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REVIEW

Micronutrients and their diverse role in agricultural crops: advances and future prospective

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Abstract In plant sciences, the prodigious significance of micronutrient is unavoidable since plant relies primarily on micronutrient as it has profound influence on array of plant activities. Although micronutrients are abundantly present in the soil but plants usually acquire them in relatively trace amounts; hence, regarded as tracer element. B, Cu, Fe, Mn, Zn are such micronutrients required in minute amounts by plants but inexorably play an eminent role in plant growth and development. Plant metabolism, nutrient regulation, reproductive growth, chlorophyll synthesis, production of carbohydrates, fruit and seed development, etc., are such effective functions performed by micronutrients. These tracer elements when present at adequate level, elevate the healthy growth in plant physiological, biochemical and metabolic characteristics while their deficiency promotes abnormal growth in plants. Prevalence of micronutrient deficiency has become more common in recent years and the rate of their reduction has further been increased by the perpetual demands of modern crop cultivars, high soil erosion, etc. On the basis of present existing condition, it is not difficult to conclude that, the regular increment of micronutrient deficiency will be mostly responsible for the remarkable degradation in substantiality of agricultural crops somewhere in near future and so that this issue has now been the subject of intensified research among the breeder, ingenuities and expertise of science. These micronutrients can also be proven toxic when present at accelerated concentrations and such toxicity level endangers the plant growth. Taking this into consideration, the current review unfolds the phenomenal participation of micronutrients in plant sciences and gives a brief overview of the current understanding of main features concerning several micronutrient acquisitions in agricultural crop plants.

Keywords Micronutrients · Agriculture · Deficiency · Toxicity · Food security

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Introduction

In the last few decades being widely cited, the term food security has raised the major concern worldwide, among the scientists, researchers, agronomists and policy makers. Owing to anticipated changes in climatic conditions and the perpetually looming anthropogenic activities, recent years have witnessed much focus on food security and now the countries from all over the world are continually paying much more attention towards the security of food and thus working under the common mission of global food security (FAOUNS 2000; Devereux and Maxwell 2001; CFS 2005; Clay 2002; Fresco 2009; Floros et al. 2010). Further, in the wake of accumulated evidence, it becomes increasingly important to broach here that food security is not only meant for securing the quantity of food which was consumed by global population but is also concerned with quality and variety of food (Maxwell 1996; Hamm and Bellows 2003; Faye et al. 2011; Chappell et al. 2013).

Nutritional insecurity, due to alarming micronutrient deficiencies has substantially contributed to the global burden of disease resulting in devastating health consequences as the people face extreme hunger, which later results into life threatening illness popularly known malnutrition or undernutrition (Flores and Gillespie 2001; Pinstrup-Andersen and Rosegrant 2001; Barrett 2002; Thompson et al. 2012). Some recent reports on micronutrient status clearly suggested that every year more than 10 million people die due to the vulnerable effects of micronutrients while micronutrient deficiency also reduces the immunological capacity of plant and animals that enable them to resist against several chronic diseases (Flores and Gillespie 2001; Pinstrup-Andersen and Rosegrant 2001; Barrett 2002; Thompson et al. 2012). Conventionally, from last many years, nutrition safety issue has been taken as the most significant realm of health professionals but still more focus is required to meet the food security challenges (Parnell et al. 2001; Floros et al. 2010; Chappell and LaValle 2011). It is reported that agri-food chain has always played a vital role to provide the sufficient nutrients either to plants or to human beings (Soil Association 2000; Thrupp 2000; Heaton 2001; Williams 2002; Maathuis and Diatloff 2013); therefore, agri-food interaction is also another venture for the food scientists. With agriculture being the prime source of nutrition in India, several government policies in this respect has been introduced to draw full attention towards higher agricultural yield and also to understand the food security goals, including nutrition security and its importance in plant and human life (Hänsch and Mendel 2009; White and Brown 2010; Marschner 2012).

From the above discussion, an integrated solution for securing sufficient and healthy food for all could preferentially be drawn as a sustainable opportunity to reduce hidden hunger because micronutrient plays an important role in plant growth, their development and more specifically it also involved in multitudinous metabolic processes (Singh et al. 2011; Marschner 2012; Tripathi et al. 2012a, b, c; 2014a, b; Kumar et al. 2014a, b). Mineral nutrients protect the plants from various hurdles and maximally perform irreplaceable role during the entire life cycle of plants (Singh et al. 2011; Tripathi et al. 2012a, b, c; Kumar et al. 2015; Liang et al. 2013; Tripathi et al. 2014a, b). Minerals nutrients that are found in the soil, water, air and plants were classified previously by imminent plant scientists on the basis of their utility and requirement (Marschner 2012; Sperotto et al. 2014). They discriminate it in two different classes, i.e., macronutrients and micronutrients, further micronutrients are those nutrients which are required by plant in lesser amount whilst macronutrients is needed in relatively larger amount to complete the life cycle of plants (Tripathi et al. 2011, 2012a, b, c, 2014a, b; 2015; Chauhan et al. 2011; Singh et al. 2011; Marschner 2012).

Owing to its increased necessity in intensive cropping system for attaining higher yield productivity, in recent years, micronutrients gained profound significance (Dell et al. 2006; Liu et al. 2015). Moreover, regarding the importance and the role of micronutrients in crop production, promising changes have been found in modern scenario of agriculture that also deals with the level of micronutrients in the main staple food crops as well as diets of humans and animals.

Micronutrients i.e. boron (B), copper (Cu), chlorine (Cl), iron (Fe), zinc (Zn), manganese (Mn), molybdenum (Mo) are regarded as essential plant nutrients taken up and consumed by the plants in relatively lesser amount. These micronutrients play an eminent role in plant growth, development and plant metabolism. However, their deficiencies may induce several diseases in plants and later, can reduce the quality as well as quantity of food. Thus investigation related to the role of micronutrients in plants has resulted in breathtaking curiosity and is a matter of a huge significance among the researchers. It has been well documented that micronutrients play multifarious roles and their adequate supply increases the growth and yield of plants, thereby protecting the plants from adverse effects of various biotic and abiotic stresses (Fig. 1). Therefore, in this current review, we have summarized the overall benefits and significance of some micronutrients in plants.

Boron (B)

Soil basically serves as the unique/prime source of trace elements for vascular plants (Fig. 2). Among them, boron has been recognized as one of the most essential, ubiquitously distributed microelements of group III of the long form of periodic table. Boron show marked difference from the other members of its group because it is a highly electronegative element and exhibits intermediary properties between metals and non-metals (Bolaños et al. 2004; Herrera-Rodríguez et al. 2010). Though its average concentration inside the soil solution is 10 ppm, but the most preferable range for which plants encounter neither deficiency nor toxicity is very low i.e., 0.3–1 ppm (Lee and Aronoff 1967; Shelp 1993; Blevins and Lukaszewski 1998). Though boron has ubiquitous distribution in nature, the important role of boron in making proper growth and productivity is still not well known. Plant acquires boron (B) basically in the form of undissociated/uncharged boric acid (H_3BO) that tends to form borate ester by reacting with apiose residues of two rhamnogalacturonan II (RGII) molecules and the resulting RGII borate dimers further show the cross-linking with pectins of the cell wall thereby

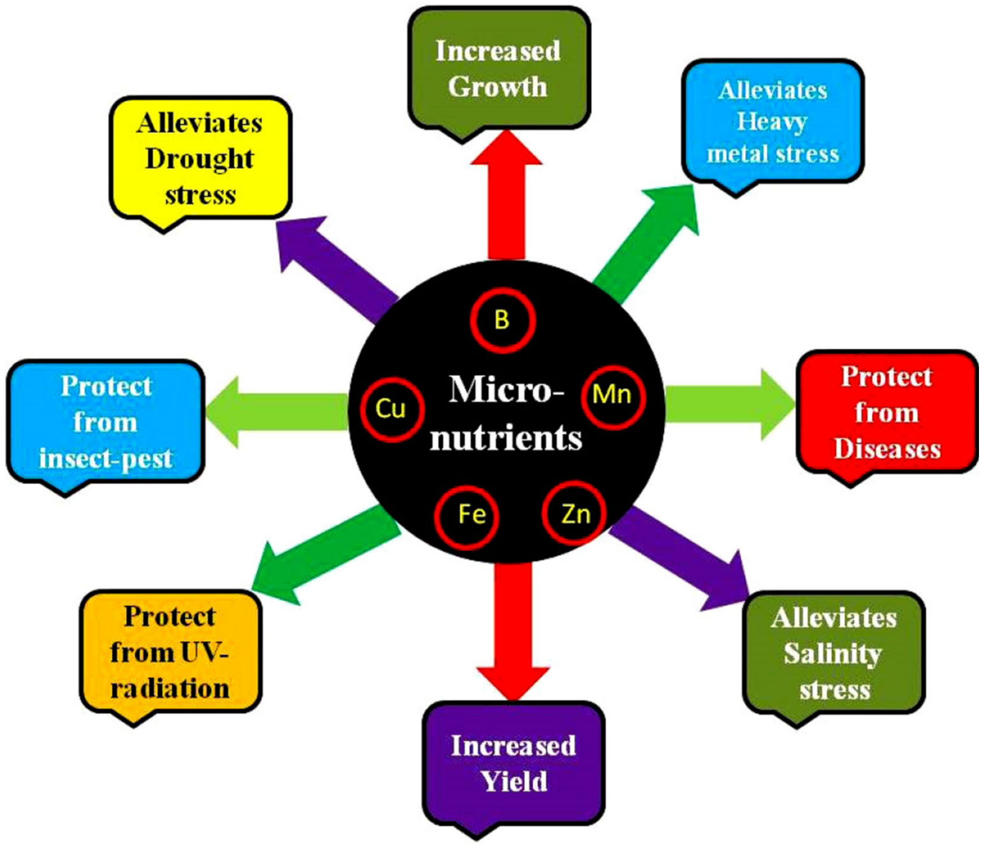

Fig. 1 Response of micronutrients in different abiotic and biotic stresses

initiating the formation of three-dimentional pectic network and thus, maintaining structural integrity of the cell wall (Kobayashi et al. 1996; Camacho-Cristóbal et al. 2008; Beato et al. 2011).

Firstly, Warington (1923) recognized boron (B), as the essential microelement and also established its importance in improving the optimal growth of plant cell. In the beginning of the twentieth century, the necessity of boron was first considered and as the time passed boron has been declared as the critically essential micronutrient by a number of investigators. It has also been well documented that smaller concentration of boron could facilitate the proper growth and development of the higher plant and their deficiency would lead to the impairment of metabolic and physiological processes (Nable et al. 1997; Blevins and Lukaszewski 1998; Bolaños et al. 2004; Reid 2007; Camacho-Cristóbal et al. 2008).

In addition to playing incredible role in the biosynthesis of cell wall and lignifications, boron is also involved significantly in a variety of physiological and biological processes such as tissue differentiation, vegetative growth, phenolic metabolism, and membrane integrity, etc. (Table 1). Apart from this, the bioavailability of boron is also necessary for nitrogen fixation and nitrate assimilation (Camacho-Cristóbal and González-Fontes 1999; Matas et al. 2009; Reguera et al. 2010; Beato et al. 2010), for oxidative stress (Pfeffer et al. 1998; Kobayashi et al. 2004) and root development (Dugger 1973; Martín-Rejano et al. 2011). However, its presence beyond the permissible limit hampers plant growth and crop productivity worldwide (Stangoulis and Reid 2002; Reid et al. 2004). Boron is an essential micronutrient required by the plant for proper growth and development (Miwa et al. 2007) and its deficiency would impose several inimical effects on plants, such as yellowing of the leaf tips, chlorosis and necrotic spot, stunted growth, and inhibition of root and shoot length, greenish-grey spots on fruits (Table 1) (Nable et al. 1997). Therefore, from the above studies and recent findings it can be well said that boron is the sole element and it has been proved beneficial for the proper growth and development of plant only if it is absorbed and accumulated in required amount (Table 1).

Copper (Cu)

The magnificent role of copper (Cu) in the plant world makes it a unique element. Being a transition element, it occupies place in 11th group of periodic table with atomic number of 29 and atomic mass of 63.5. It is considered to be a very

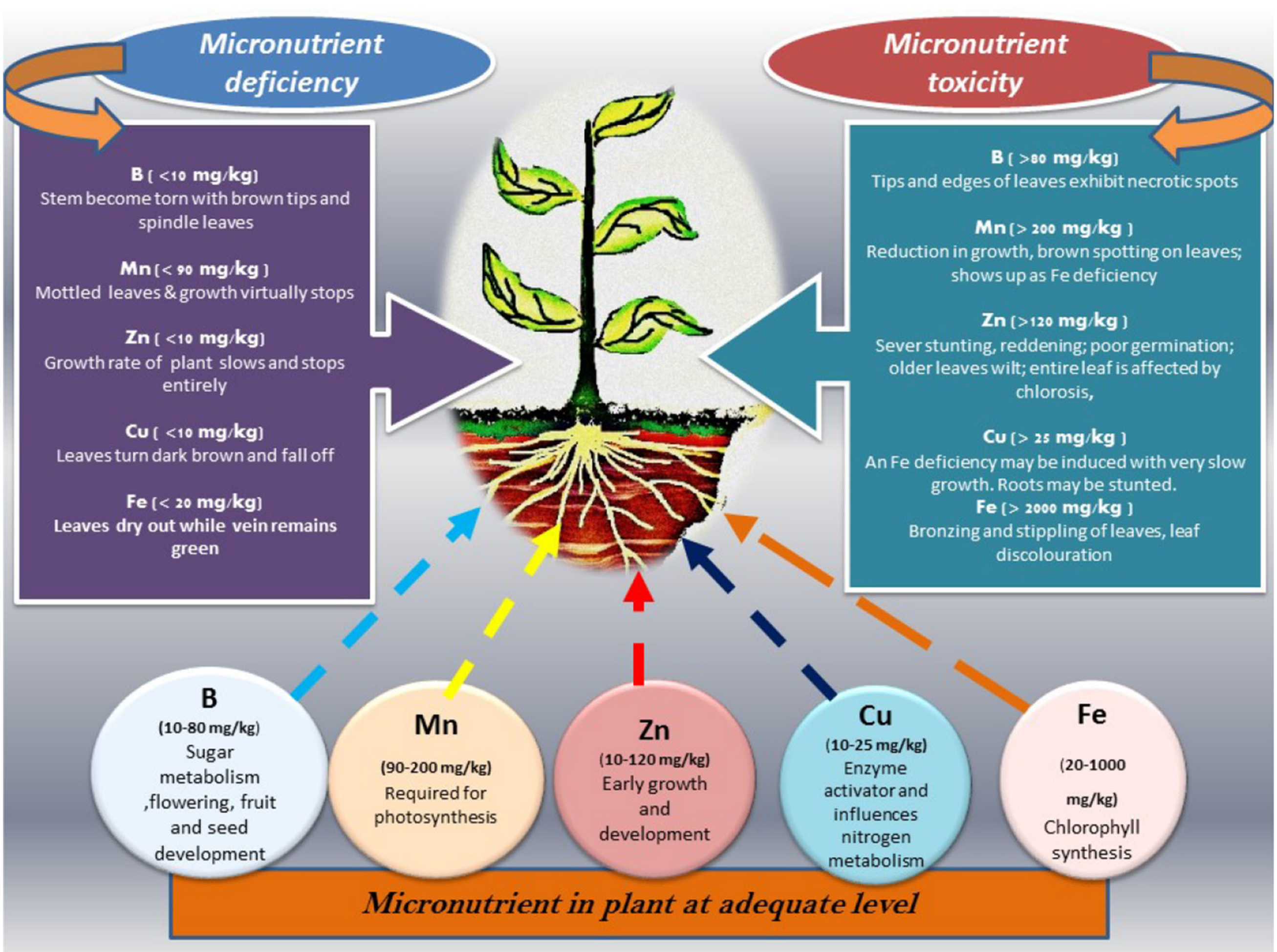

Fig. 2 Adequate level of micronutrients in plants and their diverse response under deficiency and toxicity (Epstein and Bloom 2005; Marschner 2012)

important element for every life being present on the earth due to its several characteristics. Plant growth is highly dependent on the availability of Cu as it plays pivotal role in regulating multiple biochemical reactions in plants (Table 2). Arnon and Stout (1939) declared Cu as an important nutrient for plants in their experiments with tomato.

Being the stable cofactor of various enzymes and proteins, Cu plays an indispensable role in regulating several metabolic and physiological processes of plants (Rehm and Schmitt 2002). Cu actively takes part in many physiological processes in plants as it is present in the form of oxidized Cu (II) and reduced Cu (I) states in histidine and cysteine or methionine, respectively (Yruela 2005; Gratão et al. 2005; Pilon et al. 2006; Burkhead et al. 2009a, b). It participates in oxidation-reduction reaction as an electron carrier in chloroplasts and mitochondria as well as in oxidative stress response (Raven et al. 1999; Yruela 2005; Gratão et al. 2005; Pilon et al. 2006; Krämer and Clemens 2006; Puig et al. 2007; Yruela 2009).

The other effective functions of Cu in the plant world at cellular level can be enlisted as follows:

- Significantly contributes in cell wall metabolism and signal pathway of transcription,
- Cu actively participates in oxidative phosphorylation and iron mobilization,
- Cu plays important role in the biogenesis of molybdenum cofactor and protein trafficking machinery.

As mentioned earlier, Cu acts as a cofactor of enzymes and plays significant role in respiration, photosynthesis, lignifications, phenol metabolism, protein synthesis, regulation of auxins, etc. (Table 2). Some of these Cu-enzymes are cytochrome oxidase, Cu/Zn-superoxide dismutase (Cu/ZnSOD), laccase, ascorbate oxidase, amino oxidase, polyphenol oxidase and plastocyanin (Yruela 2005; Ravet et al. 2011; Rout et al. 2013). Plastocyanin, being the most abundant copper protein promotes electron transport in the thylakoid lumen of chloroplasts (Yruela 2005; Abdel-

Table 1 Integrated response of agricultural crops towards the bioavailability, deficiency and toxicity of certain essential micronutrients influencing its probable sustainability

Microelement boron (B) in variable concentration	Symbol and the form of absorption by plants	Concentration in plant	Response of agricultural crops towards variable concentration of boron in soil solution	References
Boron (in adequate concentration)	(B) H_3BO_3 (Boric acid)	0.3–1 ppm 3–100 μg g^{-1} dry weight	Boron (B) plays an indispensable role in Biosynthesis of cell wall and lignifications Tissue differentiation Phenolic metabolism Vegetative and reproductive growth Membrane integrity Nitrogen fixation and nitrate assimilation	Reguera et al. (2010), Cristóbal et al. (1999), Matas et al. (2009), Beato et al. (2010)
Boron-deficiency		Less than 0.3 ppm and 0.14 mg kg^{-1} and	Boron deficiency in soil results in Stunted growth Inhibition of cell expansion Cracking or rotting of fruits Wilted or curled leaves Water soaked petiole	Silva and Uchida (2000), Dear and Weir (2004)
Boron-toxicity		Above 0.3–1 ppm and 3–100 μg g^{-1} dry weight	Higher concentration of boron in plants would lead to Yellowing of the leaf tips and distorted shoot growth Chlorotic and necrotic patches in the margin/older leaves spots on fruits	Nable et al. (1997), Stangoulis and Reid (2002), Reid et al. (2004), Nable et al. (1997)

Table 2 Cumulative response of agricultural crops towards variable concentration of certain essential micronutrients

Presence of Micronutrients	Symbol and the form of absorption by plants and concentration	Concentration in plant	Response of agricultural crops towards variable concentration of Zinc and Copper in soil solution	References
Adequate amount of Zinc	(Zn) and Zn^{2+}	15–20 mg Zn kg^{-1} DW	Regulates the biological membranes Zinc finger regulates transcription directly through effects on DNA/RNA binding Regulation of chromatin structure RNA metabolism and protein–protein interactions Antioxidative defence enzymes	Sinclair and Krämer (2012), Rengel (2004), Hänsch and Mendel (2009), Broadley et al. (2007)
Deficiency of Zn		Below 15 mg Zn kg^{-1} DW	Impaired stem elongation in tomato Root apex necrosis ('dieback') Interveinal chlorosis ('mottled leaf') Development of reddish-brown or bronze 'bronzing' Internode shortening ('rosetting') Epinasty, inward curling of leaf lamina 'Goblet' leaves) and reductions in leaf size (little leaf)	Tsonev et al. (2012), Alloway (2004a, b), Disante et al. (2010), Skoog (1940)
Toxicity level of Zn		Above 20 mg Zn kg^{-1} DW	Reduced yields and stunted growth Leafy vegetable crops are sensitive to Zn toxicity Soybean and rice has been recognized as Zn sensitivity crops in which Zn toxicity instigate genetic variation Phototoxic concentrations of Zn Increase lipoxygenase activity Lipid peroxidation Enhancing antioxidative activity in plants	Hafeez et al. (2013), Boawn and Rasmussen (1971); Chaney, (1993); Weckx and Clijsters (1997)
Adequate amount of copper	(Cu) and Cu^{1+}, Cu^{2+}	6 µg g^{-1} DW	Cell wall metabolism Electron transport in chloroplast, mitochondria etc. Oxidative phosphorylation and iron mobilization Biogenesis of molybdenum cofactor Nitrogen assimilation, abscisic acid (ABA) biosynthesis	Raven et al. (1999), Yruela (2005), Gratão et al. (2005), Pilon et al. (2006), Krämer and Clemens (2006), Puig et al. (2007), Yruela et al. (2009)
Deficiency of Cu		Below 5 µg g^{-1} DW	Improper growth rate and distortion or whitening (chlorosis) of young leaves Decrease in cell wall formation lignification in several tissues and curling of leaf margins Damages apical meristem, fruit formation, pollen development, the fruit and seed production, wood production Inhibits embryo development, seed viability and plant development	Marschner (1995), Epstein and Bloom (2005), Ruiter (1969), Küpper et al. (2003), Yruela (2005), Burkhead et al. (2009a, b)
Toxicity of Cu		Above 20 µg g^{-1} DW or higher	Chlorosis and necrosis, stunting, and inhibition of root and shoot growth Inhibit enzyme activity and protein function, which later produces highly toxic hydroxyl radicals leading to oxidative damage of plant cell	Gratão et al. (2005), Vinit-Dunand et al. (2002), Küpper et al. (2003), Yruela et al. (2009)

Ghany and Pilon 2008). Apart from this, some copper proteins that are localized in cytoplasm, stroma of chloroplast, peroxisomes and other plant organelles act as the most effective scavenger of reactive oxygen species (Yamasaki et al. 2008; Montes et al. 2014). Furthermore, Rehm and Schmitt (2002) suggested the unique role of Cu in optimal seed production and chlorophyll formation which is necessary for optimal enzyme activity, whereas Bernal et al. (2006) explained the prominent role in thylakoid grana stacking. Additionally, Cu plays important part in nitrogen assimilation, abscisic acid (ABA) biosynthesis. It was also confirmed by Kuper et al. (2004) that Cu ion provisionally occupies the site for Mo lodging in the bound molybdopterin substrate (Burkhead et al. 2009a, b).

Copper (Cu) levels in plants have been reported as 2–50 $\mu g\ g^{-1}$ DW (ppm) considering 6 $\mu g\ g^{-1}$ to be suitable for shoots (Epstein and Bloom 2005). Cu level below 5 $\mu g\ g^{-1}$ DW in vegetative tissues shows its deficiency while above 20 $\mu g\ g^{-1}$ DW, toxicity level of Cu has also been noticed (Marschner 1995; Burkhead et al. 2009a, b). Below 5 $\mu g\ g^{-1}$ of Cu level, several effects of deficiency can be noticed such as improper growth rate, distortion or whitening (chlorosis) of young leaves, decrease in cell wall formation and lignification in several tissues. It causes curling of leaf margins, damages apical meristem and badly hampers fruit formation, pollen development, the fruit and seed production, wood production and inhibits embryo development, seed viability and plant development (Ruiter 1969; Marschner 1995; Küpper et al. 2003; Epstein and Bloom 2005; Yruela 2005; Burkhead et al. 2009a, b).

Copper (Cu) level above 20 $\mu g\ g^{-1}$ DW or higher is proven to be toxic for plant growth and development as it causes inhibition of root and shoot growth, stunting, chlorosis and necrosis (Yruela 2005; Hossain et al. 2012). By binding to sulfhydryl groups in proteins, they inhibit enzyme activity and protein function which later produces highly toxic hydroxyl radicals leading to oxidative damage of plant cell (Yruela 2005; Hossain et al. 2012). Hence from the above it could be well documented that for the healthy growth and development of plants, proper acquisition, assimilation and regulation of Cu should be maintained in different cells and organelles (Yruela 2005). This can only be possible by detailed investigation and advanced study of application of copper in plants to explore the still hidden facts (Table 2).

Iron (Fe)

Besides silicon, oxygen, and aluminium, iron (Fe) is typically regarded as the fourth most abundant and virtually essential microelement on the earth crust. It belongs to the 4th period and group VIII of the long form of periodic table with atomic number 26 and atomic weight of 55.845 which intervene a variety of cellular processes (Puig et al. 2005). Iron is an indispensable microelement and required by plant in a tracer amount for their optimal growth and productivity (Curie and Briat 2003). Gris (1843) firstly recognized it as an essential micronutrient for plant growth and also establishes its relative significance in eliminating the adverse effect of chlorosis in plants (Table 3). Because of low soil solubility its bioavailability to plants cell in inorganic form is limited (Chatterjee et al. 2006). Fe-acquisition in plant occurs by two efficient strategies called Strategy I and Strategy II that operates in different phylogenic groups (Romheld and Marschner 1986; Romheld 1987; Ma and Nomoto 1996; Curie and Briat 2003; Schmidt 2003; Ma 2005; Donnini et al. 2010). Although vascular plant requires relatively a lower concentration of micronutrient for their optimum development, but its slighter deficiency (moderate decrease in micronutrient content) and toxicity (modest increase in micronutrient content) would lead to the impairment of several physiological and metabolic processes and thus, poses great constraint to overall crop productivity (Robinson et al. 1999; Schmidt 2003; Ma 2005; Donnini et al. 2010).

Iron is found to be localized inside the different cellular compartments such as chloroplasts, mitochondria, and vacuoles (Jeong and Guerinot 2009; Adamski et al. 2012; Vigani et al. 2013). It also acts as a redox cofactor in a variety of plant cellular metabolism (Puig et al. 2005). Iron (Fe) is an unavoidable and one of the most prominent constituent of a number of proteins and enzymes that plays important roles in key metabolic processes, including cellular respiration, oxygen transport, lipid metabolism, the tricarboxylic acid (TCA) cycle, gene regulation, synthesis of metabolic intermediates, and DNA biosynthesis as well as making it essential for photosynthesis and chlorophyll biosynthesis (Jeong and Connolly 2009; Adamski et al. 2012). To organize the range of physiological and metabolic function in a convectional manner and to minimize nutritional disorder both the abundance and deficiency of micronutrients should be maintained properly. Therefore, to conquer the ill effects imposed by iron deficiency, plants are equipped with an efficient and promising tolerance strategies that make their survival possible in such stressful conditions and such adapted mechanism of plants facilitates the controlled uptake of iron, the process termed as iron homeostasis (Marschner et al. 1986; Jeong and Guerinot 2009; Ramirez et al. 2009; Wang et al. 2012). However, homeostasis of this metal is essential for plant growth and development, because in several studies it has been demonstrated that it seems to be harmful when present in both excessive and limiting amounts (Sharma 2007; Adamski et al. 2012; Wang et al. 2012). The main and one

Table 3 List of certain essential micronutrients whose variable distribution in nature directly or indirectly influences the sustainability of agricultural crops

Microelement (in variable composition)	Symbol and the form of availability to plants	Concentration in plants	Probable response of agricultural crops	References
Manganese (in appropriate composition)	(Mn) and Mn^{2+}, Mn^{3+}	10–100 µg g^{-1}	Manganese plays a pivotal role in biosynthesis of ATP acyl lipids, proteins and fatty acids. Besides, it also participates in RuBP carboxylase reactions, oxidation-reduction process of photosynthesis, photolysis of water at PSII of photosynthesis. Bioactivation of enzymes	Pfeffer et al. (1986), Ness and Woolhouse (1980), Houtz et al. (1988)
Manganese deficiency		Less than 10–100 µg g^{-1}	Deficiency symptoms: Interveinal chlorosis, in young tissue, appearance of greenish-grey specks at the lower base of monocots, development of brown necrotic spots on the cotyledons of legume plants, premature leaf fall, white–grey spots of leaf and delayed maturity	Schulte and Kelling (1999)
Manganese toxicity		Above 10–100 µg g^{-1}	Toxicity symptoms: Higher concentration of Mn interferes with absorption and utilization of other mineral elements; it also affects the energy metabolism, decreases photosynthetic rates and also causes oxidative stress	Demirevska-Kepova et al. (2004), Clark (1982), Fecht-Christoffers et al. (2003)
Iron (in adequate concentration)	(Fe) and Fe–S–Fe, heme, nonheme, Fe^{2+}, Fe^{3+}	50–150 µg g^{-1}	Iron plays a pivotal role in biosynthesis of chlorophyll, bioactivation of certain enzymes Being a part of protein ferodoxin, Fe is required in sulphate and nitrate reduction, also associated with protein metabolism	Schulte and Kelling (1999), Chatterjee et al. (2006)
Iron (Fe) deficiency		Less than 50–100 µg g^{-1}	Deficiency symptoms: Interveinal chlorosis in young leaves, caused by decreased chlorophyll synthesis, retarded/stunted growth and reduced activity of hill reaction	Goos et al. (2004), Nikolic and Kastori (2000)
Iron (Fe) toxicity		Above 50–100 µg g^{-1}	Toxicity symptoms: Growth inhibition, reduced chlorophyll synthesis, inhibition of photosynthesis	Chatterjee et al. (2006)

of the most visually appeared characteristics features of iron deficiency is chlorosis in young leaves, which is caused by decreased chlorophyll biosynthesis (Sharma 2007; Wang et al. 2012). Several reports have shown that, those structural component that permit iron to act as an efficient catalyst and cofactor in cellular redox reactions, also have tendency to make it a potent toxin on similar structural chemical properties, when it is up taken by plants in excess of cellular needs, and as a consequence lead to overproduction of toxic oxygen radicals (Olaleye et al. 2009; Gill and Tuteja 2010; Sharma et al. 2012). Moreover, elevated iron concentrations lead to enhanced oxidative stress and the excessive production of highly reactive and toxic oxygen species (ROS) (Robello et al. 2007; Sharma et al. 2012).

ROS are extremely destructive in nature because they seriously pose a threat to a variety of cellular components, including lipids, proteins, carbohydrates, and nucleic acids, thus due to their destructive activity leading to express diverse morphological, biochemical, and physiological alterations (Fang et al. 2001; Gill and Tuteja 2010; Sharma et al. 2012). In the case of excess iron, one of the ways to limit progressive oxidative damage is to stop the uncontrolled oxidation caused by antioxidant enzymes. Superoxide dismutase (SOD) plays a protective role against the damaging effects of ROS that requires Fe, Mn, Cu, and Zn as metal cofactors and is present in various cellular compartments, and is involved in the detoxification of $O_2^{\cdot -}$ to H_2O_2 and O_2 (Sinha and Saxena 2006; Sharma et al. 2012). In addition to SOD, CAT and peroxidases have been revealed to participate in this protective mechanism (Costa et al. 2005; Sharma et al. 2012). Accelerated concentration of iron affects the uptake and accumulation of other mineral nutrients such as calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), and of iron itself (Zhang et al. 1999). Hence from the above mentioned fact and recent findings, it can be well said that the role of iron in plant metabolism is indispensible and hence efforts should be made to abolish iron (Fe) stress (deficiency or toxicity) for avoiding several nutritional disorders.

Manganese (Mn)

Manganese (Mn), after iron (Fe) is being recognized as one of the most essential and ubiquitously distributed microelement on the earth crust belonging to the group VII of the extended form of periodic table (Kluwer et al. 2010). In nature, it occurs in a variety of oxidation states 0, II, III, IV, VI but the most preferable range in biological system is II, III and IV (Hebbern et al. 2009). Bioavailability of manganese in nature is basically affected by the redox condition and pH level of the soil (Marschner 1995;

Porter et al. 2004; Millaleo et al. 2010a, b). Though its concentration inside the soil solution is relatively large but plant acquires only a small fraction of it for their optimum growth and development (Kluwer et al. 2010).

Manganese plays a pivotal role not only in variety of metabolic process but is also involved directly or indirectly in stress tolerant mechanism of higher plants by serving as the cofactor of various antioxidative enzymes (Burnell 1988). Furthermore, the role of manganese (Mn) in photosynthesis is indispensable as it participate in photolysis of water at photosystem II that provides electrons needed for the onset of electron transport system (Millaleo et al. 2010a, b).

Kenneth (2012) significantly demonstrated the efficient role of manganese during oxygen evolution step of photosynthesis. Further it has well documented that manganese is significantly involved in the biosynthesis of ATP, acyl lipids, proteins and fatty acids besides, it also participate in RuBP carboxylase reactions (Ness and Woolhouse 1980; Pfeffer et al. 1986; Houtz et al. 1988; Millaleo et al. 2010a, b).

Being the structural constituent of photosynthetic proteins and enzyme it is predominantly involved in the bioactivation of approximately 35 crucial enzymes of plants, such as: Mn-SOD, Mn-CAT, phosphoenol pyruvate carboxy kinase and pyruvate carboxylase (Burnell 1988; Ducic and Polle 2005). Biogenesis of chlorophyll, amino acid (tyrosine) and several other secondary metabolites such as flavenoids and liginin are another eminent role of manganese in plants (Lidon et al. 2004). Millaleo et al. (2010a, b) signifies the profitable role of manganese and also ascribed their distribution, accumulation and resistant mechanism inside the plant when its concentration inside the soil solution exceeds the permissible limit, it becomes severely toxic to plant cell, thereby limiting its growth and yield productivity worldwide.

Excessive-limed soil or the soil rich in organic matter (above 6.0 %) with high pH level (more than 6.5) are primarily responsible for the prevalence of manganese deficiency (Reichman 2002; Demirevska-Kepova et al. 2004; Millaleo et al. 2010a, b). But the uptake and accumulation of manganese inside the plant shows adverse relation with the available iron content of soil (Demirevska-Kepova et al. 2004; Millaleo et al. 2010a, 2010b). As a trace element it's over expression led the generation of highly reactive oxygen species (ROS) particularly OH· that ultimately triggers oxidative injuries inside the plant (Demirevska-Kepova et al. 2004; Millaleo et al. 2010a, b).

Likewise, the appearance of interveinal chlorosis, brown necrotic spots, premature leaf fall, white and gray spots of leaf and delayed maturity is another characteristic deficiency symptom of Mn resulting from its limited supply inside the plant. Therefore, its proper optimization inside the plant is necessary to further lessen the exogenous demand of fertilizers. Although the potentially significant physiological and biological role of manganese is well elucidated from the above studies however, further investigation is still needed with the insight of improving gross productivity and maintaining the human/plant nutrient status on a global scale.

Zinc (Zn)

The essentiality of zinc (Zn) as a micronutrient in plant is phenomenal, bearing atomic number 30, Zn is another transition element and observed as the 23rd most copious element on earth with five stable isotopes (Broadley et al. 2007). Zn^{2+} has distinct characteristics of Lewis acid and also considered to be the redox-stable due to completely filled d-shell orbitals by electron unlike in Fe^{2+} and Cu^{2+} (Barak and Helmke 1993; Auld 2001; Broadley et al. 2007; Sinclair and Krämer 2012; Hafeez et al. 2013). Broadley et al. (2007) mentioned that idea of importance of Zn in plants was originated for the first time when its significance was shown by Mazé (1915) in maize and barley and dwarf sunflower by Sommer and Lipman (1926). Interestingly, Zn plays eminent role by being a structural constituent or regulatory co-factor for different enzymes and proteins. At organism level, the significant role of 'zinc finger' as a structural motif is worth mentioning as it regulates transcription (Klug 1999; Englbrecht et al. 2004; Broadley et al. 2007). The optimal crop growth is generally maintained by intake of Zn in its divalent form. Henceforth, performing several important functions in different plants which can be enumerated as:

- Regulation of carbonic anhydrase for fixation to carbohydrates in plants (Carbon dioxide → reactive bicarbonate species).
- Promotion of the metabolism of carbohydrate, protein, auxin, pollen formation (Marschner 1995) etc.
- Governs biological membranes and performs defence mechanism against harmful pathogens.
- Presence of Zn in SOD and CAT as a cofactor, protects plant from oxidative stress.
- The fundamental attribute of Zn is being the component of all the six enzyme classes' → oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases.

Additionally, Zn being participatory in the structure of Rubisco, activates several biochemical reactions in the photosynthetic metabolism (Brown et al. 1993; Alloway 2004a, b; Tsonko and Lidon 2012). In the thylakoid lamellae, Zn inhibits the production of high toxic hydroxyl radicals in Haber–Weiss reactions due to its high affinity with cysteine and histidine (Cakmak 2000; Alloway 2004a, b; Brennan 2005; Disante et al. 2010; Tsonko and Lidon 2012).

Furthermore, Alscher et al. (1997) and later Cakmak (2000) confirmed the savior role of Zn against oxidative stress by being involved in multiple antioxidative enzymes such as ABX and glutathione reductase. The availability of water to plant has also been noticed to be affected by Zn (Barceló and Poschenrieder 1990; Kasim 2007; Disante et al. 2010; Tsonko and Lidon 2012). Pahlsson (1989) and Coleman (1992) suggested formation of complexes of Zn with DNA and RNA. The tryptophan synthesis and active role in signal transduction are also some of the valuable functions of Zn reported so far (Brown et al. 1993; Alloway 2004a, b; Lin et al. 2005; Hänsch and Mendel 2009). Nonetheless, prominent participation of Zn in regulation of membranes by combining with phospholipids and sulphydryl groups of membrane proteins is also equally important to be known.

The sufficient Zn concentration required for proper growth of plant is estimated to be 15–20 mg Zn kg^{-1} DW as mentioned by Marschner (1995). Deficiency of Zn has been reported below this level in several research works. For instance, Skoog (1940) observed the disturbances in stem elongation in tomato.

Several other symptoms and responses of plants towards Zn deficiency are as follows:

- Necrosis at root apex and inward curling of leaf lamina,
- Mottled leaf due to inter veinal chlorosis,
- Bronzing and internodes shortening as well as size reductions in leaf.

While on exposure of leaf with elevated level of Zn i.e. above 0.2 mg g^{-1} dry matter, multiple abnormal functioning in plant can be observed. This toxicity level gives rise to deterioration of leaf tissue and at the same time decline the productivity of plant by making their growth stagnant. Sensitivity towards toxic Zn concentration has also been noticed in Soya bean and Rice. Boawn and Rasmussen (1971) and Chaney (1993) took chance to show the effect of Zn toxicity in leafy vegetable crops as they tend to accumulate high concentration of Zn noticed in spinach and beet. Therefore, it can be interpreted that, although Zn is toxic at excess level, it is an indispensable component of thousands of proteins in plants. Hence, adequate supply of Zn is one of the prime-most demands for plants growth and development which can be reached by detail research work on understanding the concept of application, acquisition and assimilation of Zinc in plants.

Conclusion and future outlook

Micronutrients, though required in relatively tracer amount (at <100 mg kg^{-1} dry weight) by plants, play a virtually significant role in a variety of cellular and metabolic processes such as, gene regulation, hormone perception, energy metabolism and signal transductions etc. Based on their precise requirement in higher plants, boron (B), chloride (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) are typically classified under essential micronutrients. Each organism requires an adequate supply of these micro elements which subsequently requires a complete metal homeostasis networking including their uptake and accumulation inside the plant, mobilization, storage and intracellular trafficking etc. (Hänsch and Mendel 2009). Insufficient supply or low phyto-availability of these elements would result in limited crop productivity worldwide. Therefore, plants require an requisite and constant supply of these micronutrients throughout their entire growth phase for optimal productivity. But, the over expanding human population and mindless exploitation of natural repositories makes it difficult for the plants to ensure their adequate supply for future reference and therefore, causing impulsive challenge for the expertise of science. Recently, it has been well elucidated that approximately 2/3 of the world's population is being suffering from the risk of nutrient-deficiency (White and Broadley 2009; Stein 2010). However, the marked deficiency of mineral nutrient could be reduced by the judicious exogenous supply of mineral fertilizers or by the cultivation genotypically modified crops (GM crops) with higher metal concentrations. In addition, crop husbandry, breeding or genetic manipulation could also be recognized as one of the most efficient, recent and reliable technique of improving mineral status of soil (White and Broadley 2009). For sure, these above mentioned approaches can definitely create new horizon in the field of micronutrient application in plant and crop sciences, but in order to achieve greater successful results, more advanced and scientific research works on this deep topic are necessarily required.

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