Tariq Aftab Khalid Rehman Hakeem *Editors*

Plant Micronutrients

Deficiency and Toxicity Management



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This book is dedicated to Sir Syed Ahmad Khan (October 17, 1817–March 27, 1898)

Sir Syed Ahmad Khan, one of the architects of modern India, was born on October 17, 1817, in Delhi and started his career as a civil servant.

The 1857 revolt was one of the turning points in Syed Ahmed's life. He clearly foresaw the imperative need for the Muslims to acquire proficiency in English language and modern sciences, if the community were to maintain its social and political clout, particularly in Northern India.

He was one of those early pioneers who recognized the critical role of education in the empowerment of the poor and backward Muslim community. In more than one way, Sir Syed was one of the greatest social reformers and a great national builder of modern India. He began to prepare the road map for the formation of a Muslim university by starting various schools. He instituted Scientific Society in 1863 to instill a scientific temperament into Muslims and to make the Western knowledge available to Indians in their own language.

The Aligarh Institute Gazette, an organ of the Scientific Society, was launched in March 1866 and succeeded in agitating the minds in the traditional Muslim society. Anyone with a poor level of commitment would have backed off in the face of strong opposition, but Sir Syed responded by bringing out another journal, Tehzeeb-ul-Ikhlaq, which was rightly named in English as "Mohammedan Social Reformer."

In 1875, Sir Syed founded the Madrasatul Uloom in Aligarh and patterned the MAO College after Oxford and Cambridge universities that he went on a trip to London. His objective was to build a college in line with the British education system but without compromising its Islamic values. He wanted this college to act as a bridge between the old and the new, the East and the West. While he fully appreciated the need and urgency of imparting instruction based on Western learning, he was not oblivious to the value of oriental learning and wanted to preserve and transmit to posterity the rich legacy of the past. Dr. Sir Mohammad Iqbal observes:

"The real greatness of Sir Syed consists in the fact that he was the first Indian Muslim who felt the need of a fresh orientation of Islam and worked for it—his sensitive nature was the first to react to modern age."

The aim of Sir Syed was not merely restricted to establishing a college at Aligarh but at spreading a network of Muslimmanaged educational institutions throughout the length and breadth of the country; keeping in view this end, he instituted All India Muslim Educational Conference that revived the spirit of Muslims at national level. The Aligarh Movement motivated the Muslims to help open a number of educational institutions. It was the first of its kind of such Muslim NGO in India, which awakened the Muslims from their deep slumber and infused social and political sensibility into them.

Sir Syed contributed many essential elements to the development of the modern society of the subcontinent. During Sir Syed's own lifetime, "The Englishman," a renowned British magazine of the nineteenth century remarked in a commentary on November 17, 1885: "Sir Syed's life strikingly illustrated one of the best phases of modern history." He died on March 27, 1898, and lies buried next to the main mosque at Aligarh Muslim University.

Preface

Plants require essential nutrients (macronutrients and micronutrients) for normal functioning and growth. A plant's sufficiency range is the range of nutrient amount necessary to meet the plant's nutritional needs and maximize growth. This range depends on individual plant species and the particular nutrient. Nutrient levels outside of a plant's sufficiency range cause overall crop growth and health to decline due to either a deficiency or a toxicity. In addition to the macronutrients (N, P, K, H, Mg, Ca, and S), micronutrients (B, Cl, Mn, Fe, Zn, Cu, and Mo) are required for optimal plant growth. Micronutrients are required by plants in small amounts but are no less essential than macronutrients. Plant micronutrient concentrations are an integration of the dynamic processes of nutrient uptake, transport, and dry matter accumulation, but levels are ultimately dependent on sufficient available soil concentrations. Total soil micronutrients may exceed the demand of a single crop by more than a thousandfold, but the available fraction may be insufficient, resulting in crop nutrient deficiencies. Available micronutrients are dependent on soil chemical and physical properties such as pH, soil organic matter content, and clay minerals.

This book covers a wide range of topics, discussing the management approaches of plant micronutrient deficiency as well as toxicity in plants. Moreover, this will be the first reference book on the topic discussing the management of deficiency and toxicity with latest biotechnological and omics approaches. In this volume, we highlight the working solutions as well as open problems and future challenges in plant micronutrient deficiency and toxicity research. We believe that this book will initiate and introduce readers to state-of-the-art developments and trends in this field of study.

The book comprises 20 chapters, most of them being review articles written by experts from around the globe, highlighting wide range of topics, and discussing the management approaches of plant micronutrient deficiency as well as toxicity in plants. We are hopeful that this volume would furnish the need of all researchers who are working or have interest in this particular field. Undoubtedly, this book will be helpful for general use of research students, teachers, and those who have interest in plant micronutrients.

x Preface

We are highly grateful to all our contributors for accepting our invitation for not only sharing their knowledge and research, but also venerably integrating their expertise in dispersed information from diverse fields in composing the chapters and enduring editorial suggestions to finally produce this venture. We also thank Springer-Nature team for their generous cooperation at every stage of the book production.

Lastly, thanks to well-wishers, research students, and authors' family members for their moral support, blessings, and inspiration in the compilation of this book.

Aligarh, India Jeddah, Kingdom of Saudi Arabia Tariq Aftab Khalid Rehman Hakeem

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At present, Dr. Hakeem serves as an editorial board member and reviewer of several high-impact international scientific journals from Elsevier, Springer Nature, Taylor & Francis, Cambridge, and John Wiley Publishers. He is included in the advisory board of Cambridge Scholars Publishing, UK. He is also a fellow of Plantae group of the American Society of Plant Biologists; member of the World Academy of Sciences; member of the International Society for Development and Sustainability, Japan; and member of Asian Federation of Biotechnology, Korea. Dr. Hakeem has been listed in Marquis Who's Who in the World, since 2014–2020. Currently, Dr. Hakeem is engaged in studying the plant processes at ecophysiological as well as molecular levels.

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Chapter 1

An Overview of Micronutrients: Prospects and Implication in Crop Production



1

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Abstract Micronutrients are important for plant growth and they significantly play an important role in balanced crop nutrition. They are vital for appropriate growth and development of plants in their entire life span. A deficiency of any one of the micronutrients in the soil can limit the growth of plants, even when all other nutrients are available in adequate amounts. The deficiency of micronutrients is widespread in many areas due to the nature of soils, high pH, low organic matter, salt stress, continuous drought, high bicarbonate content in irrigation water and imbalanced application of fertilisers. In India, the most deficient micronutrient in the soil is Zn, followed by B. In recent years, the deficiency of micronutrient has risen to a great extent. Zn and B deficiencies are focussed mainly for their adverse impacts on

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human health and food production. This chapter attempts to examine the defects of Zn, Fe, Mn, Cu, B and Mo deficiency in the soil and crops as well as the management of micronutrient deficiencies by way of fertilisation, development of agronomic strategies and creation of awareness of micronutrient dose. Deficiencies of Zn and B cause some severe complications in crop production in India. In view of the problems, we discuss the importance of micronutrients in agriculture and their roles and ways to improve crop productivity.

Keywords Micronutrients · Soil fertility · Crop nutrient management · Balanced nutrition

Introduction

Micronutrients in small quantity are applied for healthy growth and development of plants. Micronutrients and macronutrients play an important role in completing the life cycle of plants. The role of micronutrients as balanced plant nutrition is well established. Micronutrients are essential for the maintenance of soil health as well as for the enhancement of productivity of crops (Rattan et al. 2009). Zinc, copper, manganese, iron and boron are essential micronutrients for speedy growth of plants. Micronutrients play an indispensable role in the biosynthesis of proteins, nucleic acids, gene expression, growth substances, metabolism of carbohydrates and lipids, stress tolerance, chlorophyll and secondary metabolites, etc. through their association with other physiologically active molecules and various enzymes (Singh 2004; Rengel 2007; Gao et al. 2008). Therefore, the availability of micronutrients is very much essential for proper crop nutrition and development. Geological substrate and pedogenic systems of management determine the quantity of micronutrients in soils. However, plants are unable to indicate the deficiency because the availability of micronutrients depends on organic matter content, soil pH, adsorptive surfaces and other biological, chemical and physical conditions in the environment.

Soil plays a significant role in defining the agro-system of sustainable productivity. Sustainable fertility depends on the ability of the soil to supply essential nutrients to the growing plants. Micronutrient deficiency imposes a severe constraint on productivity, stability and sustainability of soils (Bell and Dell 2008). Lack of micronutrients may be due to their low contents, or soil factors reduce plant growth. Inappropriate management of nutrients leads to multi-nutrient deficiencies in Indian soils (Sharma 2008). Moreover, continuous negligence of micronutrient application and avoidance of organic manures are the significant causes of scarcity of micronutrients (Srivastava et al. 2017). The deficiency of the nutrient in plant

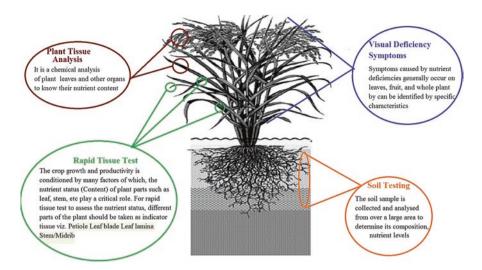


Fig. 1.1 Possible steps to identify the nutrient deficiency

and soil can be identified by several steps. Some of the so far established strategies are suggested in Fig. 1.1.

Availability of micronutrients to plants is influenced by the distribution within the soil profile (Singh and Dhankar 1989). Land-use pattern, besides soil characterisation, plays a vital role in governing the nutrient dynamics and fertility of soils (Venkatesh et al. 2003). Continuous cultivation following a particular land-use system affects physico-chemical properties of soils resulting in the modification of DTPA-extractable micronutrient content to make available to plants for their growth. It is quite impossible to get the maximum benefit from crop production without the availability of adequate micronutrients. Knowledge of the pedogenic distribution of micronutrients is crucial because the roots of many plants penetrate subsurface layers of the soil to draw required nutrients.

Role of micronutrients as a balanced nutrient of crops is well established. Micronutrients are indispensable for the growth and development of plants. The origin of micronutrient management research in India draws back to a publication by Iyer and associates in 1934. Real impetus on micronutrient research came with a report of *Khaira* disease in mid-1960s (Nene 1966). Keeping in view of the report, All India Coordinated Research Scheme of Micronutrients in Soil and Plants was established in India. The need for inclusion of micronutrients in the crop nutrition programme has become more of an essential nature in the present day (Tables 1.1 and 1.2).

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Micronutrient		Year of	
elements	Essentiality established by	discovery	Plant uptake form
Iron	E. Gris	1843	Fe ²⁺
Manganese	J. S. McHargue	1922	Mn ²⁺
Zinc	A L. Sommer and C. B. Lipman	1926	Zn ²⁺
Copper	A L. Sommer, C. P. Lipman, and C. McKinny	1931	Cu ²⁺
Molybdenum	D. L. Arnon and P. R. Stout	1939	MoO ₄ ²⁻
Boron	K. Warington	1923	H ₃ BO ₃ , H ₂ BO ₃ ⁻ , HBO ₃ ²⁻ , BO ₃ ³⁻
Chlorine	Broyer, Carlton, and others	1954	Cl-
Nickel	P. H. Brown, R. M. Welch, and E. E. Cary	1982	Ni ²⁺

Table 1.1 Micronutrient elements discovered so far

Table 1.2 The concentration of micronutrients in leaf tissue of various plants

Micronutrient	Deficient	Normal	Toxic
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
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	100–200
Ni (mg/kg)	<0.1	_	_

Sources: Tisdale et al. (1997)

Function of Micronutrients

Function of Zinc

Zinc is a constituent of enzyme carbonic anhydrase (CA), alcoholic dehydrogenase, and superoxide dismutase (SOD). The deficiency of zinc restricts RNA and protein synthesis as it plays a significant role in nitrogen metabolism and photosynthesis. Zinc also controls the concentration of auxin in plants. Zinc increases seed viability and seedling vigour and gives protection to abiotic and biotic stresses (Cakmak 2008).

Function of Copper

Copper is a constituent of polyphenol or catechol oxidase, tyrosinase, laccase and ascorbic oxidase. Copper plays a vital role in saving the plants from diseases. It improves the fertility of male flower, and it is also concerned with the oxidation of iron in plants.

Function of Iron

Iron is a component of porphyrin compounds—cytochromes, haem and haem enzymes and other functional metallic proteins. The haemoglobin of the leguminous root nodules leghaemoglobin contains iron as an essential nutrient. As a constituent of ferredoxin, iron is involved in the nitrogen fixation by a diverse group of microorganisms.

Function of Manganese

Manganese plays a crucial part in the tricarboxylic acid cycle in oxidation and reduction reactions. It activates several enzymes such as oxidoreductases, hydrolases and lyases. It also autocatalyses isocitrate dehydrogenase, malic dehydrogenase, glycocyaminase and D-alanyl synthesase. Manganese is a primary component of water-splitting enzyme related to photosystem II.

Function of Boron

Boron increases cell wall thickness by forming specific complexes. It increases flower production and retention, pollen tube elongation and germination and seed and fruit development. It also helps in the translocation of photosynthates. It inhibits IAA oxidation and gives drought tolerance to crops.

Function of Molybdenum

Molybdenum is a vital constituent of nitrogenase, sulphite oxidase, nitrate reductase and xanthine oxidase/dehydrogenase. Molybdenum aids in the synthesis of ascorbic acid. It is critical for the formation of pollens and anthers. It is a remedy of excessive copper, manganese and zinc.

Function of Chlorine

Chlorine activates enzymes that are involved in starch utilisation which affects germination and energy transfer. In moisture-stress conditions chlorine helps in the movement of water into cells and maintenance of that water. Chlorine also controls the opening and closing of stomata on leaf surfaces.

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Function of Nickel

Nickel is related to nitrogen metabolism by way of manipulating urease activity. It enables passage of nutrients to the seeds or grains.

Micronutrient Deficiency Scenario in Soils and Plants

Micronutrient content in soil is reliant on numerous factors such as parent material; soil-type inherent soil properties like pH and soluble salt concentration (EC); quality and quantity of calcium carbonate content and soil organic matter; trace elements supplied through manures and fertilisers; content of available macronutrients; micronutrient relations; and vegetation (Fageria et al. 2002; Alloway 2008; Shukla et al. 2016).

Leaching loss of micronutrients, liming of soils, limited use of manures and use of excessive micronutrient fertilisers deprived of micronutrient additions aggravate depletion of available micronutrients in soils.

Parent material and pedogenic processes govern total soil micronutrient content. Indian soils are reasonably acceptable concerning total micronutrient content. But despite the comparatively high entire contents, micronutrient deficiencies have often been reported in many crops due to low availability of available micronutrients (Singh 2008; Behera and Shukla 2014; Shukla and Tiwari 2016).

More than 50% of soils showed Zn deficiency in states like Goa (55.3%), Rajasthan (56.5%), Madhya Pradesh (57.1%) and Tamil Nadu (63.3%) and less than 10% of soils had Zn deficiency in states like Arunachal Pradesh, Uttarakhand, Tripura, Nagaland, Mizoram, Meghalaya and Himachal Pradesh. Fe deficiency of more than 20% soils was observed in states like Rajasthan (34.4%), Maharashtra (23.1%), Gujarat (25.9%) and Haryana (21.7%) although a deficiency in 10–20% of soils has been observed in states like Andhra Pradesh, Telangana, Goa, Bihar, Tamil Nadu and Uttar Pradesh. Haryana (5.1%), Rajasthan (9.2%) and Tamil Nadu (12.0%) had Cu deficiency of more than 5%. In light-textured rice-growing soils, higher Mn deficiency was reported (especially in rice-wheat systems) in states like Rajasthan (28.3%), Punjab (26.2%), Goa (16.9%), Uttar Pradesh (15.8%) and Chhattisgarh (14.8%). 5–10% Mn deficiency had been observed in the soils of states like Bihar, Haryana, Himachal Pradesh and Telangana. 35–60% of soils showed B deficiency in the states having acid soils like Jharkhand, Odisha, Karnataka, Jammu and Kashmir, Himachal Pradesh, Manipur, Meghalaya, Mizoram and West Bengal (Table 1.3) (Shukla et al. 2018).

In plants, the optimum concentrations of micronutrients are 100, 50, 100, 20, 20, 0.1, 0.1 and 6 mg kg⁻¹ of dry matter for Cl, Mn, Fe, B, Zn, Mo, Ni and Cu, respectively. Visual diagnosis of micronutrient disorders is an influential tool for the quick identification of plant health associated with fertility, micronutrient availability, uptake and confirmation of soil or foliar test results. Careful remarks of the growth of plants can deliver a direct indication of their nutritional conditions. Metabolic disturbances subsequent from micronutrient deficiencies offer relations between the

Zinc State Copper Manganese Iron Boron Andhra Pradesh 22.92 1.33 1.63 17.24 4.08 Arunachal Pradesh 4.63 1.40 3.01 1.44 39.15 Assam 28.11 2.80 0.01 0.00 32.75 Bihar 45.25 3.19 8.77 12.00 39.39 Chhattisgarh 25.29 3.22 14.77 7.06 20.59 Goa 55.29 3.09 16.91 12.21 12.94 Gujarat 36.56 0.38 0.46 25.87 18.72 Haryana 15.42 5.13 6.16 21.72 3.27 Himachal Pradesh 8.62 1.43 6.68 0.51 27.02 Jammu and Kashmir 10.91 0.34 4.60 0.41 43.03 Jharkhand 17.47 0.78 0.26 0.06 60.00 Karnataka 30.70 2.28 0.13 7.68 36.79 Kerala 18.34 0.45 3.58 1.23 31.21 Madhya Pradesh 57.05 0.47 2.25 8.34 4.30 Maharashtra 38.60 0.14 3.02 23.12 20.69 Manipur 11.50 2.46 2.06 2.13 37.17 Meghalaya 3.84 1.03 2.95 1.33 47.93 32.76 Mizoram 1.96 0.98 1.22 0.49 2.00 54.31 Nagaland 4.62 0.53 3.05 Odisha 32.12 2.12 6.42 51.88 7.11 Punjab 19.24 4.67 26.20 13.04 18.99 Rajasthan 56.51 9.15 28.28 34.38 2.99 Tamil Nadu 63.30 12.01 7.37 12.62 20.65 Telangana 26.77 1.36 3.54 16.65 16.49 Tripura 5.51 2.36 0.00 1.57 23.62 Uttar Pradesh 27.27 2.84 15.82 15.56 20.61 Uttarakhand 9.59 1.51 4.82 1.36 13.44

Table 1.3 Distribution of micronutrient deficiencies in India

Source: Shukla et al. (2018)

14.42

36.50

West Bengal

All India average

function of an element and the appearance of specific development of micronutrient deficiency in the plant:

0.98

7.10

0.03

12.8

37.05

23.4

- Step 1: Reduction of micronutrients stored in the body—lessening the degree of saturation of the carriers and enzymes.
 - Step 2: Damage of micronutrients is reliant on biochemical functions.

1.76

4.20

Step 3: Determinate changes in cellular and physiological functions.

Step 4: Presence of structural and functional lesions. When a plant lacks a particular nutrient, it reveals the injury of biological and physiological functions (up to step 3) before showing deficiency as lesions or clinical symptoms (step 4). The first three stages mark a hidden hunger, which may cause a critical loss in growth and development of plant and eventually decrease in yield, if not identified through plant tissue analysis in time (Table 1.4).

Table 1.4 The critical micronutrient concentration in crop plants

Micronutrients	Crops	Critical concentration (mg kg ⁻¹)
Zn	Cereals	15
	Millets	15–20
	Legumes	7–20
	Vegetables (French bean)	36
	Oilseeds	12–25
В	Cereals	4–10
	Millets	7–15
	Legumes	3–15
	Vegetables	3–5
	Oilseeds	5–10
Cu	Cereals	2–4
	Millets	2–3.5
	Legumes	4–8
	Vegetables	2–6
	Oilseeds	2–10
Mn	Cereals	25
	Millets	10
	Legumes	10–35
	Vegetables	30–40
	Oilseeds	5–18

Source: Shukla et al. (2018)

Micronutrient Status in Indian Soil

Iron

Iron is placed second compared to aluminium in the list of abundant metals present in the soil. It forms about 5% of the earth's crust. Although it may not be present in an available form, it is not absent from soils. Plants take up iron as either Fe²⁺ (ferrous cation) or Fe³⁺ (ferric cation). Ferric iron compounds have low solubility, and the condition which favours the formation of these compounds reduces iron availability in the soil. Sahu et al. (1990) conducted a distribution study on available Mn, Zn, Fe and Cu in both subsurface and surface soils from eight soil groups of rice-growing areas of Odisha and he observed that Fe, Mn and Cu were adequately supplied to these soils. However, the deficiency of available Zn extracted by DTPA (<0.6 ppm) was found. Further, Raj Kumar et al. (1990) made a detailed study on the depth-wise distribution of four available micronutrients, i.e. Mn, Zn, Fe and Cu, in 15 domination soil series of Bundelkhand, MP. They found higher contents of available micronutrient cations in soils developed from shale and ferruginous sand-stone as compared to the soil formed from basalt or granite. Available Mn, Fe and Cu were increased with depth up to B₂ horizon. They also observed that the horizon

in Udic Haplustalfs was developed over granite, but no uniform pattern was observed in Vertisols. Organic carbon and pH were found as the dominant factors to control the availability of micronutrient cations in these soils.

Bhogal et al. (1993) analysed the micronutrient status available in Aquic Ustifluvents and Udifluvents and its relationship with specific soil properties. Among micronutrients, they found a widespread deficiency of Zn in Aquic Ustifluvents, and Udifluvents of Bihar followed by B. The stepwise multiple regression equations indicated that the availability of Cu and Zn was predominantly controlled by organic carbon and pH. In contrast, Mn and Fe were controlled by organic carbon, pH and available P and K, and that of B were controlled by EC, pH and organic carbon of the soils. Vadivelu and Bandyopadhyay (1995) studied the DTPAextractable Fe, Cu, Mn and Zn in the soil of Minicoy Island, Lakshadweep. They observe that DTPA-extractable Fe ranged between 1.7 and 12.1 mg kg⁻¹ in the surface soil. They noted that the DTPA-extractable Fe decreased in the depth of the soils. Vijay Kumar et al. (1996) submitted detailed reports on the decrease in micronutrient contents in soils of Northern Telangana. The reports indicate that the soils of Northern Telangana are low in organic carbon and range between low and high in CEC. Fe, Cu and Mn of the soils vary widely from 19 to 59.9, 1.01 to 5.19 and 15 to 86 mg kg⁻¹, respectively. The surface of the soils contains more nutrients than the subsurface soils. Chattopadhyaya et al. (1996) studied nine soil profiles collected from three districts of the Vindhyan scrap land area to study Zn, Cu, Fe and Mn status and observed that soil in the upper elevation contained more micronutrient than that of lower altitude.

Parman et al. conducted a distribution study on the soils of vegetable-growing pockets of cold desert areas and found the deficiency of DTPA-extractable Fe, Zn and Mn. Sarkar et al. (2000) found high contents of DTPA-extractable Fe, Cu, Zn and Mn in the surface layers in almost all the soil profiles of Madhubani district of Bihar. Sharma et al. (2001) studied the samples of soil and plant collected from six tehsils of Rajgarh district of MP to know the status of different physico-chemical properties and Zn, Cu, Fe and Mn. Overall, the mean value of soil pH, EC, CaCO₃ and organic carbon in the district were 7.9, 0.21 dSm⁻¹, 3.9 and 0.57%, respectively. The DTPA-Fe in the soil ranges between 11.8 and 26.4 mg kg⁻¹, respectively.

A detailed study was undertaken by Minakshi et al. (2005) to assess the micronutrient status of the soil using Arc-info GIS to examine the physico-chemical properties of soil and DTPA-extractable micronutrients. They observed a significant and positive correlation between soil organic matter with all the micronutrient cations and Mn, Fe and Cu with clay content. However, they also noted a negative relationship between DTPA-Fe (r = -0.251) and pH. Thangasamy et al. (2005) revealed that the soils of Sivagiri micro-watershed of Chittoor district in Andhra Pradesh were deficient in Fe, between deficient and sufficient in available Zn but sufficient in available Mn and Cu. Singh et al. (2006a, b) evaluated soil samples representing widely varied land use, viz. pine, oak, deodar, forest orchard and agricultural field from Nainital and Almora district of Kumaon hills, and observed that DTPA-Fe and Zn in the soils varied from 14.0 to 84.0 and 0.09 to 8.49 mg kg⁻¹, respectively.

Zinc

Zn²⁺ cation is the predominant form available to plants. Zn in the soil occurs as divalent cation Zn2+ and may present as water-soluble Zn2+, exchangeable Zn2+ and adsorbed Zn²⁺ on surfaces of clay, organic matter, carbonates and oxide minerals. Sharma et al. (1996) investigated arid-zone soils of Punjab and reported that these soils are alkaline in nature but poor in micronutrient elements. Sen et al. (1997) observed that available Zn content of the soils of Manipur ranged between 0.2 and 1.4 mg kg⁻¹ and further decreased down the profile. They found that the soils of the valley were most miserable in Zn content as compared to the soils of inter-hill valley and hill. Singh et al. (1997) submitted a report on DTPA-extractable Zn content in the soils of rice fields of Meghalaya. They observed that DTPA-Zn in the soils decreased with the increase in altitude. Sharma et al. (1999) studied the soils developed on six physiographic units of the semi-arid Siwalik hills of Punjab in northwest India and reported widespread deficiency of Zn, Fe and Cu in the cultivated soils on foot slopes, toe slopes and floodplain of Siwalik hills. They observed that insufficiency ranges from 16% in Cu to 100% in Mn and Fe contents. From an investigation of Entisols of Punjab, Sharma et al. (2002) concluded that the total and DTPA-extractable micronutrients in the surface horizon were higher than those of subsurface soils. Its content varied from 15 to 76 mg kg⁻¹(Zn), 1 to 31 mg kg⁻¹(Cu), 100 to 1350 mg kg⁻¹(Mn) and 0.80 to 3.70% for Fe. The DTPA-extractable content varied between 0.08 and 1.88 mg kg⁻¹, 0.04 and 2.40 mg kg⁻¹, 0.20 and 27.7 mg kg⁻¹ and 0.50 and 23.0 mg kg⁻¹ for Zn, Cu, Mn and Fe, respectively.

Gupta et al. (2003) confirmed DTPA-extractable micronutrient cations (Zn, Fe, Cu and Mn) in profiles of six established series of northern Madhya Pradesh, in broad spectrum; all the micronutrient cations decreased with depth exceptionally in 15-60 cm layer where available content Cu was maximum and followed a decreasing trend down the profiles in most of the soil series. Sharma et al. (2003) studied some soils of the semi-arid region of Rajasthan to investigate the status of micronutrients and also the effect of soil properties on their status. The study showed that Zn, Fe, Cu and Mn had positive correlations with organic carbon and silt + clay but a negative relationship with calcium carbonate content and pH. Investigations of Venkatesh et al. (2003) in the soil of Ri Bhoi district of Meghalaya revealed that burning of leftover straws for cultivation resulted in decreased availability of Zn, Fe and Cu but increase in the available Mn by about fourfold on burning. However, they noticed that the soils of the valley contain the highest amount of available forms of Zn, Fe and Cu but the least amount of available Mn. Nayak et al. (2006) made a detailed study on the spatial variability of DTPA-extractable micronutrients (Zn, Cu, Fe and Mn) in the soil of Bara Tract of Sardar Sarovar Canal Command in Gujarat. The study revealed that the spatial variability of the micronutrients was described both graphically and as empirical statistics of the function of the distribution. The result of the sampled scale showed a normal distribution of the micronutrients, viz. Zn, Cu and Fe, in the soil. Talukdar et al. (2009) made an investigation on the DTPA-extractable micronutrient cations and their relationship with soil physico-chemical properties of soil in two agroecosystems of Golaghat district of Assam. Regardless of the land-use pattern, the DTPA-extractable micronutrient cations were correlated positively with CEC and organic carbon content. However, they observed that all micronutrients had a significant negative correlation with soil pH. Vijayakumar et al. (2011) studied the soils of tsunami-affected coastal areas of Nagapattinam Taluk of Tamil Nadu. The study revealed that the soil contained sufficient contents of available micronutrients, 97% of Fe and 53% of Zn. However, the study detected 100% deficiency of Mn and 45% deficiency of Cu in the soils.

Manganese

Manganese is considered to exist in three valence states in the soil as (i) divalent manganese (Mn²⁺) (adsorbed cation or in the soil solution), (ii) trivalent manganese (Mn³⁺) which exists as highly reactive oxide Mn₂O₃ and (iii) tetravalent manganese (Mn⁴⁺) which exists as very inert oxide MnO₂. They exist as deposits in cracks and veins and as a mixture of iron oxides, coating of soil particles and other constituents of soil in nodules. In soil solution, Mn increases significantly under acid soils; solubility of Mn²⁺ may be sufficiently great to cause toxicity problems for sensitive species. The primary form of manganese taken up by plants is Mn²⁺. Tripathi et al. (1994) studied the soils of Himachal Pradesh and observed that available Mn had no specific trend of distribution with depth in the soil profile. They noticed an average value of 29 mg kg⁻¹ in the soil. They also found a significant correlation of DTPA with organic carbon. They observed that Fe varied between 0.1 and 2.8, between 0.4 and 4.8 and between 4.5 and more, respectively. In general, the DTPA-Zn, -Cu and -Fe were on the decrease in the depth of the soil. However, Prasad and Gajbhiye (1999) investigated the value of available Mn and found that it was on the decrease in the depth of the profile. They observed that DTPA-extractable Mn, Zn and Cu ranged between 3.0 and 15.1, between 0.14 and 0.63 and between 1.3 and 4.6 mg kg⁻¹, respectively, in different horizons of three Vertisols of basaltic origin and occurred in the different agroecological zone of central India. Venkatesh et al. (2003) analysed samples of surface soils of various land-use patterns, viz. bun cultivation, terrace cultivation, natural forest soil cultivation and valley land cultivation of Ri Bhoi district of Meghalaya to ascertain the status of total micronutrient. They reported that burning of leftover straws and stems of other plants on the land for bun cultivation resulted in a decrease of Fe, Zn and Cu available in the soil but an increase in the Mn by about fourfold. Kher et al. (2004) examined the soils of the Kandi belt of Jammu region and noticed that almost all samples of soil were well supplied with Fe and Mn but deficient in Zn and Cu. Zn, Mn, Fe and Cu available in soils ranged between 0.28 and 2.44, between 4.52 and 21.92, between 2.02 and 5.70 and between 0.16 and 1.40 ppm with an average value of 1.62, 11.00, 3.40 and 0.55 ppm, respectively. According to the report of Satyavathi and Reddy (2004), Cu and Mn were adequate in the soils of ten pedons of Telangana region in the state of Andhra Pradesh. The study also revealed that there was a lack of a definite trend of distribution of DTPA-extractable