The Mechanisms of Trace Element Uptake and Transport Up To Grains of Crop Plants

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Abstract

Trace elements are vital for the operation of metabolic pathways that promote growth and structural integrity. Trace elements are essential for plant growth, i.e., iron, zinc, copper, manganese, cobalt, nickel, boron, molybdenum, and chlorine. Unfortunately, the first two i.e. iron and zinc deficiency in humans has increased on a global scale. The main reasons for these two micronutrients deficiency are dietary intake of food with low levels of Fe and Zn. Biofortification approaches would result in the enrichment of these two elements on target tissue to a considerable extent. Absorption of trace elements is a complex physiological trait which is mainly governed by element transporters and metal chelators of the plant system. Different factors like crop growth stage, edaphic factors, season, etc. also influence the element efficiency of a particular crop. The absorption and transport of trace elements in crop plants are based on the thermodynamics of adsorption on charged solid surfaces embedded in a solution phase of charged ions and metal-binding ligands together with redox systems in the case of iron, zinc, and some other elements. During the normal condition, constitutive absorption systems function in nutrient uptake while in deficiency inducible turbo systems function which increases the supply of a particular nutrient. Crops are divided into two groups, i.e., dicotyledonous crops and monocotyledonous crops. Fe and Zn uptakes in dicotyledonous crops have a turbo system that is an upregulated version of the constitutive system which consists of a membrane-bound reductase and an ATP-driven hydrogen ion extrusion pump while monocotyledonous crops have a constitutive system with an inducible system

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remarkably different from dicot that uses the mugenic acid class of phytosiderophores and chelators. Biofortification of these metals involves through enhancing uptake and translocation of Fe and Zn by introducing genes responsible for the biosynthesis of mugineic acid family phytosiderophores (MAs). MAs played an important role in iron transport from an iron-rich soil into the iron-starved crops. Iron is stored in crops after absorption as phytoferritin and transported to active sites by transport-specific ligands. In the grains, Fe and Zn are transported by the phloem sap system through chelation of heavy metals which is governed by three or four genes each that control chelation, membrane transport, and deposition as phytate.

Keywords

Plant nutrition · Micronutrients · Adsorption · Transport · Phytosiderophores · Chelation

6.1 Introduction

The essential micronutrients which are required by plants i.e., iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), cobalt (Co), nickel (Ni), boron (B), molybdenum (Mo), and chlorine (Cl) (Marschner 1993). Mo and Cl are present in soils as anions and undoubtedly require active transport across the plasmalemma of plant root cells for uptake while B is either an anion or neutral molecule in most soils which is fairly permeable across biological membranes (Stangoulis et al. 2001). The remaining six micronutrients are generally absorbed as divalent ions via divalent ion channels which are specific for each element (Welch 1995).

Fe is essential for plant growth. At the same time, Fe is highly reactive and toxic via the Fenton reaction. Consequently, plants tightly control Fe homeostasis and react to Fe deficiency as well as Fe overload. The ability of plants to respond to Fe availability ultimately affects human nutrition, both in terms of crop yield and the Fe concentration of edible tissues. Deficiency of Fe is a major worldwide agricultural problem. Fe is not easily available in neutral to alkaline soils which cover nearly 30% of global cultivated soils with low iron availability and present in insoluble oxidized forms (Guerinot and Yi 1994; Mori 1999). Dicots and monocots have developed the Strategy I response to iron deficiency stress (Romheld and Marschner 1986; Marschner and Römheld 1994). This response includes acidification of the rhizosphere by releasing protons, subsequent induction of Fe^{+3} chelate reductase activity that reduces Fe^{+3} to Fe^{+2}, and acquisition of Fe^{+2} across the plasma membrane of root epidermal cells (Romheld 1987). In the nutrition of chlorophyll-containing plants, Fe has multiple roles. It is a tightly bound component in a wide group of hem-proteins, which include the cytochromes system, catalase, peroxidase, and hemoglobin. Their distribution in plant tissues and cell fractions is quite varied. Deficiency of Fe suppresses cell division and leaf primordial production. Iron may be involved in some reaction of photosynthesis but its role in chlorophyll synthesis is still unsolved although correlation has been found to exist between the chlorophyll content of leaves and their Fe content (Jacobson and Oertli 1956; Hewitt 1961). Fe can be considered to be at least moderately mobile in plants (Branton and Jacobson 1962; Brown Yamaguchi and Leal-Diez 1965). While Zn is also a crucial element for the survival of most organisms including humans (Hambidge 2000). Zn acts as a cofactor of more than 300 proteins (Coleman 1998; Lopez-Millan et al. 2005) and present in all six enzyme classes i.e. oxidoreductase, transferase, hydrolases, lyases, isomerases, and ligases which regulates the activities, conformational stabilization, and folding of various proteins (enzymes). Zn also acts in membrane integrity and stabilization (Cakmak 2000; Disante et al. 2010), alleviation of oxidative stress (Cakmak 2000), and as an intracellular second messenger (Yamasaki et al. 2007). In spite of these Zn is involved in several plant physiological processes such as hormone regulation (e.g., tryptophan synthesis, a precursor of IAA), signal transduction via mitogen-activated protein kinases (Lin et al. 2005; Hansch and Mendel 2009), repair processes of PS II complex during photoinhibition (Bailey et al. 2002; Hansch and Mendel 2009), and maintenance of CO_2 concentration in the mesophyll. Peck and McDonald (2010) confirm the participation of Zn in the regulation of Rubisco activity along with alleviation from adverse effects of heat stress in wheat.

Because iron and zinc deficiencies are extremely widespread in humans and are also common in some farm animals, this article focuses on sustainable management of Fe and Zn through fortification and their uptake, transport, and loading into grains that constitute the staple foods of most of the human race. What is known about the uptake, transport, and loading of the other transition elements is generally analogous to iron and zinc.

6.2 Soil as a Medium of Plant Growth and Custodian of Plant Nutrient

Soil consists of primary minerals (i.e., sand, silt, and clay), organic matter, water, and air. Thus soil has three-phase systems: there is a solid phase consisting of innumerable minerals and organic substances; the liquid phase consisting of the soil moisture or water in which relatively small amounts of the solid phase dissolve; and the gaseous phase, the soil air which fills the pore space not occupied by the soil moisture. But a soil serving as a medium for plant growth is more than a three-phase system which is a living phase that must always be taken into account in any consideration of soil as a medium for crop production. The pH of the systems which involve many chemical reactions and, particularly biological activity and life is tremendously important. Crop plants as well as plants in general vary greatly as regards the reaction of the nutrient medium in which they grow best. Some species of plants grow best in acidic medium, some in an alkaline medium, and others in a neutral medium or nearly neutral medium. The reason for these reaction preferences is due to the direct and indirect influences of soil reaction. The nutrient elements are held or stored in soils in three degrees or categories of availability; (a) readily available, (b) moderately available, and (c) slowly available. To produce good crops, the supply of readily available forms of nutrients must be high enough so that most of which required by crops can be obtained directly from these forms.

Iron plays an important role in soil chemistry being involved in numerous reactions affecting the chemical and physical properties of soils. Due to its interaction with other elements, it may considerably affect the availability of micro- as well as macro-nutrients. The availability of Fe to plants is greatly affected by various soil properties and also by interaction with other elements. The amount of plant-available Fe in soils depends largely on soil pH and redox potential. In acid soils, Fe is usually in ferrous forms which are available to plants, but in neutral or alkaline soils it is oxidized to ferric iron which may be so insoluble that plants have difficulty in absorbing enough, e.g., at pH 7, the solubility of Fe^{+3} is only 10^{-17} moles per liter while that of Fe^{+2} is 10^{-4} (Granick 1958). Increasing oxidation potential leads to the oxidation of Fe from ferrous to ferric forms and, therefore, decreases its availability. The oxidation potential increases with increasing pH and with increasing aeration so that the reaction Fe^{+2} to Fe^{+3} due to both of these factors is likely to proceed towards Fe^{+3} and to decreasing Fe availability. Improvements in soil structure may have a similar influence (De Kock 1955; Mokady 1961; Wiklander 1958). Increasing acidity, as well as depletion in soil structure, is likely to cause a reaction towards the reduction of iron. Therefore, the portion of ferrous iron of the total Fe usually increases towards the lower soil horizons due to the decreasing aeration. In poorly drained soils the reduction of ferric to ferrous iron may be effected by decomposing organic matter, and some wet soils may contain so much ferrous iron at low pH values that they are toxic to plant roots (Bear 1965). Although the deficiency of Fe may occur on both acid and alkaline soils, it is perhaps most common on calcareous soils as a lime induced Fe chlorosis. In addition to high pH decreasing the Fe availability, high concentrations of calcium in soil solutions may not only decrease the uptake of Fe on these soils, but there is also evidence of inactivation of Fe within the plant due to abundance of Ca or Ca and P (Mc George 1949; Thorne 1957; Taper and Leach 1957; Olsen 1958; Brown et al. 1959a, b; Miller et al. 1960). Fe deficiency has been induced through both high Ca and P applications, but also through K deficiency. In all cases, the deficiency could be corrected with potassium application (Bolle-Jones 1955).

Zn is also more available in acid than in alkaline soils, the range of least availability being about pH 6.0–7.0. Increased soil pH stimulates Zn adsorption to cation exchange sites of soil constituents (e.g., metal oxides, clay minerals) which reduce Zn availability in soil solution. Moreover, at a pH range of 5.5–7.0, Zn concentration in soil solution (soluble Zn) decreases significantly by 30-fold to 45-fold for each unit increase in soil pH. It is one of the reasons for enhancing the risk of Zn deficiency in crop plants (Marschner 1993). At high pH, the formation of insoluble calcium zincates is favored and Zn may be less available. Therefore liming of acid soils decreases the availability of Zn and may produce Zn deficiency (Thorne et al. 1951). In soils of sodium alkalinity, the availability of Zn may increase with increasing pH due to the formation of relatively soluble sodium zincates (Bear 1955). In several studies, however, no apparent connection between the soil pH and Zn uptake by plants could be established (Tisdale and Nelson 1966). Soil moisture is another physical factor that affects Zn uptake by plant roots via diffusion. The role of soil moisture is very critical in soils with low Zn availability (Rattan and Deb 1981; Marschner 1993). The solubility of Zn and ratio of Zn^{+2} to organic-Zn ligand complexes increases at lower pH especially in soils of low soluble organic matter. Higher levels of soil organic matter enhance the pool of phytoavailable Zn in soil (Catlett et al. 2002; Obrador et al. 2003). In addition to soil pH, the redox potential of soil strongly influences the speed and intensity of the humification process, the redox status of the rhizosphere, and hence the mobility of Zn. In general, the physiological growth and functioning of plants take place at a redox potential range of +300 to +700 mV (Volk 1993). However, reduced conditions (+350 mV) limit the growth of many plants by depriving the oxygen pool of roots. Plant roots modify redox potential of the rhizosphere in two ways: first is through secretion of various reductants and chelating compounds in root exudates and second is through association with the microbial community (Hartmann et al. 2009). Both of the mechanisms influence availability, solubility, and oxidation–reduction state of Zn in soil solution. In conclusion, soil type, mineral and clay types, soil biota and plant uptake, etc., collectively determine Fe and Zn distribution in soil–root–plant fluxes.

6.3 Mechanism of Uptake and Transport of Iron From Roots to Stem

The contact theory distinguishes between contact intake and contact depletion of plant nutrients. Soil clays played important role in exchange reaction with root surface, and replenishment of the soil solution by replaceable metallic cations, i.e., Fe and Zn subsequent on their depletion by plants, is a prima facie evidence of the significance of the soil particle-size distribution upon nutrient availability. Plants absorb most of the minerals from the soil via their specialized organs, i.e., roots. The availability of Fe and Zn depends upon physicochemical properties of soil, the activity of plant roots, and micro flora in the rhizosphere and other non-edaphic factors. Some fraction of soil Fe and Zn exists either as insoluble complexes or in adsorbed and exchangeable form. However, another fraction exists in a water-soluble form which is freely available to plants. Root activity also makes the exchangeable form available for uptake to some extent via ion exchange and release of organic acids, etc. The major determining factor affecting soil Fe and Zn distribution is soil pH, which affects the solubility of these elements in soil solution.

At moderate and high soil pH values, Fe deficiency in crops was observed due to the low availability of Fe in the presence of oxygen. These insoluble forms of iron in the soil are solubilized either by complexation of ferric iron [Fe (III)] with chelators to ferrous iron [Fe (II)] due to lowering of the pH value. The mechanisms to adopt these two strategies vary between species by plant roots. The strategy I that is constitutive system adopted by all dicotyledonous plants together with the nongraminaceous monocotyledonous plants while Strategy II in Gramineae plants (Marschner 1995). Both groups have a constitutive system that is adequate to supply plants that are grown in fertile soils having plenty of available forms of Fe. The constitutive system consists of a membrane-bound ferric reductase that is linked to a divalent ion transporter or channel and an ATP-driven proton-extrusion pump. Single amino acid substitutions in the sequence of this channel protein create specificity for the various divalent cations (Rogers et al. 2000). These two membrane functions can supply adequate iron to most plants in healthy soil. However, leaf chlorosis symptoms occur in iron-deficient soils, in which additional mechanisms of iron acquisition are induced to restore iron status in plants. Induced responses are restricted in both strategies to the apical zones of the roots and are fully shut down again within 1 d of restoration of normal iron status. Strategy I plants respond to signals of low iron status by up-regulating the ferric reductase and the proton-extrusion pump. Also, many Strategy I plants have a mechanism for excreting iron-binding ligands and soluble reluctant, which are commonly phenols. All these changes are designed which expressed in the apical zones of the roots where the adaptations are associated with changes in root morphology and the appearance of transfer cells with invaginated membranes. The reductase is stimulated by a low pH level and thereby by the proton-extrusion pump such that its function is effectively inhibited by bicarbonate in high-pH soils. This is the basis for the severe iron chlorosis that is seen in dicotyledonous plants from high-pH soils. Insensitivity to bicarbonate is a feature of Strategy II plants, which induce an entirely new mechanism of mobilizing iron under iron stress. An induced turbo system that is an upregulated version of the constitutive system, Strategy II plants synthesize and release to the soil nonprotein amino acids are known as phytosiderophores (PS) or phytometallophores which recognizes that these amino acids can chelate most of the transition metals and not just iron. These form strong soluble chelates with ferric ions in the soil, and because they are soluble and less positively charged, they are free to diffuse towards the root in soil–water films. Additionally, Strategy II plants have constitutively a highly specific transporter protein [the genes encoding for this transporter most likely belong to the natural resistance associated macrophage protein (NRAMP) family (Curie et al. 2000; Thomine et al. 2000) or the interferon-g-responsive transcript (IRT-1) family (Eide et al. 1996)]. This highly specific transporter protein, which is not present in Strategy I plants, recognizes and transports its specific ferric chelate across the membrane. In the cytoplasm, the ligand is separated from the metal by reduction of the latter, which is then stored in phytoferritin or transported in the plant with ferrous-specific ligands such as nicotianamine. Graminaceous species contain the various members of the PS family in unique ratios: generally, the small-grain cereals such as barley, wheat, oat, and rye have the greatest expression, which explains their remarkable adaptation to the high-pH soils that are usually found in the semi-arid winter cereal-cropping belts of the world. The PS pathway appears to be a major vehicle for the entry of iron into the biosphere from the lithosphere. Curiously, the release of PS from the roots is diurnal and peaks a few hours after sunrise. As in Strategy I plants, the synthesis of PS is quickly suppressed when the plants are restored to adequate iron status, which suggests that these inducible systems are energetically demanding. PS also binds zinc, copper, and manganese and can enhance their absorption along with that of iron. However, with the possible exception of zinc, the mechanism is not induced by deficiency of these other transition metals in the plant. The constitutively expressed extrusion of protons, reductants, and metal-binding ligands will enhance the absorption of all the divalent cations. Inducible systems for upregulated absorption of micronutrients are best understood for iron, and indeed, although the existence of an inducible system in the gut of humans is generally accepted, its nature is not as clearly understood as that in plants and bacteria. The latter has an inducible system that involves the synthesis of members of the hydroxamate group of ferric-binding ligands.

6.4 Mechanism of Uptake and Transport of Zinc from Roots to Stem

Variations in Zn requirement and Zn concentration of closely related species may be due to differences in their Zn uptake, transport of root absorbed Zn to shoots, and in Zn sequestration. But downstream of such Zn differences is the tight regulation of Zn absorption for the survival of root cells and Zn homeostasis for normal functioning of physiological processes (transpiration, nutrient absorption, etc.) in which root participates. Zn is taken up mainly as a divalent cation (Zn^{+2}ion) by plant roots. However, in some cases, organic ligands-Zn complexes are also absorbed by plant roots. Depending upon the ligands secreted by plant roots, two physiological strategies are involved in the uptake of divalent cations like Zn^{+2}. The strategy I involves efflux of reductants, organic acids, and H^+ ions, which enhance the solubility of Zn-complexes (Zn phosphates, hydroxides, etc.) and release Zn^{+2} ions for absorption by root epidermal cells. The organic acids released either in root exudates/mucilage or directly by epidermal cells include citric acid, malic acid, oxalic acid or tartaric acid, etc. Strategy II involves the efflux of phytosiderophores (phytometallophores) which form stable complexes with Zn and their subsequent influx into root epidermal cells. However, this absorption mechanism (i.e., strategy II) is restricted to cereal roots. Phytosiderophores are low molecular weight organic compounds (particularly nonprotein amino acids such as nicotianamine, deoxymuigenic acid, avenic acid, etc.) that possess a high binding affinity for their respective metals resulting in their chelation and acquisition. Biosynthesis of these compounds involves condensation of S-adenosylmethionine molecules, causing the formation of nicotianamine, which is a precursor of phytosiderophores.

For an understanding of mineral absorption, one should keep in mind that roots are not just static organs. Plant roots release various organic acids, amino acids, sugars, protons, even some mineral ions, etc. in the rhizosphere that facilitate their adequate functioning and growth. Zn is absorbed as divalent metal ion Zn^{2+} through mass flow and diffusion mechanisms by roots. Passive Zn uptakes by these mechanisms involve the participation of water (solvent) molecules and differences in Zn concentrations across the root cell-plasma membrane (RCPM). The main driving force in Zn^{2+} uptake (cation uptake) is the hyperpolarization of RCPM which is mediated through the activity of the RCPM H^+-ATPase system. The RCPM H^+-ATPase system actively pumps H^+ ion extracellularly at the expense of

ATP hydrolysis. Release of H+ ion in the rhizosphere causes hyperpolarization of RCPM on one hand while reduces the soil pH on the other hand which results in increased cation uptake rate. But unlike water, charged Zn ions are not able to cross cell membranes freely (Alberts et al. 2007), so these divalent cations are transported by specific transporter proteins (Guerinot 2000; Clemens et al. 2002). These proteins are not in close association with ATP breakdown which confirms passive uptake of Zn rather than active. Furthermore, Zn^{2+} uptake also occurs by non-selective cation channels associated with the passive flux of diverse groups of cations (Demidchik et al. 2002). This additional driving force in the uptake of many metal cations is likely due to their very low cytoplasmic activity, which is a result of metal sequestration and their binding to intracellular sites (i.e., Zn finger proteins, organic acids, enzymes, etc.).

6.5 Interactive Effect of Zinc with Iron During Uptake

Transport of metal ions in plants consists of events such as uptake from soil solution to root, movement from root to shoot, and ultimately their (metal ion) supply from shoot to various sink organs of the plant. These functions are performed by specific transporter proteins that regulate both intercellular and intracellular transport. Low abundance of the metal ions/trace elements in soil explains the evolutionary development of high affinity metal transporter in plants. A number of genes have been identified till date that either encodes Zn transporter proteins or regulates their expression at transcriptional, post-transcriptional, and translational levels. Most important families of transporter proteins involved in Zn transport are: the ZIP (Zinc-, Iron-Permease family/ZRT-, IRT-like proteins) family, the HMA (Heavy Metal ATPases) family, and the MTP (Metal Tolerance Protein) family. Among these, members of ZIP family perform the function of Zn influx into the cytosol while HMA family participates in efflux of Zn to the apoplast. MTP family is involved in sequestration of Zn into intracellular compartments such as vacuole, endoplasmic reticulum (Palmer and Guerinot 2009).

Root Zn uptake from rhizosphere is greatly influenced by Fe divalent cations which compete with Zn for the same ligands binding site such as in phytosiderophores, transporter proteins like IRT1. Some metal transporters like IRT1 and non-selective cation channels transport Fe^{+2} cations in addition to Zn. Although plants have a basal metal tolerance for these cations but at higher levels, they may have detrimental effects on plant growth. Regarding Fe–Zn interactions, both metal ions have common transporter proteins required for their absorption. Expression studies of Zn deficiency response genes in Fe-deficient mutant (fit mutant) demonstrated low expression of MTP3 and HMA3 suggesting Fe deficiency induces Zn accumulation (Colangelo and Guerinot 2006). The involvement of Fe in transcriptional regulation of the ZIF1 gene has also been demonstrated (Haydon et al. 2012). In contrast, high levels of Zn cause physiological Fe deficiency which is visible as stunted plant growth and chlorotic leaves.

6.6 Path of Transport of Trace Elements in Roots

6.6.1 Radial Transport

Fe^{+2} and Zn^{+2} are transported radial within the root and pass through several tissues e.g., epidermis, cortex, endodermis, and pericycle before reaching the xylem for transport to shooting. The diameter of these tissue layers decreased when moving towards the stellar region in the center. The radial pattern of transport accelerates water flow in its path to xylem and concentration increases faster at smaller radii for the same flux (lesser solvent volume), both of which help in a large accumulation of ions (metal cations) in the pericycle, which ultimately loads the xylem (Claus et al. 2013). Although specialized transporter proteins are present on cell membranes of respective tissues, yet tight regulation of their expression and activity (rate of Zn transport in per unit time) ultimately decides the intracellular zinc content of root tissues. Several factors such as zinc compartmentation in roots, translocation and use in shoots, sink growth stage, etc. also affect xylem loading of Zn in roots and ultimately lead to differences in symplastic Zn levels.

During the transport of mineral ions to xylem, two main routes are followed: (1) Symplastic route; (2) Apoplastic route. The cytoplasms of adjacent cells in root tissues are connected by cytoplasmic bridges (plasmodesmata) in the cell wall, forming a symplastic continuum without membrane barriers. In addition to this, water and mineral ions can also move via cell wall and intercellular spaces, the apoplast, which also has significant contributions to root mineral transport (Steudle 1994). But the apoplastic route is interrupted in regions of endodermis due to deposition of suberin lamellae in the Casparian strip. Suberin is highly impermeable to water and charged ions. So mineral ions and water molecules need to pass the membrane before the Casparian strip and are transported further through a symplastic route (Yang and Jie 2005). Some of the Zn^{2+} and Fe^{2+} ions are also delivered extracellularly to stellar apoplast in regions where the Casparian band is not fully formed (i.e., near root apex and region of lateral root initiation) as depicted by White et al. (2002) and Ranathunge et al. (2005). Both symplastic and apoplastic fluxes contribute to net Zn and Fe fluxes in the shoot. The apoplastic Zn transport involves entry of Zn from the cell wall plasma membrane interface into the cytosol, making this process less selective than symplastic transport. Contrary to this, symplastic transport controls the selectivity and magnitude of nutrient delivery (Clemens et al. 2002).

6.6.2 Transport of Trace Elements in Xylem and Phloem

After crossing the barrier of Casparian strip in root endodermis, metal ions enter simplistically in living cells of pericycle and xylem parenchyma bordering the xylem. Another barrier in metal ion transport occurs at this step of nutrient transfer which is known as xylem loading. It is the key determining step in the root export of metal cations. Continuous activity of H^+-ATPase in xylem parenchyma causes membrane hyperpolarization which restricts the movement of positive ions out of the cytosol. Thus, the loading of metal cations from xylem parenchyma/pericycle cells to apoplastic xylem is an active process (Sondergaard et al. 2004). The active efflux of symplasmic Zn^{2+} is mediated by specific transporters (HMA family or P1B-type ATPase) present on pericycle cells/xylem parenchyma. Enhanced activity and higher expression of plasma membrane H^{+}-ATPase in xylem parenchyma is also responsible for the acidic nature of xylem sap (pH 5–6.5). In xylem sap, metal ions are transported mainly as metal complexes with asparagines, histidine, organic acids, and nicotianamine which was studies on chloronerva mutant of tomato that revealed these amino acid regulates metal distribution between apoplastic and symplastic compartments (Pich and Scholz 1991; Takahashi et al. 2003). Energization of nutrients uptake at the site of xylem unloading has also been reported because of dilution of xylem sap by a continuous supply of water through transpirational pull (Sondergaard et al. 2004). Specialized cells are present at such transport interfaces to enhance the symplastic transfer of solutes. These mainly involve transfer cells and vessel associated cells. Both cell types are associated with the sieve element companion cell complex of the phloem. Transfer cells are considered to be the most specialized cell type for membrane transport. Greater number of mitochondria, abundant H^{+}-ATPases, and numerous plasma membrane invaginations of these cells towards the tracheary elements help in nutrient transfer in and out of xylem. On the other hand, vessel associated cells are a special class of xylem parenchyma cells which are associated with numerous large pits to neighboring xylem vessels (Sondergaard et al. 2004). Once Fe and Zn enter the phloem, further translocation to various plant organs and developing sinks is mediated by short and long-distance pathways. Moreover, the mobility of Fe and Zn is higher in phloem than xylem due to increased concentration of chelating solutes (peptides, organic acids, etc.) in phloem sap. Metals are transported either in ionic form or as complex with chelators like Zn nicotianamine, Zn-malate, Zn-histidine complexes in phloem tissues wise versa Fe is also transported nicotianamine (NA). NA is a non-proteogenic amino acid ubiquitous in higher plants, synthesized by the condensation of 3 molecules of S-adenosylmethionine in a reaction catalyzed by nicotianamine synthase (NAS). NA complexes with Fe^{2+} and Fe^{3+}; it has a higher affinity for Fe^{3+}, but forms a more stable complex with $Fe^{2\ +\ 0}$.73 NA also readily binds Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Mn^{2+}, in decreasing order of affinity (Curie et al. 2009). Although xylem contains a lower concentration of solutes, nevertheless is important in nutrient transfer to various organs. Young sink tissues such as developing grains, tubers, etc. are mainly fed by phloem.

6.7 Mineral Nutrition During Ontogeny of Plants

Crops showed three fairly distinct stages of metabolism from the period of germination to flowering. The conspicuous stages in the nutrition of the vegetative plant comprise an initial anabolic phase (I) in which intake of inorganic nutrients and synthesis of proteins is rapid. In the second phase (II), the accumulation of carbohydrates accelerates while the rate of protein synthesis gradually diminishes. As flowering is approached, a third or catabolic phase (III) becomes evident in which hydrolysis of reserves begins to overbalance synthesis and a general internal redistribution of nutrients is initiated. Though, conditions of the environment and nutrient supply determine to a considerable degree the exact time of the shift from predominantly anabolic to catabolic activity, the latter characteristic is associated with flowering and commonly initiated before anthesis (Dennison 1945). Some studies (Briggs et al. 1920; Murneek and Wittwer 1942; Wittwer 1943; Biddulph and Brown 1945; Whyte 1946;) indicated that the phenomenon of synopsis or sporogenesis represents a turning point in nutritional metabolism (Hornberger 1882; Knowles and Watkins 1931).

(a) In monoecious species such as corn, it has been observed that the origin of the staminate and pistillate organ is associated with a transitory but systemic acceleration of anabolic over catabolic processes including more rapid nutrient absorption and dry weight gain.
(b) Under normal conditions, the metabolic stimulus associated with synapsis is brief and soon gives way to a reduction in anabolic processes during the ensuing phase of blossoming or anthesis. The flowering phase is usually characterized by subsidence of anabolic activity as well as the inauguration of fundamental modifications (Lugg and Weller 1948) and redistribution of the organic and inorganic nutrient component.
(c) The decline of anabolic activity associated with blossoming gradually gives way to what is usually the final resurgence of absorption of mineral nutrients and acceleration of organic synthesis in vegetative tissues. The anabolic stimulus is associated with the fusion of male and female nuclei in syngamy and the very early enlargement of young fruits (Wittwer 1943; Whyte and Murneek 1948).

The fruiting stage has its origin in syngamy. The early stage of fruit enlargement is commonly associated with marked increments in absorption by roots and accelerated anabolism of the younger parts of the shoot. Gains in nitrogen and potassium become appreciable higher. Absorption of phosphorus and Fe, though fairly steady at first, tend to rise, some time to surprisingly high level at maturation supervenes. There is an increase in the accumulation of protein carbohydrates, the latter usually being greater in terms of dry weight gains. As would be expected, an increasing amount of organic and inorganic reserves are diverted from vegetative to reproductive organs as more fruits are set and their enlargement accelerates. Seeds and fruits are highly selective in the elements which they accumulate from leaves and stems. Fe moves to the seeds, most likely via the phloem, as the flow of the xylem is driven by transpiration, and seeds do not transpire (Grusak 1994). Fe is received in developing seeds from the roots and from senescent leaves. The level of remobilization from shoot to seed varies by species: rice transports only 4% of shoot Fe to the seeds (Marr et al. 1995) versus wheat, that transports 77% of shoot Fe to the seeds (Garnett and Graham 2005). The timing and regulation of senescence have been shown to have a significant effect on Fe accumulation in the seeds. NAC family of transcription factors with RNAi was found to delay senescence in wheat by over 3 weeks, and to decrease seed Fe by over 30% (Uauy et al. 2006). Generally, crop breeding has been often selected for improved grain maturation time, but ignored nutrient accumulation in the grain as a desirable trait. Many staple crops are agronomically productive, but they have low levels of nutrients like Fe and Zn in the seed. Thus, fortification is necessary for sustainable crop production as well as nutrient supplement for human health. Cereal seeds provide more than 50% of the world's energy intake (Bewley 1997) and are a large part of the diet in many developing countries. As the plant based diet offers relatively low amounts of bioavailable Fe and Zn, large portions of the developing world suffer from these metal deficiency, including over 60% of all children in Africa and Southeast Asia (de Benoist et al. 1993). This chapter has focused on understanding how nutrients (particularly Fe and Zn) are transported to seeds, and how this can be increased. This shows the importance of determining how Fe and Zn levels are sensed at the tissue and intracellular level, and how this ultimately affects metal allocation to the seed.

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