

# Chapter 1

## An Overview of Micronutrients: Prospects and Implication in Crop Production



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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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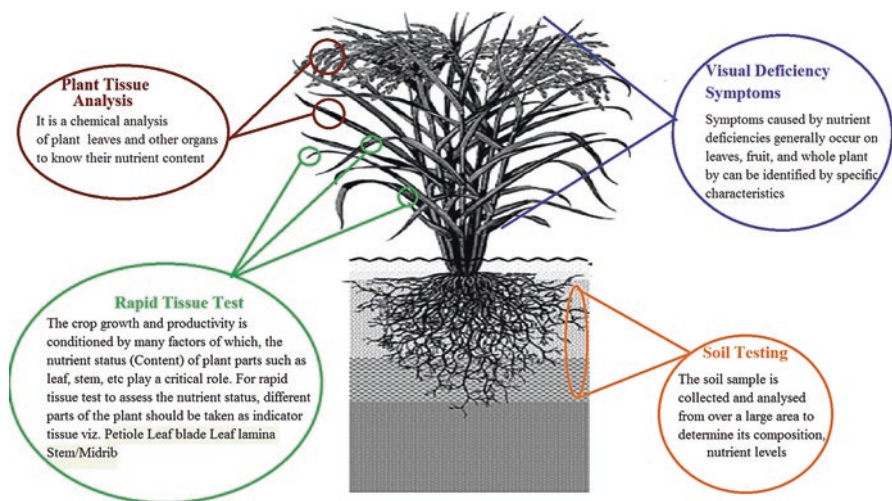
human health and food production. This chapter attempts to examine the defects of Zn, Fe, Mn, Cu, B and Mo deficiency in the soil and crops as well as the management of micronutrient deficiencies by way of fertilisation, development of agronomic strategies and creation of awareness of micronutrient dose. 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).

**Table 1.1** Micronutrient elements discovered so far

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

**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, glycoaminase and D-alanyl synthetase. 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.

## *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<sup>-1</sup> 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

**Table 1.3** Distribution of micronutrient deficiencies in India

State	Zinc	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
Mizoram	1.96	0.98	1.22	0.49	32.76
Nagaland	4.62	0.53	3.05	2.00	54.31
Odisha	32.12	7.11	2.12	6.42	51.88
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
West Bengal	14.42	1.76	0.98	0.03	37.05
All India average	36.50	4.20	7.10	12.8	23.4

Source: Shukla et al. (2018)

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

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.

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 <sup>-1</sup> )
Zn	Cereals	15
	Millets	15–20
	Legumes	7–20
	Vegetables (French bean)	36
	Oilseeds	12–25
B	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 Fe<sup>2+</sup> (ferrous cation) or Fe<sup>3+</sup> (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 sandstone as compared to the soil formed from basalt or granite. Available Mn, Fe and Cu were increased with depth up to B<sub>2</sub> 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.

Bhagal 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 DTPA-extractable 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<sup>-1</sup> 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<sup>-1</sup>, 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, CaCO<sub>3</sub> and organic carbon in the district were 7.9, 0.21 dSm<sup>-1</sup>, 3.9 and 0.57%, respectively. The DTPA-Fe in the soil ranges between 11.8 and 26.4 mg kg<sup>-1</sup>, 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<sup>-1</sup>, respectively.

## Zinc

Zn<sup>2+</sup> cation is the predominant form available to plants. Zn in the soil occurs as divalent cation Zn<sup>2+</sup> and may present as water-soluble Zn<sup>2+</sup>, exchangeable Zn<sup>2+</sup> and adsorbed Zn<sup>2+</sup> 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<sup>-1</sup> 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 north-west 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<sup>-1</sup>(Zn), 1 to 31 mg kg<sup>-1</sup>(Cu), 100 to 1350 mg kg<sup>-1</sup>(Mn) and 0.80 to 3.70% for Fe. The DTPA-extractable content varied between 0.08 and 1.88 mg kg<sup>-1</sup>, 0.04 and 2.40 mg kg<sup>-1</sup>, 0.20 and 27.7 mg kg<sup>-1</sup> and 0.50 and 23.0 mg kg<sup>-1</sup> 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 left-over 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 ( $Mn^{2+}$ ) (adsorbed cation or in the soil solution), (ii) trivalent manganese ( $Mn^{3+}$ ) which exists as highly reactive oxide  $Mn_2O_3$  and (iii) tetravalent manganese ( $Mn^{4+}$ ) which exists as very inert oxide  $MnO_2$ . 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  $Mn^{2+}$  may be sufficiently great to cause toxicity problems for sensitive species. The primary form of manganese taken up by plants is  $Mn^{2+}$ . 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

micronutrients concerning depth. Minakshi et al. (2005) observed in the soil of Patiala district of Punjab that the soil had a deficiency of 4% in Mn and deficiency of 5% in Fe. Sharma et al. (2005a) examined the soil profiles collected from concave hill slope in the Siwalik Himalaya, piedmont and plain on a topo-sequence in Punjab and observed that DTPA-extractable Zn, Cu, Mn and Fe content ranged between 0.22 and 2.30, between 0.30 and 2.58, between 2.80 and 86.5 and between 3.10 and 30.5 mg kg<sup>-1</sup>, respectively, in the soil profiles. DTPA-extractable forms decreased with depth but increased with clay content. They also found that organic carbon controlled DTPA-extractable forms.

Sharma et al. (2006) carried out a study on five representative soil profiles of the basaltic terrain of southern Rajasthan and observed that the soils of high altitude contain more cation micronutrients than those at the lesser elevation. Sharma et al. (2006) studied the soils of different blocks of Leh district to assess the available status of major micronutrients and observed a positive correlation between available micronutrients Fe, Mn and Cu (0.072, 0.029 and 0.069 mg kg<sup>-1</sup>, respectively) and the organic carbon. Sharma et al. (2003) also observed a positive correlation between organic carbon and available micronutrients in the soils.

## *Copper*

The common forms of soil copper are as follows: (i) ionic and complexes in the soil solution; (ii) on regular cation-exchange sites of clays and organic matter—held electrostatically in response to Coulombic forces; (iii) co-precipitated in soil oxide material; and (iv) in biological residues and living organisms. Sangwan and Singh (1993) studied ten profiles of semi-arid soils of southern Haryana to assess the vertical distribution of Zn, Mn, Cu and Fe concerning depth and other essential soil properties. They observed that the distribution of Mn and Fe was influenced by pH and CaCO<sub>3</sub> content, as well as clay and CEC, controlled the availability of Cu. Pradeep Kumar et al. (1996) conducted a study on the soils of lower Siwalik of Himachal Pradesh and observed that extractable form of Zn, Cu, Fe and Mn failed utterly to follow the pattern of depth-wise distribution due to stratification of these soils. Jalali and Sharma (2002) studied the soils of an intermediate mid-hill region of Jammu and found that the soil with low organic and the soil with a high pH content were generally little in Zn, Cu, Fe and Mn. Gupta et al. (2003) studied 24 profiles of 6 established series (Madhaiyapura, Palri, Taton, Bhangarh, Richarikala and Bagwai) of Northern Madhya Pradesh to evaluate the DTPA-extractable micronutrient cations (Zn, Cu, Fe and Mn) and their relationship with different soil properties. They observed in the profiles of soil series that zinc, Fe and Mn content was generally on the decrease with depth but Cu was found maximum in the layer between 15 and 60 cm and again on the decline with depth. Nayak et al. (2006) studied the soils of borehole to assess the spatial variability of DTPA-extractable Zn, Fe, Cu and Mn in the soils and reported that 10% of the areas were deficient in Zn and 5% of the area lacked in Cu and Fe, but adequate available Mn content was available in

the area. Mondal et al. (2007) investigated the surface soil samples collected from the newly established location of S.K. University of Agricultural Science and Technology Jammu, at Chatha (J&K), and reported that the soil was deficient in B. The investigation revealed that B had an average value of  $0.45 \text{ mg kg}^{-1}$  and rest of micronutrients were abundant in the surface soil samples. Sharma and Chaudhary (2007) studied the vertical distribution of available micronutrient cations (Zn, Cu, Fe and Mn) and their relation with different properties in 32 profiles of 8 tentative soil series of Mandhala watershed which represent lower Shiwaliks of Solan district in Himachal Pradesh. The study revealed that the content of available Cu was high on the horizontal surface, and decreased with depth. It ranged from  $0.30$  to  $2.80 \text{ mg kg}^{-1}$  in almost all the soil series. Rao et al. (2008) studied the significant landforms of Ramachandrapuram Mandal of Chittoor district of Andhra Pradesh and reported that soils were deficient in DTPA-extractable zinc and iron but sufficient in DTPA-extractable Cu and Mn. Those soils were slightly acidic to moderately alkaline in reaction and ranged between low and medium in organic carbon and cation-exchange capacity. Anil Sood et al. (2009) generated the maps showing the spatial variability of individual micronutrient cation (Zn, Cu, Mn and Fe) by using Arc Info GIS. The study revealed that 7% of the total geographical area (TGA) of the district was deficient in Cu. The amount of Cu available in soil ranged between  $0.08$  and  $3.36 \text{ mg kg}^{-1}$ . Sankar and Dadhwal (2009) studied the red soil of Tamil Nadu and found that available Fe, Mn, Zn and Cu contents in the soil ranged between  $6.2$  and  $71.8$ , between  $2.6$  and  $15.4$ , between  $0.8$  and  $11.5$  and between  $1.6$  and  $29.2 \text{ ppm}$ , respectively. They reported that the content of available micronutrients in the soils was in the order of  $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu}$ . Kumar et al. (2011) studied arid soils of Chura district of Western Rajasthan and observed that Fe, Mn and Cu had a significant and positive correlation with organic carbon. It showed how organic matter played an important role in promoting the availability of this micronutrient in the soils since organic matter acts as a chelating agent; the availability of this ion (Fe, Mn and Cu) increases with an increase in the organic matter.

## **Correlation Between Micronutrients (Fe, Zn, Mn and Cu) and Physical Properties of Soils**

### ***Iron***

Sahu et al. (1990) conducted a study on the distribution of clay content and observed that clay content had a significant and positive correlation with Fe, but the relationship of pH with DTPA-extractable micronutrients was negative. Bhogal et al. (1993) reported that available Fe, Zn, Cu, Mn and B correlated significantly and negatively with pH and correlated positively with organic carbon. Vadivelu and Bandyopadhyay (1995) studied the DTPA-Fe and found that DTPA-Fe correlated positively with organic carbon ( $r = 0.522$ ) and correlated negatively with  $\text{CaCO}_3$  ( $r = -0.549$ ) and

pH ( $r = -0.657$ ). Vijay Kumar et al. (1996) revealed that available Fe, Zn, Cu and Mn correlated negatively and significantly with soil pH. Chattopadhyaya et al. (1996) studied the available Fe and Mn in the soil and reported that Fe and Mn correlated significantly and negatively with pH, EC and  $\text{CaCO}_3$ . Cu correlated significantly and negatively with pH. Parman et al. (1999) concluded for their investigation that Fe and Mn had a significant and negative correlation with soil pH and also had a significant and positive correlation with organic carbon. Zinc had shown a significant and negative relationship with soil pH. Sarkar et al. (2000) concluded from their investigation that available Zn and Fe correlated significantly and negatively with pH. DTPA-extractable Fe, Mn, Cu and Zn correlated positively and significantly with organic carbon. Singh et al. (2006a, b) reported that DTPA-Mn had a negative correlation with available P content but correlated positively with pH. They also said that Fe correlated negatively with pH but correlated significantly and positively with organic carbon, CEC available N and Zn.

## ***Zinc***

Sharma et al. (1996) investigated the positive correlation of all elements with silt and clay contents as well as a negative correlation with sand content. Silt-size feldspar had a positive relationship with Cu, Zn and Mg, but other size had a negative association with Zn, Fe, Mg and Mn. Singh et al. (1997) revealed that DTPA-Cu and -Zn had a positive correlation with pH and clay. However, DTPA-Zn, -Cu and -Mn were influenced negatively and significantly by organic carbon. Sharma et al. (1999) studied the linear correlation coefficients and revealed that the total content of micronutrients increased with increase in clay content, whereas DTPA-extractable micronutrient content increased with increase in organic carbon and decreased with increase in pH. Sharma et al. (2002) reported that the total micronutrients increased with increase in clay content and CEC, whereas DTPA-extractable micronutrient increased with increase in organic carbon content and CEC and decreased with increase in pH and sand content and decrease in subsurface. Gupta et al. (2003) also confirmed that DTPA-extractable micronutrient cations (Zn, Cu, Fe and Mn) showed a positive correlation with organic carbon but had an inverse relationship with soil pH and  $\text{CaCO}_3$  content. Venkatesh et al. (2003) reported that available Zn and Cu positively correlated with organic carbon.

Sharma et al. (2003) studied molybdenum and found that the molybdenum correlated negatively with silt-added clay and organic carbon but correlated positively with pH and  $\text{CaCO}_3$  content. They found that available Zn correlated positively and significantly with clay, CEC and OC. Vijayakumar et al. (2011) studied Fe and found that Fe had a positive correlation with OC but a negative correlation with pH. Zn had a positive relationship with EC and pH but a negative relationship with OC.



## *Manganese*

Datta and Ram (1993) reported that available Mn had a negative association with clay content in upland and lowland soils of Tripura. Available Cu and Fe correlated positively with organic carbon, whereas available Zn correlated negatively with organic carbon in both upland and lowland soils. The clay content correlated positively with available Zn, Cu and Fe in upland soil. Tripathi et al. studied soils of Himachal Pradesh and observed that organic carbon correlated significantly with Zn, Cu and Fe. However, Cu failed to show any significant relationship with other soil properties. Kher et al. (2004) studied the organic carbon and found that organic carbon correlated significantly and positively with all micronutrient cations. According to the report of Satyavathi and Reddy (2004), DTPA-extractable micronutrient content increased with an upsurge in organic carbon and decreased with increase in pH. Minakshi et al. (2005) observed that all the micronutrient cations correlated significantly and positively with soil organic matter. They found a significant and positive correlation of Fe, Mn and Cu with clay content. However, DTPA-Fe correlated negatively with pH. Sharma et al. (2005a, b) observed that the soils of the area where the study was conducted were adequate in DTPA-extractable micronutrient cations and correlated significantly and negatively with pH. Sharma et al. (2006) reported that Cu and Mn correlated positively with organic carbon in the soils of Leh district of Ladakh.

## *Copper*

Pradeep Kumar et al. (1996) revealed that among the soil properties, only CEC was related positively with total and available Cu. Nayak et al. (2000) studied the alluvial soils of Arunachal Pradesh and found that available Cu correlated significantly and positively with pH, but it correlated negatively and non-significantly with sand and clay. Available Zn correlated negatively with soil pH but correlated positively with organic carbon, clay and CEC. Fe correlated negatively and significantly with pH and sand. They observed that Mn correlated positively and significantly with organic carbon. Mn and organic carbon, silt and CEC had a significant and positive relationship, but they had shown a negative correlation with pH and sand. Meena et al. (2006) conducted a study on the soils of Tonk district of Rajasthan and reported that soil pH correlated significantly and negatively with available Cu. However, available Cu correlated positively with organic carbon and clay content. Balpande et al. (2007) conducted a study on the grape-growing soils in Nasik district of Maharashtra and reported that copper had a significant and positive relationship with zinc. They said that extractable Fe did not affect DTPA-Zn whereas zinc had negative correlations with Mn. Similarly, pH influenced DTPA-extractable micronutrients negatively. Verma et al. (2007) investigated the micronutrient cations in alkaline soils of north-east Punjab and concluded that silt had a significant and

positive correlation with DTPA-Cu, -Fe and -Mn. A significant and positive relationship between organic carbon and DTPA-extractable micronutrients indicated that organic matter generates complexing agents. However, it was found that the organic carbon had a maximum positive on DTPA-Cu. Vijayakumar et al. (2011) studied the tsunami-affected areas of Sirkali Taluk of Tamil Nadu and reported that Cu had a positive correlation with organic carbon but negative correlation with pH and EC and Zn.

## Harmful Complications of Micronutrients

Usage of soluble salts may cause adverse effects as these salts get transformed into an insoluble compound and may get concentrated in the rhizosphere. Harmful effects of one element may cause other deficient, for instance, iron and manganese or calcium and boron. Determination of nutrients after leaf analysis seems to be of infinite importance. Harmful effects created by micronutrients and non-essential elements can be categorised into two categories: (1) facts that are same with iron-deficiency symptoms and can be attributed to the low availability or reduced utilisation of iron and (2) effects which are particular to the elements provided in excess. The most commonly occurring symptom of toxicity of metal is chlorosis of the young leaves, except for chromium.

### *Zinc*

In Indian soils, the available Zn ranges between 0.01 and 52.9 mg kg<sup>-1</sup>. It constitutes less than 1% of the total Zn content. At present 36.5% of soil samples across the country are deficient in available Zn; about 8%, 29% and 15% area of the country is suffering from acute deficiency, deficiency and latent deficiency of Zn, respectively. Coarse-textured (loamy sand/sandy, alkali or sodic soils) and calcareous soils, and soil organic carbon with <0.4% content soils, have acute Zn deficiency. Owing to regular and higher use of Zn fertiliser in some parts of the country, a decline in zinc deficiency was observed from 46% in 1967–1987 to 36.5% in 2011–2017. Fascinatingly, based on episodic Zn deficiency data from 1967 to 2000, Singh (2009) had forecast that Zn deficiency would rise to 63% by 2020–2025. A linear rise in the use of Zn fertiliser was witnessed after making awareness among the farmers and initiative taken by the fertiliser industry and also large research and extension undertakings on micronutrients, particularly on Zn by AICRP-MSPE.

With subsequent accumulation of Zn level in soil, Zn deficiency declined to 36.5% in 2017 and based on the present-day trends Zn deficiency would be 21% by 2025–2030 if the profuse efforts of the fertiliser industry and government support and promotion of Zn fertilisation remain. Zinc deficiency disorders are recognised by different nomenclatures like Khaira disease in rice, rosetting in wheat, white bud



in maize, little leaves and mottling in vegetables, and reduced fruit formation in citrus. Effect of Zn deficiency impacting crop productivity is established from the response obtained in a significant number of crops and cropping system across the country to applied Zn (Takkar et al. 1989; Singh 2009; Shukla et al. 2012). Soil is categorised as marginal or nonresponsive, responsive, very responsive and highly sensitive to Zn with incremental relative economic yield, REY, <200, 200–500, 500–1000 and >1000 kg ha<sup>-1</sup>, respectively, based on the level of increase in comparable economic yield (REY) of different crops in more than 15,000 trials conducted at cultivators' fields from 1967 to 2016. During 1967–1984, out of 4144 trials conducted on farmers' fields, 58% showed a response to Zn application (Takkar et al. 1989; Singh 2001). A substantial increase in the number of trials responding to applied Zn enlarged from 58% during 1967–1984 to 63% during 1985–2000, and 72% during 2000–2010 to 80% during 2011–2016. It points out that either new cultivars are more responsive to Zn application or its deficiency has intensified due to tremendous mining of Zn from the soil without its matching replacement.

## *Iron*

In India, iron deficiency is common in calcareous and sodic soils with >7.5 pH. Under drought- or moisture-stress conditions availability of Fe gets poorer owing to the transformation of Fe<sup>2+</sup> into less accessible Fe<sup>3+</sup>. From time to time, iron availability to the crop plants is also hindered by high concentrations of organic matter contents, phosphorus and nitrate N. The acute deficiency, deficiency and latent deficiency of Fe are about 4%, 9% and 6% area of the country, respectively. About 10%, 11% and 60% area is characterised by adequate, high and very high levels of available Fe, respectively. A very high level of available Fe is also associated with strong acid and waterlogged soils. As a result of Fe toxicity in submerged (paddy) rice soils, rice yields get harshly reduced. The problem of iron toxicity in rice paddies is common in the soils of north-east region Odisha and Kerala. Generally, iron chlorosis in plants, also called lime-induced chlorosis, is observed in upland crops primarily aerobic rice, sorghum, groundnut, sugarcane, chickpea grown in Fe-deficient highly calcareous soils, compact soil with limited aeration, and soils with low active Fe and high P and bicarbonate content. By and large, foliar application of 10–12 kg FeSO<sub>4</sub> ha<sup>-1</sup> or soil application of 50–150 kg ha<sup>-1</sup> FeSO<sub>4</sub> has been fruitful in easing deficiency of Fe in most of the crops (Takkar et al. 1989; Singh and Dayal 1992). On average, crop responses to soil and foliar application of Fe range from 0.45 to 0.89 t ha<sup>-1</sup> in cereals, 0.3 to 0.68 t ha<sup>-1</sup> in millets, 0.34 to 0.58 t ha<sup>-1</sup> in pulses, 0.16 to 0.55 t ha<sup>-1</sup> in oilseed crops, 0.20 to 1.53 t ha<sup>-1</sup> in vegetables and 0.39 to 9.68 t ha<sup>-1</sup> in cash and other plants (Takkar et al. 1989, Singh 2008; Shukla et al. 2012). The rates of soil application of Fe are unusually high, because of the rapid pace of oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>, and henceforth are uneconomical. Correspondingly, the farmers are discouraged from using Fe chelates due to its high cost. Foliar spray of FeSO<sub>4</sub> is recommended for

horticultural crops. For correcting Fe chlorosis in tomato, chilli, groundnut and sugarcane foliar sprays of  $\text{FeSO}_4$  are more effective and efficient than soil application.

## *Copper*

In Indian soils, copper deficiency is almost negligible. In Indian soils, available Cu varies between 0.01 and 136.4 mg  $\text{kg}^{-1}$  with an average of 2.05 mg Cu  $\text{kg}^{-1}$  (Shukla and Tiwari 2016). The country has about 2% severe deficiency, 2% deficiency and 3% latent deficiency of Cu, respectively. On the other hand, the area with an adequate level is about 11%, 14% high and 68% very high level of available Cu. pH, SOC,  $\text{CaCO}_3$  and clay content are the main factors that influence copper availability in soils. A rise in organic matter and clay content increases copper availability, while an increase in pH and  $\text{CaCO}_3$  content of the soil decreases its availability (Katyral and Agarwala 1982; Rattan et al. 1999). Soils that have copper deficiency are sandy, calcareous, eluviated and organic matter-rich soils. The  $\text{CaCO}_3$ -bound Cu fraction in the soil releases with the addition of organic matter and organic fraction it rebinds. Thus it enhances the availability of Cu in calcareous and sandy loam soils. The Cu availability in the hill (Alfisols), Histosols (organic peat soils) of Kerala and Mollisols (submontane soils) of the Himalayan Tarai zone of Uttarakhand and Himachal Pradesh is reduced by the presence of excess organic matter (Singh 2008; Patel et al. 2009; Behera et al. 2012). Reduced yields and poor crop quality are the results of the crops grown on severe Cu-deficient soils. Cu deficiency in citrus results in low juice content, abnormally shaped fruits with a rough exterior, and weak flavour and in apples small fruits of poor quality are found. In cereals, it includes reduced viability of seeds and shrivelled grains. In sugar beet, higher concentrations of nitrogenous compounds give compressed juice purity. Chlorotic leaves, lesser size, discolouration of edible portions and apparent wilt in gin vegetables lead to fewer commercial opportunities.

A typical instance of severe Cu deficiency in the wheat crop grown on organic fertile calcareous soils (a rendzina soil) of north western France exhibited characteristic symptoms; that is, plants were shorter with dark pigmentation (melanism) in the ear and had an inferior density of ears per unit area. For instance, in north western France, wheat grown on severe Cu-deficient rendzina soil (organic fertile calcareous soils) showed specific symptoms, like shorter height with dark pigmentation (melanism) in the ear and decreased density of ears (spikes) per unit area. Generally, crop responses to Cu application in cereals, millets, oilseeds, onion and sugarcane ranged from trace to 1.78 t  $\text{ha}^{-1}$ , 0.20 to 0.30 t  $\text{ha}^{-1}$ , trace to 0.80 t  $\text{ha}^{-1}$ , 4.43 to 6.18 t  $\text{ha}^{-1}$  and 0.30 to 0.50 t  $\text{ha}^{-1}$ , respectively (Takkar et al. 1989). In Typic Ustipsamments, foliar and soil application of Cu in soybean wheat cropping system proves to be useful in correcting its deficiency and use of 5.0 kg Cu  $\text{ha}^{-1}$  in the soil gave a significant response of 0.2 t  $\text{ha}^{-1}$  to the first crop. An increase of soybean grain yield from 2.18 to 2.35 t  $\text{ha}^{-1}$  was found with the foliar spray of 0.2%  $\text{CuSO}_4$  solution.

## ***Manganese***

In Indian soils, available Mn content ranges between 0.01 and 445.0 mg kg<sup>-1</sup>, with a mean of 21.8 mg kg<sup>-1</sup> (Shukla et al. 2014). The country suffers from about 1% acute deficiency, 6% deficiency and 10% latent deficiency of Mn. A very high level of available Mn has been found in 60% of the region. Mn deficiency increased from 3.0% in 1967–1987 to 7.1% in 2011–2017. Rice-wheat-growing areas of Punjab, Haryana and western Uttar Pradesh witnessed an emerging Mn deficiency due to its increase. The occurrence of Mn-deficiency problems is common in heavily weathered tropical and sandy soils (low total contents of Mn), limed acid soils or calcareous soils, mineral soils with pH values of 6.5 or above, organic-rich soils with a pH above 6 and peaty soils. In India, an increase of Mn deficiency has grown very fast mainly in sandy or loamy sand soils of Punjab and Haryana under rice-wheat cropping systems. Like Fe, crops grown at shallow moisture content have a high risk of incidence and severity of Mn deficiency. The mobility of Mn is more in waterlogged soil, and rice grown under such soil conditions often manifests Mn toxicity. The appearance of greenish-grey specks at the lower base of younger leaves in monocots, which finally become yellowish to yellow-orange, is due to the deficiency of Mn. It often results in the development of marsh spots (necrotic areas) on the cotyledon of legumes. In sugarcane, pahala blight is the name given to Mn deficiency. There was a marked response in crops on Mn-deficient soils with the application of soil and foliar of Mn; responses ranged from traces to 3.78 t ha<sup>-1</sup> for wheat, trails to 1.78 t ha<sup>-1</sup> for rice, 0.03 to 1.02 t ha<sup>-1</sup> for soybean, 0.40 to 0.70 t ha<sup>-1</sup> for sunflower, 3.63 to 4.30 t ha<sup>-1</sup> for onion and 0.30 to 0.80 t ha<sup>-1</sup> for tomato (Takkar and Nayyar 1981). Owing to oxidation of soil-applied Mn, it is challenging to manage severe Mn deficiency with soil application, especially in high-pH soil. An instant effective measure to combat Mn deficiency in wheat and berseem is the foliar application of MnSO<sub>4</sub>·H<sub>2</sub>O. In comparison to its soil application with B:C ratio of 2.1, the economic benefit of foliar application of Mn to wheat was twofold with B:C ratio of 4.5.

## ***Boron***

In India, B deficiency is next to Zn deficiency, and the total B ranges from 2.6 to 630 mg kg<sup>-1</sup> (Takkar 2011), and available (hot water soluble, HWS) B ranges from 0.04 to 250 mg B kg<sup>-1</sup>, with an average of 21.9 mg kg<sup>-1</sup> soil (Shukla and Tiwari 2016). In the country, about 4%, 19% and 21% of the area faces acute deficiency, deficiency and latent deficiency of B, respectively. The areas that has adequate, high and very high available B status are about 12%, 11% and 32%, respectively. Soil pH, CaCO<sub>3</sub> and organic matter contents govern the availability of B in plants. Besides total B content in the soil, the other factors that have a substantial impact on B availability are its interactions with other nutrients, variety or plant type and environmental factors. In some regions of Indian soils, boron deficiency is a harsh

problem in agricultural productivity. Generally, in sandy leached soils, highly calcareous soils, limed acid soils or lateritic or reclaimed yellow soils B deficiency adversely influences crop productivity.

In the eastern region of the country, the extent of B deficiency is more significant due to its excessive leaching in sandy loam soils because of high precipitation (Takkar 1996; Shukla and Behera 2012; Shukla and Tiwari 2016). The growing tips and younger leaves with stunted plant growth are the first symptoms of boron deficiency. The production of hollow heart in peanut, black heart in beet, distorted and lumpy fruit in papaya and hollow pith in cabbage and cauliflower are its outcomes. To sustain the high productivity of cereals, pulses, oilseeds and cash crops in B-deficient soils of Assam, Bihar, Orissa, Punjab and West Bengal soil application of 0.5–2.5 kg B ha<sup>-1</sup> gave a response ranging from 108 to 684 kg grain kg<sup>-1</sup> of B or 10 to 44% over NPK (Takkar et al. 1989; Sakal and Singh 1995; Shukla et al. 2012).

## *Molybdenum*

In India, the least studied micronutrient is molybdenum. In Indian soils total Mo ranges from 0.1 to 12 mg kg<sup>-1</sup> and ammonium oxalate (pH 3.3)-extracted available Mo varies from traces to 2.8 mg kg<sup>-1</sup> (Behera et al. 2011, 2014). Soil colloids and minerals (at pH <6.0) strongly adsorb the molybdate anions (MoO<sub>4</sub><sup>2-</sup>) and due to the formation of secondary minerals, it gets trapped sometimes. Mo may also be fixed firmly by the hydrous aluminium silicates. Soils developed from parent material like shale and granite are high in Mo concentrations, whereas low Mo contents characterise those soils formed from sandstone, basalt and limestone. Mo deficiency is common in some acidic, sandy and leached soil; most of the other soils are satisfactory in Mo content. In calcareous alkaline soils of semi-arid and arid, reports on Mo deficiency are hardly found as it contains relatively high Mo contents, but molybdenum deficiency has been observed in some parts of Maharashtra, and acidic soils of Odisha, West Bengal, Kerala and Himachal Pradesh. Crops like legumes, crucifer vegetables and oilseed grew on acid, and severely leached soils are severely affected by molybdenum deficiencies. Stunted plant growth and restricted flower formation are results of molybdenum deficiency, and it also causes the whiptail disease of cauliflower. Takkar et al. (1989) stated the response of crops like rice, wheat, soybean, green gram, sorghum, pearl millet, groundnut and peas to Mo application.

Response to applied Mo ranged from 0.24 to 1.01 t ha<sup>-1</sup> in rice, 0 to 0.47 t ha<sup>-1</sup> in wheat, 0.08 to 0.19 t ha<sup>-1</sup> in soybean and 0.10 to 0.40 t ha<sup>-1</sup> in green gram. In acid soil of Andhra Pradesh, the seed yields of maize and niger increased significantly as a result of soil application of 1.0 kg sodium molybdate ha<sup>-1</sup> or foliar application of 0.1% solution. In different soils, potato soaking before sowing in ammonium molybdate solution @ 0.01% for 24 h improved the tuber yield by 1.3–2.9 t ha<sup>-1</sup>

(5–8%). Yield, quality and oil content improve with the treatment of soybean seed @ 3.00 g sodium molybdate  $\text{kg}^{-1}$  (Nayyar et al. 1990).

### *Nickel*

In India, the total Ni content in the soil is between 20 and 1000  $\text{mg kg}^{-1}$ , whereas available Ni status ranges between 0.2 and 0.8  $\text{mg kg}^{-1}$  soils (Singh 2009). Reports for its deficiency in Indian soils have not yet been disclosed. It is an essential constituent of urease enzyme, required for the breakdown of urea to liberate the nitrogen into a usable form for plants. Nickel is necessary for germination of seeds and growth, and also for the engagement of iron. The production of dwarf foliage and reddish pigmentation in young leaves is associated with nickel deficiency in plants. In humans, Ni is a vital element for the heart muscle, liver and kidneys for their normal functions. On the other hand, it is involved in the metabolism of the hormone, lipid and membrane. The general requirement for Ni is met from the natural sources which are found in grains, fruits and vegetables which are readily available around.

### *Cobalt*

Depending upon the parent rock and climate of the region, the contented total Co differs extensively from traces to 277  $\text{mg kg}^{-1}$ . Available Co content varies from 0.06 to 2.1  $\text{mg kg}^{-1}$  soil and is noticeably affected by factors such as texture, organic matter content, pH,  $\text{CaCO}_3$ , soil-crop management systems and practices. In plant nutrition, the total amount of cobalt content alone is not of any importance. Nonetheless, there are reports of Co deficiency from soils with less than 0.5–5  $\text{mg kg}^{-1}$  of the entire cobalt in many cases. The available Co (extracted by 2.5% acetic acid) content is generally less than 0.25  $\text{mg kg}^{-1}$  in Co-deficient soils. Cobalt deficiency in the soil leads to its scarcity in plants and affects an animal's productivity. Soils that are high in  $\text{MnO}_2$  content have low availability of Co due to the higher affinity of  $\text{MnO}_2$  to Co (Takkar 2015). Cobalt helps in nodulation and growth of legume and brassica crops. Seed treatment with cobalt-containing salts @ 2–3  $\text{g kg}^{-1}$  seed helps increase the seed yield.

### *Vanadium*

Average vanadium (V) content is 110  $\text{mg kg}^{-1}$  in the earth's crust. The geological parent material determines the vanadium content in soils and waters (Hope 1997). It is concentrated in shales (100–130  $\text{mg kg}^{-1}$ ) and mafic rocks (basalt

200–250 mg kg<sup>-1</sup>) and V content is lowest in limestone and dolomite (10–45 mg kg<sup>-1</sup>). The soil V content is enhanced with the anthropogenic emissions, mostly from the burning of fossil fuels. Anthropological activities such as the addition of phosphate fertilisers, soil amendments and road-fill materials derived from steel slag add vanadium inputs to soils (Molina et al. 2009). Plants absorb vanadium as vanadate ion (Ullrich-Eberius et al. 1989) and can hinder hydrogen (H<sup>+</sup>) translocation ATPase in the plasma membrane, which plays an essential role in the uptake of the nutrient element by plant cells.

## *Selenium*

In soil selenium (Se) content varies from traces to 8000 mg kg<sup>-1</sup> (Singh 2009). Most of the cultivated crops do not require selenium, and it obtains maximum yield on soils characterised by traces of Se. In soils, Se exists as selenate and selenite forms; selenate is less soluble than the selenite forms and also less available to plants. Selenite forms predominate in humid regions, and it occurs as selenate form in the arid areas. In the fodders of sorghum, pearl millet, oats, cluster bean, berseem and mustard, the selenium content varies from traces to 1.5 mg kg<sup>-1</sup>, and in natural grasses and weeds, it ranged between traces and 0.54 mg kg<sup>-1</sup>. In one study, Se content in different fodders was informed as ranging from 0.9 to 6.7 mg kg<sup>-1</sup>.

For instance, in rice straw and husk, it was more than 0.5 mg kg<sup>-1</sup> and might have a toxic effect. In fodders grown in Haryana, soils have high Se content of 1.0–9.5 mg kg<sup>-1</sup> (Shukla et al. 2018).

Toxicity in the soil-plant-animal-human food chain in alkali soil areas is due to the high Se accumulation in irrigation water where after the rainy season the Se of subsurface soils is brought out through capillary rise and evapotranspiration. About 20 years back in some villages of Hoshiarpur district of Punjab irrigation of rice-wheat system with underground water which contained nearly nine times more Se (17.43 µg L<sup>-1</sup>) than that in the non-seleniferous areas (1.91 µg L<sup>-1</sup>) caused Se toxicity (snow-white chlorosis) (Takkur and Dhillon 1984). The Se content of the seleniferous regions is about 4–5 times higher than that in non-seleniferous areas. Surface and subsurface soils of seleniferous areas contain 2.12 and 1.6 mg Se kg<sup>-1</sup>, respectively.

In 45–60-day-old wheat plants, the Se content varied from 1.08 to 2.70 mg kg<sup>-1</sup> with an average of 1.91 mg kg<sup>-1</sup> and exhibited visual symptoms of Se toxicity. The Se content was 3.6 times higher than the lush green typical plants. Supplementation of Se in low-Se soil would increase Se contents of food, feed and fodder. The plant species and crop cultivars of the forages/pastures which are inefficient in Se utilisation should be preferred over efficient varieties for high-Se soils. In contrast, productive cultivars are preferred for the Se-deficient soil. Such plant species and cultivars should be identified and/or developed for cultivation in seleniferous-endemic areas.

## Management of Micronutrient Deficiencies

Micronutrient deficiencies in the soil affect the proper growth and development of plants. Hence, nutrient stress is to be managed effectively to assure food and nutritional security. To deal with the situation treatment of soil with an appropriate nutrient carrier is a crucial strategy. Sources of the nutrient may be natural or human-made. Natural manures work as soil-conditioning agents. But the inconsistent supply of micronutrients reduces their role to be a complement rather than a substitute for synthesised chemicals. Consistent soil fertility and adequate supply of organic manures are to be assured. However, it depends on the kind of extent and intensity of soil fertility decline because organic approaches alone may not and cannot cover all the deficiencies. It is beyond questions that natural resources always play a vital role in sustaining soil health in all respect to fill the gap created by the high nutrient mining happening as an aftermath of high-yield industrial agriculture.

Accordingly, consumption of micronutrient fertiliser scaled higher steadily and consistently, based on the information on soil test values which indicate the dominance of Zn deficiency. In Indian soils, maximum attention on the management of micronutrient deficiencies concentrates on this micronutrient. Approximately 80% of the micronutrient fertiliser use is constituted of  $\text{ZnSO}_4$ . Zinc sulphate is the prime Zn fertiliser. Zn fertiliser is available in two forms, i.e. heptahydrate  $\text{ZnSO}_4$  (21%) and monohydrate  $\text{ZnSO}_4$  (33%). Between the two forms, heptahydrate  $\text{ZnSO}_4$  dominates (70% of total Zn use). Zn carrier is preferable because it is (i) indigenously manufactured and available across the country, (ii) economically favourable and (iii) easy to control for soil application and liquid sprays, and (iv) above all agronomically its performance is more than chelates (Zn-EDTA). On account of the incidence of multi-micronutrient deficiencies, Zn is also supplied through multi-micronutrient mixture-customised fertilisers. FAI (2016–2017) enlists the use of some 27 customised fertilisers and 70 fertiliser mixtures containing two or more micronutrients. In the state of Tamil Nadu 14 multi-micronutrient mixtures are in use. Almost 10% of the Indian soil is plagued with multiple nutrient deficiencies, yet there is hardly any systematic data on the location-specific multi-micronutrient content. There is no information available on site-specific production of customised fertilisers, which are prepared to match local nutrient deficiencies.

Correlated to soil test values, Zn deficiency management practices are outlined as follows (Katyal and Randhawa 1983; Katyal and Agarwala 1982; Shukla et al. 2017; Rattan 2017:

- The quantity to be applied varies between 5 kg (light-textured soils) and 10 kg (heavy-textured soils)  $\text{Zn ha}^{-1}$  (25–50 kg heptahydrate zinc sulphate, 21% Zn) which may cost approximately from Rs. 500–1000. As a higher dose of monohydrate zinc sulphate, 35% Zn, is used to manage Zn deficiency, it requires adjustment of the quantity accordingly.



- Zinc sulphate is applied before sowing following the broadcast method of incorporation; band placement produces higher use efficiency; use efficiency otherwise hardly exceeds 5%.
- Root dipping in ZnO suspension (made from 1.5 kg ZnO) is comparable in agronomic efficiency to soil application; developments of nano-carriers offer unique possibilities, but the progress has to pass an economic test.
- Deficiency in the growing crops is contained by foliar sprays (0.5% zinc sulphate); the number of courses depends on the existence of symptoms; spray is applied at an emergent situation and is no replacement for soil application, even if it is essential to increase Zn content of grain.
- One soil application lasts at least for two seasons, but in the case of flooded rice and irrigated upland maize repeat application is required for every season; spray treatment needs to be followed up with every episode of Zn deficiency.
- Use of ZnSO<sub>4</sub> produces a significant response; additional yield attributable to Zn treatment was measured as more than 200 kg<sup>-1</sup> in one out of two experiments (numbering 4144) conducted in the farmer's field (Katyal 1985); in 25% of the experiments yield increase was 500 kg ha<sup>-1</sup>.
- Since the benefit-to-cost ratio has always been higher than 1, treatment with ZnSO<sub>4</sub> is economically affordable; since toxic build-up due to repeat treatment is almost precluded, it is financially safer also.
- The use of ZnSO<sub>4</sub> has tremendously increased from a few hundred tonnes in the 1970s to 180,000 tonnes in 2016–2017 (FAI 2016–2017). Out of the total Zn consumed in India, 40% use is concentrated in North Indian states, e.g. Punjab and Haryana. However, its use in the southern states, e.g. Telangana and Andhra Pradesh, seems to be far below the crop needs.

Generally, Indian soils are applied with only 1.2 kg zinc sulphate ha<sup>-1</sup>. Projected ZnSO<sub>4</sub> requirements worked out by various investigators for 2025 range between 0.3 and 0.5 Mt (Rattan et al. 1997), and 1.5 Mt (Takkar et al. 1997) is considered as insufficient. In anticipation of the demand, there is a necessity to utilise ZnSO<sub>4</sub> as efficiently as practicable. Savings in use are necessary (i) because India imports about 100,000 t Zn annually and (ii) because of 'peak zinc' mode, which means global production of Zn has reached its maximum point and extraction will reach a stage of terminal decline. It is estimated that Zn reserves will last for not more than 20 years. Besides, increasing use efficiency, harnessing natural sources of Zn (organic manures) and development of Zn-efficient varieties hold significant promise and need to be explored on priority.

In view of the recent research findings (brief by Shukla et al. 2018) B deficiency is going to assume the proportion that will be next to Zn. Attempts are being made to suggest economic sources and efficient ways of managing them. Borax or sodium tetraborate (B 10.5%) and disodium octaborate tetrahydrate (Na<sub>2</sub>B<sub>3</sub>O<sub>13</sub>·4H<sub>2</sub>O), solubor (21%), are the chief sources manufactured in India. Boric acid (H<sub>3</sub>BO<sub>3</sub>) is another B carrier like solubor that is used for foliar treatment. Borax is usually applied as soil dressing. To leach sandy soils less soluble sources (e.g. B frits) may be preferred. Boron doses require to be calibrated carefully because of the known



marginal differences between deficiency and toxicity. The optimum treatment of B for soil application varies between 0.5 kg B ha<sup>-1</sup> for less responsive crops like cereals and 2 kg ha<sup>-1</sup> for more responsive crops like fruits, vegetables and oilseeds. As for foliar treatment, 0.25% of boric acid may be sprayed 2–3 times to control deficiency. Approximately 10% of the total B fertilisers used in India (21,000 t) is imported.

Manganese deficiency is another nutritional constraint. As the manganese deficiency is of sporadic occurrence, region- and crop-specific management strategies ought to be delineated. For handling suboptimal levels of Mn in crops, a foliar spray containing 0.5% manganese sulphate (26% Mn) may be used 2–3 times repeatedly depending upon appropriate symptoms. The total consumption of manganese sulphate (4267 t during 2016–2017) is met through imports (10,000 t in 2016–2017) (FAI 2016–2017).

Iron deficiency, like that of Mn, which tends to get fixed in the soil, is managed by 0.5% iron sulphate solution (20% Fe). However, unlike manganese sulphate, the entire quantity consumed in the country (21,000 t) is produced indigenously.

Deficiency of Cu is rare in Indian soil and crops. If at all there is any incidence of lack of Cu, it is managed by copper sulphate application to soil (5 kg Cu ha<sup>-1</sup>) or by foliar spray (0.2% copper sulphate solution). Soil application, as expected, will produce residual effects; hence treatment of some crops is not undertaken. During the year 2016–2017 (FAI, 2016–2017) 1600 t of copper sulphate was used in the country.

Several methods are used to control molybdenum deficiency of acid soils and leguminous plants. As the requirement of Mo is only for a few grains, it is necessary to tune techniques for application of small amounts of Mo. Soluble sources like ammonium molybdate (52% Mo), which is an FCO-approved source of Mo in India, are not suitable for soil dressing because of the vulnerability of leaching. Application of foliar spray @ 0.1–0.3% ammonium molybdate solution or potato tuber soaking in 0.01% ammonium molybdate solution for 24 h before sowing and treatment of soybean with 3.0 g kg<sup>-1</sup> seeds are effective methods for controlling Mo deficiency. In India, around 100 t Mo was used during 2015–2016, and 90 t was used during the year 2016–2017 (FAI, 2016–2017).

## Conclusion

Micronutrients are having a greater impact on the plant as well as soil; a small amount of their deficiency can hamper the quality of agriculture product a lot. Their deficiency affects not only the quality but also shelf life of the product. The deficiency in soil also slows down the metabolic activity of several enzymes and biochemical activity of soil. Therefore, precise use of micronutrient should be done for a greater impact. Their micro quantity can show a macro effect after precise management.

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