Chapter 4
Role of Micronutrients in Biochemical Responses of Crops Under Abiotic Stresses

Shyam Narain Pandey

Abstract Essential micronutrients regulate and change the functioning of plants. The plants show tolerance in diverse ways under abiotic stress conditions, like drought, mineral deficiency, elevated salts concentrations in soil, etc., greatly contributed by the cellular biochemical reactions under suitable availability of micronutrients. Micronutrients such as zinc, copper, manganese, iron, molybdenum, boron and chloride support physiology and biochemical constituents in plants to neutralize the abiotic stresses. Under abiotic stresses, the micronutrients in plants, being constituents of biomolecules, function as an activator of many enzymes, electron carriers, etc. Also, their functions in metabolism regulations, reproduction, and protection against abiotic and biotic stress conditions are very significant. During diverse stress conditions, a large number of reactive oxygen species (ROS) are generated, and they damage the cellular metabolism of plants. The sufficient micronutrient status protects the plants against ROS by activating the enzymes and biomolecules to become a constituent or activator and directly favour the growth and cellular metabolism. This chapter describes the better interactions of plants and micronutrients for maintaining growth and metabolism and providing tolerance against abiotic stresses through changing the biochemical constituents in plants.

Keywords Abiotic stresses · Cellular metabolism · Micronutrients · Oxidative stress

1 Introduction

Today, global food demand is increasing due to the continuously growing population. Despite the development of agricultural technology for high production of food grain, abiotic stresses cause havoc on crop production. The major abiotic stresses in the world are drought, salinity, temperature (including global climatic change), mineral deficiency, heavy metals toxicity, etc. (Hussain and Shi 2014;

S. N. Pandey (✉)
Department of Botany, University of Lucknow, Lucknow, Uttar Pradesh, India

R. Roychowdhury et al. (eds.), *Sustainable Agriculture in the Era of Climate Change*, https://doi.org/10.1007/978-3-030-45669-6_4

Gautam et al. 2017). All plants require essential elements for their structure and functions. In recent decades, environmental stress conditions increased, and in this situation, the role of nutrients, particularly micronutrients, is very significant in the survival of plants (Pandey 2018). The micronutrients such as zinc, iron, copper, manganese, molybdenum, boron, chlorine, etc. along with other macronutrients play a direct role in the growth and metabolism of plants (Sharma 2006). Plants cannot survive in the absence of these micronutrients (Arnon and Stout 1939) even in normal growing conditions. The major abiotic stress conditions such as drought, salt and nutrients deficiency/toxicity are increasing day by day due to various anthropogenic activities. A large number of enzymes and organic molecules in cellular metabolism supported the defence system of plants against various stresses (Pandey et al. 2018). A large number of enzymes and biomolecules involved in plant defence system require micronutrient elements as constituents or activators (Pandey 2014). In food chains, plant nutrition effects both on plants growth and survival of other living organisms (Karthika et al. 2018). Micronutrients play their role in various biotic and abiotic stresses, because they are electron carriers, regulate cellular metabolism and play a role in osmotic regulation. Micronutrients maintain the structural integrity of the plasma membrane during abiotic stress conditions (Brown et al. 2002). Micronutrient such as iron is a cofactor of choline monooxygenase, a catalyst that helps in the biosynthesis of an osmoprotectant glycine betaine, which maintains the integrity of plasma membrane and stabilize the structure of proteins during salt and drought stress conditions (Gorham 1995).

Micronutrients play their protective role in plants during stress conditions such as drought, salt and minerals deficiency/toxicity, heavy metals, etc. Under such stress conditions, production of reactive oxygen species (ROS) creates oxidative stress damage to cellular structure and functions (Pandey 2018). Micronutrients such as iron, manganese, copper and zinc are participants in detoxification of ROS. Also, they play a role in signal transduction (Apel and Hirt 2004). In the antioxidant system of enzymes, many micronutrients are a cofactor for protecting cellular structure and functions from the excessive generation of ROS (Pandey and Gautam 2009). Under abiotic stresses, during electron transport system (in chloroplast and mitochondria), excessive ROS are produced. An important enzyme superoxide dismutase (SOD), which has micronutrient cofactors such as Cu-Zn SOD, Mn-SOD and Fe-SOD, supports the defence system against the ROS (Sharma 2006; Pandey 2014). These micronutrients containing SOD show high activity in mitochondria (Mn-SOD), chloroplast (Fe-SOD and Cu-Zn SOD) and cytosol (the activity of Cu-Zn SOD). The activity of SOD converts superoxide ions (O_2^-) into hydrogen peroxide (H_2O_2). The high concentrations of H_2O_2 are inducing lipid peroxidation and damage the cellular metabolic systems (Pandey 2018). So H_2O_2 concentration is prevented by its conversion into water (H_2O). This conversion of H_2O_2 to H_2O is catalysed by Fe-containing enzymes catalase (CAT) and ascorbate peroxidase (APX). Ascorbate peroxidase scavenges H_2O_2 in the chloroplast in combination with the ascorbate-glutathione cycle (Asada 1997). The enzyme catalase breaking down the H_2O_2 is present in peroxisomes. In peroxisomes, the conversion of glycolate to glyoxylate also contributes to accumulation of H_2O_2, thus becoming a cofactor of the above antioxidative enzymes (catalase, APX and SOD), the micronutrients involved in the cellular defence system against oxidative stress (Van Wiren et al. 1996). In cellular defence system, antioxidative enzymes decrease their activity due to limited availability of metal cofactors by various stresses in soil, which weakens the antioxidant defence system (Pandey 2014). Micronutrients are involved in various biosynthetic pathways (Pandey et al. 2018). Biosynthesis of secondary metabolites is formed with catalytic actions of enzymes. These enzymes contain micronutrient as cofactors. Also, they play a role in lignifications of the cell wall, genes regulation, hormonal balance, ionic homeostasis and cell signalling (Stiles 2013). A large number of enzymes present in the various compartment of the cell contain various micronutrients for performing their normal functions (Tej and Zeiger 2002). Even normal growth plants require a sufficient level of micronutrients. But availability of nutrients is greatly affected by soil physical, chemical and biological properties which determine the dynamics of the equilibrium of micronutrients in soil and its labile pool, from which micronutrients are absorbed by plant roots. From the labile pool, the acquisition of micronutrients is affected by the physical factors of the environment such as light intensity, pH, temperature, moisture, etc. and soil cultural practices. In addition, the genetic composition and stress disposition of plants influence the acquisition of micronutrients (Brady and Weil 1999; Karthika et al. 2018).

Salt stress conditions (salinity and sodicity) are a major threat to crops responsible to yield less by 4–6.5% annually across the world. In salt-affected soils, high concentration of sodium and chloride ions impairs the availability of essential nutrients to plant roots for absorption (Chakraborty et al. 2016), and these results in a reduction of crop productivity (Pandey 2014). Similarly, the stress in soil due to excessive heavy metals activity affects plant growth and contaminates our delicate food chain (Naaz and Pandey 2010; Roychowdhury and Tah 2011; Basu et al. 2012; Roychowdhury et al. 2018, 2019). Soil salinity causes nutrient loss, poor soil characteristics and essential nutrients imbalance. High concentration of salts in saline soils affects osmotic potential. Mostly, micronutrients such as Zn, Fe, Cu and Mn are less available for plants under high soil pH (alkaline) range, low soil moisture, high temperature and low organic matter content conditions (Brady and Weil 1999; Pandey et al. 2018). The status of some micronutrients influences plants-water relations. The role of chlorine in osmoregulation involves cell osmotic relations and turgor-dependent extension growth of cells (Sharma 2006).

2 Zinc (Zn)

Zinc is an essential micronutrient for the structural and functional role of all living organisms (Pandey et al. 2002). Mostly, plants absorb zinc from the soil as Zn^{++} ion. The uptake of zinc from the soil and translocation to plant shoot portion are concentration-dependent, and some workers have reported carrier-mediated transport of Zn^{2+} (Norvell and Welch 1993). In adverse soil conditions such as calcareousness, low temperature, salinity and alkalinity, zinc is less available in the soil for plants root absorption (Gautam et al. 2017). The zinc-deficient soil conditions induce the plants for the secretion of phytosiderophores which mobilize zinc (Treeby et al. 1989) and help their uptake in plants. Plant genotypes are variable in the secretion of phytosiderophores and efficiency of zinc uptake (Van Wiren et al. 1996). Several identified transporters such as *ZIP* (Guerinot 2000) and CDF (cation diffusion facilitator) family (Williams et al. 2000) facilitated zinc transport in plants. Zinc transporter genes (ZIP 1, 2, 3 and 4) have been isolated from *Arabidopsis,* and these genes are expressed in plant roots due to zinc deficiency (Guerinot 2000). A large number of proteins contain zinc as their structural component for performing their catalytic functions of more than 250 enzymes. These metal chelates with polypeptides are synthesized during heavy metals stress conditions in plants (Gautam et al. 2017). Zinc provides stability of various proteins involved in regulatory functions, and such proteins are zinc fingers, RING finger domains and zinc clusters. Under excessive heavy metals concentrations in plant tissues, metallo-polypeptides help tolerance in plants against heavy metals in tissues (Pandey et al. 2002).

2.1 Enzymes

Zinc does not function during oxidation-reduction reactions due to its single oxidation state (Zn^{2+}). Some important enzymes playing a vital role in cellular metabolism contain zinc as cofactor or activator, and these are DNA-dependent RNA polymerases, carbonic anhydrases, superoxide dismutase, carboxypeptidase A, etc. Zinc is used as a substrate by the enzyme H^+ ATPase and functions as Zn-ATPase. Most enzymes contain zinc as constituents catalyse hydrolysis reactions (Sharma 2006). The carbonic anhydrase catalyses the reversible conversion of carbon dioxide to bicarbonate (HCO_3^-) and is therefore critical to photosynthesis in C_4 plants growing in drought and high-temperature conditions. In C_4 plants in carboxylation reaction, bicarbonate is used as substrate and enzyme is PEPCase. Carbonic anhydrase enzyme is localized in mesophyll chloroplast in C_3 plants, while cytosol of mesophyll cell in C_4 plants. The cytosol is also the site for phosphoenolpyruvate carboxylase (PEPCase) using bicarbonate as substrate (Hatch and Burnell 1990). The active sites of SOD contain copper and zinc. SOD (Cu-Zn SOD) protects plant cells against ROS. Zinc is also a constituent of some DNA-dependent RNA polymerases involved in transcription (Petranyl et al. 1978). A large number of enzymes required zinc as a cofactor in animals, bacteria and fungi. The availability of zinc is influenced under various stress conditions or zinc deficiency, and the activity of all zinc-related enzymes is adversely affected. The decrease in the activity of carbonic anhydrase in leaves is a strong indicator of zinc deficiency (Rengel 1995). Zinc-deficient plants also show decreased activity of SOD (Pandey et al. 2002). The low activity of catalase and ascorbate peroxidase in plants due to zinc deficiency has been reported (Yu et al. 1998; Pandey et al. 2002). The role of glutathione reductase (GR) is increased in response to environmental stresses and xenobiotics which provide tolerance to the plants against these stresses. The decrease in GR activity in response to zinc deficiency in bean plant has been reported by Cakmak and Marschner (1993). Under stress conditions, zinc protects plants by an inhibitory effect on plasma membrane-bound NADPH oxidase (catalyses the production of superoxide ions).

2.2 Physiological Role

Plants show zinc deficiency grown under soil salinity, sodic or calcareousness stresses performed poor photosynthetic functions (Karthika et al. 2018). Low zinc in cells changes chloroplast structure, electron transport and carbon dioxide fixation (Sharma et al. 1994). The production of ROS increases due to zinc deficiency in plant tissues, and ROS damage in the thylakoid membranes consequently decreases the photosynthetic active area in leaf (Cakmak and Engels 1999; Henriques 2001). Carbonic anhydrase catalyses the production of the substrate (HCO_3^-) in C_4 plants and maintains CO_2 concentration in C_3 plants at the site of carboxylation by the conversion of HCO_3^- to CO_2 under the role of RuBP carboxylase (Hatch and Burnell 1990). The activity of carbonic anhydrase is inhibited in plants under the influence of zinc deficiency (Badger and Price 1994). In zinc-deficient plants, decrease in catalase and peroxidase activity, photosynthetic rate and accumulation of essential oil in leaves have been studied (Pandey 2018; Srivastava et al. 1997). Marschner et al. (1996) observed increased accumulation of carbohydrates in leaves of zinc-deficient plants. The increased accumulation of starch in zinc-deficient condition correlates the role of zinc in sucrose biosynthesis (Shrotri et al. 1980) and starch metabolism. Zinc is also involved in auxin metabolism by the help of tryptophan-dependent auxin biosynthesis. Tryptophan is a significant precursor of auxin which is a growth-promoting plant hormone. Zinc deficiency reduces the protein content, while increases the non-protein nitrogen in plants (Bisht et al. 2002) indicates the role of zinc in protein synthesis. The metabolism of nucleic acids and ribosome and zinc as a constituent of a transcription factor may also affect zinc deficiency which leads to decrease in protein synthesis. Low zinc status in plants suppressed the various stages of reproductive development (Pandey and Gautam 2009) such as flowering, male and female gametogenesis, seed development, development of anther, etc. (Sharma 2006; Pandey 2014). Zinc is a critical nutrient element for microsporogenesis and pollen fertility. Pollen tube accumulated zinc at their part that participated in fertilization. Zinc finger protein (TFIIIA type) controls the development of the flower. The zinc finger proteins (anther-specific) play a role in microsporogenesis (Kobayashi et al. 1998). Zinc-deficient plants accumulate high proline content which is indicative of water stress (Sharma and Sharma 1987; Pandey 2018).

2.3 Oxidative Stress

Plants produce high reactive oxygen species when influenced with zinc deficiency. Also, the power of defence system decreases which neutralizes the toxic effects of ROS (Cakmak 2000; Pandey and Gautam 2009; Singh and Pandey 2011). The activity of copper-Zn SOD, ascorbate peroxidase and catalase antioxidant enzymes is reduced in plants due to zinc deficiency (Yu and Rengel 1999; Naaz and Pandey 2009; Gautam et al. 2017). High production of free oxygen radicals oxidizes lipid in membrane causing leakage of cell sap due to structural changes in the plasma membrane. The toxic effect of ROS also leads damage to the photosynthetic apparatus (Cakmak and Engels 1999; Henriques 2001).

3 Copper (Cu)

Copper exists in Cu^+ (cuprous) and Cu^{++} (cupric) oxidation states, particularly in oxidation-reduction reactions. In cellular metabolism, many copper-containing proteins act as enzymes and electron carriers. It is an important constituent of cytochrome C oxidase. In the mitochondrial electron transport system, copper as constituents of cytochrome C oxidase is the terminal component. The copper protein (plastocyanin) is an electron carrier in the light reaction phase of photosynthesis. Copper is a component of many proteins detoxifying the effect of reactive oxygen species highly produced during abiotic stress conditions. Copper is taken by plants roots through active transport proteins across the plasma membrane (Fox and Guerinot 1998). Copper transporter proteins COPT1, COPT2, COPT3, COPT4 and COPT5 have been identified from *Arabidopsis* (Kampfenkel et al. 1995; Sancenon et al. 2003). These copper transporters have been detected in leaf, stem, flowers and roots, but their expression was different in different parts of the plant. The cupric ions long-distance transports are facilitated by Cu^{++}-amino acid complex formation, and the amino acids involved in the transport process are asparagine, histidine and glutamic acid (Loneragan 1981). Under copper deficiency, transport from leaves to grains is poor (Loneragan 1981), particularly at the time of seed-filling stage.

3.1 Physiological Functions

Copper causes reduction of one atom of O_2 to water and another atom of O_2 to hydroxylation of substrates such as phenolase complex (Sharma 2006). It is a cofactor of a large number of enzymes in plants such as Cu-Zn SOD and cytochrome C oxidase. The metal receptor protein (metallochaperones) delivers copper metal Cu-proteins (Lippard 1999). Some important copper-containing enzymes are ascorbate oxidizer, SOD, cytochrome C oxidase, diamine oxidase, etc. Catechol oxidase (copper proteins) or polyphenol oxidases are important for secondary metabolism in plants. They play a role in the biosynthesis of lignin and alkaloids. Also, in the formation of phytoalexins, they have antifungal activity. Therefore, phenolases involved in metabolism provide strength to the cell wall for the protection of pathogens (Pandey et al. 2018). Laccase or p-diphenols oxidase contains four copper ions (both Cu^+ and Cu^{++}) acting as a catalyst in the oxidation of p-diphenols to p-quinones. Laccase is involved in the synthesis of plastoquinones, useful in PS-II (Ayala et al. 1992). Tyrosinase enzyme was identified as mushrooms involved in the conversion of tyrosine to dopa-quinone. The Cu-Zn SOD enzyme involved in the conversion of ROS to H_2O_2 and oxygen, therefore, provides protection of cells from ROS. The enzymes SOD and ascorbate peroxidase are attached to the chloroplastic thylakoids in the vicinity of the PS-I. Ascorbate peroxidase is involved in the reduction of H_2O_2 to H_2O and protects cellular lipid peroxidation (Pandey 2018). Copper is a constituent of single-electron carriers protein plastocyanin found in chloroplasts. Plastocyanin is an electron carrier linking two pigment systems (PS-I to PS-II). Copper element that binds to polypeptides forms copper-chelating biomolecules (Maksymiec 1997). Copper deficiency causes a reduction in photosynthesis (Ayala et al. 1992; Pandey 2018). In some blue-green algae, plastocyanin synthesis is with the availability of copper. Under salinity and alkali soil conditions, low availability of Cu inhibits the Cu-Zn SOD activity and plastocyanin-mediated transport of electrons within the chloroplasts (Shikanai et al. 2003). Low copper in plants causes ultrastructural changes in chloroplast thylakoids in grana and decrease in chlorophyll content (Casimiro et al. 1990).

3.2 Stress Neutralization

Copper involves in the disproportion of superoxide ions (O_2^-) produced due to abiotic stresses because it is constituent of the enzyme Cu-Zn SOD for the conversion of H_2O_2 and molecular oxygen. Therefore, low copper weakens the oxidative defence system in plants. Copper plays a protective role in plants against pathogens through their involvement in the synthesis of lignin (Graham 1983). Copper-deficient plants are more vulnerable to pathogenic infections. During stress conditions, copper induces the formation of ROS and activates copper diamine oxidases that trigger defence mechanisms in the plant (Sharma 2006).

4 Iron (Fe)

Iron exists in ferric (Fe^{+++}) and ferrous (Fe^{++}) oxidation states and participates in oxidation-reduction reactions. It participates in the electron transport system, and it is a cofactor of several enzymes. They play important roles in fatty acids metabolism and biosynthesis of terpenoids, signalling molecules and growth hormones.

The role of iron is known for induction to produce and detoxification of reactive oxygen species. The biochemical reactions related to iron are very complex. Iron also plays a very important role in signal transduction and biosynthesis of Jasmonic acid (Sharma 2006). Under Fe deficiency conditions, mostly plants uptake reduction-based iron (Bienfait et al. 1983). The ferric ion chelate reduced into ferrous ion chelate by the catalytic activity of an enzyme known as Fe (III) chelate reductase. This reductase enzyme is induced in the plasma membranes of root epidermal cells under Fe deficiency (Sharma 2006). Yi and Guerinot (1996) described that the *Arabidopsis* mutants ferric reductase defective 1, 2 and 3 suppress the activity of Fe^{+++} chelate in *Arabidopsis* as reported by Robinson et al. (1999) and named it ferric reductase oxidase 2 (FRO2). The various genes involved in uptake in roots, as well as their distribution in shoot portions, are characterized (Robinson et al. 1999; Waters et al. 2002). Extracellular pH influences the solubility of Fe^{++} in the root zone area, which is observed maximum at pH 5.0. High pH reduces the Fe^{+++} reduction (Manthey et al. 1996; Zheng et al. 2003). Plant hormone ethylene helps in the uptake of iron in roots (Zaid et al. 2003) by changing the root morphology of iron-deficient plants (Schmidt et al. 2000). Several Fe transports proteins in plasma membranes, and several transporter genes of different gene families have been identified and characterized such as iron-regulated transporter (IRTI) belonging to ZIP family identified in *Arabidopsis* (Eide et al. 1996). Nramp family transporters are also involved in the uptake of iron (Thomine et al. 2000). The strategy of the plant to uptake the iron with the reduction of Fe^{3+} to Fe^{2+} by the catalytic activity of Fe chelate reductase is established only under iron deficiency condition. The second strategy is established for iron uptake by the formation of Fe complex of phytosiderophores. The mugineic acid forms complex with Fe^{3+} that is prerequisite for its recognition by the specific Fe^{+++} transport system in roots (Ma and Nomoto 1996; Ma et al. 1993). Mugineic acid synthesizes from methionine chelate $Fe^{3}+$ with their carboxyl groups and amino groups. The graminaceous plant species secrete mugineic acid (phytosiderophores, when soil is deficient in iron), but the secretion of specific mugineic acids (non-proteinogenic amino acids) is different (Sharma 2006). The mugineic acids (MA) are secreted by rice, corn and wheat. Soybean genotypes are 2-DMA, 3-HMA (3-hydroxyl mutagenic acid) and 3-epihydroxy mugineic acid (epi-HMA). These MAs provide tolerance to plants against iron chlorosis. The transport of iron to the shoot portion takes place through xylem as ferric citrate organic complex (Cataldo et al. 1996).

4.1 Physiological Roles

A large number of iron (Fe)-containing enzymes and carrier proteins are present in electron transport systems. These enzymes are essential for the biosynthesis of secondary metabolites, plant hormones and some other biomolecules significant as signalling molecules and developmental activities. Some enzymes are di-iron enzymes in which two iron atoms forming an Oxbridge are bound to two histidine and four carboxylate residues such as mitochondrial alternative oxidase (Sharma 2006). In non-haem iron enzymes, Fe cofactor is present as Fe-sulphur cluster which enables iron-sulphur proteins to be as donors or acceptors of electrons. The iron clusters are Fe-S, 2Fe-2S (two Fe ions are coordinated to two inorganic sulphide ions) and 4Fe-4S (contains four Fe ions and four sulphide ions). The enzymes containing Fe as activator are catalase, cytochrome C oxidase and peroxidases, and they are iron bound to the apoprotein as iron porphyrin. There, Fe ion is complexed to the four nitrogen atoms of the four pyrrole groups. Some non-haem iron enzymes are superoxide dismutase (SOD), lipoxygenase, alternative oxidase and 2-oxoglutarate-dependent enzymes. Some important non-haem iron enzymes with Fe-S cluster cofactor are nitrite reductase aconitase, sulphite reductase, formate dehydrogenase, succinate dehydrogenase, NADH-Q oxidoreductase and FDX-thioredoxin reductase. The various groups of enzymes containing Fe involved in detoxification of reactive oxygen species are SOD, catalase, peroxidase, alternative oxidase, etc. A large number of Fe proteins are electron carriers, a significant part of mitochondrial and chloroplastic electron transport system including ferredoxins and cytochromes. Leghaemoglobin in leguminous plants has a high affinity for O_2 molecule. The phytoferritin serves as a store of cell's excess iron in plants (Sharma 2006). Haem protein cytochromes are localized in chloroplasts, in mitochondrial inner membrane and in the endoplasmic reticulum, and cytochromes are involved in reversible reactions of two iron oxidation states ($Fe^{+++} = Fe^{++}$). Ferredoxins (2Fe-2S)-type iron-sulphur clusters function in electron transport in between iron oxidation states, mainly localized in chloroplasts and root plastids. Chloroplastic ferredoxin is reduced by taking electrons from P700, and it is an electron donor for several reductive reactions such as glutamine to glutamate and reduction of nitrite and sulphite. The phytoferritins in plants constitute a major sink of iron accommodating about 4500 iron atoms (Smith 1984). Iron plays a significant role in photophosphorylation and, as a part of ferredoxin and ferredoxin-thioredoxin reductase, functions in the photoreduction of thioredoxin. In the case of some plants, the ferredoxin-thioredoxin regulates the activity of Rubisco (Zhang and Portis 1999) and also functions in the Calvin cycle. The iron proteins NADH-cytochrome b_5 reductase, cytochrome b_5 and a desaturase are membrane-bound proteins involved in fatty acid metabolism (Sharma 2006).

4.2 *Free Radical Production*

The reduction of O_2 and H_2O_2 generates superoxide ions which are dissimulated by SOD and make two ROS causing lipid peroxidation damaging cellular components (Pandey 2018). Superoxide ions react to H_2O_2 to produce hydroxyl radicals

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\circ} + OH^{-}$$

These ROS damage proteins, lipid and DNA and induce mutations. Ferrous ions also react with oxygen molecules to generate $Fe^{2+}O$ (ferryl) and $Fe^{2+}O_2$ (per ferryl), which are more toxic compounds. The activity of lipoxygenase (iron enzyme) in the hydroxylation of linoleic acid catalyses the production of singlet oxygen species ($^1O_2$).

4.3 Protective Role

In plants, iron also participates in the defence system against salt stress, oxidative stress and various pathogens attack. Although iron ions promote the production of ROS, iron-containing enzymes are participating in detoxification of ROS (Roychowdhury et al. 2018, 2019). The iron-SOD detoxify the superoxide ion (O^{2-}) conversion into H_2O_2. Other enzymes catalase and ascorbate peroxidase (haem enzyme) detoxify the H_2O_2 by converting them into H_2O. In the iron-deficient plant, decrease in the activity of ascorbate peroxidase and consequently increase in H_2O_2 concentration in sunflower have been reported (Ranieri et al. 2001). Quinol reacting with oxygen generates ROS, and iron enzyme alternative oxidase reduces quinol by providing an alternate pathway in the mitochondrial electron transport system, thus preventing the production of ROS. Iron plays a role as an osmoprotectant through biosynthesis of glycine betaine against high temperature and high salinity (Gorham 1995). Also, iron is involved in the biosynthesis of lignin, which provides mechanical strength to cell wall against pathogens (Caruso et al. 2001).

5 Manganese (Mn)

Manganese (Mn) exists in various oxidation states such as Mn^{2+}, Mn^{3+}, Mn^{4+} and Mn^{5+}, out of which the most prominent is Mn^{2+}. It forms a rapid bond with oxygen-containing species. Mn behaves as an activator of enzymes, plays a catalytic role in cellular metabolism and also functions in CO_2 fixation in CAM and C_4 plants. It also plays a significant role in scavenging oxygen free radicals. Mn^{2+}ions are absorbed by plant roots through facilitated diffusion. The acidification outside the plasma membrane by H^+ efflux increases uptake of Mn (Yan et al. 1992). Several genes have been identified and characterized, and they are encoding Mn transporter proteins (Hall and Williams 2003). The P-type ATPase is involved in Mn transport. The transporter ECA1 in *Arabidopsis* functions as an endoplasmic reticulum-bound Ca^{2+}/Mn pump, which also provides tolerance to the plants to excess manganese (Wu et al. 2002). Mn anti-portal Sh MTP1 confers tolerance to manganese in plants through internal sequestration (Delhaize et al. 2003). Nramp family transporter participates in manganese transport, and Nramp 3 plays a role in long-distance transport of manganese (Thomine et al. 2003). The translocation of manganese to developing grains is slowly observed in wheat.

5.1 Physiological Role

Over 30 enzymes contain Mn as constituents. Some important enzymes with Mn are Mn-SOD (manganese superoxide dismutase), PEPCK (phosphoenolpyruvate carboxyl kinase), NAD + malic enzyme, IDH (isocitrate dehydrogenase), NADP + malate enzyme, PEPCase (phosphoenolpyruvate carboxylase), glutamine synthetase, enolases, etc. PEPCK catalyzes the decarboxylation of oxaloacetate to PEP in the chloroplast of bundle sheath in C_4 plant. The released carbon dioxide is the starting point of the Calvin cycle.

$$\text{Oxaloacetate} + \text{ATP} \rightarrow \text{Phosphoenolpyruvate} \ + \text{ADP} + \text{CO}_2$$

The significant role of Mn is the oxidation of water in PS II (Ono and Onone 1991). Many enzymes in C_4 plants containing Mn^{2+} as cofactor help in photosynthesis in C_4 plants. Manganese is also involved in the decarboxylation of C_4 acids to generate carbon dioxide in bundle sheath cells. Such produced CO_2 is again fixed in a C_3 compound by Rubisco (Sharma 2006). Manganese-activated enzymes catalyse the biosynthesis of secondary metabolites in plants. It is also involved in biosynthesis pathway systems of pigments as an activator of many enzymes. The manganese plays a significant role in the biosynthesis of aromatic amino acids (tyrosine, tryptophan and phenylalanine). These amino acids are precursors of flavonoids, indole and lignin (Burnell 1988). Manganese is the activator of arginase and plays a role in the synthesis of polyamines. Polyamines are important for plant growth and development. Deficiency of Mn decreases photosynthesis in plants because Mn is an important constituent of PS II (Yachandra et al. 1993), and leaf ultrastructure changes are induced by Mn deficiency (Polle et al. 1992). Plants show an increase in soluble carbohydrate and a decrease in fatty oil content under manganese deficiency (Campbell and Nable 1988). Increase in soluble nitrogenous compounds due to Mn deficiency has been reported in plants because Mn is an activator of arginase and allantoate amidohydrolase (Winkler et al. 1985). Also, Mn deficiency is related to the accumulation of arginine and uriedes and reduction in nucleic acids (Chatterjee et al. 1994).

5.2 Protective Role

Manganese-SOD (superoxide dismutase) localized in mitochondria is an important enzyme of the antioxidant system; thus, Mn is involved in the defence system against reactive oxygen species. It prevents the accumulation of superoxide ions by dismutation of them and converts it to hydrogen peroxide (Sharma 2006). Low Mn in plants shows oxidative stress. Overexpression of Mn-SOD in transgenic tobacco increases tolerance in plant against oxidative stress as reported by Slooten et al. (1995). The Mn-SOD also contributes tolerance to plants against drought stress.

Increased Mn-SOD expression induced under drought stress has been observed in wheat seedlings as reported by Wu et al. (1999). The concentrations of tissue manganese are related to disease in plants, and it supports the resistance in plants to pathogenic diseases (Graham 1983). Manganese contributes protection and strength in plants to fungal infection through its involvement in the biosynthesis of phenolics and lignin (Morab et al. 2003).

6 Molybdenum (Mo)

Molybdenum (Mo) is a second transition series metal that exists in several oxidation states, and the most stable is the Mo VI (hexavalent) form. Molybdenum has an affinity for sulphur-containing groups. It participates in oxidation-reduction reactions due to its variable and easy convertibility oxidation states. Molybdenum is a cofactor of several enzymes. Mo plays a role in dinitrogen fixation and assimilation of nitrate in plants, and it is also essential for free-living and symbiotic bacterial nitrogen fixation processes. Plants take Mo as Mo O_4^{2-} (molybdate ion). Molybdenum follows some transporter path as transport of phosphate. A higher concentration of sulphate decreases the uptake of molybdenum (Marschner 1995). For redox reactions in plants and microbes, Mo is a cofactor of several enzymes (Sharma 2006). Xanthine oxidase and nitrate reductase are Mo-containing enzymes. These enzymes involve in catalysing the reactions for nitrogen and nitrogenous compounds. Aldehyde oxidase contains iron and MoCo as prosthetic groups catalyse the terminal reaction of the biosynthetic pathway of abscisic acid and auxins (Taylor 1991). Molybdenum-containing enzymes also contain additional cofactors such as Fe-S, iron, haem, etc. (Koshiba et al. 1996).

6.1 Physiological Roles

The molybdoenzyme nitrate reductase is very significant to catalyse the conversion of nitrate to nitrite, and the enzyme plays a role in the synthesis of organic nitrogenous compounds. The bacterial and eukaryotic nitrate reductase enzymes belong to two different families of molybdoenzymes (Sharma 2006). The enzyme nitrate reductase distribution differs in different plant species but is localized in the cytosol in all plant species. The molybdoprotein xanthine dehydrogenase has two similar and catalytically independent subunits. Each subunit contains a molybdoprotein, two Fe-S clusters and one flavin cofactor which catalyses oxidative degradation of xanthine to uric acid with the use of NAD^+ as an electron acceptor (Sharma 2006). Sulphite oxidase works in plants and human beings, and it is an essential liver enzyme. Sulphite oxidase is a molybdoprotein but lacks the redox-active centres (Mendel and Hansch 2002). Aldehyde oxidase contains FAD (flavin), iron and MoCo as prosthetic groups, it catalyses the oxidation of the abscisic aldehyde to abscisic acid (Seo and Koshiba 2002) and indole-3-acetic acetaldehyde to indole-3-acetic acid, and it regulates growth in plants. Dinitrogenase (Mo-Fe protein) and dinitrogenase reductase (Fe protein) are nitrogenase (prokaryotic enzyme) that catalyses the nitrogen fixation process. Several other non-molybdoenzymes such as catalase (Agarwala et al. 1986), cytochrome oxidase (Chatterjee et al. 1985) and succinate dehydrogenase (Agarwala et al. 1986) are influenced by Mo status in plants. Deficiency of Mo induces changes in several organic compounds (Sharma 2006).

7 Boron (B)

Boron (B) is metalloid that exists in three-valence status with high affinity to oxygen. Boron-diol complexes are formed between as-diol furanoid groups of sugars (apiose and fucose) and boric acid. Therefore, boron plays an important role in the structural and functional process for plant cell walls and membranes (Roychowdhury et al. 2019). Boron bridging the hydroxyl groups gives a large number of boron-containing compounds in plants (Dembitsky et al. 2002). The important role of boron is cross-linking of cell wall polysaccharides which has been established (O' Neill et al. 2004). A most significant form of boron in soils is boric acid (B [OH] $_3$) that exists mostly at pH 7.5 in the cytoplasm (Woods 1996). The uptake of boron from the soil is a passive process with formation of boron complexes which create concentration gradient. A investigation has also been reported for the uptake of boron is active or passive or both (Pfeffer et al. 1998). The transport of boron for long distances is facilitated by transpiration stream through the xylem, whereas retranslocation of boron to sites that do not lose water such as fruits, inflorescence, etc. involves phloem (Brown et al. 2002).

7.1 *Physiological Role*

Boron plays an important structural role in the cell wall as it binds with dial groups of polysaccharides. It is also highly accumulated in the cell wall as an integral component of polysaccharide complexes (Moth et al. 1993). Boron influences the uptake of ions from roots. Its effect on membrane potential (Em) is demonstrated by Schon et al. (1990). Boron-deficient plants show high efflux of K^+, sucrose and amino acids (Cakmak et al. 1995) due to structural changes in the cell wall. Short-term boron deficiency increases the accumulation of actin and tubulin involved in alteration in the polymerization pattern of the cytoskeletal assemblies as investigated in maize root apices by Yu et al. (2002). Boron increases photosynthetic oxygen evolution and photosynthetic efficiency in leaves. The supply of boron in plants affects the metabolism of carbohydrate, affecting the activity of related enzymes. The pentose phosphate pathway (alternative to glycolysis) is influenced by boron concentration in the plant (Sharma 2006). The activity of glucose-6-phosphate dehydrogenase and 6-phosphogluconate dehydrogenase increases in response to boron deficiency in plants (Lee and Aronoff 1967). In boron-deficient plants, the activity of acid phosphatase increases (Agarwala et al. 1991).

8 Chlorine (Cl)

Chlorine is a halogen element (group VII) with a single oxidation state as Cl^- ions. These ions are mostly bound to organic molecules or exchange sites. Among chlorine-containing organic compounds, 4-chloroindole acetic acid shows high auxin activity (Flowers 1988). The absorption of the free anion of chloride is by plant roots and also by shoot portion of plants in gaseous form or as chloride ions (White and Broadley 2001). Chloride uptake through plasma membrane occurs either by active transport (by H^+ ATPases) or by facilitated diffusion. The active transport with ATP hydrolysis involves a Cl^-/nH^+ symporter (Sharma 2006).

8.1 Physiological Roles

In manganese-linked oxygen evolution complex (of photosystem II), chlorine is a structural constituent. Chlorine deficiency in plants decreases photosynthesis and evolution of O_2 by chloroplasts of higher plants (Kelley and Izawa 1978). Chlorine deficiency inhibits extension growth of cells and cell division, and consequently, leaf area for photosynthesis is reduced (Terry 1977). Stomatal functioning indirectly affects photosynthesis process because proton pumping across vacuolar membrane induces an influx of chloride simultaneous with K^+, followed by water movement in guard cells, increase turgor and the opening of stomata, and affects the exchange of carbon dioxide (Schnabl 1980). Chlorine does not function as a catalyst, directly. It stimulates asparagine synthetase, which is important to catalyse the glutamate-dependent synthesis of asparagine. Asparagine synthetase also catalyses the amination of aspartate to asparagine. The synthesis of asparagine resulted in the storage of nitrogen and its transportation from source to sink (Rognes 1980).

8.2 Osmoregulation

Chlorine functions as osmoregulator in plants and therefore affects plant-water relations. The osmoregulatory functions such as cell division in shoot and root apices, stomatal functioning and development of stigma require chlorine. It causes turgor-induced extension cell growth in the apical portion of root and shoot. The rapid growth of stigma induces extension growth of cells which increases cell turgidity followed by quick mobilization of Cl^- and K^+ ions from the neighbouring cells as reported by Heslop-Harrison and Roger (1986). Such osmoregulatory functions of chlorine are very significant in reproductive biology. A carbon dioxide-induced chlorine efflux from guard cells into the apoplastic fluid is linked to the activation of the anion of protein channels in the plasma membrane of guard cells (Hanstein and Felle 2002) observed in faba bean. The concentrations of chlorine for osmoregulation process are variable from plant to plant, and osmotic responses are also variable under abiotic stress conditions (Sharma 2006; Roychowdhury et al. 2013; Ganie et al. 2014; Roychowdhury 2014; Hasanuzzaman et al. 2015; Pandey 2018).

9 Conclusions

The role of micronutrients in plant's biochemistry is very significant, particularly during biotic and abiotic stress conditions, because they play a significant role in the regulation of enzymatic reactions and biosynthesis of organic molecules. During abiotic stress conditions, the strength of the defence system, new synthesis and induction of biomolecules, induction of signalling, etc. are facilitated by appropriate concentration of essential micronutrients in plant tissues. The critical normal range of micronutrients not only promotes the growth but also protects cellular metabolism against abiotic stresses such as drought, mineral deficiency, salinity, adverse temperature, heavy metals and chemical toxicity.

Acknowledgements I acknowledge late Prof. C. P. Sharma (former head of Department of Botany and Dean Faculty of Science, University of Lucknow, India) for various discussions during the research and study on the physiological role of micronutrients in plants. I also acknowledge Ms. Isha Verma and Mithlesh Kumar for providing help in the preparation of this chapter.

References

Agarwala SC, Nautiyal BD, Chaterjee C (1986) Manganese, copper and molybdenum nutrition of papaya. J Hortic Sci 61:397–405

Agarwala SC, Abidi A, Sharma CP (1991) Variable boron supply and sugarbeet metabolism. Proc Natl Acad Sci (India) 61:109–114

Arnon DI, Stout PR (1939) The essentiality of certain elements in minute quantity for plants with special reference to copper. Plant Physiol 14:371–375

Asada K (1997) The role of ascorbate peroxidase and monodehydroascorbate reductase in H_2O_2 scavenging in plants. In: Scandalios JG (ed) Oxidation states and the molecular biology of Antioxidative defenses. Cold Spring Harbour Laboratory Press, Cold Spring Harbour, pp 715–735

Apel K, Hirt H (2004) REACTIVE OXYGEN SPECIES: Metabolism, Oxidative Stress, and Signal Transduction. Annual Review of Plant Biology 55:373–399

Ayala MB, Lopez GJ, Lachica M, Sandmann G (1992) Changes in carotenoids and fatty acids in photosystem II of Cu-deficient pea plants. Physiol Plant 84:1–5

Bisht SS, Nautiyal BD, Sharma CP (2002) Zinc nutrition dependent changes in tomato (*Lycopersicon esculentum* Mill) metabolism. J Plant Biol 29:159–163

Badger M, Price DG (1994) The role of carbonic anhydrase in photosynthesis. Annu Rev Plant Physiol Plant Mol Biol 45:369–392

Basu A, Roychowdhury R, Bhattacharyya SS, Tah J (2012) Estimation of major heavy metals (Fe, Cu and Zn) in the fruit part of *Cucumis sativus* L. World J Sci Technol 2(7):01–03

Bienfait HF, Bino RJ, Van Der Blick AM, Duivenvoordan JF, Fontain IM (1983) Characterization of ferric reducing activity in roots of Fe-deficient *Phaseolus vulgaris*. Physiol Plant 59:196–202

Brady NC, Weil RR (1999) The nature and properties of soils, 12th edn. Prentice Hall Inc. International (UK), London

Brown PH, Bellalovi N, Wimmer MA, Bassil ES, Ruiz J, Hu H, Pfeffer H, Dannel F, Romheld V (2002) Boron in plant biology. Plant Biol 4:205–223

Burnell JN (1988) The biochemistry of manganese in plants. In: Graham RD, Hannam RJ, Uren NC (eds) Manganese in soils and plants. Klumer Academic, Dordrecht, pp 125–137

Chatterjee C, Nautiyal N, Agarwala SC (1985) Metabolic changes in mustard plants associated with molybdenum deficiency. New Phytol 100:511–518

Chatterjee C, Nautiyal N, Agarwala SC (1994) Influence of changes in manganese and magnesium supply on some aspects of wheat physiology. Soil Sci and Plant Nutr 40:191–197

Cakmak I (2000) Possible roles of zinc in protecting plant cells from damage by reactive oxygen species. New Phytol 146:185–205

Cakmak I, Engels C (1999) Role of mineral nutrients in photosynthesis and yield formation. In: Rengel Z (ed) Mineral nutrition of crops: fundamental mechanisms and implications. Haworth Press, New York, pp 141–168

Cakmak I, Marschner H (1993) Effect of zinc nutritional status on activities of Superoxide radical and hydrogen peroxide scavenging enzymes in bean leaves. Plant Soil 155:127–130

Chakraborty K, Bose J, Shabala L, Eyles A, Shabala S (2016) Evaluating relative contribution of osmotolerance and tissue tolerance mechanisms toward salinity stress tolerance in three species. Physiologia Plantarum 158:135–151

Campbell LC, Nable RO (1988) Physiological functions of manganese in plants. In: Graham RD, Hannam RJ, Uren NC (eds) Manganese in soils and plants. Klumer Academic Publishers, Dordrecht, pp 139–154

Casimiro A, Barroso J, Pais MS (1990) Effect of copper deficiency on photosynthetic electron transport in wheat plants. Physiol Plant 79:459–464

Cakmak I, Kurz H, Marschner H (1995) Short-term effects of boron, germanium and high light intesity on membrane permeability in boron-deficient leaves of sunflower. Physiol Plant 95:11–18

Caruso C, Chilosi G, Leonardi L, Bertini L, Magro P, Buonocore V, Caporale C, (2001) A basic peroxidase from wheat kernel with antifungal activity. Phytochemistry 58:743–750

Cataldo DA, McFadden KM, Guerinot ML (1996) A novel iron-regulated metal transporter from plants identified by functional expression in yeast. Proc Natt Acad Sci U S A 93:5624–5628

Delhaize E, Katnoka T, Hebb DM, White RG, Rayan RR (2003) Genes encoding proteins of the cation diffusion facilitator family that confer manganese tolerance. Plant Cell 15:1131–1142

Dembitsky VM, Smoum R, Al-Quntar AA, Ali HA, Pergament I, Srebnik M, (2002) Natural occurrence of boron-containing compounds in plants, algae and microorganisms. Plant Sc 163:931–942

Eide D, Broderius M, Feit J, Guerniot ML (1996) A novel iron regulated metal transporter from plants identified by functional expression in yeast. Proc Natl Acad Sci U S A 93:5624–5628

Flowers TJ (1988) Chloride as a nutrient and as an osmoticum. In: Tinker B, Läuchii A (eds) Advances in plant nutrition. Prager, New York, pp 55–78

Fox TC, Guerinot ML (1998) Molecular biology of cation transport in plants. Annu Rev Plant Physiol Plant Mol Biol 49:669–696

Ganie SA, Karmakar J, Roychowdhury R, Mondal TK, Dey N (2014) Assessment of genetic diversity in salt-tolerant rice and its wild relatives for ten SSR loci and one allele mining primer of *salT* gene located on 1st chromosome. Plant Syst Evol 300(7):1741–1747

Gautam S, Rathoure AK, Chhabra A, Pandey SN (2017) Effects of nickel and zinc on biochemical parameters in plants- a review. Octa J Environ Res 5:14–21

Gorham J (1995) Betains in higher plants-biosynthesis and role in stress metabolism. In: Wallsgrove RM (ed) Amino acids and their derivatives in higher plants. Cambridge University Press, Cambridge, pp 171–203

Guerinot ML (2000) The ZIP family of metal transporters. Biochimica et Biophysica Acta (BBA) - Biomembranes 1465:190–198

Graham RD (1983) Effect of nutrient stress on susceptibility of plants to disease with particular reference to trace elements. Adv Bot Res 10:221–276

Hanstein SM, Felle HH (2002) CO_2-triggered chloride release from guard cells intact faba bean leaves. Kinetics of the onset of stomatal closure. Plant Physiol 130:940–950

Hasanuzzaman M, Roychowdhury R, Karmakar J, Dey N, Nahar K, Fujita M (2015) Recent advances in biotechnology and genomic approaches for abiotic stress tolerance in crop plants. In: Devarajan T, Jeyabalan S (eds) Genomics and proteomics: concepts, technologies and applications. Apple Academic Press, Canada, pp 333–366

Hatch MD, Burnell JN (1990) Carbonic Anhydrase Activity in Leaves and Its Role in the First Step of C Photosynthesis. Plant Physiology 93:825–828

Hall JL, Williams LE (2003) Transition metal transporters in plants. Journal of Experimental Botany 54:2601–2613

Henriques FS (2001) Loss of blade photosynthetic area and of chloroplasts photochemical capacity account for reduced CO_2 assimilation rates in zinc-deficient sugarbeet leaves. J Plant Physiol 158:915–919

Heslop-Harrison JS, Roger BJ (1986) Chloride and potassium ions and turgidity in the grass stigma. J Plant Physiol 124:55–60

Hussain SS, Shi B (2014) Role of miRNAs in abiotic and biotic stresses in plants. In: Emerging technologies and management of crop stress tolerance., Biological techniques, vol 1. Elsevier, pp 181–207

Kampfenkel K, Kushnir S, Babiychuk E, Inze D, Van Montagu M (1995) Molecular characterization of a putative *Arabidopsis thaliana* copper transporter and its yeast homologue. J Biol Chem 270:28479–28486

Karthika KS, Rashmi I, Sreekumar PM (2018) Biological functions, uptake and transport of essential nutrients in relation to plant growth. In: Plant nutrients and abiotic stress tolerance. Springer, Singapore, pp 1–49. https://doi.org/10.1007/978-981-10-9044-8_1

Kelley PM, Izawa S (1978) The role of chloride ion in photosystem II 1. Effects of chloride on photosystem II electron transport and hydroxylamine inhibition. Biochem Biophys Acta 502:198–210

Koshiba T, Saito E, Ono N, Yamamoto N, Sato M (1996) Purification and Properties of Flavin- and Molybdenum-Containing Aldehyde Oxidase from Coleoptiles of Maize. Plant Physiology 110:781–789

Kobayashi A, Sakamoto A, Kubo K, Rybka Z, Kanno Y, Takatsuji H (1998) Seven zinc-finger transcription factors are expressed sequentially during the development of anther in petunia. Plant J 13:571–576

Lee S, Aronoff S (1967) Boron in Plants: A Biochemical Role. Science 158 (3802):798–799

Lippard SJ (1999) Free copper ions in the cell. Science 284:748–749

Loneragan JF (1981) Distribution and moment of copper in plants. In: Loneragan JF, Robson AD, Graham RD (eds) Copper in soils and plants. Academic, London, pp 165–188

Marschner H (1995) Mineral Nutrition of Higher Plants. Academic Press, London

Ma JF, Nomoto K (1996) Effective regulation of iron acquisition in graminaceous plants. The role of mugineic acid as phytosiderophores. Physiol Plant 97:609–617

Ma JF, Kusano G, Kimura S, Nomoto K (1993) Specific recognition of mugineic acid ferric complex by barley roots. Phytochemistry 34:599–603

Manthey JJ, Tissarat B, Crowley DE (1996) Root responses of sterile grown onion plants to iron deficiency. J Plant Nutr 19:145–161

Moth T, Ishigaki K, Ohno K, Azuma J (1993) Isolation and characterization of a boron-polysaccharide complex from radish roots. Plant Cell Physiol 34:639–642

Marschner H, Kirkby EA, Cakmak I (1996) Effect of mineral nutritional status on shoot-root partitioning of photoassimilates and cycling of mineral nutrients. Journal of Experimental Botany 47:1255–1263

Mendel RR, Hansch R (2002) Molybdoenzymes and molybdenum cofactor in plants. J Exp Bot 53:1689–1698

Morab H, Koti RV, Chetti MB, Patil PV, Nalini AS (2003) Role of nutrients in inducing rust resistance in soybean. Indian J Plant Physiol 8:85–88

Maksymiec W (1997) Effect of copper on cellular processes in higher plants. Photosynthetica 34:321–342

Naaz S, Pandey SN (2009) Growth and biochemical responses of tomato irrigated with industrial effluent. Res Environ Life Sci 2:91–94

Naaz S, Pandey SN (2010) Effect of industrial waste water on the uptake of certain heavy metals on growth and biochemical responses of lettuce (Lactuca sativa L.). J Environ Biol 31:273–276

Norvell WA, Welch RM (1993) Growth and nutrient uptake by barley (*Hordeum vulgare* L. cv Herta): studies using an N- (2 hydroxyethy) ethylene dinitrilotriacetic acid buffered nutrient solution technique I. Zinc ion requirements. Plant Physiol 101:619–625

Ono T, Onone Y (1991) A possible role of redox-active histidin in the photoligation of manganese into photosynthetic O_2-evolving enzyme. Biochemistry 30:6183–6188

O'Neill MA, Ishii T, Albersheim P, Darvill AG, (2004) Rhamnogalacturonan II: Structure and Function of a Borate Cross-Linked Cell Wall Pectic Polysaccharide. Annual Review of Plant Biology 55:109–139

Pandey SN (2014) Effect of soil sodicity on growth, biochemical constituents and zinc content in wheat plants. J Biol Chem Res 31(1):317–324

Pandey SN (2018) Biomolecular functions of micronutrients toward abiotic stress tolerance in plants. In: Hasanuzzaman M, Fujita M, Oku H, Nahar K, Hawrylak-Nowak B (eds) Plant nutrients and abiotic stress tolerance. Springer, Singapore, pp 153–170

Pandey SN, Gautam S (2009) Effect of zinc supply on its uptake, growth and biochemical constituents in lentil. Indian J Plant Physiol 14:67–70

Pandey N, Pathak GC, Singh AK, Sharma CP (2002) Enzymic changes in response to zinc nutrition. J Plant Physiol 151:1151–1153

Petranyl P, Jendrisak JJ, Burgess RR (1978) RNA polymerase II from wheat germ contains tightly bound zinc. Biochem Biophys Res Commun 74:1031–1038

Pandey SN, Abid M, Abid Ali Khan MM (2018) Diversity, function and stress responses of soil microorganisms. In: Egamberdieva D, Ahmad P (eds) Plant microbiome:stress responses. Microorganisms for sustainability, vol 5. Springer, Singapore, pp 1–17

Pfeffer H, Dannel F, Römheld V (1998) Compartmentation of boron in roots and its translocation to the shoot of sunflower as affected by short term changes boron supply. In: Boron in Soils and Plants. Bell RW, Rerkasem B (eds.). Kluwer Academic Publishers, Dordrecht: 203–207

Polle A, Chakrabarti K, Chakarbarti S, Seifert F, Schramel P, Rennenberg H (1992) Antioxidant and manganese deficiency in needle of Norway spruce (*Picea abies* L.) trees. Plant Physiol 99:1084–1089

Ranieri AM, Cartanga A, Baldan B, Soldatini GF (2001) Iron deficiency affects peroxidase isoforms in sunflower. J Exp Bot 52:25–35

Robinson NJ, Protor CM, Connolly EL, Guerinot ML (1999) A ferric chelate reductase for iron uptake from soils. Nature 397:694–697

Rognes SE (1980) Anion regulation of lupin asparagine synthetase. Chloride activation of glutamine- utilizing reaction. Phytochemistry 19:2287–2293

Roychowdhury R (2014) Crop improvement in the era of climate change. IK International Publishing House, New Delhi, p 496

Roychowdhury R, Tah J (2011) Differential response by different parts of *Solanum melongena* L. for heavy metal accumulation. Plant Sci Feed 1(6):80–83

Roychowdhury R, Karmakar J, Karmakar J, Adak MK, Dey N (2013) Physio-biochemical and microsatellite based profiling of lowland rice (*Oryza sativa* L.) landraces for osmotic stress tolerance. Am J Plant Sci 4(12):52

Roychowdhury R, Khan MH, Choudhury S (2018) Arsenic in rice: an overview on stress implications, tolerance and mitigation strategies. In: Hasanuzzaman M, Nahar K, Fujita M (eds) Plants under metal and metalloid stress. Springer, Singapore, pp 401–415

Roychowdhury R, Khan MH, Choudhury S (2019) Physiological and molecular responses for metalloid stress in rice – a comprehensive overview. In: Hasanuzzaman M, Fujita M, Nahar K, Biswas J (eds) Advances in rice research for abiotic stress tolerance. Woodhead Publishing/ Elsevier, USA, pp 341–369

Rengel Z (1995) Carbonic anhydrase activity in leaves of wheat genotypes differing in zinc deficiency. J Plant Physiol 147:251–256

Sancenon V, Puigs MH, Thiele DJ, Peoarrubia L (2003) Identification of a copper transporter family in *Arabidopsis thaliana*. Plant Mol Biol 51:577–587

Schmidt W, Tillel J, Schikora A (2000) Role of hormone in induction of iron deficiency responses in *Arabidopsis* roots. Plant Physiol 122:1109–1118

Schnabl H (1980) Anion metabolism as correlated with volume changes in guard cell protoplasts. Z Naturforsch 35c:621–626

Shrotri CK, Tewari MN, Rathore VS (1980) Effect of zinc nutrition on sucrose biosynthesis in maize. Phytochemistry 19:139–140

Slooten L, Capiau K, Van Camp W, Van Montagu M, Sybesma C, Inze D (1995) Factors Affecting the Enhancement of Oxidative Stress Tolerance in Transgenic Tobacco Overexpressing Manganese Superoxide Dismutase in the Chloroplasts. Plant Physiol 107:737–750

Singh K, Pandey SN (2011) Effect of nickel-stresses in uptake, pigments and antioxidative responses of water lettuce, *Pistia stratioes* L. J Environ Biol 32:391–394

Schon MK, Novacky A, Blevins DG (1990) Boron induces hyperpolerization of sunflower root cell membranes and increases membrane permeability to K^+. Plant Physiol 93:566–571

Seo M, Koshiba T (2002) The complex regulation of ABA biosynthesis in plants. Trends Plant Sci 7:41–48

Sharma PN, Kumar N, Bisht SS (1994) Effect of zinc deficiency on chlorophyll contents, photosynthesis and water relations of cauliflower plants. Photosynthetica 30:353–359

Sharma CP (2006) Plant Micronutrients. Science Publishers, Enfield

Sharma CP, Sharma PN (1987) Mineral nutrient deficiencies affect plant water relations. J Plant Nutr 10:1637–1643

Shikanai T, Muller-Moul P, Munekage Y, Niyogi KK, Pilon M (2003) PAA1, P-type ATPase of *Arabidopsis* functions in copper transport in chloroplasts. Plant Cell 15:1333–1346

Smith BN (1984) Iron in higher plants: storage and metabolic rate. J Plant Nutr 7:759–766

Stiles W (2013) Trace elements in plants. Cambridge University Press, New York

Srivastava NK, Mishra A, Sharma S (1997) Effect of zinc deficiency on netphotosynthetic rate, ^{14}C partitioning and oil accumulation in leaves of pepperment. Photosynthetica 33:71–79

Thomine S, Wang R,Ward JM, Crawford NM, Schroeder JI (2000) Cadmium and iron transport by members of a plant metal transporter family in Arabidopsis with homology to Nramp genes. Proceedings of the National Academy of Sciences 97 :4991–4996

Thomine S, Lelievre F, Debarbieux E, Schroeder JI, Barbier-Brygoo H (2003) At NRAMP3, a multispecific vacuolar metal transporter involved in plant responses to iron deficiency. Plant J 34:685–695

Tej L, Zeiger E (2002) Plant physiology. Sinauer Associates, 3rd ed. Publisher, pp 103–124. ISBN: 0-878930831-1

Terry N (1977) Photosynthesis, growth and role of chloride. Plant Physiol 60:69–75

Treeby M, Marschner H, Römheld V (1989) Mobilization of iron and other micronutrient cations from a calcareous soil by plant-borne, microbial, and synthetic metal chelators. Plant and Soil 114:217–226

Taylor IB, (1991) genetics of ABA synthesis. In: Abscisic Acid, Physiology and Biochemistry (Davis WJ, Jones HG, eds.). Bios Publishers, Oxford 23–37

Van Wiren W, Capiau K, Van Montgu M, Inze D, Slooten L (1996) Enhancement of oxidative stress tolerance in transgenic tobacco plants overproducing Fe- superoxide dismutase in chloroplasts. Plant Physiol 112:1703–1714

Waters BM, Blevins DG, Eide DJ (2002) Characterization of FRO1, a Pea Ferric-Chelate Reductase Involved in Root Iron Acquisition. Plant Physiology 129:85–94

Woods WG (1996) Review of possible boron speciation relating to its essentiality. The Journal of Trace Elem Exp Med 9:153–163

White PJ, Broadley MR (2001) Chloride in soils and its uptake and movement within in the plants. A review. Ann Bot 88:967–988

Winkler RG, Palacco JC, Blevims DG, Randall DD (1985) Enzymatic degradation of allantoate in developing soybeans. Plant Physiol 79:878–893

Williams LE, Pittman JK, Hall JL (2000) Emerging mechanisms for heavy metal transport in plants. Biochimica et Biophysica Acta (BBA) - Biomembranes 1465:104–126

Wu G, Wilen RW, Robertson AJ, Gusta LV (1999) Isolation, Chromosomal Localization, and Differential Expression of Mitochondrial Manganese Superoxide Dismutase and Chloroplastic Copper/Zinc Superoxide Dismutase Genes in Wheat. Plant Physiol 120:513–520

Wu Z, Liang F, Hong B, Young JC, Sussman MR, Harper JF, Sze H (2002) An Endoplasmic Reticulum-Bound Ca /Mn Pump, ECA1, Supports Plant Growth and Confers Tolerance to Mn Stress. Plant Physiol 130:128–137

Yachandra VK, De Rose VJ, Latimer MJ, Mukerji I, Sauer K, Klein MP (1993) Where plants make oxygen: a structural model for the photosynthetic oxygen-evolving manganese complex. Science 260:675–679

Yan F, Schubert S, Mengel K (1992) Effect of low root medium pH on the net proton release, root respiration and root growth of corn (*Zea mays* L.) and broad beans. Plant Physiol 99:415–421

Yi Y, Guerinot ML (1996) Genetic evidence that induction of root Fe (III) chelate reductase activity is necessary for iron uptake under iron deficiency. Plant J 10:835–844

Yu Q, Rengel Z (1999) Micronutrient deficiency influences plant growth and activities of superoxide dismutase in narrow-leafed lupins. Ann Bot 83:175–182

Yu G, Osborne LD, Rengel Z (1998) Micronutrient deficiency changes activities of superoxide dismutase and ascorbate peroxidase in tobacco plants. J Plant Nutr 21:1427–1437

Yu Q, Hlavacka A, Matoh T, Volkmann D, Menzel D, Goldbach HE, Baluška F (2002) Short-Term Boron Deprivation Inhibits Endocytosis of Cell Wall Pectins in Meristematic Cells of Maize and Wheat Root Apices. Plant Physiol 130:415–421

Zaid H, El Morbat R, Diem HG, Arahou M (2003) Does ethylene mediate cluster root formation under iron deficiency. Ann Bot 92:673–677

Zhang N, Portis AR (1999) Mechanism of light regulation of Rubisco: A specific role for the larger Rubisco activase isoform involving reductive activation by thioredoxin-f. Proceedings of the National Academy of Sciences 96:9438–9443

Zheng SJ, Tang C, Avakawa Y, Masaoka Y (2003) The responses of red clover (*Trifolium pratense* L.) to iron deficiency: a root Fe (III) chelate reductase. Plant Sci 164:679–687