cellulose degraders like *Trichoderma viride*, *Trichurus spiralis*, *Aspergillus niger*, *Paecilomyces fusisporus* have been prepared and used with advantage, and found to reduce decomposition period by several weeks. Lignin degrading fungi include *Clavaria* sp., *Cephalosporium* sp. and *Humicola* sp.

Another major development has been the nutrient enrichment of compost (P,S,N,) by addition of rock phosphate and pyrite and inoculation of microorganisms like *Aspergillus awamori*, *Trichoderma viride*, *Azotobacter chroococcum* in the mesophilic phase. Another improvement in composting is the use of two-stage composting, first in the pit and then *in situ* in the field to reduce decomposition time and minimize losses. Another innovation has been the alternate layering of *Azolla* with rice straw in rectangular heaps in North-East India, which results in rapid decomposition and reduces the composting period.

Organically farmed soils have been shown to have higher organic matter levels, improved soil physical properties and increased microbial populations *vis-à-vis* chemically farmed soils. However, differences in microbial communities in soils under different management practices (conventional, organic, integrated, etc.) are subtle, rather than dramatic (Shannon *et al.*, 2002). Organically managed soils have been shown to have higher population of microbial antagonists to commonly occurring soil borne plant pathogens compared to the conventional farming. Higher incidence of mycorrhiza in organically managed soils has also been known since long. Biodynamic field sprays and compost preparations have not been shown to have any additional effect over and above the conventional organic management.

11. Biofertilizers

Microorganisms play an important role in the service of mankind, ranging from fermented foods and beverages to transformation of plant nutrients. They are being exploited since long by the food and beverage industry. However, their use in agriculture is relatively recent. Besides development of biofertilizer for nitrogen fixation and P-solubilization/mobilization, considerable work has been done on biopesticides for the control of plant diseases, pests, weeds and detoxification of industrial wastes using soil microorganisms.

Biofertilizers are biologically active products containing live microorganisms on a suitable carrier used to inoculate seed or soil or both for (i) improving plant nutrition, (ii) stimulating plant growth, and (iii) accelerating decomposition of plant residues. The importance of biofertilizers is due to accruing of larger benefits relative to the costs involved, recycling of plant nutrients and their environment-friendly nature.

Use of biofertilizers helps in mobilizing plant nutrients through the activity of organisms contained in it. If these organisms are not present in adequate numbers in soil, they have to be inoculated by using biofertilizers to get the desired effect.

There are mainly two types of biofertilizers:

(i) *Rhizobium* used for inoculating legumes, and

(ii) Plant growth promoting bacteria (PGPR) which include phosphatic biofertilizers (PBF) used for inoculating all crops.

Rhizobium fixes atmospheric nitrogen in root nodules of legumes and adds nitrogen into soil following the decomposition of nodule and root tissues. Following types of biofertilizers are commercially produced in our country:

(a) *Rhizobium* which is crop-specific and is used to inoculate leguminous crops. This type of biofertilizer is most popular and shows consistent benefit.

(b) *Azospirillum* which is non-crop-specific and is mainly used for cereal crops.

(c) *Azotobacter*, a non-symbiotic nitrogen fixer used for inoculating a wide range of crops.

(d) Blue green algae cultures used for rice crops.

(e) Phosphatic biofertilizers contain live cells of phosphate solubilizing bacteria (PSB) belonging to the genera *Pseudomonas* and *Bacillus* and fungi of the genera *Penicillium* and *Aspergillus*. The performance of PBF is not uniform as these cultures are likely to be more successful in soils with high organic matter content or when added along with organic matter application. Cultures of Vesicular Arbuscular Mycorrhizae (VAM) are also being used on a limited scale. VAM helps in P nutrition by not only increasing P availability but also increasing its mobility. Through VAM, plants are able to take P from soil zone not visited by the root system. As VAM fungi cannot be grown on a synthetic medium, its large-scale application is limited to perennial crops and transplanted crops where the requirement of the inoculum is reduced by about 20-times due to less area to be covered in the nursery.

A number of experiments have shown that dual inoculation of *Rhizobium* along with plant growth promoting bacteria (mostly P-solubilizers like *Bacillus polymyxa or Bacillus megaterium*) for pulses results in better nodulation and N fixation and grain yield. Beneficial consortia of microorganisms including *Rhizobium*, PSB and PGPR (*Pseudomonas fluorescens*) for grain legumes and *Azospirillum/Azotobacter,* PSB and PGPR for other crops are being increasingly used as multi-strain inoculants to obtain benefits of BNF, P-solubilization, plant growth promotion and disease control.

Adequate precautions need to be taken in the use of biofertilizers. Since biofertilizers contain live cells, care should be taken during their transportation and storage. They should be kept in a cold place and not exposed to sunlight. Legume cultures are crop-specific and they must be used for the crop for which they are meant. If they are to be used under adverse soil conditions, appropriate remedial measures like liming and use of gypsum should accompany their application to soil. At present about 20,000 tonnes of biofertilizers are produced in India in nearly 165 production units. In majority, the carrier is a solid support like lignite or charcoal. Strictly sterile conditions are required to be maintained in its production at all stages to obtain a good quality product alongwith proper storage conditions to ensure acceptable cell count (> 5 × 10^7 cells/g) at the end of six-month expiry period.

Liquid biofertilizers with added cell protectants to improve survival of bacteria have been shown to have higher shelf-life, up to one year. The use of microbial inoculants is now finding increasing acceptance in many areas and farming situations, particularly in organic farming pockets. But, there are serious concerns about the poor quality of inoculants from many production units who employ unsterile carriers and unhygienic production methods, resulting in high level of contaminants. The Bureau of Indian Standards has produced quality standards for most inoculants. The Government of India has included biofertilizers in the Fertilizer Control Order making it mandatory for the manufacturers to register themselves with the state governments. A quality control mechanism has been put in place and responsibility entrusted to the National Centre on Organic Farming of the Government of India.

12. Biocontrol of Plant Pathogens

There is increasing interest in seed and soil inoculation with a group of bacteria called plant growth promoting rhizobacteria (PGPR) or plant health promoting rhizobacteria most of which have poly-functional abilities, including ability to suppress pathogens. Biological control of soil-borne plant pathogens and nematodes involve use of one specific organism to control another. For example, crown gall induced by *Agrobacterium tumefaciens* can be controlled by using strain 84 of the non- pathogenic *A. radiobacter*, which produces an unusual antibiotic belonging to the group of bacteriocins, Agrocin-84. Rapid colonization by specific strains of *Pseudomonas fluorescens-putida* group in the rhizosphere of potato, sugarbeet and radish increases the crop yields. The siderophore, pseudobactin, produced by *Pseudomonas* sp. which sequesters and removes the iron required for the growth of pathogens, has been implicated in the control of soft rot of potato caused by *Erwinia carotovora. Gaeumannomyces gramini* var. *tritici* causes 'take-all' of wheat and barley, a serious root disease. Inoculation with fluorescent *Pseudomonas* is effective in preventing disease of barley in take-all conducive soils as well as in *Fusarium*-wilt conducive soils and was attributable to siderophore production. One of the most exciting prospects for biological control is the use of *Bacillus penetrans* against the nematode *Meloidogyne* sp. as also the use of the fungus *Nematophthora gynophila* to control *Heterodera.*

13. Soil Bioremediation

In agricultural practices for crop production, many harmful chemicals are used to control insect, pests, diseases and weeds. These are applied to plants as well as to soil. These chemicals are, however, normally detoxified in soil in a reasonable time, if used in recommended amounts. The detoxification of such poisonous chemicals is done by soil organisms. A voluminous research work has already been done on these chemicals, which indicates that when applied in recommended amounts, most of these chemicals are detoxified within the acceptable period and soil fertility processes are not affected adversely. Moreover, an adverse effect on any of the processes is generally not long-lasting. Hence, it is essential that every new chemical applied to soil for any specific reason should be examined for its persistence in soil and effect on soil organisms and their activities. In addition to pesticides, many other chemicals and heavy metals may find entry into soil through addition of city garbage, sewage and sludge. Soil organisms decompose these unusual chemicals and save the plants from their adverse effects. Soil microorganisms transform the heavy metals and reduce their toxic levels through one mechanism or the other. For example, some of the bacteria can volatilize mercury from the soil when it is in toxic amounts.

Improper disposal, misuse or accidental release of toxic organic or inorganic compounds in soil results in widespread pollution not only of the soil but also of groundwater environment. Similarly, mining and brick kilns also spoil the arable soils. Bioremediation covers varoius types of contaminations of soil and diverse techniques of their treatment. However, truly speaking, bioremediation involves the use of microorganisms in association with plant host, soil amendments and agronomic technique to remove, contain or render harmless the soil contaminant. Sometimes instead of bioremediation, the term 'phytoremediation' is also used when contaminated soils are exposed to different kinds of vegetation along with a lot of irrigation water.

13.1. Pollution by Pesticides

The transformation of pesticides added to soil depends upon their adsorption onto clay and organic matter, leaching, volatilization, uptake by soil organisms and plants, movement with runoff water, microbial and chemical degradations and photolysis (Adhya *et al.*, 1994).

Persistence is a relative term, usually quantifying the time taken for 75% to 100% loss of a pesticide in a normal arable soil under recommended practices of application, is taken as the persistence value of an agrochemical. Organochlorines are highly persistent and typical values are: DDT, 4 years; BHC, 3 years; aldrin and dieldrin, 1-3 years. Persistence of organophosphorus and carbamate insecticides is low — diazinon, 3 months; phorate, 2 weeks and malathion and parathion, 2 weeks. Persistence of herbicides, however, varies depending upon the active principle, e.g., propazine and picloram, 18 months; simazine, 12 months; atrazine, 10 months; trifluralin, 6 months; 2,4,5-T, 5 months and 2,4-D, 1 month. Most fungicides remain only for a few months in soils and most of the fumigants disappear in 3 to 4 weeks.

Most of the fungicides, nematicides and insecticides applied to soil temporarily suppress the microbial activity which is alleviated sooner than later. While some insecticides are inhibitory, some are stimulatory and others are innocuous. There is an initial depression, followed by recovery of microbial population. Addition of organic matter helps reduce toxicity due to adsorption as well as greater break-down due to enhanced microbial population. Many pesticides at concentrations in excess of the recommended doses reduce soil respiration. The minimum inhibitory concentration of various herbicides to *Rhizobium* sp. is very high, ranging from 7000 to 15000 mg/kg in soil and much greater than that for plants, showing that they can be safely used. Blue green algae are unaffected in the presence of recommended quantity of herbicides and contribute to N build-up of soil.

Pesticides have adverse impact on soil fauna affecting the populations of arthropods (insects, mites, spiders, millipedes and centipedes), molluscs (snails, slugs), annelids (earthworms) and protozoans (*Paramecium*, *Amoeba*), etc., which are very important in maintaining soil structure and nutrition. Earthworms concentrate DDT manifold and show higher respiratory metabolism. Earthworm feeding is very important in breakdown of deciduous tree litter. Enchytraeid worms, Collembola, some Acarina and dipterous larvae help to dis-integrate plant material. Hence, any chemical which affects soil organisms adversely influences soil fertility.

Of the soil processes, ammonification is comparatively resistant. Insecticides do not appear to harm nitrification when applied at recommended field doses. Microorganisms are more important in the degradation of pesticides than physico-chemical mechanisms. The major biochemical reactions involved in pesticide breakdown are: oxidation, reduction, hydrolysis and synthetic reactions. The idea of using microorganisms or their enzymes to degrade pollutants is not new and was suggested by Audus as long ago as 1951 for the removal of 2,4-D from soil. The degradation of 2,4-D is shown in Box 3. Disappearance of DDT has been shown from soil after heavy inoculation with a DDT-degrading *Aerobacter aerogenes.*

Accelerated hydrolysis of parathion in a flooded soil by inoculating a parathion-hydrolyzing *Pseudomonas* sp. was demonstrated. In one study, inoculation of contaminated soil with PCP degrading *Arthrobacter* led to ten-fold increase in the degradation rate and reduction in half-life from 2 weeks to < 1 day. *Pseudomonas cepacia* removed 95% of a 1000 mg/kg soil application of 2,4,5-T in one week. Alternately, pesticides breakdown can be accelerated by enriching the microbes already present, e.g., 2,4-D mineralization was stimulated by the addition of sachharides and other organic substances. However, there are limitations to microbial application since acclimatized cultures can develop sensitivity to degradation products, viz., *p*-nitrophenol resulting from parathion degradation and also there can be limitation of substrate availability and preference. These limitations can also be due to soil conditions. Hence, enzymes can be used as they have other advantages like ability to withstand higher concentration of salt, solvent and temperature than microorganisms. Immobilized enzymes have been used, e.g., trickling filters and activated sludge system for the removal of 2,4-D, continuous flow fibre wall biological reactor for the removal of PCP, activated carbon column with fixed film bacteria for the removal of chlorinated organics have all been successfully used for the removal of pollutants from wastewaters.

Genetic engineering is another exciting possibility. During the past 20 years numerous genes in bacteria coding for enzymes involved in pesticide degradation have been shown to be plasmid encoded, e.g., 2,4-D gene coding for dehalogenases, parathion, DDT, kelthane, 3-chlorobenzoate, etc. Using recombinant DNA techniques, it was possible to produce soil microbial populations that carry extrachromosomal elements conferring ability to degrade recalcitrant pesticide molecules such as 2,4,5-T *(P. cepacia)* and its potent contaminant 2,3,7,8-tetrachloro-di-benzo-para-dioxin. The potential applications of genetically engineered strains are still speculative and till date, genetically engineered strains have not been actually used for pollution control to any significant.

13.2. Acid Mine Spoils

The over-burden left from the mining operations is a mixture of soil and rock, mixed with low grade ores or coal. These are levelled and revegetated. Pyrite is the most common reduced form of S in rocks and soils. Oxidation of pyrite primarily by the chemoautotroph *Thiobacillus ferroxidans* produces and releases large quantities of sulphuric acid during strip mining, resulting in the acidification of waterways, soils and sediments. The strong

Box 3. Pathway showing degradation of 2,4-D (2,-4-dichlorophenoxy acetic acid) in soil

2,4-D ⟶ 2,4-Dichlorophenol ⟶ 3,5-Dichlorocatechol
↓
cis, cis-2,4-Dichloromuconic acid
↓
Succinic acid ← Chloromalethyl acetic acid ⟵ 2-Chloro,4-carboxymethylene-bis-2-enolide

Source: Alexander (1977)

acid producing pH values of < 2.5 dissolves soil minerals, produces toxic concentrations of Fe, Al, Mn and trace elements and results in high salt levels. Drainage from coal mines invariably contains high concentrations of potentially toxic metals like Zn, Cu, Ni or Mn. This environment is hostile to the growth of microorganisms, other soil fauna and flora as well as higher plants. Nitrification of added ammonium is severely restricted (7%) in surface mined soils as compared to undisturbed site (93%). Mine spoil materials are unlikely to adequately supply the N-requirement of a reseeded plant community. N-mineralization rates in spoil material were very slow, averaging one-fifth the rate of associated top soil.

The key to the reclamation of abandoned mine lands is burial of mine spoil and establishment of an active biological surface zone by vegetation, preferably forestry. Disturbance of soils by mining reduces population of and root colonization by VAM fungi which are an important and essential component in re-establishing plant communities on disturbed sites. *Pisolithus tinctorus* is the dominant mycorrhizal partner in mine spoils to which it is admirably adapted. Mycorrhiza can induce greater root ramification. Plants colonizing mine spoils and other industrial wastelands are usually legumes because they can fix their own nitrogen. When plants like legumes or mycorrhizal trees are grown, they decontaminate the soil and stabilize the contamination, as shown in Figure 7.

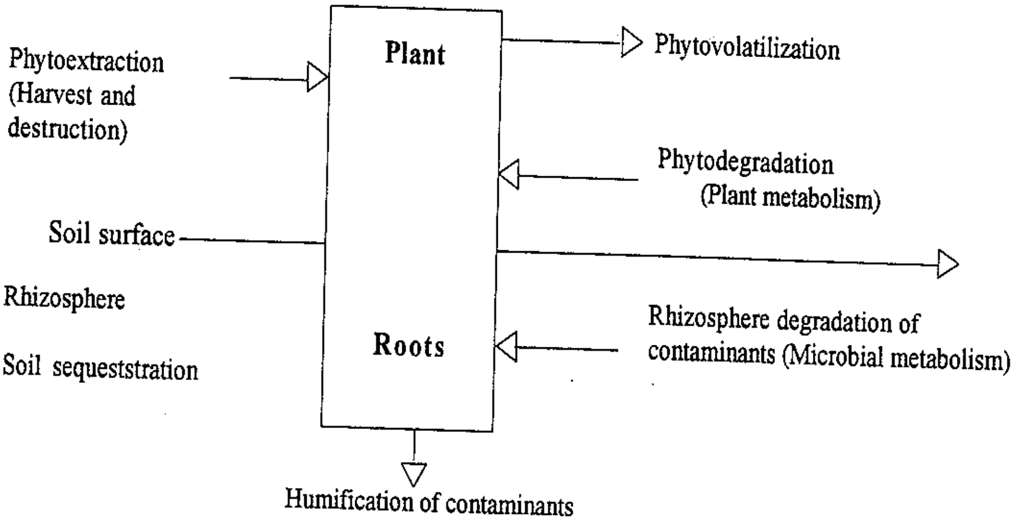
13.3. Other Organic Pollutants

Numerous organic compounds other than pesticides enter soils as a result of industrial activities, including chemical synthesis, processing of petroleum, coal tars, oil shales and other energy-related materials. Generally much more dramatic effects on microbial communities and their activities have been observed for toxic organics than for pesticides which generally have undergone extensive screening for ecotoxicological effects prior to release.

The best known application of *biodegradation* is for the *in-situ* clean up of oil spills. In contrast, pentachlorophenol (PCP), phenol and 2,4-D are biodegraded in contained facilities. Microbial species grow and consume the target pollutant. Co-metabolic biodegradation processes are used for the recalcitrant halogenated compounds like trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) at pilot scale. Biodegradation can completely mineralize a xenobiotic compound, resulting in a clean-up or partial degradation to products that are subsequently detoxified by abiotic mechanisms or spontaneous breakdown or biotically by another group of microbes. Degradation of compounds like tetrachloroethylene (TCE) and dioxin (2,3,7,8-tetrachloro-dibenzodioxin) is a challenge. Biotransformation without biodegradation can ameliorate the toxicity associated with the organic pollutants via humification or polymerization. Microbial populations and abiotic mechanisms in soil transform pesticides into intermediates which are incorporated into humus, but this is not confined only to pesticides. Polycyclic aromatic hydrocarbons, refractory compounds like PCBs and PCP can also be incorporated into humic material. Biostabilization reduces the risks associated with the leaching of organics from soil. Bioremediation applications for clean-up of soil, sediments, groundwaters or industrial waste streams are urgent priorities for soil and environmental microbiologists.

14. Gaseous Emissions from Soils and Environmental Pollution

There is a worldwide concern over the large increases in the emissions of CO_2, CH_4, oxides of nitrogen, chlorofluorocarbons, etc. into the atmosphere. These are causing global warming and having serious consequences for agriculture and environment. Microorganisms, either directly through their metabolism or indirectly through their alterations of the organic matter, are the principal sources of biologically derived gases in the atmosphere. The concentration of CO_2 in the atmosphere has increased from 280 ppm in pre-industrial age to 379 ppm at present and is likely to increase to 460 ppm by 2030 and 555 ppm by 2100 AD. Deforestation accounts for 10-30% of annual anthropogenic CO_2 emissions. When forest cover is removed, the organic matter is rapidly degraded by the soil microbes. Emissions of CO_2 in India



(On decomposition of such plants, the contaminant gets bound in humus)

Figure 7. Schematic representation of decontamination of soil-plant-root system

are nearly 1190 Tg (Tg = 10^{12} g) as per a 2000 estimate and it is rising at the rate of 6% every year. Of this amount, the net CO_2 emission from agriculturally impacted soils in India is estimated at 19,788 Gg, which is around 2% of global CO_2 emissions.

On a global basis, atmospheric methane (CH_4) arises from bacterial decomposition of organic matter under anaerobic conditions as exist in lakes, ponds, marshes, rice fields and swamps. Figure 8 depicts the microbiological transformations occurring under anaerobic conditions in rice soils. The methanogenic bacteria are anaerobes belonging to the genera *Methanosarcina*, *Methanobacillus*, *Methanobacterium*, *Methanospirillum* and *Methanococcus*. Some other methanogenic bacteria reduce carbon monoxide to methane, while some metabolize methyl mercaptan and dimethyl sulphide to CO_2 and CH_4. Annual emissions of CH_4 are of the order of 500 Tg. CH_4 has 23-times greater radiative forcing than CO_2. There is increasing concern about emissions of CH_4 from rice fields and rumen of cows and buffaloes from the Indian sub-continent which was based on both from experimental studies and extrapolations. But, field studies on a large scale in a net work project by National Physical Laboratory (NPL) and Central Rice Research Institute (CRRI) have shown that CH_4 emissions from rice is only between 4-6 Tg/yr against the Environmental Protection Agency of the United States of America (USEPA) estimate of 37.8 Tg/yr. Rice soils that are prone to CH_4-production mainly belong to the orders of Entisols, Inceptisols, Alfisols, Vertisols and Mollisols.

Denitrifying bacteria in soils and aquatic environments account for most of the production of nitric (NO) and nitrous oxides (N_2O) and N_2, the former two have a high potential for warming, 230-times greater radiative force than CO_2. N_2O contributes to the stratospheric ozone depletion by producing NO_x as it breaks up in the atmosphere. N_2O emissions (0.31 Tg/yr) result from fossil fuel combustion, biomass burning, nitrogenous fertilizer use, land clearing and natural processes in soils, oceans and fresh water ecosystems, of which agriculture contributes above 90%; nitrogen fertilizers contribute 0.14-2.4 Tg/yr. N_2O is simultaneously produced and consumed in soils via the microbial metabolic pathways of denitrification, nitrification, nitrate assimilation and nitrate dissimilation. The denitrifiers are facultative aerobes such as *Pseudomonas denitrificans*, *Paracoccus denitrificans* and *Thiobacillus denitrificans*. N_2O is also formed by the oxidation of ammonium by the autotrophic nitrifier, *Nitrosomonas europea*, by the reduction of nitrate by heterotrophic bacteria such as *B. subtilis*, *E. coli* and *Aerobacter aerogenes* and by the reduction of nitrite by soil fungi such as *Aspergillus flavus*, *Penicillium* *atrovelltum, Fusarium oxysporum* and *F. solani*. Photosynthetic microbes located in the top layers of soil are capable of reducing nitrate to nitrite and are presumably another source of NO and NO_2.

Nitrous oxide is formed both during oxidation of NH_4 and on reduction of NO_3. Therefore, oxidized as well as reduced conditions both may result in the emission of N_2O. In well-aerated soils, nitrification, after application of nitrogenous fertilizers increases nitrous oxide emission. N_2O production increases with increasing temperatures, increasing water contents to field capacity and increases in pH from 4.7 to 6.7. Very high N_2O-emissions have been recorded from well-drained cultivated organic soil, which is attributed to high mineralization of organic N. Alternate oxidation and reduction strongly enhance N_2O emissions, while continuous flooding on the contrary gives mainly N_2 with little N_2O production. Therefore, N_2O from flooded rice fields although substantial, is low. However, under upland rice cultivation and in light-textured soils that drain rapidly, the soils may undergo cycles of wetting and drying, resulting in much higher emissions of N_2O.

15. Soil Genomics

Biological soil quality parameters mentioned previously are sufficiently discriminatory for soil health purpose, but they cannot provide information on differences in the structure of the microbial community or its potential functional significance. The DNA extracted from soils can be analyzed for specific marker gene pools (Entry *et al.*, 2007). Combinations of specific polymerase chain reaction (PCR) amplification of target gene pools and genetic fingerprinting techniques, such as restriction fragment length polymorphism (RFLP), denaturant/temperature gradient gel electrophoresis (DGGE/TGGE), single strand conformation polymorphism (SSCP), ribosomal intergenic spacer analysis (RISA), terminal restriction fragment length polymorphism (T-RFLP), etc. are applied. Soil microarrays, fluorescent *in-situ* hybridization (FISH) and stable isotope probing have been developed to identify and track specific soil microorganisms. Many investigations have focused on the amplification of specific marker genes from total soil DNA by using specific probes like nif H (for diazotrophs), nirK/nirS (denitrifiers), amo A

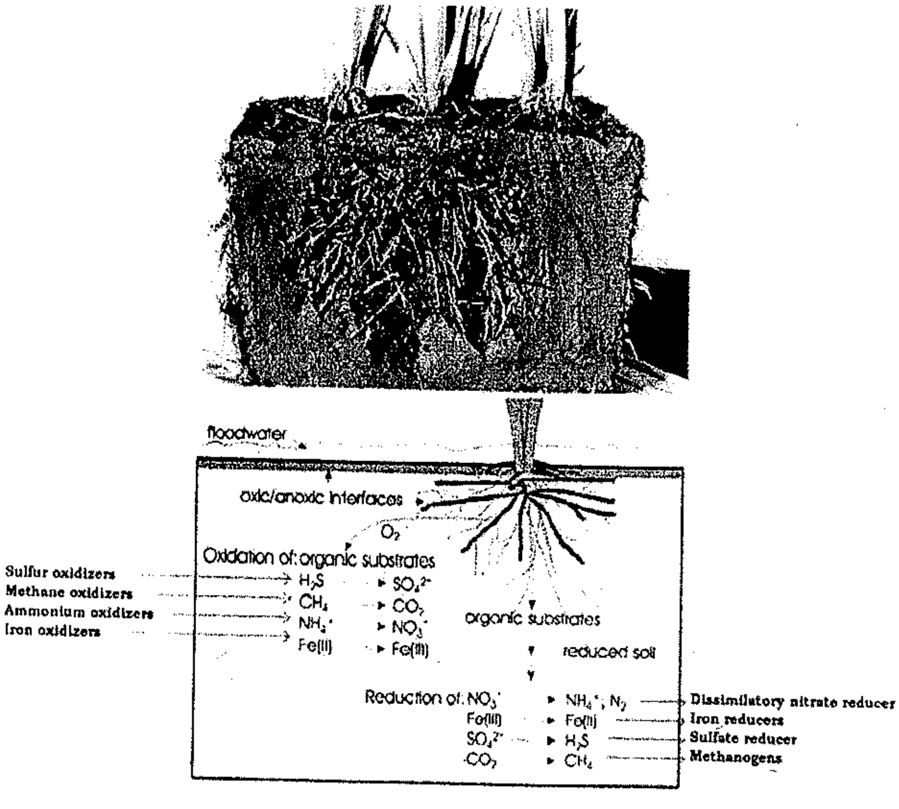


Figure 8. Microbiological transformations occurring in flooded rice soils

(nitrifiers), nod C (rhizobia), as well as genes involved in P and S cycling. These analyses yield DNA banding patterns (genetic fingerprints), which can be quantified and compared among different soil samples. Although such data represent an image of the soil microbial community, but as mentioned in a previous section, an accepted definition of the taxonomic unit, which can be used for defining soil microbial diversity, is still lacking at this point. But, there is hope that scientific advancements in the future would lead to more robust assessment of biological conditions and devising of genomic kits for assessment of soil health and soil contamination.

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Chapter 24

Soil Organic Matter

KUNAL GHOSH, K.K.R. BHARDWAJ and MOHAN SINGH

1. Introduction

Organic materials are intrinsic and essential components of all soils. Whether it be the soils in cold deserts of Tundra or the humid tropical Amazonian forest, organic matter is ubiquitous. Whereas the body of the soil is constituted by the inorganic materials, one may look upon the organic matter as its life. Organic matter (OM) is what makes the soil a living, dynamic system that supports all life on this planet. The immense importance of soil organic matter (SOM) accrues from the following facts :

(i) It is the food source for soil microorganisms and soil fauna. Without OM, the soil would be almost sterile and consequently, extremely infertile.

(ii) It is the soil's storehouse for nitrogen supply to higher plants. There is very little inorganic nitrogen in soils and much of it is obtained by conversion of the organic forms. Plants are, therefore, dependent either directly or indirectly, for their nutritional requirement of nitrogen on SOM.

(iii) It functions as a storehouse of phosphorus and sulphur and thereby contributes significantly to the supply of these nutrients to higher plants.

(iv) It improves various other chemical properties of soil. For example, the increased cation exchange capacity and enhanced ligancy help in trapping nutrient cations like potassium, calcium, magnesium, zinc, copper, iron, etc. Improved soil buffering is its another important contribution.

(v) Apart from the nutrients within the soil organics themselves, SOM contributes to nutrient release from soil minerals by weathering reactions, and thus helps in nutrient availability in soils.

(vi) Plant growth and development are benefited by the physiological action of some organic materials that are directly taken up by plants.

(vii) Another important influence of SOM is on soil physical properties. Improvement in soil structure, porosity, water holding capacity, soil drainage, etc., is direct consequence of organic matter in soils.

(viii) The organic substances influence various soil processes leading to soil formation.

(ix) It is the prime decider of soil health and soil quality.

In brief, OM as a single entity, is the most important soil component.

1.1. Nature and Amount of Soil Organic Matter

The term SOM refers to those organic materials which are a part of the soil matrix. This includes :

(a) The litter layer which consists of dead plant residues at the uppermost layer of the soil,

(b) Partly decomposed plant residues formed by the action of soil fauna and microorganisms on the litter,

(c) Biological organic molecules (both macromolecules and small molecules) which are components of plant or animal tissues, e.g., proteins, carbohydrates, lignins, lipids, peptides, amino acids, organic acids, alcohols, etc.; these are collectively called the non-humic substances, and

(d) Humic substances which are the stable end products of decomposition of plant and animal residues.

Since agricultural soils contain little litter and decomposed litter layers, SOM generally refers to non-humic substances which constitute 10-15% of total organic materials, and the humic substances which comprise the largest fraction (85-90%).

Special mention may be made to soil microbial biomass which is currently defined as the living pool of SOM, excluding plant roots and larger soil fauna (above 5×10^3 micro m^3), and is made up of a genetically and functionally diverse range of organisms able to perform under a wide range of environmental conditions. Soil biomass is usually treated as a whole because that enables the study of flux of energy and material through soil population. However, comprehensive understanding is only obtained by recording the roles played by the different component systems like bacteria, fungi, algae, etc. as well as their interactions amongst themselves and also with larger soil fauna and plant roots.

Contents of OM in soils vary and largely depend on the environmental conditions. In general, cultivated soils in temperate regions have high OM levels (5-10%) in their surface horizon, whereas similar soils in the tropics have only one-fifth or one-sixth as much (often less than 1%). The reasons for these differences in OM levels have been attributed to certain 'factors of soil formation' and are represented as relation (1) :

$$\text{Organic matter} = f\,(\text{climate, time, vegetation, parent material, topography,} \ldots\ldots) \quad \ldots(1)$$

Climate (temperature and rainfall) plays one of the most important roles in determining the extent of SOM accumulation. It has been observed that SOM contents decrease 2 to 3 times for every 10 °C rise in mean temperature. Apparently, the decomposition loss of SOM (to CO_2) increases more rapidly with temperature than the rate of its formation. Therefore, in warmer climates, SOM levels are generally lower than in cooler regions. In general, the activity of soil microorganisms and decomposition of SOM increase with rise in temperature from 0 to 35 °C; but above this temperature, the microbial decomposition gets suppressed. The decomposition of OM is also influenced by rainfall and, therefore, the soil moisture levels. Intensity of decomposition increases with moisture and reaches a maximum at 60-80% of the maximum water holding capacity. The marked differences in OM levels between the temperate and tropical regions are mainly due to climatic factors.

The second important factor influencing OM levels in soil is the nature and amount of vegetation. Vegetation provides the basic input in the form of leaf litter, branches, roots, etc. The effect of vegetation on OM accumulation is best seen in the tropics. In tropical evergreen forests, where litter input is very high, the soils are very rich in OM; soils under grass cover in the same region have much lower OM levels since litter input to the soil is relatively less; cultivated areas with limited vegetative cover have very low levels of OM (Saikh *et al.*, 1998). It follows that within a particular climatic zone, vegetation is the major factor of OM accumulation.

Other factors, which influence OM accumulation, are soil minerals and soil texture. Soils rich in montmorillonite favour OM accumulation. OM is easily lost from light-textured sandy soils, whereas loamy soils tend to accumulate OM. This can best be seen along river banks in areas otherwise covered by sandy soils.

Topography influences the OM levels through soil drainage and moisture levels. Soils in depressions and valleys may accumulate more OM than those at the slopes. If all other factors remain constant, OM accumulations reach equilibrium levels with time. Further increase will not occur after a certain period of time, which is normally a few years. However, the stable fraction (humus) can persist in the soil for as long as 250 years to about 2000 years. This stable fraction takes a much longer time to accumulate and has an average 'turnover period' of about 150 years. These functional pools of SOM may be classified as:

(A) **Decomposable :** (i) metabolic litter (plant and animal residues like cellulose; 1-6 months), (ii) structural litter (plant residue like lignin; 3 months-2 year),

(B) **Resistant :** (i) active pool (labile fraction, viz. microbial biomass; 2 months– 1.5 years), (ii) slow pool (labile fraction, viz., particulate OM; 8-50 years), (iii) passive pool (humus; up to 2000 years).

Physical fractionation based on density and size can provide a fair estimate of slow and passive pools.

Organic carbon content of soils decreases drastically on cultivation; a significant reduction occurs even within 5-15 years of cultivation (Saikh *et al.*, 1998). These workers observed that there appears to be a tendency to reach some "quasi-equilibrium" values (1-2 %) which are broadly similar for all soils, irrespective of their initial C levels.

2. Humic Substances

Humic substances are considered as the most important constituents of soils. They form the largest fraction of soil OM and play the most dominant role in improving soil productivity. Humic substances are formed by the decomposition of plant and animal residues by microorganisms. They are colloid-sized, polymeric substances having dark colours (black and brown-black to yellow). Because of their wide range of molecular sizes and properties, humic substances are usually fractionated in order to obtain materials with similar properties. The three fractions of humic substances are: (i) fulvic acid (FA), (ii) humic acid (HA), and (iii) humin. FA is the most soluble fraction being soluble in water, acids and alkalis; FAs have yellow to brownish-yellow colours. HA is that fraction which is soluble only in alkalis; it is not soluble in water and acids. It has a dark brown to black colour. The most insoluble fraction of humus is humin, which is neither soluble in acids nor alkalis. This fraction is very strongly bound to the soil mineral matrix and is difficult to extract.

2.1. Chemical Nature of Humic Substances

Humic substances are polymeric compounds, built up mainly of aromatic units. The major units are: phenols, quinones and aromatic carboxylic acids which together with nitrogenous compounds form long chains linked by -O-, -NH-, =N-, $-(CH_2)-$, etc. bridges. Aliphatic structures (fatty acids, etc.) are also present as branches on the chain. Some of the units which form the humic polymer include, mono-, di- and tri-hydroxybenzenes, benzene carboxylic acids, heterocyclic nitrogenous compounds, amino acids, aromatic amines and small amounts of fatty acids, carbohydrates, polypeptides, etc.

Since the basic building blocks in humic substances consist of a wide variety of compounds, they cannot be described by any single repeating unit like other organic polymers; for the same reason, they cannot be described by any single structural formula.

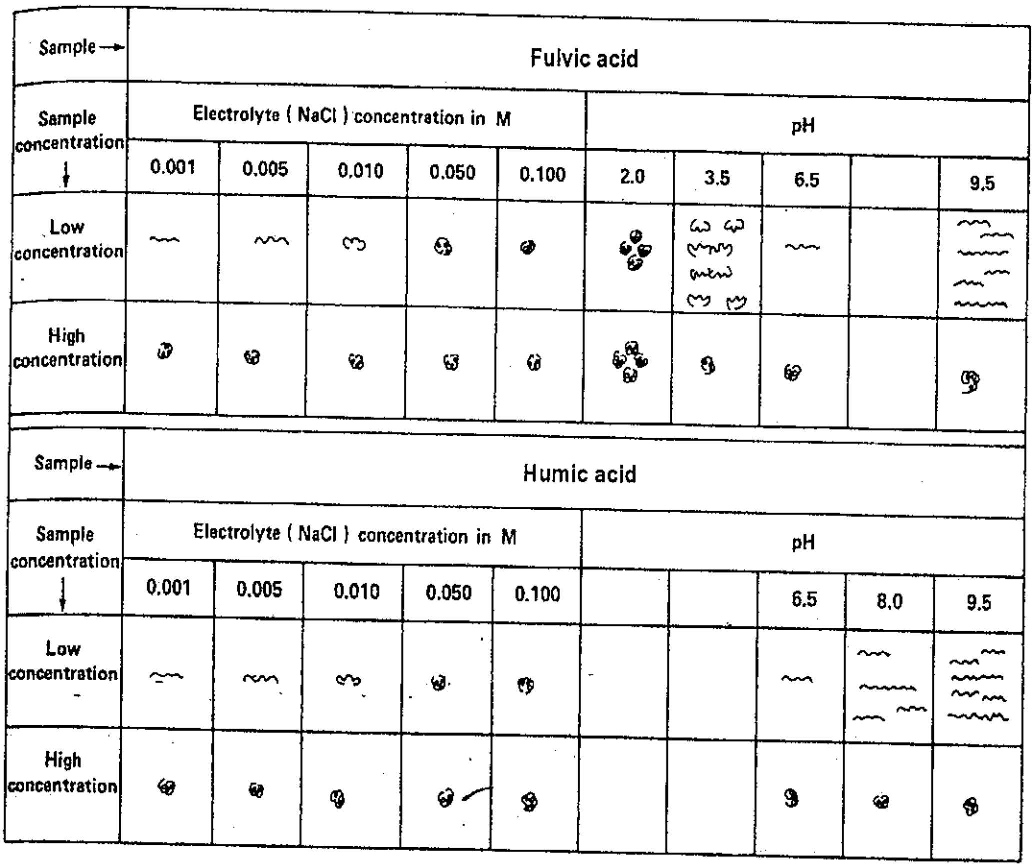
Major functional groups in humic substances are carboxyl, phenolic hydroxyl, amino, quinone, ketone, etc. Functional group contents in humic substances are also variable. The chemical composition and functional groups in HA and FA are listed in Table 1. HAs have higher carbon and lower oxygen contents than FAs. The FAs are more acidic and contain more hydrophilic (water-loving) groups, they dissolve readily in water unlike HAs, which are richer in aromatic and hydrophobic (water-repelling) groups.

Another major difference between HAs and FAs is in their molecular sizes or molecular weights. Molecular weight of HA may be anywhere between 10,000 to over 200,000, whereas for FA, it is much lower (between few hundreds to few thousands). Thus, FAs are the less polymerized fractions, whereas HAs are longer chain, more polymerized compounds. In the solution phase, interconversion of HA to FA and *vice versa* may occur. Thus, a suspension of HA in water will have a yellowish colour after a few days of contact; a concentrated solution of FA will form dark colour precipitates. In the former case, FA is produced by cleavage of HA molecule; in the latter case, several FA molecules undergo reaction to form the larger HA molecules. Factually, all the fractions and sub-fractions of humus represent a group of polymers linked together by a chain of interconversions (Mukherjee and Ghosh 1984).

Transmission electron microscopy (TEM) has shown that humic molecules have diameters of the order of 60-100 Å ($0.6\text{-}1.0 \times 10^{-10}$m) and each particle is a globular sphere.

Table 1. Characteristics of humic substances

Humic substances	Elemental composition (%)					Functional goups (cmol/kg)			E_4/E_6
	C	H	N	S	O	Total acidity	-COOH	Phenolic-OH	
Humic acids	54-59	3-6	1-4	0.1-1.5	33-38	500-900	150-600	200-600	3-5
Fulvic acids	41-51	4-7	1-4	0.1-3.5	40-50	700-1400	500-1100	100-600	6-9



Note: The straight wavy structures represent linear colloids, while the other structures show spherocolloidal configuration

Figure 1. Model macromolecular structures

Source: Ghosh and Schnitzer (1980)

These individual spheres coalesce to form network structures, fibre-like structures or spongy structures with voids.

The humic polymer chain is highly flexible and can coil or uncoil in solution. At high dilutions or under alkaline conditions, the negatively charged groups on the macromolecule repel one another and the molecule becomes uncoiled and straightened. At high concentrations or in the presence of salts or acids, the molecules become coiled. Individual coils may also come together forming larger aggregates (Ghosh and Schnitzer, 1980). These macromolecular configurations are shown in Figure 1.

The detailed chemical structure of humic substance is, however, not known with certainty. Due to its non-crystalline nature and heterogeneous chemical character, there is still much that needs to be known before humic substances as chemical compounds can be fully understood (Aiken *et al.*, 1985; Clapp *et al.*, 2001; Gieseking, 1975; Kononova, 1966; Schnitzer, 2000; Stevenson, 1994).

2.2. Extraction of Humic Substances from Soils

Humic substances in soil occur in chemical combination with various inorganic constituents (minerals, metallic cations, etc.). The extraction methods, therefore, involve breaking of such bonds so that the humic molecules can be brought into solution. The extracted material is subsequently purified to remove unwanted substances.

The common method of extracting humic substances is by treatment with alkali; dilute NaOH or Na_2CO_3 is generally used. Treatment with alkali converts the insoluble polyvalent cation humates and mineral humates, to soluble sodium humates. The reaction may be represented by Equation (2) :

$$\text{Ca-HA/ Clay-Al-HA} + 2\text{NaOH} \rightarrow \text{Na}_2\text{-HA} + \text{Ca(OH)}_2\text{/ Clay-Al-(OH)}_2 \quad \ldots(2)$$

If the soil is very rich in Ca^{2+} ions or contains $CaCO_3$ concretions, it is treated with dilute HCl prior to alkali extraction, otherwise the humate may re-precipitate as calcium humate. Acid pretreatment is, therefore, recommended as it improves the efficiency of humus extraction.

The alkaline humate solution is then treated for the separation of HA and FA. As can be seen in Figure 2, the solution is acidified to pH 2 using dilute HCl, whereupon HA precipitates and FA remains in the solution; HA and FA are separated by centrifugation. The residue containing HA and some clay impurities is redissolved in a dilute alkali and centrifuged at high speed to remove clay. The supernatant liquid is again acidified with dilute HCl to pH 2. The precipitated HA is treated with HCl-HF mixture to reduce the ash content, i.e. to remove cations like Fe^{3+}, Fe^{2+}, Al^{3+}, Si^{4+}, etc., which are still bound to HA. In spite of these treatments, some amounts of ash (inorganic cations) are always present even in the most purified samples. The HA, after treatment for ash removal, is dialyzed till free of salts and then dried under vacuum.

The purification of the FA solution involves precipitation as Ba-fulvate by treatment with a Ba-salt, dialysis of Ba-fulvate and treatment with an H^+ form of a cation exchange resin. The FA solution is concentrated and dried under vacuum. Ash is removed from FA by repeatedly passing it through H-resin columns. If humus from humin needs to be extracted, the soil residue (after the alkali treatment) is alternatively treated with dilute acid and dilute alkali at elevated temperatures.

Sometimes, non-humic substances are removed prior to the alkali treatment; the method involves either treatment with acetyl bromide

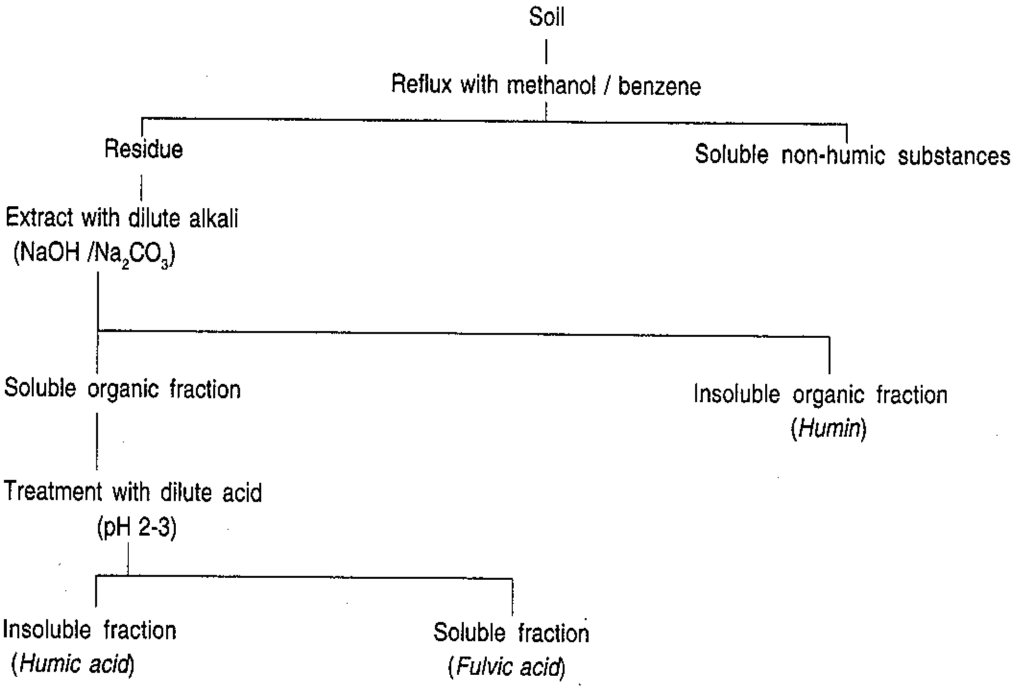


Figure 2. Scheme for extraction and fractionation of humic substances

(Source: Biswas and Mukherjee, 1994)

or refluxing with a mixture of methanol and benzene.

2.3. Experimental Methods for the Study of Humic Substances

2.3.1. Elemental Analysis

Humic substances are analyzed for their contents of C and H by combustion, N and S by Kjeldahl and Zeisel methods, respectively; O is determined by difference. The ranges of C, H, N, S and O in HA and FA are shown in Table 1.

2.3.2. Total Acidity

HA and FA exhibit weak acid behaviour owing to the presence of carboxyl and phenolic hydroxyl groups; some of these groups are not neutralized by alkali in aqueous medium. To determine the total acidic groups, $Ba(OH)_2$ titration may be done in a non-aqueous (organic solvent) medium under an inert (N_2) atmosphere.

2.3.3. Molecular Weight

Viscosity measurements of HA/FA solutions provide the simplest technique for determining their average molecular weights. Using a viscometer, the time of flow of water and HA/FA solutions of various concentrations are measured at constant temperature. Greater the molecular size, the more viscous the solution is and, consequently, the time of flow will also be longer. A mathematical relation is derived, which relates viscosity parameters to molecular weight. Since HA and FA solutions contain molecules having a range of sizes, values determined by experimental means provide an estimate of average molecular weights.

2.3.4. Functional Groups and Structure

Spectroscopic methods are mostly used to study the chemical nature of humic substances. These methods are based on the principle that the interaction of electromagnetic (light) waves with molecules depends on the molecular parameters. Molecules may interact in various manners over a range of wavelengths from the radiofrequency (long wavelength) to the visible (medium wavelength) and even to the x-rays (short wavelength). The technique chosen depends on the structural entity being investigated.

Infrared (IR) spectroscopy is the absorption of IR radiation by molecules due to the vibrations of their functional groups. In HA/FA, reactive functional groups are studied by IR spectroscopy, e.g., –COOH, phenolic and alcoholic –OH, >C=0, $-NH_2$, etc. Such groups show characteristic absorptions which vary with the change in the environment of that group. Thus, whereas the carboxyl group in HA shows absorption at about 1720 cm^{-1}, the carboxylate ion absorbs at 1590 cm^{-1}. IR spectroscopy thereby provides a measure of the qualitative changes in functional groups.

Ultraviolet (UV) and visible absorption spectroscopy measures the absorption of UV-visible light by HA/FA solutions. As such absorption is directly related to the concentration of HA/FA in solution, this technique is useful for quantitative analysis of humic substances in solution.

Another important parameter is the E_4/E_6 ratio, which is the ratio of optical density of HA/FA solutions at 465 nm and 665 nm respectively; this ratio is considered as an inverse index of particle size and aromaticity. Thus, FAs have higher E_4/E_6 ratios than HAs (Table 1).

Fluorescence is another noteworthy property of humic fractions and is characterized by a band at 465 nm in their fluorescence (excitation) spectra.

Nuclear magnetic resonance (NMR) spectroscopy involves the absorption of radiowaves by the atomic nucleus in a strong magnetic field. Only atoms with an odd number of nucleons (total number of neutrons and protons in the atom, i.e., mass number), e.g., ^{13}C, ^{1}H or ^{31}P can be studied by NMR spectroscopy. The ^{13}C NMR of HA/FA gives information on the various types of carbons, e.g., aromatic C, aliphatic C, etc. Proton magnetic resonance (^{1}H NMR) is similarly used for studying the various hydrogens in HA/FA.

Humic substances also contain unpaired electron spins. Electron spin resonance (ESR) spectroscopy is used to probe both the nature of such spins and the spin concentrations. These spins are responsible for various reactions of humic substances, especially their interaction with some of the transitional metal ions.

2.3.5. Crystallinity

X-ray diffraction (XRD) is the technique used for studying the crystalline structure of substances. Humic materials are found to be poorly crystalline and hence their structure analysis gives poor results.

2.3.6. Morphology

Since humic substances are extremely small in size, ordinary (light) microscopes cannot be used for studying the humic morphology. Scanning electron microscopy (SEM), which gives much higher magnifications, is used for this purpose. SEM reveals modifications in surface morphology owing to environmental changes like change in pH, ionic concentration, etc.

2.4. Reactions of Humic Substances with Metal Ions

Humic substances contain several reactive functional groups which make them efficient soil complexants for transitional metal ions like Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, etc. The functional groups of HA/FA involved in complexation with these ions include -OH, -NH_2, -COO^-, >CO, etc. Two kinds of bonding may be involved :

(a) Coordinate bonding wherein a pair of electrons is donated by the functional group to a vacant orbital in the transition metal ion, e.g., $H_2N: \rightarrow Cu$, and

(b) An electrovalent linkage in which a negative group bonds with the positively charged cation, e.g. $COO^- \ Zn^{2+} \ COO^-$.

Either one or both types of linkages may be present.

Bonding strength with HA varies with the metal ions. Amongst the highly stable complexes (where there is strong bonding between the metal and humus), stability of metal-HA complexes follows the order:

$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$.

The maximum amount of metal ion that can be bound by humic substances is roughly equal to its total acidic group content, since these are the groups that primarily take part in the reaction. Metal ions bound to humic substances may be recovered by treatment with a strong cation exchange resin. However, sometimes bonding is so strong that a part of the ions is not recoverable. Plant root hairs, which also function as ion exchangers, can extract the metal ions complexed by humic substances.

The importance of metal-humic complexes lies in the function as carriers of trace elements for plants. Their role in weathering and release of micronutrients from primary minerals and insoluble precipitates is also critical (Barman *et al.*, 1992). Complexation reduces precipitation and leaching losses. Toxic concentration of pollutant metal ions (e.g., Pb or Cd) may be reduced to non-toxic levels by bonding with humic substances.

2.5. Reactions of Humic Substances with Clay Minerals

Reactions between clay minerals and humic substances are primarily responsible for the formation of stable soil aggregates with important consequences in improving almost all soil properties. The formation of clay-humus complexes also retards microbial decomposition of humus. In mineral soils, almost all humus occurs in combination with clay. In spite of this, the picture of clay-humus complexes in soil is still not very clear (Varadachari *et al.*, 1991).

The reaction between HA/FA and clay is similar to that with metal ions; same groups in the humus molecules are involved. Clay minerals, on the other hand, contain cations at basal surfaces and edges to which the acidic groups of HA can bond. The primary chemical bonds in clay-humus complexes are the electrovalent bonds and coordinate bonds; physical bonding may also occur (Theng, 1979).

In chemical bonding between clay and humus, the metal ion forms a bridge linking the two, viz. clay-Ca^{2+}-HA. In montmorillonite, bonding is at the basal surface of the mineral. Both basal surface of illite plates as well as their edges are involved in complexation with humus. In kaolinite, almost all humus is bound to the edges. Humus in soils also forms complexes with sesquioxide (Varadachari *et al.*, 2000). Thus, bonding of HA to hematite (Fe_2O_3) is very strong and occurs both by electrostatic bonding to the charged surface as well as by the formation of coordinate bonds.

A similar mechanism also operates in humus-goethite [FeO(OH)] complexes, but the strength of bonding is much weaker. Recent studies with various types of clay-humus complexes have pointed out the primary importance of cations in the bonding of humus to clay.

2.6. Formation of Humus in Environment

Humic substances are produced (Varadachari and Ghosh, 1984) when plant residues and other organic debris are broken down and/or chemically altered by microorganisms and subsequently recombined under the influence of enzymes (Figure 3). Plant residues contain mainly lignin, carbohydrates and proteins, all of which are very high molecular weight, large sized compounds and are also chemically bound to one another. Microorganisms exude extracellular enzymes which break down these macromolecules to smaller units. These are taken up by the microorganisms as food; a part of it is oxidized to CO_2 and the rest is exuded in the form of different waste products. These waste products are different from the original compounds. Thus, when lignin is utilized, polyphenols, phenolic acids, etc. are produced. Similar compounds may also be produced from carbohydrates. Proteins are broken down into polypeptides and amino acids, much of which are used by the organism itself.

Polyphenols, phenolic acids, etc. appear to be the common molecular wastes, which find little use as a food (energy) source by microorganisms. Such compounds, therefore, accumulate in the soil. Phenolic compounds are highly unstable in air and rapidly polymerize by an oxidative process. Phenol polymerization

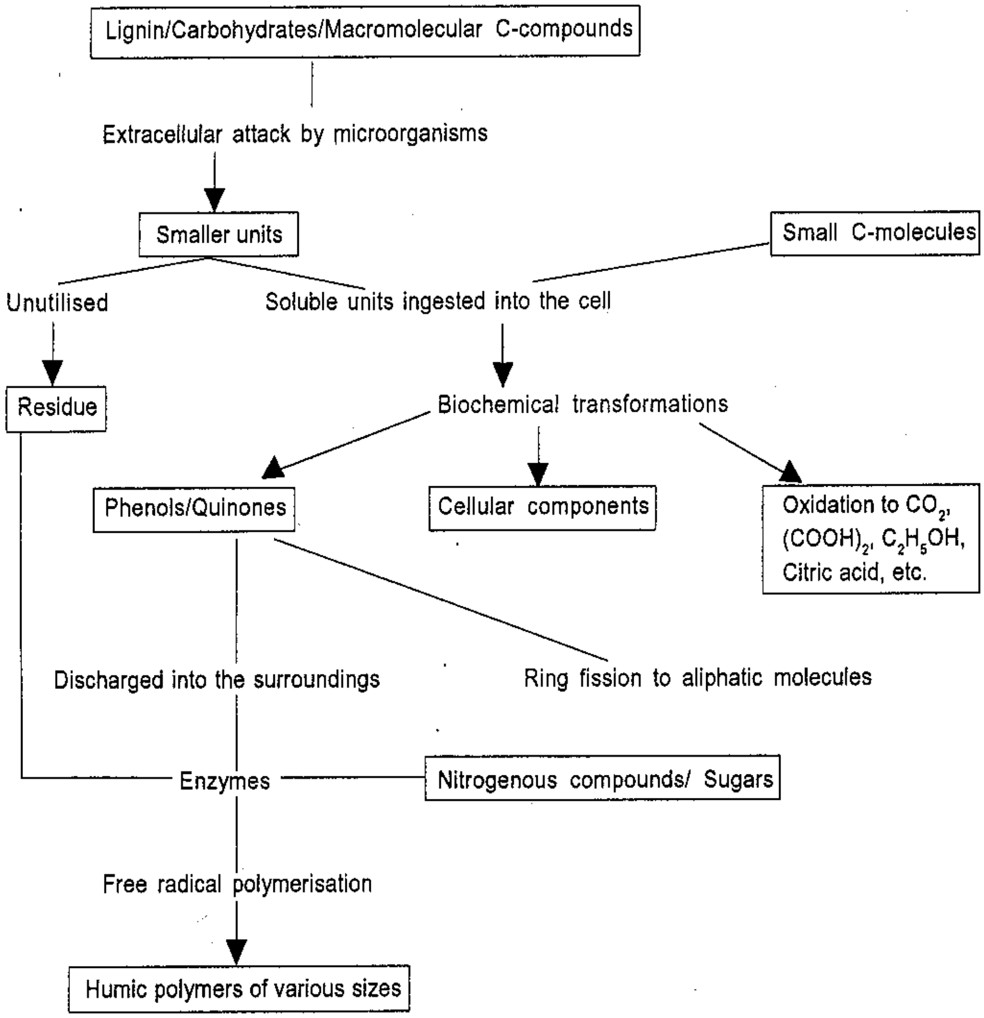


Figure 3. Humus formation — A schematic representation

(*Source:* Varadachari and Ghosh 1984)

also occurs under the influence of certain enzymes (called phenol oxidases) exuded by microorganisms. Phenols may also copolymerize with nitrogenous compounds (amino acids, polypeptides, etc.), sugars and various other degradation products in the soil.

As polymerization proceeds, the compound becomes dark brown or black and gets precipitated. Molecules which are polymerized more and have higher molecular weights, are the HAs, while the less polymerized compounds are FAs. The proportion of HA and FA in soils is determined by the O_2 availability and moisture levels. Under anaerobic conditions, phenol oxidation will be less than that under aerobic condition and, therefore, the less polymerized FA will predominate. Drying of the soil facilitates polymerization and thereby promotes HA over FA. The extent of N, P and S in the HA/FA form depends on the proportion of such compounds in the soil. However, since the ratios of C : N, C : P and C : S are within a fairly narrow range in soils, their relative proportions in HA or FA also vary within small limits.

Although microorganisms play a critical role in humus formation, soil fauna also has an essential part. Soil fauna, like earthworms and arthropods, breakdown the macroscopic plant residues into smaller fragments and excretory products which are more readily and rapidly assimilable by microorganisms. Without soil fauna, the production of humus in soil would be indeed exceedingly slow.

3. Management of Soil Organic Matter

3.1. Sources of Organic Matter

Plant, animal and microbial materials are the primary sources of OM. Plant tissues and microbial cells contain approximately 40 to 50% carbon on dry weight basis. The amounts and types of materials that are added to the soil depend upon the climatic conditions and vegetation systems. Forest systems add larger and more diverse amounts of OM to soils than grassland systems, which, in turn, provide higher amounts of OM than crop production systems. Large amounts of crop residues are produced but only a fraction of it is returned to the soil.

Sources of organic matter for use in agriculture can be broadly grouped into two classes: (i) On–farm sources, and (ii) Off–farm sources.

3.1.1. On-farm Sources of Organic Matter

Crop residues, roots, root exudates, and green manure crops contribute significantly towards build-up of SOM. The integrated use of manures and chemical fertilizers with greater frequency of leguminous crops in the cropping sequence is the most effective way to increase SOM under the given climate. Livestock wastes provide an excellent opportunity to transform wastes of one system into the input to the other. Crop residues are important feed to the livestock, while livestock wastes are good source of manures or compost. Cattle dung, urine, poultry and swine wastes are some of the resources commonly available at farms. These biodegradable wastes are transformed into a high quality compost. Regular application of good quality compost even at low rates (5 t/ha) along with chemical fertilizers improves soil health and soil quality. Such additions together with beneficial microorganisms such as *Rhizobium*, *Azotobacter*, *Azospirillum*, and *Pseudomonas* spp. have been found to enhance biological N-fixation, increase nutrient-use efficiency and suppress soil-borne diseases.

3.1.1.1. Organic Manures

Compost, manures and organic fertilizers are widely used. The term compost is often used interchangeably with manures and organic fertilizers. Cattle wastes or mixture of farm wastes dumped into pits for six or more months produce manures of uncertain quality, contaminated with weeds. Organic materials such as de-oiled cakes, bone meals, etc. are used as organic fertilizers.

In India, farmyard manure (FYM) provides a significant source of OM, more so, because of the removal of most crop residues and natural grasses for use as animal feed and/or as fuel. OM is also provided by green manuring (Bhardwaj and Kanwar, 1991). A well-grown green manure crop can easily provide 15-20 tonnes of green matter corresponding to 3-4 tonnes of dry matter per hectare of cultivated land.

3.1.1.2. Composts

Composting is a process of biological decomposition and stabilization of organic materials in wastes, under conditions that allow development of thermophilic temperature (55-65 °C) for a minimum duration of 3-4 weeks. The biologically-produced heat in this process sanitizes the material and minimizes the generation of odorous compounds and leachates. It leads to a final product of pre-determined quality that is stable, free of pathogens and plant seeds, and can be beneficially applied to land. Composting is actually a highly complex biodegradable process carried out by a diverse group of microorganisms in which the environment created by one community invites the activity of the successor group. Different types of microorganisms are, therefore, active at different times and sites in the composting mixture, depending on the food availability, oxygen supply and moisture content.

The decomposing materials during composting passes through two distinct stages: (a) thermophilic (sanitization), and (b) mesophilic (decomposition). The former phase utilizes easily degradable organic substances and the pile temperature rises up to 55-60 °C within 2-7 days. Microorganisms mainly involved here are thermo-tolerant fungi and thermophilic bacteria and actinomycetes. In the latter stage, degradation of complex organic molecules occurs, leading to the synthesis of dark brown humus like materials and the compost gets stabilized. Here, bacteria represent 80% of microbial population.

Vermicomposting uses the earthworms which can consume practically all kinds of organic materials. The excreta or "castings" of the worms are rich in nitrate and available forms of phosphorus, potassium, calcium and magnesium. The passage of soil through earthworms promotes bacterial and actinomycetes growth; actinomycetes thrive well in the presence of worms and their content in worm casts is several fold higher than in the original soil.

3.1.2. Off-farm Sources of Organic Matter

Rapid urbanization and advancement in food, agro-based and processing industries have resulted into generation of large volumes of biodegradable wastes with potential to supply OM and nutrients to crops. Presently, these wastes are unscientifically disposed either on land or into water bodies, leading to the contamination of our valuable natural resources. Broadly these biodegradable wastes are subclassed into: (i) Agro-industrial wastes, and (ii) Municipal wastes.

The agro-industrial wastes include biodegradable wastes of sugar industry, fruits and vegetable processing plants, slaughter houses, fisheries and marine catches.

Municipal solid wastes (MSW) are highly heterogeneous, only partially bio-degradable and contain a number of pollutants. Sewage sludge is another organic waste material of microbial origin which contains significant amounts of N, P and other nutrients, but often contain high amounts of heavy metals like Pb, Cd, Cu, Zn, etc., posing environmental threat.

3.2. Management Practices

In view of the vital functions of OM in soil productivity, it is essential that the potential sources of OM are judiciously managed. Particular attention is needed for cultivated soils in which organic carbon levels usually remain low. Intensive cultivation stimulates decomposition of native soil OM; excessive dependence on chemical fertilizers and neglect of adequate input of OM for plant nutrient supply, are the main factors responsible for relatively low carbon-content of cultivated soils. Attempts are, therefore, needed to provide sufficient amount of OM to these soils in order to maintain their productivity.

3.2.1. Crop Management Practices

Addition of carbonaceous materials low in nitrogen is not desirable. It is necessary to maintain the C: N ratio of the soil. If materials of high C: N ratio are incorporated into the soil, an appreciable amount of mineral nitrogen will be immobilized. This may happen when residues having C: N ratio wider than 30:1 are decomposed. The requirement of N can be met by either including legumes or addition of inorganic nitrogenous fertilizers. A suitable legume crop grown for about two months and ploughed under the soil can provide 75 to 100 kg of N to the soil. In situations not allowing green manuring for economic reasons, grain legumes may be included in the crop rotations.

For efficient management of nitrogen-deficient crop residues, incorporation of these materials well in advance of the crop sowing is essential so that the added OM gets enough time for decomposition and re-mineralization of the microbially immobilized nitrogen. Three-to-four weeks are usually required for adequate transformation of crop residues before the next crop can be successfully grown. Management of legume residues is easier than non-leguminous materials. Being relatively rich in N, these materials do not immobilize any significant quantity of inorganic nitrogen during decomposition. Also, their rate of decomposition is faster than that of other crop residues.

Keeping plant residues on the soil surface and resorting to minimum tillage slows down decomposition. In the course of time, this increases OM in the soil as compared to the practice of residue incorporation and intensive tillage. However, SOM management through minimum tillage is feasible only under such situations as can provide convenient tools for seed sowing. Increased use of fertilizer and herbicides is another requirement for minimally tilled soil.

4. Microbiological Aspects of Organic Matter Decomposition

Organic matter decomposition is primarily a microbiological process. Decomposition is carried out by heterotrophic microflora and microfauna comprising bacteria, fungi, actinomycetes and protozoa. In contrast to autotrophic organisms which can synthesize their own food from simple substances, heterotrophs derive energy and carbon for their growth solely from organic compounds. Besides the microflora and microfauna, many species of mesofauna such as earthworms also play an important role in the initial breakdown of organic residues.

In the decomposition process, two stages are noticeable. Microbial populations developing during the initial period of 2 to 3 weeks constitute primary flora, while those developing at later stages are made up of secondary flora. Organisms forming secondary flora act upon the compounds produced by the primary flora or dead cells of the primary flora. Numerically, microorganisms developing at the primary stage of decomposition are much larger than those appearing at the secondary stage. Accordingly, maximum decomposition of organic materials is accomplished in the first two weeks.

Organic matter decomposition serves three functions for the microflora: (i) providing energy for growth, (ii) supplying carbon for the formation of cell material, and (iii) providing other nutrient elements needed for cell growth. Carbon is continuously incorporated into the microbial cells. This process is known as 'assimilation'. Other elements, such as nitrogen, are also assimilated. Under aerobic conditions, about 20 to 40% of the substrate is assimilated into the microbial biomass. The rest is mineralized, i.e. converted to CO_2 or accumulated as products of decomposition, e.g., organic acids, alcohols, etc. However, the ability to assimilate carbon varies across microbial groups. Fungi may assimilate 30 to 40% of the carbon, whereas aerobic bacteria assimilate only 5 to 10% and anaerobic bacteria incorporate only 2 to 5% carbon.

Organic matter decomposition is largely an enzymatic process. Constitutional enzymes are produced by microbial cells, irrespective of the substrate in the environment; inducible enzymes are formed in the presence of a specific substrate. Further, an enzyme may metabolize its substrate within or outside the cell. Accordingly, they are known as intracellular or extracellular enzymes. Extracellular enzymes are essential for the decomposition of polysaccharides because the microbial cell is impenetrable to the large polysaccharide molecules. Monosaccharides, such as glucose, are metabolized by intracellular enzymes. Organic residues added to the soil are first broken down into their basic components by extracellular enzymes; and the basic components are subsequently utilized by intracellular enzymes.

Under anaerobic conditions, organic matter decomposition is considerably lower than that under aerobic conditions. It is because, in the absence of O_2, oxidation to CO_2 is incomplete and much of the carbon remains in the form of intermediate products of decomposition. Due to low carbon metabolism, energy yield and synthesis of microbial biomass are also lower than those under aerobic systems. Organic acids, alcohols, hydrogen, methane, etc., are produced under anaerobic or waterlogged conditions. Decomposing plant residues in such soils may accumulate appreciable amounts of organic acids, which are detrimental to plant roots. Common organic acids in flooded soils are: acetic acid, formic acid, butyric acid, lactic acid, succinic acid, phenolic acids, etc.

A large amount of energy is released during the decomposition of organic residues. The ratio of the amount of energy captured by the biological system to the amount released during the decomposition is termed as 'free energy efficiency'.

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Chapter 25

Fertilizers, Manures and Biofertilizers

G. NARAYANASAMY, B.R. ARORA, D.R. BISWAS and S.S. KHANNA

1. Introduction

Fertilizers are materials (solid, liquid or gas) containing one or more nutrient elements in the form of chemical compounds of the organic or inorganic nature. These occur either as a natural deposit or are synthesized in a chemical factory. These may be regarded as concentrated plant foods. Upon application to soil, these materials dissolve fully or sparingly in the soil-water system and release the nutrient(s) in the ionic form which are absorbed by the plants. However, some fertilizers after application to soil, undergo chemical transformations before releasing the nutrients in plant-available form. Irrespective of the mode of release, a nutrient has to be present in a specific ionic form, so that plants can absorb it from soil solution through the root system. At the point of absorption of a nutrient ion, there is no difference between an ion released by a fertilizer and another ion contributed by the soil nutrient pool, or the soil organic matter component.

2. Manuring in Ancient India

The art of manuring as a part of sound crop husbandry in ancient India (3250 BC – 1200 AD) is documented in the *Vedas* and the *Upanishads* (Raychaudhuri, 1984). Use of animal excreta, fish and bones, beef and fish washings and various kinds of decoctions is mentioned in the literature of that period. Apart from cow dung and fish manure, use of green manure and wood ash was common during the Medieval period (1200-1800 AD) in India. Farmers acquired traditional knowledge about these materials through experience. They knew the benefits of fallowing, mixed cropping or rotation of crops to enrich the soil.

During the 19th Century, when the then British East India Company brought under its fold a large part of India, it viewed with concern the inadequate productivity of the land to produce commercial crops and had wanted to improve it. A proposal was mooted around 1805 AD to set up one or more experimental farms in Lower Bengal (present-day Bihar and Orissa). Thus, a farm came up at Barrackpore near Calcutta (now Kolkata), followed by one at Pusa village in Bihar. Not much emerged from these experimental farms and the next few decades saw hardly any activity on agricultural front. The Famine Enquiry Commission of 1866 suggested the establishment of an Agriculture Department and the subsequent Famine Enquiry Commissions constituted during the last quarter of 19th Century recommended setting up of agricultural schools. In 1882, Imperial and provincial Agricultural Departments were established. The first expert to be appointed at the Imperial Department happened to be an

Agricultural Chemist, who recommended chemical analysis of soil, manure, etc. to understand soil exhaustion, nitrogen balance, and similar other characteristics of soil. This paved the way for commencement of scientific research for improvement in crop productivity at the turn of the 20th Century in India (Ghosh, 1984).

With the establishment of the Agricultural Research Institute at Pusa (Bihar) (renamed later as Imperial Agricultural Research Institute) in 1905, systematic research work started in the country. Dr J.W. Leather, who as the first Imperial Agricultural Chemist at this Institute initiated soil studies, can be well regarded as the Father of Soil Science and Agricultural Chemistry in India. Later, permanent manurial experiments were started by Dr Leather at Cawnpore (now Kanpur) and Coimbatore following the Rothamsted model. The former was, however, abandoned during the 1930s while the one at Coimbatore is still continuing, testifying the foresightedness and vision of those who started those experiments and the dedication of all others who followed to nurture and maintain these plots during the past about 100 years.

During the first half of the 20th Century, considerable research was done on Indian soils by several scientists. 'Nitrogen' received special attention, while phosphate was also studied. Yet, manurial practices or fertilizer management did not attract the attention of policy makers, administrators or agricultural scientists of that time. Studies on soil fertility and fertilizer use were brought to the central stage after Stewart (1947) in his report made specific recommendations for conducting large scale manurial trials in farmers' fields. Thus, use of fertilizers in appreciable amounts in Indian Agriculture commenced only in the 1950s.

3. Fertilizers in Indian Agriculture

The amount of fertilizer nutrients ($N+P_2O_5+K_2O$) used in India during the year 1950-51 was 69,800 tonnes, which grew to 784,600 tonnes in 1965-66 (Table 1). The year 1965-66 marks a watershed in Indian agriculture. The 'Green Revolution' (a seed - fertilizer revolution) period started around this time. The fertilizer usage increased rapidly. During the next 10 years, the fertilizer consumption quadrupled to 2.9 million tonnes in 1975-76, which further tripled to 8.5 million tonnes in 1985-86. During 1995-96 fertilizer use rose to 13.9 million tonnes and in 2005-06 it was 20.3 million tonnes. The fertilizer use during 2010-11 further increased to 28.3 million tonnes. During 2009, India was the second largest consumer of fertilizer nitrogen (the top country being China), second in phosphorus (the top country being China), and third in potassium usage (the others being China and USA, in the decreasing order). Thus, India uses worldwide large quantities of fertilizers in agriculture, without which it would not be able to produce the foodgrain and other agricultural commodities needed to sustain its burgeoning population, which crossed the 1.21 billion mark in the year 2011 AD.

A strong link between fertilizer consumption and foodgrain production is evident from Table 1. Foodgrain production virtually increased from 108 million tonnes in 1970-71 to 241.6 million tonnes in 2010-2011, owing to increase in the productivity (yield per unit area). There has been little change in the cultivated area under foodgrain crops during this period. Fertilizer alone is considered to account for nearly one-half of this increased productivity. Undoubtedly, fertilizers are used not only for foodgrain production, but also for other crops such as oilseeds, sugarcane, tea, coffee, etc. At this juncture, use of fertilizers in Indian agriculture to improve crop productivity is inevitable and cannot be replaced to any great extent by other means of meeting crop nutritional needs.

3.1. The Fertiliser (Control) Order

The Fertilizer (Control) Order, (FCO) (2006) is a set of legally enforceable executive orders issued by the Govt. of India under the Essential Commodities Act, 1955 passed by the Parliament. This Order came into force in 1957, essentially to regulate the sale, price and quality of fertilizers in India. Amendments are made from time to time as per the exigencies and need of the hour and therefore, a large number of amendments were made over a period of time. Consequently, after an overall review of the various provisions of the Order, a revised

Table 1. Consumption of fertilizer nutrients and foodgrain production in India

(in '000 tonnes)

Year	N	P_2O_5	K_2O	Total ($N + P_2O_5 + K_2O$)	Total foodgrain production
1950-51	55.0	8.8	6.0	69.8	50,825
1955-56	107.5	13.0	10.3	130.8	68,850
1960-61	211.7	53.1	29.0	293.8	82,018
1965-66	574.8	132.5	77.3	784.6	72,347
1970-71	1479.3	541.0	236.3	2,256.6	108,422
1975-76	2148.6	466.8	278.3	2,893.7	121,034
1980-81	3678.1	1,213.6	623.9	5,515.6	129,589
1985-86	5660.8	2,005.2	808.1	8,474.1	150,440
1990-91	7997.2	3,221.0	1,328.0	12,546.2	176,390
1995-96	9822.8	2,897.5	1,155.8	13,876.2	180,415
2000-01	10,920.2	4,214.6	1,567.5	16,702.3	196,814
2005-06	12,723.3	5,203.7	2,413.3	20,340.3	208,602
2006-07	13,772.9	5,543.3	2,334.8	21,651.0	217,282
2007-08	14,416.1	5,514.7	2,636.3	22,570.1	230,670
2008-09	15,090.5	6,506.2	3,312.6	24,909.3	233,880
2009-10	15,580.0	7,274.0	3,632.4	26,486.4	218,100
2010-11*	16,890.2	8,001.4	3,391.4	28,282.9	241,600

*Provisional

Source: FAI (2011)

Fertilizer (Control) Order 1985, was issued, which came into effect on September 25, 1985.

FCO consists of two Schedules (I and II), besides Forms of Registrations and Appendices. Schedule I comprises Part A and B. While Part A provides the specifications (like minimum nutrient content, maximum moisture content, range of physical parameters, maximum levels of impurities/ contaminants, etc.), of all the fertilizers that can be marketed in India (no material not listed in the FCO can be sold as fertilizer), Part B lists the tolerance limits in plant nutrients and physical parameters for various fertilizers. Schedule II encompasses again two parts, with Part A describing the procedures for drawal of samples of fertilizers, and Part B elaborating detailed methods of analysis of fertilizers.

FCO is legally enforceable throughout the country. The provisions of this Order needs to be followed scrupulously and completely by the agencies identified and ordained to enforce this Order, both for drawing of samples and subsequent analysis. No deviation of any kind is permitted in this regard, as any dispute arising between the enforcement agency and the offending party/ parties will be adjudicated by an appropriate court of law.

4. History of Fertilizer Production

4.1. Global Scene

Use of ground bone as fertilizer was practised in England in the 17th Century. In the United States of America, its use started in 1825. A fertilizer by the name Peruvian guano (sodium nitrate) was discovered by the German botanist, Humboldt in 1802, but its mining and extensive use, mainly in Europe and America, started around 1840. Estimated to be around 12 million tonnes in 1840, this deposit depleted fast so that in 1875 only about 2 million tonnes was left. Yet, its mining and export continued at a decreasing rate till the turn of the 19th Century. During the second half of 19th Century, both Peruvian and Chilean deposits of sodium nitrate became well known in Europe and America. Besides natural materials such as bonemeal and bird guano, ammonium salts were first produced as by-product and used in England in 1840. In 1842, John B. Lawes took a patent to manufacture a fertilizer which he called *'Superphosphate'.* He ac-

Table 2. Production of fertilizers in India — An historical account

Sl No.	Year	Fertilizer material	Name of first manufacturer	Total No.of units (as on 1-11-2008)
1	1906	Single superphosphate	EID-Parry (India) Ltd., Ranipet	79
2	1906	Fertilizer mixtures		75#
3		Ammonium sulphate		10
	1933	(a) As a by-product of steel industry	Tata Iron & Steel Co. Ltd., Jamshedpur	6
	1941	(b) Using sulphuric acid	Mysore Chemicals & Fertilizers Ltd. Belagula*	
	1947	(c) Using gypsum as raw material	FACT, Udyogamandal (Alwaye), Kerala	
	1974	(d) As a by-product of polymer/caprolactum	GSFC, Baroda	4
4	1959	Ammonium sulphate nitrate	FCI Ltd., Sindri*	**
		Urea	FCI Ltd., Sindri*	28$
		Ammonium chloride (Agri. Grade)	New Central Jute Mills Co. Ltd., Varanasi*	**
5	1960	Ammonium phosphate	FACT, Udyogamandal (Alwaye), Kerala	3@
6	1961	Calcium ammonium nitrate	NFL, Nangal	1$
7	1965	Nitrophosphate	RCFL, Trombay, Mumbai	2$
8	1967	Diammonium phosphate	Gujarat State Fertilizers & Chemicals Ltd., Baroda	11
9	1968	Triple superphosphate	Dharamsi Morarji Chemical Co. Ltd. Ambernath	**
		Urea ammonium phosphate	Coromandel Fertilizers Ltd., Vizag (Visakhapatnam)	2
		NPK complex fertilizers	RCFL, Trombay, Mumbai	10@@
10	1973	Pelofos	Orissa Fertilizers and Chemicals, Rourkela	**

*: Not in operation now (closed)
**: Not manufactured now
#: Exact number is not available
$: Plant(s) in operation
@ : During 2007-2008, nine plants manufactured ammonium phosphate sulphate (20-20-0)
@@: Plants manufacured NPK complex fertilisers in 2007-08.
Note: Fertilizer plants with multiple products have been counted more than once under respective product categories
Source: FAI (2011)

tually produced it in 1843 by treating coprolites (a fossilized dung) with sulphuric acid. This may be considered as the first commercially successful venture of fertilizer production. German potassium salts were first used as a fertilizer around 1860 and by the end of the 19th Century, potassium salts became thoroughly established in the market as fertilizer.

Another milestone in the fertilizer production is the mining of phosphate rock in the USA (around 1868) and in the North Africa (around 1899). Around the same period (about 1880), basic slag (a by-product of steel industry) was used as a fertilizer in England. Mixed fertilizers were produced in the USA in 1849. Thus, the fertilizer industry continued to expand in the Europe and the USA during the latter part of the 19th Century. During the first decade of the 20th Century, prior to World War I, German chemists developed some economically feasible methods for the fixing of atmospheric nitrogen. This paved the way for the synthesis of many nitrogenous fertilizers subsequently (Collings, 1955).

4.2. Developments in India

In India, the first fertilizer produced in 1906, was single superphosphate. In the same year fertilizer mixtures also appeared in the market. Another chemical compound ammonium sulphate – a by-product of steel industry (by absorbing the ammonia gas obtained during coking of coal in sulphuric acid) was produced in 1933 (Table 2). In 1941, ammonium sulphate was produced as the main product using sulphuric acid. In 1947, the manufacture of this compound started using gypsum as a raw material, and in 1974 as a by-product of polymer industry. The year 1959 saw the production of urea, ammonium sulphate

Table 3. Sector-wise and material-wise capacity for the production of fertilizers in India
(Capacity: Situation as on 1.11.2008) (Figures in '000 tonnes material)

Sector	Urea	Ammonium sulphate	Calcium ammonium nitrate	Ammonium chloride	Complex fertilizers	Single super-phosphate
Public	6594.3 (5934.3)$^{\#}$	407.9	800.0$^+$	-	2134.5	-
Private	9024.5 (8302.5)$^{\$}$	208.6	142.5	105.0$^+$	6773.6	7526.2
Cooperative	5418.6	-	-	-	4336.4	-
Total	***21037.4*** ***(19655.4)***	***616.5***	***942.5***	***105.0+***	***13243.5****	***7526.2***

*: Out of which DAP capacity is about 6972 thousand tonnes.
+: Idle capacity
: Urea plants of FACT-Cochin i and RCF-Trombay V are lying idle.
$: Urea plant of DIL-Kanpur is lying idle.
Figures within the brackets denote operating capacity
Source: FAI (2011)

nitrate and ammonium chloride. Calcium ammonium nitrate (CAN) was produced in 1961 by diluting the explosion-prone ammonium nitrate with dolomitic limestone. Nitrophosphates appeared in 1965 and diammonium phosphate was produced for the first time in 1967. The `Triple superphosphate', `Urea ammonium phosphate' and NPK complex fertilizers arrived in the market in 1968. Today, large capacities for the production of nitrogenous and phosphatic fertilizers (Table 3) have been created in public, private and cooperative sectors. However, since India lacks in the mineral deposits containing potassium salts, no potassic fertilizer is produced here.

5. The Fertiliser Association of India (FAI)

This organization, set up in 1955 and registered as a company, is the national representative body of all fertilizer manufacturers in India, comprising public, private, joint and cooperative sectors. It is a non-profit, non-trading organization of fertilizer manufacturers, distributors, technologists, plant/equipment manufacturers, research institutes and others interested in fertilizers. Among others, FAI performs the following functions:

(i) Acts as a bridge between fertilizer industry and Government,
(ii) Maintains close liaison with international bodies,
(iii) Provides various fora for exchange of views at regional, national and international levels,
(iv) Carries out studies on specific topics,
(v) Acts as a clearing house for technical, commercial and statistical information concerning the industry,
(vi) Provides training programmes at different levels and in all the disciplines of the industry,
(vii) Administers a number of annual awards to promote healthy competition and to reward outstanding work, and
(viii) Publishes quality journals of different periodicity besides the annual publication of 'Fertiliser Statistics', which is regarded as a reference book on Indian fertilizer and agriculture, containing detailed information on production, distribution, consumption, prices and related statistics from India as well as abroad.

6. Classification of Fertilizers

Fertilizers can be classified into three categories:

(i) Straight fertilizers,
(ii) Compound or complex fertilizers, and
(iii) Mixtures.

A straight fertilizer is a single compound containing one primary (N, P or K) nutrient only. A compound or complex fertilizer is also a single compound, but contains two or more nutrients, of which at least two primary nutrients are in chemically combined form. Mixed fertilizers are prepared by physically mixing two or more fertilizers. Such mixtures can be prepared by mixing two or more straight fertilizers or one or more straight fertilizers with one or more complex fertilizers. Usually fertilizer mixtures are prepared to meet specific needs of a crop. These are usually prepared locally on a small scale a little before its actual use.

The straight fertilizers can be classified as: (a) nitrogenous, (b) phosphatic, and (c) potassic fertilizers. With the emergence of deficiency of nutrients other than N, P or K, other fertilizers are also gaining importance, such as carriers of sulphur, zinc, manganese, iron, molybdenum, boron, etc.

7. Nitrogenous Fertilizers

These contain N in the form of either ammonium (NH_4^+), nitrate (NO_3^-), amide ($-NH_2$), or cyanamide ($-CN_2$). The first two forms are inorganic in nature, and the latter two are constituents of organic molecules. Fertilizers containing either ammonium or nitrate or both, are readily soluble in water and dissociate spontaneously to release the ion(s) in the soil solution. Nitrate is readily absorbed by most of the plants, but ammonium is taken up by only certain plants like rice, tomato, etc. However, under certain soil conditions, ammonium ions are rapidly converted to nitrate ions by a group of soil-borne microorganisms. This process is termed as 'nitrification'. This transformation is brought about mainly by two groups of bacteria. There are two steps in this process. In the first step, *Nitrosomonas* sp. converts ammonium to nitrite through enzyme mediated biochemical pathway and in the second step, nitrite serves as a substrate to another group of bacterium, *Nitrobacter* sp. and owing to the biochemical oxidation, the end product is nitrate. Evidently nitrite is the intermediate product in the nitrification process. It is a potential toxicant to plants. Fortunately, the conversion of nitrite to nitrate is usually fast and therefore, nitrite concentration seldom builds up to the toxic levels. Nitrate, unlike ammonium, is not retained by the soil to any great extent, and is therefore liable to leaching along with drainage water, if not absorbed by plant roots. Ammonium, being a positively charged ion (cation) behaves much like other cations, such as K^+, Na^+, Fe^{2+}, Ca^{2+}, Mg^{2+}, etc. in the soil system and is retained by the negatively charged soil colloids of both inorganic and organic types.

The amide and cyanamide forms of nitrogen are organic in nature and need to be converted first to inorganic (ionic) forms for the uptake by plants. This conversion involves many biochemical reactions brought about by specific microorganisms. One such process is ammonification in which nitrogen in organic forms is converted to the ammonium form. Once ammonium ion is released into the soil solution, it is subjected to either physicochemical reaction with soil colloids or biochemical conversion to nitrate ions.

7.1. Synthetic Nitrogenous Fertilizers

The industrial production of synthetic nitrogenous fertilizers is done by three processes, which were developed in the 20th Century. These are: (i) cyanamide, (ii) arc, and (iii) direct synthetic ammonia processes, yielding crude calcium cyanamide, dilute nitric acid and anhydrous ammonia, respectively.

7.1.1. Calcium Cyanamide Process

This process was developed in Germany during the period 1897-1905 by two chemists, Prof. Dr Adolph Frank and Dr Nicodem Caro (though the discovery is reportedly done by two other chemists, namely Rothe and Freudenberg employed by them). Frank obtained a patent in 1900 for a process converting cyanamide to ammonium ion. But calcium cyanamide became an important fertilizer during the first few decades of the 20th Century, especially during the World War I. This was mainly because of:

(i) the relatively cheap raw materials required, namely coal and limestone, both being abundantly available,

(ii) distinctly lower (less than one-fourth) amount of electrical energy needed in comparison to arc process, and

(iii) the ease with which calcium cyanamide can be converted to ammonia and then to nitric acid, which was largely used in the manufacture of explosives.

In the production of calcium cyanamide, the first step is the burning of limestone (calcitic) in a kiln (vertical or rotary) at about 1100 °C, leading to the decomposition of limestone [Equation (1)]:

$$CaCO_3 \xrightarrow{\text{Heating}} CaO + CO_2 \quad \text{... (1)}$$

Calcium carbide is next produced by heating the lime with coal or coke in an electric furnace [Equation (2)]:

$$CaO + 3\,C \rightarrow CaC_2 + CO \quad \text{...(2)}$$

Pure nitrogen (obtained through fractional distillation of liquefied air), is then reacted with fine powdery calcium carbide at about 1000 °C to obtain calcium cyanamide [Equation (3)]:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \quad \text{...(3)}$$

(Calcium cyanamide can also be produced by heating a mixture of limestone and coke or coal in an atmosphere of nitrogen. But this route is stated to be uneconomical compared to the process technology involving discrete steps described above).

Calcium cyanamide fertilizer is not produced in India.

7.1.2. Arc Process

This is the simplest process of nitrogen fixation, imitating a reaction that takes place between N_2 and O_2 in the atmosphere due to lightning discharge of electric storms. It is estimated that about 100 million tonnes of the atmospheric nitrogen is fixed through this natural process and a considerable part reaches land mass along with the rainwater, with the remainder falling into the water bodies of the world. The first commercial venture based on arc process was established by C.S. Bradley and R. Lovejoy in the USA during 1902-1904, but this turned out to be an unsuccessful one. However, two Norwegians, Prof. Christian Birkland and Samuel Eyde (an engineer), successfully established a plant around the same time. Since then a few more attempts were made, but this route of fixing atmospheric nitrogen remained an unattractive one. The major defects of this process are the requirement of enormous amount of power (almost 5-times of that is needed in the cyanamide process) and high capital cost.

The arc process involves a reaction between N_2 and O_2 in an electric arc field at a temperature of 3500 °C. This is accomplished by blowing air through a flaming electric arc, when about 2% of air combines to yield nitric oxide (Equation 4), which is then allowed to combine with O_2 and water to yield nitric acid (Equation 6):

$$N_2 + O_2 \xrightarrow{\text{Heat}} 2\,NO \quad \text{...(4)}$$

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad \text{...(5)}$$

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO \quad \text{...(6)}$$

7.1.3. Synthetic Ammonia Process

This process is widely used for fixing atmospheric nitrogen as ammonia. The first plant of synthetic ammonia was built in 1910 in Germany, where Prof. Fritz Haber worked out a method for combining N_2 and H_2 for synthesizing ammonia. During 1905-1908, he perfected this process involving a certain gas pressure, temperature and a catalyst. This process consumes much less power as compared to the cyanamide and the arc processes and therefore became the most popular route of nitrogen fixation. Subsequently, the technical difficulties of handling inflammable gases at high temperature and pressure were tackled by Dr Carl Bosch by making certain modifications and today the modified Haber-Bosch process forms the basis for the modern direct synthetic ammonia process technology.

Synthetic ammonia process needs two gases, nitrogen and hydrogen. Nitrogen is obtained from atmospheric air by fractional distillation of liquefied air. Alternatively, N_2 can be secured by blowing air over burning coal, or natural gas, when O_2 of the air combines with carbon of the coal or natural gas to form CO or CO_2, leaving N_2 unchanged. The resultant mixture is the well known 'producer gas' containing both N_2 and H_2.

The production of hydrogen gas is the challenging aspect of synthetic ammonia process. The material used as a source of hydrogen is called 'feedstock' and this includes an array of materials starting with simple natural gas (mostly methane) to complex naphtha and heavy fuel oil.

Natural gas is a mixture of alkanes with chain length 1 (CH_4, methane) to 5 (C_5H_{12}, pentane). Naphtha is a distillate obtained during fractional distillation of petroleum in a temperature range 200-250 °C and consists of hydrocarbons having ring structures such as benzene (C_6H_6), toluene ($C_5H_5C\text{-}CH_3$), and xylene ($C_4H_4C\text{-}CH_3C\text{-}CH_3$). Liquefied petroleum gas, also obtained from petroleum, consists mainly of propane (C_3H_8) and butane (C_4H_{10}). Hydrogen is present in the molecules of all these feedstocks. The process of extraction of hydrogen from feedstock involves the following five steps:

(i) Desulphurization, a process of removing sulphur, which poisons the catalysts;
(ii) Primary reformation, when at high temperature around 1300 °C in the presence of a Ni-catalyst, steam at high pressure breaks down the hydrocarbons, releasing the carbon as CO and CO_2 and hydrogen as H_2 gas;
(iii) Secondary reformation, where a major part of CO is converted to CO_2 in the presence of Ni as catalyst;
(iv) Shift converter, where Fe_2O_3 and Cr_2O_3 catalysts convert the remaining traces of CO to CO_2 by reacting with H_2O and thereby, releasing more H_2; and
(v) Carbon dioxide absorber, where CO_2 present in the stream is finally removed, leaving H_2 gas in tact.

Hydrogen can also be obtained by electrolysis of water. But this is feasible only where low cost electric power is available.

Other sources of hydrogen include water gas, coke-oven gas and refinery gas. Water gas is a mixture of H_2, CO and a few impurities and is produced by passing superheated steam over red hot coke, when carbon of the coke combines with oxygen of the water molecule to form carbon monoxide, thereby releasing the hydrogen of water as a gas.

Synthesis of Ammonia — The chemistry of synthesis of ammonia is simple:

$$3\,H_2 + N_2 = 2\,NH_3 \qquad ...(7)$$

The reaction (7) is exothermic (647 kcal/kg of NH_3) and is usually carried out at 400-450 °C using an iron catalyst promoted with alumina and potassium. A gas mixture consisting of N_2 and H_2 in the ratio of 1:3 plus 10 to 14% inerts (mainly methane, argon and sometimes helium) and about 2% ammonia is used. Two types of ammonia synthesis convertors are employed. In the first type, a multiple catalyst bed is used with the provision for "quenching" the gas between beds, and in the second type, a continuous catalyst bed with built-in heat exchangers is used. The gas leaving the convertor may contain 12-18% ammonia which is cooled first and then refrigerated to condense most of the ammonia in liquid form. The gas remaining after the ammonia condensation is recycled through the convertor. Ammonia can be stored under atmospheric pressure if it is cooled to −33 °C. Alternatively, it can be stored under high pressure also.

Storage of Ammonia — Once produced ammonia is either used for production of one or more of the several fertilizers possible in the same factory or supplied to other producers of fertilizers or farmers who will use it for direct application to soil. Anhydrous ammonia is the most concentrated form of nitrogenous fertilizer as it contains 82% N. Ammonia is stored as a liquid under either fully refrigerated, semi-refrigerated or pressurized conditions.

Transport of Ammonia — There are several modes of transportation of ammonia as liquid, depending on the distance and other factors: (i) Ships are commonly used. (ii) Shipment of anhydrous ammonia is done through barges. (iii) Transportation of anhydrous ammonia by pipeline is also followed over long distances. (iv) It can be transported by rail cars. (v) Transportation of anhydrous ammonia by truck is also possible but is economical only for short distances.

7.2. Production of Nitrogenous Fertilizers

The nitrogenous fertilizers generally produced are: ammonium sulphate, ammonium chloride, ammonium nitrate, calcium ammonium nitrate (CAN) and urea. Production processes, in brief, are presented below.

7.2.1. Ammonium Sulphate

It contains 20.6% N and was a leading nitrogenous fertilizer at one time but now accounts for only a small percentage of the total N fertilizers. Depending upon the availability of raw materials, the principal methods are:

(i) Reacting ammonia and sulphuric acid in a saturator evaporator:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \quad ...(8)$$

(ii) Scrubbing coke-oven gas with sulphuric acid.

(iii) Reacting ammonium carbonate with gypsum (natural or by-product origin) and removing the calcium carbonate by filtration followed by evaporation and crystallization of ammonium sulphate:

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3 \quad ...(9)$$

(iv) Evaporating the by-product liquors containing ammonium sulphate produced in other processes.

(v) Reacting gaseous ammonia with sulphuric acid in a spray tower to form a dry amorphous product.

(vi) Reacting ammonia with mixed acids to get ammonium sulphate and other ammonium salts simultaneously as granulated fertilizer materials containing phosphates, nitrates, etc.

7.2.2. Ammonium Chloride

Among the several methods available for producing ammonium chloride (25% N), the following are the important ones:

Dual Salt Process — In this process ammonium chloride and sodium carbonate are produced simultaneously (Solvay Process). In the conventional Solvay plants, ammoniated solution of about 30% sodium chloride is treated with carbon dioxide in large absorber towers to form ammonium carbonate [Equation (10)]:

$$2\,NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3 \quad ...(10)$$

Additional carbonation produces ammonium bicarbonate [Equation (11)]:

$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3 \quad ...(11)$$

Addition of sodium chloride yields sodium bicarbonate and ammonium chloride [Equation (12)]:

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + 2NH_4Cl \quad ...(12)$$

Sodium bicarbonate is separated out and calcined to obtain sodium carbonate and carbon dioxide. The mother liquor is then ammoniated and salted out by the addition of washed solid sodium chloride. The precipitated ammonium chloride is centrifuged, washed and dried.

Direct Neutralization Process — Ammonia is neutralized with hydrochloric acid. This process yields salts of high purity [Equation (13)]:

$$NH_3\,(g) + HCl\,(l) \rightarrow NH_4Cl\,(s) \quad ...(13)$$

7.2.3. Nitric Acid

Nitric acid is an important intermediate compound in nitrogen fertilizer industry and it is produced by the oxidation of ammonia at 800-1000 °C in the presence of catalysts consisting of platinum and rhodium. The first step is oxidation of ammonia to nitric oxide (NO), followed by oxidation of NO to NO_2 (nitrogen dioxide) and conversion of NO_2 to nitric acid [Equations (14) - (16)]:

$$4\,NH_3\,(g) + 5\,O_2\,(g) \rightarrow 4\,NO\,(g) + 6H_2O \quad - 54.14 \text{ kcal/g-mole} \quad ...(14)$$

$$2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g) \quad - 13.6 \text{ kcal/g-mole} \quad ...(15)$$

$$4\,NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 4\,HNO_3\,(aq) \quad - 20.8 \text{ kcal/g-mole} \quad ...(16)$$

It is used mainly for production of fertilizers such as ammonium nitrate, complex fertilizers, nitrophosphates, nitrogen solutions and mixed salts.

7.2.4. Ammonium Nitrate

It is one of the most popular fertilizers (35% N) in several countries, since it contains N in the readily available nitrate form of N along with the ammoniacal form, both being present in equal amounts. But, because of the risk of fire or sometimes even explosion, in some of the countries including India, straight ammonium nitrate is not permitted to be sold as a fertilizer. It is mixed with limestone and sold as calcium ammonium nitrate (CAN) (26% N).

Several methods are followed for the production of ammonium nitrate, using different combinations of neutralization, evaporation and drying and finishing. Neutralization of anhydrous ammonia is carried out with nitric acid of more than 50% concentration ($NH_3 + HNO_3 \rightarrow NH_4NO_3$). The concentration of ammonium nitrate is usually about 80%, which becomes 99.8% after evaporation. If CAN is to be produced, the concentrated ammonium nitrate solution is mixed with ground calcitic or dolomitic limestone ($NH_4NO_3 + CaCO_3 \rightarrow CAN$) and the resultant mixture is granulated. Usually a clay conditioner is used as surface coating to improve the physical properties of CAN.

7.2.5. Urea

Urea was first identified in 1773 after isolation in crystalline form from urine. It was synthesized in the laboratory in 1828 by Wöhler from ammonia and cyanuric acid [Equation (17)]:

$$NH_3 + HCNO \rightarrow CO(NH_2)_2 \qquad ...(17)$$

It is the first organic compound prepared by synthesis from the inorganic materials. However, now-a-days it is manufactured from ammonia and carbon dioxide [Equations (18) - 19)]:

$$2\,NH_3 + CO_2 \rightleftharpoons NH_2CO_2NH_4 \qquad ...(18)$$

$$NH_2CO_2NH_4 \rightleftharpoons CO(NH_2)_2 + H_2O \qquad ...(19)$$

While the first reaction is highly exothermic (37.7 kcal/g-mole), the second one is moderately endothermic (-7.7 kcal/g-mole).

The methods used for production of urea (45- 46% N) follow either once-through partial recycle or total recycle process. The once-through method is the simplest one in which liquid ammonia and gaseous carbon dioxide are pumped into a urea reactor maintained at about 185 °C and 200 atmosphere pressure. About 35% of the ammonia and 75% of the carbon dioxide are converted into urea. The reactor effluent solution contains about 80% urea. The unconverted ammonia and carbon dioxide are driven off by steam heating. In the partial recycle process, a portion of the carbon dioxide and ammonia gases is recycled to the urea reactor. In the total recycle process, all the unconverted ammonia and carbon dioxide mixture is recycled to the urea reactor, thereby leading to a conversion of 99%.

In India, urea is marketed mainly in the form of prills, though other solid forms of urea include flake, granule and crystal. Molten urea is prilled by spraying it from the top of a prilling tower. The droplets formed by the prilling device cool and solidify as they fall through an ascending gas stream.

To improve the physical strength and increase the resistance to caking, urea is often treated with a conditioner like formaldehyde (0.3 to 0.4%). Alternatively, coating of prills can also be followed by using powdery materials like china clay, talc, etc. Even a medium viscosity oil (without clay) can be used for coating prilled urea to retard moisture absorption.

Effect of Biuret — During synthesis of urea, a compound called biuret (NH_2-CO-NH-CO-NH_2) is also formed in small quantities. It is not an undesirable compound by itself, but when urea solution containing biuret more than 2% is sprayed onto crops, it may cause some damage to foliage. Certain crops like citrus are more sensitive to biuret.

8. Phosphatic Fertilizers

Phosphatic fertilizers are basically produced by converting certain P-containing minerals occurring in nature into fully (or partially) water-soluble compounds.

8.1. Raw Materials

Phosphate rock and sulphuric acid are the two major raw materials required for the manufacture of a number of phosphatic fertilizers.

8.1.1. Sulphuric Acid

Nearly half of the total sulphuric acid produced worldover is used for the manufacture of phosphatic fertilizers. About 60% of the world's production of sulphuric acid is based on elemental sulphur, 25% on pyrites, and the rest on other sources. Elemental sulphur is burnt in the presence of dry air at a temperature of 950-1100 °C to produce sulphur dioxide (SO_2) which is converted to sulphur trioxide (SO_3) through catalytic oxidation. Sulphur trioxide is subsequently absorbed in dilute sulphuric acid. The end product is sulphuric acid, usually of 98% concentration. The two principal processes used for conversion of SO_2 to SO_3 are known as (i) 'chamber' and (ii) 'contact' processes. The 'contact process' is more commonly followed, where a metal or a metal oxide (vanadium oxide) (platinum was widely used once) is used as a catalyst.

8.1.2. Phosphate Rock

The term phosphate rock means any rock containing large proportion of phosphate minerals that can be used for such commercial purposes as manufacture of fertilizers, direct application to soil or production of industrial phosphorus compounds. Usually, it is produced by mining and beneficiation, though some phosphate rocks are used as such without beneficiation. About 150 minerals containing more than 1% P_2O_5 occur in nature. But minerals belonging to two groups, namely 'apatites' and 'aluminous phosphates', alone are of commercial importance. In most of the commercial grade phosphate rocks, the P_2O_5-content is around 32% (w/w).

The commercial production of phosphate rock began in the 19th Century and its production was around 147 million tonnes in 2004. Though many countries produce phosphate rocks, nearly three-fourths of these are produced by the USA, China, Morocco, Russia and Tunisia. Amongst other phosphate rock producing countries are Togo, Jordan, Senegal, Israel and Algeria.

Aluminous Phosphates — This group of minerals is fairly widespread in nature. The principal aluminium phosphate minerals are:

Crandallite ($CaO.2Al_2O_3.P_2O_5.5H_2O$),
Wavellite [$4AlPO_4.2Al(OH)_3.9H_2O$], and
Millisite ($2CaO.Na_2O.6Al_2O_3.4P_2O_5.17H_2O$).

These are directly applied to soil after calcination (a thermal treatment of the mineral under controlled condition). The contribution of aluminous phosphate to fertilizer usage is very small.

Apatites — These are basically calcium phosphates and almost the entire quantity of fertilizer phosphorus and other industrial phosphorus compounds is produced from these minerals. Commercial phosphate rocks generally contain a variant of fluorapatite [$Ca_{10}(PO_4)_6F_2$] as the primary source of phosphorus.

Apatites occur in igneous, metamorphic and sedimentary rock formations. Sedimentary deposits are the most important ones yielding large proportion of commercial phosphate rocks at present. In these materials, a group of carbonate-substituted minerals called francolite or carbonate apatites is the important phosphorus-bearing mineral having the following general empirical formula:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$$

where, 'a' represents the molar substitution of Na for Ca, 'b' represents the molar substitution of Mg for Ca, and 'x' is the molar substitution of CO_3 and F for PO_4. The value of x ranges from 0 to 1.2 in naturally occurring apatites in commercial phosphate rocks.

Accessory Minerals — Apatites occur in natural deposits along with an array of accessory (impurity) minerals. The most common ones are: silica, clays and other silicate minerals, mica, and carbonates (mainly calcite and dolomite). A crude mined ore containing these minerals is usually purified to some extent by a process known as 'beneficiation' to get apatite-rich phosphate rock (30% - 38% P_2O_5). It is then ground into fine powder form (90% of the material passing through 100 mesh screen) for subsequent use as raw material in phosphate industry.

8.1.3. Phosphoric Acid

This is an important intermediate product and to a less extent, an end product in phosphate fertilizer industry and contributes to nearly 90% of the P produced in the form of fertilizers. Two types of processes are used for the production of phosphoric acid: (i) Furnace Processes, and (ii) Wet Processes.

8.1.3.1.Furnace Processes

In these processes, a mixture of phosphate rock (or other phosphate-bearing mineral), silica and coke is fed into a furnace. The P-mineral and silica are fused with the help of an arc produced with carbon or graphite electrodes. The carbon in the coke reduces the phosphate to elemental form. A mixture of elemental phosphorus vapour and carbon monoxide gas is withdrawn continuously from the furnace. Molten calcium silicate slag and other melt are tapped from the furnace periodically. Elemental P thus produced is burnt in the air to get phosphorus pentoxide, which in turn is reacted with water to get phosphoric acid. The principal reactions are represented by Equations (20) - (22):

$$Ca_{10}(PO_4)_6F_2 + 15\,C + 6\,SiO_2 \longrightarrow 1.5P_4 + 15CO + 3(3CaO.2SiO_2) + CaF_2 \quad ...(20)$$

$$P_4 + 5O_2 \rightarrow 2\,P_2O_5 \quad ...(21)$$

$$P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4 \quad ...(22)$$

The 'thermal grade acid' produced by this route is highly pure but very expensive and therefore is rarely used for the production of phosphate fertilizers.

8.1.3.2. Wet Processes

These involve disintegration of apatite in a mineral acid to release the phosphorus as phosphoric acid. Wet processes are classified according to the acid used to decompose phosphate rock. Hydrochloric, nitric or sulphuric acid is used in commercial processes. Processes using nitric acid lead to the production of nitrophosphates, use of hydrochloric acid is rather uneconomical while sulphuric acid is the most common means of producing phosphoric acid for fertilizer use. The main chemical reaction in the wet (sulphuric acid) process may be represented by the Equation (23), using pure fluorapatite to represent phosphate rock:

$$Ca_{10}(PO_4)_6F_2 + 10\,H_2SO_4 + 10n\,H_2O \longrightarrow 10\,CaSO_4.nH_2O + 6\,H_3PO_4 + 2\,HF \quad ...(23)$$

where, n = 0, 0.5 or 2, depending on the hydrate form in which calcium sulphate crystallizes. The reaction in fact represents the net result of two stages. In the first stage, sulphuric acid reacts with the apatite forming monocalcium phosphate and in the second stage, monocalcium phosphate reacts with sulphuric acid to form phosphoric acid and calcium sulphate. These two stages of reaction take place simultaneously in a single reactor.

As mentioned earlier, phosphate rock contains many impurities and therefore these impurities participate in several side reactions leading to the formation of many compounds besides the major ones given in the above equation. Large amount of heat is released during these reactions.

Commercial wet processes may be classified according to the hydrate form in which calcium sulphate crystallizes (Anhydrite - $CaSO_4$, hemihydrate - $CaSO_4.0.5H_2O$ and dihydrate - $CaSO_4.2H_2O$). The dihydrate processes are most popular because they are relatively simple and adaptable to a wide range of grades and types of phosphate rocks. But hemihydrate processes have the advantage of producing phosphoric acid of a relatively high concentration. The dihydrate route involves four essential steps:

(i) Disintegration of apatite in sulphuric acid (3-5 minutes) and release of phosphoric acid.

(ii) Holding the slurry for sufficiently long time (1.5 to 12 hours) to allow growth of gypsum crystals of adequate size.

(iii) Separation of phosphoric acid from residue (phosphogypsum and other insoluble materials) by filtration.

(iv) Concentration and the clarification of product acid.

Phosphoric acid produced by most of the dihydrate processes contains 26-32% P_2O_5 and this is usually concentrated to 52-54% P_2O_5 strength by evaporation.

8.2. Phosphates

8.2.1. Single Superphosphate (SSP)

This fertilizer, also known as normal superphosphate and ordinary superphosphate, is the first fertilizer to be produced industrially and its production started in as early as 1843 in England. But, its contribution to world phosphate supply is shrinking and its present share among phosphate fertilizers is not more than 20% in India. Yet, SSP is an important phosphate fertilizer and is likely to remain so because of the following advantages.

(i) The production process of SSP is simple, requiring little technological skill.
(ii) Single superphosphate supplies two secondary nutrients (Ca and S) also, besides P.
(iii) The fertilizer effectiveness of SSP is unquestioned.
(iv) Economies of scale are minor, thus small plants can also be viable.
(v) As the process is not capital-intensive, SSP plants can operate on a planned seasonal schedule.

Though SSP has several advantages, its major disadvantage is its low analysis, 16%-22% P_2O_5 and consequent high distribution and application costs per unit of P_2O_5 compared to that of high analysis fertilizers like triple superphoshpate (TSP) and ammonium phosphates.

The production of SSP involves following operations:

(i) The powdered phosphate rock (containing 30%-38% total P_2O_5) is mixed with sulphuric acid (65%-75% H_2SO_4) to form a slurry.
(ii) Solidification of the slurry in a den (denning), where continued reactions and crystallization of monocalcium phosphate take place (time required 0.5 to 4 hours).
(iii) The wet material is subjected to final curing, when some of the slow reactions reach a state of near completion and the excess water evaporates. The curing time is 2-6 weeks. The dried material is crushed into a coarse powder before it is distributed as SSP.
(iv) If granular SSP is desired, it can be granulated either before or after it is cured.

The overall reaction between apatite and sulphuric acid can be represented by Equation (28):

$$Ca_{10}(PO_4)_6F_2 + 7\,H_2SO_4 + 3\,H_2O \longrightarrow 3\,Ca(H_2PO_4)_2.H_2O + 7\,CaSO_4 + 2\,HF \qquad ...(28)$$

It is generally agreed that the reactions proceed in two stages: (a) Sulphuric acid reacts with a part of apatite, yielding phosphoric acid, and (b) the resultant phosphoric acid subsequently reacts with the remaining apatite forming monocalcium phosphate. While the first stage is rapid, the second one proceeds slowly. It may also be seen that SSP is a mixture of calcium sulphate (usually gypsum) and water-soluble monocalcium phosphate with the former compound being the dominant member and this is the reason for its low analysis (16%-22% P_2O_5).

8.2.2. Enriched Superphosphate

Also known as 'double superphosphate', it essentially is a mixture of SSP and TSP. It is produced by reacting rock phosphate with a mixed acid system consisting of variable proportions of sulphuric and phosphoric acids. The advantage of this material is a fairly high P_2O_5-content (25%-35%) and the presence of some amounts of sulphate and calcium.

8.2.2. Fertilizers Derived from Phosphoric Acid

Theoretically any phosphate can be made from phosphoric acid. However, the commercial fertilizers produced are: triple superphosphate (TSP), ammonium phosphates and other complex fertilizers.

8.2.2.1. Triple Superphosphate (TSP)

This is produced by reacting phosphate rock with phosphoric acid [Equation (24)]:

$$Ca_{10}(PO_4)_6F_2 + 14\,H_3PO_4 + 10\,H_2O \longrightarrow 10\,Ca(H_2PO_4)_2.H_2O + 2\,HF \qquad ...(24)$$

The TSP is a highly concentrated phosphatic fertilizer containing P in the form of water-soluble monocalcium phosphate. Another advantage is that a part of its P-content is derived directly from phosphate rock. Some of the disadvantages of TSP are its acidic character, which may cause deterioration of storage bags (jute/ hemp/ paper) and its unsuitability for blending with urea. The TSP fertilizer may be produced in either granular or non-granular form, with 46% total P_2O_5 and 42.5% water-soluble P_2O_5 content .

8.2.2.2. Ammonium Phosphates

Ammonium phosphates, particularly diammonium phosphate (DAP), are the most popular phosphate fertilizers which are either used as such or are present in several complex fertilizers. These have high nutrient content with good physical properties and water solubility. Three ammonium phosphates can be obtained when the tribasic phosphoric acid is reacted with ammonia. Of these only mono-ammonium phosphate (MAP) ($H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$) and diammonium phosphate (DAP) are produced, while triammonium phosphate (TAP) is not produced as a fertilizer because it is an unstable compound (decomposes due to its own alkalinity and releases part of ammonia and converts itself into diammonium phosphate).

Again between the two stable ammonium phosphates, diammonium phosphate (18-46-0) is preferred over monoammonium phosphate (11-52-0) because of the relatively large nitrogen content in DAP compared to MAP (plants usually need more nitrogen at planting time such as is provided by DAP). However, crystalline MAP is produced on a limited scale, mainly for the preparation of clear non-pressure type liquid fertilizers. Granular DAP is commonly produced by a slurry process in which wet process phosphoric acid of about 40% P_2O_5 is allowed to react with ammonia in either a single step or two stages such that the mole ratio of $NH_3 : PO_4$ in the final product is maintained around 2:1. The overall reaction can be represented by Equation (25):

$$H_3PO_4 + 2\,NH_3 \rightarrow (NH_4)_2HPO_4 \qquad ...(25)$$

8.2.2.3. Ammonium Polyphosphates

A group of high analysis fertilizers is produced by reacting superphosphoric acid (polyphosphoric acid) with ammonia. Superphosphoric acid is produced by concentrating phosphoric acid of wet process origin or by absorbing phosphorus pentoxide in less water than needed to get normal orthophosphoric acid. It is a mixture of several species of phosphoric acid in equilibrium proportions. Orthophosphoric (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and longer chain-length acids [P_3 to P_{10}, namely, $H_5P_3O_{10}$ (tripolyphosphoric acid), $H_6P_4O_{13}$ (tetra-polyphosphoric acid), etc.] with empirical formula $H_{n+2}P_nO_{3n+1}$ constitute the equilibrium mixture. As the concentration of the superphosphoric acid increases, the proportion of short-chain species decreases and the number and proportion of long-chain species increase. Superphosphoric acid of 69-75% P_2O_5 strength is of interest in fertilizer industry.

Upon ammoniation, a superphosphoric acid yields a number of compounds in a mixture in an equilibrium proportion, as determined by the degree of ammoniation and the composition of the superphosphoric acid itself. In ammonium polyphosphates, only a portion of P is present as orthophosphate and the remainder exists in non-orthophosphate form, which has to undergo hydrolysis to orthophosphate form before becoming a plant-usable form.

8.2.2.4. Other Fertilizers from Phosphoric Acid

Ammonium Phosphate Sulphate (APS or ASP)— It contains two salts of ammonia. In this category the best known grade is 16-20-0, consisting essentially of MAP and ammonium sulphate. In this double salt, the presence of sulphate makes it an eminently suitable fertilizer material to correct the deficiency of N, P and S together. Because of the high critical relative humidity of MAP (91.6% at 30 °C), this fertilizer has very good physical properties. The usual method of production involves reaction of sulphuric and phosphoric acids with ammonia. Alternatively, ammonium sulphate from by-product sources and phosphoric acid can also be used to ammoniate to get ASP.

Ammonium Phosphate Nitrate — These double salts contain ammonium phosphate and ammonium nitrate. Mixed phosphoric and nitric acids are used to neutralize ammonia to get the desired grade material (25-25-0, 30-10-0, etc.). The presence of ammonium nitrate makes this material somewhat hygroscopic.

Urea Ammonium Phosphates (UAP) — Combinations of urea with ammonium phosphate represent this group. Ammonium phosphate is produced in the form of a slurry by neutralizing phosphoric acid with ammonia in the desired ratio, to which urea is added as a solid melt or concentrated solution. The mixture is then granulated to UAP grades such as 28-28-0, 22-22-11, 18-18-18, etc.

8.3. Nitrophosphates

A group of fertilizers is produced by the treatment of phosphate rock with nitric acid. The main advantage of these processes is that nitric acid serves two purposes: (i) converts phosphate rock into more soluble form, and (ii) provides fertilizer nitrogen to the product. In this category, the simplest process involves the reaction between nitric acid with phosphate rock to produce monocalcium phosphate and calcium nitrate [Equation (26)]:

$$Ca_{10}(PO_4)_6F_2 + 14\,HNO_3 \longrightarrow 3\,Ca(H_2PO_4)_2 + 7\,Ca(NO_3)_2 + 2\,HF \quad ...(26)$$

This reaction is analogous to that of single superphosphate production, except that nitric acid replaces sulphuric acid. The product may contain about 8% N and 16% P_2O_5. The presence of calcium nitrate makes this product hygroscopic, limiting thereby its wide scale adoption.

Most of the nitrophosphate processes involve dissolution of phosphate rock in nitric acid (50%-60% HNO_3) to form phosphoric acid and calcium nitrate [Equation (27)]:

$$Ca_{10}(PO_4)_6F_2 + 20\,HNO_3 \longrightarrow 6\,H_3PO_4 + 10\,Ca(NO_3)_2 + 2\,HF \quad ...(27)$$

Nitrophosphate processes differ mainly in the subsequent treatment of phosphoric acid and calcium nitrate solution. For this the options available are:

(i) Removal of calcium nitrate by cooling of mother liquor and crystallization of calcium nitrate;

(ii) Removal of calcium by ion exchange by passing the mother liquor through a potassium-loaded resin;

(iii) Precipitation of calcium as calcium sulphate by the addition of soluble sulphate and its removal; and

(iv) Adjusting the CaO : P_2O_5 ratio to a desired level by the addition of soluble phosphate (instead of removing the calcium).

After tackling calcium nitrate by any one or more of the above techniques, ammoniation is carried out under defined controlled conditions. The final slurry after ammoniation is granulated with or without addition of potassium salts by a variety of methods. Nitrophosphates are produced with different water solubility (30%-70% of total P soluble in water). The grades of nitrophosphates are: 13-13-20, 15-15-15, 20-20-0, 23-23-0, etc.

8.4. Other Phosphate Fertilizers

8.4.1. Basic Slag

Also called Thomas slag, it is a by-product of steel industry. The usual range of P_2O_5-content in it is 10-20%. But, the basic slag produced in India is rather poor in phosphate content (2-5% P_2O_5). Phosphate in basic slag is present mainly as calcium silicophosphate, which is not soluble in water, but a small fraction of it, soluble in 2% citric acid, is considered to be potentially plant available.

8.4.2. Potassium Phosphates

These are excellent water-soluble compounds with very high nutrient contents (monopotassium dihydrogen phosphate, KH_2PO_4: 0-52-35; dipotassium hydrogen phosphate, K_2HPO_4: 0-40-54; tetrapotassium pyrophosphate, $K_4P_2O_7$: 0-43-57; potassium metaphosphate, KPO_3: 0-60-40). These can be produced by reacting potassium hydroxide or potassium carbonate with phosphoric acids of the appropriate category. But, there is no commercial production of these materials.

8.4.3. Bone Meal

This is a good source of P in acid soils and its slow solubility has a long-term effect. But, it is too expensive to be used widely as fertilizer. Most of the bone meal is used in animal feeds.

8.4.4. Fused Calcium Magnesium Phosphate

These are produced by fusing phosphate rock with olivine or serpentine (magnesium silicate) in an electric furnace. These glass-like products contain about 20% P_2O_5 and 15% MgO; and nearly 90% of P present in these fertilizers is soluble in citric acid.

8.4.5. Defluorinated Phosphate Rock

Powdered high grade phosphate rock is mixed with small quantity of sodium carbonate or sodium sulphate and phosphoric acid. This mixture is calcined at a temperature of 1350 °C and the product contains 38%-42% P_2O_5, of which about 90% is soluble in 2% citric acid.

8.4.6. Rhenania Phosphate

It is another thermal phosphate made by calcining a mixture of phosphate rock, sodium carbonate and silica in a kiln at 1250 °C. The product contains 28%-30% P_2O_5, most of which is soluble in neutral or alkaline ammonium citrate solution.

8.4.7. Dicalcium Phosphate

It is a common constituent of nitrophosphates and is also present in ammoniated superphosphates. Straight dicalcium phosphate is produced by dissolving phosphate rock in hydrochloric acid and precipitating dicalcium phosphate by stepwise addition of limestone or slaked lime. The product is recovered by filtration and washing.

8.4.8. Direct Application of Phosphate Rocks

Application of raw ground mineral phosphate rock to soil as a fertilizer is an old practice in most of the countries. But, the contribution of this source to total P consumption is only marginal and it may not exceed 5% of fertilizer phosphate consumption. The efficiency of directly applied phosphate rock varies widely and the agronomic response depends on soil characters (acidic reaction, P-deficiency, Ca status, etc.) to a great extent and on several other factors such as the reactivity of the phosphate rock, crop and climatic conditions, etc.

9. Potash Fertilizers

Potash was first mined commercially in Germany in 1861. Annual production of about 26 million tonnes of K_2O as fertilizer remains steady since 1999-2000; mostly by Canada, Russia, Belarus, Germany, Israel and Jordan. Some of the important K-bearing minerals are: sylvite, langbeinite, kainite and carnallite. Sylvinite, a mixture of sylvite (potassium chloride) and halite (sodium chloride) crystals, is the most extensively mined mineral ore and is easy to process. About 95% of all the potash mined is used as fertilizers, with the remaining 5% going into other industrial applications. Potash reserves on the global scale are enormous and sufficient to meet the requirements for many centuries to come. Canada and Russia have more than half of the world reserve. The other important regions having potash minerals are: the USA, Europe, the Middle East, Thailand and South America.

9.1. Potassium Chloride: Mining and Beneficiation

Potash is largely extracted from underground deposits of sylvinite. Shaft mining is generally practised when the ore body is less than 1300 metres deep from the surface. At greater depths, another method called "solution mining" is adopted. Potash is also recovered in much smaller quantities from brines such as those in Great Sea Lake and the Dead Sea.

Crude potash ore mined by any of the above three methods is normally subjected to 'beneficiation'. This process removes a part of the impurities (usually sodium chloride) present in the sylvinite ore and also upgrades the quality of the finished product. Three principal methods followed by beneficiation of sylvinite are:

Table 4. Sulphur and micronutrient containing fertilizer sources

Fertilizer source	Formula	
A. Sulphur sources		*Sulphur content (%)*
Single superphosphate	$Ca(H_2PO_4) + CaSO_4{\cdot}2H_2O$	12-14
Ammonium sulphate	$(NH_4)_2SO_4$	24
Ammonium phosphate sulphate	$(NH_4)_2SO_4 + NH_4H_2PO_4/(NH_4)_2HPO_4$	13
Potassium sulphate	K_2SO_4	18
Gypsum	$CaSO_4.2H_2O$	16
Pyrites	FeS_2	About 20
B. Micronutrients sources		*Micronutrient content (%)*
Zinc sulphate heptahydrate	$ZnSO_4.7H_2O$	Zn, 21
Zinc sulphate monohydrate	$ZnSO_4.H_2O$	Zn, 33
Manganese sulphate	$MnSO_4.H_2O$	Mn, 30.5
Ferrous sulphate	$FeSO_4.7H_2O$	Fe, 19
Copper sulphate	$CuSO_4.5H_2O$	Cu, 24
Sodium borate (Borax)	$Na_2B_4O_7.10H_2O$	B, 10.5
Ammonium molybdate	$(NH)_6Mo_7O_{24}.2H_2O$	Mo, 52

(i) Froth floatation,
(ii) Heavy media separation, and
(iii) Solution - crystallization.

Among these, froth floatation is widely practised. This is a method of floating-off of the crystals of either potassium chloride or sodium chloride on a froth and subsequent harvest of the froth. After beneficiation, the material is dried and marketed as 'muriate of potash'.

9.2. Production of Potassium Sulphate

Potassium sulphate as an independent mineral does not exist in nature and therefore cannot be directly mined and processed like potassium chloride (sylvite). It is produced by treating potassium chloride with sulphuric acid in a two-stage reaction [Equations (29) and (30)]:

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl \quad \text{(an exo-thermic reaction)} \qquad ...(29)$$

$$KHSO_4 + KCl \rightarrow K_2SO_4 + HCl \quad \text{(an endo-thermic reaction)} \qquad ...(30)$$

Potassium sulphate is also produced by treating potassium chloride with hot sulphur dioxide [Equation (31)]:

$$4\,KCl + 2\,SO_2 + O_2 + 2\,H_2O \rightarrow 2\,K_2SO_4 + 4\,HCl \qquad ...(31)$$

10. Secondary Nutrients

Interest in sulphur nutrition remained marginal till about 1980, due to inadvertent application of sulphur in large quantities in fertilizers like ammonium sulphate, single superphosphate and sulphate of potash, besides insecticides, fungicides and manures. However, now there are increasing number of reports of sulphur deficiencies in soils.

The principal source of S in the fertilizers commonly manufactured in India, is the elemental sulphur which is totally imported. During 2005, India imported about 2 million tonnes of elemental S. The major source of S-containing fertilizers manufactured in India, their chemical formula and S-content are given in Table 4.

The atmosphere is also a source of sulphur which is brought down by snow and rainfall. Atmospheric sulphur is mainly in the form of sulphur dioxide which is produced due to the burning of coal, oil and gas, smelting of sulphide containing ores and different chemical operations. While the amount varies, depending on the industries located in the vicinity of the farm, it has been found that rainfall contributes 3 to 30 kg of sulphur per ha per year.

11. Mixed Fertilizers

Mixed fertilizers are physical mixtures of fertilizer materials, containing two or more major plant nutrients. Mixed fertilizers are made by thoroughly mixing the ingredients, either mechanically or manually. Such mixtures are usually in powder form in India. However, due to several advantages of granulated fertilizer mixtures over physical mixtures described below in another section, granulated mixtures are becoming increasingly popular.

In dealing with mixed fertilizers, it is necessary to understand a few terms which are commonly used in their references. These are: (i) Fertilizer grade, (ii) Fertilizer ratio, (iii) Conditioner, and (iv) Filler.

11.1. Fertilizer Grade

It refers to the guaranteed minimum percentage of nitrogen (N), phosphate (P_2O_5) and potash (K_2O) contained in the mixed fertilizer. Thus, 100 kg of a mixture of a grade 12-6-6 will contain a minimum of 12 kg of nitrogen, 6 kg of phosphate in terms of P_2O_5 and 6 kg of potash in terms of K_2O. The numbers representing the grade are separated by hyphens and are always stated in the order of N, P_2O_5 and K_2O.

11.2. Fertilizer Ratio

This refers to the ratios of the percentages of nitrogen (N), phosphate (P_2O_5) and potash (K_2O) in the fertilizer mixture, e.g. the fertilizer grade 12-6-6 has a fertilizer ratio of 2:1:1.

11.3. Conditioners

These are materials which are added to fertilizer mixtures during their preparation for reducing hygroscopicity and improving their physical condition. Such materials are low-grade organic materials.

A *'filler'* is a weight makeup material added to fertilizer ingredients to produce a mixture of the desired grade. Such materials may be sand, soil, coal powder, filler china clay, etc.

11.4. Types of Fertilizer Mixtures

11.4.1. Open-formula Fertilizer Mixtures

The formula of each fertilizer mixture in terms of kinds and quantities of the ingredients mixed are disclosed by the manufacturers. The formula enables the farmers to know the kind and quality of the nutrients and their suitability for specific soils and crops and consequently, to determine roughly the quantity of sand or other inert material contained in any fertilizer mixture.

11.4.2. Closed-formula Fertilizer Mixtures

The ingredients or straight fertilizers used in such mixtures are not disclosed. So these mixtures have the disadvantage that the farmer cannot know the kind and quality of the nutrients in them.

11.5. Materials Used in Fertilizer Mixtures

Different materials are used for the production of mixed fertilizers. In accordance with their principal function in the mixture, the materials could be grouped into four categories as follows:

11.5.1. Suppliers of Plant Nutrients

These are straight fertilizers added to supply the plant nutrients mentioned in the grade. Nitrogen is supplied in the form of a large number of straight fertilizers, like ammonium sulphate, urea, calcium ammonium nitrate, calcium cyanamide, sodium nitrate, oilcakes and sludge. Phosphoric acid comes mainly from superphosphate and bone meal. Muriate of potash and potassium sulphate are used to supply potassium. Complex fertilizers are also used for the production of fertilizer mixtures.

11.5.2. Conditioners

To prepare mixed fertilizers in good drilling condition and to reduce caking, low-grade organic materials are usually added at the rate of about 100 kilograms per tonne. These materials, known as conditioners, are tobacco stems, peat, groundnut shell and paddy husk.

11.5.3. Neutralizers of Residual Acidity

If the nitrogenous fertilizers are acidic in nature, like ammonium sulphate and urea, a basic material like dolomitic limestone is added to counteract the acidity. Such a material is known as neutralizer of residual acidity.

11.5.4. Filler

A filler is the make-weight material added to a fertilizer mixture. The common filler materials used are: sand, soil, ground coal, ashes, and various other waste products.

11.6. Incompatibilities in Fertilizer Mixtures

The preparation of satisfactory mixed fertilizers requires a comprehensive knowledge of the chemical and physical characteristics of the individual fertilizer materials, their behaviour in mixtures under different conditions of storage, transportation as well as under varying circumstances of atmospheric temperature and humidity. In mixing straight fertilizers, the following points should be kept in view:

(i) Fertilizers containing ammonia (e.g. ammonium sulphate, ammonium nitrate) should not be mixed with basically reactive fertilizers (e.g. lime, basic slag, phosphate rock, calcium cyanamide) as losses of nitrogen may result through escape of gaseous ammonia.

(ii) No water-soluble phosphatic fertilizer (superphosphate, triple superphosphate and ammonium phosphates) should be mixed with those fertilizers that contain free lime, because this converts a portion of the soluble phosphate into an insoluble form.

(iii) Easily soluble and hygroscopic fertilizers (like calcium ammonium nitrate, urea and potash salts) tend to cake or form lumps after mixing. Such fertilizers should be mixed shortly before use.

(iv) Slightly acidic superphosphate may liberate acid from certain fertilizers (e.g. nitrates and chlorides) and this may damage the gunny bags and drilling implements.

11.7. Guide for Mixing Fertilizers

The diagram in Figure 1 shows which fertilizers can be mixed and which cannot be mixed.

11.8. Methods of Preparing Fertilizer Mixtures

Fertilizer mixtures may be prepared either manually by farmers or in factories with the help of special equipments. The former are known as 'farm-mixed' fertilizers, while the latter are termed as 'factory-made' mixtures.

11.8.1. Farm-mixed Fertilizers

Some fertilizer materials can be mixed satisfactorily on the farm without using special equipment. The method is economical. Mixing on the farm should be done on a cement floor. The equipment required would be a spade, a screen, a hammer/mallet to break the lumps and a weighing balance or scale to weigh the exact quantities of different fertilizers and filler. It is desirable to mix the fertilizers on the day of application or a day before, to avoid caking. If the fertilizer mixture cannot be immediately used, a certain amount of filler like sand may be added to check the mixture from caking into hard mass.

11.8.2. Factory-made Mixtures

There are, in general, four different types of fertilizer-mixing plants:

(i) Dry-mix plant in which all straight fertilizers are mixed in dry form.

(ii) Plants in which ammonia is added to phosphatic and potassic fertilizers.

(iii) Plants in which superphosphate is manufactured from phosphate rock and locally purchased sulphuric acid and superphosphate are utilized for the preparation of mixed fertilizers.

(iv) Plants which, manufacture their own requirement of sulphuric acid to prepare superphosphate which is further used in preparing mixed fertilizers.

11.9. Granulated Fertilizer Mixtures

Recently, manufacturing of fertilizer mixtures in granulated form has been started in India by various firms. Granulated fertilizer mixtures are normally of high analysis. Advantages of granulation are:

(i) Every granule is complete plant food containing major nutrients in balanced quantities.

(ii) This ensures easier and uniform absorption by crops, resulting in vigorous and healthy plant growth.

(iii) Granular fertilizers are dry, free flowing and easy to apply. Thus, they can be applied through a seed drill.

(iv) There is no loss due to dusting during transport and handling or due to wind in the fields.

Potassium chloride	Potassium sulphate	Potassium schoenite	Ammonium sulphate	Calcium ammonium nitrate	Urea	Superphosphate, single and triple	Ammonium phosphates	Basic slag	Rockphosphate (powdered)	Calcium carbonate (Lime)	
☐	☐	☐	☐	☒	☒	☐	☐	☐	☐	☐	Potassium chloride
☐	☐	☐	☐	☒	☒	☐	☐	☐	☐	☐	Potassium sulphate
☐	☐	☐	☐	☒	☒	☐	☐	☐	☐	☐	Potassium schoenite
☐	☐	☐	☐	☐	☒	☐	☐	■	☒	■	Ammonium sulphate
☒	☒	☒	☐	☐	☒	☒	☒	■	☐	☐	Calcium ammonium nitrate
☒	☒	☒	☒	☒	☐	☒	☒	☒	☒	☒	Urea
☐	☐	☐	☐	☒	☒	☐	☐	■	■	■	Superphosphate, single and triple
☐	☐	☐	☐	☒	☒	☐	☐	■	■	■	Ammonium phosphates
☐	☐	☐	■	■	☒	■	■	☐	☐	☐	Basic slag
☐	☐	☐	☒	☐	☒	■	■	☐	☐	☐	Rockphosphate (powdered)
☐	☐	☐	■	☐	☒	■	■	☐	☐	☐	Calcium carbonate (Lime)

☐ Fertilisers which can be mixed

☒ Fertilisers which may only be mixed shortly before use.

■ Fertilisers which cannot be mixed (for chemical reasons).

Bonemeal which is often used as "drier" may be mixed with other fertilisers.

Figure 1. Guide for mixing fertilizers

(v) Being high analysis, they are considerably more economical in transport and application costs.

(vi) There is less possibility of adulteration.

11.10. Application of Fertilizer Mixtures

Fertilizer mixtures can be applied to the soil in the same manner as a straight or a complex fertilizer is applied. Some advantages and disadvantages of fertilizer mixtures are given below.

11.10.1. Advantages of Fertilizer Mixtures

(i) Less labour is required to apply a fertilizer mixture than to apply its various components separately.

(ii) If a proper mixture is used to suit a particular soil type and crop, the use of a fertilizer mixture leads to balanced manuring.

(iii) The residual acidity or sodicity of fertilizers can be effectively controlled by the use of a proper quantity of liming material or gypsum in the mixtures.

(iv) Micronutrients, which have to be applied in small amounts to soil can be more evenly applied if they are incorporated in fertilizer mixtures.

(v) Mixtures have a better physical condition and are more easily applied than many straight fertilizers. This advantage is most marked when mixtures are prepared in a granular form.

11.10.2. Disadvantages of Fertilizer Mixtures

(i) Their (indiscriminate) use does not permit application of individual nutrients which may best suit the needs of a crop at a specific time.

(ii) Cost of plant nutrients per kilogram is usually higher in mixtures than in individual fertilizers used in such mixtures.

(iii) Farmers may use mixtures without a careful study of their needs, thus they may apply lesser quantity of some nutrients and more of others, leading to imbalanced manuring of their soils and crops.

12. Characteristics of Fertilizers

The physical and to some extent chemical properties of fertilizers have a strong bearing on their storage, bagging, transportation and distribution. The physical characteristics relevant to transportation and distribution are of two types:

(i) *Physical Form* – Powdery, crystalline, prills, granules, etc., and

(ii) *Intrinsic Physical Properties* – Hygroscopicity, melting point, bulk density, specific gravity, and solubility. The intrinsic properties depend more on the chemical nature of the fertilizers.

12.1. Physical Properties of Fertilizers

Physical properties of fertilizers affect their packaging, storage including warehousing, transportation and application at the farm level.

12.1.1. Hygroscopicity

Hygroscopicity or moisture absorption is an important property because of its effect on caking and drillability of a fertilizer material. All soluble substances, to which most fertilizers belong, have the property of absorbing moisture from the air when the humidity reaches a value that is characteristic of each substance. One measure of hygroscopicity is the critical relative humidity (CRH). When the relative humidity of the atmosphere is higher than the CRH of a fertilizer, the fertilizer absorbs moisture from the atmosphere. Hence, it is desirable that the CRH of a fertilizer should be high. The critical relative humidity of different fertilizers is given in Table 5.

12.1.2. Free Moisture Content

High moisture content in a fertilizer primarily reduces the concentration of plant nutrient and increases its tendency to cake or set. A high moisture content in conjunction with a low critical humidity may induce caking or a sticky condition of the fertilizer.

12.1.3. Particle Size

Apart from the fact that the particle size of a fertilizer affects the release of plant nutrients, it is known that fine particles, almost irrespective of their constitution, have a tendency to cohere and cake under pressure that occur in bulk bag storage pile.

12.1.4. Melting Point

The melting point of fertilizer materials is of interest when the products are dried during manufacture, since it limits the maximum temperature in the drier. The melting point also indicates the possible adaptability of the product to drilling or other melt granule processes. Low melting soluble materials are highly hy-

Table 5. Relative humidity of air in equilibrium with saturated solutions of fertilizer materials

S.No.	Fertilizer material	Critical relative humidity at 30 °C
1.	Ammonium sulphate	79.2
2.	Ammonium chloride	77.2
3.	Urea	75.2
4.	Triple superphosphate	93.6
5	Muriate of potash	84.0
6.	Diammonium phosphate	82.5
7.	Urea-ammonium phosphate (29:29:0)	50.5
8.	Nitrophosphate	55.6

Table 6. Melting point and specific gravity/bulk density of important fertilizers

S. No.	Fertilizer material	Melting point (°C)	Specific gravity
1.	Ammonium sulphate	512	1.50
2.	Urea	132	1.30
3.	Ammonium chloride	Decomposes at 350	1.70
4.	Muriate of potash	772	1.98
5.	Diammonium phosphate	Decomposes at very low temp.	1.60
6.	Nitrophosphate (20:20:0)	152	

Table 7. Solubility of important fertilizers in water at 20° C

S. No.	Fertilizer material	Solubility (% by wt in water)
1.	Ammonium sulphate	42.8
2.	Urea	52.0
3.	Ammonium chloride	27.1
4.	Muriate of potash	16.1
5.	Diammonium phosphate	40.8

groscopic (Table 6).

12.1.5. Solubility

The solubility of a fertilizer is one of its most important properties. This property, besides being indicative of the solubility of the compounds in soil water, influences the storage and handling properties, particularly hygroscopicity and the granulation of the salts and their mixtures (Table 7).

12.2. Characteristics of Individual Fertilizers

In this section some of the important properties of common fertilizers are described.

12. 2.1. Straight Fertilizers

(a) Nitrogenous Fertilizers

Urea – It is available in free flowing round white prills. Being highly hygroscopic, it requires special packing. It contains 46% total nitrogen, the whole of which is in amide form. It should be applied to soil under moderately wet condition and thoroughly mixed with soil. It leaves slightly acidic reaction in soil. It can be applied to soil at sowing or used as a solution for top-dressing. Its contact with seed should be avoided when applied at sowing to reduce the adverse effects on germination.

Calcium Ammonium Nitrate — It is a mixture of ammonium nitrate and powdered chalk and is made into free flowing grey or light brown granules coated with soapstone. It is highly hygroscopic in nature and contains 25% nitrogen; half in ammoniacal and the other half in nitrate form. It is a neutral and quick acting fertilizer and is especially useful for top-dressing.

It can be mixed with phosphate and potassic fertilizers but these mixtures should be used immediately. As the mixtures absorb moisture and form lumps on storage, they should be packed in moisture-proof bags.

Ammonium Sulphate — It is a white, grey, brown, red or yellow colour crystalline salt. It is non-hygroscopic and has excellent physical properties. It is readily soluble in water and contains 20.6% nitrogen, all in ammoniacal form. It can be applied at the time of sowing or used for top-dressing. It should not be mixed with seed as germination of seed may be affected. As it is retained by soil colloids and not lost by leaching, it is an excellent fertilizer for rice. It has an acidic residual effect on the soil. Because of excellent physical properties, it is suitable for use in dry mixtures with phosphatic and potassic fertilizers. However, it should not be mixed with fertilizers containing lime, as this would result in volatilization loss of ammonia . Since it contains 24% sulphur, it can be used as a source of sulphur too.

Ammonium Chloride — It is a white crystalline salt which contains a minimum of 25% nitrogen, all in the water soluble form. It has excellent properties and an acidic residual effect. In respect of its agronomic suitability, it is at par with other nitrogenous fertilizers. It is not recommended for potato, as its chloride content might affect keeping quality of potato. It can be conveniently mixed with phosphatic and potassic fertilizers.

(b) Phosphatic Ferilizers

Single Superphosphate — It is a grey or brownish powder or granular material containing monocalcium phosphate and gypsum. It contains some free acid which causes rotting of bags. It is slightly hygroscopic and forms lumps during storage. It contains 16% water-soluble P_2O_5. When applied to neutral and alkaline soils, it gets converted into dicalcium phosphate which is less but still available to plants. Reversion and fixation can be reduced by applying it in bands 2-3 cm away from the seed rows at a depth of 4 to 8 cm. It should be applied before or at seeding or transplanting stage. Since it contains 12% S too, its application to oilseed crops and wheat grown in sulphur-deficient soils is particularly beneficial. It can be freely mixed with other fertilizers, except those like CAN which contain free lime, as their mixture cannot be stored for a long time.

Triple Superphosphate — It is a concentrated form of superphosphate and is available in greyish colour granules. It is slightly hygroscopic and contains 46% P_2O_5, out of which 42.5% is in water-soluble form. It is used in the same way as single superphosphate and is especially useful in the preparation of high analysis fertilizer mixtures.

(c) Potassic Fertilizers

Muriate of Potash (Potassium Chloride) — It is a crystalline white to red material and contains 60% K_2O, all in water-soluble form. On application to the soil, the potassium ions are retained by soil colloids and thus not lost through leaching. It is neutral in reaction. It can be applied at the time of or prior to or after sowing. On heavy soils, placement of this fertilizer in bands is better, as in the case of phosphatic fertilizers. It can be applied to all soils and crops; however for potato, potassium sulphate may be preferred. It can be safely dry mixed with all fertilizers, yet its mixtures with urea should not be stored for a long time.

Potassium Sulphate — It is a white crystalline salt and contains 50% potassium as K_2O. It is least hygroscopic and readily soluble in water and neutral in reaction. It can be applied to all soils and all crops at or prior to sowing. It possesses good physical properties and can be safely used in the preparation of mixed fertilizers.

12.2.2. Complex Fertilizers

Diammonium Phosphate — It is a whitish-grey granular material, non-hygroscopic and possesses excellent physical properties. It contains 18% nitrogen (all in ammoniacal form), 46% total P_2O_5 and 42.5% water-soluble P_2O_5. It is an acidic fertilizer. It is easy to drill at sowing. However, mixing it with seed should be avoided.

12.2.3. Secondary and Micronutrient Fertilizers

Gypsum — It is a white powdery material. Agricultural grade gypsum with 70-80% purity contains about 16% S. Its solubility is 0.25%. Since S is present as sulphate (SO_4^{2-}) in this material, it is readily available to plants. In sulphur-deficient soils, it is applied before sowing the crop by uniform broadcast, followed by mixing in the soil. If the deficiency symptoms appear in a standing crop, it can be top-dressed also, followed by mixing in the soil and irrigation.

Zinc Sulphate (Heptahydrate) — It is a white, light greyish and sometimes brownish and light green crystalline material, containing 21% Zn (zinc sulphate monohydrate contains 30.5% Zn). Among all the zinc fertilizers, it is the most efficient and economical one. Though it can be applied both to soil and crop foliage, application to soil is easy and economical. Foliar application can be a good practice to correct Zn-deficiency in a standing crop. The soil applied zinc is known to meet the requirement of the following 2-3 crops.

Ferrous Sulphate — It is a light greenish crystalline material, contains 19% iron in ferrous form and is easily soluble in water. When applied to soil, it is rapidly converted into unavailable form (mostly ferric) and plants cannot use it. Because of this characteristic its foliar application is recommended for correcting iron-deficiency.

Manganese Sulphate — It is a white material with a pinkish tinge. It contains 30.5% Mn and is easily soluble in water. Though it can be applied both to soil and crop, its foliar application should be preferred as that is more economical than soil application.

13. Manures

Manures are organic materials containing plant nutrients relatively in small concentrations. These are derived from plant, animal and human residues. Thus, manures may be called low analysis organic fertilizers. Organic manures usage is an ancient practice in India and remained as the main source of replenishing soil fertility until 1950s when chemical fertilizers began to gain popularity on account of these being less bulky (high analysis), cheaper to transport, handle and store and amenable to precise application. Thus, the use of organic manures progressively declined in Indian agriculture. But, in many regions where fertilizer consumption is still low, manures are the main source of replenishing soil fertility.

Organic manures are presently used regularly for growing high-value crops, like potato, sugarcane, vegetables, fruits, medicinal and aromatic plants, plantation and other crops. In recent years, however, a renewed emphasis on use of organic manures as an important component of integrated use of fertilizers is evident in order to sustain high yields and higher efficiencies, while maintaining optimal physical, chemical and biological properties of soils.

14. Classification of Manures

Manures may be broadly classified as: (i) bulky organic manures, e.g. farmyard manure (FYM), compost, green manure and crop residues; and (ii) concentrated organic manures. Concentrated organic manures may be either of plant origin, namely different types of oilcakes or of animal origin like bonemeal, bloodmeal, meatmeal, hoofmeal, fishmeal, etc.

Bulky organic manures are those that are voluminous in nature and supply all the major plant nutrients, though in small concentrations. They are, however, rich in organic matter. Thus, in addition to supplying all the nutrients in limited quantities to plants, these contribute to the much-needed organic carbon to the soil. Farmyard manure, farm compost, urban compost, vermicompost, green manure, sewage sludge and other bulky sources of organic matter comprise this class of manures. Out of these, farmyard manure, compost and green manure are by far the most important and widely used ones in agriculture. Crop residues also make a significant contribution to organic matter content of soil and fall under bulky organic manures category. In contrast, concentrated organic manures contain relatively higher proportion of one or more of the major plant nutrients, namely, N, P and K than bulky organic manures.

15. Farmyard Manure

Farmyard manure (FYM) is a traditional organic manure and its nutrient value in increasing crop production is recognized from time immemorial. It is the most commonly used organic manure by farmers in India. FYM can be prepared by using three components, namely (i) solid excreta or dung of animals, (ii) liquid excreta or urine of animals, and (iii) litter used as bedding material in animal shed. In India, usually most of the urine is wasted in animal shed as it is not collected systematically. Litter on the other hand, is rarely used as bedding material, as it is generally fed as fodder. So, FYM as prepared in the country mainly consists of cattle dung together with the waste from the fodder fed to animals. Further, about 50% of the cattle dung produced in the country is burnt as fuel in rural homes and is thus lost. Moreover, the traditional method of preparation and storage of FYM is generally faulty.

For the preparation of FYM, sufficient quantity of dry litter is spread under the animal in the evening for absorption of urine. Next morning, the materials consisting of dung and urine soaked in litter are collected and placed in trenches or pits or heaps. Ideally, the size of the trench should be 6 m × 2 m ×1 m. Two such trenches are sufficient for preparation of FYM for one year having 3-4 cattle head, which give 5-6 tonnes of manure per year per head of cattle. Addition of substrate should be in sections of 1 m length. When one section is filled up to a height of about 0.5 m above the ground level the top of the trench/pit/heap is made into dome-shape and plastered with a slurry made up of cowdung and little amount of soil. After 4 to 6 months, well-decomposed material becomes ready for use.

The composition of FYM varies according to the composition and proportion of the substances used in its preparation. Dung is a major component of FYM, which consists mainly of that portion of the food that has not been digested or only partially digested by animals. It also contains dead or living bacterial cells, which constitute nearly 50% of N in the dung.

15.1. Factors Affecting Quality of FYM

Following factors influence the quality and general characteristics of FYM:

(i) *Source of Excreta:* The average percentage of N, P_2O_5 and K_2O in the fresh excreta of different animals is given in Table 8. It shows that sheep and poultry excreta are richer than those of cow, horse and pig. Urine of all the animals contains more N and K_2O than dung. Urine of cow, bullock and horse contains practically nil or trace amount of P_2O_5.

(ii) *Food of Animal:* The quality of manure is also linked to the kind of feed given to cattle. Concentrated feeds like oilcakes, wheat bran, grain husk, gram, horse gram, etc. are rich in N, P, K, Mg and S. In contrast, manure from cattle fed on cereal straws and grass hay, is much less valuable than that from animals fed on legume hays, grains and concentrates. About 60-90% of N and P_2O_5, 90-99% of K_2O and 50% of organic matter in the food consumed by animals are excreted through dung. So, richer the food fed to animals, richer will be the composition of FYM prepared out of excreta of such animals.

(iii) *Age and Condition of Animal:* Young and healthy animals consume more nutrients from the fodder fed to them than mature and sick animals. Therefore, FYM prepared from the dung of latter is richer than the former.

(iv) *Function of Animal:* Animals producing milk and wool consume more nutrients from their feed than animals at rest or working. Therefore, FYM prepared from the dung of latter is richer than of former. It is generally noticed that in the case of adult working-cattle about 80% of N and other mineral elements contained in the feed, are recovered in urine and dung.

(v) *Manner of Storage/ Condition of Cattle Shed:* If the cattle shed is having mud (uncemented) flooring, most of the N in urine is lost due to leaching and if any drainage is there, substantial amount of potassium is lost. Under such conditions, FYM produced is nutritionally poor.

(vi) *Nature of Litter:* The composition of FYM varies considerably depending on the type of substrates used as litter. In general, the nature of litter used as bedding material should have high absorptive capacity so that it can absorb large amount of urine. If good quality litter is used, naturally the FYM would be better.

On an average, well-decomposed FYM contains 0.5% N, 0.2% P_2O_5 and 0.5% K_2O. Based on this analysis, an average dressing of 25 tonnes of FYM per ha gives 125 kg N, 50 kg P_2O_5 and 125 kg K_2O, respectively. When FYM is applied to soil about 30% of N, 60-70% of P_2O_5 and 75% of K_2O are available for the first crop and the remaining nutrients to the subsequent crops, depending upon the transformation of each nutrient element in the soil matrix.

15.2 Loss of Nutrients during Collection, Preparation and Storage

Loss of nutrients takes place due to inadequate collection of animal excreta and litter and improper preparation of manure and sub-

Table 8. Average percentage of N, P_2O_5 and K_2O in the fresh excreta of different animals

Source of animal	Dung			Urine		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O
Cow and bullock	0.40	0.20	0.10	1.00	Trace	1.35
Sheep and goat	0.75	0.50	0.45	1.35	0.05	2.10
Horse	0.55	0.30	0.40	1.35	Trace	1.25
Pig	0.55	0.50	0.40	0.40	0.10	0.45
Poultry	1.46	1.17	0.62			

Source: Yawalkar (1996)

sequent storage. Significant amount of N from urea is lost as NH_3 gas and escapes into atmosphere. The smell of NH_3 in cattle shed is a clear sign of loss of N from the urea present in urine. The following reactions are involved:

$$NH_2CONH_2 + H_2O \rightarrow NH_4COONH_2 \quad \ldots(32)$$

$$NH_4COONH_2 + H_2O \rightarrow (NH_4)_2CO_3 \quad \ldots(33)$$

$$(NH_4)_2CO_3 \rightarrow 2NH_3(\uparrow) + CO_2(\uparrow) + H_2O \quad \ldots(34)$$

The most serious loss of dung is through cakes used as fuel in rural homes. Secondly, it is practically not possible to collect the dung dropped in the field during grazing. Approximately two-thirds of the dung is either utilized for the preparation of cakes or lost during grazing.

Nutrients are also lost in the following ways during storage:

(i) *Leaching:* If the manure gets exposed to rain water, extensive loss of water-soluble constituents occurs through leaching. It is observed that about 50% of N and P_2O_5 and 90% of K_2O of FYM are water-soluble, and are susceptible to leaching by rain water. The actual losses of nutrients by leaching will however, depend on the surface exposed, intensity of rainfall and slope of land on which the manure is heaped.

(ii) *Volatilization:* Considerable amount of NH_3 gas is produced during storage in the manure heap from the decomposition of urea and other nitrogenous compounds present in the urine and dung. The loss of NH_3 as gas into the atmosphere increases with (a) increase in ammonia vapour pressure; (b) increase in temperature; and (c) air movement. More than 50% of the nutrient value of FYM is lost due to leaching and volatilization when the manure is exposed to the weather during storage.

15.3. Improved Methods of Handling FYM

It is practically impossible to check completely the losses of nutrients during handling and storage of FYM. However, by following improved methods, such losses can be minimized:

15.3.1. Preparation of FYM by Trench Method

The manure is prepared in trenches or pits of suitable sizes. The size of trench or pit may be 1 m in depth, 1.3-1.5 m in width and 4.5-6 m in length, depending upon the number of cattle on a farm. All the available crop residues/ farm and house refuse are heaped near the cattle shed and a suitable portion of litter mixed with earth, if available, is spread under the feet of the cattle in the shed in the evening, approximately, 2.0-2.5 kg material per animal for the absorption of urine. The urine-soaked litter and dung are well mixed and accumulated into the trench next morning. The filling of the trench or pit should be done section-wise and when each section of about 1.0 m in length is filled to about 0.5 m above the ground level, the top of the heap is made dome-shaped and plastered with 2.5 cm layer of a mixture of mud and dung in equal proportion. Before plastering, sufficient amount of water is to be added to the manure pit for decomposition of organic matter. Plastering conserves moisture and nitrogen and also prevents housefly nuisance. If the heaps lie exposed to the sun for a long period, the raw organic matter dries up quickly and proper decomposition is affected. When the trench is completely filled up, say in about three months time, a second trench is taken up for filling in a similar way. If urine is not conserved in the bedding used for cattle it must be collected in covered masonry drain and then added to the dung in the manure pit. The manure becomes ready for use in about 4 to 5 months after plastering. The nutrient content of FYM prepared by this method is about 0.7 to 0.8% N on fresh weight basis or 1.4 to 1.6% N on dry weight basis.

15.3.2. Biogas-compost Plant

In India more than 50% of the cowdung is made into cowdung cakes and burnt as fuel for cooking by the rural households. Therefore, use of biogas plant or *gobar* gas-compost plant to produce a combustible gas called methane (CH_4) is an improved method of handling dung. In this method, different gases are generated of which CH_4 is the major component, due to anaerobic fermentation of most of the common organic materials such as cattle dung, horse and pig manure, grasses, vegetable wastes and human excreta. An approximate composition of biogas by volume is: 50-60% CH_4; 5-10% H_2; 30-45% CO_2; 1-2% N_2 and traces of H_2S and O_2. Besides the generation of biogas, which is used for cooking and lighting purposes, huge quantity of biogas slurry is also produced during the process. Biogas slurry is a very good source of plant nutrients and can be used after drying the slurry. It is richer in plant nutrients compared to FYM and compost having 1.6-1.8% N, 1.0-1.2% P_2O_5 and 1.2-1.8% K_2O. The main disadvantage is its excessive water content. Thus, it should be dried before use, which becomes difficult during rainy season. Biogas plant provides both fuel (biogas) and manure (slurry). One tonne of biogas slurry provides about 44 kg of nutrients as compared to about 19 kg by FYM and 27 kg by compost.

15.3.3. Use of Chemical Preservatives

In order to minimize the losses of N from FYM, a number of chemical preservatives have been suggested, which when added to fresh dung/urine would either combine with the ammonia and prevent its volatilization or by reducing the bacterial action, formation of NH_3 is curtailed. The preservatives are applied in the cattle shed for getting better results. It will permit direct contact of preservative with the liquid portion of excreta or urine, thereby decrease the loss of N from urine. The commonly used chemicals as preservatives are: (i) gypsum and (ii) superphosphate.

(i) Gypsum: Gypsum ($CaSO_4 . 2H_2O$) has been found effective as an ammonia-absorbing agent. When gypsum is added, it reacts with the unstable ammonium carbonate, appearing as an intermediate product of decomposition of urea present in urine, leading to the formation of stable ammonium sulphate as per the reaction:

$$(NH_4)_2CO_3 + CaSO_4.2H_2O \longrightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O \quad ...(35)$$

As long as the manure is moist, no loss of NH_3 will occur, but if the manure becomes dry, the above chemical reaction is reversed and loss of NH_3 may occur. The drawback to the use of gypsum lies in the fact that it is required in large quantities, as gypsum is a sparingly soluble salt, the actual quantity of gypsum required for an efficient fixation of ammonia is much higher than that of theoretically calculated quantity.

(ii) Single Superphosphate: Since single superphosphate (SSP) contains up to 50-60% gypsum ($CaSO_4$) besides the highly acidic monocalcium phosphate (MCP) [$Ca(H_2PO_4)_2$], it can be effectively used as a chemical preservative of manure. Superphosphate, besides absorbing ammonia, supplies additional amount of phosphorus and, thus, improves the quality of manure. Its mode of action is similar to that of gypsum in reducing the loss of N as NH_3 volatilization. About 450 to 900 g of SSP per day per animal can be spread in the cattle shed, preferably in places where animals pass urine for better effectiveness.

16. Compost

Composting is advocated for recycling of different types of biodegradable organic matter by converting them into a valuable manure.

Composting is largely a biological process in which aerobic and anaerobic microorganisms decompose organic matter and narrow down the C/N ratio of substrate used. The final product formed after composting is an amorphous, brown to dark brown humified material known as compost. It is a more stable, well-rotten material containing high organic matter and relatively higher proportion of major nutrients compared to FYM. Composting also takes care of killing most of the pathogens present in the substrates. Basically, compost and FYM are the same, except the type of substrate. In FYM, the substrates are dung, urine and litter, whereas in compost, the substrates are plant residues of different types.

Among the various options of waste recycling, composting is widely followed for handling diverse waste organic materials. Compost can be produced from waste materials of various kinds, such as cereal straws, crop stubbles, cotton stalks, groundnut husk, farm weed and grasses, leaves, leaf-mould, biodegradable segment of household, factories and food processing plants refuse, wood ash, litter, urine-soaked earth from cattle-sheds and other similar substances. These raw materials are rich in cellulose and other readily decomposable carbohydrates and have a C/N ratio of 40 or more to 1. The direct application of such undecomposed, low-nitrogen organic matter as manure brings about a temporary deficiency of mineral nutrients (especially nitrogen) in soil by stimulating the growth of microorganisms, which in turn, compete with crop plants for available N, P and other elements. Hence, before using them as manure, it is necessary to convert them into compost or partially decompose them. This process narrows the C/N ratio to about 15:1 and thus, the required quality of manure is attained. Further, the quality of compost produced depends upon the composition of organic wastes and the process involved in its bio-conversion.

16.1. Classification of Composting

Composting can be classified on the following four general ways:

(a) Based on Substrates Used: Composts commonly prepared in India are categorized as rural compost and urban compost.

(i) *Rural Compost or Compost from Farm Litter:* This utilizes different types of organic substrates generated in the farm such as cereal straws, crop stubble, cotton stalks, groundnut husk, farm weed and grasses, leaves, wood ashes, litter, urine-soaked earth from cattle-sheds and other similar substances.

(ii) *Urban Compost or Compost from Town-Refuse*: The major components of urban compost are night soil, wastes from fruit and vegetable market *(Mandi)*, business centres, offices, street and household refuse and other wastes.

(b) Based on Oxygen Usage: Based on oxygen usage during decomposition, two methods of composting are usually recognized, viz. aerobic and anaerobic.

(i) Aerobic composting takes place in the presence of air or oxygen, as in the Indore method. Aerobic composting is generally characterized by high temperature, optimum moisture, presence of aerobic microorganisms, absence of foul odour and is more rapid than anaerobic composting.

(ii) Anaerobic composting takes place in the absence of air or oxygen, as in Bangalore method. It is characterized by low temperature, production of foul odour because of production of many intermediate products and generally proceeds at a slower rate than does aerobic composting. The main advantage of anaerobic composting is that the process can be carried on with due care and as such can be sealed from the environment. The methane released can be used for energy generation.

(c) Based on Temperature: Based on temperature, it may be classified as mesophilic and thermophilic.

(i) Mesophilic composting requires moderate temperature, ranging from 15 to 50 °C, which is the ambient temperature.

(ii) Thermophilic composting on the other hand is carried out at 45 to 65 °C.

In practice, most processes include the above two ranges of temperature.

(d) Based on Technological Approach: It may be open or windrow and mechanical composting.

(i) *Open or Windrow Composting:* Compost systems falling under this category are those in which the entire process is carried out in open. The material is usually stacked in elongated windrow.

(ii) *Mechanical Composting:* It is carried out in an enclosed unit known as digester during the initial part of composting, and involves windrowing towards the end of the process.

16.2. Factors Affecting Rate of Composting

The rate of composting process is affected by the following environmental factors: (i) moisture content, (ii) temperature, (iii) pH, (iv) C/N ratio, (v) aeration or oxygen supply, and (vi) inoculants.

(i) Moisture Content: Moisture content in the composting pit plays a very important role in the decomposition of organic matter. Water is required for microbiological activities as well as for many reactions that occur during decomposition. Large quantity of heat is generated during decomposition and unless sufficient water is present in the pile, it will tend to dry out and decomposition rate will drop to almost zero. For fibrous materials like straw, dry grasses and leaves, the moisture content should be around 75 to 85%, while for green vegetation like vegetable wastes and wet garbage, it should be maintained at 50 to 60%.

(ii) Temperature: The range of optimum temperature for the composting process is broad, i.e. from 35 to 50 °C, to facilitate many groups of microorganisms (mesophillic and thermophillic) that take part in the decomposition process. High temperature, up to 70 °C is essential for the destruction of pathogenic organisms and weed seeds. Decomposition rate is faster in the thermophillic stage, but this temperature should not be kept for a longer period, while temperature below 20 °C lowers down the rate of decomposition. Further, the rise of temperature is governed by the C:N ratio, moisture content, aeration, microbial activity and size of the heap/trench. However, leaving the closely controlled digester, a uniform temperature does not prevail throughout the mass of composting material at any particular time, except at the start of the process when all materials are at ambient temperature.

(iii) pH: An optimum pH range for most bacteria is between 6 and 7.5; and for fungi between 5.5 to 8.0. The pH drops from about 6.5 to 5.5 in the early stage of mesophillic digestion and then rises rapidly during the thermophillic stage to slightly more than 8.0 and falls to 7.5 during cooling and maturing stage.

(iv) C/N Ratio: Nitrogen is required for the microorganisms, which decompose organic matter for their growth and activities. Microorganisms use C as an energy source and N for cell building. Thus, during decomposition, a substantial amount of C is lost as CO_2 and the C/N ratio changes from the original level of 70:1 to 20:1. This continues till the C is decreased to the minimum and activities of microorganisms cease. The final C/N ratio usually lies between 15:1 and 20:1. The initial C/N ratio of the substrate is the deciding factor in the speed at which decomposition takes place. The ideal initial C/N ratio ranges from 30:1 to 35:1. Thus, addition of nitrogen source such as legume residues, aquatic weeds (water hyacinth), slaughter-house waste, green leaves, etc. can enhance microbial activity and thereby hasten the decomposition process.

(v) Aeration: Aeration of the composting pit is necessary to (i) provide oxygen to support aerobic microorganisms; (ii) carry away heat generated in the pit by biological action; and (iii) remove excess moisture from the pit. The supply of oxygen is usually provided by natural aeration through the porous mass of biodegradable materials, particularly during the initial period of composting. Periodic turning of composting mass assists in aeration and tends to enhance thermophillic activity and maintain a uniform moisture content and temperature.

(vi) Inoculants: Addition of inoculants like cellulolytic and lignolytic microorganisms enhances the process of composting and decomposition, particularly of the material rich in cellulose and lignin. Addition of fresh cowdung slurry has been found to accelerate the composting process, as it acts as natural inoculant.

16.3. Common Composting Methods

Two important composting methods usually followed in India are: (i) Indore method, and (ii) Bangalore method.

16.3.1. Indore Method

This method is known as 'heap' or 'aerobic' method of composting. The method was first developed at the Institute of Plant Industry, Indore (Albert Howard and Y.D. Wad between 1924 and 1931). Animal dung is used as the catalytic agent along with different types of organic wastes available in the farm. A trench or pit of suitable size say, 3 m × 1.5 m × 1 m is prepared. The site selected for the compost pit should be near the cattle shed and water source and at an elevated site so that rain water does not flood into the composting pit during rainy season. Organic wastes of different sources are accumulated near the trench and mixed thoroughly and a layer of about 30-cm thick is spread at the base of the trench and slurry of cowdung and water is sprinkled onto the refuse. A second layer (30 cm thick) of wastes is then spread followed by a layer of slurry of cowdung and water. The layering is continued till the heap is raised to a height of 50 cm above the ground level. The top is then covered with a thin layer of soil. The filling is completed within 6 to 7 days to fill three-fourths length of the trench, leaving one-fourth length empty to facilitate subsequent turnings. Water is added so as to raise the moisture content to about 60 to 80%. Turning is done three times, approximately at 15, 30 and 60 days of composting in order to facilitate aeration. At each turning, the whole mass is mixed thoroughly. The main advantage of this method is that the matured compost is ready within 4 to 5 months. However, as it requires extra labour for 2-3 turnings, the cost of preparation of compost is more. During rainy seasons or in regions with heavy rainfall, the compost may be prepared in heaps above the ground level. When sufficient nitrogenous material is not available, a green manure or leguminous crop like sunnhemp is grown on the fermenting heap after the first turning. The green matter is then turned in at the second mixing.

16.3.2. Bangalore Method

This is an anaerobic process, and was developed at the Indian Institute of Science, Bangalore (C.N. Acharya, 1939). The mixed farm residues are spread at the bottom of a trench or pit of a convenient size, similar to that of Indore method. The pit is filled layer-wise till the raw material reaches about 50 cm above the surface, and then plastered with a 2-5 cm layer of a mixture of mud and cowdung. Under such conditions, decomposition is largely anaerobic and high temperatures do not develop. Organic nitrogenous compounds gradually become soluble and the carbonaceous matter is broken down into CO_2 and H_2O. The loss of ammonia is negligible because in high concentrations of CO_2, ammonium carbonate is stable. The material undergoes anaerobic decomposition at a very slow rate and it takes about 6 to 8 months to obtain the finished product. Plastering of pit also prevents the fly nuisance. This method effectively controls foul smell and kills pathogenic organisms. The anaerobic process is particularly suited for use by gardeners in or near cities and towns. The well-decomposed compost contains 0.8-1.0% N. The recovery of the finished product is greater in this process than in aerobic composting. Labour requirements are less than those for the Indore method, as turning of material is not done; labour is needed only for digging and filling the pits.

16.4. Municipal Solid Waste Composting

Municipal solid waste (MSW) or Urban solid waste (USW) composting or mechanical composting is followed in big cities, particularly where huge quantities of garbage rich in organic matter are generated. The metropolitan cities like Mumbai, Kolkata, Delhi, Chennai generate about 2000 to 6000 tonnes garbage per day, posing considerable disposal problems.

Mechanical composting plant with capacities of 500-1000 t/day of city garbage or MSW could be conveniently installed in big cities and 250 t/day plants in the small towns in India. The adoption of accelerated fermentation treatment enables 70% of the refuge to be available as refined compost in the form of a dry, black, free-flowing material, easy to transport and handle. Such refined mechanical compost contains generally about 40% mineral matter and 40% organic matter with organic C about 15%. The composition of the compost would vary depending on the raw materials used. On an average, it may contain 0.7% N, 0.5% P_2O_5 and 0.4% K_2O and the C/N ratio of 15-17.

The mechanical composting using municipal solid waste has several advantages such as (i) environmental sanitation to minimize pollution; (ii) recycling of discarded wastes into a value-added product; and (iii) production of composts within a short period.

16.5. Characteristics of Compost

The composition of compost depends on the type of substrates as well as method of composting. On an average, based on dry weight basis, a well-decomposed compost should conform to the specification of Fertiliser (Control) Amendment Order 2006 (Table 9).

Table 9. Composition of well decomposed compost (% dry weight basis)

Characteristic	Value
Moisture (% by weight)	15.0-25.0
Colour	Dark brown to black
Odour	Absence of foul odour
Particle size	Min. 90% material should pass through 4.0 mm IS sieve
Bulk density (g/Mg^3)	0.7-0.9
pH	6.5-7.5
EC (dS/m)	≤ 4.0
Total organic C (% by weight, min)	≥ 16.0
Total N (% by weight, min)	≥ 0.50
Total P_2O_5 (% by weight, min)	≥ 0.50
Total K_2O (% by weight, min)	≥ 1.00
C:N ratio	≤ 20:1
Pathogens	Nil
Heavy metal content	
Zn (mg/kg)	≤ 1000
Cu (mg/kg)	≤ 300
Cd (mg/kg)	≤ 5
Pb (mg/kg)	≤ 100
Ni (mg/kg)	≤ 50
Cr (mg/kg)	≤ 50

17. Enriched Compost

In general, the bulky organic manures like FYM and compost contain, on an average, 0.5-1.0% N, 0.2-0.5% P_2O_5 and 0.5-1.0% K_2O. Thus, if 120 kg of N is to be supplied through these organic manures, one has to add 20 to 25 t of compost per ha, which is not feasible as only limited quantity of organic matter is available in our country. Moreover, the cost of preparation, storage, transport and application of FYM or compost to soils is high. The demerits of these bulky manures can be overcome to a certain extent through preparation of enriched compost by adding nitrogen, phosphorus, potassium and micronutrients either alone or in combination.

17.1. Advantages of Enriched Compost

Enriched composts have the following advantages:

- Enriched compost is a more concentrated manure compared to compost or FYM, thereby it reduces the bulk to be handled per unit of nutrient.
- It may increase fertilizer nutrient use efficiency and maintain soil organic matter.
- It prevents the nutrient losses due to immobilization by microorganisms during decomposition of organic residues and due to adsorption of cations on account of high exchange capacity of organic matter.
- Lesser problems in handling, storage and transportation.
- Offers a potential avenue for the efficient utilization of low-grade materials such as rock phosphate and waste mica (a K-bearing mineral).

Enrichment of compost can be done in two ways, namely (i) addition of fertilizer materials during composting, and (ii) addition of fertilizer materials with ready compost or FYM by physical mixing. Incorporation of fertilizers during composting leads to immobilization of fertilizers into microbial cells and insertion into molecules of humic substances formed during decomposition. A substantial part of added inorganic nutrients may also be adsorbed onto exchange sites or chelated by humic substances. On the other hand, physical mixing of fertilizers with finished product of FYM or compost provides for only adsorption and chelation of fertilizer elements by humic substances, which are already present in the decomposed product.

17.2. Enrichment with Nitrogen

17.2.1. Enrichment during Composting

During the preparation of compost from wide C/N ratio substrates, such as straws, incorporating fertilizer N like ammonium sulphate or urea @ 0.7 to 0.8% of raw materials hastens the decomposition by serving as starter. The wide C/N ratio plant materials require addition of mineral N to narrow down the C/N ratio. The Adco process of preparation of N-enriched compost developed by Hutchinson and Richards (1921) is based on this principle. Enrichment of N during composting with inorganic N can be done up to 1.8-2.5%, but cannot be improved beyond 2.5% N, because of the associated losses of N with higher level of N-addition. Composting with an initially high level of N includes the production of free NH_3 because all N cannot be converted into microbial cells or incorporated into humic substances.

17.2.2. Enrichment with Ready Compost or FYM

It is recommended that compost or FYM with a C/N ratio of about 20:1 should be treated with ammonium sulphate or urea so as to bring the C/N ratio to <10:1 and N-content >2.5%. Thus, by spraying a solution of $(NH_4)_2SO_4$ or urea on finished product of compost or FYM followed by physical mixing, the N-content can be increased up to 5 to 7%. As most of the added inorganic N remains in the fertilizer form without much of chemical or biological reaction with the manure it is difficult to justify the utility of using fertilizers to raise N-content of the finished product above 5 to 7%.

17.3. Enrichment with Phosphorous

17.3.1. Enrichment during Composting

Phosphorus-enriched compost can be prepared by adding superphosphate (SP), dicalcium phosphate (DCP) and rock phosphate (RP) during composting. Enrichment with soluble phosphate is expected to remain as such, though a small amount of immobilization of soluble P into microbial P may be expected. But, with most plant material containing sufficient P to satisfy microbial demands during decomposition, assimilation of P from external sources is seldom needed. On the other hand, addition of insoluble sources of P like low-grade RP to enrich compost is a more rational and practical approach, since solubilization of insoluble P occurs during composting. Early work has shown that by adding RP to farm composting materials to a thickness of about 5 mm per layer, nearly 50-70% of insoluble P becomes soluble and readily available to plants.

For production of one tonne of phosphocompost (6-8% P_2O_5), the ingredients required are: 800 kg of organic refuse, crop residues, leaves, grasses, weeds, etc.; 100 kg of cattle dung or biogas slurry; 100 kg of soil; 50 kg of well-decomposed FYM or compost; and 265 kg of low-grade RP. The compost is ready in 3 months with significant transformation of insoluble P in RP (about 50% insoluble P) to citrate soluble P taking place during composting. However, total N-content decreases because of dilution.

17.3.2. Enrichment with Ready Compost or FYM

Addition of soluble P-fertilizers to finished compost or FYM offers a better scope for increasing the efficiency of fertilizer-P as well as manure-P. Thorough mixing of fertilizers may reduce P-fixation. The mineralization of manure-P may also be accelerated due to increased solubility of organic-P in the presence of fertilizers. Blending of compost with SSP could raise phosphorus-content of the enriched manure up to 5% P_2O_5.

17.4. Enrichment with Potassium

Potassium-bearing minerals like feldspars and mica can be added during composting to enrich compost. The availability of potassium in K-bearing minerals may improve due to production of organic acids such as citric, tartaric, acetic, etc.

17.5. Enrichment with Nitrogen, Phosphorus and Potassium

Attempts have been made to prepare N, P and K enriched compost by adding urea, low-grade rock phosphate and waste mica during composting. The raw materials required for preparation of one tonne of enriched compost are: 1000 kg crop residues/ biodegradable wastes, 45 kg urea, 200 kg rock phosphate and 200 kg waste mica. The enriched compost thus prepared contains: 1.4-1.5% N, 5.0–6.0% P_2O_5 and 2.5-3.0% K_2O. Therefore, addition of one tonne of enriched compost will substitute about 14-15 kg of N, 50-60 kg of P_2O_5 and 25-30 kg of K_2O, respectively.

17.6. Enrichment with Bioinoculant

Enrichment of composts with nitrogen-fixing bacteria and/ or phosphate and potassium solubilizing microorganisms is one of the possible means of improving nutrient content of the final product of compost. Inoculation of *Azotobacter chroococcum* to the compost heap enhances N-content by fixing atmospheric N_2. Phosphate solubilizing bacteria such as *Bacillus polymyxa, Pseudomonas striata*, and fungi such as *Aspergillus awamori* can be introduced into the composting mass along with rock phosphate. These microorganisms help in solubilizing sparingly soluble inorganic phosphates due to production of organic acids such as citric, tartaric, gluconic, etc., thereby increasing available P-control (water-soluble and citrate soluble P) of compost. Some cellulolytic and lignolytic microorganisms, such as *Trichoderma viride, Trichurus spiralis, Paeciliomyces fusisporus* and *Phaenerocheate crysosporium* are used as compost accelerators to hasten the process of composting.

18. Vermicomposting

Vermicompost is a composting process aided by earthworms. Earthworms can consume practically all kinds of organic matter. They consume daily about 2 to 5 times of their body weight, retain 5-10% of the feedstock for their own growth and excrete the mucus-coated undigested matter known as wormcasts or vermicast that has undergone physical and chemical breakdown through the activity of the muscular gizzard present in the intestine.

Vermicomposting is an appropriate technique for disposal of non-toxic solid and liquid organic wastes. It helps in cost-effective and efficient-recycling of animal wastes like poultry manure, piggery excreta and cattle dung, agricultural residues and industrial wastes. It has been estimated that one tonne moist organic matter can be converted into 300 kg of compost by earthworms. The castings of earthworms are rich in nutrients (N, P, K, Ca and Mg), which are in readily available form. Wormcasts are also rich in vitamins, enzymes and growth promoting substances. The introduction of worms into compost heap has been found to mix the materials, aerate the heaps and hasten decomposition. Turning the heaps is not necessary which is taken care of by the earthworms. Besides rural and urban wastes, effluents from agro-industries, viz., dairy, tannery, pulp and paper mill, distillery, etc. can be treated by using earthworms. The main advantage of use of earthworms for composting of a wide variety of organic residues is the reduced time required for maturity of compost. They can hasten the rate of decomposition, thereby reduce the time for composting and the product is ready for use within three months.

18.1. Species for Vermicomposting

There are about 3,000 species of earthworms in India, which can be classified broadly as surface living (epigeic) and burrowing (epianecic) worms. Epigeic or compost worms are found on surface and are reddish brown in colour (red worms). The epigeic group prefers organic wastes to process, while the other species (epianecic) burrow and mix the soil from different horizons in the profile and ingest organic and mineral fractions of soil; thereby promote the formation of organo-mineral complexes. Of the many species of earthworms tested for mass culture all over the world, *Eisenia foetida, Pheritima elongata, Eudrilus eugeniae* and *Perionyx excavatus* come in the above order of preference for their ability to compost organic wastes.

18.2. Method of Vermicomposting in Pits

For the preparation of a good quality of vermicompost, a number of steps are followed as mentioned below:

- *Selection of Earthworm*: The locally available earthworms native to a particular soil may be used for vermicomposting.
- *Size of Pit*: Any convenient dimension such as 2 m × 1 m × 1 m may be prepared. This can hold 20,000-40,000 worms, giving one tonne manure per month.
- *Preparation of Vermibed*: A thick layer of 15-20 cm of good loamy soil above a thin layer (5 cm) of broken bricks and sand should be made. This layer is made to inhabit the earthworms.
- *Inoculation of Earthworms*: About 100 earthworms are introduced as an optimum inoculating density into a composite pit of about 2 m × 1 m × 1 m, provided with a vermibed.
- *Organic Layering*: It is done on the vermibed with fresh cattle dung. The compost pit is then layered to about 5 cm with dry crop residues. Moisture content of the pit is maintained at 60-70% of water holding capacity.
- *Wet Organic Layering*: It is done after one month with moist/green organic waste, which can be spread over it to a thickness of 5 cm. This practice can be repeated every 3-4 days. Mixing of wastes periodically without disturbing the vermibed ensures proper vermicomposting. Wet layering with organic waste can be repeated till the compost pit is nearly full.
- *Harvesting of Vermicompost:* The moisture content in the compost is brought down by stopping the addition of water for 3-4 days before maturation that ensures drying of compost and migration of worms into the vermibed. The mature compost, a fine loose granular mass, is removed out from the pit, dried and packed.
- *Rate of Application*: Mature vermicompost is recommended @ 5 t/ha.

To boost vermicompost production following suggestions are offered:

(i) A mixture of cattle, sheep, and horse dung with gram and wheat bran and vegetable wastes forms the ideal feed for worms.

(ii) Mixing of gram/bran with dung in the ratio of 3:10 increases the biomass. Mixing of wheat bran with dung in 3:10 ratio hastens the growth of worms. Addition of kitchen waste in the same proportion increases the worm population.

(iii) The biogas sludge and poultry dropping in equal quantities enhance the worm population and the biomass.

18.3. Nutrient Content of Vermicompost

The nutrient content of vermicompost varies depending on the raw materials as well as different species of earthworms used. Thus, the final product is not a single standard product. The average nutrient content of vermicompost is: N 0.6-1.2%, P_2O_5 0.13-0.22%, K_2O 0.4-0.7%, CaO 0.4% and MgO 0.15%. On an average, it contains more C and P, but less K and micronutrients than FYM, while it contains comparable N and wide C:N ratio as in FYM. On the whole, vermicompost cannot be described as being nutritionally superior to other organic manures. Yet, the unique way in which it is produced, even in the field condition and at low cost makes it very attractive for practical application.

Vermicomposting of animal and agricultural residues results in significantly higher nutrient content and microbial population within a short period of 8 weeks. The excess worms that have been harvested from the pit can be used in the other pits, sold to other farmers for compost inoculation, and may be used as animal and poultry feed or fish food.

19. Green Manuring

Green manuring is the practice of enriching soil by growing of a crop and ploughing *in situ* or turning it into the soil as undecomposed green plant materials for the purpose of improving physical properties as well as fertility of the soil. The crops grown for green manuring are called green manure crops. The green manure crop supplies organic matter as well as additional nutrients, particularly N, if it is a legume crop, which has the ability to fix nitrogen from the atmosphere with the help of its root-nodule bacteria.

The practices of green manuring are classified as:

(i) *In-situ* Green Manuring: In this practice, green manure crops are grown and buried in the same field either as pure crop or as an intercrop with the main crop. The commonly used crops are: sunnhemp (*Crotalaria juncea*), *dhaincha* (*Sesbania aculeata*), cluster bean *(Cyamopsis tetragonoloba)*, *senji (Melilotus parviflora)*, horse gram *(Dolichos biflorus)*, pillipesara *(Phaseolus trilobus)*, cowpea (*Vigna sinensis*), berseem (*Trifolium alexandrinum*) and lucerne (*Medicago sativa*), etc.

(ii) Green Leaf Manuring: In this practice, plants that are grown elsewhere are brought in for incorporation into the soil as green leaves or tender green twigs. e.g. *Leucaena leucocephala* (*Subabul*), *Glyricidia maculata*, *Sesbania speciosa*, *Pongamia pinnata* (*Karanj*), *Pongamia glabra*, *Cassia tora*, etc.

In general, the green manure crops should preferably have the following characteristics:

- Legume with good nodulation growth, and good N_2-fixing capacity.
- Fast in growing even under water and nutrient stress conditions.
- Deep rooted system to absorb moisture and nutrients from deeper layers.
- Leafy habit/ tender leaf permitting rapid decomposition.
- Low water requirement for its own growth.
- Short duration (4-6 weeks).
- Rapid decomposability – non-fibrous and succulent.

19.1. Fate of Green Manuring

Decomposition of added plant materials depends on its chemical constituents and the physical conditions in the surrounding environment. For a proper decomposition of the green manure, it is necessary that the green material should be succulent and there should be adequate moisture in the soil. Plants at the flowering stage contain the maximum amount of succulent organic matter with a low C/N ratio. The incorporation of the green manure crop into the soil at this stage facilitates a quick liberation of N in the available form. With advancing age, the percentage of carbonaceous matter in the plants increases and that of N decreases. If the material with a wide C/N ratio is ploughed, microorganisms bring about its decomposition, draw upon the released N and mineral nutrients and consequently, cause a temporary nutrient-deficiency.

20. Concentrated Organic Manures

Concentrated organic manures are those that are organic in nature and contain higher percentages of major essential plant nutrients, namely N, P and K compared to bulky organic manures like FYM and compost. These concentrated manures are derived from raw materials of either animal or plant origin, such as oilcakes, fish manure, dried blood, bone meal, etc.

20.1. Oilcakes

Oilcakes are the residues left after the edible or non-edible oil is extracted from oil-bearing seeds. Oilcakes of different kinds are produced in India to the tune of about two million tonnes annually. They contain not only N but also substantial amounts of P and K along with organic matter. In addition to the major nutrients, the oilcakes invariably contain varying amounts of oil, depending upon the manufacturing process employed, namely indigenous oil press (*ghani*) (10-15% oil), hydraulic press (8-10% oil), expeller (5-8% oil) and solvent (1-2% oil). In general, oilcakes containing higher amount of oil decompose more slowly than those containing less oil. As a result, the availability of nutrients decreases

The C/N ratio of oilcakes is relatively narrow, being 3-15 for most of the oilcakes. Because of this it mineralizes readily and nearly 50-80% of its N is made available in about 2-3 months. However, certain oilcakes like *mahua* cake are exceptions, as their N does not become available till about two months. The use of oilcakes is limited to irrigated crops or those areas having sufficiently high rainfall, as it require moisture for its decomposition.

Oilcakes can be grouped into two categories, namely (i) edible oilcakes, which are suitable for feeding cattle, and (ii) non-edible oilcakes that are not suitable for feeding cattle. The average chemical composition of the major oilcakes available in the country is given in Table 10.

Owing to the importance of using edible oilcakes like groundnut, mustard, coconut, linseed, etc. as a cattle feed, their utilization as fertilizers is undesirable. They should be fed to cattle and the excrements may be used as manure. Non-edible cakes like castor, *neem, mahua, karanj*, undecorticated cottonseed and safflower cake, however, are recommended for use in conjunction with chemical fertilizers. Non-edible oilcakes are relatively slow acting, but they supply available N for a longer period.

Table 10. Average chemical composition of major oilcakes available in India

Oilcakes	N (%)	P_2O_5 (%)	K_2O (%)
Edible oilcakes			
Groundnut	7.3	1.5	1.3
Rapeseed/mustard	5.2	1.8	1.2
Linseed	4.9	1.4	1.3
Sesame	6.2	2.0	1.2
Coconut	3.0	1.9	1.8
Cottonseed (decorticated)	6.4	2.9	2.2
Safflower (decorticated)	7.9	2.2	1.9
Non-edible oilcakes			
Castor	4.3	1.8	1.3
Mahua	2.5	0.8	1.8
Neem	5.2	1.0	1.4
Karanj	3.9	0.9	1.2
Cottonseed (undecorticated)	3.9	1.8	1.6
Safflower (undecorticated)	4.9	1.4	1.2

Source: Yawalkar (1996)

20.2. Concentrated Organic Manures of Animal Origin

20.2.1. Bones and Bone Meals

Bones consist of apatite, a form of calcium phosphate, along with organic matter consisting mainly of fats and proteins. Hence, these are good sources for the supply of lime, phosphate and nitrogen. The presence of fats, however, slows down the process of mineralization. Therefore, bones are often first treated with steam to remove fat and then crushed to make into powder form. Steamed bones are more brittle and easy to crush and they decompose more readily. Steaming, however, reduces the N-content of the treated product. Steaming process increases phosphate and lime contents. It also increases the citrate-soluble P-content of calcium phosphate. For agricultural purpose, most of the bone meal is marketed as crushed, unsteamed raw bones. Bone meal is a slow acting manure. It is essentially a phosphatic fertilizer. It is suitable for acid soils or soils rich in sesquioxide (Fe_2O_3 and Al_2O_3). The composition of raw and steamed bones as specified by the Bureau of Indian Standards (BIS) is given in Table 11.

20.2.2. Dried Blood or Blood Meal

It contains 10-12% N, 1.0-2.0% P_2O_5 and 0.6-0.8% K_2O. It is a very quick-acting manure and effective on all crops and all types of soils. It should be used in the same way as oilcakes.

20.2.3. Meat Meal

It is also a quick-acting manure and effective to all crops. It contains 10-11% N, 2.0-2.5% P_2O_5 and 0.7-1.0% K_2O.

20.2.4. Fish Manure

Fish manure is available as either dried fish or fish-meal or powdered fish. In regions where fish oil is extracted, the residue can be used as manure. Depending on the type of fish, its manurial constituents vary from 5-8% N, 3-6% P_2O_5 and 0.3-1.5% K_2O. It is quick-acting and suitable for all crops and soils. It can be used either at planting or for top-dressing. Sometimes, the whole fish or small pieces are

Table 11. Bureau of Indian Standards Specifications for bone meal

(% by weight)

Composition	Raw bone meal	Steamed bone meal
Moisture (maximum)	8.0	7.0
Total N (minimum)	3.0	-
Total P_2O_5 (minimum)	20.0	22.0
Citrate-soluble P_2O_5 (minimum)	8.0	16.0

pushed into the soil while transplanting. However, its use is restricted mainly to coastal areas because of likely good supply and low cost.

20.2.5. *Guano*

It is the dried excreta of sea birds. It also contains the remains of their dead bodies and fish they consumed. It contains 7-8% N, 11-14% P_2O_5 and 2-3% K_2O. However, for commercial use this manure is not produced in India.

20.2.6. *Other Manures*

Some byproducts of small-scale industries are often used as concentrated organic manures. These are available in small quantities and used locally wherever they are produced. The most important organic manures of this type are:

Slaughterhouse Waste: It consists mainly of waste meat, intestines, etc. and has a good manurial value. It is practically wasted at present, though some municipalities use it for compost making along with night soil and town refuse. If dried and ground, it makes a very valuable manure containing 8.0-10% N and 3.0% P_2O_5.

Wool and Silkworm Wastes: Wool waste is a slow-acting manure and contains 4.0-7.0% N and 1.0-5.0% K_2O. This manure is suitable for growing potatoes and other vegetables. Silkworm waste contains N up to 10% and decomposes fairly quickly.

Press Mud: Press mud (PM) is a byproduct of sugar industry. It is also known as 'filter cake'. The raw juice contains suspended and dissolved impurities like dispersed soil particles, bagasse particles, wax, fats, proteins, gums, pectin, and inorganic salts of Na, K, P, etc. These impurities have to be removed from the juice in order to obtain sugar crystal. Usually two types of processes namely, sulphitation and carbonation are followed to clarify the cane juice. In sulphitation process, lime and SO_2 are used to get a clear juice. Here, calcium sulphite ($CaSO_3$) is obtained along with other impurities in the form of sulphitation press mud (SPM). While, in the carbonation process, lime and CO_2 are used to get clear juice. In this case, calcium carbonate ($CaCO_3$) is precipitated along with other impurities, which is known as carbonation press mud (CPM).

Press mud is a soft, spongy, amorphous and dark brown to brownish white material. Its composition is highly variable. On an average, it consists of about 60-70% moisture and 20-25% organic matter, besides mineral matter. Of the mineral matter, it is contained 1.0-1.5% N, 4-5% P_2O_5, 2-7% K_2O and 3-5% lime on dry weight basis. Besides its fertilizer value, press mud can be used for ameliorating acidic (carbonation press mud) and saline-sodic (sulphitation press mud) soils. It can be used as a carrier medium for biofertilizers. It can also be used for raising sugarcane seedling.

21. Sewage and Sludge

Sewage and sludge constitute the liquid and solid wastes from city sewerage system, which pose a problem of disposal. The raw or crude sewage consists mainly of water carrying various solids partly in solution and partly in suspension. Thus, it contains suspended solids in the form of solid organic matter. Therefore, before it is disposed off, the organic matter in the sewage has to be reduced. Thus, in many cities, the sewage is purified or treated before it is let out so that it does not pollute the river or stream water.

Several methods are employed for treating sewage, namely (a) septic tank method, (b) filter bed or percolation method, and (c) activated sludge method. They all work on the principle of biological oxidation of organic substances. In the septic tank method, the decomposition is mainly anaerobic, while filter bed method allows aerobic decomposition of the colloidal solids in suspension. In the activated sludge method, the raw sewage is stirred with a large excess of air so that the decomposition takes place under super-aerobic conditions. The sludge that settles at the bottom in this process is called 'activated sludge'. It has the remarkable property of bringing about rapid oxidation of the organic matter present in the fresh sewage. It is also inoffensive and on dry-weight basis, contains 3 to 6% N, about 2% P_2O_5 and 1% K_2O in forms that can become readily available when applied to soil.

In all the treatment methods, the raw sewage is separated into two main fractions, liquid fraction is called as effluent or sewage and the solid portion is called as sludge. The resultant products, viz., the effluent and the sludge, can be utilized as manure as they contain large amounts of plant nutrients. Sewage is used for irrigation purposes and sludge is used as manure.

Sewage has been used in agriculture from the beginning of civilization. But in earlier days, as there were not many industries and automobiles, contamination of sewage with heavy metals and other pollutants was limited. With development of more industries, pollution of sewage with heavy metals and other toxic substances becomes more intractable. Today, the total sewage generation from 200 major cities of India is 2600 million m^3 per year. Due to the high cost of treatment and lack of infrastructure and awareness, 65-70% of sewage does not get any treatment before its discharge into water bodies. As a result of high organic and salt load of untreated sewage, its disposal into water bodies causes water pollution. Almost all major rivers in India are now threatened with such problems. In view of the presence of toxic substances like heavy metals and pathogens in sewage, its recycling in an economically and environmentally acceptable manner is a great challenge.

Nutrient supplying potential of sewage is directly related to its composition, which in turn depends on the extent of industrialization and urbanization of the area from where sewage is generated. In general, the sewage generated in India contains more than 90% water and is used for irrigation purpose. On an average, the sewage sludge has the following composition on oven dry basis:

Composition	*Amount on oven dry basis, %*
Organics	40-50
Inert materials	30-40
Bio-resistant organics	10-15
Miscellaneous substances	5-8

It has been calculated that sewage available from big cities in India could annually contribute about 33,000 tonnes of N, 7,000 tonnes of P and 20,000 tonnes of K. According to other estimates, sewage and sludge from urban areas can provide about 1.2 Mt of N, 1.0 Mt of P and 0.8 Mt of K.

Sewage water can be used as an irrigation source. However, it should be treated before application to fields. Soil sickness results from excessive organic and N loading, which causes anaerobiosis and imbalance in C:N and C:P ratios. Excessive N-loading also induces production of more foliage, resulting in less fruiting, particularly in the case of vegetables like brinjal, okra, chillies, etc. The yield decline due to continuous application of untreated sewage water is primarily due to the blocking of soil pore spaces by colloidal matter. The soil quickly becomes 'sewage sick' owing to the clogging of pores and the development of anaerobic organisms, which not only reduce the nitrates already present in the soil but also produce alkalinity. Bacterial contamination makes the eating of raw vegetables grown by using untreated sewage a real danger to human health. This ill effect can be overcome by using treated sewage. Dilution of secondary treated sewage with good water (1:1) helps in increasing yield.

The main disadvantage of using sewage and sludge in agriculture is its heavy metals content, particularly Pb and Cd, due to electroplating and other industries. However, the extent of heavy metals depends on the source of sewage and sludge. Thus, repeated application of sewage tends to increase the concentration of metals in soils and the availability of metal to plants, which in turn get into our food chain.

22. Distillery Effluents (Spent wash)

Distillery is one of the most important agri-based industries in India for manufacturing of ethyl alcohol from molasses. A large volume of foul smelling effluent which is commonly known as distillery effluent or spent wash is generated. Usually with each litre of alcohol production, 12-15 L of spent wash effluent is generated. Approximately 40 billion litres of spent wash is generated per annum from 285 distilleries in the country, which is usually discharged into the water courses under untreated or partially treated conditions, causing environmental pollution owing to its very high organic load. In order to reduce its high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), many distilleries recycle these effluents to produce methane (CH_4) by passing them through biomethanation digesters and the effluent thus obtained is known as post-methanation effluent (PME). In general, a very high organic load, as measured by BOD and COD, has been recorded in spent wash (Table 12). Post-methanation effluents contain reduced organic matter load but still have considerable organic and salt load making its disposal a problem. Raw spent wash and PME contain considerable amounts of organic matter and plant nutrients, particularly K and S and appreciable amounts of N and P, which can be applied to arable land as irrigation water and as an amendment. The pH and nutrient concentrations of the effluents increase while EC decreases due to methanation.

Table 12. Characteristics of raw and post-methanation spent wash effluents

Parameter	Raw spent wash effluents	Post-methanation effluents
BOD (mg/L)	50,000	5,000
COD (mg/L)	95,000	25,000
EC (dS/m)	15	8.5
pH	4.5	5.9
N (mg/L)	1000	300
P (mg/L)	40	20
K (mg/L)	11000	6000
SO_4 (mg/L)	1500	

When applied to crops, these effluents may act as source of plant nutrients and have been reported to increase the yield of crops. It is reported that crops like sugarcane have been found to withstand application of spent wash effluents without showing yield reduction. Cereals like wheat and rice, on the other hand, grow well after suitable dilution to BOD levels of 500-1000 mg/L. Diluted spent wash is considered as organic fertilizer having high K-content and N is in organic form but becomes available slowly (slow release fertilizer). About 67% of P is also in organic form. It also contains large amounts of secondary elements like S, Ca, and Mg as well as micronutrients like Cu, Mn and Zn. The post-methanation effluents show positive effect on crops like sugarcane, rice, wheat and mustard. Even after 20 consecutive irrigations with 30% PME, none of the crops showed any toxicity symptoms. Thus, application of this effluent to arable land as irrigation water and as a source of plant nutrients offers a promising alternative for its safe disposal.

Addition of spent wash is beneficial for improving soil health. However, continuous and indiscriminate use of high BOD and COD materials for a long time poses the risk of deteriorating the physical and physicochemical properties of the soil, resulting in adverse effect on soil health. As post-methanation effluents have nearly 60% less organic load and higher pH value than raw effluents, they have shown positive impact on soil health. The nutrients in effluent irrigation are more effective in respect of the bioavailability of nutrients to plants as compared to chemical fertilizers. Significant increase in pH, EC, OC, SAR, KAR, exch.-Na and exch.-K and available nutrients are observed in spent wash effluents irrigated soil compared to normal water irrigated soil. Distillery waste water also poses a serious threat to water bodies. Addition of distillery effluents to river results in high concentration of organic load and depletion of oxygen due to increase in microbial population in the water bodies and causing wide spread mortality of fish and other aquatic organisms. Sometimes, the colour of groundwater is so dark that the water becomes unsuitable for drinking.

23. Biofertilizers

Biofertilizers are the products containing one or more species of microorganisms which have the ability to mobilize nutritionally important elements from non-usable to usable form through biological processes such as nitrogen fixation, phosphate solubilization, excretion of plant growth promoting substances or cellulose and lignin biodegradation in soil, compost and other environments. In brief, biofertilizers refer to living organisms which augment plant nutrient supplies in one way or the other. They are environment-friendly and cost effective supplement to chemical fertilizers and organic manures. Biofertilizers play a significant role in improving nutrient availability to crop plants. They are recognized as one of the components of integrated plant nutrient supply (IPNS) system.

23.1. Classification of Biofertilizers

Biofertilizers may be broadly classified into nitrogen fixing bacteria, phosphate solubilizing microorganisms and organic matter decomposers (Figure 2).

23.1.1. Rhizobium

Among biofertilizers, *Rhizobium* inoculants are of greatest importance because of their ability to fix atmospheric N_2 in association with certain legumes. It is estimated that N_2-fixation by *Rhizobium* in root nodules of legumes is of the order of 14 Mt on a global scale and is almost 15% of industrial N-fixation (88 Mt). It is now known that yield of many leguminous crops can be stepped-up substantially by the use of appropriate *Rhizobium* cultures. *Rhizobium* bacteria live in the root nodules of legume plants through a symbiotic relationship. There are six distinct species under the genus *Rhizobium* which is classified on the basis of cross inoculation group concept. The assumption of this concept is that those legumes falling within a particular infection group can be inoculated by a particular species of nodule bacteria.

According to other school of concept, it can be grouped into two categories. The slow-growing *Rhizobia* are grouped under the genus *Bradyrhizobium* and fast-growing ones under the genus *Rhizobium*. However, the latter classification is more complex and usually the concept of cross inoculation classification is used frequently.

23.1.2. Azotobacter

Azotobacter fixes atmospheric N_2 non-symbiotically and the extent of fixation is directly dependent upon the amount of carbohydrates utilized by them. It is an aerobic, chemo-heterotrophic and free-living bacterium. Hence, they work better in the root region of crop non-symbiotically when adequate organic matter is present. They are very effective in enhancing yield of crops like wheat, rice, sorghum, etc. and vegetable crops like onion, brinjal, tomato, cabbage, etc.

23.1.3. Azospirillum

Azospirillum is a chemo-heterotrophic bacteria associated to live within the roots of sorghum, pearl millet, rice, maize, wheat and sugarcane crops. They can fix atmospheric N_2 to the extent of about 15-30 kg N/ha.

23.1.4. Frankia

It shows symbiotic association with certain non-legumes, mainly with trees and shrubs. It has modest agricultural importance because its potential in fixing N from atmosphere is not widely known. However, its potential could be harnessed in agroforestry.

23.1.5. Azolla

Azolla is known as free floating water fern. *Azolla* fixes atmospheric N_2 in symbiotic association with blue green algae (*Anabaena azollae*) in rice fields. This association is a live, floating N_2-factory using energy from photosynthesis to fix atmospheric N_2, amounting to 40-60 kg N/ha/rice crop. *Azolla* contains 0.2-0.3% N on fresh weight basis and 3-5% N on dry weight basis. There are seven species of *Azolla* out of which *Azolla pinnata* is most widely distributed in India. *Azolla* can be used both as a green manure before transplanting and as a dual crop after transplanting of rice.

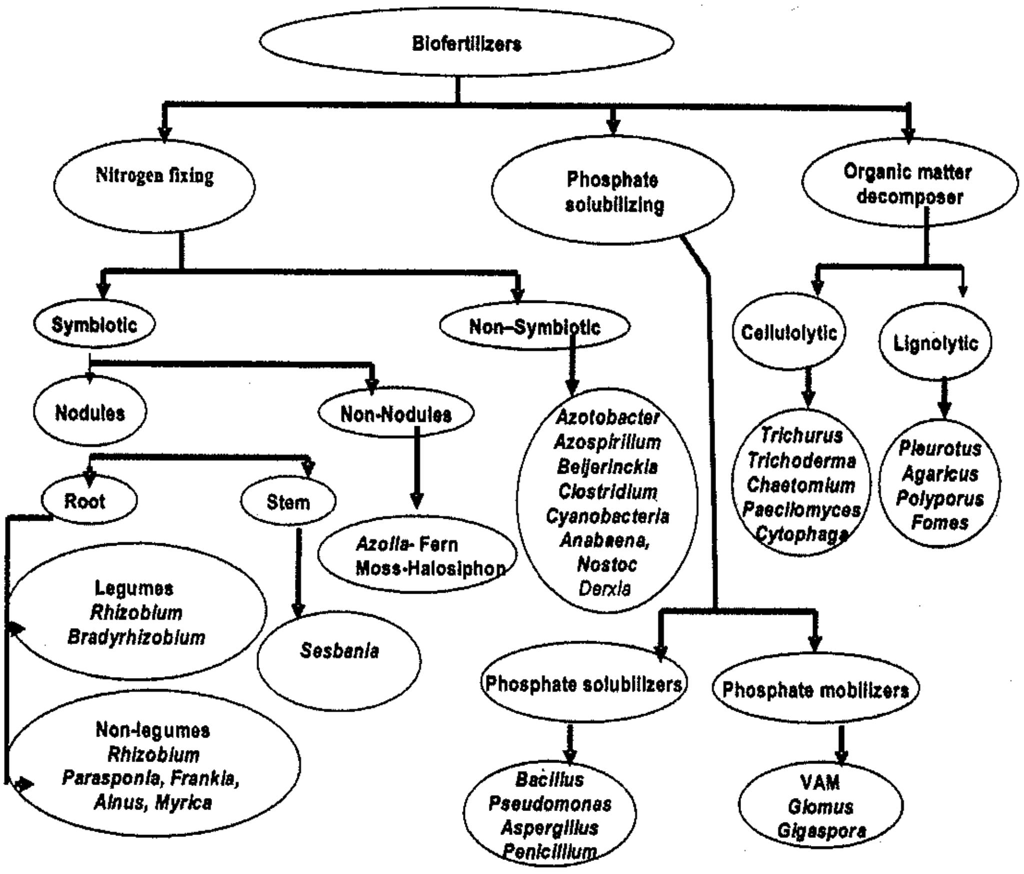

Figure 2. A broad classification of biofertilizers

Azolla supplies N to rice after its decomposition just like any other organic matter. It takes about 8-10 days to decompose and release about 67% of its N within 35 days.

23.1.6. Blue Green Algae

Blue green algae (BGA) are also known as cyanobacteria. Cyano means blue that means it is blue bacteria. The first account of agronomic potential of BGA in rice was presented by P.K. De (1939), who attributed the natural fertility of tropical rice field to these N_2-fixing organisms. The N_2-fixing potential of BGA can be estimated by evaluating its biomass, N-content and N_2-fixing activity. Nitrogen fixed by BGA becomes available to the rice crop after their decomposition as the case with *Azolla* or any organic sources. BGA can contribute about 20-30 kg N/ha.

23.1.7. Phosphate Solubilizing Microorganisms (PSM)

A group of heterotrophic microorganisms possesses the ability to solubilize inorganic P from insoluble sources to soluble forms. They may be efficient strains of bacteria, namely *Bacillus megatherium, B. polymyxa, B. subtilis, B. circulance, Pseudomonas striata*, etc.; fungi, namely *Aspergillus awamori, A. niger, Penicillium digitatum, Trichoderma* sp.; and yeast like *Schwanniomyces occidentalis*. In earlier work carried out in the erstwhile USSR, it was observed that inoculation with *Bacillus megatherium* var. *phosphaticum* popularly known as 'Phosphobacterin' increased crop yield by 5-10%. Significant increase in yields due to inoculation of *B. polymyxa, P. striata, Aspergillus awamori* along with rock phosphate has been reported by many workers.

The principal mechanism for mineral phosphate solubilization due to inoculation with PSM is the action of organic acids like citric, oxalic, tartaric, acetic, lactic, gluconic, α-ketogluconic, succinic, glyoxalic, maleic, fumaric, α-ketobutyric, etc. produced by microorganisms. These acids are sources of H^+ ions and are able to dissolve the mineral phosphate and make it available to the plant. In addition to pH reduction, organic acid anions can solubilize phosphate through chelation reactions. Organic acid anions through their hydroxyl and carboxyl groups, have the ability to form chelates with cations such as Ca^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+}, that are often bound with phosphate, the latter being converted to soluble forms. In addition to P-solubilization, these microorganisms can mineralize organic P into a soluble form. The reaction takes place in the rhizosphere and because the microorganisms render more P into solution than is required for themselves for their own growth and metabolism, the surplus is available for plants.

The PSM also produce growth promoting substances which influence plant growth. Acid phosphatases play a major role in the mineralization of organic P in soil. These microorganisms are quite useful in the utilization of low grade rock phosphates. Field experiments conducted with P-solubilizers significantly increased the yields of various crops in the presence of rock phosphate, and a saving of nearly 30 kg P_2O_5/ha has been noticed.

23.1.8. Vesicular-arbuscular Mycorrhiza (VAM)

The symbiotic association between plant roots and fungi is termed as 'mycorrhizal association' which is known to improve the growth and yield of crops in nutrient-deficient conditions. There are two types of mycorrhiza, namely ectomycorrhiza and endomycorrhiza. VAM fungi fall under endomycorrhiza group. These are obligate symbiont with a network of hyphae in soil and extensive growth within the plant roots. They have an important role in efficient use of P-fertilizers and improving N_2-fixation. Reports dealing with the interaction of VAM fungi and N_2-fixers present in soil are increasing. VAM fungi infect the plants, spread inside the root and produce highly branched hyphal structure, known as vesicles and arbuscules, within the host cells. The arbuscules help in the transfer of nutrients from the fungus to the root systems and the vesicles store P as phospholipids.

Mycorrhizal association is generally found very effective in agroforestry. The other crops where VAM infections have shown beneficial effects are sorghum, barley, wheat, rice (upland), tobacco, cotton, soybean, cassava, grape, citrus, apple, etc. Mycorrhizal roots can take up several times more P per unit root length than non-mycorrhizal roots, primarily because of larger surface area resulting from the growth of hyphae. Mycorrhizal infection can also increase the uptake of nutrients like K, particularly in seedlings of forest trees, and S, Cu and Zn.

23.1.9. Organic Matter Decomposer

Composting is a key technology to use a wide variety of organic wastes, including crop residues and rural and urban wastes (discussed in detail elsewhere in this chapter). However, it takes about 4-6 months for its maturity for use as source of plant nutrients. In order to hasten the decomposition of these organic wastes, some efficient cellulolytic and lignolytic microorganisms are introduced into the composting mass. These microorganisms decompose organic matter at a faster rate and make it ready for use within 2-3 months. The efficient cellulolytic and lignolytic cultures used for rapid decomposition are *Trichoderma viride, Trichurus spiralis, Aspergillus niger, Phaenerocheate crysosporium, Paecilomyces fusisporus*, etc.

23.1.10. Plant Growth Promoting Rhizobactreia (PGPR)

Plant growth promoting rhizobactreia are also known as 'rhizosphere bacteria' that exert beneficial effect on plant growth. PGPR belong to several genera, viz., *Agrobacterium, Arthrobacter, Bacillus, Pseudomonas, Zanthomonas, Rhizobium, Azotobacter, Enterobacter*, etc. The primary mechanism of PGPR is to improve the plant growth by colonizing the root system and/or pre-empting or suppressing the establishment of deleterious or harmful microorganisms in root-rhizosphere. The presence of large population of PGPR on planting materials and roots plays an important role in recycling plant nutrients and reducing the growth of harmful pathogen in rhizosphere.

Use of PGPR has been found to improve potato growth and yield primarily by suppress-

Table 13. Biofertilizers and their mode of action, host crops, methods of application and rate of inoculants used

Name of organism	Mode of action	Host crops for which used	Method of application	Rate of inoculant	Remarks
Rhizobium strain	Symbiotic N_2 fixation	Legumes like pulses, soybean, groundnut	Seed treatment	200 g per 10 kg seed	Leaves residual N in soil for next crop
Azotobacter	Non-symbiotic N_2 fixation	Cereals, millets, cotton, vegetables	Seed treatment	200 g per 10 kg seed	Also controls certain diseases
Azospirillum	Associative N_2 fixation	Non-legumes like maize, barley, oats, sorghum, millet, sugarcane, rice, etc.	Seed treatment	200 g per 10 kg seed	Produces growth promoting substances Can be applied to legumes as coinoculant
Phosphate solubilizers	Phosphorus solubilization	Soil application for all crops	Seed treatment	200 g per 10 kg seed	Can be mixed with rock phosphate
Blue green algae (BGA)	Non-symbiotic N_2 fixation	Rice	Soil application	10 kg/ha	Reduces soil alkalinity, has growth promoting effects
Azolla	Symbiotic N_2 fixation	Rice	Soil application	1 t dried material/ha	
Mycorrhiza (VAM)	Symbiotic association	Many tree species, wheat, sorghum, ornamentals	Soil application		Usually seedlings are inoculated

ing cyanide-producing deleterious or harmful microorganisms. The suppression of pathogen growth due to inoculation of PGPR includes substrate competition, production of siderophores and antibiotics and induced resistance. Siderophores are the Fe-chelating compounds produced by certain soil microorganisms. Their role in P-solubilization appears to be important in acid soils where ferric phosphate is one of the major forms of insoluble phosphates.

Commonly produced biofertilizers and their mode of action, host crops, methods of application and rate of inoculants are given in Table 13.

23.2. Methods of Application of Biofertilizers

23.2.1. Seed Treatment

For treating seeds, 200 g of biofertilizer is suspended in 300-400 mL of water and mixed gently with the seeds (10 kg) using an adhesive like gum acacia, jaggery solution, etc. so that the bioinoculants may get energy for their prolonged survival. Care should be taken to avoid any damage to seed coat. The seeds are then spread on a clean sheet/ cloth under shade to dry and used immediately for sowing.

23.2.2. Seedling Root Dip

For rice crop, a bed is made in the field and filled with water. Recommended biofertilizers are mixed in this water and the roots of seedlings are dipped for 8-10 h and transplanted.

23.2.3. Soil Treatment

Four kilogram each of the recommended biofertilizers is mixed in 200 kg of compost and kept overnight. This mixture is incorporated in the soil at the time of sowing or planting.

23.3. Precautions for Using Biofertilizers

- Biofertilizer packets need to be stored in a cool and dry place, away from direct sunlight and heat.
- As *Rhizobium* is crop-specific, one should use it for the specified crop only.
- While purchasing one should ensure that each packet is provided with necessary information like name of the product, name of the crop for which intended, name and address of the manufacturer, date of manufacture, date of expiry, batch number and instructions for use.
- The packet has to be used before its expiry date, only for the specified crop and by the recommended method of application.
- Both nitrogenous and phosphatic biofertilizers are to be used to get the best results.
- It is important to use biofertilizers along with chemical fertilizers and organic manures.
- Biofertilizers are not replacement of fertilizers but can supplement plant nutrient requirements.

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Chapter 26

Soil Fertility Management

V.K. NAYYAR and K. SUDHIR

1. Introduction

In developing countries like India, where the land-person ratio is rapidly narrowing, the only means of meeting the needs of agricultural produce is through increased productivity without detriment to environment and sustainability. The per capita land availability in the country has decreased from 0.48 ha in 1951 to 0.14 ha in 2001 and is projected to be further reduced to 0.10 ha by the year 2025. Not only the land available for cultivation is decreasing, the quality of land available for cropping is also declining due to urbanization, industrialization, etc. This has led to the cultivation of marginal lands and destruction of forests, resulting in impoverishment of soil quality and making the land more prone to floods and erosion. Consequently, the country's productive resource base is being affected adversely. This calls for the management of soil fertility in the context of shrinking soil resource base in terms of both quantity and quality.

Soil fertility refers to the inherent capacity of a soil to supply essential nutrients to plants in adequate amount, in correct proportion and at right-time for their optimum growth. Management of the fertility of soils demands its build-up and sustenance at a high level to produce adequate food, feed, fodder and fuel for the ever-increasing population of human beings and animals. Fertilizers, therefore, assume a great significance and constitute one of the key inputs for achieving high productivity. The Green Revolution in India would not have been possible without spectacular increase in fertilizer input, which could exploit the potential of fertilizer-responsive high-yielding varieties in the presence of adequate water and pest management.

India is not self-sufficient in producing primary plant nutrients. A large part of nitrogenous and phosphatic fertilizers and entire quantity of potassic fertilizers are imported. Efficient management of soil fertility is, therefore, of prime concern to the scientists in view of the increasing gap between production and consumption of fertilizers with time as well as of increasing threat to the environment. Efficient management of soil fertility requires knowledge about the nutrient needs of the plants, cycling of nutrients in soils, soil fertility constraints and efficient nutrient management. These aspects are briefly discussed in the following sections.

2. Plant Nutrient Requirement

Plants need a variable quantity of a nutrient within a narrow range and in an optimum proportion with respect to other nutrients for their vegetative growth and ultimate yield. The amounts of nutrients required to produce a given quantity of grain, however, varies with the crop (Table 1); generally higher the yield, greater is the nutrients requirement. A shortage of one or more nutrients can inhibit or stunt plant growth, but their oversupply can also be a problem, causing economic ineffi-

Table 1. Nutrient requirement in kg to produce 100 kg grain

Crop	N	P_2O_5	K_2O
Rice	1.58-2.37	0.33-1.88	2.42-3.24
Wheat	2.08-2.70	0.38-1.50	1.28-4.13
Maize	2.02-2.71	1.09-1.11	0.87-2.95
Ragi	2.16-4.04	1.51-1.73	2.05-3.68
Chickpea	2.69-6.10	0.92-1.58	3.53-4.22
Cotton	2.51	1.56	4.31
Groundnut	3.94-4.76	0.75-1.58	1.30-2.83
Sunflower	2.21-2.94	2.27-2.62	2.52-2.94
Cabbage	0.13	0.04	0.08
Potato	0.34	0.12	0.65

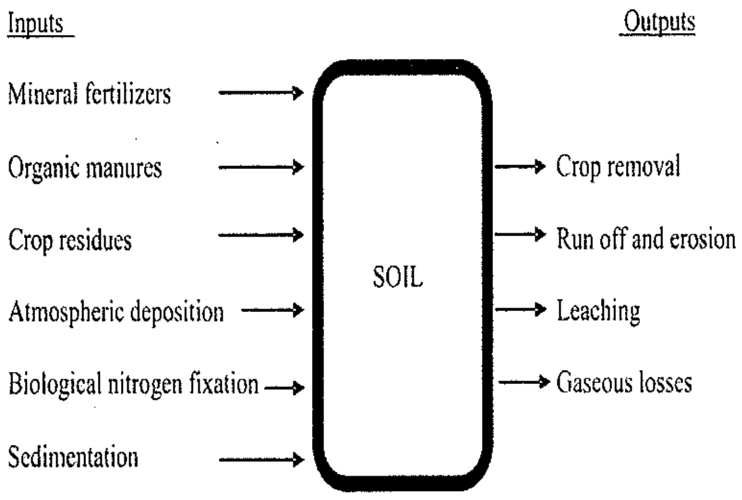
Source: Muralidharudu *et al.* (2007)

ciency, damage to the environment and in some cases, may even harm the plants themselves and the animals and humans who consume them. Hence, efficient management of the soil storehouse as well as of added nutrients is essential for maintaining soil fertility and sustaining high yields. To achieve healthy growth and optimal yield levels, nutrients must be available not only in the correct quantity and proportion, but also in usable forms at the right time. Soil testing and plant analysis (Chapter 22) can help provide the needed information for realizing optimum yield of crops and cropping systems under different soil situations. However, economic optimum may differ from the physical optimum, depending on the added cost of inputs and the value of benefits derived from any increased output.

3. Nutrient Cycle

Soil is a storehouse of nutrients and the nutrients are not locked up in one form only. Natural processes constantly change them from one form to another. The availability of nutrients in soil, therefore, changes over time due to their continuous addition and removal from the system (Figure 1) and the complex geological, chemical and biological processes occurring in soil. The continuous recycling of nutrients into and out of the soil is known as the nutrient cycle and involves complex physical, chemical and biological interactions, some of which are not yet fully understood.

The difference between the volume of inputs and outputs constitutes the nutrient balance. Positive nutrient balances in the soils (when nutrient additions to soil are higher than their removal from soil) indicate that farming systems are inefficient and they may pollute the environment. Negative balances, on the other hand, indicate that the soils are being mined and that the farming systems are unsustainable over the long-term. Thus, maintaining proper nutrient balances require understanding and proper planning over a long period of time to make the system viable and sustainable. Several studies have indicated a net negative balance in respect of the three major nutrients in most of the Indian soils. Based on nutrient input through fertilizers, an annual depletion of 8.4 million tonnes (Mt) for N + P_2O_5 + K_2O on gross basis and 9.7 Mt on net basis has been shown (Table 2) and thus emphasize the



Input – output = nutrient balance

Figure 1. The plant nutrient balance system

Table 2. A balance sheet of NPK in Indian agriculture

Nutrient	Gross balance sheet ('000 t)			Net balance sheet ('000 t)		
	Addition	Removal	Balance	Addition	Removal	Balance
N	10923	9613	1310	5461	7690	-2229
P_2O_5	4188	3702	486	1466	2961	-1496
K_2O	1454	11657	-10202	1018	6994	-5976
NPK Total	16565	24971	-8406	7945	17645	-9701

The net balance sheet has been arrived at by adjusting fertilizer inputs for their use efficiency @ 50% for N, 35% for P (including residual effect), and 70% for K. For removal, this is taken as 80% of crop uptake for N and P and 60% in case of K.

Source: Tandon (2004)

need for regular addition of nutrients in adequate amounts to maintain soil fertility and productivity.

4. Soil Fertility Constraints

A careful identification of the constraints of current nutrient deficiencies and monitoring the changes in soil fertility to predict the areas of emerging deficiencies is a pre-requisite for soil fertility management. Intensive agriculture using high-yielding and hybrid varieties without the application of the required amounts of nutrients through fertilizers to supplement the supply from the soil sources has been leading to the depletion of more and more number of nutrients in the soil below the critical level over the years (Figure 2). It is not a good trend in terms of keeping the soil in a healthy and productive condition for sustainable agriculture. Soils in India, in general, are inherently low-to-medium in the available status of most of the nutrients. They are also low in their organic matter status, which is a key factor in the supply of many nutrients to the crops. Table 3 indicates the percentage of soil samples falling under the low, medium and high categories in respect of the three major nutrients.

4.1. Nitrogen

Indian soils are largely low in total nitrogen, except in the hilly regions of north, where its content is relatively higher, and the response to fertilizer nitrogen is good. The total nitrogen-content in a soil-depends on its organic matter content, which decreases with deforestation, erosion and high temperature. Barring 18 districts in the hilly region of north-eastern India and Himachal Pradesh which were high in organic carbon and hence in available nitrogen, others are low or medium in available nitrogen (Yadav *et al.*, 2000).

4.2. Phosphorus

Most of the Indian soils are low in available phosphorus, some are medium and very few are high. Soils of 59% districts of Uttar

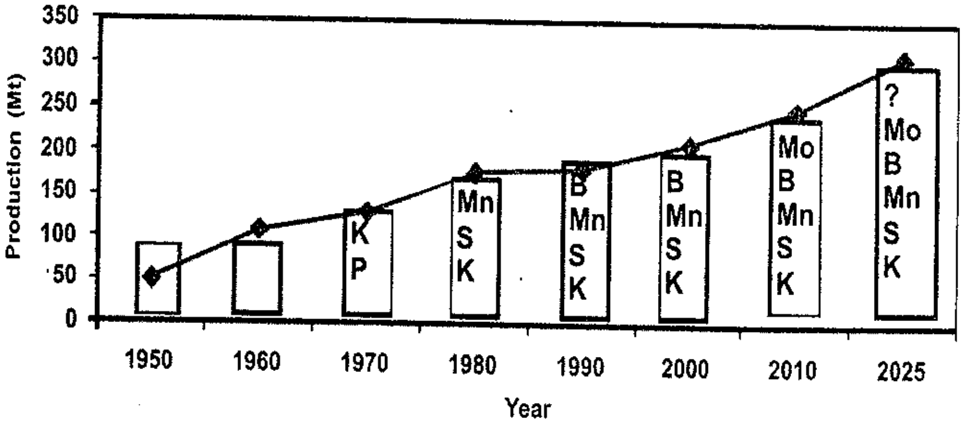


Figure 2. Trends in deficiency of plant nutrients in relation to food grain production

Source: Subba Rao and Srivastava (2007)

Table 3. Extent of macronutrient deficiency in India

Nutrient	No. of samples analysed	Samples by category (%)		
		Low	Medium	High
N	3650004	63	26	11
P	3650004	42	38	20
K	3650004	13	37	50
S	27000	40	35	25

Source: Mostara (2002)

Pradesh, Uttarakhand, Bihar, Jharkhand, Haryana, Punjab, Andhra Pradesh and Tamil Nadu are low in available phosphorus. The deficiency is more in the soils of Uttar Pradesh, Uttarakhand and Andhra Pradesh than those of Punjab and Haryana (Yadav *et al.*, 2000). Under intensive cropping in the irrigated areas, it is not possible to reap high yields without the application of phosphorus along with nitrogen. The uptake of phosphorus by crop is generally less than 30% of the applied quantity and the rest largely remains in the soils and becomes available to subsequent crops. Hence, there is need to increase the efficiency of phosphorus utilization by crops, especially when grown in a sequence.

4.3. Potassium

A large percentage of Indian soils are medium to high in available potassium (Table 3). Total potassium is high in forest hill soils of erstwhile Uttar Pradesh, alluvial soils of Punjab, and desert soils of Rajasthan and low in acid soils of Kerala and many districts of Jammu and Kashmir, erstwhile Uttar Pradesh and Himachal Pradesh (Chapter 18). The non-exchangeable potassium is more abundant in some alluvial, Vindhyan and Bundelkhand soils of Uttar Pradesh and desert soils of Rajasthan and is less in low-level laterites and acid soils of Kerala, and in red and laterite soils of the Peninsular India. The exchangeable and water-soluble forms of potassium follow roughly the same order.

4.4. Calcium and Magnesium

Most of the Indian soils contain enough of calcium and magnesium in plant-available forms. The available calcium and magnesium contents of several soil series in India are given in Table 4. The calcium deficiency is widespread in acidic soils. The total CaO-content of these soils ranges from less than 0.1% to about 1.0% with calcium saturation of the cation exchange capacity being 20–25% of the total. The alluvial soils of the Indo–Gangetic Plains, being neutral to moderately alkaline in reaction, have sufficient bases on their exchange complex and calcium deficiency is, therefore, rarely encountered in these soils. However, alkali soils may contain inadequate quantities of calcium due to dominance of sodium on the exchange complex. Sandy soils with low exchangeable Mg, acid soils and those high in native or applied K are likely to exhibit hidden or even apparent hunger for magnesium. In the irrigated eco-system, magnesium deficiency can be a problem in acid laterite soils of southern Plateau and black cotton soils of Andhra Pradesh.

4.5. Sulphur

With increase in the use of fertilizers like diammonium phosphate in place of single superphoshate coupled with intensive cropping, the incidence of sulphur-deficiency in Indian soils has increased. Recently, analysis of more than 60,000 surface soil samples carried out under the All India Coordinated Research project on micro- and secondary-nutrients and pollutant elements in soils and plants revealed that sulphur deficiency ranged between 5 and 83% with an overall mean of 41% (Singh, 2006). Sulphur deficiency is generally widespread in coarse-textured alluvial, red and laterite, leached acidic and hill soils, black clayey soils as well as soils with low organic matter content. Saline, alkali and eastern coastal soils contain adequate amounts of available sulphur.

4.6. Micronutrients

Crop requirements for micronutrients increase with rise in crop productivity. In the absence of their replenishment, potential threats of deficiencies in soils, followed by in crops increase. The availability of micronutrients, therefore, has become an important limiting factor in the present day intensive and exploit-

Table 4. Soil properties and nutrient status of some soil series in India

Soil series	Horizon/Depth	pH	Organic carbon ($g/10^3g$)	CEC [$cmol(p^+)kg^{-1}$]	Exchangeable cations [$cmol(p^+)kg^{-1}$]			
					Ca	Mg	K	Na
Patancheru, Udic Rhodustalf, Andhra pradesh								
1	0-10	6.5	0.84	8.1	5.8	1.9	0.3	0.1
	10-20	6.5	0.79	8.4	5.6	2.1	0.3	0.2
Pusaro, Typic Paleustalf , Bihar								
2	0-9	5.1	0.26	8.5	2.4	1.6	0.5	0.2
	9-30	5.5	0.23	8.8	3.6	2.0	0.5	0.1
Kabilpur, Typic Ustochrept, Gujarat								
3	0-19	7.5	0.64	24.7	18.2	4.2	0.3	1.5
	19-72	7.5	0.21	23.1	17.6	3.8	0.3	1.8
Lukhi, Typic Ustochrept, Haryana								
4	0-8	8.3	0.13	7.3	3.2	2.5	0.4	0.5
	8-27	8.4	0.14	7.6	3.7	2.2	0.4	0.6
Vijayapura, Typic Kandi Ustalf, Karnataka								
5	0-7	5.6	0.44	3.0	1.7	0.6	0.2	0.1
	7-21	5.2	0.42	3.0	1.0	0.7	0.1	-
Thiruvananthapuram, Ustoxic Dystropept, Kerala								
6	0-9	4.5	1.39	6.7	1.7	0.4	0.2	Tr
	9-25	4.5	1.10	5.8	1.0	0.2	0.2	Tr
Sundra, Chromic Haplustert, Madhya Pradesh								
7	0-12	8.9	0.7	34.4	24.0	6.5	0.6	1.9
	12-40	7.9	0.6	37.5	26.3	5.0	0.5	2.0
Wadgaon, Vertic Ustropept, Maharashtra								
8	0-16	7.1	0.31	54.9	40.1	11.9	-	-
	16-52	7.1	0.28	60.1	40.4	14.9	-	-
Sidhamula, Aquic Ustifluvent, Orissa								
9	0-15	6.9	0.38	6.8	3.2	1.6	0.2	0.3
	15-50	7.0	0.06	1.6	0.8	0.4	-	0.1
Tulewal, Typic Ustochrept, Punjab								
10	0-23	8.4	0.15	4.9	2.0	1.5	0.3	0.7
	23-68	7.8	0.12	9.8	5.2	3.2	0.4	0.5
Thar, Typic Torrisamment, Rajasthan								
11	0-38	8.0	0.10	2.4	0.7	0.8	0.3	0.3
	38-92	8.2	0.12	2.2	0.7	0.9	0.1	0.4
Coimbatore, Vertic Ustropept, Tamil Nadu								
12	0-15	8.7	0.35	39.1	30.8	6.1	0.9	1.3
	15-42	8.8	0.40	45.2	34.0	7.0	0.5	3.7
Anantapur, Typic Endoaqualf, West Bengal								
13	0-12	5.1	0.49	13.6	4.2	2.2	0.5	1.0
	12-21	6.1	0.30	13.6	5.2	2.8	0.6	1.0

Source: Lal *et al.* (1994)

ative agriculture aiming at increased productivity. Soil properties have much influence on the availability of micronutrients. The extent of micronutrient deficiency therefore varies not only in different states but also in different districts of the same state or in various blocks of the same district, depending upon the soil characteristics and other management conditions.

Analysis of about 2.5 lakh soil samples in different states of India carried out under the All India Coordinated Research Project on micro- and secondary-nutrients and pollutant elements in soils and plants has revealed predominance of Zn-deficiency in divergent soils. Of these samples, 48%, 12%, 5% and 3% samples were deficient in available Zn, Fe, Mn and Cu, respectively. Analysis of more than four thousand samples carried out recently under the same project (Singh, 2006) has revealed that the incidence of Zn-deficiency in the country has decreased (39% samples deficient in Zn) due to regular use of zinc sulphate, the decrease has been sharper in some states like Punjab (Nayyar *et al.*, 2001), where use of zinc sulphate is much higher as compared to other states. Compared to Zn, deficiency of other micronutrients is less in proportion, although extent of boron-deficiency is next to that of Zn (Table 5).

Soils have different inherent problems because of which soil fertility management differs from one set of soils to others. For example, the deficiencies of calcium and boron and toxicity of aluminium are the major fertility constraints to high productivity in acid soils. On the other hand, the concentration of soluble salts and boron are high, while those of Ca and micronutrients are low in the saline sodic soils. Similarly, low nutrient reserves and excessive leaching in sandy soils and impeded drainage and high fixation in black soils require different nutrient management practices. Soil fertility management, thus, involves, many other factors besides nutrients, which all need considerations for its success at a satisfactory level.

Soil fertility management also differs with the cropping pattern because of the differential requirement and preferential absorption of different nutrients. Even in the same cropping system, on different soils, fertility management is likely to differ. For example, in rice–wheat system on sandy soils, the management of nitrogen, phosphorus, zinc, and manganese and on sodic soils, the management of nitrogen, phosphorus, calcium and zinc are the major challenges.

5. Management of Soil Fertility

Efficient nutrient management is the prime concern in the management of optimum soil fertility. It has received maximum attention during the past four decades, as is evident from the fertilizer consumption pattern and its contribution to increasing crop production

Table 5. Extent of micronutrient deficiencies in soils of India*

Name of the state	Per cent deficient samples					
	Zn	Cu	Fe	Mn	B	Mo
Andhra Pradesh	49.4	< 1	3	1	-	-
Assam	34.0	< 1	2	20	-	-
Bihar	54.0	3	6	2	38	-
Gujarat	23.8	40	8	4	2	10
Haryana	60.5	2	20	4	0	28
Himachal Pradesh	42.0	0	27	5	-	-
Jammu & Kashmir	12.0	-	-	-	-	-
Karnataka	72.8	5	35	17	32	-
Kerala	34.0	31	< 1	0	-	-
Madhya Pradesh	43.9	< 1	7	1	22	18
Maharashtra	86	0	24	0	-	-
Meghalaya	57.0	2	0	23	-	-
Orissa	54.0	-	0	0	-	-
Pondichery	8.0	4	2	3	-	-
Punjab	48.1	1	14	2	13	-
Rajasthan	21.0	-	-	-	-	-
Tamil Nadu	58.4	6	17	6	21	-
Uttar Pradesh	45.7	1	6	3	24	-
West Bengal	36.0	0.0	0.0	3.0	68.0	-
All India	48.8	3	12	5	33	13

Source: Singh (1999b)

*Based on 2.5 lakh samples for Zn,Cu, Mn and Fe and 36,825 samples for B.

(Chapter 25). During the early stages, the increase in foodgrain production was mainly due to increase in area of cultivation but after 1970-71, it has largely been due to increase in the productivity. In a successful management of soil fertility, following aspects need consideration:

- Optimum fertilizer rates
- Balanced use of fertilizer nutrients
- Efficient use of fertilizers
- Nutrient needs of cropping system, and
- Integrated nutrient management.

5.1. Optimum Fertilizer Rates

The amount of fertilizer needed by a soil depends upon its nutrient supplying capacity to crop and the requirement of crop *per se*. It is also influenced by soil and climatic conditions and management practices.

Nitrogen is the most limiting nutrient for crop production in Indian soils because of their poor organic carbon content. The response of crops to nitrogen is nearly universal in India, except in hilly region soils containing high organic matter. The chemistry of applied fertilizer in aerobic soils is substantially different from that under submerged rice culture. The efficiency of N-utilization in rice is low and it is a matter of concern because rice alone accounts for about 40% of the total fertilizer N-consumption in India. Rice, wheat, and maize generally respond significantly up to 120 kg N/ha, though at some places responses up to 150-180 kg N/ha have also been reported. (Narang and Bhandari, 1992). Leguminous crops generally require a starter dose of 10 kg N/ha as a bulk of the requirement is met through fixation of atmospheric N.

Deficiency of phosphorus is also widespread in Indian soils. Soils testing low or medium in P require the application of P for realizing optimum yields. Wheat crop is generally highly responsive to P-application compared to rice. In general, wheat responds to P applied up to 60 kg P_2O_5/ha, while in mixed black and red and yellow soils, its response continues up to 120 kg P_2O_5/ha. Similarly, rice also responds generally up to 60kg P_2O_5/ha. However, in medium black soil, very low in available P, it responds up to 90 kg P_2O_5/ha. Studies in the Indo-Gangetic Plains of India have indicated that submergence of soils causes an increase in the solubility of soil phosphates and consequently, rice crop generally shows small or no response to P-application even on soils testing low in available-P.

Response to potassium application on crops is modified by the amount of reserve K and several other factors. Crop responses to K are large on laterites, red, red and yellow, and mixed red and black soils. Crops grown on coarse-textured alluvial soils and some shallow black soils need K fertilization for optimum crop production (Subba Rao and Srinivasa Rao, 1996). Both wheat and rice respond to 25-75 kg K/ha on soils testing low in available-K, depending on soil texture and rate of release of K from clay minerals (Yadvinder-Singh and Bijay-Singh, 2001).

Sulphur deficiency is also becoming widespread in different soils of India. Differential response to sulphur application of different crops has been reported. In Punjab and erstwhile Uttar Pradesh, 20 kg S/ha to groundnut, linseed, pigeon pea and sorghum, 30 kg S/ha to groundnut, wheat, potato, chickpea, black gram and maize and 40 kg S/ha to green gram, and lentil corrected the S-deficiency in crops. In black soils, 30 kg S/ha to green gram, soybean and 50 kg S/ha to potato and 20 kg S/ha to groundnut efficiently corrected S-deficiency. Rice and maize responded significantly up to 60kg S/ha, whereas wheat, and berseem responded up to 90 kg S/ha. Field experiments on oilseeds and pulses with S-application showed a response of 9-19 kg grain per kg of S-applied in the case of oilseeds and 4-10 kg grain per kg of S-applied to pulse crops (Singh, 1999a). The beneficial effects of sulphur application ranging from 2 to 12 q/ha in different cropping systems have earlier been reported (Tandon, 1999).

All acid soils and many sodic soils are inherently deficient in Ca and/or Mg and crops respond to the application of these elements.

Among the micronutrient disorders of crops, zinc-deficiency is critical in many states of India. Response to zinc differs widely among crops in each state as well as across the states. *Kharif* crops generally give a better response to zinc application than *rabi* crops; the magnitude is generally influenced by several factors, such as crops and their cultivars, soil types, deficiency status of zinc and other nutrients, soil environment, climate and cultural practices, etc. The deficiency of zinc, copper, iron and manganese is more common in soils having high pH, high calcium carbonate content, and low organic carbon and clay contents. On the other hand, deficiency of boron and molybdenum is more prevalent in acidic soils; B is also deficient in highly calcareous soils. Over the years, many workers have reviewed the crop response to micronutrient application (Takkar and Nayyar, 1984; Rattan *et al.*, 1997; Nayyar *et al.*, 2001; Chhibba and Nayyar, 2002).

5.2. Balanced Use of Fertilizer Nutrients

Crops remove nutrients continuously from the soils and therefore, their replenishment through fertilizers and manures is essential. The ideal ratio of nutrients for optimal growth varies with soil type, available nutrient status, crops and cropping systems, weather, amounts and kinds of fertilizers applied and their time of application, and use of soil amendments. When the added fertilizer contains nutrients in less (Table 6) or higher amount than that required by the crop, the imbalance thus caused results in poor crop growth. The application of phosphorus along with nitrogen increases the nitrogen-use efficiency. Sometimes even with NP application, decrease in yield occurs because K becomes the limiting factor. Similarly, with optimum dose of NPK, the deficiency of zinc may appear. Soil test based fertilizer recommendations ensure balanced use of fertilizers and increase yield and profits. Balanced fertilizers encompass, besides major nutrients, secondary and micronutrients whose deficiencies appear in different soils in various agro-eco regions due to intensive cultivation.

5.3. Efficient Use of Fertilizer

Increasing nutrient efficiency is the key to the management of soil fertility. The proportion of the added fertilizer actually used by plants is a measure of the fertilizer efficiency. Soil characteristics, crop characteristics and fertilizer management techniques are the major factors that determine fertilizer efficiency.

5.3.1. Soil Characteristics

Nutrient Status of Soil — The response of any crop or a cropping system to added nutrient depends largely upon the inherent capacity of soil to supply that nutrient as per the requirement of the crop. Chemical tests have long been used to estimate the nutrient availability in soils to predict the probability of obtaining profitable response to applied nutrients. On the basis of soil testing, soils are rated low, medium and high in plant nutrients and suitable fertilizer amounts are recommended. In a low nutrient soil, crop responds remarkably to its application. On the other hand, in a high nutrient soil, the crops may show little or no response. In medium test soil, the response is intermediate. Soil testing helps in adjusting the amount of fertilizer and in enhancing the efficiency of fertilizer-use. By demarcating the areas responding differently to different plant nutrients, right type and proper amount of fertilizer can be applied to them.

Table 6. Effect of inadequate and imbalance application of nutrients and integrated management of nutrients on crop yield

Treatments	Yield of finger millet plus maize (q/ha)		
	Mean of initial four years (1987-88 to1990-91)	Mean of last four years (1999-00 to 2002-03)	Mean of 16 years (1987-88 to 2002-03)
50 % NPK	41.1	35.94	41.7
100 % NPK	54.0	65.0	64.6
100 %NPK + FYM	64.1	72.6	73.8
100% NP	30.8	9.6	17.3
100 %N	20.5	7.3	12.4
Control	10.9	7.4	9.1

Source: Sudhir *et al.* (2004)

Table 7. Effect of method of application of nitrogen on ammonia volatilization loss under well-drained conditions as obtained in upland crops such as wheat

Method ofapplication	Ammonia volatilization loss					
	I week		II week		III week	
	mg N	% of applied	mg N	% of applied	mg N	% of applied
Broadcast	13.3	4.4	16.4	5.5	18.8	6.2
Incorporation insurface soil	7.7	2.5	10.4	3.5	12.4	4.1
Placement 2–3 cm below surface	1.6	0.5	3.3	1.1	5.1	1.7

Source: Prasad *et al.* (1999)

Soil testing laboratories in India currently follow identical critical limits for sufficiency or deficiency of plant nutrients, irrespective of the mineralogy or texture of soil or even crop species. However, the amounts of available nutrients depend on the amounts and kinds of nutrient reservoirs and environmental conditions, which influence losses, or transformations of nutrients to less available forms. Hence, critical limits for deficiency or sufficiency of plant nutrients need to be refined for different agro-ecological zones of the country for various crops and cropping sequences to enhance fertilizer-use efficiency.

Forms of Nutrients — Not all pools of nutrients present in soil are available equally to crops. Some nutrient pools even do not show in soil tests but may supply considerable amounts of the nutrient during the crop growth period. For example, sandy soils high in mica may supply sufficient potassium to crops even though the soil tests indicate low available potassium. Responses to potassium in such soils are not expected in a short period but may show up in long-term experiments.

Nutrient Losses and Transformations — The amount of a nutrient estimated by soil tests may not be entirely available to plants because of its leaching, volatilization, denitrification and transformation to unavailable forms. Leaching losses are important for nitrate nitrogen because exchange sites in the soil do not hold it and as such it is lost. Such losses are of particular significance in sandy soils and in situations if heavy rain or irrigation follows its application. In acid soils, leaching losses of calcium, sulphate, potassium and magnesium are more common. Volatilization of ammonia in high pH surface soils is considerable when urea is applied at the surface. Volatilization losses can be significantly reduced when nitrogen is either incorporated or placed below the surface as compared to its broadcast application (Table 7).

Denitrification loss of nitrogen mainly occurs under waterlogged conditions (Table 8) prevailing during rice cultivation, particularly under high temperatures and in the presence of easily decomposable organic materials.

The conversion of a portion of soluble nutrients into insoluble mineral forms is also important. The efficiency of the highly-reactive nutrients like P and Zn is much lower as compared to less-reactive nutrients like N and S due to their interaction with soil components. Thus, the efficiency of added phosphorus is 20-30% and that of Zn is only less than 3%. Microbial immobilization also converts temporarily the soluble forms of nutrients into unavailable forms.

Soil characteristics play a dominant role in the transformation of nutrients. Soil reaction (pH) is one of the important soil properties that affect plant growth. The harmful effects of soil acidity are more due to secondary effects, except in extremes cases. The important secondary effects of high acidity or low pH in a soil are the inadequate supply of calcium, phosphorus and molybdenum on one hand and the excess of soluble aluminium, manganese and iron on the other. Likewise, in saline-alkali soils, the deficiency of Ca, Mg, P, Zn, Fe

Table 8. Proportion of fertilizer N lost and N used under different crop growing environments

Crop	Rate of fertilizer N (kg N/ha)	Fertilizer N lost (%)	Fertilizer N use (%)
Rainfed sorghum	60	10	65
Irrigated wheat	120	25	45
Lowland rice	120	45	35

Source: Katyal (2003)

and Mn is very common. The fertilizer practices are, therefore, to be modified accordingly for soils with different soil reactions. The main aim of liming of acid soils and addition of gypsum to alkali soils is to change the soil pH suitable for the availability of most plant nutrients.

Soil Organic Matter — Soil organic matter is generally considered as the index of soil fertility and sustainability of agricultural systems. It improves the physical and biological properties of soil, protects soil surface from erosion and provides a reservoir of plant nutrients. In tropics, the maintenance of soil organic matter is very difficult because of its rapid decomposition under high temperatures. The cultivation of soil generally decreases its organic carbon content because of increased rate of decomposition by the current agricultural practices. In cultivated soils, prevalent cropping system and associated cultural practices influence the level at which organic matter would stabilize in a particular agro-ecosystem.

Long-term fertilizer experiments have shown that the integrated use of organic manures and chemical fertilizers can maintain high productivity and sustainable crop production (Table 6). Recent studies have indicated that a periodic addition of a large quantity of crop residue to the soil maintains the nitrogen and organic matter contents in adequate levels, even without using legumes in the rotation (Table 9). The application of FYM, compost and cereal residues effectively maintain the soil organic matter. There is a significant increase in soil organic matter due to incorporation of rice or wheat straw into the soil instead of removing or burning it. Yields are, however low in residue-incorporated treatments due to wide C: N ratio of the residues. This ill effect, however, can be avoided if the rice straw is incorporated at least 20 days before seeding wheat.

Soil Moisture — Fertilizer application facilitates root extension into deeper layers and leads to deeper root proliferation in the root zone. Irrigated wheat fertilized with nitrogen used 20-38 mm more water than the unfertilized crop on loamy sand and sandy loam soils and increased dry matter production (Gajri *et al.*, 1989). Soil moisture also affects root growth and plant nutrient absorption. The nu-

Table 9. Effect of soil fertility management on SOC content (g/kg) in long-term fertilizer experiments at some locations in India

Centre	Treatments				
	Control	N	NP	NPK	NPK+FYM
Ludhiana	3.6	3.5	3.7	3.9	4.2
Jabalpur	5.7	6.8	7.5	7.5	11.2
Bangalore	4.4	4.5	4.9	5.6	7.5
Ranchi	3.0	3.0	3.1	3.5	4.0
Bhubaneswar	3.8	4.6	4.6	5.6	8.4

Source: Ghosh *et al.* (2004)

trient absorption is affected not only directly by soil moisture but also indirectly by the effect of water on metabolic activities of plant, soil erosion, soil aeration and concentration of soil solution. If soil moisture becomes a limiting factor during critical stages of crop growth, fertilizer application may adversely affect the yield.

Fertilizer-use efficiency, therefore, depends on a good and steady moisture supply. The interactive effects of nitrogen rates and irrigation levels in a fine loamy Udic Haplustalf are shown in Table 10. With 30 kg N/ha, N-use efficiency was found to significantly increase initially, but decreased when water supply was enhanced further. With 60 kg N/ha, higher water supply was needed as compared to 30 kg N/ha for realizing the maximum nitrogen-use efficiency. Thus, the efficiency of applied N depends on the rate of N-application and the amount of water supply. It is, therefore, desirable to define optimum nutrient needs of soils in relation to available amounts of rainfall and irrigation water in an area. On sandy loam soils, the range of fertilizer N and water supply manipulation is wide for medium yield targets (4-5 tonnes of wheat grain/ha) as compared to higher yield targets (6 tonnes/ha), for which requirements of fertilizer N and water are high.

Physical Conditions of Soil — Despite adequate nutrient supply, unfavourable physical conditions resulting from a combination of the size, shape, arrangement and mineral composition of the soil particles, may lead to poor crop growth and activity of microorganisms. Soil nitrogen generally increases as the texture becomes finer. The basic requirements for crop growth in terms of physical conditions of soil are adequate soil moisture and aeration, optimum soil temperature and freedom from mechanical stress. Tillage, mulching, irrigation, incorporation of organic matter and other amendments like liming of acid soils and addition of gypsum to sodic soils are the major field management techniques that aim at creating soil physical environment suitable for crop growth.

Tillage affects water use by crops not only through its effect on root growth but also by modifying the hydrological properties of soils. Mulching with residues (Table 11), plastic film, etc. influences evaporation losses from soil by altering the hydro-thermal regime of the soil, besides affecting root growth and rooting pattern. Use of organic mulch also decreases maximum soil temperature in summers and increases minimum soil temperature in winters and helps in the conservation of soil moisture.

5.3.2. Crop Characteristics

Nutrient Uptake — The total amount of nutrients removed by a crop may not serve as an accurate guide for fertilizer recommendations; it does, however, indicate the differences in their requirements among crops and the rate at which the nutrient reserves in the soil are depleted. The nutrient uptake may vary depending upon the crops and their cultivars, nutrient levels in the soil, soil type, soil and climatic conditions, plant population and management practices. It is estimated that 8 tonnes of rice

Table 10. Effect of irrigation (I) and nitrogen (N) on nitrogen-use efficiency in sunflower crop

(kg of seed / kg of N)

Nitrogen rate (kg/ha)	Irrigation (IW/CPE)			
	$I_{0.6}$	$I_{0.8}$	$I_{1.0}$	$I_{1.2}$
N_0	1.00	1.00	1.00	1.00
N_{30}	7.60	19.94	19.03	17.40
N_{60}	5.27	10.90	12.90	9.93
N_{90}	5.94	7.54	8.00	7.29
	Nitrogen (N)	Irrigation (I)	Interaction (I×N)	
CD (P = 0.05)	0.17	0.50	0.34	

Source: Taha *et al.* (1999)

Table 11. Effect of mulches on the grain yield and partial factor productivity N (PPF_N) of wheat under rainfed conditions at Palampur

Mulch	60 kg N/ha		120 kg N/ha	
	Grain (t/ha)	PPF_N	Grain (t/ha)	PPF_N
No mulch	1.7	-	2.0	-
Lantana	3.1	23.3	3.5	12.5
Eupitorium	2.3	10.0	3.2	10.0

Source: Prasad (2007)

grain remove about 160 kg N, 38 kg P, 224 kg K, 24 kg S, and 320 g zinc as compared to a removal of 125 kg N, 20 kg P, 125 kg K, 23 kg S and 280 g zinc by 5 tonnes of wheat from one hectare field (Tandon and Narayan, 1990).

Root Characteristics — Roots are the principal organs of nutrient absorption. A proper understanding of their characteristics helps in developing efficient fertilizer practices. The absorption of nutrients depends upon the distribution of roots in soil. The shallower the root system, the more dependant is the plant on fertilizers. Hence, any soil manipulation, which encourages deep rooting, will encourage better utilization of fertilizers. It is well known that some plants are better scavengers of certain nutrients than others. This is mainly because of the preferential absorption of these nutrients by the roots of those plants. For example, legumes have a marked preference for divalent cations like Ca^{2+}, whereas grasses feed better on monovalent cations like K^+.

The efficiency of applied fertilizers can be improved considerably if the rooting habits of various plants during the early growth are known. This is particularly true for relatively immobile nutrients and for situations where the fixation of applied nutrients is very high. If a plant produces tap root system early, fertilizer can best be placed directly below the seed. On the other hand, if lateral roots are formed early, side placement of fertilizer would be helpful.

Mycorrhizal fungi often associated with plant roots, increase the ability of plants to absorb nutrients, particularly under low soil fertility. However, fertilizer additions generally reduce their presence and activity.

Crop Rotation — The nature of cropping has a profound effect on the fertilizer requirement and its efficiency. Crops are known to differ in their feeding capacities on applied as well as native nutrients. The crops requiring high levels of fertilizers such as maize, potato, may not use the applied fertilizer fully and some amount of the nutrients may be left in the soil, which can be utilized by the succeeding crop. Phosphorus, among the major nutrients, is worthy of consideration because not more than 20% of the applied phosphatic fertilizer is usually utilized by the first crop. Similarly, such direct usage is even less than 3% of the applied zinc. The magnitude of the residual effect is, however, dependent on the rate and kind of fertilizer used, cropping and management system followed and to a great extent on the type of soil. Crops have a tendency of luxurious consumption of N and K and may not leave any residual effect unless doses in excess of the crop requirement are applied. On the other hand, if sub-optimal doses of fertilizers are applied to a crop, they may leave the soil in a much-exhausted condition and the fertilizer requirement of the succeeding crop may increase. The legumes leave nitrogen-rich root residues in the soil for the succeeding crop and thus reduce its nitrogen requirement.

5.3.3. Fertilizer Characteristics and Management Techniques

The efficiency of a fertilizer varies to a large extent on the type of fertilizer, time of application and method of application.

Type of Fertilizer — Fertilizers differ in both their nutrient content and forms. In the case of nitrogenous fertilizers, the nutrient may be present in ammonium, nitrate or amide form. Similarly, in the case of phosphatic fertilizers, phosphorus may be present in water-soluble, citrate-soluble, or citrate-insoluble form. The nutrient content of a fertilizer may also differ considerably. Thus, the total nitrogen-content of calcium ammonium nitrate is 25% as compared to 46% of urea, 20.5% of ammonium sulphate and 82% of anhydrous ammonia. Nitrogen may also be present as one of the components of the combined fertilizer sources such as 18% in diammonium phosphate, 13% in potassium nitrate. Similarly single superphosphate will supply only 16% P_2O_5 as compared 46% P_2O_5 supplied by diammonium phosphate or triple superphosphate. The K_2O content of potassium chloride is 60%. The fertilizers may also differ in their water solubility and their ability to get fixed in the soil. Nitrate fertilizers have higher water solubility and are subject to leaching in higher rainfall areas or due to heavy irrigation, as these do not interact with the soil constituents upon their addition to soil and thus move to greater depths.

Generally, all sources of fertilizer N have been shown to be equally efficient in upland soils, but ammoniacal and amide forms of N are more efficient as compared to nitrate sources of N for submerged rice soils. Phosphatic fertilizers containing phosphorus in water-soluble forms like diammonium phosphate and single superphosphate have been found superior for most of the crops in neutral or alkaline soils as compared to citrate-soluble or citrate-insoluble form. Both single superphosphate and diammoinium phosphate have proved equally efficient on the basis of equivalent phosphate content, but single superphosphate has the advantage in soils low in available sulphur and particularly for sulphur-loving crops like oilseeds and pulses. Rock phosphate, which has phosphate in water-insoluble form, has proved useful in acid soils, rice soils or for long-duration legumes. Nitrophosphates with more than 60% water-soluble P have shown promise as efficient sources of P in alkaline soils.

The entire quantify of fertilizer K used in Indian agriculture is imported and is largely in the form of muriate of potash with only about 1% as sulphate of potash. In highly leached acid soils, where sulphate leaching is expected to have caused S-deficiency, potassium sulphate should be preferred. For certain crops like tobacco, which are chloride sensitive, potassium sulphate should be applied.

Straight micronutrient carriers like zinc sulphate, ferrous sulphate, manganese sulphate and copper sulphate have been found to be superior and economical as compared to other sources of micronutrient cations. Management of micronutrient deficiencies in Indian soils have been reviewed by several workers (Takkar and Nayyar, 1986; Takkar 1996; Nayyar 1999; Nayyar *et al.*, 2001; Chhibba and Nayyar, 2002).

Time of Application — Time of fertilizer application is important, particularly for those nitrogenous fertilizers which tend to leach with irrigation water or rainfall. Split application of nitrogen is the common and widely accepted practice for almost all crops. The basic concept is to apply nitrogen in two or more splits to coincide with peak period of nitrogen requirements of the crop. Nitrogen application in split doses is particularly beneficial on light-textured soils for increasing its efficiency. Its application in three split doses to rice at transplanting, tillering and panicle initiation and at planting, knee high stage and teaselling stage of maize, is usually recommended. In general, crops grown in rainy season should receive nitrogen fertilizers in split doses so that the leaching of nutrients during heavy rains may be reduced and an adequate supply of the nutrient at critical stages is ensured.

For crops like wheat, barley, *Brassica* sp, which are grown in winter when the rains are scanty, best results are obtained when the entire dose of nitrogen is applied as a basal dose in medium to heavy textured soils and on light soils in two equal splits at sowing and at first irrigation. Some studies have shown that nitrogen application in the form of urea preceding pre-sowing irrigation even in a loamy sand soil gives higher grain yield of wheat as compared to its application at preparatory tillage and increases both nitrogen-use efficiency (7 to 34%) and water-use efficiency (2 to 24%) at different nitrogen and irrigation levels (Sidhu *et al.*, 1994). For unirrigated crops, however, split application is useful. Plant N status has been used to indicate the time of application of N, particularly for rice using Minolta™ chlorophyll meter (SPAD 502 model) or leaf colour chart (LCC). Researches have shown that LCC-based fertilizer N management saved 27-56 kg N/ha in Punjab, 19-39 kg N/ha in Haryana, 30 kg N/ha in Uttarakhand, 30-40 kg N/ha in Bihar and 20 kg N/ha in West Bengal as compared to fixed-time blanket N recommendation or farmer's practice (Yadvinder-Singh, 2005).

In the case of phosphatic and potassic fertilizers as well as for zinc and copper among micronutrient cations, all the quantity applied at sowing gives the best results with most of the crops. However, in the case of iron and manganese, foliar sprays of these nutrients are recommended. In the case of manganese, foliar sprays initiated 2-3 days before the first irrigation to wheat, have been found to be significantly superior to their application after the first irrigation (Takkar *et al.*, 1986). Similarly, foliar application of iron should be initiated as soon as the symptoms of its deficiency appear on crops.

Method of Application — Various techniques have been developed to improve the efficiency of applied nutrients. Since nitrates are easily leached and lost by denitrifiaction, retardation of the nitrification of ammonium-containing or ammonium-producing fertilizers by using nitrification inhibitors in rice fields subjected to intermittent flooding has been found helpful in increasing the nitrogen-use efficiency. Chemical nitrification inhibitors as well as indigenous materials such as *neem* (*Azadirachta indica*) and *karanj* (*Pongamia glabra*) cakes have been successfully used, except on highly coarse-textured soils of Punjab. Also, some slow release nitrogen materials like urea-form, isobutylidene diurea as well as coated fertilizers such as sulphur-coated urea, lac-coated urea, etc. have been used to reduce the nitrogen losses.

Root zone placement of urea supergranules or urea briquettes appears to be a better way of placing N (although it presents some difficulties) in rice fields for reducing volatilization losses as ammonia, particularly in high pH soils. In coarse-textured soils of Punjab, urea applied in three equal splits has shown a better performance than urea supergranules and *neem*-coated urea applied at transplanting. Single application of sulphur-coated urea has been found to be more efficient than urea application in three splits (Table 12). Placement of fertilizer N in both summer and winter crops is superior to its broadcast application in increasing the yield of crops. Placement of N also prevents volatilization losses. Foliar application of nitrogen as supplement to soil application has been found useful under rainfed conditions.

The band placement of water-soluble phosphatic fertilizers is better than its broadcast as it reduces its fixation (Table 13). However, phosphates of low water solubility react slowly in soil and are usually more effective as a source of phosphorus when broadcast. When rock phosphate is used in rice culture, it should

Table 12. Relative efficiency of modified urea fertilizers applied basally @ 40 kg N/ha in flood prone lowland rice at Cuttack

Urea fertilizers	Relative grain yield	Agronomic efficiency (kg grain/kg N)	Apparent N recovery (%)
No N	100	-	-
Prilled urea	140	26	18
Urea supergranules	158	39	40
Sulphur-coated urea	164	45	45
Lac-coated urea	140	29	26
*Neem*cake-coated urea	135	22	16
Coal tar-coated urea	128	18	15
FYM-enriched urea	147	30	29

Source: Sharma (1994)

Table 13. Relative efficiency of methods of application of P on grain of crops under dryland agriculture conditions

Method of P application	Finger millet	Chikpea	Soybean
Broadcast	100	100	100
Drilled	132	137	169
Mixed with seed	129	118	135

Source: Srinivasa Rao *et al.* (2003)

be mixed with soils 15-30 days before rice planting.

Split application of potassium is expected to increase its efficiency in situations where leaching losses are considerable either because of light texture of the soil or long duration of the crop. Beneficial effects of split application have been observed in sugarcane and rice. For fruit crops, 2–6 splits have been recommended, depending upon the crop.

Application of sulphur in neutral to calcareous soils is equally efficient in correcting its deficiency whether broadcast, drilled or applied in split doses. In standing crop of wheat, top dressing of ammonium sulphate is beneficial.

For efficient utilization of applied zinc, the best time of its application for wheat and rice is at seeding or transplanting of the crop (Takkar, 1996). Among different methods, broadcasting and mixing of zinc is more efficient than its drilling or band placing and top dressing 60 days after seeding. Application of zinc sulphate @ 25-50 kg /ha to soil is superior to foliar spray of 0.5% zinc sulphate solution neutralized with lime. The lower efficiency of the foliar mode is primarily due to delayed cure of the deficiency as well as the low concentration of Zn in the spray solution. Other methods of zinc application such as coating or soaking of seeds in zinc solution, dipping rice seedling roots in ZnO suspension and transplanting zinc enriched nursery have proved either inferior to or at par with soil application of zinc (Nayyar *et al.*, 2001).

Foliar sprays of 0.5 to 1.0% manganese sulphate solution have been found more effective and economical as compared to soil application of manganese (20 kg Mn/ha) in manganese-deficient sandy loams of Punjab (Nayyar *et al.*, 2001).

Soil application of ferrous sulphate in coarse-textured soils for rice is less efficient than foliar sprays. However, for upland crops, the soil-applied iron has been found to be as effective as foliar sprays (Nayyar *et al.*, 2001).

5.4. Nutrient Needs of Cropping System

The needs of a cropping system should take into account the long-term implications of nutrient management where direct, residual, and cumulative effects of applied fertilizers are taken into consideration. The cropping pattern in irrigated ecosystem at present is a cereal-cereal system due to its higher yields, low risks and adequate support price from the government. Most of the long-term studies thus far have been focussed on such cropping systems.

The cropping system approach helps in optimizing the scheduling of fertilizer application, especially for immobile nutrients like phosphorus and zinc. The phosphorus should preferably be applied to *rabi* crops in the cropping sequence and has been confirmed in maize-wheat, groundnut–wheat and pigeonpea–wheat rotations. However, soils, which are highly deficient in available phosphorus, may be the exceptions where fertilizer P application is needed to all the crops in a system.

5.5. Integrated Nutrient Management

Integrated nutrient management (INM) envisages the use of chemical fertilizers in conjunction with organic manures, legumes in cropping systems, biofertilizers, crop residues and other locally available nutrient sources for sustaining soil health and productivity. The combined application of organic manures and chemical fertilizers generally produces higher crop yields than when each is applied alone. This increase in crop productivity may be due to the combined effect of nutrient supply, synergism and improvement in soil physical and biological properties. Farmyard manure constitutes an important component of integrated nutrient management for maintaining soil fertility and yield stability. The long-term fertilizer experiments, which are in operation in different agroecological regions on intensive cropping under irrigated conditions, have revealed that only optimum doses of NPK in combination with FYM can sustain high yields.

Green manures are also valuable sources of N to a considerable extent and of organic matter to a lesser extent. Sesbania, sunnhemp and cowpea incorporated before transplanting rice partially meet the nutrient requirement, especially of N, of the crop. In upland crops, the most efficient time of incorporation of green manure crops has been found to be 15 days before seeding the main crop. Besides being a source of P, K, S and micronutrients, green manure influences availability of the most of the nutrients through its favourable impact on oxidation-reduction regime, pH, and increased chelation capacity. In permeable coarse-textured soils, green manuring helps in correcting the iron chlorosis in rice. Green manuring helps in the reclamation of salt-affected soil and improvement in physical and biological properties of soil.

Growing legumes in rotation and incorporation of legume residues after picking of pods also significantly improve the yield of cereal crop in rotation. The efficiency of incorporation of *Azolla* in increasing grain yield and nitrogen uptake of rice depends on the temperature of a region. Also, several problems like very high or very low temperature, grazing by invertebrates, pesticides, irrigation and drainage limit widescale use of *Azolla*, besides it being labour-intensive.

The integrated nutrient management approach has now assumed great importance in view of the increasing negative nutrient balance as well as realization of the fact that neither chemical fertilizers nor the organic sources alone can achieve the production sustainability of crops and cropping systems under highly intensive cropping systems. The integrated nutrient management helps in restoring and sustaining soil fertility and crop productivity by optimizing the physical, chemical and biological environment of soils and bringing economy and efficiency in fertilizers applications.

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Chapter 27

Soil and Water Quality

M.C. MANNA and K.L. SHARMA

1. Introduction

It is only after meeting the basic physiological needs of air, water and food that the humankind begins to consider about safety and other aspects of life, like the environment in which it lives. Sustaining soil quality is the most effective method for ensuring sufficient food to support life. By soil quality we mean suitability or limitation of a soil for a particular use. Some scientists define it as the 'fitness for use' (Pierce and Larson, 1993), and others as the 'capacity of the soil to function' (Karlen *et al.*, 1997). For improving and ensuring soil and water quality, the main considerations should be identification and development of suitable methods to measure their quality. Then, the management-sensitive key indicators of soil and water quality should be identified and used for monitoring and predicting the changes periodically.

2. Soil Quality and Soil Health

The term *soil quality* and *soil health* are often used interchangeably in the scientific literature; scientists, in general, prefer 'soil quality' and producers prefer 'soil health' (Harris and Bezdicek, 1994). '*Soil quality*' is the capacity of a specific kind of soil to function within ecosystem and land-use boundaries, to sustain biological productivity, maintain environmental quality, and sustain plant, animal, and human health (Doran and Parkin, 1994). '*Soil health*' is defined as being a state of dynamic equilibrium between flora and fauna and their surrounding soil environment in which all the metabolic activities of the former proceed optimally without any hindrance, stress or impedance from the latter (Goswami and Rattan, 1992). Soil health is considered as the state of a soil at a particular time, equivalent to the dynamic soil properties that change in short-term, while soil quality may be considered as soil usefulness for a particular purpose over a long time scale, equivalent to intrinsic or static soil quality (Goswami, 2006).

Soil quality lists at least six diverse simultaneous functions, viz. (i) Biomass production, (ii) Filtering, buffering and transformation actions, (iii) Source of biodiversity, (iv) Infrastructure development (roads, railways, waterways, homestead/farmstead, etc.), (v) Source of geogenic, and (vi) Cultural heritages of landform/ soilscape and in some cases concealing paleontological/ archaeological treasurers that must be optimized to achieve high rating of soil quality, to sustain (1) plant and animal productivity, (2) maintain or enhance water and air quality, and (3) support human health and habitation.

The perception that soil is a "living" matter, though disputed by some, results from the observation that the number of living organisms in a fertile soil (10 g) can exceed nine billion, one and a-half times of the human population on the earth. Soils form slowly, averaging 100-400 years per centimetre of topsoil, through the interaction of climate, topography and a myriad of living organisms (earthworms, insects, bacteria, fungi, algae, nematodes, animals, plants, human kind, etc.). Thus, the physical and chemical attributes of soil regulate biological activity and interchanges of molecules/ions between the solid, liquid and gaseous phases, which influence nutrient cycling, plant growth, and organic matter decomposition. The inorganic components of soil play a major role in retaining cations through ion exchange and non-polar organic compounds and anions through sorption reactions.

3. Specific Soil Functions

The sustenance of soil quality depends on the understanding of how soils respond to agricultural use and practices over time. In order to develop best management practices, it is necessary to develop methods to assess the soil quality over a period of time. The standards of soil quality are needed to determine what is sustainable and what is not, and to determine if soil management systems are functioning at acceptable levels of performance (Figure 1). Karlen *et al.* (1997) have defined five major soil functions, which are:

1. Sustaining biological diversity, and productivity;
2. Regulating and partitioning water and solute flow;
3. Filtering, buffering, degrading, immobilizing, and detoxifying organic and inorganic materials, including industrial and municipal by-products and atmospheric deposition;
4. Storing and cycling nutrients and other elements within the earth's biosphere, and
5. Providing support of socioeconomic structures and protection for archeological treasures associated with human habitation.

4. Interrelationship among Soil Quality, Soil Resilience and Soil Resistance

4.1. Soil Degradation

Soil degradation is an autonym of soil quality. Soil degradation is a major concern of modern times because of its adverse impacts on productivity, human and animal health, air and water quality, especially on local, regional and

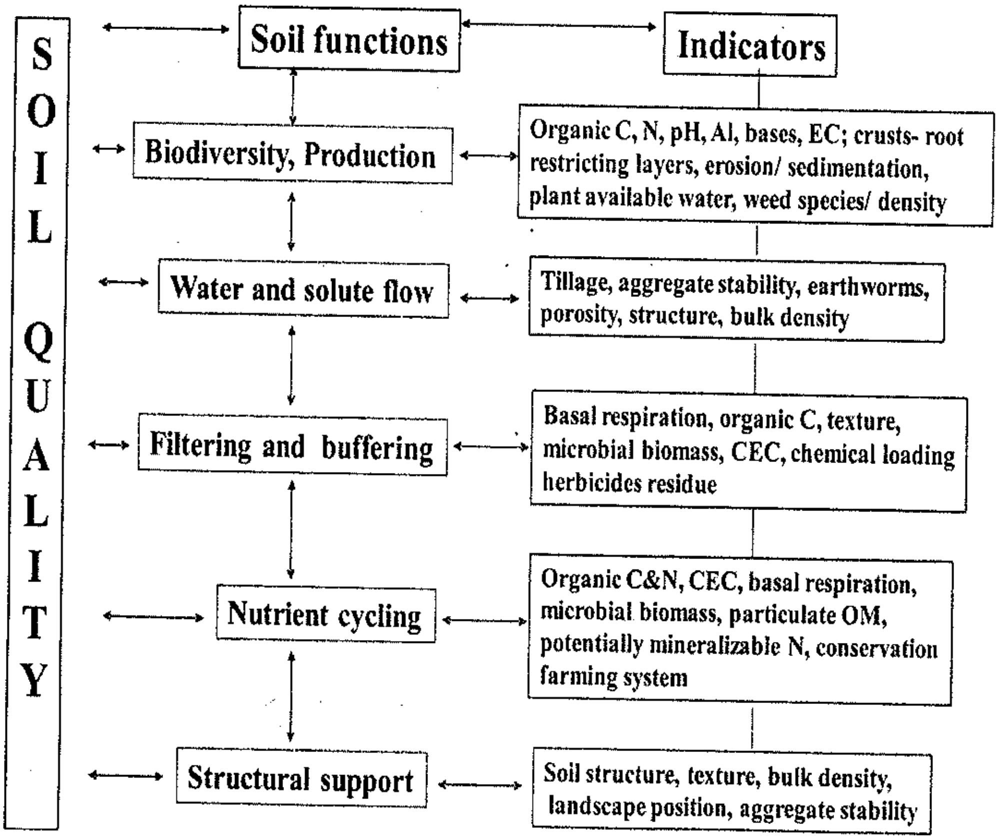

Figure 1. A schematic representation of the concept of soil quality

Source: Seybold *et al.* (1996)

Table 1. Common soil stress and related degradative processes

Stress	Principal degradative processes
Heavy load due to extensive mechanization (vehicular traffic)	Physical degradation, e.g., crusting, compaction, structural decline and poor soil tilth
High intensity rain and overland flow, high wind velocity	Accelerated erosion by water and wind
High evaporation demand and high salt concentration in the profile	Drought, aridization or desertification, salinization or sodification
Poor internal drainage, and slow surface drainage	Soil wetness and anaerobiasis
Intensive cropping	Chemical degradation, nutrient imbalance and soil organic matter depletion
Intensive use of agrochemicals and monoculture	Biological degradation, acidification and reduction in soil biodiversity

global scales. About 43% of earth's vegetated surface has diminished its capacity of supplying benefits to humankind as a result of improper land-use decisions (Daily, 1995). Common soil degradative process in agricultural systems may be erosion, leaching, hard setting and compaction, fertility depletion, loss of organic matter, etc. Each degradative process is involved with specific stress (Table 1). There are no critical limits of soil degradative processes because they depend on intrinsic soil characteristics. Intrinsic properties governing soil resilience, which are related to soil quality include, soil structure, soil water retention and transmission properties, cation-exchange capacity, exchangeable cations, soil organic carbon (SOC), nutrient supplying capacity, and soil pH, etc.

4.2. Soil Resilience

'Soil resilience' means ability of a system to return after disturbance to a new dynamic equilibrium or ability of a soil to resist adverse changes under a given set of ecological and land-use conditions and to return to its original dynamic equilibrium after disturbance. It was introduced to create a common theory that describes the reaction of soil to a range of impacts or disturbances. A disturbance is broadly defined as any event that causes a significant change from the normal pattern or functioning of an ecosystem. Whether an event is considered to "cause a significant change from the normal pattern or functioning" depends on the temporal and spatial scale of interest. Natural disturbances and causes of disturbance include fires, earthquakes, floods, landslides and high-intensity storms. Anthropogenic disturbances include human activities associated with land use and land management. These 'disturbances', encompass waterlogging, grazing, urban and industrial developments, recreation, annual cropping, etc.

4.3. Soil Resistance

'Soil resistance', distinct from soil resilience, is defined as 'the capacity of a soil to continue to function without change throughout disturbance'. The magnitude of decline in the capacity to function defines the degree of resistance to change (Figure 2a). A small decline indicates a high resistance, whereas a relatively large decline indicates a low resistance to change through a disturbance. The distinction between soil resistance and soil resilience has been illustrated in an example using soil function related to soil physical properties on an annual time scale (Figure 2b). The resistant soils can maintain their functioning capacity at a higher level throughout the year than those that have a lower resistance, but are resilient on an annual time scale. Resistance and resilience are the two key measures of sustainability and both are dependent on soil type (including soil biota) and vegetation, climate and land use, disturbance regime at temporal as well as spatial scales. Sustainability is based on a long-term maintenance of soil functions or soil quality. The capacity of a soil to resist and recover from the minor stresses and disturbances can be enhanced through appropriate management (Figure 2c). Management of soil quality enhances soil resilience, and the resilient soils respond to management. For example, management practices that increase soil organic matter levels will improve most of the soil functions. Soil resistance can indicate the degree to which a soil will recover from a particular cropping or management system. In an annual cropping system, soil may recover in a hysteretic manner in which it doesn't fully recover before the next cropping cycle is imposed (Figure 2d). Each year the same hysteretic effect occurs until, eventually, the soil's capacity to restore itself and its quality are significantly degraded. This concept explains the decline in organic matter levels of tilled soils from the time they were brought under agricultural operations.

4.3.1. Quantitative Assessment of Soil Resilience

Three primary approaches for determining soil resilience are: (i) measuring the recovery of soil after degradation directly, (ii) identifying and quantifying the integrity of the mechanisms that contribute to soil resilience after disturbance, and (iii) measuring specific properties that serve as indicators of soil recovery mechanisms. This first approach requires monitoring of the rate and mode of recovery of soil after it is degraded. Long-term studies may be required if the soil has low resilience to a particular disturbance. The second approach to gauging resilience requires quantifying the functioning capacity associated with the recovery mechanisms after a disturbance. If critical recovery mechanisms are still functioning, recovery can occur. However, it will depend on the rate or kinetics of the recovery processes or mechanisms. If a soil has completely lost its recovery processes, the soil and ecosystem it supports, may become permanently degraded, resulting in lower production capacity. This new, stable lower functioning capacity can become very resistant to change. In the third approach, indicators of soil resilience are used to measure the capacity of the soil to restore

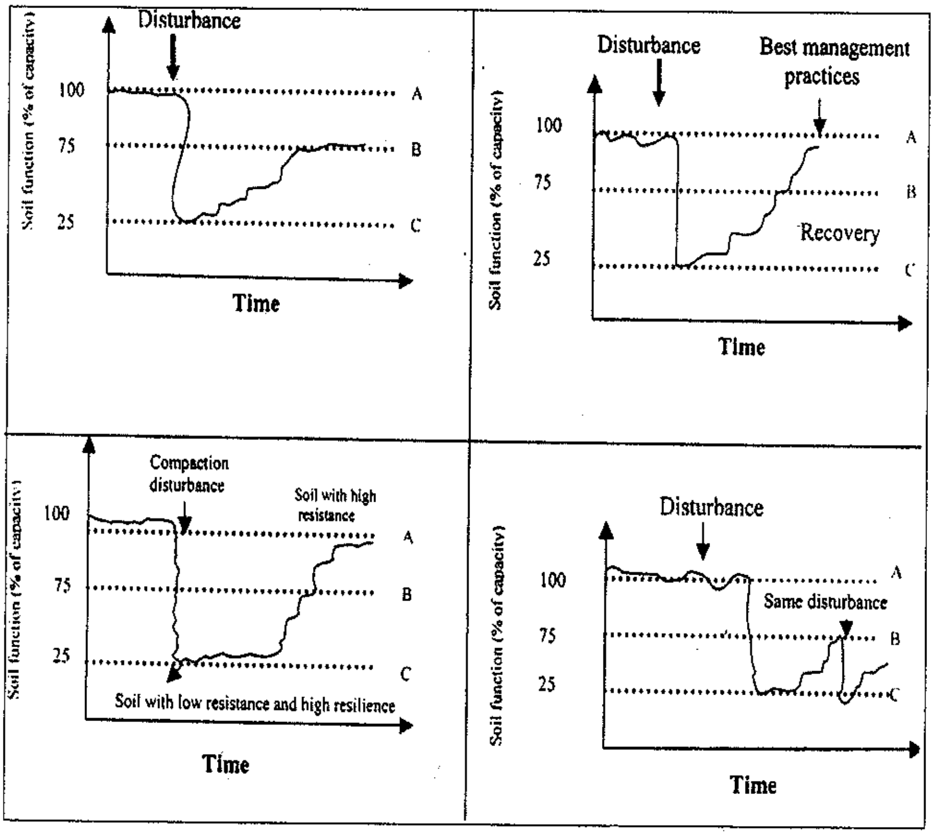

Figure 2. Effects of disturbance and resilience on soil functions: (a) general concept; (b) two soils with difference in resilience and resistance; (c) positive management impacts on soil resilience; and (d) repeat disturbances without sufficient recovery

or recover its function. This aspect is similar to that proposed for the assessment of soil quality.

Soil resilience is a dynamic property and it depends on the soil's status at the time of assessment. Herrick and Wander (1998) have observed that the time scale of interest, nature of disturbance, level of recovery expected, and the type and amount of inputs needed to support recovery must be known for assessment of soil resilience. It can be quantified experimentally by measuring the rate [Eq. (1)] or extent [Eq. (2)], of recovery after a disturbance. Resistance can be expressed simply as the ratio of the capacity of the soil to function after a disturbance to its pre-disturbance capacity [Eq. (3)] (Herrick and Wander, 1998):

$$\text{Recovery rate} = d[(B - C)/(A - C)]/dt \quad \ldots(1)$$

$$\text{Recovery extent} = (B - C)/(A - C) \quad \ldots(2)$$

$$\text{Resistance} = C/A \quad \ldots(3)$$

where, A is the pre-disturbance functioning capacity of the soil, B is the level of recovery to a stabilized equilibrium level of soil functioning, and C is the level of soil function immediately after the disturbance (Figure 2a). Therefore, soil resilience is directly related to the soil quality and the factors affecting it. The capacity of a soil to function (soil quality) cannot be measured directly, but it can be gauzed indirectly through indicators of those functions (Karlen *el al.*, 1997; Seybold *et al.*, 1998).

4.3.2. Mechanism of Soil Recovery

Recovery of different soil functions varies widely. Often multiple mechanisms occur simultaneously, and each may affect one or more soil functions. A multitude of soil and plant community processes, including physical, chemical and biological mechanisms, contribute to soil recovery (Table 2). Many resilience mechanisms can be viewed as they contribute directly to various soil functions (Table 2). Nearly all processes associated with soil formation contribute to soil resilience. The most important factors controlling recovery of degraded soil are floral and faunal activities, including microbial activity and climate.

Soil quality can be expressed by Equation [4]:

$$\text{Soil quality (SQ)} = f(W_c \times S_c \times R_d \times E_d \times N_c \times B_d)t \quad \ldots(4)$$

where, SQ is the soil quality, t is time, W_c is water capacity or non-limiting water range, S_c is structural index, R_d is rooting depth, E_d is charge density or measurement of CEC, N_c is nutrient supplying capacity, and B_d is soil biodiversity.

From Equation (4), soil resilience can be expressed as:

$$S_r = f(\text{SQ, land use, management})\ t \quad \ldots(5)$$

where, S_r is soil resilience. Resistance is inversely proportional to loss of soil functional integrity following perturbation, while resilience is proportional to the recovery of functional integrity (Figures 2a, 2b, 2c and 2d).

5. Assessment of Soil Quality

Ecosystem concept such as functions, processes, attributes, and indicators is a useful

Table 2. Soil function and associated recovery processes or mechanisms

Soil function	Recovery processes or mechanism
Nutrient cycling	Biological activity, biological diversity and plant growths, partitioning of water, soil faunal activity, shrink-swell cycles, plant growth. Freeze-thaw cycles, aggregation, vegetation establishment.
Productivity	C-sequestration, aggregation, nutrient cycling, biological diversity
Water storage	C-sequestration, aggregation process, biological activity
Decomposition	Biological activity
Absorption and detoxication of pollutants	Biological activity, C-sequestration, biological diversity, mineral weathering, clay formation

framework to describe soil quality. Soil quality has two aspects: (i) "intrinsic" part covering a soil's inherent capacity for crop growth, and (ii) "dynamic" part, which is influenced by the soil users.

5.1. Inherent Soil Quality

The quality of a soil depends on its natural or inherent composition, which is a function of geological and topographical features. Attributes of inherent soil quality, such as mineralogy and particle size distribution, are mainly viewed as almost static and usually show little change over time. Characterization of inherent soil quality for crop production also involves consideration of "extrinsic factors" that influence crop yield, such as climate (i.e. precipitation, evaporation and air, temperature).

Generally, inherent soil quality for crop production cannot be evaluated independent of extrinsic factors. For example, high clay content may be favoured in a semiarid region, where soil moisture retention is an advantage, but may be understandable in humid conditions in which poor internal drainage may limit crop yields. Similarly, a certain soil bulk density can be optimal under a semi-arid moisture regime, but it may not be so under a humid moisture regime due to changes in relative saturation and the subsequent poor soil aeration. Thus, there is no universally applicable set of inherent soil quality criteria and optimum values. "Inherent soil quality" can be assessed using national land resource or soil survey inventories.

5.2. Dynamic Soil Quality

'Dynamic soil quality' encompasses those soil properties that can change over a relatively short time period (i.e. soil organic matter, labile soil organic carbon (SOC) fractions, soil structural components, and macro-porosity) in response to human activities and management and are strongly influenced by agronomic practices.

'Soil quality attributes' are the measurable soil properties that influence the capacity of a soil to perform a specific function. In many cases, a specific property may be difficult to measure directly. *'Soil quality indicator'* is used to serve as an indirect practical measurement of the attributes. For the dynamic soil quality, indicators are most useful when they indicate or measure changes in the attribute. Various studies have attempted to identify sets of attributes or properties that can characterize a soil process or processes with regard to a specific soil function. Assessment of each of the chosen indicators is completed with a quantitative measurement, made either in the field or laboratory. The soil quality indicators should be estimated easily, cost-effective and highly reproducible, and should be useful across a range of ecological and socioeconomic situations. An indicator should:

1. Correlate well with natural processes in the ecosystem,
2. Integrate soil physical, chemical and biological properties and processes and serve as basic inputs needed for estimation of soil properties or functions, which are more difficult to measure directly,
3. Be relatively easy to use under field conditions and be assessable by many users.
4. Be sensitive to variations in management and climate. The indicator should be sensitive enough to reflect the influence of management and climate on long-term changes in soil quality, but not be so sensitive as to be influenced by short-term weather patterns, and
5. Be the components of the existing soil databases, wherever possible.

The suitability of indicators (soil properties) used for assessing soil quality can vary from location to location, depending on the kind of land or land-use, soil function, and soil forming factors.

5.3. Minimum Dataset for Soil Quality Assessment

Effective identification of appropriate indicators for soil quality assessment depends on the ability of any approach to consider the multiple components of soil function for productivity in particular and environmental well-being in general. Identification of indicators and assessment approaches are further complicated by the multiplicity of physical, chemical and biological factors, which control biogeochemical processes and their variations in intensity over time and space. The two highest priority needs are: (i) establishment of reference guidelines and thresholds for indicators of soil quality that enable identification of relationships between measured soil attributes and soil function which permit valid comparisons across variations in climate, soils, land-use and management systems, and (ii) development of a practical index for on-site assessment of soil quality and health for use by farmers, researchers, extension workers, and environmental monitors. It can also be used by resource managers and policymakers to determine the sustainability of land management practices. The proposed minimum data set has been described in Table 3.

The assessments of production sustainability should be based on two components; first, non-declining crop yield trends, and second, stability of yield from crop cycle to crop cycle. A good ecological indicator should be one that is universal in distribution, reflects crucial aspects of the functioning of the ecosystem, shows prompt and accurate response to an external perturbation and is readily and economically measurable. Based on many studies, the widely used indices of biological soil quality are: soil organic matter, soil respiration, specific activity ratio and nitrogen mineralizations. Soil microbial biomass carbon, particulate organic matter and hydrolysable carbohydrates are considered as biologically active fractions of soil organic matter and are sensitive indicators of management-induced changes. Dehydrogenase activity, has been widely used as a generalized comparative index of microbial activity, but it has not always been correlated with microbial activity.

Once the indicators of soil function are selected, reference/ baseline values for these indicators need to be established for a compari-

Table 3. Minimum data set recommended for physical, chemical and biological indicators for screening the quality or health of soils

Indicators	Relationship to soil conditions and functions
	Physical
Texture	Retention and transport of water and chemicals; modelling use, soil erosion and variability estimate
Effective depth of soil and rooting	Estimates of productivity potential and erosion; normalizes landscape and geographic variability
Infiltration and soil bulk density	Potential for leaching, productivity, and erosivity; bulk density
Water holding capacity (water retention characteristics)	Related to water retention, transport, and erosivity; available H_2O calculated from bulk density, texture, and SOM
	Chemical
Soil organic carbon	Defines soil fertility, stability, and erosion extent; use in process models and for site normalization
pH	Defines biological and chemical activity thresholds; essential to process modelling
Electrical conductivity	Defines plant and microbial activity thresholds; presently lacking in most process models
Extractable N, P, and K	Plant-available nutrients and potential for N loss; productivity and environmental quality indicators
	Biological
Microbial biomass C and N	Microbial catalytic potential and repository for C and N; modelling: early warning of management effects on SOM
Potentially mineralizable N	Soil productivity and N-supplying potential; mineralizable N; process modelling (surrogate indicator of biomass)
Soil respiration	Microbial activity measure (in some cases plants); process modelling; estimate of biomass activity

Source: Doran *et al.* (1996); Larson and Pierce (1994) son, so that a soil's degree of excellence can be ascertained. Following two approaches are used for quantifying and assessing soil quality:

- Monitoring of Trends Approach, and
- Reference Values.

5.3.1. Monitoring of Trend Approach

Monitoring trends are useful for the soil quality evaluation at plot, field and farm scales. Individual indicators may evaluate trend lines. If the change in a soil quality indicator is positive, and 'more is of better quality', then the soil can be regarded as improving or aggrading in quality with respect to that indicator (Figure 3.). If the trend line is negative for that indicator, then quality is degrading. A no-change in soil quality or its indicators means sustaining. A disadvantage of this approach is that it requires measurement of soil quality over a period of time. In addition, this approach is somewhat misleading if a soil is functioning at the highest level attainable and cannot improve, or if it is functioning at its lowest level and cannot go lower; both cases show a static or no-change trend, indicating a sustaining system.

The trend line equation can be written as per Equation (6):

$$Y = a + bt \qquad \ldots(6)$$

where, 'Y' is the individual indicator, 'a' is the intercept (indicates initial value) and 'b' is the slope (magnitude or rate of change).

From Equation (6), the negative or positive yield trend could be significantly related with soil organic matter trend under long-term field experiment. This indicates that soil organic matter is one of the soil quality indicators and its maintenance in soil improves the physical, chemical and biological properties of a soil. Negative values indicate that long-term application of imbalanced fertilizer degrades the soil quality attributes as well as its productivity, whereas a balanced use of fertilizer in combination with organics either sustains or improves soil quality attributes (Table 4).

5.3.2. Reference Values

In 'reference approach', soil quality requires establishment of baseline values for various indicators, and measuring changes in those indicators over time. Changes in the indicators reflect the combined effects of land-use and climate. Three different situations for which a specific kind of soil may function at maximum capacity are: (1) the native state, (2) the intensively managed state (the capacity to function is usually lower than the native state), and (3) the altered state (the capacity to function is usually higher than at the native state).

Reference values are developed for each indicator and consist of a maximum value and baseline value, and the values in between are target values for good soil quality (Figure 4). The maximum value represents the maximum potential that can be obtained by an indicator under a given land-use, and the baseline value represents the minimum acceptable potential. For the soils in their native condition, reference values represent the inherent ability of a

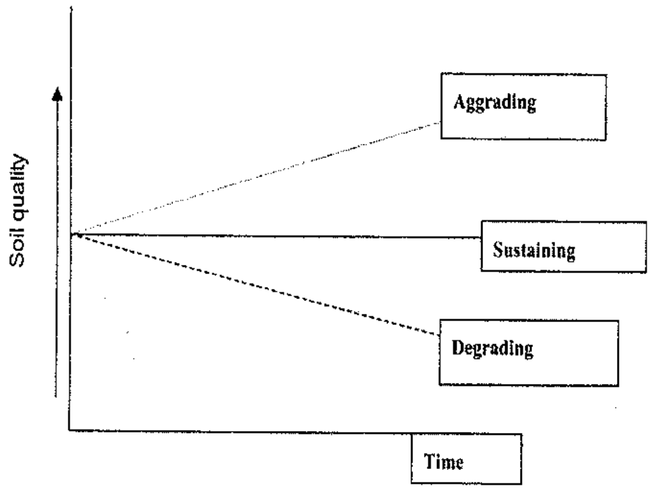

Figure 3. Monitoring trends in soil quality over time

Table 4. Relationship between soil organic carbon (SOC) and yield trends at different locations under different nutrient management systems

Location	Treatments	Rate of yield change magnitude (Mg/ha/yr) *(b)*	Intercept / Initial value of yield (Mg/ha) *(a)*	Rate of SOC changes magnitude (Mg/ha/yr) *(b)*	Initial value of SOC (g/kg) *(a)*
Barrackpore	N	-0.054	3.29	-0.044	6.35
(Rice-Wheat-Jute, 30 years)	NP	-0.044	3.21	-0.017	5.00
(Typic Eutrochept)	NPK	-0.046	3.35	0.078	4.64
	NPK+FYM	-0.030	3.30	0.066	5.05
Ranchi	N	-0.020	0.71	-0.008	3.7
(Soybean-wheat, 30years)	NP	-0.013	1.78	-0.017	3.8
(Typic Haplustalf)	NPK	0.034	1.87	-0.011	4.1
	NPK+FYM	0.002	1.97	0.003	4.2
Akola	N	-0.82	2.11	0.032	4.5
(Sorghum-wheat)	NP	-0.68	2.60	0.066	4.6
(Typic Haplustert)	NPK	0.048	2.48	0.076	4.5
	NPK+FYM	0.077	2.53	0.115	5.8

Note: Intercept *(a)* is considered as initial value either yield or SOC; *(b)* is the slope value indicating the rate of change of magnitude. *Source*: Modified from Manna *et al.* (2005)

soil to function, as defined by the soil forming factors and processes. Scoring functions for soil quality indicators can be developed from the reference values for each group of similar soils. Sometimes, the references values of scoring functions do not represent real situations.

6. Major Factors Affecting Soil Quality

The major causes of poor soil quality are:

(1) Wide gap between nutrient demand and supply,

(2) High nutrient turnover in soil plant system coupled with low and imbalanced fertilizer use,

(3) Emerging deficiency of secondary and micronutrients due to improper use of inputs such as water, fertilizers, pesticides, etc.,

(4) Insufficient use of organic inputs,

(5) Acidification and Al^{3+} toxicity,

(6) Development of salinity and alkalinity in soils,

(7) Development of adverse soil conditions such as heavy metal toxicity,

(8) Disproportionate growth of microbial population responsible for soil sickness, and

(9) Natural and manmade calamities such as erosion, deforestation occurring due to rapid industrialization and urbanization, etc.

7. Quantitative Estimation of Soil Quality

There are many approaches that are used for soil quality evaluation. In all these cases, minimum data set can be used. Among them, the following approaches are more important:

(i) Comparative assessment,

(ii) Dynamic assessment,

(iii) Common statistical approach — Regression analysis,

(iv) Pedotransfer functions,

(v) Standardize scoring function based on threshold limits and base line values, and

(vi) Principal component analysis (PCA).

(i) Comparative Assessment

In a comparative assessment of soil quality, the performance of a system can be evaluated in relation to alternatives at a given time

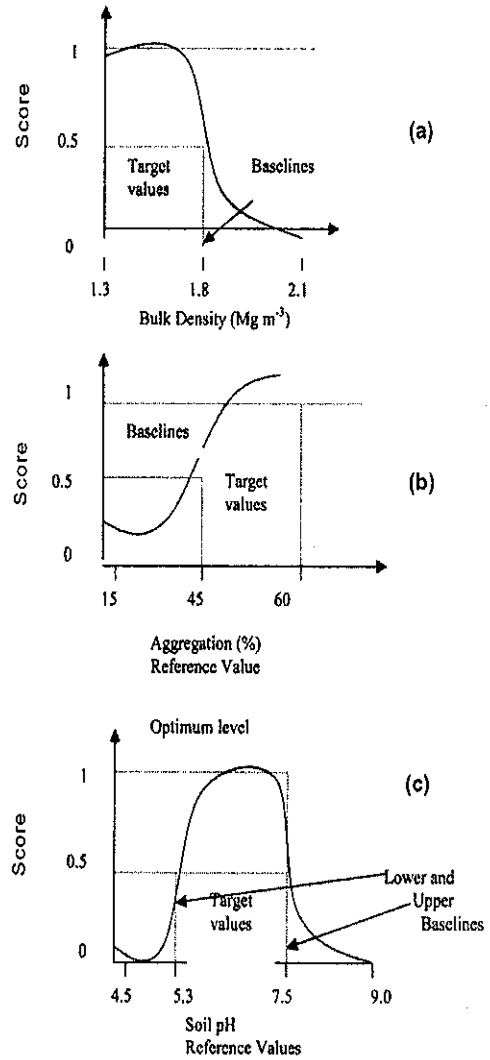

Figure 4. Scoring functions for soil quality indicators developed from reference value. Three situations are (a) less is better, (b) more is better, and (c) optimum level
Source: Karlen *et al.* (1994)

only. For example, after 15-30 years of cultivation, some soil quality parameters get significantly changed over the initial soil quality attributes due to land-use management practices (Table 5).

ii) Dynamic Assessment

In a dynamic assessment, performance of a system can be evaluated in relation to alternatives across time. The dynamic assessment approach should include the following steps:

- Explicit identification of the desired outputs of a management (productivity, erodability, human, animal health, etc.)
- Assessment of the design of the system to determine if it will produce the desired output,
- Identification of soil quality parameters,
- Establishment of the starting point for evaluation of a management system; historical record of the site should be maintained, and
- Stabilization of a system process that is out-of-control. A stable system of variation is one of which the variation is solely a result of the system in place; and there are no special causes of variation.

Larson and Pierce (1991) proposed that soil quality (Q) can be expressed as a function of attributes of soil quality (q_i) that can be written as Equation (7):

$$Q = f(q_i, \ldots\ldots, q_n) \qquad \ldots(7)$$

In the recent literature the term 'indicators' has been used rather than attributes and soil quality index (SQI) has been used to represent Q. Examples of soil quality attributes (q_i) are soil organic matter, texture, structure, pH, electrical conductivity, etc. From Equation (7), the magnitude of Q is the collective contribution of all qs, from q_i to q_n.

It is also suggested that soil degradation can be evaluated by measuring q_i at different time periods. Then, the dynamic change in soil quality, dQ/dt, can be quantified as per Equation (8):

$$dQ/dt = f\,[\,(\{q_{it} - q_{ito}\}/q_{ito} \ldots\ldots\ldots\ldots(\{q_{nt} - q_{nto}\}/q_{nto})]/dt \qquad \ldots(8)$$

where, dQ/dt is the dynamic change; t_0 is the initial time and t is the time when q is measured.

An aggrading soil would have a positive dQ/dt and a degrading soil would have a negative dQ/dt. The functional relationship from Equation (8) is difficult to define, and it is impossible to describe Q in terms of all soil attributes. Thus, Larson and Pierce (1991) proposed a minimum data set in combination with pedotransfer function to monitor the changes in soil quality.

(iii) Regression Analysis: Multiple Regression Model

Multiple linear regressions can be used to calculate soil quality index of crop productivity using soil attributes as

Table 5. A comparative assessment of some indicative soil quality parameters of long-term effect of fertilizer and manure experiments in Inceptisols (30 years), Alfisols (30 years) and Vertisols (15 years) of India

Soil quality parameters	Inceptisol Typic Eutrochrept			Typic Haplustalf			Typic Haplusters		
	Initial	NPK	NPK+FYM	Initial	NPK	NPK+FYM	Initial	NPK	NPK+FYM
Bulk density (g/cm)	1.35	1.3	1.27	1.35	1.36	1.28	1.26	1.26	1.25
Water stable aggregates (WSA) (%) (< 250 mm)	39.3	24.0	40.4	25.2	21.6	24.8	73.12	71.7	80.19
Organic carbon (g/kg)	7.14	7.4	7.9	4.5	4.2	4.5	4.6	6.1	7.0
Total N (mg/kg)	960	867	927	500	505	570	440	486	590
pH (1:2, soil:water)	7.1	6.9	7.28	5.3	4.9	5.31	8.1	8.1	8
Cation exchange capacity [cmol(p$^+$)kg^{-1}]	19.1	24	31	7.8	7.2	9.9	48.1	48.2	49.9
Available-N (kg/ha)	223	273	285	295	331	392.9	120	290	319
Available-P (kg/ha)	41.5	63	83.7	12.6	64.35	75.5	8.4	25.6	29.56
Available-K (kg/ha)	143	192	225	157.6	164.1	177.8	358	356	445
Soil microbial biomass carbon (SMBC) (mg/kg)	-	398	576	-	210	231		382	465
Soil microbial biomass nitrogen (SMBN) (mg/kg)	-	14	18.7	-	13.62	14.5		13.3	16.4
Hot water soluble C (mg/kg)	-	69	80.4	-	18.5	23.5		22.3	27
Soluble carbohydrates (mg/kg)	-	689	845	-	466	517		625	796
Soil respiration (SR) (mg CO_2-C/100g/10days)	-	37	49.7	-	22.7	24.1	-	25.9	33.3
	-	86	118.4	-	54.7	62.6	-	41.3	44.41
Alkaline phosphatase (*p*-nitrophenol, g/hour)	-	191	223.2	-	170.8	301.5	-	220	225.3

$$Y = (a+b_1X_1+b_2X_2+\ldots\ldots\ldots\ldots+b_nX_n) \qquad \ldots(9)$$

where, Y is the crop yield; X_1, X_2,......., X_n are different soil properties; and a, b_1, b_2,......,b_n are coefficients of soil attributes.

The significant coefficient values of soil attributes are selected for calculating soil quality index.

In the next step, the actual value of soil attributes and crop yield are normalized as Xi by the relation:

$$Xi = \frac{\text{Observed value of the soil attributes or crop yield } (X_0)}{\text{Maximum value of the soil attributes or crop yield } (X_m)}$$

The Xi may be taken as 1 for the values of X_0 exceeding X_m. The normalization can be done to extend the applicability of the model under diverse soils and climates.

In the next step, the normalized values of the selected soil properties are individually subjected to regression with normalized crop yield to determine their coefficient of determination, R^2, whose proportionate variation can be obtained and expressed as Ai. Thus:

$$Ai = Ri^2 / \Sigma Ri^2 \qquad \ldots(10)$$

And the soil quality index (SQI) can be calculated as per Equation (11):

$$SQI = \sum_{i=1}^{n} Ai * Xi \qquad \ldots(11)$$

where, n is the number of properties, and Xi should be significant by *t*-test. Thereafter, SQI can be calculated for the normalized values of soil properties and plotted against the corresponding normalized crop yields. A second-degree polynomial can be fitted to the data. Higher the SQI, better is the performance.

(iv) Pedotransfer Functions

A pedotransfer function is a mathematical function that relates soil characteristics and properties with one another using minimum data set for evaluation of soil quality. Many pedotransfer functions (PTFs) occur in the literature and are statistical or empirical in nature. Some selected PTFs are given in Table 6.

These mathematical functions are related to soil characteristics and properties with one another for use in the evaluation of soil quality.

(v) Scoring Functions

Scoring functions are based on threshold limits and base line values (Karlen and Scott, 1994). These functions are used to transform the measured indicator values into performance-based score for soil quality index. The five steps followed in this method are:

(i) Choosing the function for soil quality as related to defined goal.

(ii) Selecting the minimum data set of indicators that best represent soil functions.

(iii) Assigning relative weights to each function. All weights within each function must

Table 6. A list of selected pedotransfer functions

Estimate	Relationship
Cation exchange capacity	CEC= a OC +bC
Phosphate–sorption capacity	PSC = 0.4 (Al_{ox} + Fe_{ox})
Change in organic matter	C = a + b OC
Bulk density	Db = f (OC + clay)
Water retention	Q = b_1 (% Sa) + b_2 (% Si) + b_3 (% C) + b_4 (% OC)
Porosity increase	P = f (MR + IP + Clay + Si + OC)
Hydraulic conductivity	K^s = f (texture)
Soil productivity	PI = f (Db+ AWHC + pH + EC + ARE)

Db = Bulk density; Si = Per cent silt; Sa = Per cent sand; C = Clay; PSC= Phosphate sorption capacity; Al_{ox} = Oxalate extractable aluminium; Fe_{ox} = Oxalate–extractable iron; OM = Organic matter; IP = Initial porosity; ARE = Aeration; AWHC = Available water holding capacity; EC = Electrical conductivity.

sum to 1.0 or the decimal equivalent of 100 %. Use standard scoring functions by converting numerical or subject rating to unitless values on 0-1 scale.

(iv) Establishing an appropriate scoring function and realistic base line and threshold values for each indicator. Information from specific database can be used for these processes, but the source and reason for selection must be documented. Four of the most common shapes for scoring functions are: grouped together and assigned a relative weight based on importance (Figure 5). For example, the function of plant productivity 'more is better' for SOC, 'less is better' for bulk density, and 'an optimum range' for pH (Wymore, 1993).

(v) Scoring the indicators based on their performance of soil function. After scoring each factor, the value is multiplied by the appropriate weight. When all the indicators for a particular function are scored, the user has to prepare a matrix that can be summed to provide a soil quality rating as related to productivity or any degradative process such as soil erosion by water, etc.

For example, to compute an index based on nutrients, water, and plant rooting relationships for the various management practices, the parameters affecting each of them are grouped, as shown in Table 7. It should be noted that some parameters such as SOC are included in more than one of the critical relationships. During the grouping of the parameters for the scoring function, the prime requirement is that the rationale such as expected ranges, base line and threshold values, should be well documented. A relative weight or importance for each parameter associated with a specific relationship is then chosen and entered into a spreadsheet. Measured values for each management practices are entered in this spreadsheet. This value is scored based on the mathematical equations that describe the various standard-scoring functions. Soil quality rating with regard to score can be computed by summing the weighted score for each critical function using Equation (12):

$$SQI = q_{nr}(wt) + q_{wr}(wt) + q_{rr}(wt) \qquad \ldots(12)$$

where, SQI is the soil quality index; q_{nr} is the nutrient relation; q_{wr} is the water relation and

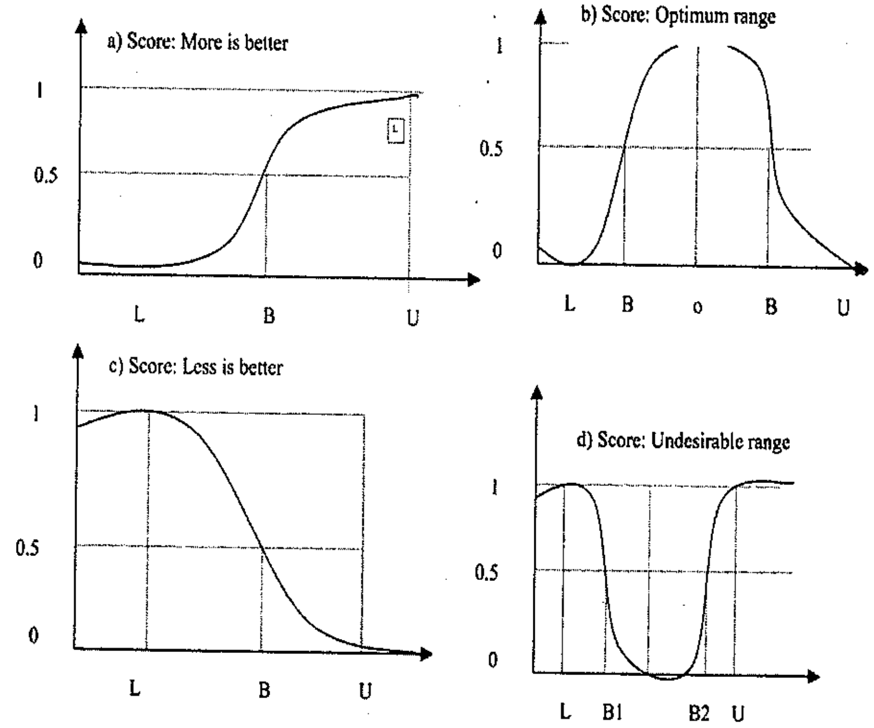

Figure 5. The general shapes for standard scoring functions, (a) more is better; (b) optimum range; (c) less is better; and (d) undesirable range. The letters L, B, U refer to lower threshold, baseline, upper threshold values, respectively

Source: Wymore (1993)

Table 7. Soil quality functions and indicators related to erosion by water

Function	Weight	Level I	Weight	Level II	Weight	Level III	Weight
Accommodate water entry	0.50	Infiltration rate	1.0	Surface crust	0.20	Texture	0.50
						Thickness	0.20
						Strength	0.20
						Formation rate	0.10
				Surface roughness	0.20		
				Crop residue cover	0.50		
				Macropores	0.10	Plant root	0.40
						Earthworms	0.60
Facilitate water transfer and absorption	0.10	Hydraulic conductivity	0.60	Soil texture	0.50		
				Capillary water content	0.30		
				Bulk density	0.20		
		Porosity	0.15				
		Macropores	0.25	Plant roots	0.40		
				Earthworms	0.60		
Resist degradation	0.35	Aggregate stability	0.80	Mineralogy	0.20	Physical bonding	0.50
		Shear strength	0.10			Chemical bonding	0.50
		Soil texture	0.05	Soil carbohydrates	0.35	Labile organic C	0.60
		Heat transfer capacity	0.05			Recalcitrant organic C	0.40
				Microbial biomass	0.30	Fungal hyphae	0.50
						Actinomycetes	0.30
						Bacteria	0.20
				Available cations	0.15		
Sustain plant growth	0.05	Rooting depth	0.25	Restrictive layer depth	0.70		
				Texture	0.30		
		Water relations	0.35	PAWC*	0.70		
				Drainage	0.20		
				Organic C	0.10		
		Nutrient relations	0.30	pH	0.15		
				Organic C	0.25		
				Macronutrients	0.40	N	0.50
						P	0.25
						K	0.25
				Secondary nutrientsCa,Mg, S	0.10		
				Micronutrients B,Cu,Fe, Mn,Zn	0.10		
		Chemical barriers	0.10	Salinity	0.50		
				Heavy metals	0.15		
				Pesticides	0.25		
				Radioactive elements	0.10		

*PAWC= Plant available water capacity; *Source:* Larson and Pierce (1994)

q_{rr} is the rooting relations. From this hypothetical example, SQI can be assessed for computing plant productivity index component of SQI using scoring function approach (Table 8). From this scoring function, the relative performance of management can be evaluated without the use of simulation model. This simplest technique can be used for the assessment of soil quality.

(vi) Principal Component Analysis

The principal component analysis (PCA) is a useful multivariate statistical tool that has the advantage of generating relationships among many correlated variables into a few principle components (PCs). These can be classified as soil quality indicators with respect to the specific soil functions. Changes in the properties or soil attributes associated with a PC can be used to classify soil quality as aggrading, degrading or stable. In this method, four steps are followed: (i) define the goal, (ii) select a minimum data set (MDS) of indicators that best represent soil function, (iii) score the MDS based on performance of soil function, and (iv) integrate the indicator scores into a comparative index of soil quality.

Step-1: The first step in evaluating soil quality, as with any ecosystem management practice, is the identification of management goals (or soil functions) specific to the site in question. Some of the goals could be, crop yields, productivity, sustainability yield index, water erosion, etc.

Step-2: Selection of a minimum data set (MDS): Minimum Data Set is considered as the smallest set of soil properties that can best represent human-induced changes in the area, which could be used either individually or in combination, as in a soil quality index, to assess this effect on soil condition (Larson and Pierce, 1991; Gregorich *et al.*, 1994; Yemefack *et al.*, 2006). In other words, MDS for evaluating soil quality is the smallest set of chemical, physical, and biological indicators that account for at least 70% of the variability in the whole soil data set at each site obtained through multivariate statistical techniques. To select a representative MDS, only those soil properties that show significant treatment variation are selected. For choosing a MDS multivariate statistical techniques, viz. principal component analysis could be employed to minimize disciplinary bias (Andrews and Carroll, 2001). The measured soil properties and yield of crop are performed using a correlation matrix of the statistical analysis.

The principal component analysis for a data set is defined as a linear combination of variables that account for the maximum variance within the set by describing vectors of closest fit to the "n" number of observations in p-dimensional space, subject to being orthogonal to one another. In other words, Principal Component Analysis (PCA) is a mathematical procedure that transforms a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables called principal components. The principal components receiving high eigen values and variables with high factor loading are assumed to be variables that best represent systems attributes. Therefore, only PCs with eigen values ≥ 1 and those that explain at least 5 % of the variation in the data are examined. Within each PC, only highly weighted factors are retained for MDS. Highly weighted factor loadings are defined as having absolute values within 10% of the highest factor loading. When more than one factor is retained under a single PC, multivariate correlation coefficient will be employed to determine if the variables could be considered redundant and therefore, eliminated from the MDS.

To maximize the correlations between PCs and measured attributes, the retained PCs are subjected to varimax rotation. Well-correlated variables are considered redundant and only one is considered for the MDS. The rest are eliminated from the data set. If the highly weighted variables are not correlated, each of them is considered important and will be retained in the MDS. As a check of how well the MDS represents the management system goal, multiple regressions are performed using the indicators retained in the MDS of independent variables and end point measures like yield as dependent variables. If any variable within the MDS does not contribute to the coefficient of determinant of multiple regressions of the variables, it is also dropped from the MDS.

Table 8. Spreadsheet for computing the plant productivity component of a SQI using scoring function approach

Function	Weight	Attributes	Expected range	Type of curve	Weight	Lower threshold	Upper threshold	Lower base line	Lower slope	Optimum value	Measured value	Score	Score × weight
Nutrient relation	0.33	Bray P	7.5-150 mg/kg	Optimum	0.15	7.5	150	16	0.235	30	38	0.999	0.150
		Exchangeable K	45-525 mg/kg	Optimum	0.15	45	525	85	0.050	175	267	1	0.150
		pH	3.5-9.5	Optimum	0.20	3.5	9.5	5.3	1.67	6.50	6.30	0.999	0.200
		Organic carbon	5-65 g/kg	More is better	0.40	5	65	20	0.133	-	23.9	0.889	0.356
		NO_3^--N	3-50 mg/kg	Optimum	0.10	3	50	12	0.222	25	1.00	0	0.000
Water relation	0.33	Surface residue	1000-18000 Mg/ha	Optimum	0.25	1000	18000	3000	0.001	10000	7620	1	0.250
		Porosity	20-80%	Optimum	0.20	20	80	40	0.200	50	60	0	0.000
		Organic C	5-65 g/kg	More is better	0.20	5	65	20	0.133	-	23.9	0.889	0.178
		Aggregate stability	15-70%	More is better	0.35	15	70	30	0.133	-	40	0.995	0.348
Rooting relation	0.34	pH	3.5-9.5	Optimum	0.35	3.5	9.5	5.3	1.67	6.50	6.30	0.999	0.350
		Bulk density	1.2-2.1 g/cm	Less is better	0.35	1.20	2.10	1.45	-8.00	-	1.07	1	0.350
		Rooting depth	60-250 cm	More is better	0.20	60	250	125	0.031	-	150	0.956	0.191
		Organic C	5-65 g/kg	More is better	0.10	5	65	20	0.133	-	23.9	0.889	0.089
Nutrient relation (Nr)												0.856^A	0.282
Water relation (Wr)												0.776^B	0.256
Rooting relation (Rr)												0.980^C	0.333

For computing the plant productivity component of a soil quality index using scoring function = (0.282 +0.256+0.333) = 0.872

A =Score × weight of Nutrient relations (Nr); B= Score × weight of water relations (Wr); and C= Score × weight of rooting relations (Rr) 0.40

Step-3: After determining the MDS indicators, every observation of each MDS indicator should be transformed using a linear scoring method (Andrews *et al.*, 2002). Indicators should be arranged in order depending on whether a higher value is considered " good" or "bad" in terms of soil function. For 'more-is-better' indicators, each observation should be divided by the highest observed value so that the highest value should receive a maximum score of 1. For 'less-is-better' indicators, the lowest observed value (in the numerator) will be divided by each observation (in the numerator) such that the lowest observed value receives a score of 1.

Step-4: Once transformed, the MDS variables for each observation are weighted using PCA results. Each PC explains a certain amount (%) of the variation in the total data set. This per cent variation, divided by the total percentage of variation explained by all the PCs with eigen vectors >1, provides the weighted factor for variables chosen under a given PC. The weighted MDS variable scores for each observation should be summed up using Equation (13):

$$SQI = \Sigma\, Wi \times Si \qquad \ldots(13)$$

where, Si is the score for the subscripted variables and Wi is the weighted factor derived from the PCA. The calculated SQI treatment means could be compared using ANOVA and student's t at $P = 0.10$. There is no standard threshold limit of SQI values. Here, the assumption is that higher index scores meant better soil quality or greater performance of soil function.

7.1. Soil Health Scorecard

The preparation of a soil health card is a qualitative approach, which depicts both the capacity of a soil to perform certain functions (infiltration, decomposing, cycling of nutrient and others) and soil attributes (structure, soil colour, root morphology, earthworms and others).

In the scorecard, each soil health indicator is operationized to conform to the following subject rating scale:

1. **Healthy:** Performance of function is optimal and structure is normal.
2. **Impaired:** An abnormality in function and or structure.
3. **Unhealthy:** Severe restriction or inability to perform normal function, severe deformity or loss of structure, disabled.

In the scorecard's soil health scale, the majority of indicator properties are directly measured by the senses (look, smell, or feel). Indicators of soil health vary in quality or character rather than in a specific measurable quantity. The scale used in the scorecard does not measure the exact magnitude of difference among healthy, impaired, and unhealthy categories, meaning that the scale is at the ordinary level of management. Farmer's based soil health scorecard can be computed from Table 9.

8. Soil Organic Matter and its Significance in Soil Quality

Soil organic matter (SOM) is an important attribute of soil quality. It influences the physical, chemical and biological properties and processes of soil. It regulates energy and nutrients for soil biota, aggregates stability, water retention, hydraulic properties, resistance or resilience to compaction, buffering capacity, cation exchange capacity, and formation of soluble and insoluble complexes with metals. The most important biological properties of organic matter are: (i) its role as a reservoir of metabolizable energy for soil microbial and faunal activities, (ii) its effects in stabilizing enzyme activities, and (iii) its values as a source of plant nutrition through mineralization.

Soil organic matter attributes (microbial biomass C and N) are very sensitive to changes in total soil organic matter and could be utilized, based on their relative simple and straightforward methodology, as indicators of change. Recently, a wider range of labile soil organic matter attributes such as light fraction of organic matter, particulate organic matter (POM, < 53 μm), water-soluble carbon, acid-hydrolysable carbohydrates and potentially-mineralizable fraction of carbon are more sensitive to changes in management. Little attention has been paid towards labile pools of carbon as compared to total organic carbon in most agricultural soils. Typically, organic mat-

Table 9. Farmer's based assessment for soil health scorecards (Scale corresponding to healthy (3-4); impaired (1.5-2.5), and unhealthy (0-1)

Score	Soil health state
	1. Earthworms
0	Little sign of worm activity
2	Few worms holes or casting
4	Worm holes and casting are numerous
	2. Erosion
0	Serve erosion, considerable topsoil moved and gullies formed.
2	Moderate erosion, signs of sheet and rill erosion and some top soil blows
4	Little erosion evident, topsoil resist erosion by water and wind
	3. Tillage
0	Plough scours hard and soil never works down.
2	Soil grabs plough, is difficult to work, and needs extra passes.
4	Plough field in higher gear and soil flows and falls apart and is mellow.
	4. Soil Structure
0	Soil is cloddy with big chunk or is dusty and powdery
2	Soil is lumpy or does not hold together.
4	Soil is crumbly and granular.
	5. Colour (moist)
0	Soil colour is tan, light yellow, orange, light gray.
2	Soil colour is brown, gray or reddish
4	Soil colour is black, dark brown or dark gray
	6. Compaction
0	Soil is tight and compacted, cannot get into it, and there is a thick hard pan.
2	Soil packs down, thin hardpan or plough layer.
4	Soil stay loose, does not pack, and there is no hard pan
	7. Infiltration
0	Water does not soak in; it sits on top or runs off.
2	Water soaks in slowly and is slow to dry out.
4	Soil drains at good rate for crops, and water moves through.
	8. Drainage
0	Poor drainage, soil, if often waterlogged or oversaturated,
2	Soil drains slowly and is slow to dry out
4	Soil drains at good rate for crops, and water moves through.
	9. Water retention
0	Soil dries out too fast and is droughty.
2	Soil is drought-prone in dry weather.
4	Soil holds moisture well and gives and takes water easily.
	10. Decomposition
0	Residue and manure do not break down in soil.
2	Slow rotting of residues and manures.
4	Rapid rotting of residues and manures.
	11. Soil fertility
0	Poor fertility, nutrient don't move, and potential is very low.
2	Fertility not balanced and needs help
4	Fertility is balanced, nutrients available, and potential is high
	12. Feel
0	Soil is mucky, greasy or sticky.
2	Soil is smooth or grainy and compressed when squeezed.
4	Soil is loose, fluffy, and opens up after being squeezed.
	13. Surface crust
0	Soil surface is hard, cracked when dry, and compacted
2	Surface is smooth with few holes and has thin crust.
4	Surface does not crust, is porous, and digs easily with hand.
	14. Surface cover
0	Soil surface is clean, bare, and residue is removed or buried following harvest.
2	Surface has little residue, it is mostly buried.
4	Surface is trashy, lots of mulch left on top or cover crop used.
	15. Hardness
0	Soil is hard, dense or solid, and will not break between two fingers.
2	Soil is firm and break up between fingers under moderate pressure.
4	Soil is soft and crumbles under light pressure.
	16. Smell
0	Soil has a sour, putrid, or chemical smell.
2	Soil has no odor or mineral smell.
4	Soil has an earthy, sweet, fresh smell.
	17. Soil texture
0	Texture is a problem; extremely sandy, clayey, or rocky.
2	Texture is too heavy or too light but presents no problem.
4	Texture is loamy.
	18. Aeration
0	Soil is light, closed, and there are almost no pores.
2	Soil is dense and has a few pores.
4	Soil is open, porous, and breathes.
	19. Biological activity
0	Soil shows little biological activity, no signs of soil microbes
2	Moderate biological activity; some worm like threads, moss, and algae.
4	Biological activity is high; white worm like threads, moss and algae are plenty.
	20. Top soil depth
0	Subsoil is exposed or near surface.
2	Topsoil shallow.
4	Topsoil is deep.

ter levels decline rapidly when soil under native vegetation is converted to arable agriculture in the first 10-20 years and then stabilize at a new equilibrium level. Many factors contribute to loss of SOM levels such as lower allocation of carbon to the soil, removal or burning of crop residue, tillage-induced aggregates disruption, more favourable condition for decomposition and greater losses of surface soil by water erosion.

Factors that increase organic matter under arable agriculture include a decreasing proportion of fallow in rotation, an increase in the proportion of cereal as compared to root crops, an increasing proportion of perennial crops in rotation, return of crop residue rather than burying or removal, improve root biomass and crop growth with better fertilizer and irrigation conditions and addition of organic manure or other organic wastes. Similarly, perturbations to the soil system such as conversion of native vegetation to arable agriculture cause large changes in SOM-content in soil. These are reflected in labile and stabilized SOM-fractions in soil. In addition, labile fraction (LF) has a disproportionately large effect on nutrient supplying capacity and structural stability of soil. In agricultural soil, the light fraction typically contain 20-30% C, 5-20% N, 22-18% of total C, and 1-16% of total N in the whole soil. Particulate organic matter contains 20-45% of TOC and 13-40% of TON in the whole soil. Particulate organic carbon is the precursor for formation of soil microbial biomass carbon, soluble fractions of carbon, humic and non-humic fractions of carbon in soil and thus, it is a key attribute of soil quality. It is the major source of cellular C and energy for the heterotrophic microorganisms.

The particulate organic matter (POM) decomposition is also the major pathway by which nutrients are recycled from crop residues back to the soil and release nutrients by mineralization during decomposition of POM. The large POM maintains soil structure and macro-aggregation. The large amount of microbial community associated with the decomposing POM produces binding agents such as exocellular mucilaginous polysaccharides. It acts as a major food and energy for endogenic soil fauna. Thus, POM is associated with a multitude of soil processes and functions and is therefore, a key attribute of soil quality.

Acid hydrolysable carbohydrate (AHC)-C (32-37% of TOC) is a labile C-fraction and has been found more rapidly in response to changes in management than TOC contents. The $KMnO_4$–oxidizable C-fraction accounts for 5-30% of organic C. This oxidizable fraction usually is more sensitive to soil management than TOC. Simple measurement of soil aggregate stability, POM, light fraction of carbon, and acid-hydrolysable carbohydrates have been evaluated for their sensitivity to changes in different soils and crop management systems (Table 10).

Soil organic matter serves many soil functions, so the critical value or range would vary according to a function. The critical level could be established for specific soil types or site and soil management scenarios, related to a single soil process or function, and is based on a range rather than a set value. Generally, at present, two main approaches utilized to establish critical levels are:

(a) Use of average or base line SOM values under local soil conditions and soil types to establish an initial reference level of threshold based on general consensus, and

(b) Characterization for critical levels of SOM based on empirically derived relations between SOM and specific soil process and conditions. Close relationship should be quantified between SOM and soil fertility indices, crop productivity, soil erodibility and soil aggregation.

Factors that regulate SOM functioning in soil are related to (i) organic matter addition or inputs, which influence particulate or macro-organic matter, and (ii) the relation between SOM and soil aggregates. Functions of SOM are differentiated on the basis of total SOM or aggregated SOM. Monitoring is important, but the usefulness of the data will only be realized if it is used in the management decisions to correct deficiencies or improve the quality of the soil resources. Additions of organic matter to the soil, in the form of crop residues or organic amendments, increase the level of low-density macro organic matter. This form of SOM improves the mechanical properties of soil (Table 11).

Table 10. Long-term effect of manure and fertilizer applications on active and slow fractions of soil organic carbon under Inceptisol (Rice-Wheat-Jute, R-W-J) and Vertisol (Sorghum-Wheat, S-W) system at 0-15 cm soil depth

Locations	Treatments	LF-C (mg/kg)	LF-N (mg/kg)	AHC (mg/kg)	SOC	POM in SOC (%)
Inceptisol (R-W-J)	Control	169	11.4	526	5.4	10.6
	N	162	10.7	580	5.7	16.5
	NPK	327	15.2	689	7.4	20
	NPK+FYM	486	20.2	845	7.9	27
Vertisol (S-W)	Control	201	8.6	462	3.6	10.3
	N	220	10.2	590	5.2	23.3
	NPK	328	13.3	725	5.6	30.1
	NPK+FYM	465	16.4	840	6.1	39.7

Source: Manna *et al.* (2006; 2007)

LF = Labile fraction, AHC = Acid-hydrolysable carbohydrate; SOC = Soil organic carbon; POM = Particulate organic matter

Table 11. Functions of soil organic matter and its relations to soil processes

Location of SOM	Functions or processes involved
SOM in the whole soil	• Compatibility and strength • Water holding capacity
SOM in particles and aggregates	• Conservation of nutrients and energy • Erodibility

9. Water Quality

Soil and water quality are inherently linked; conserving or enhancing soil quality is a fundamental step towards improving water quality. On the other hand, soil and water systems are interrelated through a complex web of interactions and any change in one system will cause varying degree of changes in the other. Water quality refers to the characteristics of a water supply that influences its suitability for a specific use, i.e., how well the quality meets the needs of a user. Unlike soil quality, water quality implies analysis of specific pollutants below set concentrations, thresholds and with limited exceptions, and the standards in the pure state.

The water quality can be evaluated by its aesthetic, physical, chemical and biological properties, which gets influenced by means of agricultural, industrial and anthropogenic uses. Aesthetic properties include colour, smell, odour and appearance. Physical properties that influence water quality include turbidity and clarity, dissolved solids, sediment load and suspended organic and inorganic materials. Important chemical properties in relation to water quality include pH, salinity, alkalinity, dissolved oxygen, dissolved load of chemical constituents, especially nitrate, phosphorus, fluoride, arsenic, heavy metals, pesticides and other toxic compounds. Among biological properties, the presence and number of microorganisms and their biomass and the presence of pathogens (bacteria and algae, etc.), phytoplankton and zooplanktons are used to assess the impact of water quality.

9.1. Soil Processes Affecting Water Quality

Principal soil processes that affect water quality in relation to agricultural activities include accelerated soil erosion, macro pore flow, leaching, microbial by-product and transformations and mineralization of humus (Lal and Stewart, 1994).

9.1.1. Accelerated Soil Erosion

During the process of accelerated soil erosion, transport of suspended and dissolved loads with overland flow through surface runoff from agricultural land is a major process affecting non-point source water pollution. Compaction, crusting, and accelerated soil erosion are the important soil physical processes which affect water quality. Physical processes are set in motion by the decline in soil structure with resultant decrease in water infiltration capacity and increase in surface runoff. Decline in structural stability also increases soil erodability and risks of inter-rill and rill erosion. Surface runoff and erosion enhance transport of suspended and dissolved chemicals and sediment-borne pollutants into natural waters.

9.1.2. Leaching

Leaching, transport of chemicals from surface into the sub-soil with percolating water, is another major process affecting water quality. Concentrations of soluble nutrients may be several orders of magnitude higher in seepage water than in surface runoff. Leaching is generally more severe during off-season when crops are not actively growing. Active crop growth removes readily soluble chemicals, e.g. NO_3^-, NH_4^+, P, K, Ca, Mg, etc. The process of leaching is predominantly influenced by several factors such as soil texture, rainfall, soil moisture and amount of water percolated, nature of chemicals and their solubility, retention capacity of soil, etc.

9.1.3. Macropore Flow

Macropore flow is one process of transport of nutrients and agricultural chemicals from surface into sub-soil and eventually into groundwater and interflow that feeds streams. Macropores flow can also occur through cracks. Water flow through cracks is a dominant process of water movement in the heavy-textured soils, e.g. Vertisols. In general, the rate and magnitude of macropore flow are inversely related to those of surface runoff. Leaching can be accentuated by macropore flow or by-pass flow. This involves rapid transport of water and chemicals from surface into the sub-soil through large pores made by biotic activity, e.g. worm holes, root channels, burrows by large animals.

Macropores are large soil pores that have minimum equivalent cylindrical diameters ranging from 0.075 mm to 1.0 mm, which can promote rapid and preferential transport of water and chemicals through agriculturally and environmentally important soil surface layers to sub-surface and into a drainage system. In soil, sometimes macropore prefer transport of water and chemicals in incomplete saturated transport pathway, which is called as bypass-flow. In general, macropores are classified into three types as large macropore (1mm), intermediate macropore (> 0.075 – < 1mm), and small macropore (0.075mm). Macropore-flow initiates when the soil is saturated with water ponded on the entire soil surface. Factors that affect macropore-flow initiation include soil texture, soil morphology, antecedent soil moisture content, and rainfall intensity. The rapid arrival of chemicals from agricultural land at some depth is often the first clue that macropore flow is occurring. However, solute transport literature considers it as either reactive (inorganic cations) or non reactive (inorganic anions). Non-reactive anions are highly mobile and thus NO_3^-, Br^- and Cl^- are highly mobile as a result of water pollution.

9.1.4.Mineralization of Humus and Microbial Byproduct Transformation

In addition to nutrient application through fertilizers, plant nutrients also become available through mineralization of humus and soil organic matter. The process of humification releases plant nutrients immobilized in organic matter and makes them readily soluble and mobile. The biomass, active and dead, is a major buffer against nutrient loss (by erosion or leaching) out of the ecosystem. Therefore, decrease in total biomass, activity and species diversity of soil fauna can have serious adverse impact on water quality. Besides this, the transport of microbes and microbial by-products from soil into surface and groundwater is another cause of non-point source pollution. Transport of biomass carbon is usually more in overland flow than groundwater because of the nature of the process of soil erosion. Microbial processes that aggravate adverse effects on water quality are mineralization, solubilization, and exudates or microbial by-products.

9.2. Interrelationship between Soil and Water Quality

Soil and water quality are very much associated with each other. Soil quality degradations causes both direct and indirect degradation of water quality. Direct degradation of water quality occurs from erosion through the delivery of sediments and attached agricultural chemicals to surface waters. The indirect effects on water quality may be as important as the direct damages, which are often overlooked. Some of the indirect effects are: (i) soil erosion and compaction degrading the capacities of watersheds to capture and store precipitation, altering stream flow regimes by exaggerating seasonal patterns of flow; (ii) increasing the frequency, severity, and unpredictability of high-level flows; and (iii) extending the duration of low-flow periods and causing stream channels to erode, adding to sediment loads and degrading aquatic habitat for fish and other wildlife.

On the other hand, use of nutrients, pesticides, and irrigation water to compensate for the declining soil quality may be an important cause of water pollution. Even if soil quality is very high, producers who mismanage inputs may still have unacceptable losses of nutrients, pesticides, and other pollutants from their farming systems. Improvements in soil quality alone, however, will not be sufficient to address all water quality problems unless other elements of the farming system are addressed.

9.3. Impact of Agricultural Management on Surface Water Quality

In the humid tropics, greater soluble-N losses usually occur with subsurface flow than with surface runoff. Excessive amount of N-application in agriculture is not only waste of resources, but can be detrimental to human and animal health. The excessive NO_3^- and NO_2^- in water and food have adverse impact on human health such as methemoglobinaemia in infants. The production of nitrosamines from NO_2^-, and secondary amines are the major causes of cancer. Similarly, peroxyacyl nitrates, alkyl nitrates, NO_3^- aerosols, and HNO_3 aerosols in rainfall are the causes of respiratory illness. High levels of NO_2^- in soils create plant toxicity. In drinking water, NO_3^- content limit is 10-44.5 mg NO_3^-/L for human intake. Similarly, emission of nitrous oxide from denitrification under anaerobic soil-water environment resulted in the depletion of stratospheric ozone layer. Loss of N associated with sediment is usually several times higher than soluble N-loss in surface runoff. Water infiltering into the soil or moving through macropores, also has the potential to move soluble-N. Thus, various reduced or conservation tillage practices reduce runoff and erosion, losses of sediment associated N and soluble N. Much is known about how to use N for efficient crop production and minimize its adverse impacts on surface and sub-surface water quality. Research is needed on the levels of inorganic and organic N accumulation acceptable without posing a potential groundwater quality problem. NO_3^- has a very low affinity, or ability to bind, to either soil particles or organic materials. Therefore, once it is dissolved in water, NO_3^- will remain dissolved until physically or biologically removed by either plants, by anaerobic microbial conversion such as denitrification or by some physical processes. The most feasible physical process for NO_3^- removal from contaminated water is ion exchange and reverse osmosis. Use of denitrification is not suitable under borehole, but it is useful for NO_3^- removal from large waterbodies, because during anaerobic processes, bacterial proliferation, methanol production, organic metabolites organochlorinated compounds are the major byproducts associated with denitrification.

The transport of soluble-P and particulate-P in surface runoff, streambanks and channel beds is initiated by the desorption-adsorption, dissolution and fixation characteristics. The loss of fertilizer or manure P is influenced by the rate, time, and method of application, form of fertilizer or manure; amount and time of rainfall after application; and vegetative cover. In peaty or organic soils, organic matter may accelerate the downward movement of P together with organic acids and Fe and Al. Similarly, P is more susceptible to movement through sandy soils with low P-adsorption capacities and in soil that have been waterlogged, where a decrease in Fe-content occurs. The loss of P in subsurface runoff is appreciably lower than that in surface runoff because of sorption of P from infiltrating water as it moves through the soil profile. In general, P concentration and loss in natural subsurface runoff is lower than in tile drainage due to the longer contact time between subsoil and natural subsurface flow than in tile drainage. Increased sorption of P from percolating water also accounts for lower total P loads. Conservation tillage can reduce soil and P transfer in surface runoff. The soluble-P and total-P concentrations of runoff are consistently above the critical values associated with accelerated eutrophication of a waterbody (0.01 mg/L and 0.02 mg/L, respectively; Vollenwieder and Kerekes, 1980).

9.4. Influence of Animal and Municipal Wastes on Water Quality

The waste products of animals are feaces, urine and bedding materials. Improper recycling of these wastes is considered to be one of the point sources of water pollution. Fresh feaces of animal waste contain acetic, propionic, butyric, valeric and isovaleric acids. In poultry excreta, uric acid is the most abundant nitrogen metabolite, which degrades into urea through *Pseudomonades* with the following degradation pathway:

Uric acid → Allantoin → Allantoic acid → Urea or Glyoxylic acid

Municipal biodegradable solid waste such as household materials, industrial by-products and sewage-sludge often contain undesirable contaminants. Incorporation of these materials in agricultural soil may introduce heavy metals, xenobiotic organic compounds and pathogens to human food chain. Municipal solid wastes contain heavy metals and pathogens. Nitrogen in municipal compost is mainly present in organic form and contents of ammonium and nitrate are low. The chemical compounds found in sewage-sludge are: phenol, phthalate esters, polyaromatic hydrocarbon, polychlorinated biphenyls, triaryl phosphate esters, monocyclic aromatics, halogenated aliphatics, chlorinated pesticides, aromatic and alkyl amines, etc. The civil construction for industrialization, urbanization intensification and diversification around the rivers have contributed a lot in disrupting wastes, which in turn, have vitiated the water quality and biota to the extent of irreparable state in certain stretches.

Excessive loading of organic matter into water has all the potentialities of pollutants to upset the ecological balance of an ecosystem, particularly in floodplain lakes known as 'Eutrophication'. All the above-mentioned organic compounds decompose aerobically or anaerobically from manure, slurry and sewage-sludge. It pollutes groundwater quality through surface runoff or overland flow occurs at sloping sites when the infiltration rate of water into soil is lower than the rate of precipitation. The losses of N through runoff amounts to 25-50 % of the manure-N applied to soil. For the microbial characterization of runoff waters from soils amended with organic wastes, the number of feacal colifoms, total coliforms and feacal streptococci are the major dominant microorganisms, which create water pollution. The chemical characterizations include inorganic ions such as nitrogen, phosphorus, chloride, fluoride, iron, manganese, copper, zinc, boron, silver and also surfactants, hydrocarbons and organochlorine compounds.

9.5. Soil and Water Contamination by Heavy Metals

Various metals such as Cd, Cr, Co Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sn and Zn are used in industry and out of them Cd, Cu, As, Cr, Hg, Ni, Pb and Zn are considered most dangerous for animal and human health. Heavy metals are distributed in solid and liquid phases, and the partitioning of heavy metals between solid and liquid phases is influenced by a number of factors such as complexation with various organic and inorganic ligands, oxidation-reduction, ion exchange adsorption reactions and dissolution –precipitation reactions. These interactions are main controlling factors for mobility and bioavailability of heavy metals in soils and water systems. Heavy metals which are present in rocks, soils and originated from geological materials, directly or indirectly, affect the chemical composition of water, soil, animal feed and foodstuff. Some igneous rocks (basalt and granite) and sedimentary rocks (limestone and sandy stone) contain heavy metals. In soil heavy metals are derived either from the weathering of the parent materials or from numerous external contaminating sources. Two physical factors such as the residence time and the pathways along which the water moves through the system are important with respect to chemical composition of water quality. The larger is the residence time, the greater is the reaction opportunity between water and heavy metals in contact with it. In general, water flowing in shallow pathways gets in contact with more weathered and consequently less reactive materials along with deeper pathways. Regarding heavy metals, various processes are influenced by anthropogenic activities and cause water pollution:

1. Runoff from agricultural and urban areas,
2. Discharge from mining factories and from municipal areas,
3. Leaching from waste dumps,
4. Atmospheric deposition, and
5. Leaching from natural soils and vegetation previously contaminated by air pollution.

Groundwater is insignificant from purely ecological point of view because overlying soils generally protects groundwater reservoirs, thus it is not severely affected by human activities. Since it is more alkaline than surface water, their heavy metal contents are generally low compared to standard values, except some elements such as arsenic and molybdenum, which tend to become more soluble with higher pH. Acidification of shallow groundwater appears to be a significant problem, which is likely to be accompanied with increased solubility of heavy metals in subsoil.

The upper permissible limits of some elements in irrigation water are presented in Table 12.

Table 12. Recommended maximum concentrations of trace elements in irrigation waters

Elements	For irrigation water quality (for use in all soils (mg/L)
Mn	0.2
Pb	5.0
Mo	0.01
Ni	0.2
Se	0.02
Al	5.0
As	0.1
V	0.1
Cu	0.2
Cd	0.01
Co	0.05
Fe	5.0
Zn	2.0

Source: Adapted from National Academy of Sciences (1972) and Pratt (1972)

9.6. Water Quality for Irrigation in Agriculture

Quality of irrigation water is one of the main factors that affect the physical and chemical properties of the soil and ultimately, the crop growth. The irrigation water must be free form excess soluble salts and from concentrations of specific chemical substances that may create soil quality problem such as salinity, sodicity, permeability and specific ion toxicity. These problems do not occur in short-term application and therefore, in classifying water quality for irrigation it is not necessary to include all of them. Sometimes, the point sources of irrigation create hazards to soil quality. In the semiarid and arid regions, irrigation is essential for successful crop production, but the main source of irrigation is groundwater, which is usually saline with varying degrees of salt concentration and their continuous application affects crop growth. Some ion limits for irrigation water for agricultural use are given in Table 13.

9.7. Standard Water Quality for Human and Livestock

There is a need to establish and standardize critical or tolerable limits with regard to concentration of major pollutants in natural waters. Though tolerable limits vary from regions and countries and between humans and livestock consumption, some of water quality standards are listed in Table 14.

Table 13. Guidelines for interpretations of water quality for irrigation

Parameters	Suitable	Moderately suitable	Not suitable
EC (milliSiemens per metre, mS/m)	25	25-75	>75
Sodium absorption ratio (SAR)	<10	10-18	>18
Sodium (as adjusted SAR)	3.0	3-9.0	.9.0
Residual sodium carbonate (RSC) (me/L)	<1.25	1.25-2.5	>2.5
HCO_3 (me/L)	<1.5	1.5-8.5	>8.5
NO_3-N (me/L)	<5.0	5.0-30.0	>30.0
B (mg/L)	<0.75	0.75-2.0	>2.0
Cl (me/L)	<4.0	4.0-10.0	>10.0
F (me/L)	<1.0	1.0-15.0	>15.0
pH	6.5-8.4	0-5	>9.5

Source: FAO (1994)

Table 14. International water quality standards for human and livestock consumption

Chemical element/ compound	Concentration, mg/L	
	Human	Livestock
Pb	<0.1	0.05
Mo	—	0.01
As	<0.05	0.05
Se	<0.01	0.01
Zn	<15	<20
Cd	<0.01	0.01
Ba	<1.0	-
Ca	<200	<1000
Mg	<0.01	0.002
Hg	<45	<200
NO_3^-	<0.05	-
NH_4^+	<400	<1000
Cl^-	<200	-

Source: From Edwards *et al.* (1983), van der Leeden *et al.* (1990).

Table 15. Threshold limits for drinking water as recommended by World Health Organization

Water quality parameters	Threshold limits for human consumption
Aesthetic	
Colour	>5 –15 degree colour unit
Odour & appearance	Acceptable to consumers
Physical	
Turbidity and clarity	>2 degree
Dissolved solids	500 mg/L
Sediments load	-
Suspended organics & inorganics	-
Hardness	300 mg/L
Chemical	
pH	6.5-8.5
EC	250 µS/cm
NO_3^-	10-50 mg/L
NH_4^+	<0.05 mg/L
SO_4^{2-}	250-500 mg/L
Chloride	200-250 mg/L
Flouride	0.8-2 mg/L
Na	180-200 mg/L
Ba	0.2-0.7 mg/L
Ca	300 mg/L
As	0-0.007 mg/L
Zn	1-5 mg/L
Se	0.01-0.05 mg/L
Cd	0.002-0.01 mg/L
Pb	0-0.01 mg/L
Hg	0.001-0.005 mg/L
Ni	0.02
Al	0.02
Fe	0.01-0.03
Biological	
Total coliform	0/100 mL
E. coli	0-<1/100 mL

It is imperative that aggressive campaign for environmental awareness should be the order of the day. The maximum permissible limits, as given by World Health Organization (WHO) for human consumption, are given in Table 15.

10. Impact of Land Use and Management on Soil and Water Quality Sustenance

The periodical soil quality assessment is suggested to evaluate the effectiveness of various land-use practices that will improve land use, enhance plant, animal and human health and sustain biological diversity within natural management ecosystem. To accomplish this goal, indicators that are sensitive, reliable and capable of detecting changes in soil physical, chemical and biological parameters and their interaction must be developed. Many studies on soil quality have revealed that soil quality would improve by increasing organic carbon in soil. The resulting changes are expected to improve soil structure with reduced surface crusting, increased water filtration rate, lowered runoff, and reduced soil erosion.

Extensive cultivation and greater reliance on chemical fertilizers and pesticides have resulted in many-fold increase in crop production. However, in some cases, these management practices have also resulted in decreased SOC, increased soil erosion, and surface and groundwater contamination. However, awareness is needed among the farmers to shift from input-extensive management to reduced external input farming system which may protect soil quality and human health and environment. The quality of many soils in India and many other countries has declined significantly under imbalanced fertilizer management practices in arable agriculture. A continuous application of balanced NPK fertilizer helps in improving the soil quality as well as yields. Reports are also available that decline in yields is more pronounced with concomitant decrease in SOC-content under imbalanced fertilizer application.

Mechanical cultivation and production of continuous row crops have resulted in soil and nutrient losses through erosion. Large decrease in SOC-content and concomitant increase of CO_2, nitrous oxide and methane from soil to atmosphere pollute atmosphere. Soil erosion by water is estimated to be 6.9 metric tonnes per hectare per year on 155 hectares of crop land (Kellog *et al.*, 1994). The practice of conservation agriculture would maintain better soil quality as compared to conventional agriculture. The legume based-cropping systems sustain large soil quality parameters as compared to conventional system. Soil and nutrient management practices such as tillage, residue application, and conjunctive nutrient-use especially when practised over long periods, significantly influence various key soil quality indicators and relative soil quality indices (RSQI), besides improving the sustainability yield indices (SYI) (Sharma *et al.* 2005; 2008).

Acidification in soils results in loss of exchangeable Ca^{2+} and Mg^{2+}, a decrease in effective cation exchange capacity, and an increase in exchangeable Al^{3+}. Long-term application of imbalanced nutrients and sub-optimal or no use of organic and inorganic fertilizers into soil are the main reasons for low productivity in acid soils. Solubility of Al, Fe and Mn being high in acid environment, they are available quite in excess, at times causing toxicity to microbes. Ordinarily, boron should be available under acid conditions but porous nature of topsoil allows the soluble boron to leach down in the profile beyond the reach of the plant roots. Excess of Al in soil solution reduces the uptake and transport of P in plants. Long-term uses of chemical fertilizers along with organic manure or lime improve the acid-soil quality indicators and sustain crop productivity.

Salts in the soil and groundwaters are of fossil origin and under favourable conditions, have been accumulated at or near the surface, rendering many productive soils into barren lands. The salt-affected soils are characterized by the presence of electrolytes capable of alkali hydrolysis with or without the dominant presence of neutral salts and often impregnated with calcium carbonate at some depth in soil profile. The other major occurrence of salt-affected soils is the inland saline soils mostly in arid and semi-arid regions. The coastal salt soils are subject to inundation by seawater during high tides. Excessive amounts of salts present in the soil have an adverse impact on soil biological quality such as microbial biomass, soil respiration, dehydrogenase activity, etc. The decrease of microbial biomass C was evident at ECe > 32 and 19 dS m^{-1} in the 0-15 cm and 0-30 cm soil layer. Dehydrogenase activity declined by 71 to 87% at ECe of 28 and 40.8 dS m^{-1} due to carbon stress, and in high saline soils low biological activity is predominantly due to exo-osmosis in microbial cell (Batra and Manna, 1997). Improvement of rhizosphere soil biological activity through agroforestry, agri-pastoral, and silvipastoral are the viable options to improve soil quality in saline sodic soil.

Heavy metal and toxic element contamination, on the other hand, is generally more identifiable as a soil health problem. Such problems may result from geological factors such as high natural occurrence of the elements of interest in bedrock, or could be related to poor agricultural management. The sewage possesses excellent manurial value and its application may act as a good source of organic matter. However, it is rich in toxic metals and has the potentialities of transmitting and accumulating substantial amount of these metals in soil. Continuous application of sewage rich in heavy metals might be responsible for deterioration of soil biological activity.

Perhaps more profound outcome of a soil function as a living community would be the degree of resilience and stability that develops over time. A decrease in tillage intensity results in greater production of soil microbial biomass as well as organic carbon. The microbial biomass can be considered as one of the important management sensitive early indicators of soil health.

Improved soil and water management practices along with integrated nutrient management, use of cover crops, increasing N-use efficiency and site-specific management of plant nutrients have the potential to maintain productivity, and soil and water quality. Generally, farming practices that enhance soil erosion decrease soil quality as well as surface and groundwater quality. There is a need of future research to generate information on the long-term effects of farming practices on soil and water quality, especially on the contamination of surface water and groundwater with chemical pollutants derived from plant nutrients and plant protection chemicals used in intensified systems.

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Chapter 28

Soil Pollution and its Control

BIJAY-SINGH and DILIP KUMAR DAS

1. Introduction

The agricultural activities involve addition of nutrients, pesticides and sediments to soil. On the other hand, industry and urbanization pollute the soil with solid wastes, heavy metals, solvents and several other organic and inorganic substances. As the world population grows, increasing amounts of wastes are produced and most often soil is the medium for disposal of wastes, Dispersal of waste from its source can be through the atmosphere, via the water bodies or directly into the soil itself. Once in the soil, not only can it enter the food chain thereby affecting plants, animals and humans but in some cases, alters also the composition of the soil and its ability to perform its many functions. For example, some forms of pollution can diminish the populations of soil organisms such as earthworms and microbes, which decrease the biotic capabilities of the soil. Also, pollutants can often be transported from the soil to the water bodies where they contribute to further damage of the environment. Although soil acts as a physical filter by its sieving action, a chemical filter by adsorption, precipitation and transformations of chemical substances, and a biological filter by decomposing organic materials, it does not have infinite capacity to perform these functions..

Any addition to soil of substances that may exert adverse effects on its functioning can be defined as soil contamination. Since soils possess buffering capacity, it usually takes some time for the negative effects to become visible and then the soil can be considered polluted and the process as soil pollution. Many pollutants reaching the soil can build up to such concentrations which pose serious threats to plants and animal health. Soil pollution is not apparent immediately and shows its effects sometimes only after many years. Some pollutants can remain in the soil for centuries, thus prohibiting its normal use for extended periods.

In general, two types of environmental pollution activities are associated with soil. First are those, which pollute the soil itself, making it unfit either as a medium for plant growth or for growing crop plants that do not contain enough toxic substances so as to be suitable for human/ animal consumption. Even essential plant nutrients like nitrogen and some micronutrients can pollute the soil if applied in excessive amounts. An indiscriminate land application of wastes considering soil as nature's dispose-all may often lead to such pollution problems. In the second category, the management of soil may contribute to the pollution of water, such as leaching of nitrate to groundwater. Under these situations, intensive food production merely to feed the under-nourished will not be acceptable because in doing so the atmosphere or the water no longer remains life sustaining.

2. Land Application of Wastes

The term *waste* is defined as useless , unwanted or discarded material. It can be distinguished into solid and liquid wastes. Liquid waste is frequently referred to as recycled 'effluent'. With increase in population and revolution in industry and agriculture, huge amounts of wastes containing different types of pollutants are being produced and ultimately deposited in the soil and water. Soils can get polluted from sewage (or municipal), agricultural, industrial, and nuclear wastes.

2.1. *Sewage Wastes*

For centuries, the people in India have recycled the animal excreta through the soil to utilize the nutrients and the organic matter it contains. In the nineteenth century, it became relatively common for municipalities to install sewage system in cities and to operate sewage farms. More than 450 cities in India generate more than 17 × 10^6 m^3 of raw sewage per day. With available treatment plants, production of sewage sludge is estimated to be around 1,200 tonnes per day; although there exists a potential to produce 4,000 tonnes of sludge per day. The nutrient potential of available sewage in India is estimated to be more than 350,000 tonnes N, 150,000 tonnes P and 200,000 tonnes K per year (Juwarkar *et al.*, 1991). Obviously, all the sewage sludge, a period of long yrs will eventually be applied to soil.

During the past couple of decades, land application of wastewater is being re-emphasized as an alternative technology for waste treatment. The hydraulic and nutrient (in terms of N) loading in different sewage farms in India varies from 22 to 340 m^3/ha/year and 400 to 6,000 kg/ha/year, respectively (Juwarkar *et al.*, 1991). Thus, the present day system is inclined towards disposal of sewage rather than appropriate nutrient management. The organic and inorganic loading is also increasing beyond the assimilation capacity of the soil. The excessive N-loading induces more foliage and creates an imbalance in the C:N ratio of the soil. The application of industrial effluents to soil is governed primarily by the nature of its constituents. For example, toxic elements present in industrial effluents when applied to agricultural lands may enter food chain. These may also leach to groundwater or reach surface waters through runoff and deteriorate their quality.

2.1.1. *Composition of Sewage*

For allowing the wastewater to be cleaned by percolation through soil or dumping the sewage sludge on agricultural lands, it must be ensured that these do not leave undesirable residues in the soil. In this regard, the characteristics of wastes assume great importance. The composition of sewage wastes is highly variable depending upon the contributing source, method of collection and treatment procedure. In India, most of the raw sewage is a mixture of domestic, commercial and industrial activities. Therefore, although a large proportion of this wastewater is organic in nature and contains essential plant nutrients, sometimes toxic elements are also present in considerable amounts (Table 1). Municipal wastewaters contain conspicuously high amounts of organic matter, particularly where a large number of dairy farms or food processing units are located. The composition of wastewaters also varies with season.

2.1.2. *Effect of Sewage Waste Application on Soil Characteristics and Crop Responses*

The application of sewage wastes, in general, favourably influences the soil fertility. The contents of organic carbon, N, P and K are substantially increased by irrigating soils with sewage water (or application of sewage sludge) rather than with tube-well (groundwater) or canal water (Table 2), thereby resulting in improved soil fertility and productivity. Most of the crops show substantial yield responses when irrigated with sewage waters or grown on soil amended with sewage sludge. In the Nagpur sewage farm where for more than two decades an area of 1,500 ha spread over 21 villages is being irrigated with treated and untreated sewage, yields of different crops have always been higher in sewage-irrigated fields, the primary-treated sewage performed better than the untreated and the 1:1 diluted sewage (Juwarkar *et al.*, 1991). Similar results have been obtained at the Pune sewage farm.

A continuous application of sewage waste over several years may result in enrichment of heavy metals in the top soil. The availability of accumulated heavy metals is governed by the

Table 1. Composition of sewage sludge from different cities in India

City	N	P	K	Organic matter (%)	Cu	Zn	Cd	Cr	Ni	Pb
		%					mg/kg			
Ahmedabad	1.18	0.56	0.23	33.5	535	2147	3.5	60.4	32.3	76.8
Delhi	1.67	0.56	0.11	54.7	440	1610	5.5	53.5	815	34.5
Nagpur	1.08	0.51	0.21	39.1	272	832	1.5	49.2	14.8	24.3
Chennai	0.82	0.65	0.12	40.2	210	935	8.3	38.5	60.5	16.6
Jaipur	2.34	0.94	0.12	39.1	265	1720	7.3	176	37.5	66.9
Kolkata										
Tolly's Nalla	–	0.06	0.23	–	11.4	41	–	86.1	–	–
Tapsia	–	0.16	0.23	–	9.9	507	–	740	–	–
Kanpur	–	0.17	0.15	–	13.0	229	–	571	–	–
Bikaner	–	0.11	0.19	–	13.6	49	–	35.6	–	–
Bombay	–	0.23	0.11	–	108	234	–	378	–	–

Sources: Juwarkar *et al.* (1991); Garg *et al.* (1997)

Table 2. Effect of sewage irrigation on soil organic matter and nutrient content of surface soils

Organic matter or nutrient content	Sewage-irrigated soil	Canal/groundwater irrigated soil
Organic carbon (%)	0.86-2.34	0.18-0.22
Available N (kg/ha)	88-142	45-65
Available P (kg/ha)	14-44	4-17
Available K (kg/ha)	153-360	66-162
Available S (kg/ha)	4-16	3-12

Source: Singh and Kansal (1985)

soil properties– pH and organic carbon, but the enhanced organic matter level due to application of waste generally results in increased availability of metals by forming organo-metallic complexes. The long-term irrigation of soils using sewage water increases the contents of not only micronutrients like Zn, Cu, Fe and Mn but also of toxic elements like Cd (Table 3).

The plants grown in sewage-treated soils always contain more nutrients and heavy metals than those grown in an untreated soil (Table 4). Due to the genetical characteristics, plant species and even varieties differ in their susceptibility and tolerance to heavy metals. The leafy vegetables and root crops accumulate larger amounts of heavy metals than grain crops. For example, spinach can absorb large amounts of Pb and Cd, whereas, wheat grains accumulate very small amounts of toxic heavy metals.

2.2. Industrial Effluents and Soil Pollution

The industrial effluents are usually discharged on land or into sources of water. These effluents have variable chemical characteristics and metal contents that may prove harmful to soil environment (Table 5). It causes soil degradation and environmental pollution. This problem will be further aggravated with increase in the industrial activity. On the other hand, a large quantity of wastewater generated from some of the industries will play an important role in the context of scarcity of fresh water resources for irrigating agricultural land. Besides being a useful source of plant nutrients (N, P, K, S, etc.), these effluents often contain high amounts of various organic and inorganic materials as well as toxic trace elements. These may accumulate in soils in excessive quantities on long-term use. Subse-

Table 3. DTPA–extractable heavy metals in soils under different crops irrigated with sewage and underground water

Crop	Source of irrigation water	Zn	Fe	Cu	Mn	Cd
				mg/kg		
Berseem	Sewage	13.4	75.3	24.4	33.2	0.119
	Underground	4.2	38.0	7.8	28.4	0.074
Spinach	Sewage	41.2	65.6	32.2	28.8	0.253
	Underground	4.2	59.4	7.0	24.4	0.079
Coriander	Sewage	21.1	69.0	49.4	23.0	0.208
	Underground	6.6	32.4	9.5	18.4	0.054

Source: Sharma and Kansal (1986)

Table 4. Heavy metal contents in crops grown on sewage effluents and tubewell water-irrigated soils

Crops	Metal contents (mg/kg)									
	Zn		Cu		Fe		Mn		Ni	
	S	T	S	T	S	T	S	T	S	T
Rice (*Oryza sativa* L.)										
Grain	49.6 (27)	29.6 (4)	51.6	23.0	122	186	53.3	88.1	10.1	9.85
Straw	58.9 (27)	61.9 (4)	57.2	59.8	233	202	208	229	10.4	5.27
Wheat (*Triticum aestivum* L.)	65.3 (88)	47.5 (27)	9.39	7.45	404	336	15.3	13.6	20.0	19.7
Sorghum (*Sorghum vulgare* Pers.)	54.2 (38)	73.4 (9)	16.9	115.5	526	485	40.6	44.8	14.8	11.6
Maize (*Zea mays* L.)	78.8 (15)	67.6 (1)	14.9	13.3	531	99.0	26.0	15.3	16.5	5.20
Oats (*Avena sativa* L.)	59.0 (7)	44.3 (2)	8.71	6.35	458	400	23.8	29.2	18.3	37.3
Gobhi sarson (*Brassica napus*)	66.9 (17)	38.7 (3)	23.1	14.1	454	401	69.0	104	12.0	3.73
Spinach (*Spinacea oleraceae* L.)	77.1 (17)	38.4 (2)	20.6	16.1	711	734	39.3	87.8	18.4	13.2
Indian rape (*Brassica campestris* var. toria Dutch)	52.5 (10)	–	5.42	–	475	–	42.6	–	8.78	–
Cauliflower (*Brassica oleracea* L.)	46.7 (11)	–	10.8	–	328	–	31.8	–	14.4	–
Cucumber (*Cucumis sativus* L.)	79.4 (5)	–	19.3	–	932	–	19.9	–	21.5	–
Radish (*Raphanus sativus* L.)										
Leaf	60.8 (7)	–	14.6	–	358	–	41.9	–	9.26	–
Root	58.9 (7)	–	10.4	–	166	–	16.7	–	11.5	–
Egyptian clover (*Trifolium Alexandrinum* L.)	91.9 (15)	–	18.3	–	623	–	20.7	–	20.6	–

Note: Figures within the parentheses indicate number of samples analysed; S: Sewage-irrigated; T: Tubewell water-irrigated.

Source: Rattan *et al.* (2005)

Table 5. Some characteristics of wastewater from domestic and industrial locations in Ludhiana — An industrial city of Punjab

Location	pH	Biological oxygen demand	Chromium - hexavalent	Nickel	Cyanides
			(mg/L)		
Electroplating industry	6.2-7.2	60-380	0.2-2.5	1.0-3.0	0.42-0.97
Sugar industry	7.1-7.9	1058-1640	–	–	–
Paper industry	7.0-10.1	560-1113	–	–	–
Household	6.7-7.8	80-460	0.1-0.2	0.2-2.0	0.05-0.07
Maximum limits for disposal on agricultural lands	5.5-9.0	100	0.1	0.005	0.2

Source: Tiwana *et al.* (1987)

quently, these toxic elements may cause physical problems to human beings and animals by entering into the food chains. However, industrial wastewater could be used safely and effectively with proper precautions to increase the soil productivity. The utilization of industrial effluents for agricultural purpose could also provide a solution to their disposal problems.

2.2.1. Distillery and Paper Mill Effluents

In India, large amounts of wastewater generated in the form of distillery and paper mill effluents are discharged on land or into the running water. The distillery and paper mill wastewaters are characterized by low pH, high BOD (biological oxygen demand) and COD (chemical oxygen demand) values and contain high percentages of organic and inorganic materials. The wastewater also contains considerable amounts of N, P, K, S and Ca. The use of distillery effluents results in a significant increase in the electrical conductivity (EC), organic carbon, exchangeable Na as well as available N, P and K in soils. Similarly, pH, organic carbon, cation exchange capacity, available N, P and K and micronutrient contents of soils irrigated with paper factory effluents are reported to be increased. Some of the field crops show positive response to the post-methanation effluent application with irrigation water (Chhonkar *et al.*, 2000).

The paper mill effluents adversely affect the seed germination and seedling growth of various crops; however, these aspects of crops are stimulated if these effluents are applied after proper dilution. Increase in organic load, depletion of oxygen content and destruction of aquatic life in water courses are some of the major problems created due to the disposal of these effluents in rivers and other water bodies. A few evidences are available to show the impact of pulp and paper mill effluents on soil health. The irrigation of sugarcane crop with pulp and paper effluents increases pH, organic carbon and N, P and K status of soils. The application of these effluents over a period of 15 years has been found to increase the exchangeable Na by 4-5 fold compared to wellwater-irrigated soil, and it ultimately raised the sodium adsorption ratio (SAR) of these soils.

The soils of tropical regions are low in organic carbon. Therefore, addition of organic matter is always beneficial for improving the soil fertility status. But, the application of materials with high values of BOD and COD may have adverse effect on soil health by increasing pCO_2 and formation of organic acids during decomposition which lead to net immobilization of plant nutrients. It is also likely that the application of nutrients in the form of effluents from distillery plants may be more effective in increasing the bio-availability of nutrients to plants as compared to the synthetic inorganic fertilizers.

2.2.2. Tannery and Textile Industrial Effluents

The effluents generated from tanning and textile industries are characterized by high values of BOD, COD, Na and dissolved solids. The addition of tannery effluents causes deflocculation of soil particles and increases N, P and K levels in soil. Similarly, deleterious effects such as increase in sodicity, EC and pH have been observed by the discharge of textile effluents on land. Salinization and alkalization of groundwater occur on land on which tannery and textile effluents are applied.

There are about 3000 tanneries in India spread mostly over Tamil Nadu, West Bengal, Uttar Pradesh, Maharashtra, Karnataka, Punjab and Rajasthan. The leather processing requires large quantities of chemicals like sodium chloride, chromium sulphate, calcium and ammonium salts and organic dyes. The tannery effluents are ranked as the highest pollutants amongst all industrial waters. The effluents from chrome tannery generally contain much higher suspended solids, dissolved salts, and chlorides as compared to those from vegetable tanning. The effluents arising from tanneries of North Arcot (now Vellore) district of Tamil Nadu are generally discharged into neighbouring fields in untreated form. These effluents finally reach the Palar river and leach down. The wells and bore-wells in the area thus tap the contaminated water. The Periyar district (Erode) in this state also has a large number of tanneries which discharge their effluents into irrigation canal as well as the river Cauvery.

The application of tannery effluents has undesirable effect on soil properties. The total porosity and hydraulic conductivity of soil decreases as a result of application of these effluents, while the bulk density of soil gets increased. This is attributed to the accumulation of large quantities of inorganic and organic materials as well as the interaction of Na with the exchange complex, which causes deflocculation of the soil particles. The tolerance limits for disposal of tannery effluents are given in Table 6.

In the textile industry, a large number of chemicals including different salts of sodium, bleaching powder, mordants and detergents are used. The effluents emanating from hand processing textile units of Pali (Rajasthan) have been characterized by high salinity, BOD, COD, and excessive concentration of sodium and carbonate ions. Large quantities of these effluents are discharged into the nearby seasonal rivers which cause serious geo-environmental pollution and anthropogenic hazards.

Table 6. Tolerance limits for disposal of tannery effluents

Parameters	Effluents to be discharged	
	Into inland surface water	On land for irrigation
pH	6.0-9.0	6.0-9.0
BOD	30	100
Suspended solids	100	200
Chloride (as Cl)	1000	200
Chromium (as Cr)	2.0	2.0
Sulphides (as S)	2.0	-
Sodium (%)	-	60
Oil and grease	10	10

All parameters except pH are expressed in mg/L or otherwise stated

Source: Environmental (Protection) Rules (1986)

The application of effluents from the textile industries near Jodhpur has revealed high build up of Na in soils (Nema *et al.,* 1990). The clogging of fields that sometimes turn the land barren has also been noticed. The application of textile effluents even on short-term basis increases the amount of water-soluble salts, organic matter, Na and Ca. The occurrence of salinization and alkalization of groundwater has been seen due to the textile hand-processing industries in Pali (Rajasthan). A substantial increase in sodium, carbonate and bicarbonate contents as well as SAR (sodium adsorption ratio) and RSC (residual sodium carbonate) has been found in waters of wells in the nearby areas (Table 7).

2.2.3. Metal Finishing Industries Effluents

In India, there are over 50,000 large, medium and small metal finishing industries including electroplating units, scattered mostly in the urban areas. The variety of processes and methods of operation in the metal finishing industry gives rise to a wide range of effluent compositions. Electroplating industry effluents can be expected to contain cyanides of potassium or sodium, complex cyanides, copper, nickel, zinc and cadmium in acid solution, hexavalent chromium, oil wastes and solvents. When these effluents end up in the soil environment, heavy metals which can potentially

Table 7. Effect of textile effluents on quality of water of the riverine wells, located on the bank of the effluent-carrying river Bundi

Parameter	Raw effluents	Polluted well (near river)	Unpolluted wells (away from river)
EC (dS m^{-1})	8.5 - 13.9	5.2 - 12.5	2.4 -7.4
Sodium	73.0 - 124.0	38.0 - 112.0	12.0- 47.0
Ca + Mg	0.5 - 2.0	0.3 - 1.2	4.8-17.0
Carbonates	4.0 - 16.0	2.0 - 6.0	-
Bicarbonates	14.0 - 40.0	28.0 - 38.0	4.0 - 16.5
Sulphates	9.0 - 15.0	9.8 - 15.4	2.6 - 16.5
Chlorides	75 - 112	40 - 90	20 - 60
Sodium adsorption ratio (SAR)	60 - 100	39.7 - 200	4.2 - 23.9
Residual sodium carbonate (RSC)	30 - 43	8.0 - 47.7	0.0

All parameters except EC are expressed in milliequi/L

Source: Gupta and Jain (1992)

Table 8. Average DTPA-extractable heavy metal contents in soils in the Coimbatore district of Tamil Nadu contaminated with effluents from different kinds of industries

Industry emitting the contaminating effluents	DTPA-extractable heavy metal (mg/kg)					
	Ni	Pb	Cd	Cr	Cu	Zn
Electroplating	6.34	2.67	0.33	4.21	3.53	0.53
Textile	0.83	2.53	0.17	3.62	0.50	3.31
Dyeing	2.49	2.27	0.05	0.58	0.65	0.72
Foundry	0.81	1.22	0.02	0.26	0.43	0.57

Source: Malarkodi *et al.* (2007)

accumulate to levels which can be toxic for the plants or the consumers of plant products are of major concern. A typical wastewater from an electroplating industry is likely to have (in mg/L): 20-100 Cr(VI), 30-150 total Cr, 5-25 Cu, 15-70 Ni and 10-200 Zn. The permitted levels of metal contaminants in the electroplating wastewater to be discharged, as applicable in various parts of the world as well as in India, are very low. Existing wastewater discharge standard for electroplating industry in India are (in mg/L) 2.0 Cd, 3.0 Ni, 0.1 Cr(VI), 2.0 total Cr, 3.0 Cu, 0.1 Pb. In a detailed study based on the analysis of 500 soil samples contaminated with effluents originating from different kinds of industries in the Coimbatore district in Tamil Nadu, it was observed that soils receiving wastewaters from electroplating industry contained the largest amounts of DTPA-extractable heavy metals, posing a threat to crop plants as well as the food chain for animals and humans (Table 8).

3. Mechanism of Interaction of Waste with Soil

The mechanisms of interaction of waste with the soil can be categorized as physical, chemical and biological. Different processes involved within each category can be schematically shown as depicted in Figure 1.

The behaviour of wastewater in soil is influenced by the nature of pore spaces and in turn, is governed by the characteristics of min-

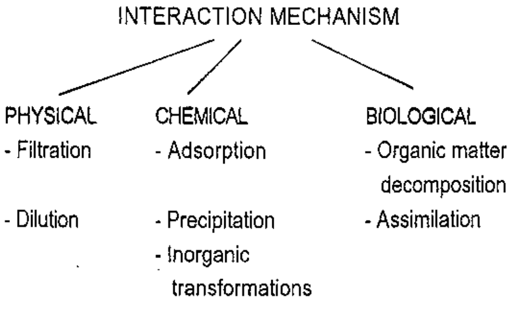

Figure 1. Mechanisms of interaction of wastes with soil

eral particles and organic matter. The accumulation of organic matter in soil as a result of waste application is the prime agent for manipulating the infiltration rate. The residence time of waste constituents increases rapidly with water storage capacity of the soil, thus promoting interaction of wastes with the soil. The retention and transmission of dissolved ions and compounds in wastes are governed by the cation exchange capacity of soil. In fact, the cation exchange capacity is a rough index of all the reactions between charged pollutants and soil colloids. The dissolved ions or compounds in wastewaters are retained in soil primarily through adsorption and chemical precipitation. Specific adsorption occurs when soils retain certain cations and anions so tightly that they are not exchangeable. Heavy metal cations such as Zn, Cu, Ni, Cd and Pb, can be incorporated into the soil via this mechanism. The application levels of Zn, Cu and Ni, which can be phytotoxic and, Cd, which can accumulate in plants to levels toxic to animals/ human consuming them, have been proposed according to relative toxicity of metals, soil texture, organic matter and cation exchange capacity.

The biological transformations of wastes in the soil occur primarily in the root zone. The diversity of organisms in wastewaters enhances the soil's ability to degrade a wide variety of organic substances. The amount of oxygen present in soil largely determines the rate at which the organic matter decomposes and the end products that are formed. Initially, the organisms digest the easily-decomposable materials. The 5-day biochemical oxygen demand (BOD_5) gives the amount of oxygen consumed at this stage. In the second stage of biological transformation, the microbial tissues from organisms die off, and some resistant compounds are partially degraded. This leads to the formation of humus, which is degraded by highly specialized organisms during the final stage of biological transformation.

The soil permeability and nitrogen content limit the waste application rates long before the maximum loading capacity for organics is reached. The general limitations for waste application to soils are described in Table 9. Nitrogen is often the major limiting factor governing the application of wastes. Using these criteria, an added degree of safety occurs in terms of loading values of toxic constituents. For example, if nitrogen requirement of a soil is fifteen-times that for permissible level of toxic elements, there exists a 15-fold safety factor for the application of toxics. In other words, it will be safe to apply wastes containing toxic constituents less than 1/15th of the amount of nitrogen that will become available to crop plants.

Table 9. Summary of general limitations for waste material application to soils

Constituent	Limitation
Organics	
BOD_5	4,480 kg/ha perapplication period[a]
Suspended solids	672 kg/ha per application period[a]
Nutrients	
P	168-336 kg/ha-year
Total N	112-560 kg/ha-year
Toxic materials	
Zn, Cu, Ni, Cd	Depends on soil cation exchange capacity
Sodium	SAR<10

[a] It is assumed that the waste application period is followed by a drying period of at least 3-5 days

Source: Loehr *et al.* (1979)

4. Fertilizers

Several problems linking excessive use of fertilizer with environment have been identified. The increase of nitrates in the drinking water, a development about which general public is greatly concerned, and believed to be due to the excessive use of N fertilizers and animal manures, is regarded as the most important fertilizer-related pollution issue. Nutrient enrichment, eutrophication and deterioration of surface-water quality due to transportation of nutrients applied through fertilizers via leaching and/or runoff and sediment erosion is another problem. As the reactive nitrogen can swiftly move across different media of air, soil and water, it can contribute to higher levels of ozone in the lower atmosphere, causing respiratory ailments and damaging vegetation. A portion of fertilizer nitrogen applied to soil is converted into nitrous oxide which contributes to both the greenhouse effect and stratospheric ozone depletion. From the soil, nitrogen can be lost to atmosphere also as ammonia gas which can fall to the surface as atmospheric deposition after undergoing oxidation to nitric acid, leading to acidification of soils and water bodies, and inadvertent fertilization of trees and grasslands, creating unnatural growth rates, nutrient imbalances, decreasing or altering biodiversity and corrosion of buildings, bridges and other man-made and natural structures. The contamination of soils by heavy metals through fertilizers such as cadmium from phosphatic fertilizers, is also receiving increasing attention of environmentalists.

Fertilizer application to cultivated soil as an element of intensive agriculture is also partly responsible for the less thought of impact of modern farming activities on the environment in terms of impairment, reduction in size, splitting up and destruction of natural and semi-natural biotopes and rural landscape elements. In the developed nations, there has been an intensive use of fertilizer for the past 3-4 decades. If the polluting effects of fertilizers are being observed there now, then similar problems in the developing countries like India should be expected in the near future.

4.1. Pollution due to Excessive Nitrate in Soil

Nitrate can be absorbed by crop plants, lost beyond the rooting zone of the crops via leaching or denitrified to N_2 and N_2O gases. Nitrate leaching below the root zone of crop constitutes a potential pollution threat for surface and groundwater bodies. The production of N_2O through nitrification-denitrification reaction represents a potential danger in terms of damage to both the stratospheric ozone layer and the green-house effect. Nitrate can also be absorbed in large amounts by plants, particularly fodders and vegetables, and may result in nitrate toxicity to the consumers. Thus, a majority of the environmental issues related to N-use in agriculture revolve around transformations leading to the production of nitrate in soil.

The plants, particularly those belonging to the *Chenopodiaceae* family, growing in soils containing high nitrate levels tend to accumulate nitrates because their uptake by roots exceeds reduction and assimilation. Environmental factors, fertilizer-N management and crop production practices besides genetic potential of the plant, control the extent of nitrate accumulation in plants. The amount, source, time and method of application govern the effects of fertilizer-N application on nitrate concentration in plants. In general, longer the plant is in contact with nitrate, greater will be the tendency to accumulate nitrate. Thus, urea or ammonium fertilizers when side-dressed will result in less nitrate accumulation in plants than when source of N is a nitrate fertilizer. Slowly mineralizing organic manures result in less accumulation of nitrate in plants.

4.2. Nitrate Pollution of Groundwater

Two major factors controlling the leaching losses of nitrate are: (i) concentration of nitrate in the soil profile at the time of leaching, and (ii) quantity of water passing through the soil profile. High soil nitrate levels and sufficient downward movement of water to move nitrate below the rooting depth are often encountered in soils of the humid and sub-humid zones, to a lesser extent in soils of the semi-arid zone and quite infrequently, if at all, in arid zone soils (Bijay-Singh and Yadvinder-Singh, 1993). Substantial leaching losses occur if rainfall is received when the soils are at or approaching field capacity. Both intensity and amount of rainfall or irrigation are important in determining the rate and extent of leaching. When high fertilizer rates are combined with heavy irrigation regimes on coarse-textured soils, leaching losses of nitrate can be substantial. Where summer fallow is followed by monsoon type heavy rainfall, leaching of N can occur to a serious extent (Bijay-Singh and Sekhon, 1979).

4.2.1. Health Problems Associated with Nitrate Pollution of Groundwater

The consumption of water containing high levels of nitrate-N can lead to methemoglobinemia (blue baby syndrome), particularly in infants (< 6 months old). The World Health Organization's standard for drinking water is 10 mg NO_3^--N/L. The effects of nitrate on livestock are similar to those on human beings. The ruminants are particularly susceptible because rumen microorganisms can easily reduce nitrate to nitrite which leads to methemoglobinemia. Cattle are more susceptible to nitrate poisoning than sheep and if pregnant, may even abort. An excessive ingestion of nitrates may also increase the risk of cancer in human population through *in-vivo* formation of carcinogenic nitrosamines by the reaction of ingested amines with nitrite in the human stomach.

4.2.2.Nitrate Concentration in Groundwater

Nitrate concentrations in groundwater have increased in several parts of the world in recent years. From 1974 to 1981, nitrate concentrations in the groundwater in the USA had increased up to 60-fold, while in other parts of the world, these are rising at rates of 0.2 - 1 mg NO_3^--N/L/year (Hallberg, 1989).

A significant correlation exists between the amount of fertilizer-N applied per unit area per year and nitrate-N concentration of well-water in Punjab. The geometric mean of nitrate-N content has registered an increase from 0.42 mg/L to 2.29 mg/L during 1975 to 1988 (Table 10). At many places, nitrate levels have exceeded the safe limit of 10 mg NO_3^--N/L (Table 11). An appraisal of risk of nitrate leaching related groundwater pollution in different parts of India can be made by considering together the fertilizer N-use per unit area and the extent of groundwater development for irrigation purposes. Using the data generated by the reconnaissance of nitrate content in shallow groundwaters by the Central Ground Water Board, Agrawal *et al.* (1999) have categorized different states with respect to the potential hazard of nitrate pollution of groundwaters (Table 12). With the highest groundwater development, average nitrate content in groundwater and average fertilizer N-use, the states of Punjab and Haryana have been placed in the high risk zone. Irrigation

Table 10. Nitrate concentration (mg NO_3^-–N/L) in water samples from shallow wells (4 to 10 m deep) located in cultivated areas of Ludhiana district (central Punjab) during 1975 to 1988

	1975		1982		1988
	June	Sept.	June	Sept.	Nov. / Dec.
Number of observations	46	33	26	26	28
Range (mg NO_3^--N/L)	0.04-6.15	0.05-7.90	0.35-10.11	0.23-15.17	0.31-13.30
Geometric mean (mg NO_3^--N/L)	0.42	0.42	1.48	2.13	2.29
Correlation coefficient (r): fertilizer-N applied vs. NO_3^-–N in well water	NS	051*	NS	0.51*	0.59*

*Significant at 5% level of significance

Source: Bijay-Singh *et al.* (1995)

Table 11. Nitrate-N content (mg N/L) in tubewells and hand pumps in four blocks of Ludhiana district in July 1999

Block	Tubewells		Hand pumps	
	Range	Mean	Range	Mean
High Fertilizer Use				
Jagraon	2.46-16.16	6.49	3.57-49.74	12.6
Samrala	1.44-8.73	4.06	0.92-29.58	12.4
Low Fertilizer Use				
Pakhowal	1.67-4.41	2.82	2.95-13.19	6.75
Dehlon	1.32-9.25	4.29	0.15-20.64	8.67

Mean values of nitrate-N in 1992 were: Tubewells = 3.62±1.52 (n = 236), Hand pumps = 5.72±2.09 (n = 367)

Sources: Bijay-Singh *et al.* (1995), Roopna-Kaur (2000)

Table 12. Extent of groundwater enrichment with nitrate pollution in different parts of India

Risk zone	Average fertilizer N consumption (kg/ha)	Average NO_3 in groundwater (mg/L)	Groundwater development (% of total available in 1990)	Region (states)
Little or no risk	2	6-8	< 2	Jammu and Kashmir, North-Eastern states
Low risk	4-11	8-45	5-22	Himachal Pradesh, Madhya Pradesh, Orissa, Maharashtra
Moderate risk	14-53	13-50	16-40	Uttar Pradesh, Uttrakhand, Bihar, Jharkhand, West Bengal, Andhra Pradesh, Gujarat
High Risk	118-163	55-100	70-100	Punjab, Haryana

Source: Agrawal *et al.* (1999)

without artificial drainage in the poorly-drained flat plains of Punjab and Haryana increases the nitrate pollution hazard compared to that in the freely-drained regions of northern and north-eastern states and the peninsular plateau in the southern parts of the country. Agriculture is not intensive in the northern and north-eastern states, as is reflected in the meagre consumption of N-fertilizers and negligible groundwater use. The situation in the peninsular states is in between the two extremes.

The traditional animal waste disposal practices and the presence of manure pits on the village periphery possibly create potential sources of nitrate pollution of groundwater under village habitations. Although animal manures (such as farmyard manure, poultry manure, pig manure) are applied to the cultivated area along with N-fertilizers, crop plants absorb a sizeable portion of the N applied from both organic and inorganic sources, so that only a small fraction of the applied N is leached beyond the root zone.

There are several other sources of nitrate-N, namely sewage effluents, animal excreta, natural soil nitrates and decomposition products of soil organic matter. In many regions, natural deposits of nitrate may constitute a major source of nitrate pollution of groundwater. For example, in some selected locations in Punjab, Haryana and western Uttar Pradesh, nitrate-N concentration in well-water samples is several-fold higher than its upper safe limit.

4.3. Eutrophication

Eutrophication refers to the process of enrichment of surfacewater bodies with nutrients. The nutrient enrichment of water bodies results in intense proliferation and accumulation of algae and higher aquatic plants in excessive quantities that can result in detrimental changes in the water quality and can significantly interfere with man's use of the water resources. For example, decomposition of the algae and macrophyte biomass reduces dissolved oxygen and leads to fish mortality, thus further impairing the water quality.

Not only groundwater, but surfacewater too receives large contribution of nutrients from non-point sources such as agricultural lands. Estimates indicate that more than 90% of the N entering the surfacewaters originates from non-point sources and that more than 80% of that portion is from agricultural lands. High levels of total-N in surfacewaters are generally related to the agricultural activities. The spreading of fertilizers and manures in the drainage basin enhance the nutrient load of the water body. A large part of the nutrient load generated from the agricultural land is related to the natural nutrient-content of the soil. Practices that do not allow for the proper incorporation of fertilizers applied at excessive rates can cause short-term elevated nutrient concentrations in the runoff.

Both N and P are important in stimulating eutrophication. In most of the low producing oligotrophic (low in nutrients) surfacewater bodies, P rather than N is a limiting constituent. In many of the eutrophic lakes, biotic productivity is controlled by N because the N/P ratios of pollutants from many sources are far below the ratios required for the plant growth. Also, in some oligotrophic lakes where N is the limiting nutrient, the input from groundwater, surface runoff or precipitation may be essential to maintain the biological productivity. The urban and industrial wastes usually account for most of the phosphate loading. However, surface runoff (including soil erosion) from cultivated land can contribute to phosphate loading of surfacewaters. The best management practices recommended for a particular soil, crop and region are highly effective in eliminating this possibility and at the same time, allow the most efficient use of fertilizers by crops to ensure optimum food production.

4.4. Nitrous Oxide Emissions from Soil in Relation to Climate Change Effects

Nitrous oxide (N_2O) is a trace gas that is formed during the microbial processes of nitrification and denitrification in soils. The natural emissions of N_2O can be increased by a variety of agricultural practices and activities, including the use of synthetic and organic fertilizers, production of nitrogen-fixing crops, cultivation of high organic content soils, and the application of livestock manure to croplands and pastures. All of these practices directly add additional nitrogen to soils, which can then be converted to N_2O. Water management in fields greatly influences the extent of N_2O emission. Up to 50% of the applied-N can be lost through denitrification when alternating aerobic – anaerobic conditions prevail in the rice fields. A vast majority of soils in the Indo-Gangetic Plains of India are relatively coarse-textured and experience frequent alternating aerobic – anaerobic conditions.

Nitrous oxide is one of the greenhouse gases and contributes around 6% to the anthropogenic greenhouse effect (IPCC, 2001). It also contributes to the depletion of stratospheric ozone. The global atmospheric N_2O concentration increased from a pre-industrial value of about 270 parts per billion (ppb) to 319 ppb in 2005. The growth rate has been approximately constant since 1980. More than a third of all N_2O emissions are anthropogenic and are primarily due to agriculture (IPCC, 2007). Following Intergovernmental Panel on Climate Change (IPCC) methodologies, Garg *et al.* (2006) have estimated direct N_2O emissions from soils (including use of synthetic fertilizers), field burning of agriculture crop residues, manure management, indirect soil emissions, fossil fuel combustion, industrial activities, namely production of nitric acid, and waste sector in India (Table 13). Agricultural sector activities account for more than 80% of the total N_2O-emission, including 60% from the use of synthetic fertilizer, about 12% each from agriculture residue burning and indirect soil emissions and about 3% from manure management (Garg *et al.*, 2006). Production of N_2O occurs by both nitrification and denitrification during the storage of animal manures. Emission factors for N_2O for solid storage of

Table 13. N_2O emissions from various source categories in India

Source categories	1985	1990	1995	2000	2005	Compounded annual growth rate (%)
	Gg-N_2O					
Synthetic fertilizer use	80	94	109	129	151	3.2
Field burning of agricultural residues	15	18	21	21	20	1.4
Indirect soil emissions	17	19	21	25	30	2.9
Manure management	4	5	6	6	8	3.9
Fossil fuel combustion	7	9	12	15	19	4.9
Industrial processes	6	7	9	12	16	5.0
Wastes	5	6	7	8	9	2.8
Total N_2O	134	158	185	217	253	3.2

Source: Garg *et al.* (2006)

animal manure in India, as worked out by Gupta *et al.* (2007), varies from 3 to 11.7 mg/head/year for different categories of bovine with a total annual emission estimate of about 2344 kg N_2O for the country.

4.5. Ammonia Emissions from Soil and Environmental Degradation

Application of nitrogen fertilizers to soil and the livestock are the major contributors to ammonia emissions. Out of all the fertilizers, urea application is responsible for more than 90 % of the total contribution due to fertilizers. Loss of N via ammonia volatilization can be substantial when urea is top dressed, particularly on alkaline soils. Deep placement of urea in the soil as such or its application before irrigation results in substantial reduction in ammonia volatilization losses from agricultural fields. In the atmosphere, ammonia is either deposited or transformed into an ammonium aerosol. Before deposition, ammonium aerosols contribute to fine particulate matter and regional haze concentrations in the atmosphere. Ammonia plays an important role in the direct and indirect effects of aerosols on radiative forcing and thus in global climate change (Bijay-Singh *et al.*, 2008). About half of the ammonia that is volatilized is deposited in downwind ecosystems within a 50-km radius, while the other half is deposited over a much broader region.

The estimates of ammonia emission in India are highly uncertain as no country-specific emission factors are available. Parashar *et al.* (1998) estimated that the fertilizer applications in India were responsible for the emission of about 1.17 Tg NH_3 during 1993-94; the emission from livestock sector was estimated to be 1.43 Tg NH_3. Losses of ammonia following fertilizer applications to upland and lowland cropping systems can range from ~0 to > 50%, while losses from flooded rice can reach as high as 80%. Fertilizer placement, the timing of application, soil temperature and fertilizer type determine the ammonia loss rates.

4.6. Strategies for Minimizing the Adverse Effects of N–use on Environment

There can be two general approaches to minimize the environmental pollution arising due to N–use in agriculture. One is the optimum use of the ability of crop plants to compete with processes that lead to losses of N from soil-plant system to the environment. Second approach can be the direct reduction in the rate, duration and extent of loss of N to the environment by loss processes themselves. Some of the management practices, listed in Table 14, ensure that fertilizer N is efficiently utilized by crop plants while the other prac-

Table 14. Management practices that can reduce environmental pollution by N originating from agricultural lands

Improved Fertilizer N–use Efficiency

- Apply optimum dose of fertilizer N
- Time the fertilizer N applications to coincide with crop needs
- Apply N fertilizer in split doses
- Apply balanced doses of N, P and K
- Incorporate or deep place fertilizer N into soil
- Use slow release fertilizers
- Use urea and nitrification inhibitors

Land Management Techniques

- Use of crop rotations and catch crops
- Improve irrigation scheduling to encourage plant growth and minimize leaching
- Conservation tillage to control surface runoff
- Crop residue recycling
- Use of animal manures
- Use of terrace, contouring and retention bases to catch sediments
- Genetic manipulation of plant material to be more efficient at N-recovery and N_2-fixation

Source: Cameron and Haynes (1976)

tices influence the behaviour of N so as to reduce its entry into the environment.

Obviously, the fertilizer N–use efficiency as a factor deserves the most careful attention if agriculturists are to obtain maximum crop yields and prevent pollution of the environment. It varies with the type of fertilizer and the rate at which N is applied, the nature of the chemical and biochemical reactions between soil and fertilizer, the timing and placement of fertilizer, the type of crop and its N-requirement, the adequacy of other nutrients and a number of soil, climatic and management factors. Under favourable conditions, 80% or more of the fertilizer N may be utilized by the crop, but usually efficiencies of 50% or even less are common. Low fertilizer-use efficiency is caused by the loss of N from the soil-plant system via mechanisms such as leaching, ammonia volatilization and denitrification.

4.7. Heavy Metal Contaminants in Fertilizers as Soil Pollutants

Recently, there has been increasing concern towards the health hazards associated with heavy metals entering the food cycle via soil. Fertilizers contain heavy metals as impurities; rock phosphate being a highly potential source. The application of rock phosphate or its products to soil always implies the addition of a significant amount of lead and cadmium into the soil. The analysis of lead and cadmium content of different commercial fertilizers suggests that a combination of low analysis and straight fertilizers can add more lead and cadmium to soil than high analysis and mixed fertilizers.

The heavy metals applied to soil through different derivatives of rock phosphate accumulate almost completely in the surface layer of the soil and in forms generally easily available to plants. In soils with coarser textures and acidic reaction, heavy metals, applied through fertilizers, are available more than in those containing large amounts of clay and with alkaline reactions.

Although relevant data from soils in India are not available, it is interesting to note that less than 6% of the annual deposits of cadmium to the soil of European Economy Community come from the use of phosphate fertilizers, with a further 2% from phosphoric acid manufacturing, whereas two-thirds is attributable to solid wastes and excrement, aerial deposition and use of pigments and stabilizers (Anonymous, 1992).

5. Pesticides

The use of pesticides (insecticides, fungicides, herbicides) in India is increasing at the rate of 2-5% per annum. A large portion of the pesticides applied to control pests and weeds eventually finds its way into the soil, which acts as a reservoir for these residues. Inappropriate pesticide application can also lead to off-target contamination due to spray drift and run-off from plants, causing contamination of the soil. From the soil, pesticide residues enter into the bodies of invertebrates, get transported into water or air or are broken down into innocuous substances.

The effectiveness of a pesticide as well as the hazards of its harmful residues depend largely on the duration for which a pesticide remains in the soil. For example, DDT has a half-life of three years in cultivated soils, while organophosphate insecticides persist for only a few days or months. A grouping of pesticides based on persistence in soil has been provided in Table 15. The chlorinated hydrocarbons persist longer in soils having a large amount of organic matter, although more amount of the chemical must be applied to these soils to kill pests. Insecticides persist longer if worked into the soil than if left on the surface. Herbicides applied to soils may not persist at all or may persist for very short durations, depending on the individual compound. Ultimately, pesticides disappear because of evaporation and vaporization, leaching, plant uptake, chemical and microbial decomposition, and photodecomposition.

When a pesticide enters the soil, some of it is adsorbed to soil particles, particularly organic matter, and some gets dissolved and mixed with the soil water. As more water enters the soil through rain or irrigation, the adsorbed pesticide molecules may be desorbed from soil particles. One of the most useful indices for quantifying pesticide adsorption on soils is the partition coefficient. The partition

Table 15. Grouping of pesticides based on persistence in soils

Non-persistent (half-life less than 30 days)	Moderately persistent (half-life greater than 30 days but less than 100 days)		Persistent (half-life greater than 100 days)
Aldicarb	Aldrin	Heptachlor	Bromacil
Captan	Atrazine	Linuron	Chlordane
Dalapon	Carbaryl	Parathion	Lindane
Dicamba	Carbofuran	Phorate	Paraquat
Malathion	Diazinon	Simazine	Picloram
Methyl parathion	Endrin	Terbacil	Trifluralin
Oxamyl	Fonofos	TCA	
2,4-D	Glyphosate		
2,4,5-T			

Source: Rao *et al.* (2008)

Table 16. Partition coefficients for selected pesticides (generic name only)

Pesticide	Partition coefficient	Pesticide	Partition coefficient
Aldicarb	10	Carbaryl	229
Chloramben	13	Monolinuron	237
Carbofuran	29	Prometone	300
2,4-D	32	Ametryn	380
Fenuron	34	Diuron	389
Terbacil	46	Promethryn	513
Propham	51	Trietazine	549
Bromacil	72	Chlorpropham	589
Monuron	135	Linuron	841
Simazine	158	Ipazine	1,161
Dichlobenil	164	Malathion	1,778
Atrazine	172	Chloroxuron	4,986
Fluometuron	174	Methyl parathion	7,079
Cynazine	190	Parathion	7,161
Propazine	207	Chloropyriphos	13,490
		DDT	243,000

Source: Rao *et al.* (2008)

coefficient value is defined as the ratio of pesticide concentration in the adsorbed state and the solution-phase. Thus, for a given amount of pesticide applied, smaller is the partition coefficient value, higher is the concentration of pesticide in solution. Pesticides with small partition coefficient values are more likely to be leached compared to those with large partition coefficient values. Partition coefficients of several chemicals, shown in Table 16, are independent of soil type and are characteristic of each pesticide. The partition coefficient is determined by chemical properties like solubility and melting point of a pesticide.

The activities of diverse soil microorganisms and the associated soil microbial processes may be adversely affected by pesticides because (a) these are chemicals that have deleterious effect even on non-pest species, and (b) being organic in nature, these can be metabolized, resulting in modification of their activities. The pesticides decrease biodiversity in the soil because they do not just kill the intended pests and when soil biology is affected, the soil quality deteriorates as complex interactions which result in good soil fertility also break down. It is now apparent that pesticides can have unforeseen effects on non-target organisms and can thus influence crop productivity to an extent even more than the pests these are intended to control.

5.1. Insecticides

In almost all the soils that have been surveyed for insecticide residues in India, the most common chemical, and the one that is found in the largest amounts is DDT, followed by HCH and dieldrin. In a study in Punjab, out of 106 soil samples, 91 were found contaminated with insecticide residues. The highest level of 0.08 mg/g DDT-R was found in the cotton-growing areas, which is four-times of its permitted level of 0.02 mg/g. The presence of cholinesterase inhibitors in 19% soil samples indicated contamination with organophosphates and carbamate insecticides.

The reactions, movements and degradation of insecticides affect the persistence of these chemicals in soils and determine the risk of soil pollution. The biochemical degradation by soil organisms is the single most important mechanism that can remove insecticide residues from the soil. However, insecticides like DDT are subject to slow photodecomposition activated by solar radiation and organophosphates are subject to hydrolysis and subsequent degradation in the soil.

5.2. Fungicides

The residues of fungicides based on the inorganic compounds of sulphur, copper and mercury accumulate in soil because the heavy metals contained in them are irreversibly adsorbed on soil colloids. Under certain soil conditions, toxicity from the accumulation of copper-based fungicides may render the soil useless for growing crops. Similarly, the oxidation of sulphur contained in fungicides can alter the chemistry of organic matter in the surface horizon of soils in a way that decline in yield of some crop plants may occur. Other fungicides like captan, carboxin, benomyl, etc. are decomposed very rapidly through the biochemical processes. Within a few weeks of their application, the presence of these compounds becomes negligible.

5.3. Herbicides

In the intensive and diversified crop rotation systems, a herbicide applied to one crop may persist in the soil at concentrations high enough to damage the subsequent sensitive crops. For example, atrazine is the most selective and widely-used herbicide for controlling weeds in several crops. It has revolutionized the cultivation of sorghum, maize and millets in the semi-arid tropics, but when applied repeatedly, it starts building undesirable residues in the soil. Under Indian conditions, when a herbicide dose of 0.5 to 2.0 kg/ha is applied, it results in a build-up of residues in the range of 0.25 to 1.0 mg/g, which is safely below the potential residual effect. At different locations in India, it has been observed that several herbicides including fluazifop-butyl, metolachlor, oxadiazon, nitrofen, 2,4-D, metoxuron, isoproturon, oxyfluorfen and tribunil leave a little or no residual effect on the crops (Saraswat and Jayakumar, 1994). But, the residues of some herbicides, viz. fluchloralin, metabenzthiazuron and atrazine were detected in amounts that could adversely affect not only other crop plants but also several processes in soil, leading to inefficient nutrient management and in turn, reduced crop yields. The most sensitive systems are soil organic matter decomposition and different aspects of nitrogen cycle in the soil.

A normal dose (less than 40 mg/g) of DDT does not adversely affect nodulation and nitrogen fixation by *Rhizobium.* On the other hand, lindane applied at normal rates considerably reduces the number and weight of nodules in crops like groundnut. The nodule number is not adversely affected by fungicides. The herbicide, 2,4-D restricts the growth of *Azotobacter.* Blue green algae can tolerate endrin up to 6,000 mg/mL, but HCH has been found to be more toxic to it due to the suppression of heterocyst frequency.

5.4. Reducing the Pesticide Levels in Soil

Degradation of even the most resistant pesticides is encouraged by conditions that favour overall microbial proliferation in the soil. The biochemical degradation by soil organisms is the single most important method by which pesticides are removed from the soil. The polar groups, such as –OH, –COO– and $-NH_2$ on the pesticide molecules are the favourable points of attack by the microorganisms. The application of easily decomposable organic matter can help reduce pesticide levels in the soil. The application of large quantities of organic manures and raising high N cover crops also prove useful. Other practices to reduce pesticide levels in the soil include growing of crop plants that have a tendency to accumulate the pesticide or following of soil management practices leading to increased leaching of the pesticides. However, some of these practices result in only transferring the pesticide chemicals from the soil to some other part of the environment.

Application of the same pesticide on the same piece of land can lead to increased rates of microbial degradation of the chemical. This may be advantageous in the case of insecticides and fungicides in relation to environmental quality, but the rapid breakdown may result in a reduced effectiveness of herbicides.

6. Potentially Toxic Elements

The toxic elements can be air borne or may reach soil through native rocks and mining operations or get applied to agricultural land as impurities of agricultural inputs such as fertilizers, manures, fungicides, wastewaters and sludges. Additions through aerial sources, native rocks or mining operations are largely localized. Thus, as already discussed, the industrial and sewage wastes, fertilizers and manures constitute the main sources of toxic elements in the soil-plant system.

In the soil, toxic elements interact with both organic and inorganic matter and may become available to vegetation and subsequently, to the animals/human beings consuming that vegetation. It is at this point that the toxicity potential of these elements should be realized. The effect is visible in the form of reduced crop yields or sick animals. Not only crop plants exhibit varying response to potentially toxic elements, but also the behavior of different elements in the soil-plant system varies considerably.

6.1. Cadmium

High levels of cadmium in soil (>1 mg/kg) presently found in some mining and industrialized areas (such as Orissa), are largely the result of emissions in the past when smelters were operating under less stringent conditions and when cadmium was not recovered during zinc production. Cadmium is toxic to a number of plant species at relatively low concentrations in the soil. Cadmium in the soil also adversely affects microbial activity involved in nutrient cycling and maintenance of soil fertility. Uptake of Cd by plants from soils is primarily controlled by the concentration of Cd in soil solution. Accumulation of Cd varies with plant species, varieties, plant part under consideration and soil properties. Cadmium has a tendency to concentrate in the leafy vegetable tissues rather than in fruits and grains/seeds. Factors such as soil pH, applied fertilizers, presence of other heavy metals, temperature and soil organic matter exert a profound influence on Cd uptake by plants. An increase in soil pH reduces the availability of Cd to crop plants. In soils containing free $CaCO_3$, availability of Cd may be reduced due to adsorption of Cd^{2+} on the surface of the $CaCO_3$ or due to effect of increased soil pH. Although incidence of *itai-itai* disease in the Jintsu valley of Japan occurred because of the high Cd-content of rice, reducing soil conditions hinder the uptake of Cd by rice. Anaerobic conditions during the grain filling stage depress the Cd-content of grains.

6.2. Lead

Wide variations in Pb levels in the soil have been reported, ranging from less than 100 mg/kg to well over 11,000 mg/kg. Natural levels of lead in surface soils are usually below 50 mg/kg. The accumulation of Pb in soil is primarily a function of the rate of deposition from the atmosphere or through additions from sewage and different kinds of industrial wastes. The fate of Pb in soil is affected by the specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and the formation of relatively stable organo-metal complexes or chelates with the organic matter in soil. Lead is converted rapidly to lead sulphate at the soil surface. Lead sulphate is relatively less soluble, and could leach through the soil if it is not transformed further. In soils with pH 5 or more and with at least 5% organic matter, Pb is retained in the upper 2-5 cm of undisturbed soil.

Lead may mobilize from soil when lead-bearing soil particles run off to surfacewaters during heavy rains. Lead may also mobilize from soil to atmosphere by downwind transport of smaller lead-containing soil particles entrained in the prevailing wind. The downward movement of Pb from soil by leaching is very slow under most natural conditions. The conditions that induce leaching are the presence of Pb in soil at concentrations that either approach or exceed the sorption capacity of the soil, the presence in the soil of materials that are capable of forming soluble chelates with Pb, and a decrease in the pH of the leaching solution (e.g., acid rain).

Very high concentrations of Pb in the soil are necessary to produce toxic response. It is fixed in the soil by hydrolysis and polymerization. Soil factors such as high cation exchange capacity, alkaline pH, high organic matter and P-content in the soil reduce Pb-uptake by plants. It implies that if wastes rich in phosphorus and organic matter (such as sewage waters and sludges) are applied to the soil, very little hazards due to Pb are expected.

6.3. Mercury

In the uncontaminated environment, Hg-content of plant tissues seldom exceeds 500 parts per billion (ppb). In naturally contaminated areas (near Hg-bearing deposits), its level can be as high as 3500 ppb. Mercurial fungicides such as Ceresan M., constitute an important source of Hg for crop plants. The behaviour of Hg in the soil is controlled primarily by adsorption and desorption processes. Depending on complexation, the most important ligands in solution are OH^-, Cl^-, and organic anions. Since the solubility of $HgCl_2$ and $Hg(OH)_2$ is high, the affinity of Hg to these ligands leads to an increased mobility. This is particularly true for $HgCl_2$, whereas the hydrolysis of Hg^{2+} may result in the specific adsorption of Hg on mineral colloids. The high affinity of Hg to S explains the strong binding of Hg to soil organic matter and also the stability of HgS. Precipitation products other than HgS are unlikely to occur, since the activity of Hg^{2+} remains too low to exceed the solubility product of any other defined Hg compound. It is mainly the physical state of soil organic matter (dissolved or adsorbed) that determines the behaviour and distribution of Hg in soil.

Mercury is strongly held by the soil and the adsorption sites for the element never approach saturation before another toxic element becomes hazardous. Mercury content of the above-ground plant parts is generally low despite Hg seed treatment or its addition to soil. In general, Hg hazards in intensive agriculture are much less than in aquatic food chain.

6.4. Nickel

Much of the Ni released into the environment ends up in the soil or sediment where it is strongly attached to particles containing iron or manganese. Soil usually contains between 4 and 80 mg Ni/kg soil. The highest soil concentrations (up to 9,000 mg/kg) are found near industries where Ni is extracted from ore. Nickel pollution may affect microbial community development and its activity in soil and, therefore, its fertility, while organic amendment may affect Ni mobility and bioavailability. Although Ni can occur in several oxidation states, its chemistry in the soil is based on its divalent ion (Ni^{2+}). Nickel(II) is the most stable state over a wide range of pH and redox conditions found in surface soils. Under acidic and reducing conditions, the sulphides of Ni(II) are the most likely to control its concentration in the soil solution. As alkalinity of soil increases, Ni(II) more likely forms sulphate, phosphate, carbonate and hydroxy complexes if the bulk solution chemistry permits. The mobility of Ni in soils increases as the pH and the cation exchange capacity decreases. Binding of Ni to the organic fraction of soil can be important, for example, in the release of Ni from soil amended with sewage sludge.

Nickel content in the range of 50 to 100 mg/g (dry weight basis) is indicative of its toxicity in plants. Nickel behaves largely like Zn in the soil-plant system, but it forms stronger chelates with soil organic matter, thereby showing closeness to Cu. Possibility of Ni-toxicity to plants cannot be ruled out when industrial or municipal wastes with high Ni concentrations are applied to agricultural lands. Nevertheless, like Zn and Cu, phytotoxicity of Ni appears to provide an effective barrier against Ni-toxicity to human population and animals.

6.5. Chromium

Chromium is essential to human and animal life but non-essential for the vegetable kingdom. In the soil environment, Cr can be found in two main oxidation forms — Cr(III) and Cr(VI), which show contrasting properties. The trivalent Cr is apparently useful or harmless to living organisms at reasonable concentrations, while Cr(VI) is extremely toxic. In addition, Cr(III) is not mobile in soil, therefore risks of its leaching are negligible. On the other hand, Cr(VI) is mainly present in the forms of chromates (CrO_4^{2-}) and dichromates ($Cr_2O_7^{-2}$) and is generally mobile and often a part of crystalline minerals (ophiolites, serpentines). Chromium-rich soils (serpentine soils) exist in many countries and Cr-content in these soils may exceed 10,000 mg/kg.

Chromium shows a low (normally less than 5) soil-plant transfer factor (the amount of metals that passes from the soil to the plants). The main barrier to the entry of Cr in plants is represented by the roots. Cr(III) is fixed on the roots and the amount that crosses the cellular wall is negligible. Thus, plants do not accumulate Cr even when it is present in the soil in high concentrations. When applied to the soil in the soluble trivalent form, Cr is rapidly transformed to insoluble hydroxides or oxides forms, which are relatively insoluble. As Cr (VI) is reduced to Cr (III) during digestion of the sludge, it appears that Cr applied to the soil through sewage sludge presents little hazard to food chain.

6.6. Selenium

Selenium is essential for animals and humans, but not for plants. A dietary concentration of less than 4-5 mg/kg is often suggested as the maximum amount that will avoid Se-toxicity. Se in wastewater and sludge is generally present as elemental Se, selenites bound to hydrous iron oxides, heavy metal selenides or trimethyl selenonium salts. These Se-forms when applied to soil are not easily available to plants. Thus, chances for the occurrence of Se-hazards through the application of wastewater or sludge containing Se are little. In soils, Se becomes available to plants primarily as selenate under aerobic conditions and as selenite under reduced conditions. Soils containing Se in toxic levels are termed as seleniferous soils and crop plants grown on these soils contain Se in levels toxic for animal and human consumption. Some pockets of seleniferous soils have been identified in the north-western parts of India (Dhillon and Dhillon, 1997).

6.7. Arsenic

Arsenic builds up in the soil environment through natural processes of weathering of arsenic-bearing rocks or use of arsenic-contaminated groundwater for irrigation or through a host of anthropogenic activities such as mining operations, smelting of base metal ores, combustion of coal and application of arsenical pesticides. The arsenic content of contaminated soils varies widely. In general, soils overlying sulphide ore deposits or derived from shales and granites and those surrounding geothermal activity, have high arsenic contents.

Arsenic can be released into underground water from sediments through natural chemical and biochemical processes like the oxidation of arsenic-rich sulphide compounds and the reduction of arsenic-containing iron oxides. In West Bengal, water samples from about 55% tube-wells have been found to contain arsenic in concentrations more than 10 µg/L, which is the maximum permissible limit of World Health Organization (Roy Chowdhury *et al.*, 1999). The soils being irrigated with As-contaminated waters showed the presence of 6-10 mg/kg of EDTA-extractable As. Arsenic retention by soils is governed largely by the adsorption process rather than the precipitation of sparingly soluble arsenic compounds.

The toxicity of arsenic compounds in the soil environment is determined by its oxidation state (redox state and pH) and its presence in the organic/inorganic combination. The arsenites are highly soluble, mobile and toxic than the arsenates. Under aerobic condition, As(V) form predominates. Phosphate ion is an analogue of As(V), making it an important factor in the behaviour of As in aerobic soils. Both ions compete for uptake by plants. The effect of phosphate additions to aerobic soils on the uptake of As will therefore depend on the balance between competition for sorption sites and competition for uptake. The biological availability and phytotoxicity of As in soil increases on reduction to the As(III) state which is facilitated on flooding of the soil. As(III) is not an analogue of phosphate ion so that its presence is less relevant to As behaviour under flooded soil conditions. Different crop plants vary in their tendency to accumulate As from the soil (Table 17). Irrigated wetland rice is the crop most vulnerable to arsenic toxicity in the irrigation water-soil system in South Asia. This is because wetland rice is grown under anaerobic soil conditions (soil kept under 5-10 cm water), which makes arsenic mobile and bioavailable. The amount of extractable As in soil increases with the extent of submergence or decreasing E_h and decreases with zinc application. The arsenic-content in soil markedly decreases due to application of organic manures, especially farmyard manure (Das *et al.*, 2008).

6.8. Reducing Heavy Metal Pollution in Soil

The prevention of soil contamination by inorganic toxic compounds, particularly heavy metals, can be achieved by either eliminating or drastically reducing the application of the toxins to soil or by managing the soil-crop system in a manner that leads to the prevention of further recycling of the toxins. Industrial managers and decision-makers need to recognize that soil is an important natural resource with finite capacity and it can be damaged by accidental contamination through the addition of inorganic toxins. There must also be judicious reductions in the intended applications to soil of the wastes containing toxic compounds in quantities that may interfere with the normal behaviour of the soil.

Table 17. Arsenic uptake by different crops at harvest

Crop	As concentration (mg/kg)		
	Leaf	Stem	Root
Elephant foot yam	4.60	8.30	-
Green gram	5.28	5.70	6.00
Cowpea	5.00	5.38	6.10
Maize	3.80	6.19	6.32
Rice (summer)	8.42	7.32	8.30
Rice (wet season)	5.12	6.30	8.23
Jute	3.69	9.30	11.02
Potato	5.20	7.80	12.20
Mustrad	6.96	7.00	7.23
Groundnut	2.12	2.43	3.10
Sesame	2.12	0.83	5.60
Wheat	5.80	6.93	14.00

Source: Das (2007)

The continuous cycling of toxic inorganic chemicals can be reduced by following such judicious soil and crop management practices, which keep the chemicals in the soil and reduce their uptake by plants. The cycle of soil-plant-animal (human) through which toxic elements exert their effect is broken by immobilizing the toxins in the soil. The soil becomes a sink for the toxic elements. For example, if the soil pH can be maintained neutral or above (by liming of acid soils), most of the toxic elements are rendered less mobile and less available. Similarly, the drainage of wet soils helps in the formation of oxidized forms of several toxic elements, which are generally less soluble and less available for plant uptake. Heavy phosphate applications to soil can also lead to reduced availability of toxic cations.

The fact that crop species or varieties differ in extracting toxic elements from the soil can be used to decontaminate the soils, though to a limited extent. The removal of Se in large quantities by some crop species as compared to others demonstrates the effectiveness of phytoremediation for reducing the amount of Se in the soil. The accumulator plants should, however be avoided if the harvests are to be fed to human beings or domestic animals.

7. Radionuclides

The radioactive elements emit radiations which could be gamma rays, beta rays, alpha particles or neutrons. The interaction of a living body with radiations brings about a number of changes such as modification of cells or even death of cells. Persons exposed to high radiation levels experience nausea, diarrhoea, vomiting, hemorrhages, leukemia, sterilization or death. Even at low dosage levels, a reduction in the count of white blood cells is common due to the damage caused to cell membranes.

There are several sources from which radioactive contamination might be occurring. The fallout from testing of nuclear weapons has resulted in worldwide contamination, while waste products and effluents from nuclear reactors have been the principal sources of localized contamination. As the use of nuclear energy is expanding for various peaceful applications, more and more radioactive fission products are expected to be released into the biosphere. Sooner or later, some of these radionuclides will find their way into the human food chain. Contaminated soils and plants are important links in the movement of radionuclides through the food chain leading to man. The serious nuclear accident at the Chernobyl power plant on 26 April 1986 in the erstwhile U.S.S.R. demonstrated the vulnerability of agricultural soils to radioactive contamination from atmospheric fallout. It affected large areas across Europe up to thousands of kilometers from the accident site.

Of the numerous radionuclides formed as a result of application of atomic energy, the nuclides that could be of great significance in food chain are: $^{89\text{-}90}$Sr, ^{137}Cs and ^{131}I. The radioactive elements in the soil are absorbed into plants, as other elements, and become a part of whatever is consumed by the plants. The uptake of radionuclides from the soil by plants depends on the solubility of fallout debris, the chemical reactivity of individual radionuclides in soils and the absorption power of plant roots. In general, the relative order of magnitude of plant uptake of fission products has been found to be: $^{89\text{-}90}\text{Sr} > {}^{131}\text{I} > {}^{140}\text{Ba} > {}^{137}\text{Cs}$ (Nishita *et al.*, 1964). Although the relative order of magnitude varies little, the absolute magnitude of uptake depends upon soil management practices such as cultivation, fertilization and organic matter application. Fortunately, the transfer factor of radionuclides to plants is generally very low, especially for the more radiotoxic actinides. For example, Bannai *et al.* (1995) have reported transfer factors of radioactive Cs, Sr, Mn, Co and Zn from soil to edible parts of leafy vegetables as 0.11, 0.24, 0.61, 0.05 and 0.52, respectively. Soil-plant transfer factors tend to decline slowly with time for various reasons.

The soil-plant step largely reduces the transfer of radionuclides into the food chain, and thus the potential hazard to man. However, pollution from radioactivity is of great concern because of its invisibility, insidious damages and the fact that there is no known way yet to reduce or stop a radiation process. Even when it is known that soil has been contaminated with radionuclides, only known way to eliminate the hazard is by scraping and carrying off the contaminated soil.

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Chapter 29

Soil Management for Sustainable Farming

J.S. KANWAR

> *"Upon this handful of soil our survival depends. Husband it and it will grow our food and fuel and our shelter and surround us with beauty; abuse it and the soil will collapse and die, taking man with it"*

1. Introduction

Sustainable farming is the successful management of resources for agricultural production to satisfy the human needs while maintaining or enhancing the quality of environment and conserving natural resources. A farming system can be considered sustainable if it ensures that "today's development is not at the expense of tomorrow's development prospects" (World Commission on Environment and Development, 1987).

No system of farming will be sustainable unless the soil which forms its pivot and is the most important natural resource is managed scientifically to meet the present and future needs, its productivity and quality are maintained continuously and there is no reduction of output, with inputs.

Following are a few important aspects of sustainable farming:

(i) Meeting the developing needs of today and tomorrow without deceleration of growth rate with constant inputs,

(ii) Economic viability and enhanced productivity,

(iii) Successful management of resources — internal or external, renewable or non-renewable,

(iv) Maintenance, preferably enhancement, of quality of environment, and

(v) Conservation of natural resources of soil and water.

Sustainable farming system should be considered a management system that uses inputs, whether produced on the farm or purchased externally, most efficiently to maximize the productivity and profitability from the operation, while minimizing their adverse effects on the quality of soil and water and keeps it buffered against risks. It is a dynamic and not a static system. The tribal shifting cultivation system of "Slash and Burn" of 25-year rotation of north-east India, which was sustainable at low level of productivity and was considered adequate to meet the needs of low population pressure, is no longer sustainable for meeting the needs of higher human and animal pressure and increased demands for better nutrition and economic needs of today. The question is whether the replacement of shifting cultivation system of low productivity with a settled agricultural system of high productivity with agricultural inputs of modern agriculture is sustainable. Can this strategy continuously meet the growing needs for food and other agricultural products of the present generation and of the successive generations without detriment to environment?

Sustainability has several dimensions — technological, ecological, economic, social and cultural. For those engaged in the development of sustainable farming technology, it is essential to ensure that the technology is based on remunerativeness, including high-yielding varieties (HYV) and agricultural inputs (both internal and external), such as fertilizers and manures, energy, water and management practices. It should be environment-friendly and buffered against risks.

Soil and climate are the pivotal factors which determine the suitability of a farming system. It is the utilization of agricultural inputs and technology based on the most harmonious use of seed, fertilizer, manure, pesticide, energy and management practices that determine the productivity, efficiency and sustainability of a farming system.

It was believed that generally climate does not change much, though the microclimate can be modified within certain limits through the use of irrigation water and other inputs. However, of late, the world's concern about global warming signals is the indicator of climatic changes, with consequences about soil quality and agricultural productivity. How to meet these impending changes is also an agenda for soil science research. Soil is considered to be a non-renewable resource, as it takes a few hundred years for building one cm of soil which can be lost through negligence of man within a year. Man's activities can exhaust the soil in a short time through exploitative agriculture if the nutrient input-output relations are not balanced.

A degraded soil can be improved and made suitable for profitable production using proper management technology and inputs. Thus, man has the ability and capacity to reclaim and improve the degraded soils and make them productive using a proper management system. However, the time and cost involved in reclaiming a degraded soil are the serious limitations. History is full of examples where bad management turned good soils into deserts and *vice versa*. And it is a continuous process. Thus, desertification and physical, chemical and biological degradations are serious problems of today's agriculture in the absence of proper soil ameliorative practices to counter the effect of soil degrading processes.

2. Soil Management for Sustainable Farming

There are many parameters for measurement of soil maintenance or improvement. Soil quality is a yardstick of good soil management for sustainable farming. Following are some of the parameters for estimating soil quality:

(i) Soil depth and water holding capacity.

(ii) Nutrient availability — capacity and intensity factors.

(iii) Soil reaction (pH), soil salinity and sodicity.

(iv) Physical environments — structure, aeration, drainage.

(v) Hydrological regimes — waterlogging, drainage, water deficiency, etc.

(vi) Soil erosion and soil and water loss.

(vii) Soil biology, microorganisms and integrated activity.

(viii) Soil productivity as an integrated index of all these factors.

Any system of farming which causes adverse effect on these parameters of soil quality is unsustainable. The sustainability has a time dimension and cannot be assessed over a short period.

3. Important Factors of Soil Management

The most important factors which are conducive to high productivity are nutrients, water, energy and management for a cropping system. This system includes high-yielding cultivars, tolerant to biotic and abiotic stresses, and has a restorative crop in the crop rotation, which builds soil fertility. The productivity over a large number of years or crop-cycles, determines the sustainability of a high productivity system. Short-term measurements of productivity are poor indicators of sustainability; in fact, the short-term perspectives lead to long-term disasters.

3.1. Nutrient Management

Fertilizers and manures are the king pins of improved technology, contributing about 50 to 60% increase in productivity of foodgrain in India, irrespective of soil and agroecological zone. But, without an integrated use of fertilizers and manures, increased production is not possible. The high-yielding varieties produce dramatic increases in yields through conversion of chemical energy of fertilizers and manures into biomass with higher grain : straw ratio. For the land-short countries, use of fertilizers provide the best strategy for land saving. But for this strategy, India and China would have required to put 2-3 times more area under cereals to produce the same quantity of foodgrains in 1992 as was produced in 1961 (Figure 1) (Borlaugh, 1994)

The new series of long-term fertilizer experiments in India which have been in progress since 1970 in intensive cropping systems under different agro-ecological regions, provide much interesting information. It has been found that, even with the required NPK treatment (based on soil test results), yields could not be maintained at high level continuously and the deficiency of S, Zn, Fe, Mn and B or some other micronutrients started limiting the yield after different periods. For instance, in low pH Alfisols of Palampur and Ranchi, N alone reduced the pH of the soil and seriously limited the crop yields because of deficiency of Ca and toxicity of Al. Also, without liming or FYM treatments, the high yield could not be sustained (Figure 2). At many other sites, application of N alone even aggravated the deficiency of P and K, resulting in reduced yields. In the case of N and P application alone, deficiency

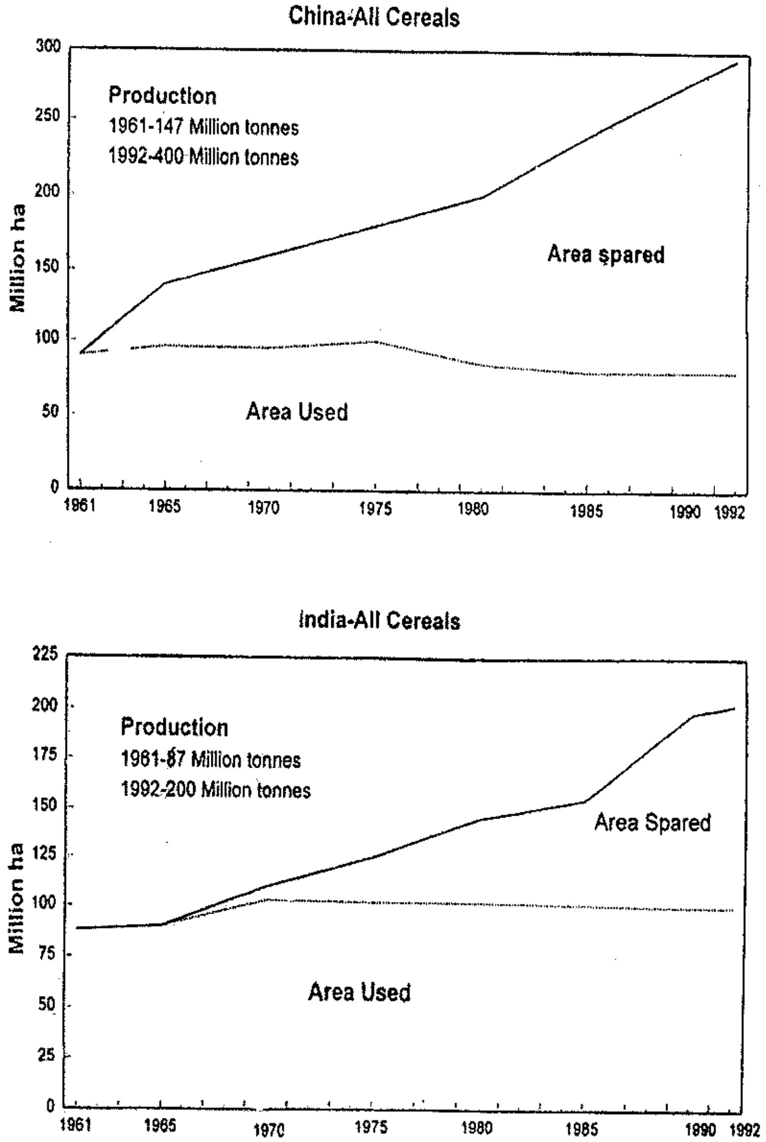

Figure 1. The land that farmers spared through cereal yield in India and China

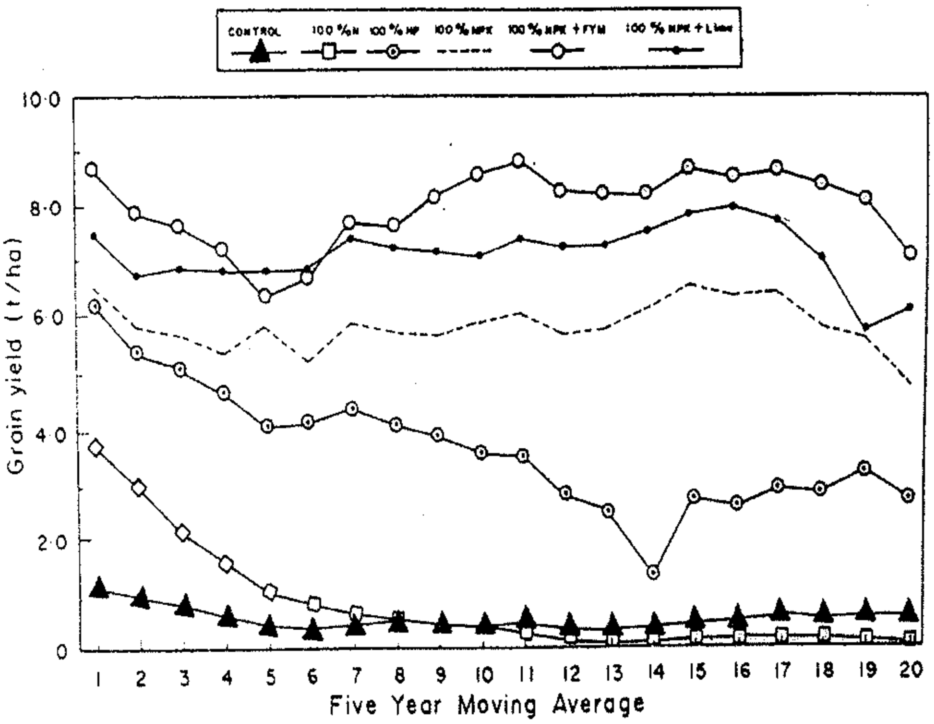

Figure 2. Effect of different treatments on grain yield of maize-wheat crops at Palampur

of K became evident within a few years. The soil analysis data from these long-term fertilizer experiments (Figure 3) clearly indicate that the imbalanced use of fertilizer over a long period usually leads to deficiency of nutrients not included in the fertilizer schedule. In some cases, even with the application of N, P and K, the yield curve tended to decline, which however showed considerable improvement with the additional application of FYM (10-15 tonnes FYM/ha) (Figure 4). This emphasizes the necessity of an integrated nutrient management with a harmonious combination of chemical fertilizers, organic manures and biofertilizers. There is no assurance that even with a combined application of N, P and K and FYM, some of the micronutrients will not become the yield-limiting factors after sometime, as even FYM may not provide all the micronutrients needed by a crop.

Generally, there exists a direct relationship between consumption of plant nutrients (NPK) and grain productivity. The National Academy of Agricultural Sciences, India, has estimated that for meeting the food needs of India's increased population by 2025, India may have to increase its plant nutrient supply through fertilizers and organic manures from the current 13 million tonnes of nutrients to 45 million tonnes, of which 35 million tonnes should be from fertilizer sources and 10 million tonnes from organic sources (Kanwar and Katyal, 1997). For high sustainable productivity, integrated plant nutrient system (IPNS) assumes highest priority. As the plant nutrients are mostly supplied by chemical fertilizers which are the purchased inputs and their costs continue to increase, improving their use efficiency is of paramount importance. The main features of this management are as follows:

(i) Integrated use of inorganic and organic sources of nutrients is essential for maintaining soil health and optimising crop productvity.

(ii) With increasing productivity, the response per unit of fertilizer decreases. Hence, the problem of maintaining high degree of efficiency assumes importance. For instance, in rice the efficiency of nitrogen fertilizers ranges from 30 to 50%, depending upon the management system. The coating of nitrogenous fertilizers, use of slow release N-compounds, split application, drilling fertilizer into the soil instead of broadcasting it on the surface, balanced use of N with

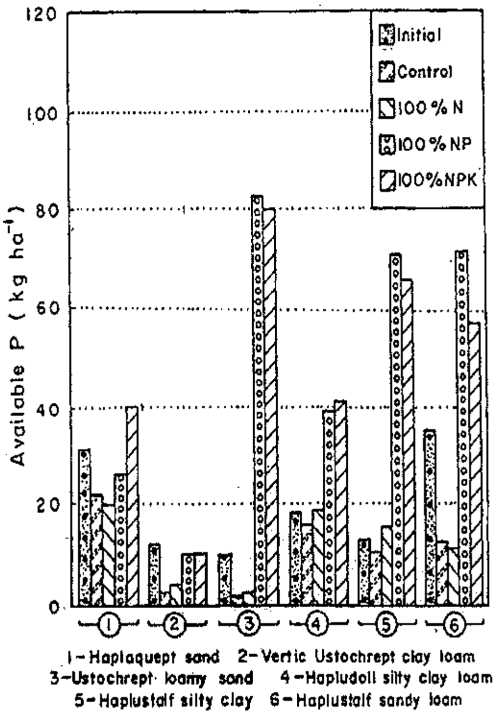

Figure 3a. Changes in available P after 25 years of cropping

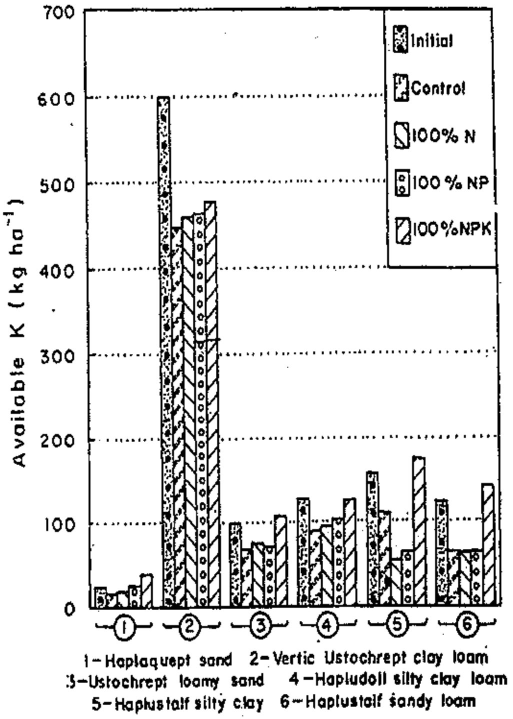

Figure 3b. Changes in available K after 25 years of cropping

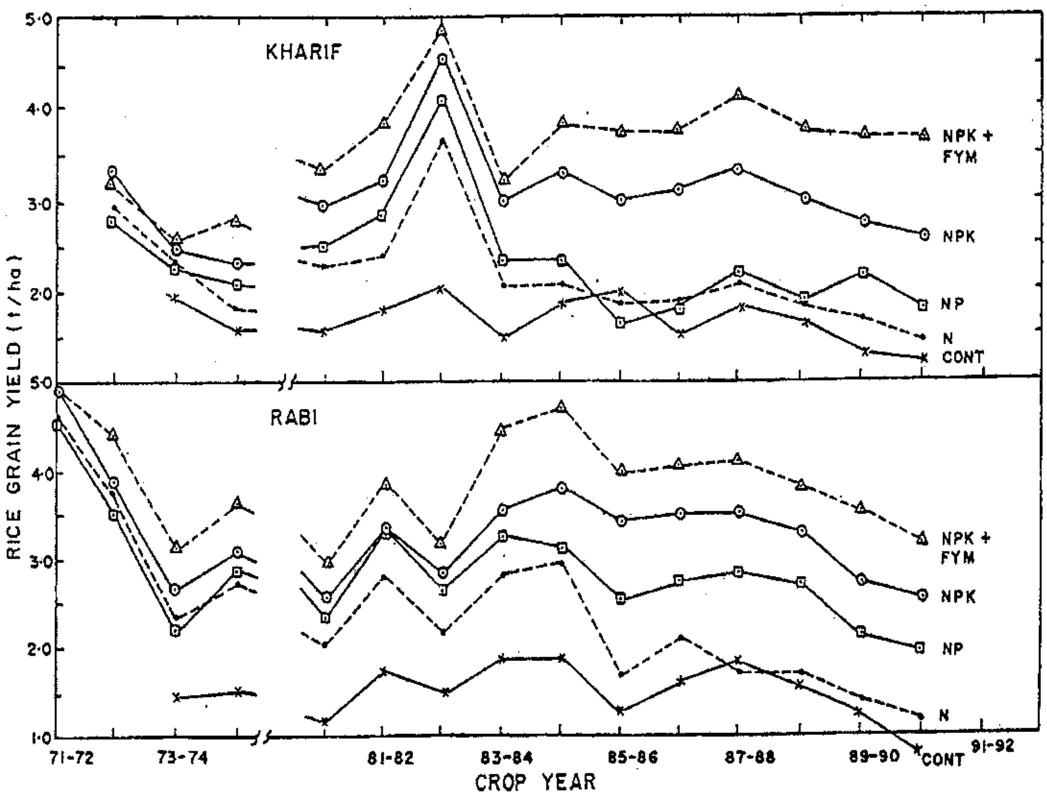

Figure 4. Effect of different treatments on grain yield of *kharif* rice at Bhubaneswar

other major and micronutrients, etc. become important management practices to increase the N-use efficiency. In a cropping system, the choice of a crop to receive a particular nutrient helps in increasing its efficiency. For instance, in rice-wheat system, the P application for wheat, Zn application for rice, and green manuring for rice to supplement nitrogenous fertilizers lead to a higher fertilizer-use efficiency and profitability. The green manuring with *dhaincha* (*Sesbania aculeata*) in rice-wheat system in northern India is reported to contribute about 30-40 kg N/ha and sustains high productivity of the system. Some biofertilizers could also be used to supplement but not to substitute nitrogenous fertilizers in, an intensive cropping system.

(iii) Reducing loss of nutrients through leaching, volatilization and removal of crop bye-products, crop residues, straw husk, etc. also increases the efficiency of fertilizer use.

(iv) Reducing environmental pollution is a matter of concern for modern agriculture based on a high input strategy. In recent years, fertilizers have received attention of environmentalists as the potential pollutants of groundwater and reducers of quality of agricultural produce. The fault lies not with fertilizers but with their inefficient and imbalanced use and poor management of soil and water. Thus, for sustainable high productivity and eco-friendly soil management strategy, integrated use of organic, biological and inorganic sources of plant nutrients is essential.

(v) An important criterion for maintaining sustainable farming is the stipulation that the productivity enhancement should not be at the cost of soil quality. Long-term fertilizer experiments have clearly shown that the balanced and integrated nutrient management improves the soil organic matter content as well as soil quality which is an index of better soil health and sustainability of the system.

3.2. Water Management

Water is a limiting factor for crop production and scientific water management is the key to development of sustainable agriculture for both irrigated and rain-fed farming systems. The low water-use efficiency, prohibitive costs of irrigation development, increasing problems of salinity, sodicity and waterlogging in the wake of development of irrigation and increasing competition for good quality water between agriculture, industry and urban uses necessitates assignment of high priority to the development of efficient system of irrigation water management. The fullest impact of irrigation on productivity and sustainability of agriculture and environment can be realised only when water use is integrated with efficient soil, water, crop, fertilizer and other agronomic management systems. Drainage is an essential component of the irrigation system. It is overuse of irrigation and, lack of adoption of best soil and water management techniques, and mismatch of nutrient inputs and agronomic management of a farming system which lead to lower efficiency of irrigation water.

The modern irrigation techniques such as drip irrigation, can become remunerative if these are used for high-value crops, with high technology and optimum agricultural inputs. Its demand for irrigated farming in the future, specially for horticulture and vegetable farming is increasing in India. While in the developed countries this system is getting computerized, in India it is still in its infancy and needs to be considered as an innovative technology for sustainable high productivity, profitability and sustainability of farming systems.

For dryland farming, increased efficiency of rain water is essential and it can be achieved in the following ways:

(i) Retain precipitation *in situ* and minimize the run-off,

(ii) Reduce evaporation in relation to transpiration,

(iii) Use drought-tolerant crops that fit in the rainfall pattern,

(iv) Use watershed concept for maximization of rainwater harvesting and recycling, and

(v) Recycle the run-off and drainage water for high-value crops adopting life-saving irrigation approach.

In fact, it is the combination of all these practices that ensures the best results with minimum degradation of environment. Since the crucial factors of rainfed farming are moisture stress and nutrient-deficiency stress, an integrated technology is needed for removing these stresses to ensure successful sustainable farming.

The Rio de Janeiro declaration of 1992 emphasized the following principles relevant to sustainable farming:

(a) Human beings are at the centre of concern for sustainable development and environmental issues are best handled with the participative co-operation of all concerned people.

(b) The criteria of productivity, equity and environmental safety are critical for the present and future generations for development of sustainable farming

(c) For sustainability it is necessary to remove all negative factors associated with unsustainability

3.3. Energy Management for Sustainable Farming

Next to fertilizer and water, the availability of energy from mechanical, chemical, electrical, human and animal sources has become the pace setter for realising the yield potential of high-yielding crop varieties. The states which have increased the use of various forms of energy for mechanisation of agricultural operations, timely and precision farm operations, tillage, fertilizer application, weeding, pest management, irrigation, harvesting and post-harvest operations, etc. have continuously obtained high crop yields. The wheat revolution would not have been possible without the use of threshers. Similarly, a wheat-rice system would not be efficient without the use of mechanised operations. The increasing use of tractors and the decreasing availability of animal power in agriculture is also an index of the future trends in harnessing the various forms of energy. How far is the use of energy essential, economical and efficient for sustainable farming? Also, how many of the traditional farming operations such as tillage are really essential for sustainable farming? In the developed countries, minimum tillage is gaining popularity because with excess tillage, the problem of soil degradation is accentuated. In India also, for rice-wheat system in northern India minimum tillage seems to give the most economic returns and optimum yields.

There is a dearth of information on long-term tillage system in the tropics for sustained productivity of farming. Inferences from short-term tillage experiments vary. While some experiences indicate the ephemeral benefits in terms of increased infiltration and yield, others show permanent advantage of tillage over no-tillage system in the tropics (Lal, 1994). However, there is enough evidence that in the case of crusting soils such as Alfisols of the semi-arid tropics, some form of tillage is essential to loosen them so as to increase infiltration and reduce run off water, where organic materials are not available for the purpose. In the humid tropics where vegetative growth is rapid and surface protection by vegetation is provided, no-tillage and minimum tillage methods have given more sustainable production over long periods.

3.4. Removing Physical Soil Constraints to Productivity

If physical soil constraints limit the crop production, the removal of such constraints through mechanical, hydrological and chemical methods generally result in sustained high productivity, provided the operations are repeated after periodical intervals and do not damage the soil structural elements permanently.

The All India Coordinated Research Project on Improvement of Soil Physical Conditions to Increase Agricultural Production of Problematic Soils has provided adequate information on the amelioration of such soils to sustain high productivity. Compaction technology suitable for management of highly permeable and low water retaining sandy and loamy sand soils, increases the productivity of rainy season crops and reduces the irrigation water needs of succeeding wheat crop. In the case of rice soils of lateritic type and of sandy loam texture, the compaction helps in reducing percolation losses of water from upland rice fields. Chiselling of dry soil up to 40 cm depth and at 50-120 cm interval has been found suitable for management of shallow-soils with highly impermeable subsoil. The broad bed and furrow

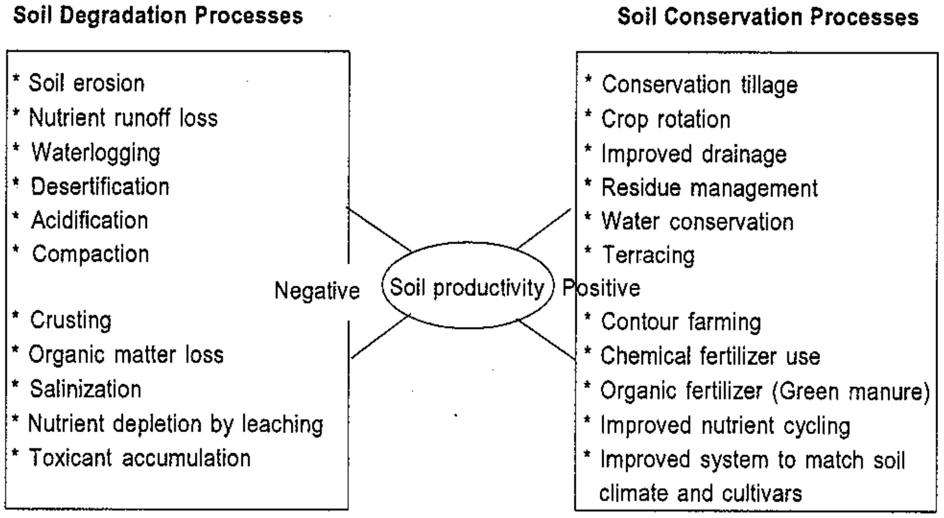

Figure 5. The relationship between soil degradation processes and soil conservation practices

system developed by ICRISAT for improving the surface drainage of Vertisols has been found effective for increasing not only yields but also cropping intensity. This system has been found effective in sustaining high productivity of sorghum, pigeonpea or maize-chickpea system and reducing soil erosion. The system could also provide opportunity for water harvesting and its reuse. Likewise at Jabalpur in a higher rainfall area of >1000 mm, raised bed and sunken bed technology on Vertisol made the rice-based cropping system sustainable. The crop residue recycling technology for the management of Alfisols – the red sandy loam soils, which are prone to crusting, has been found to improve productivity and sustainability of the farming systems.

The best means of improving and maintaining soil quality which determines soil productivity and environmental quality is adoption of alternative agricultural practices such as crop rotation, recycling of crop residues and animal manures, green manures, biofertilizers and integrated nutrient management for encouraging balanced use of fertilizers and manures, and reduced use of pesticides. These are some of the components of a strategy for obtaining sustainable high productivity in any farming system. The relationship between the soil degradation processes and soil conservation practices as outlined by Hamick and Parr (1987) is shown in Figure 5.

4. Problems of Sustainable Soil Management

The main problem of sustainable soil management is linked up with the sustainable land management and it has many technological, socio-economic and environmental aspects. A sustainable land management includes a set of technologies, policies and activities aimed at integration of socio-economic principles with environmental concerns so as to simultaneously

- Maintain or enhance productivity and production,
- Reduce the level of production risks,
- Achieve environmental stability, and
- Be economically viable and socially acceptable.

Sustainable land management system is more comprehensive than the sustainable farming. It is because, the latter is concerned with the on site constraints, whereas the former deals with the offsite or watershed-based issues and sustained productivity.

Agricultural sustainability may be defined as a function described by Equation (1) (Lal, 1994):

$$\text{Agricultural sustainability} = d\,(P_t \times S_p \times W_t \times C_t)\,dt \quad \ldots(1)$$

where, P_t is the productivity potential with input of the limiting or non-renewable resource; S_p is the measure of critical soil property, i.e. rooting depth, soil organic matter content, cation exchange capacity; W_t is the plant available water resource and quality; and C_t is the climatic factor with reference to evaporation and soil temperature flux of radioactive gases.

Thus, it is a product of numerous parameters affecting productivity and sustainability.

5. Sustainability Index

Agricultural sustainability depends on soil quality and resilience. Soil resilience is defined as the ability of soil to resist degradation or change under a perturbation or ability of soil to tolerate its continuous use without appreciable adverse changes (Lal, 1993). Soil quality refers to the capacity of soil to perform three principal functions, namely (i) economic productivity, (ii) counter environmental degradation, and (iii) aesthetic or cultural values. In the context of sustainability index, it is important that these concepts are objective, precise, quantifiable, and operational.

Sustainability of an agricultural system can be assessed on the basis of two potential approaches. In the first, important indicators of sustainability are location specific and change with situations prevailing on a farm. For example, soil erosion has a major impact on sustainability in the steep lands, whereas in flat lowland rice fields, it may not be a useful indicator. Thus, the protocol for working out sustainability index starts with the selection of a subset of indicators that a practitioner feels to be appropriate for the particular farm being evaluated. Under the other approach, the sustainability is defined by a set of requirements that must be met by a farm regardless of the diversity of situations prevailing on different farms. While major drawback with location specific approach is the difficulty of comparing results from farms where different indicators have been selected, the strength of second approach lies in using similar indicators across all farms.

Embodied in the concept of sustainable productivity is a recognition that land use and management of crop production is a hierarchy of systems operating in and interacting with economic, ecological, social and political components. Four major categories of indicators that quantify the changes occurring in a crop production system over time at different hierarchical levels are : (i) crop productivity, (ii) socio-economic, (iii) resource, and (iv) ecological. Thus, even with simplified requirements for sustainability at the farm level, there could be a long list of indicators, although several indicators are closely related to each other and it may not be necessary to measure all of them.

To arrive at a meaningful sustainability index, the indicators must be easy to measure, respond easily to changes and have thresholds for separating sustainable from unsustainable conditions. Following these guidelines, Gomez *et al.* (1996) selected yield, profit and frequency of crop failure as field indicators for farmer's satisfaction, and soil depth, organic carbon content, and percentage of ground cover for resource conservation.

An indicator is said to be sustainable if it exceeds a threshold level as given in Table 1. The thresholds are tentatively set as improvements on community averages. Those for resource conservation include an absolute minimum. For computing the sustainability index, all measurements are converted into threshold units and threshold levels are specified for each indicator using the norms given in Table 1. Indices for farmer's satisfaction and resource conservation are computed as the average of their respective indicators. These two averages must be more than 1.0 for the system to be adjudged sustainable. For sustainable cases, the average of the two indices is computed. This average is the final index of sustainability and no index is computed for farms that are adjudged non-sustainable. An interesting feature of the procedure described by Gomez *et al.* (1996) to compute sustainability index is that there is no difficulty in accommodating additional indicators under both the main pillars— farmer's satisfaction and resource conservation. Since the indices are averaged across indicators, adding more indicators should not complicate either the procedure or the level of comparability among indices.

Table 1. Threshold levels for sustainability indicators

Indicator	Threshold level	Threshold formulae
Yield (x_1)	20% more than average yield in the community	1.2 (Mean x_1)
Profit (x_2)	20% better than average in the community, whichever is lower	1.2 (Mean x_2)
Frequency of crop failure (x_3)	20%, or average frequency for the community, whichever is lower	0.20 when the mean of $x_3 > 20$, mean of x_3 otherwise
Soil depth (x_4)	50 cm or the average of similar soil types in the community, whichever is more	Mean x_4 or 50 cm, whichever is more
Organic C (x_5)	1%, or average of community, whichever is higher	0.01 when mean $x_5 < 0.01$, mean x_5 otherwise
Permanent ground cover (x_6)	15%, or average of community whichever is higher	0.15 when mean $x_6 < 0.15$, mean x_6 otherwise

Source: Gomez *et al.* (1996)

6. Sustainability of Farming and Soil Management Issues of a Few Agro-ecological Regions of India

6.1. High Productivity Areas of Intensive Agriculture in Rice-Wheat Belt of North India

The rice-wheat belt of north India is the major contributor to the foodstock buffer of the Government of India. However, it is a matter of concern that there are wide variations in productivity within the irrigated areas of this region. Even in Punjab and Haryana, the two leading states of this region, the average yield of the two crops together is hardly 6 to 7 tonnes per ha of foodgrain, whereas the best farmers are harvesting 12-13 tonnes per ha and the maximum production trials report 14-15 tonnes per ha. Long-term experiments in Punjab have shown that it is possible to have a sustainable yield of wheat plus rice of more than 10 t/ha over a period of 25 years without detriment to soil and environment but the system requires balanced use of NPK plus FYM or NPK plus Zn plus S or any other micronutrient which becomes a critical limiting factor.

In the absence of integrated nutrient management and adequate soil and water management, the intensive rice-wheat system in this region is showing signs of stagnation or even of declining yields. There are increasing trends of the appearance of the following problems also:

- Declining response per unit nutrient,
- Increasing deficiency of K, S, Zn, Fe and Mn,
- Rapidly declining water-table in some areas and increasing water-table in others,
- Increasing problem of salinization, and
- Increasing deterioration of water quality.

Thus, the sustainability of high production lies in the solution of these problems.

6.2. Semi-arid Tropics (Vertisols/Vertic Soils)

In India, nearly one quarter of land has Vertic and Vertisol order of soils and most of it lies in semi-arid tropics, some with dependable and some with not-so-dependable rainfall. The long-term studies on watershed basis at ICRISAT Centre at Patancheru, in Andhra Pradesh, have shown that under rainfed farming with appropriate soil and rain water management in Vertisols, yield of about 4 t/ha of cereals plus pulses (pigeonpea or chickpea) are obtained, without any detriment to soil and environment. Sustainable yields have also been obtained on soybean-wheat system with balanced application of NPK and FYM at the

Indian Institute of Soil Science, Bhopal. However, due attention has to be paid to monitor the changes in availability of essential major and micronutrients and to supplement the critical limiting nutrient through balanced manuring. The long-term fertilizer experiments on soybean-wheat system at Jabalpur also indicate that recommended amounts of N, P and K unless supplemented with FYM cannot produce sustainable yields, as S and Zn become limiting factors in course of time.

Another problem of this region is that with irrigation, salinity and waterlogging increase. Under unirrigated farming in some parts, it is not so much the moisture stress; rather the excess of water in the root zone of the crops and the lack of surface drainage that are the major constraints to productivity. The sustainability of agriculture at high level of productivity in vertic soils of shallow depths is even more difficult, necessitating greater emphasis on rainwater management and crop management system. The current practice of low input, particularly adequate amount of balanced fertilizers, lack of drainage and minimum tillage at appropriate time largely contributes to unsustainability of productive farming.

6.3. Alfisols of Semi-arid Tropics

Alfisols, which occupy more than 70 million hactare land in India, continue to produce low and unstable crop yields. The erratic weather, soil-related constraints such as low fertility, low water-holding capacity, high crusting and high erodibility are the serious limitations to their high productivity and sustainability. However, a holistic approach of integrating all the soil management practices aimed at removing the soil-related constraints should result in high and sustainable productivity.

6.4. Soils of Deltaic and Coastal Regions

These soils cover a large area and also a range of farming systems such as rice-based system, plantation crop-based system, tree-crop and fish culture system and agro-forestry system. The sustainability of high productivity in these regions can be assured through more location-specific and holistic soil management technology. Nutrient management, drainage improvement and soil conservation are some of the important components of such a technology.

6.5. Dilemma of Arid Regions

In low rainfall regions, the pressure of human and animal population far exceeds the carrying capacity of the environment. Crop-animal based system, and agro-foresty system are more sustainable than the crop-based system followed there. However, under irrigation, the crop-based systems also can be made sustainable provided the soil and water management practices, conducive to high productivity without detriment to environment are used as otherwise desertification, salinization and waterlogging problems would increase.

The National Bureau of Soil Survey and Land Use Planning (NBSS&LUP) has delineated 20 agro-ecological regions and 60 agro-ecological sub-regions in the country based on the data of soil, climate, physiography and length of growing period calculated on the basis of rainfall, temperature, evaporation parameters, according to the FAO system. The soil management related constraints of every region and sub-region have been discussed in detail in the publications of NBSS&LUP, Nagpur. This basic knowledge can be used with advantage for developing a technology suitable for high productivity and sustainability of a farming system for alternate land use options.

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SI Units

Names and Symbols of SI Units

Physical quantity	*Symbol for physical quantity*	*SI Unit*	*Symbol for SI Unit*	*Remarks*
Primary Units				
Length	l	metre	m	
Mass	m	kilogram	kg	
Time	t	second	s	
Electric current	I	ampere	A	
Thermodynamic temperature	T	kelvin	K	*The symbol (°) and the word degree should not be used with kelvin*
Luminous intensity	I_v	candela	cd	
Quantity of substance	n	mole	mol	*Not yet officially adopted*
Secondary Units				
Plane angle		radian	rad	
Solid angle		steradian	sr	

Derived SI Units with Special Names

Physical quantity	*Symbol for physical quantity*	*SI Unit*	*Symbol for SI Unit*	*Relation to other SI Units*
Force	F	newton	N	kg m s^{-2}
Energy	E, W	joule	J	N m
Power	P	watt	W	J s^{-1}
Electric charge	Q	coulomb	C	A s
Electric potential	V	volt	V	J Q^{-1}
Electric resistance	R	ohm	Ω	V A^{-1}
Frequency	f	hertz	Hz	s^{-1}
Temperature	t	degree Celsius	°C	t °C

Metric Multiples and Sub-multiples

Prefix	*Abbreviation*	*Value*
yotta	Y	10^{24}
zetta	Z	10^{21}
exa	E	10^{18}
peta	P	10^{15}
tera	T	10^{12}
giga	G	10^{9}
mega	M	10^{6}
kilo	k	10^{3}
hecto	h	10^{2}
deka	da	10^{1}

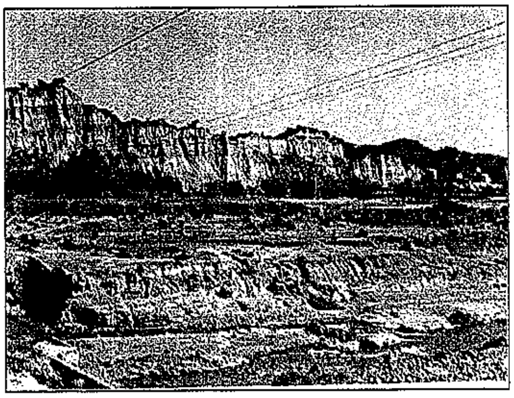
Prefix	*Abbreviation*	*Value*
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	m	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}
atto	a	10^{-18}
zapto	z	10^{-21}
yocto	y	10^{-24}

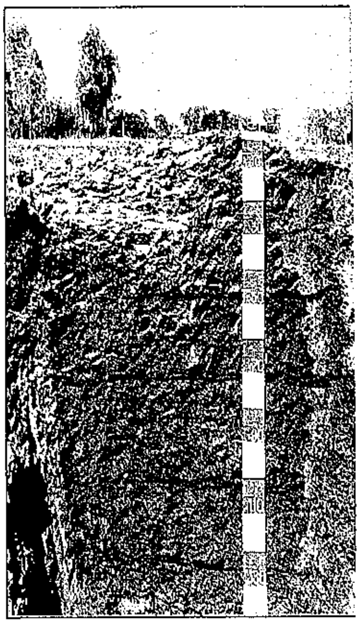
Conversion Factors for SI and non-SI Units

To covert Colm.1 into Colm. 2, multiply by	Column 1 (SI Unit)	Column 2 (Non-SI Unit)	To convert Colm.2 into Colm. 1 multiply by
		Length	
0.621	kilometre, km (10^3 m)	mile, mi	1.609
1.094	metre, m	yard, yd	0.914
3.28	metre, m	foot, ft	0.304
1.0	micrometre, μm (10^{-6} m)	micron, μ	1.0
3.94×10^{-2}	millimetre, mm (10^{-3} m)	inch, in	25.4
10	nanometre, nm (10^{-9} m)	Angstrom, Å	0.1
		Area	
2.47	hectare, ha	acre	0.405
247	square kilometre, km^2 (10^3 m)^2	acre	4.05×10^{-3}
0.386	square kilometre, km^2 (10^3 m)^2	square mile, mi^2	2.590
2.47×10^{-4}	square metre, m^2	acre	4.05×10^3
10.76	square metre, m^2	square foot, ft^2	9.29×10^{-2}
1.55×10^{-3}	square millimetre, mm^2 (10^{-3} m)^2	square inch, in^2	645
		Volume	
9.73×10^{-3}	cubic metre, m^3	acre-inch	102.8
35.3	cubic metre, m^3	cubic foot, ft^3	2.83×10^{-2}
6.10×10^4	cubic metre, m^3	cubic inch, in^3	1.64×10^{-5}
3.53×10^{-2}	litre, L (10^{-3} m^3)	cubic foot, ft^3	28.3
0.265	litre, L (10^{-3} m^3)	gallon	3.78
33.78	litre, L (10^{-3} m^3)	ounce (fluid), oz	2.96×10^{-2}
		Mass	
2.20×10^{-3}	gram, g (10^{-3} kg)	pound, lb	454
3.52×10^{-2}	gram, g (10^{-3} kg)	ounce (avdp), oz	28.4
2.205	kilogram, kg	pound, lb	0.454
0.01	kilogram, kg	quintal (metric), q	100
1.10×10^{-3}	kilogram, kg	ton (2000 lb), ton	907
1.102	megagram, Mg (tonne)	ton (U.S.), ton	0.907
1.102	tonne, t	ton (U.S.), ton	0.907
		Yield and Rate	
0.893	kilogram per hectare, kg ha^{-1}	pound per acre, lb acre^{-1}	1.12
7.77×10^{-2}	kilogram per cubic metre, kg m^{-3}	pound per bushel, bu^{-1}	12.87
0.107	litre per hectare, L ha^{-1}	gallon per acre	9.35
893	tonnes per hectare. t ha^{-1}	pound per acre, lb acre^{-1}	1.12×10^{-3}
893	megagram per hectare, Mg ha^{-1}	pound per acre, lb acre^{-1}	1.12×10^{-3}
0.446	megagram per hectare, Mg ha^{-1}	ton (2000 lb) per acre, ton acre^{-1}	2.24
2.24	metre per second, m s^{-1}	mile per hour, mi h^{-1}	0.447
		Specific Surface	
10	square metre per kilogram, m^2 kg^{-1}	square centimetre per gram, cm^2 g^{-1}	0.1
1000	square metre per kilogram, m^2 kg^{-1}	square millimetre per gram, mm^2 g^{-1}	0.001
		Pressure	
9.90	megapascal, MPa (10^6 Pa)	atmosphere	0.101
10	megapascal, MPa (10^6 Pa)	bar	0.1
1.00	megagram per cubic metre, Mg m^{-3}	gram per cubic centimetre, g cm^{-3}	1.00
2.09×10^{-2}	pascal, Pa	pound per square foot, lb ft^{-2}	47.9
1.45×10^{-4}	pascal, Pa	pound per square inch, lb in^{-2}	6.90×10^3

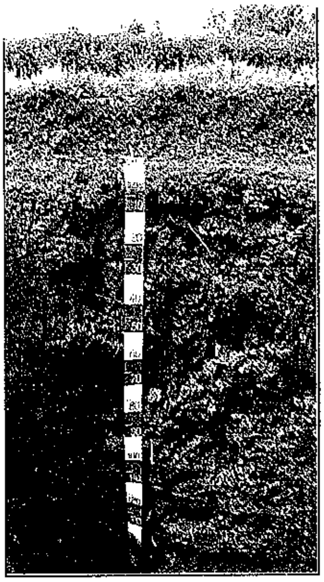
To covert Colm.1 into Colm. 2, multiply by	*Column 1 (SI Unit)*	*Column 2 (Non-SI Unit)*	*To convert Colm.2 into Colm. 1 multiply by*
Temperature			
1.00 (K – 273)	Kelvin, K	Celsius, °C	1.00 (°C+273)
(9/5 °C) + 32	Celsius, °C	Fahrenheit, °F	5/9 (°F – 32)
Energy, Work, Quantity of Heat			
9.52×10^{-4}	joule, J	British thermal unit, Btu	1.05×10^{3}
0.239	joule, J	calorie, cal	4.19
10^{7}	joule, J	erg	10^{-7}
0.735	joule, J	foot-pound	1.36
2.387×10^{-5}	joule per square metre, J m^{-2}	calorie per square centimetre (langley)	4.19×10^{4}
10^{5}	newton, N	dyne	10^{-5}
1.43×10^{-3}	watt per square metre, W m^{-2}	calorie per square centimetre minute (irradiance), cal cm^{-2} min^{-1}	698
Transpiration and Photosynthesis			
3.60×10^{-2}	milligram per square metre second, mg m^{-2} s^{-1}	gram per square decimetre hour, g dm^{-2} h^{-1}	27.8
5.56×10^{-3}	milligram (H_2O) per square metre second, mg m^{-2} s^{-1}	micromole (H_2O) per square centimetre` second, μmol cm^{-2} s^{-1}	180
10^{-4}	milligram per square metre second, mg m^{-2} s^{-1}	milligram per square centimetre second, mg cm^{-2} s^{-1}	10^{4}
35.97	milligram per square metre second, mg m^{-2} s^{-1}	milligram per square decimetre hour, mg dm^{-2} h^{-1}	2.78×10^{-2}
Plane Angle			
57.3	radian, rad	degrees (angle), °	1.75×10^{-2}
Electrical Conductivity, Electricity, and Magnetism			
10	siemen per metre, S m^{-1}	millimho per centimetre, mmho cm^{-1}	0.1
10^{4}	tesla, T	gauss, G	10^{-4}
Water Measurement			
9.73×10^{-3}	cubic metre, m^3	acre-inches, acre-in	102.8
9.81×10^{-3}	cubic metre per hour, m^3 h^{-1}	cubic feet per second, ft^3 s^{-1}	101.9
4.40	cubic metre per hour, m^3 h^{-1}	U.S. gallons per minute, gal min^{-1}	0.227
8.11	hectare-metres, ha-m	acre-feet, acre-ft	0.123
97.28	hectare-metres, ha-m	acre-inches, acre-in	1.03×10^{-2}
8.1×10^{-2}	hectare-centimetres, ha-cm	acre-feet, acre-ft	12.33
Concentrations			
1	centimole per kilogram, cmol kg^{-1}	milliequivalents per 100 gram, meq 100 g^{-1}	1
0.1	gram per kilogram, g kg^{-1}	percent, %	10
1	milligram per kilogram, mg kg^{-1}	parts per million, ppm	1
Radioactivity			
2.7×10^{-11}	becquerel, Bq	curie, Ci	3.7×10^{10}
2.7×10^{-2}	becquerel per kilogram, Bq kg^{-1}	picocurie per gram, pCi g^{-1}	37
100	gray, Gy (absorbed dose)	rad, rd	0.01
100	sievert, Sv (equivalent dose)	rem (roentgen equivalent man)	0.01
Plant Nutrient Conversion			
	Element	Oxide	
2.29	P	P_2O_5	0.437
1.20	K	K_2O	0.830
1.39	Ca	CaO	0.715
1.66	Mg	MgO	0.602

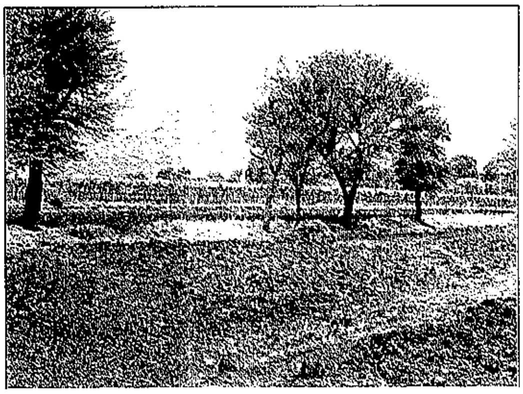
Soilscape and Soil Profiles



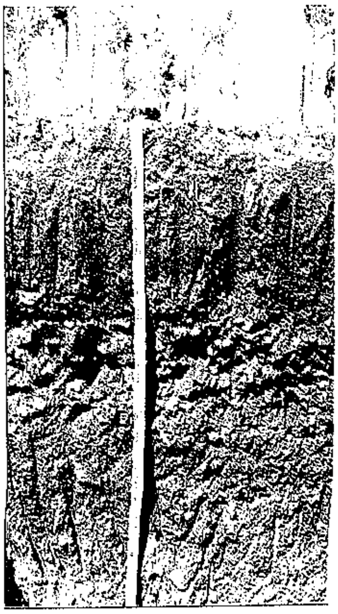


Soilscape (above) and profile (right) of an alluvial soil (Typic Haplustept)
(*Location:* 31°20' N-75°35' E, Kanga village, Jalandhar district, Punjab)
Courtesy: NBBS&LUP, Nagpur



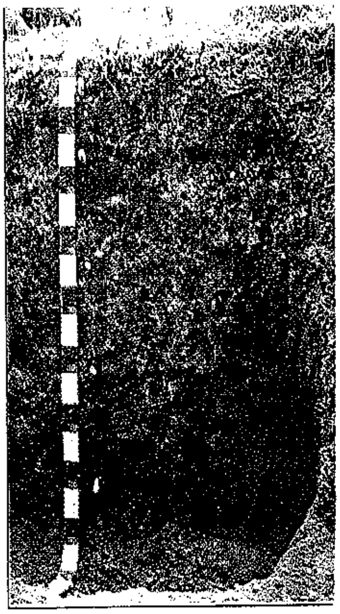


Soilscape (above) and profile (left) of a basaltic soil (Typic Haplustert)
(*Location:* 21°06' N-79°03' E, Saongi watershed, Hingna *Tehsil*, Nagpur district, Maharashtra)
Courtesy: NBBS&LUP, Nagpur

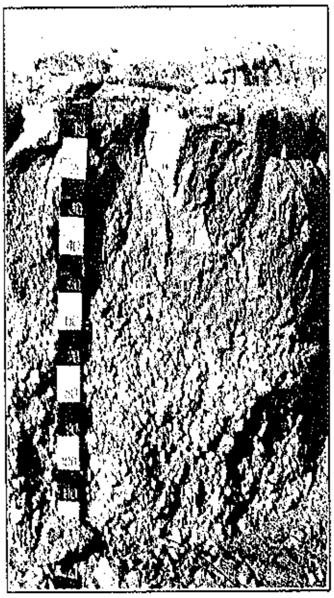


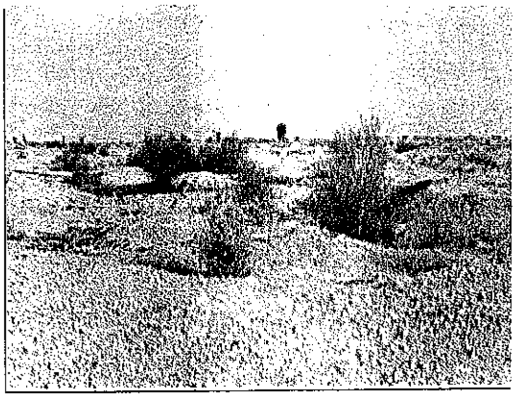
Soilscape (above) and profile (right) of a red soil (Typic Rhodustalf)
(*Location:* 12°58' N-77°35' E, Chokanhalli watershed, Bangalore district, Karnataka)
Courtesy: NBBS&LUP, Nagpur

Soilscape and Soil Profiles

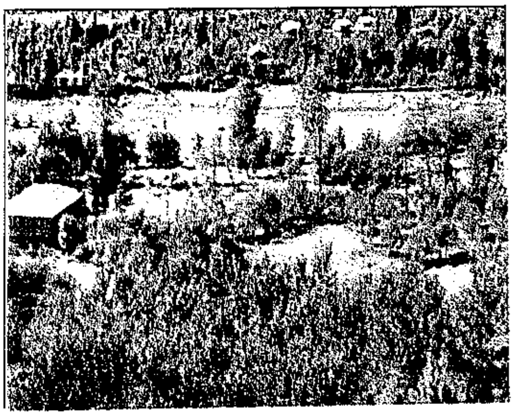


Soilscape (above) and profile (right) of a lateritic soil (Typic Haplustox)
(*Location:* 18°32' N-73°51' E, near Bhimashankar, Pune district, Maharashtra)
Courtesy: NBBS&LUP, Nagpur



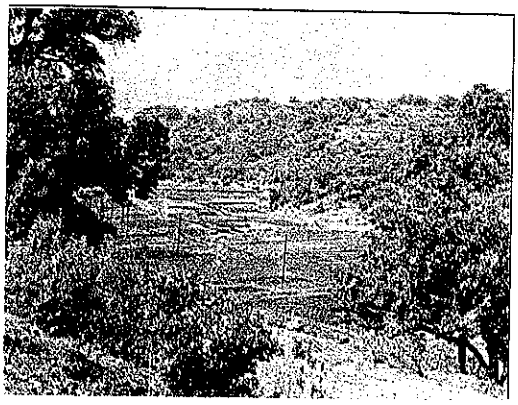


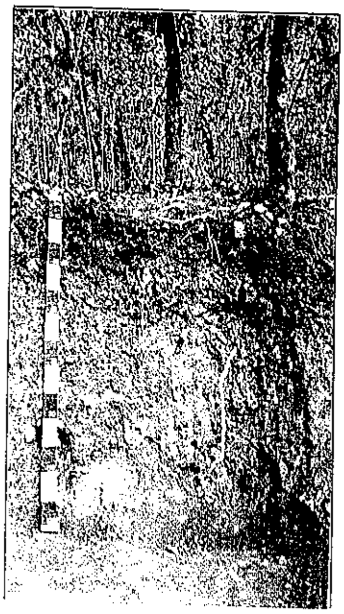
Soilscape (above) and profile (left) of a desert (arid) soil (Typic Haplargid)
(*Location:* 28°00' N-73°18' E, near Bajju village, Bikaner district, Rajasthan)
Courtesy: NBBS&LUP, Nagpur



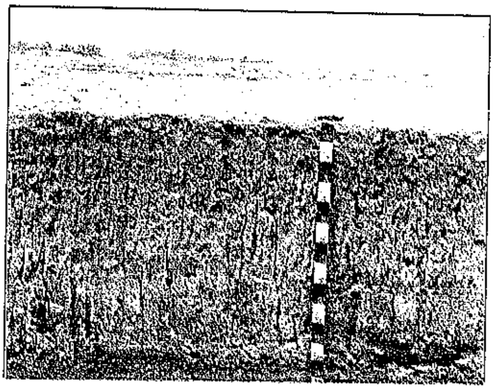
Soilscape (above) and profile (right) of a forest & hill soil
(Typic Ustorthent)
(*Location:* 32°16' N-76°23' E, Kangra, Kangra district, Himachal Pradesh)
Courtesy: NBBS&LUP, Nagpur

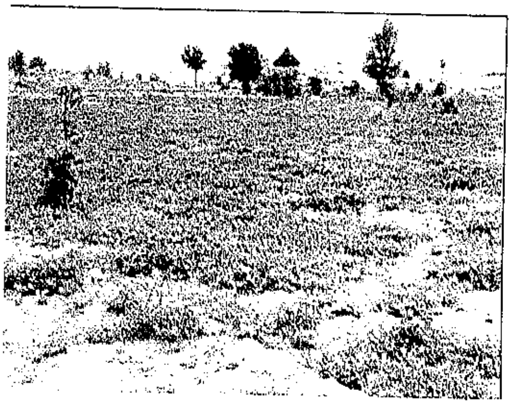
Soilscape and Soil Profiles





Soilscape (above) and profile (right) of a brown forest soil (Typic Haplusalf)
(*Location:* 17°00'N-73°16'E, Khumbhave watershed, Dapoli *tehsil,*
Ratnagiri district, Maharashtra)
Courtesy: NBBS&LUP, Nagpur

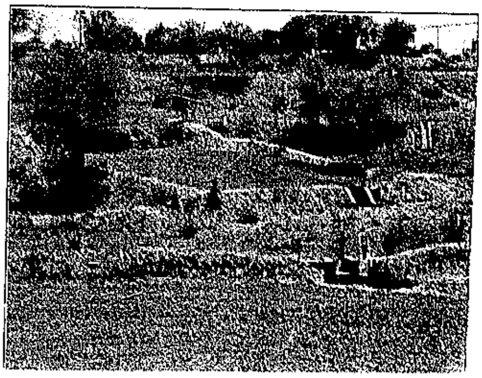




Soil profile (left) and soilscape (right) of a salt-affected soil (Typic Haplusalf)
(*Location:* 28°20' N-73°18' E, near Lunkarson village, Bikaner district, Rajasthan)
Courtesy: NBBS&LUP, Nagpur

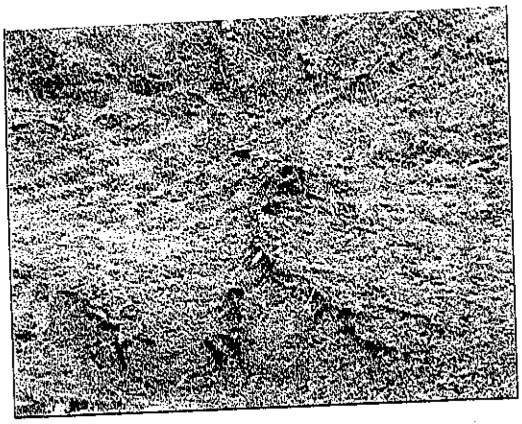
Soil and Water Conservation Measures

Highly eroded ravine land
Courtesy : Dr J.S. Samra, New Delhi

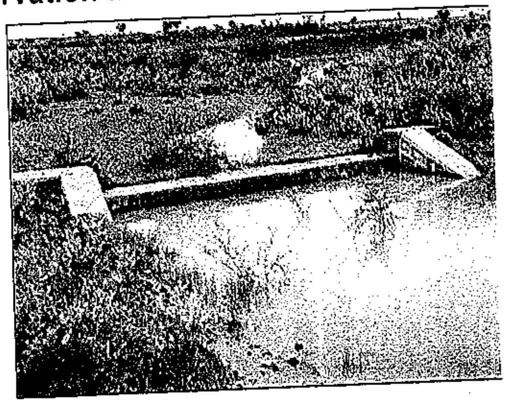


A ravine land has been conserved by bench terracing
and providing safe water disposal structure.
Courtesy : Dr J.S. Samra, New Delhi

Soil and Water Conservation Measures

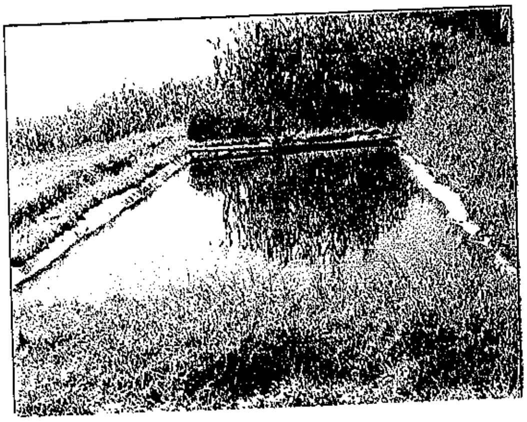


Rill erosion which ultimately gets converted into deep channels
Courtesy : Dr J.S. Samra, New Delhi

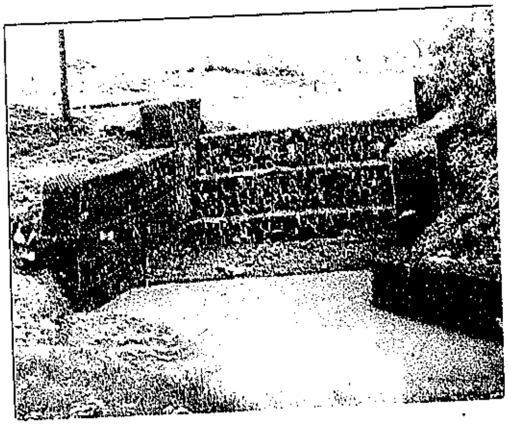


A deep channel treated with weir structure for promoting recharging
Courtesy : Dr J.S. Samra, New Delhi

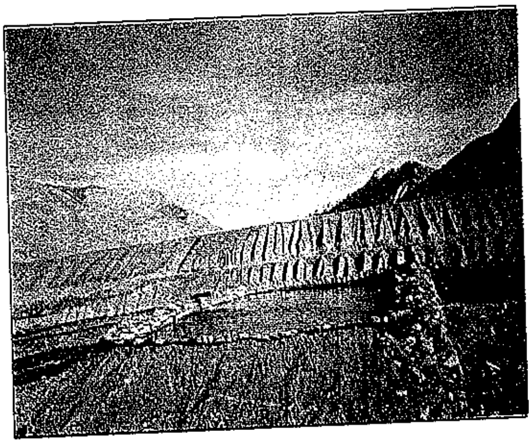
Watershed at Palampur showing bench-terraces and water harvesting reservoirs
Courtesy : Dr C.L. Acharya, Bhopal



Intra-terrace water harvesting in dug-out poly-lined tank
Courtesy : Dr C.L. Acharya, Bhopal



A gabion structure used as a spill way for a water harvesting structure
Courtesy : Dr C.L. Acharya, Bhopal

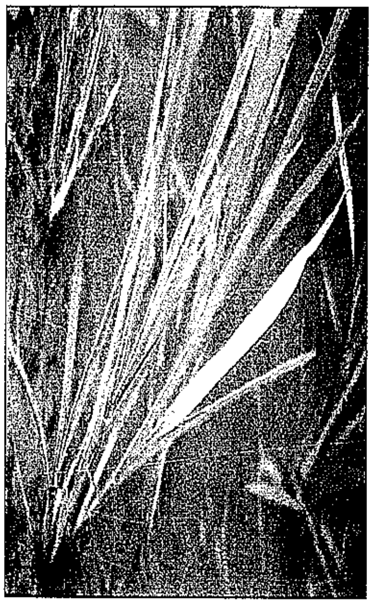


Silpaulin-lined tank for water storage in the cold desert area of Spiti valley, Himachal Pradesh
Courtesy : Dr C.L. Acharya, Bhopal

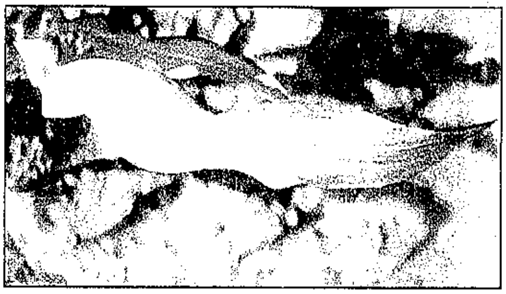
Nutrient Deficiency Symptoms

Nitrogen deficiency symptom in wheat plant
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana

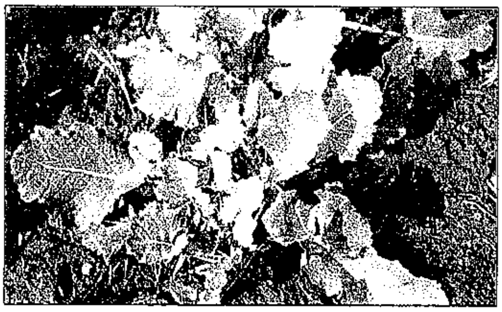
A close-up of nitrogen dificiency symptom in maize leaf
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana



Nitrogen deficiency symptom in rice plant
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana



A close-up of phosphorus deficiency symptom in maize leaf
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana

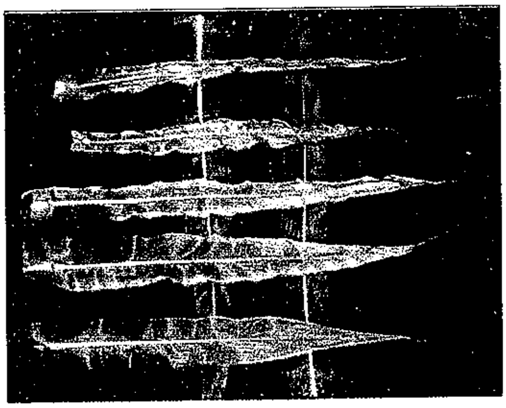


A close-up of phosphorus deficiency in *gobhi sarson* plant
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana

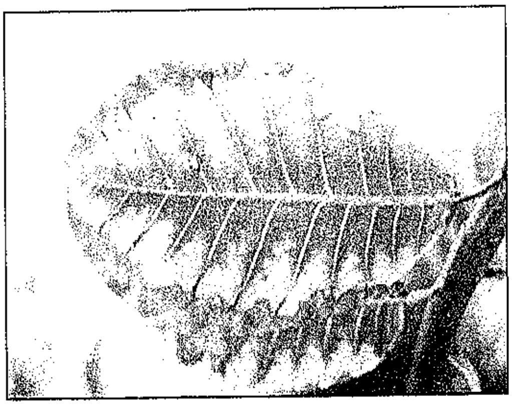
Phosphorus deficiency in sorghum plants
Courtesy : Potash and Phosphate Institute of Canada

Nutrient Deficiency Symptoms

Phosphorus deficiency symptom in sugarcane
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana



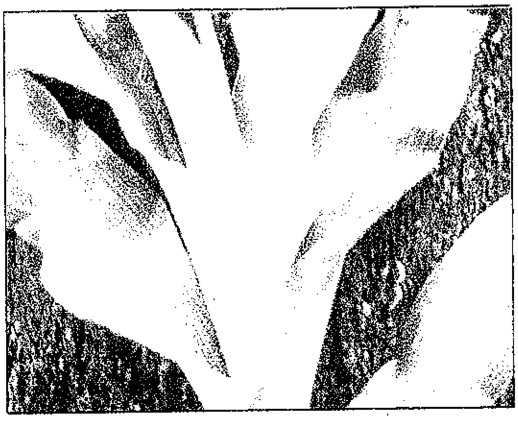
Potasium deficiency in maize
Courtesy : Potash and Phosphate Insititute of Canada



Potasium deficiency in cashew
Courtesy : Potash and Phosphate Institute of Canada

Potasium deficiency in grapes
Courtesy : Potash and Phosphate Insititute of Canada

Potasium deficiency in potato
Courtesy : Potash and Phosphate Insititute of Canada



Sulphur deficiency in maize
Courtesy : Potash and Pnosphate Insititute of Canada

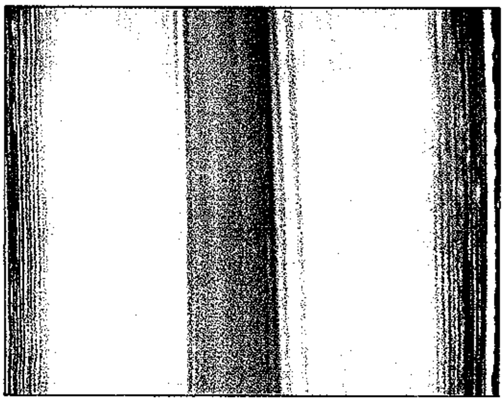
Nutrient Deficiency Symptoms

Sulphur deficient wheat crop
Courtesy : Potash and Phosphate Insititute of Canada

Sulphur deficiency in cotton
Courtesy : Potash and Phosphate Insititute of Canada

A close-up of zinc deficiency symptom in rice leaf
Courtesy : Drs V.K. Nayyar and I.M. Chhibba, Ludhiana

Zinc deficiency in cotton
Courtesy : Potash and Phosphate Insititute of Canada



Zinc deficiency in sugarcane
Courtesy: Potash and Phosphate Insititute of Canada

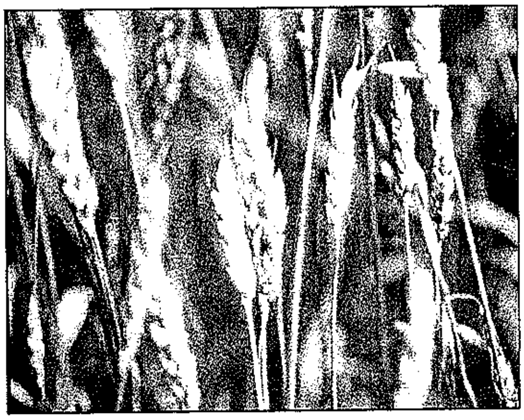
Iron-deficient bed-planted rice field
Courtesy: Dr A.K. Singh, New Delhi

Nutrient Deficiency Symptoms

Iron deficiency in maize
Courtesy: Potash and Phosphate Insititute of Canada

Iron deficiency in groundnut
Courtesy: Potash and Phosphate Insititute of Canada

Manganese deficiency symptom in flag leaf of wheat
Courtesy: Drs V.K. Nayyar and I.M. Chhibba, Ludhiana



Copper deficiency in wheat
Courtesy: Potash and Phosphate Institute of Canada

Boron deficiency in cauliflower
Courtesy: Potash and Phosphate Institute of Canada

Molydenum deficiency in cauliflower
Courtesy: Potash and Phosphate Institute of Canada