# Role of Plant Nutrients in Plant Growth and Physiology

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A mineral element is considered as essential based on the criteria of essentiality given by Arnon (1954) according to which a plants cannot complete it life cycle due to its deficiency, the deficiency must be corrected only by supplying the element in question and when the element is directly involved in the metabolism of the plant. Based on these criteria, sixteen elements so far were identified as essential: carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, zinc, copper, boron, molybdenum and chlorine. Of these C and at times S are taken up from air as $CO_2$ and $SO_2$ and oxygen and hydrogen are taken up in form of water. The rest of the elements are taken up from the soil solution as mineral nutrients.

The mineral nutrient elements play essential roles that can be broadly grouped as follows:

(i) As constituent of cell structures and cell metabolites.

(ii) In cell osmotic relations and turgor related processes

(iii) In energy transfer reactions

(iv) In enzyme catalyzed reactions

(v) In plant reproduction

Based on their requirements plant nutrients have been classified as macronutrients and micronutrients. Elements required by plants in concentration exceeding one part per million (ppm) are called macronutrients C, H, O, N, P, K, Ca, Mg, S. Those nutrients required in concentration below 1 ppm are micronutrients eg. Fe, Mn, Cu, Zn, Mo, B and Cl. This classification is arbitrary and has been found to differ with different plant groups and species. Physiologically also it is difficult to justify this classification of plant nutrients into macronutrients and micronutrients. Classification of plant nutrients according to biochemical

behaviour and functions therefore seems more appropriate. Mengel and Kirkby (1987) have classified plant nutrients into four groups according to their biochemical functions.

1. The first group includes C, H, O, N and S which are taken up as ions from the soil solution or in gaseous form from the atmosphere as $CO_2$, $HCO_3^-$, $H_2O$, $O_2$, $NO_3^-$, $NH_4^+$, $N_2$, $SO_4^{2-}$ and $SO_2^-$ These elements form the major constituents of organic material. They form the essential elements of atomic groups which are involved in enzymic processes: C and O as components of carboxylic group; N and O in oxidation-reduction processes; N in the form of $NH_2$, NH, and $N^+$ and S in the form of SH group. They are thus assimilated by oxidation-reduction reactions and are reactants in all fundamental processes.
2. The second group includes P and B which show similarity in biochemical behaviour. They are absorbed from soil solutions as anions or acid: phosphates, boric acid or borate and silicate. They occur as such in plant cell or are bound to the alcohol group of sugars forming phosphates-borate- esters. The phosphate esters are involved in energy transformations and sugar translocation.
3. The third group is made up of K, Na, Ca, Mg, Mn and Cl. These are present in free ionic state or are absorbed to organic anions (Ca) or present as chelates (Mg). They have nonspecific ionic cellular functions such as establishing osmotic potential in cell organelles or maintaining ionic balance or controlling membrane permeability, electropotentials and conductance ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$). In addition these nutrients carry out specific functions in which the ions bring about structural influences by binding to organic molecules particularly enzyme molecules and altering their conformation for optimum activation ($K^+$, $Mg^{2+}$, $Ca^{2+}$, $Mn^{2+}$). By formation of Lewis acid, $Mg^{2+}$, $Ca^{2+}$ and $Mn^{2+}$ are also able to accept an electron pair and thus catalyze or polarize reactive groups.
4. The fourth group consists of Fe, Cu, Zn and Mo which are predominantly present in the plants as chelates incorporated in prosthetic group and thus enable electron transport by

valency change in a number of enzyme reactions as they are able to accept electron pair and thus catalyze reactive enzyme groups.

## Physiological Roles of Macronutrients

### Nitrogen

After C, H and O, nitrogen is the fourth most abundant element occurring as a major structural constituent of plants. Combined with carbon, hydrogen, phosphorus and sulphur, it functions as a structural constituent of a wide variety of organic nitrogenous compounds of plants like proteins, nucleotides, porphyrins and alkaloids. In order to be incorporated into organic structures and to fulfill its essential functions as a plant nutrient, nitrogen has to be reduced to ammonium. Reduction of nitrate to ammonium involves firstly a two electron reduction of $NO_3$ to $NO_2$ catalyzed by nitrate reductase and a second step involving six electron reduction of nitrite to ammonium catalyzed by nitrite reductase. Glutamine and asparagine constitute the main assimilatory amino acids formed by amination of glutamate and aspartate.

Three main N fractions involved in N metabolism are: inorganic N, low molecular weight organic N and macromolecular organic N compounds (Table 1). In green plants, protein N is the largest N fraction and amounts to about 80 to 85% of total N. The N of nucleic acid makes up about 10% and the soluble amino N about 5% of the total N present in plant material. In order to minimize the carbon loss, low molecular weight nitrogen rich compounds such as glutamine, asparagine (amides), arginine (amino acid) and the ureide allantoin are dominant products. These low molecular weight organic nitrogen compounds are the important storage and long distance transport forms. In higher plants low-molecular weight nitrogen components are precursors of amine synthesis and also act as intermediates between the assimilation of inorganic nitrogen and the synthesis of high molecular weight

compounds. Amines are the components of lipid fraction of biomembranes eg. ethanolamine. Low molecular weight organic nitrogen compounds are also involved in osmoregulation in higher plants. Under saline conditions or water stress amino acid derivatives proline and glycine betaine counteract the high concentrations of $Na^+$ and Cl and protect enzymes from inactivation.

The amino acids form the building blocks of proteins. The amino acids and the sequence in which they join to produce a polypeptide and proteins is determined genetically. Through the process known as *transcription*, the genome (DNA) produces a template for the synthesis of protein in the form of mRNA. The sequence of nucleotides in the mRNA determines the sequence of amino acids in a protein. The functional properties of a protein are determined by *the folding of the polypeptide chains that provides them a three dimensional structure*. Many proteins form ligands with metal cofactors to acquire high catalytic efficiency. As intrinsic integrated components of the plasma membranes, the proteins function as ion channels across the membranes. A special class of proteins, known as defense related proteins, such as *lectins* and *systemins* contribute to plant's defense mechanism against pathogens and mechanical injury (wounding).

Amino acids perform several other functions besides functioning as building blocks of proteins. They may undergo decarboxylation and generate precursors of polyamines, which protect the cellular membranes against toxic effects of superoxide ions, inhibit ethylene biosynthesis and function as signalling molecules. Nicotianamine derived from L-methionine functions as a precursor of phytosiderophores involved in uptake of ferric chelates by strategy II plants and in iron homeostasis.

As a constituent of the purine and pyrimidine bases, nitrogen plays a key role in metabolism of nucleic acids. The purine and pyrimidine bases bind to pentose sugars producing

nucleosides, which link up through phosphodiester bonds to produce nucleotides that are polymerized to produce the nucleic acids (RNA, DNA).

Nitrogen is a structural component of several alkaloids known for their pharmacological properties and also a protective role against tissue damage caused by herbivores. Most alkaloids are synthesized from amino acids - phenylalanine, tyrosine, tryptophan, arginine and lysine.

Several roles have recently been attributed to nitric oxide (NO), produced primarily by conversion of L-arginine to L-citruline, catalyzed by nitric oxide synthetase. Nitric oxide is a highly diffusible gas that functions as a signal molecule in response to a wide range of external and internal factors and also contributes to disease resistance and protection against toxic effects of oxidants. Variations were observed in the antioxidant system in nitrogen deficient plants which were also mediated by NO signaling showed that the biosynthesis of phenylpropanoids with antioxidant function was increased, probably to support the oxidative status under nitrogen deficiency.

**Phosphorus**

The uptake of phosphorus is active and unlike nitrate and sulphate, phosphate is not reduced in plants but remains in its highest oxidized form. After uptake mainly as $H_2PO_4^-$, it remain either in its inorganic form (Pi) or as organophosphorus compounds. Phosphate is bound in a diester linkage (C-P-C) to form essential compounds of biological membranes. It is esterified through hydroxyl group to carbon unit (C-O-P) as a simple organic phosphate ester (e.g. Sugar phosphate) or attached to another phosphate by the energy rich pyrophosphate bond P~P e.g. ATP. Another organic P compound is phytin a storage form which occurs as Ca and Mg salts of phytic acid formed during seed formation.

The structural role of phosphorus is as a constituent of biomembranes and nucleotides. It is a major component of the lipids of the plant membranes occurring as phospholipids eg.

phosphatidyl choline. The phospholipids form the central hydrophobic barriers of the cell membrane and the ease with which they move freely in the plane of the membrane and undergo reorientation within the lipid bilayer account for the fluidity of the membranes. Gniazdowska et al. (1999) reported that the decrease in phospholipid concentration and modification of relative composition of membrane would accentuate lipid peroxidation.

Structurally phosphorus is involved in linking up of nucleosides to produce nucleotides that polymerize to produce long chains of nucleic acids nucleic acids- DNA molecules which are carriers of genetic information and RNA which is responsible for translocation of genetic information. The phosphate groups join the 5′ carbon of one nucleoside to 3′ carbon of the next nucleoside by a covalent phosphodiester bond. The directional nature of these bonds accounts for two distinct ends (5′ or 3 ′) of the nucleic acids.

Phosphorylated compounds that contain pyrophosphate bonds (Ⓟ~Ⓟ), function as an energy conserving mechanism. The most important compound is adenosine triphosphate (ATP) through which energy can be conveyed to various endergonic process such as active uptake and biosynthesis of organic compound by transfer of phosphoryl group. . Energy rich pyrophosphate bond of adenine triphosphates can also be transferred to other nucleoside phosphates (UDP-Ⓟ; GDP~Ⓟ). Hydrolysis of pyrophosphate bond yields energy that activates enzymes and drives reactions which are otherwise energetically unfavorable. Energy released by hydrolysis of pyrophosphates by proton pumping phosphorylases located in the tonoplast drives the proton pump leading to acidification of the vacuole and generation of electrochemical gradients driving membrane transport. Phosphorylation of enzyme proteins by protein kinases plays an important role in regulation of enzyme activities (eg. nitrate reductase, phosphoenolpyruvate carboxylase).

The role of phosphorus in energy transduction also stems from its role as a structural constituent of the coenzymes NAD, NADP, FAD and FMN, which function as redox agents during mitochondrial electron transport. Thiamine pyrophosphate, with a high-energy group transfer potential, plays a key role in carbohydrate metabolism. Coenzyme A is involved in the metabolism of fats, proteins and carbohydrates. Several phosphorus containing compounds such as inositol-1, 4, 5-triphosphate, cAMP, cGMP and phosphatidic acid function as second messengers or signalling molecules. They have also been shown to be involved in activation of phospholipase C and opening and closing of transmembrane channels for $K^+$, $Na^+$ and $Ca^{2+}$.

Phosphate esters play an important role in cellular metabolism and photosynthetic pathways. As many as 50 sugar phosphates are known from plants. Plants have two major phosphate pools. One of these pools, the *hexose phosphate pool*, is made up of three intermediates of the glycolytic pathway – glucose-6-phosphate, glucose-1-phosphate and fructose-6-phosphate, maintained in equilibrium by phosphoglucomutase and glucose-6-phosphate isomerase. This pool provides the precursor for synthesis of sucrose and starch. The other pool -the *triosephosphate/ pentosephosphate metabolic pool*, is made up of several sugar phosphates maintained in equilibrium through enzyme catalyzed interconversions. This pool contributes to the energy conserving reactions (ATP synthesis) during the later phase of glycolysis, and also for the synthesis of nucleic acids. Fairly large quantities of phosphorus may be stored in seeds in the form of a mixed cation salt of *myo*-inositol hexaphosphoric acid, commonly known as *phytate*. The function of phytate is evident during seed germination where it provides the large requirement for nutrients. Phytates form a major site for the storage of K, Mg and Ca. As phytic acid has a high affinity for Zn, Fe and heavy metals, it binds to them, reducing their free concentration in the cytoplasm.

**Potassium**

Potassium is taken up at a very high rate by the plants due to the high permeability of plant membranes to $K^+$. A closely knit regulation between the water channels and the potassium uptake channels helps to maintain plant water status. It is the most abundant in cytoplasm and helps in neutralizing insoluble macromolecular anions to maintain cation anion balance and osmoregulation in plant cell. Its large accumulation in cell vacuoles contributes to turgor driven extension growth of cells. Deficiency of potassium leads to decrease in turgor and cell size which is reflected in decrease in leaf area and stem elongation. Inadequate supply of potassium restricts meristematic growth and cambial activity. Beneficial effect of potassium on cambial growth and wood formation has been suggested to be related to potassium involvement in osmoregulation in the expanding cambial cells. Potassium plays a role in regulation of stomatal opening. Activation of membrane bound proton pumping ATPases causes increased uptake of $K^+$ which increases the osmotic pressure, causing uptake of water from the adjacent cells. The resulting increase in turgor leads to opening of stomata. Reversal of the process in dark tends to close the stomata.

In cytosol and chloroplasts, where potassium concentrations is sufficiently high (100-200 µM), potassium neutralizes the anionic charges ($NH_3^-$, $Cl^-$, $SO_4^-$). It also forms electrostatic bonds with the carboxylic groups of organic acids produced during cellular metabolism. Neutralization of acid groups by potassium leads to stablization of cytosolic and chloroplastic pH to a slightly alkaline reaction (pH 7 to 8), which is favored for optimal activation of most enzymes localized in cytoplasm or chloroplasts.

Potassium activates about 50 enzymes by inducing conformational changes in enzyme protein. Potassium is an activator of formate-formyl tetrahydrofolate synthetase and succinyl-Co A synthetase. Together with $Mg^{2+}$, it activates acetic thiokinase, pyruvate kinase and glutathione synthetase. It has been suggested that potassium activation of enzymes involve a conformational change in the enzyme protein which augments the rates of catalysis and in

some cases the affinities of the enzymes for the substrates. Low activities of certain enzymes such as Rubisco in potassium deficient plants have been attributed to potassium effect on protein synthesis, that involves a role of potassium in binding of tRNA to the ribosomes.

Potassium also plays a important role in providing tolerance to plants exposed to various biotic and abiotic stresses including diseases, pests, drought, salinity, cold and frost and water logging. Potassium effect on cells turgor also accounts for its role in light driven movements. In cereals, potassium is known to contribute to mechanical strength of the straw that provides protection against lodging. Potassium also improves resistance of plants against pathogenic fungi, nematodes and other microorganisms.

**Sulphur**

Plants take up sulphur largely from soil as sulphate ($SO_4^{2-}$) and assimilate it into several organic compounds. Conversion to organic sulphur compounds may take place both as $SO_4^{2-}$ and after its reduction to sulphide ($S_2^{2-}$). The reduced and oxidized forms are easily interconvertible ($SO_4^{2-} \leftrightarrow S_2^{2-}$). Sulphate is directly incorporated into sulpholipids, polysaccharides, glucosinolates and certain phytoalexins. Reduction of sulphide leads to its incorporation into many other organic compounds such as amino acids (cysteine and methionine), coenzymes and secondary metabolites. Both cysteine and methionine are essential constituents of plant proteins. These amino acids acquire added significance because animals and humans lack the ability to reduce sulphur and depend on plants for meeting their dietary requirements. Decrease of storage proteins (albumin, globulins, glutelins and prolamins) especially globulins, has been reported in response to sulphur deficiency in soyabean seeds.

The cysteine residues of proteins are critical for their structure and function. Oxidation of the thiol (SH) group of two cysteine residues of a protein produces a covalent disulphide bond (S-S). The disulphide bonds are involved in determining the tertiary structure of proteins.

Interconversion of thiol and disulphide bonds also provides a mechanism for regulation of enzyme activities. Cysteine functions as a precursor of some low molecular weight peptides of high biological activity. Important amongst these are glutathione and thioredoxins. Glutathione (γ Glu-cys-gly) is a tripeptide. Predominantly present in the reduced form (GSH), it can be readily converted to its oxidized form (GSSG), a property which enables it to function as a buffer of cell's redox potential. Enzymatic interconversion of GSH and GSSG provides an efficient mechanism for regeneration of ascorbate oxidized to dehydroascorbate by ascorbate peroxidase as a part of cells antioxidant mechanism. Glutathione also offers protection to plants against toxic effects of xenobiotics.

Sulphur offers protection against toxic accumulation of heavy metals by phytochelatins. Plants subjected to excess concentrations of heavy metals show induction of phytochelatin synthase, which catalyzes the synthesis of the low molecular weight polypeptides known as *phytochelatins* from glutathione. A group of cysteine rich polypeptides known as *metallothioneins* are also formed in response to toxic accumulation of heavy metals (Cd, Zn). Phytochelatins and thioneins provides a mechanism for their detoxification by binding of the free heavy metal cations to their thiol groups.

The sulphur thioredoxins and the assocoaited enzyme thioredoxin reductase play an important role in regulation of enzyme activities. Thioredoxin mediated thiol-disulfide reduction is also involved in the activity of *peroxiredoxins*, which not only catalyze peroxidation reactions but also play a role in antioxidant defense mechanism and modulation of redox signaling during development.

Sulphur binds to iron to produce iron-sulphur clusters (Fe-S), that form integral part of several iron proteins. The low molecular weight (9 kD) electron carrier protein ferredoxin that is widely and abundantly present in plants, plays a major role as a donor or acceptor of electrons in plant metabolism .

Sulphur, in reduced form, is also a constituent of many vitamins and coenzymes –biotin coenzyme A, thiamine pyrophosphate. Biotin functions as a mobile carbonyl group carrier in a variety of enzyme catalyzed carboxylation reactions involved in lipid biosynthesis, leucine catabolism and isoprenoid metabolism. Secondary metabolites such as glucosinolates, stored in plant vacuoles of brasicaceae and several other dicotyledonous families, and of allin, present in *Allium* sp are also sulphur compounds.

**Calcium**

Calcium occurs in plant tissue as free $Ca^{2+}$, or as $Ca^{2+}$ absorbed to carboxylic, phosphorylic and phenolic hydroxyl groups present as Ca -carbonate, -phosphate and -oxalate. The uptake of $Ca^{2+}$ is very slow as it is absorbed only by young root tips. The uptake is a passive process and is competitively depressed by presence of $K^+$ and $NH_4^+$. A low level of calcium is maintained in the cytoplasm to prevent unfavorable interactions with other nutrient ions ($PO_4^-$, $Mg^{2+}$) and inactivation of enzymes. It is also a prerequisite for its functioning as a second messenger. Low concentration of calcium in cytoplasm (~0.2 μM) is maintained by regulation of $Ca^{2+}$ fluxes across the cellular and sub cellular membranes involving membrane transporters ($Ca^{2+}$-ATPase). Efflux of $Ca^{2+}$ from cytosol into the vacuole involving V-$Ca^{2+}$-ATPase activity builds up high concentration of $Ca^{2+}$ in vacuoles, where it plays a role in neutralization of anions and in osmoregulation. Formation of Ca-oxalate in vacuoles is important for osmoregulation of cells. Calcium thus plays an electrochemical role by functioning as counter ion for anions of inorganic and organic acids. Pumped into the vacuole by the membrane transporter (V-$Ca^{2+}$-ATPase), calcium neutralizes the anions- phosphate, citrate, malate and/or oxalate that may get accumulated in vacuoles in high concentrations.

Calcium functions as a structural constituent of cell walls since a high proportion of total calcium is located in the cell wall (apoplasm) in the region of middle lamella and exterior surface of plasmamembrane. Calcium is bound to RCOO-group of polygalacturonic acid

(pectin) in the middle lamella and thus it perfoms the most essential function of regulating membrane permeability and strengthening the cell walls. When calcium supply is limiting, the growth of middle lamella during the cell expansion is inhibited. Calcium pectate makes the tissue resistant to degradation by polygalacturonase. Ability of calcium to act as a bridge between phosphates and carboxyl groups of phospholipids and proteins accounts for its role in providing stability to cellular membranes. Calcium deprivation of plants leads to disintegration of membrane structure, loss of $Ca^{2+}$ compartmentation and leakage of low molecular weight solutes. Therefore calcium deficiency, results in impairment of membrane permeability and their disintegration. High calcium content in fruits therefore increases firmness of fruit. During ripening intracellular redistribution of $Ca^{2+}$ results from increased activity of polygalacturonase so that the ethylene generating system is activated thus enhancing fruit ripening.

Calcium plays an important role in cell extension. Root growth is inhibited by calcium deficiency. Pollen tube growth and direction of pollen tube is controlled by extracellular calcium gradient. Calcium regulates selectivity of ion uptake and prevents solute leakage from cytoplasm by its membrane protecting effect. Calcium is present in very small amounts in cytoplasm and this is important as calcium inhibit enzymes located in cytoplasm and chloroplast eg. PEP carboxylase and hexodiphosphatase. Calcium increases activity of certain enzyme like α amylase, phospholipase and ATPases. Activation of α- amylase in aleurone layers by gibberellic acid and its inhibition by abscisic acid is attributed to their effect on transport of calcium to endoplasmic reticulum, which forms the site for the synthesis of the enzyme. Mitochondrial enzymes may be activated by calcium eg. Glutamate dehydrogenase. Calcium plays a regulatory role by activating biochemical events in response to environmental stresses, mechanical stimuli and pathogen infections (Bush 1995; Knight 2000).

A recent role assigned to calcium is that of a second messenger in plant cell growth and development. Perception of stress signals cause transient opening of calcium channels and pumping of calcium into the cytoplasm causing increase in its cytosolic concentration. This activates calcium binding proteins such as calmodulin. Calmodulin is a polypeptide which binds four $Ca^{2+}$, forming a compact structure, which is heat stable and insensitive to pH changes. Calmodulins are also involved in synthesis of actin filaments, cell division cycle and pollen-stigma interaction in plants. Binding of $Ca^{2+}$ to calmodulin changes its tertiary structure exposing a patch of methionine, leucine and phenylalamine involved in binding of calmodulin to the target proteins and their activation. Calmodulin is involved in $Ca^{2+}$-dependent responses to light, gravity, mechanical stress, phytohormones, pathogens, osmotic stress, salinity, heavy metals, xenobiotics, annoxia, oxidative stress, temperature stress as well as phospholipid signaling. The calcium binding protein calmodulin plays a key role in regulation of free calcium in cytosol and enzyme activation such as $Ca^{2+}$ dependent protein kinases. Calmodulin is known to activate several higher plant enzymes. It activates a number of enzymes like cyclic nucleotide phosphodiesterase, adenylate cyclase, NAD kinase including $Ca^{2+}$ ATPases and protein kinases involved in cell signaling.

**Magnesium**

Even though abundant in soil solution, magnesium ($Mg^{2+}$) is taken up by plants in much lower amounts than the other cationic macronutrients. This is possibly because of strong cation competition in uptake and lack of magnesium transporters in plasmalemma. The uptake of $Mg^{2+}$ is depressed by low pH and cations like $K^+$, $NH_4^+$, $Ca^{2+}$ and $Mn^{2+}$. The uptake rate is very slow and passive. Magnesium performs very diverse functions. The function of magnesium is related to its mobility within cells. A major function is its role as the central atom of chlorophyll molecule. A central magnesium atom is coordinated to the nitrogen atoms of the four modified pyrrole rings forming a porphyrin like structure. Chlorophyll

magnesium may constitute 10% or more of the total leaf magnesium. In leaf cells 25% of total protein is localized in chloroplasts and therefore magnesium deficiency results in poor chlorophyll content, size and function of the chloroplasts including electron transfer in photosystem II. Magnesium is important for structural integrity of ribosomes and binding of the ribosomal aggregates to t-RNA, a process necessary for protein synthesis.

Only a relatively small proportion of total plant $Mg^{2+}$ (20%) is required for various function in chloroplasts and cytoplasm. The rest of $Mg^{2+}$ occurs as counter ions for organic acid anions and inorganic anions in the vacuole and for pectates in the middle lamella of cell walls. Like potassium, magnesium is also important in maintenance of ionic balance and stabilization of pH. Vacuolar concentration of magnesium is particularly important for osmoregulation and turgor driven cell growth.

Magnesium is an activator of several enzymes. Some of these are activated by $Mg^{2+}$ along with another cation (usually $K^{+}$). In most cases, activation by magnesium is not specific and can be achieved, to varying extents, by other cations, mostly $Mn^{2+}$. Most magnesium activated enzymes catalyze transfer of a phosphate group or a carboxyl group. Magnesium functions in enzyme activation in two ways. In some enzymes, it functions as a freely dissociable cofactor. In others, it binds to the substrate modifying it to a form that is more favourable to enzyme- substrate interaction. ATPases, phosphorylases and phosphokinases belong to the second category. $Mg^{2+}$-ATP, and not free ATP, forms the substrate for ATPases. The high concentration of $Mg^{2+}$ are required in chloroplasts and cytoplasm to maintain a high pH to form the Mg-ATP complex which can be utilized by the active sites of ATPases for the transfer of energy rich phosphoryl groups. The synthesis of ATP has a requirement for $Mg^{2+}$ as a bridging component between ADP. In plants that are adequately fed with magnesium, essentially all nucleoside triphosphates occur in the form of their magnesium complexes. The enzyme fructose-1,6-diphosphatase and RuBP carboxylase

requires $Mg^{2+}$ and high pH for optimum activity. Key enzyme glutamate synthetase has magnesium requirement. Magnesium is also required for RNA polymerase and hence formation of RNA. Deficiency of magnesium therefore depresses protein synthesis.

**Physiological Roles of Micronutrients**

**Iron**

Iron is a transitional metal that exists in two oxidation states, ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$). The easy conversion of the two forms ($Fe^{2+} \leftrightarrows Fe^{3+}$) accounts for its role in a wide range of redox reactions. Iron has high affinity for oxygen and forms stable complexes with organic ligands. It acquires high biological activity by binding to proteins. Iron proteins function as enzymes catalyzing redox reactions and as electron carriers in photosynthetic and mitochondrial electron transport systems. Iron is bound to the apoprotein in four forms:

(a) It forms ionic bonds with the protein amino acids; e.g. Superoxide dismutase (Fe-SOD). Bonds are also formed between two coupled iron atoms and a protein e.g. alternative oxidase.

(b) Iron ions form coordination bonds with sulfide ions and binds to the apoprotein in the form of iron-sulfur clusters (Fe-S, 2Fe-2S, 4Fe-4S, as ferredoxin.

(c) Iron sulfur cluster along with a flavin nucleotide (FMN or FAD) forms the cofactor; e.g. succinic dehydrogenase.

(b) Iron ion is chelated to nitrogen of the four pyrrole groups of porphyrin IX to form a heme prosthetic group; e.g. catalases, peroxidases and cytochrome c oxidase.

Iron is a cofactor of many di-oxygenases and mono-oxygenases, which catalyze the incorporation of oxygen ($O_2$) directly into the substrates. Iron dioxygenases are best exemplified by lipoxygenases that are involved in the metabolism of hydroperoxy fatty acids, and production of oxylipins, derivatives of which function as signaling molecules. Some iron

containing dioxygenases require an additional substrate, generally 2-oxoglutarate. Several iron containing gibberellin oxidases belong to this category. The iron enzyme 1-aminocyclopropane-1-carboxylic acid oxidase, involved in ethylene biosynthesis, is an ascorbate dependent dioxygenase. Several $P_{450}$ mono-oxygenases are involved in biosynthesis of gibberellins and jasmonic acid. Many genes encodcoding far the cytochrome $P_{450}$ monooxigenases (the CYP gene family) have been cloned and characterized.

Iron enzymes and electron carrier proteins are essential components of mitochondrial and photosynthetic electron transport. Mitochondrial electron transport involves transfer of electrons from NADH and $FADH_2$, produced during the citric acid cycle, to molecular oxygen through the electron carrier proteins localized in the mitochondrial membrane which contain iron as an integral constituent. Transport of electrons through the electron carrier proteins generate a proton motive force required for the synthesis of ATP (oxidative phosphorylation). Iron is essential for harvesting of solar energy and transport of electrons resulting from splitting of water ($H_2O$) through photosystem II and photosystem I. It is a constituent of the PSII reaction center and that of ferredoxin, the terminal component of the electron transport chain of PSI. The former contains iron in the ionic form and the latter in the form of iron-sulfur (4Fe-4S) cluster. Transport of electrons from PSII to PSI is linked through the heme protein complex cytochrome *bf* and the copper protein plastocyanin.

Iron is a constituent of enzymes involved in nitrogen metabolism. In the reduction of nitrate to ammonium two iron enzymes are involved - nitrate reductase and nitrite reductase. Nitrate reductase has three domains- heme, molybdopterin and flavin. Nitrite reductase is a 4Fe-4S siroheme. Glutamate synthase (GOGAT), which converts glutamine to glutamate also requires iron for catalysis. In legumes iron also acts as a cofactor of dinitrogenase and dinitrogen reductase in fixation of atmospheric nitrogen. The inactivation of nitrogenase is prevented by iron protein leghemoglobin, which has higher affinity for $O_2$, Iron fertilization

of nodulating legumes benefits both dry matter production and nitrogen contents. Some important iron enzymes of higher plants and reactions catalyzed by them are listed in Table 2. Iron is important component of the electron transport chain in chloroplasts and mitochondria and deficiency of iron impairs the electron transport and leads to the production of ROS. The $Fe^{3+}/Fe^{2+}$ redox potential imparts a dual role to iron in free radical chemistry. Thus it functions as a prooxidant by generating the highly toxic $OH^{\cdot}$ radical on one hand and at the same time it acts as an antioxidant by being a constituent of several antioxidant enzymes. A high level of iron in plant tissue may be responsible for initiation of oxidative stress thereby increasing the production of toxic oxygen species and extensive cellular damage. This is so because the powerful oxidant $OH^{\cdot}$ is produced by the iron catalyzed Haber-Weiss reaction. Free $Fe^{2+}$ reacts with $H_2O_2$ to produce hydroxyl radicals (Fenton reaction). The $Fe^{3+}$ produced by Fenton reaction, on reacting with superoxide ions, is cycled back to $Fe^{2+}$

$$Fe^{3+}\ O_2^{\bullet-\cdot} \leftrightarrow\ O_2 + Fe^{2+}$$

$Fe^{2+}$ may also react with molecular oxygen ($O_2$) to produce still more toxic compounds such as ferryl ($Fe^{2+}O$) or perferryl ($Fe^{2+}\ O_2$). These highly reactive oxygen species cause damage to membrane lipids, proteins, and DNA and induce mutations. Enhanced iron accumulation stimulates free radical reactions by binding to critical cell constituents such as proteins, phospholipids and DNA. Another way iron could contribute to production of ROS is through action of lipoxygenase. This iron enzyme may also catalyze the production of $^1O_2$.

While free ionic iron accelerates the generation of reactive oxygen species iron proteins contributes to their effective detoxification as an important constituent of heme enzymes (CAT, POD and APX) or non-heme enzymes Fe-SOD. The oxidative stress induced by iron deficiency occurs as the activities of some enzymes involved in scavenging ROS decrease. The iron isoenzymes of superoxide dismutase (Fe-SOD) carries out the detoxification of $O_2^-$ by dismutating them to $H_2O_2$. Another Fe enzyme alternative oxidase (AOX) of the

mitochondrial ETC provides an alternate pathway to the reducing equivalents from quinol and prevents them from interacting with oxygen to generate ROS). The heme enzyme CAT, POD and APX are important for $H_2O_2$ detoxification in plants and their activities are affected by iron deficiency.

**Manganese**

Manganese is a transition metal that exists in several oxidation states of which the most dominant oxidation state is manganous ($Mn^{2+}$) which is easily oxidized to the less stable manganic ($Mn^{3+}$) form. It functions as a co-factor or activator of several enzymes (Table 3). Manganese activation of enzymes accounts for its role in photosynthesis, carbohydrate metabolism, nitrogen metabolism and biosynthesis and metabolism of aromatic aminoacids and secondary plant products.

The most significant role of manganese is as a component of the oxygen evolving complex associated with photosystem II. The complex associated with the PSII reaction center contains a cluster of four manganese ions bound to the amino acid residues of the D1 protein ($P_{680}$). The Mn cluster functions as a mechanism for charge accumulation that enables it to oxidixe the water molecule bound to it. In another role manganese enzymes $NAD^+$ malic enzyme and phosphenol pyruvate carboxykinase play a critical role in decarboxylating the C4 acids to release $CO_2$ that can be fixed by Rubisco and incorporated in the carbohydrate pool.

As a co-factor of enzymes involved in glycolysis and gluconeogenesis, manganese is involved in sugar metabolism. It functions as an activator of enolase and phosphoenol-pyurvate carboxylase, catalyzing terminal steps of glycolysis. The manganese enzyme-phosphoenolpyruvate carboxykinase (PEPCK) catalyzes the decarboxylation of oxaloaccetate, produced during citric acid cycle, to phosphoenol pyruvate, which is then converted to fructose-6-phosphate and glucose-6-phosphate and finally to sucrose.

Manganese catalyzes the first step of the shikimate pathway that provides the precursors for the biosynthesis of aromatic aminoacids -tyrosine, phenylalanine and tryptophan. The reaction involves the condensation of phosphoenol pyruvate and erythose-4-phosphate to produce 3-deoxyarbinoheptulosonate-7-phosphate (DAPH) catalyzed by the $Mn^{2+}$ activated enzyme DAHP synthetase. Manganese activated enzymes also figure in the biosynthesis of gibberellins and polyamines. Kaurene synthase, which catalyzes the synthesis of *ent*-kaurene, the first committed precursor of gibberellins, is specifically activated by manganese. Arginase, which catalyzes the conversion of arginine to ornithine, is also activated by manganese.

Manganese functions in prevention of toxic effects resulting from enhanced production of reactive oxygen species in response to environmental stresses. As a cofactor of the mitochondrial superoxide dismutase (Mn-SOD), manganese provides protection against oxidative damage.

**Copper**

Copper is an essential redox-active transition metal with high redox activity that is involved in many physiological processes. It has two oxidation states –cuprous ($Cu^{+}$) and cupric ($Cu^{2+}$), which are readily interconvertible. The less stable $Cu^{+}$ is readily oxidized to the stable $Cu^{2+}$. Like iron, copper has high affinity for oxygen ($O_2$) and readily binds to organic ligands. Copper acts as a structural element in regulatory proteins and participates in photosynthetic electron transport, mitochondrial respiration, oxidative stress responses, cell wall metabolism and hormone signaling. Most copper in plants is complexed to proteins. Several copper containing enzymes catalyze redox reactions (Table 4). As a constituent of the copper protein plastocyanin, copper plays a key role in photosynthetic electron transport, linking photosystem II to photosystem I. Plastocyanin activity is also involved in cyclic transport of electrons coupled to ATP production. Involvement of plastocyanin in electron transport

accounts for decrease in photosynthetic rates and change in PSI:PSII rates in copper deficient plants.

As a cofactor of several oxidases, including monooxygenases, copper plays a role in metabolism of quinones and phenols affecting synthesis of secondary metabolites including lignins. Inadequate supply of copper leads to decreased activities of copper enzymes – polyphenol oxidase, ascorbate oxidase and copper amine oxidase which accounts for increased accumulation of phenolics in copper deficient plants.

Copper plays a protective role against abiotic and biotic stresses. Superoxide dismutase with Cu/Zn cofactor (Cu-Zn SOD) is localized close to the PSI complex, and catalyzes rapid detoxification of superoxide ions ($O^{\cdot -}_2$) generated under photoinhibitory condition. Copper involvement in lignin biosynthesis contributes to resistance against penetration of pathogens. Protection against pathogens is also offered by elevated levels of copper amine oxidases which generate reactive oxygen species that are cytotoxic to pathogens and activate defense mechanism of the host.

Copper plays a major role in reproductive development of plants, which accounts for severe limitations in seed yield under copper deficiency. Several aspects of reproductive development are influenced by Cu. Copper deficiency has been reported to delay flowering and cause reduction in the number of flowers in large number of. Development of anthers and pollen grains is very sensitive to plant Cu status and higher concentration of Cu in anthers and ovaries than in other floral parts suggests involvement of Cu in their development. The role of copper in microsporogenesis and pollen fertility may account for the more severe reduction in seed yield than dry matter production by copper deficient plants. Inadequate supply of copper not only limits the size of anthers but flowers formed were male sterile showing either staminodes or arrow shaped shriveled stamen without tetrads and reduced lignification The failure of anther dehiscence in copper deficient plants is due to poor

lignification of anther cell walls resulting from decrease in activity of copper containing enzymes involved in biosynthesis of lignins.

**Zinc**

Zinc has a single valency state ($Zn^{2+}$) which makes it different from the other redox active micronutrients. The zinc ion ($Zn^{2+}$) binds to nitrogen and sulfur containing ligands through ionic bonds forming a tetrahedral geometry. Zinc is stable in the biological medium since it is inert to oxidation-reduction and therefore it has a number of structural and functional roles in plants. One of the important roles of Zn is to maintain the structural integrity and permeability of the plasma membranes. Loss of membrane integrity is the earliest biochemical change caused by Zn deficiency. In plants that are not adequately supplied with zinc, the root plasma membrane shows loss of structural integrity and enhanced leakage of ions. This is attributed to low concentration of phospholipids and thiol (-SH) groups in membranes of zinc deficient plants, possibly because of zinc involvement in protection of thiol groups.

Zinc serves as a structural or catalytic cofactor for many proteins. It is a cofactor of a multitude of enzymes that regulate various metabolic activities in plants. The zinc proteins, of which over 300 are known, function as enzymes, transcription factors and regulatory proteins. The enzymatic function and reactivity are determined by the geometric and binding characteristic of $Zn^{2+}$-ligand complexes. Three $Zn^{2+}$-ligand binding sites are recognized: structural, catalytic and co-catalytic. Some important enzymes with $Zn^{2+}$ cofactor and reactions catalyzed by them are listed in Table 5.

Apart from being a constituent of Zn-metalloenzymes, Zn is involved in stabilizing the protein of the DNA-binding domains of regulatory proteins or transcription factors. The Zn binding domains have been termed as ‘Zn-finger’ and are widespread in nature. The ‘zinc fingers’ function in folding of sub-domains of regulatory proteins enabling them to recognize and bind

to specific DNA sequence, inducing gene expression. The term ‘Zn-finger’ represents the sequence motifs (CX2_4CX3FX5LX2HX3_5H) which contains two cysteines and two histidines that coordinate a Zn atom, creating a compact nucleic acid-binding domain. About 30 C2H2 Zn-finger proteins have been identified in higher plants which play a role in many important plant developmental processes, including flower development, leaf initiation, lateral shoot initiation, gametogenesis and seed development.

Zinc also plays a key role in controlling both generation and detoxification of free oxygen radicals, which are potentially damaging to membranes and are catalyzed by superoxide radical generating NADPH oxidase. It was shown that loss of Zn from biological membranes increases their susceptibility to oxidative damage and impairs their function. Zinc offers protection against cellular damage caused by ROS by restricting overproduction of ROS, and by their rapid detoxification. The former is caused by zinc inhibition of membrane localized NADPH oxidase which catalyzes the production of superoxide ions. The latter is caused by rapid dismutation of the superoxide ions to hydrogen peroxide by the chloroplastic superoxide dismutase (Cu-Zn SOD). If not effectively detoxified, the superoxide ions ($O_2^{\bullet-}$) are converted to even more toxic $OH^-$ ions through Haber-Weiss reaction. Photooxidative damage in zinc deficient plants could also result due to impaired photosynthetic $CO_2$ fixation. Zinc is an essential element for photosynthesis and its deficiency may play a role in the reduction of photosynthesis in higher plants by changes in chloroplast structure, photosynthetic electron transport, $CO_2$ fixation ability and photochemical membrane function. Zinc is required for the synthesis of tryptophan, a precursor of IAA which acts as a growth promoting substance.

Zinc is critical for reproductive development of plants. Inadequate supply of zinc affects different aspects of reproduction – flowering, floral development, anthesis, gametogenesis, fertilization and seed maturation.

**Molybdenum**

Molybdenum is a metal of the second transitional series. It has four oxidation states, of which the most stable is the hexavalent form Mo(VI). Easy convertibility of different oxidation states of molybdenum enables it to participate in redox reactions. Over thirty enzymes catalyzing oxidation-reduction reactions contain a molybdenum cofactor. The molybdenum cofactor (Moco) is in the form of a molybdopterin (MPT). The more important molybdenum enzymes of higher plants are listed in Table 6. The molybdenum enzymes also contain other cofactor(s), such as the Fe-S cluster, heme and flavin. The molybdenum enzyme nitrate reductase has recently been shown to be a homodimer, each subunit containing three cofactors – a molybdenum cofactor (Moco), a β-type cytochrome (heme) and a flavin (FAD). As a constituent of prokaryotic nitrogenase, molybdenum plays a key role in symbiotic nitrogen ($N_2$) fixation in leguminous and some non-leguminous plants (*Alnus glutinosa)*. The nodulating leguminous plants have a higher requirement of molybdenum than the non-nodulating plants because the former require molybdenum both for root nodule development and growth of the host.

Role of molybdenum as a cofactor of assimilatory nitrate reductase accounts for accumulation of nitrate in plants grown with nitrate nitrogen. This is associated with reduced levels of protein and total organic nitrogen. Plants grown with reduced (ammonical) form of nitrogen do not show such effects, and their molybdenum requirement is also low. Molybdenum is also involved in ureide metabolism.

Molybdenum nutrition has a profound effect on plant reproductive development and seed yield. Molybdenum deficient plants of maize show reduction in cob size, failure of styles (silk) to protrude out of the husk and poor seed set. Molybdenum also effects seed development and vigor.

**Boron**

Boron is a metalloid and exists in several different forms, the most important of which is boric acid ($H_3BO_3$). It forms complexes with hydroxyl radicals of compounds having two closely situated $^{-}$OH groups in *cis* configuration. Important amongst these are the *o*–diphenols and sugars. The property of boric acid to form strong complexes with cis-diol groups (apiose and fucose) forms the basis of its structural role in plant cell walls. Recent researches have provided evidence to show that boron forms covalent bonds with two monomeric rhamnogalacturonan II groups of the cell wall pectic polysaccharides to produce a dimeric rhamnogalacturonan II – boron complex. The borate ions bind to the apiose residue of the two RG II monomers through a diester bond and functions as ubiquitous carrier of boron in higher plants cell walls. Boron cross-linking of cell wall RG II provides the cell walls with a structure capable of turgor driven growths.

The importance of boron for the maintenance of structural integrity of plasma membranes may also protect plasma membranes against peroxidative damage by toxic $O_2$ species Enhanced generation of toxic $O_2$ species in boron deficient tissues can be expected as a result of enhanced production of quinones (Fig 6). In boron deficient tissues, generation of toxic $O_2$ species can also result directly from phenolics during their oxidation. For example, enzymatic oxidation of catechin by mushroom tyrosinase and potato phenolase produced both $O_2^{-}$ and $H_2O_2$ (Jiang and Miles 1993). Moreover, some polyphenols and quinones are known to be phototoxic and can be excited by light, producing toxic oxygen species such as singlet oxygen ($^1O_2$) and $H_2O_2$ (Bakker et al. 1983). Accumulation of phenolic compounds, particularly caffeic acid and quinones, which are highly reactive, leads to enhanced generation of the superoxide ions ($O_2^{-}$), which are known to cause peroxidative damage to cellular membranes.

Boron plays an important role in plant reproductive development. Often, the effect of boron deficiency is more pronounced on reproductive yield than on biomass production. The

reproductive parts of flowers – anthers, ovary, stigma – possess a relatively higher concentration of boron than in other plant parts and show aberrations when plants are not adequately supplied with boron.

**Chlorine**

Chlorine is a halogen element having only one oxidation state. It occurs in plants as a free anion ($Cl^-$) bound to exchange sites and as chlorinated organic compounds. Chlorine functions as a structural component of the manganese cluster involved in charge accumulation and oxidation of water by photosystem II. Another important function of chlorine in plants pertains to maintenance of turgor and osmoregulation. The osmoregulatory roles of chlorine include its involvement in turgor driven growth of cells and stomatal functioning. Chlorine accumulates in relatively high concentrations in root and shoot apices, where it functions in the turgor induced extension growth of cells. Chlorine deprivation of maize plants leads to inhibition in root elongation. In a recent study, stomatal response to enhanced concentration of $CO_2$ in fava bean leaves has been shown to be associated with enhanced flux of $Cl^-$ from guard cells into the neighbouring apoplasmic fluid. Enhancement of $Cl^-$ flux is attributed to $CO_2$ induced activation of anion channels of the guard cell plasma membranes. Other examples of chlorine involvement in turgor driven responses include seismonastic movement of *Mimosa pudica* and circadian rhythms of *Samanea saman* leaf movements. Chlorine also regulates the activities of certain enzymes. It is known to activate asparagine synthetase, which catalyzes the glutamate dependent synthesis of asparagine.

**Table 1. The nitrogen fractions involved in nitrogen metabolism**.

| Inorganic nitrogen | Low-molecular weight organic nitrogen compounds | Macro-molecular organic nitrogen compounds |
|---|---|---|
| $NO_3^- \rightarrow$ | Amino acids | Proteins |

| | | |
|---|---|---|
| $NH_4^+$ → | Peptides | Nucleic acids |
| $N_2$ → | Amides | Co-enzymes; |
| | Ureides | Secondary products; |
| | Amines | Membrane constituents |

**Table 2 Some important iron enzymes in plants**.

| Enzyme | Reaction catalyzed |
|---|---|
| Superoxide dismutase (Fe-SOD) | $2O_2^{\cdot-} + 2H^+ \longrightarrow H_2O_2 + O_2$ |
| Alternative oxidase | Ubiquinol + $O_2 \longrightarrow$ Ubiquinone + $H_2O$ |
| Lipoxygenase | Linoleic acid $\longrightarrow$ 13 or 9 hydroperoxylinoleic acid |
| Aconitate hydratase | Citrate $\longrightarrow$ Isocitrate |
| Nitrite reductase | $NO_2^- + 6Fdx_{(red)} + 8H^+ \longrightarrow NH_4^+ + 6Fdx_{(ox)} + 2H_2O$ |
| Sulfite reductase | $SO_3^{2-} + 6Fdx_{(red)} \longrightarrow S_2^- + 6Fdx_{(ox)}$ |
| Glutamate synthase | Glutamine + 2 oxo-glutarate + $2Fdx_{(red)}$ or NADH $\longrightarrow$ glutamate + $2Fdx_{(ox)}$ or $NAD^+$ |
| Succinate dehydrogenase | Succinate + FAD $\longrightarrow$ Fumarate + $FADH_2$ |
| NADH – Q oxidoreductase | $NADH + UQ + 5H^+_{(matrix)} \longrightarrow NAD^+ + UQH_2 + 5H^+_{(Cytsol)}$ |
| Succinate – Q oxidoreductase | Succinate $\xrightarrow{e}$ FAD $\xrightarrow{e}$ UQ $\xrightarrow{e}$ $UQH_2$ |
| Fdx - $NADP^+$ oxidoreductase | $2Fdx_{(red)} + NADP^+ \longleftrightarrow 2Fdx_{(ox)} + NADPH + H^+$ |
| Catalase | $H_2O_2 + H_2O_2 \longrightarrow H_2O + O_2$ |
| Peroxidases | $H_2O_2 \longrightarrow H_2O$ + A |
| Cytochrome c oxidase | $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ |
| Cytochrome c reductase | $QH_2 + 2Cyt\ c_{(ox)} + 2H^+ \longrightarrow Q + 2Cyt\ c_{(red)} + 4H^+$ |

**Table 3 Some enzymes in plants activated by manganese.**

| Enzyme | Reaction catalyzed |
|---|---|
| Superoxide dismutase (Mn-SOD) | $2\ O_2^{\bullet-} + 2H \rightarrow H_2O_2 + O_2$ |
| $NAD^+$ -Malate oxidoreductase (Malic anzyme) | Malate + $NAD^+$ + $H^+$ → Pyruvate + NADH + $CO_2$ |
| Phosphoenolpyruvate carboxykinase | Oxaloacetate + ATP → Phosphoenolpyruvate + ADP + $CO_2$ |
| Allantoate amidohydrolase (Mn containing) | Allantoate + $H_2O$→ Uredoglycine + $NH_3$ + $CO_2$ |
| Arginase | L-Arginine + $H_2O$ → L-Ornithine + Urea |
| Glutamine synthase | Glutamate + $NH_4$ + ATP → Glutamine + ADP + Pi |

**Table 4 Copper enzymes in plants.**

| Enzyme | Reaction catalyzed |
|---|---|
| Polyphenol (catechol) oxidase | 2*O*- Diphenol + $O_2$ → 2*O*- Quinone + $2H_2O$ |
| Laccase | 2*p*-Diphenol + $O_2$ → 2-*p*-Quinone + $2H_2O$ |
| Ascorbate oxidase | 2*L*-Ascorbate + $O_2$ → 2 Dehydroascorbate + $2H_2O$ |
| Monophenol monoamine oxidase (Tyrosinase) | Tyrosine + Dihydroxy phenylalanine + $O_2$→ Dihydroxyphenylalanine + Quinone + $H_2O$ |
| Diamine oxidase (Cu containing) | $RCH_2NH_2 + O_2 + H_2O \rightarrow RCHO + NH_4 + H_2O_2$ |
| Superoxide dismutase (Cu-Zn SOD) | $2\ O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2$ |

**Table 5** Some important Zn enzymes and their reactions.

| **Enzyme** | **Reaction catalyzed** |
|---|---|
| Alcohol dehydrogenase | $CH_3CH_2OH + NAD^+ \rightarrow CH_3CHO + NADH^+ + H^+$ |
| Glutamate dehydrogenase | L-Glutamate + $NAD^+ \longleftrightarrow$ α-Ketoglutarate + $NH_4$ $NADH + H^+$ |
| Superoxide dismutase (Cu/Zn SOD | $2\ O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2$ |
| RNA Polymerase | Nucleoside triphosphate → pyrophosphate + RNA |
| Alkaline Phosphatase | Orthophosphoric monoester + $H_2O$ → Alcohol + orthophosphate |
| Phospholipase | Phophatidylcholine+$H_2O$→ Choline + Phosphatidate |
| Carboxypeptidase A | Peptidyl-L aminoacid + $H_2O \longleftrightarrow$ Peptide + Aminoacid |
| Ribulosebiphosphate Carboxylase | D-Ribulose 1,5-biphosphate+$CO_2$ → 2,3- phospho-D-digylcerate |
| Fructose-biphosphate aldolase | Fructose-1,6-bisphosphate ⟷ Dihydroxy acetone $PO_4$ + D-Glyceraldehyde-3-$PO_4$ |
| Carbonic anhydrase | $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$ |
| Porphobilinogen synthase (ALA dehydratase) | 2δ-Aminolevulenic acid ⟶ Porphobilinogen |
| Carbonic anhydrase | $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$ |

**Table 6 Molybdenum enzymes in plants.**

| Enzyme | Reaction catalyzed |
|---|---|
| Nitrate reductase | $NO_3^- + NAD(P)H + H^+ \longrightarrow NO_2^- + NAD(P)^+ + H_2O$ |
| Xanthine dehydrogenase | Xanthine + $O_2$ + $H_2O \longrightarrow$ Uric acid + $H_2O_2$ |
| Aldehyde oxidase | Oxidation of aldehydes (eg. abscissic aldehyde) to corresponding acids |
| Sulfite oxidase | $SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+$ |

**Suggested reading:**


**1.**Marschner's Mineral Nutrition of Higher Plants (2011), Petra Marschner; Elsevier Science Publishing Co Inc.

2. Plant Physiology (2006), Lincoln Taiz, Eduardo Zeiger, 4th edition; Sinnauer Associates, USA.

3. Sharma, C. P. 2006. *Plant Micronutrients.* New Hampshire, USA: Science Publishers.