
18 Some Interactions of Mineral Nutrients and Organic Substances in Plant Nutrition

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18.1 INTRODUCTION

The mineral nutrition of plants is dependent upon complex inorganic and organic sources of essential plant nutrients. Carbon is assimilated from the air by photosynthetic plants, and parasitic plants absorb some or all of their nutrients from other plant or animal material. Essential plant nutrients other than carbon are absorbed directly through cells in contact with the environment (e.g., roots, leaves, and surface of cells of other organs) or from other plants, in the case of parasitic plants such as *Cassytha* spp. or *Striga* spp. The acquisition of mineral nutrients can be directly facilitated by other organisms, such as mycorrhizae, which can increase the surface area of the root system of a plant, and indirect action by organisms such as fungi and bacteria can mineralize elements, making them available for absorption by plants. The purpose of this chapter is not encyclopedic, but rather to orient the reader regarding various aspects of interaction of mineral nutrients with organic substances in plant nutrition; further, in-depth information is available via the references.

18.2 PROPERTIES OF THE ESSENTIAL PLANT NUTRIENTS

There are 17 essential plant nutrients, and an element is essential if it fulfills either one or both of two criteria: (1) it is part of a molecule that is an intrinsic component of the structure or metabolism of a plant, or (2) plants deprived of this element exhibit abnormalities in growth, development, or reproduction (Epstein and Bloom, 2005). For the purpose of better understanding of interactions of organic (carbon-containing) substances with mineral nutrients (elements other than carbon), it is useful to categorize the 17 essential plant nutrients as 9 metals and 8 nonmetals. The metals are calcium, copper, iron, magnesium, manganese, molybdenum, nickel, potassium, and zinc, and the nonmetals are boron, carbon, chlorine, hydrogen, nitrogen, oxygen, phosphorus, and sulfur. Of the metals, molybdenum is found principally in anionic form (MoO_4^{2-})

in well-aerated agricultural soils with $\text{pH} > 5.0$ (Lindsay, 1972). Cationic competition in nutrient uptake by plants was clearly shown by Martin (1933).

Plants accumulate more base cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) than anions from the soil, so in the plant, the electrical imbalance between cations and anions is eliminated, or balanced, with organic anions. In terms of equivalents of inorganic cations (C_i), inorganic anions (A_i), and organic anions (OA), $C_i - A_i - \text{OA} \approx 0$ in biomass. Inorganic cations (mainly K^+ and Ca^{2+}) and organic anions (anions of weak acids such as malate and citrate) buffer the internal pH of plants in a physiological range near pH 6.5. One consequence of the $C_i - A_i$ imbalance in biomass, however, is a surplus of A_i relative to C_i in soil, so for each organic anion created in plant metabolism, one H^+ accumulates in soil. Another cause of acidity produced as a result of biological activity in soils is acidity that occurs when NH_4^+ is oxidized, producing H^+ and NO_3^- as the result of microbial processes (Loomis and Conner, 1992).

18.3 PROPERTIES OF SOIL ORGANIC MATTER

Soil organic matter (SOM) from outside the plant contains and interacts with mineral nutrients outside the plant. SOM can be divided into nonhumic and humic substances, and SOM can facilitate transport and absorption of mineral nutrients. Nonhumic substances such as carbohydrates, proteins, amino acids, fats, waxes, alkanes, and low-molecular-weight organic acids are readily attacked by microorganisms and can disappear rapidly (Schnitzer, 1978). Humic substances in soils comprise most of SOM, and they decompose slowly under natural conditions. The chemical composition of SOM is approximately 50% C, 39% O, 5% N, 5% H, 0.5% P, and 0.5% S (w/w), but these values can vary from soil to soil (Barber, 1995). There is a synergistic effect of mineral nutrients and humic substances on plant growth. Long-term experimentation since 1852 at Rothamsted, United Kingdom, has shown that spring barley grown on soil that was amended with farmyard manure yielded more barley grain than did the same soil that was fertilized only with mineral (NPK) fertilizers (Johnston et al., 1994). Stimulatory effects of SOM on plant growth can be considered indirect by improving supply of nutrients, improving soil structure, increasing soil microbial population, increasing cation exchange capacity (CEC) and buffering capacity of the soil, supplying defined biochemical compounds to plant roots, and supplying humic substances that serve as carriers of micronutrients or growth factors. Direct stimulatory effects of humic substances on plant growth include those that require uptake of organic macromolecules resulting in various biochemical effects in the cell wall, cell membrane, or cytoplasm (Chen et al., 2004). Some specific indirect effects of humic substances on mineral nutrition of crop plants include (Stevenson, 1994)

- Thorough incorporation of N and S into stable structures of humic substances during mineralization/immobilization
- Chemical transformations of inorganic N forms, namely, stabilization of N through chemical fixation of NH_3 and conversion of $\text{NO}_2^- - \text{N}$ to N_2 and N_2O through nitrosation
- Solubilization of phosphates by complexation of Ca in calcareous soils and Fe and Al in acid soils
- Alleviation of metal ion toxicities, including Al^{3+} in acid soils

Direct or indirect effects of organic matter in soil can influence the incidence of pathogenic organisms, since an abundant supply of organic matter may result in more growth of saprophytic microorganisms relative to pathogenic microorganisms, reducing populations of the latter. Moreover, biologically active organic compounds in soil, such as antibiotics or certain phenolic acids, may protect plants from soil-borne pathogens (Stevenson, 1994).

Organic matter is present as solid material in soils and is also present in soil solution. Humus that can be extracted from mineral soils in alkali can be separated into humic and fulvic acids, which are

procedural artifacts existing only in the laboratory. Another way of characterizing humic substances is to use a mild step-wise fractionation of the components of supramolecules by a “humeomics” approach using various advanced analytical techniques (Nebbioso and Piccolo, 2011). Particulate organic matter, often used as an index of SOM, contains humic materials that are heterogeneous in age and function. SOM can be categorized in pools and related fractions: labile or active SOM with half-life of days to a few years; slow or intermediate SOM with half-life of a few years to decades; and recalcitrant, passive, and stable SOM with half-life of decades to centuries (Wander, 2004). The bulk of organic matter in most soils occurs as stable humus (Stevenson, 1994). A recent conference in Hangzhou, China, was devoted to analytical and ecological aspects of natural organic matter (Xu et al., 2012), and a partial bibliography of recent humic literature is available at the website of the International Humic Substances Society (Olk, 2006).

The importance of CEC in soils is that it serves to store essential plant nutrient cations that can then be released to the soil solution by cation exchange with other cations, such as hydrogen ion, becoming available for uptake by plants. SOM, depending upon pH, may be more effective in cation exchange per unit mass than are clay minerals (Bohn et al., 1979). Metal cations exchange readily with protons of the amino ($-\text{NH}_2$), carboxyl ($-\text{COOH}$), and hydroxyl ($-\text{OH}$) groups of SOM. Representative CEC values for clay range from 30 to 100 meq/100 g, while humus may be as great as 300 meq/100 g (or cmol (+)/kg). Although humus usually constitutes only 2%–5% of the weight of agricultural soils, it makes a significant contribution to the CEC (Loomis and Conner, 1992). CEC, when viewed as the ability of a negatively charged surface to be saturated with hydrogen ions, can be considered “acidity.” Soil scientists tend to view this property as “CEC,” whereas many chemists view the same property as “acidity.” Humus is highly colloidal and amorphous, rather than crystalline, and the absorptive capacities of humus are greater than those of layer silicate minerals. The surface properties of humic materials are significant. For example, the ion exchange capacities of well-developed humus can range from 150 to 300 meq/100 g, and surface areas of well-developed humus may be as high as 800–900 m^2/g (Bohn et al., 1979). There are a variety of functional groups of organic matter in soils, including carboxyl ($-\text{COOH}$), phenolic, hydroxyl ($-\text{OH}$), quinone, hydroxyquinone, lactone, ether, and alcoholic hydroxyl ($-\text{OH}$). Fulvic acids have somewhat higher contents of $-\text{COOH}$ groups than humic acids. The $-\text{COOH}$ content of humic substances appears to be inversely related to molecular weights, and the proportion of oxygen that occurs in the form of $-\text{COOH}$ is higher for fulvic acids than for humic acids. The reactivity of humic substances, compared to that of clay minerals, is due in large measure to their high content of oxygen-containing functional groups, including $-\text{COOH}$, phenolic- and/or enolic $-\text{OH}$, alcoholic $-\text{OH}$, and the $\text{C}=\text{O}$ of quinones, hydroxyquinones, and possibly α,β -unsaturated ketones. Total acidities of fulvic acids (640–1420 cmol (+)/kg) are generally higher than total acidities of humic acids (560–890 cmol (+)/kg, and the content of oxygen-containing functional groups in fulvic acids appears to be substantially higher for any other naturally occurring organic polymer (Stevenson, 1994). In 20 Colorado soils, the organic matter in soil solution was measured in the range of 2–25 mmol (+)/L, and in 10 New York soils, organic matter in soil solution was measured in the range of 15–75 μmol (+)/L (Hodgson et al., 1966).

Two types of cation–organic matter interactions are the interactions of mineral nutrient cations with negatively charged carboxyl groups or hydroxyl groups and more complex interactions where coordinate linkages with organic ligands are formed (Baldock and Nelson, 2000). Complexation of inorganic cations by SOM can influence soil properties and processes in the following, among other, ways: increased availability of insoluble mineral P through complexation of Fe^{3+} and Al^{3+} in acid soil and Ca^{2+} in calcareous soil, competition for P adsorption sites, and displacement of adsorbed P (Stevenson, 1994; Cajuste et al., 1996) and release of plant nutrients through weathering of rocks and soil parent materials by the removal of structural cations from silicate minerals (Robert and Berthelin, 1986; Tan, 1986). Recent investigation into the interaction of Fe with humic substances of high molecular weight has shown that cucumber plants can absorb Fe^{2+} from Fe^{2+} complexed with high-molecular-weight humic substances (Colombo et al., 2011).

18.4 INTERACTION OF MINERAL NUTRIENTS AND ORGANIC SUBSTANCES NEAR AND AT THE SOIL–ROOT INTERFACE

The soil–root interface, or rhizosphere, is that zone of the soil influenced by the plant, as compared to the “bulk soil,” which is the zone of soil that lies outside the rhizosphere zone and is not directly influenced by growing roots except by the withdrawal of water and nutrients. Biological aspects of the rhizosphere include the walls of the outermost root cells that form the inner boundary of the interface. In relatively young roots, these tissues are the epidermis and root hairs, and other principal components of the rhizosphere are mucigel, soluble exudates, and the microbiological flora of the rhizosphere and rhizoplane, the substrates of which are mucigel, soluble exudates, and, in some cases, cellular contents of living plant tissues (Russell, 1977). The provision of plant nutrients by the cycling of minerals is one of the most significant activities of microorganisms in soil (Lynch, 1983).

It has been proposed that the macronutrients, N, P, and S, are made available to plants in the soil by the mineralization of these elements from organic matter through a dichotomous system involving both biological and biochemical mineralization (McGill and Cole, 1981). Biological mineralization is the result of microbial decomposition of organic matter as an energy source, resulting in the mineralization of N- and C-bonded S. Biochemical mineralization refers to the release of oxidized forms of P and S—phosphate and sulfate—from the P and S ester pool via enzymatic hydrolysis outside the cell membrane.

Rhizosphere studies have, in part, focused on the exudation of organic substances from roots, which can increase the uptake of essential mineral nutrients. Several investigators have reported that carbon released from roots growing in soil amounted to approximately 20% of total plant dry matter (Rovira, 1979). Wheat roots have been reported to lose to the soil up to 39% of carbon translocated to the roots (Martin, 1977). In wheat and barley, with a 16 h photoperiod, growth at 15°C constant or 18°C day/14°C night gave a loss of 33%–40% of the total net fixed carbon (defined as ^{14}C retained in the plant plus ^{14}C lost from the root). Photoperiod can affect the loss of organic compounds from the roots to the rhizosphere. With a 12 h photoperiod and a temperature regime of 18°C/14°C, carbon loss from the roots was decreased to 17%–25% of the total fixed carbon. The proportion of ^{14}C translocated to the roots that was released into the soil did not change with temperature, so carbon distribution within the plant must have changed (Whipps, 1984).

Although some P enters the soil solution through dissolution of precipitates of phosphate, decomposition of organic matter is a more important source. Decay and mineralization of phytic acid and polyphosphates occur slowly, but decay of nucleic acids (such as DNA and RNA) and phospholipids is rapid (Lynch, 1983). Corn roots have been shown to be able to enrich the phosphatase activity in the rhizosphere between 17% and 40%, which enables increased liberation of phosphorus from organic sources. The experiment did not allow determination as to what proportion of the increased phosphatase activity in the rhizosphere was due to exudate from the corn roots and what proportion was contributed by soil microbes growing on or near the roots. Phosphatase activity, measured in $\mu\text{mol/g/h}$ was highest at the root surface and decreased by about 5% or less at a distance of 15 mm from the root surface (Boero and Thien, 1979).

Rhizosphere acidification as a result of exudation of H^+ by plant roots in an alkaline soil will generally be the sole process stimulating the solubilization of alkaline rock phosphates and of native or residual soil phosphates. Such rhizosphere acidification can result from (1) exudation of H^+ due to (a) excess cation-over-anion uptake, (b) excess cation-over-anion uptake as a consequence of NH_4^+ nutrition, and (c) excess cation-over-anion uptake as a consequence of symbiotic N_2 fixation; or (2) exudation of organic acids as a reaction to P starvation (Van Diest, 1991).

Biological fixation of gaseous N (N_2) in nodules of legumes (plants in the family Fabaceae [identified by others as Leguminosae]) by nitrogen-fixing bacteria is an organic system that produces ammonia that is assimilated into the amide group of glutamine. Most often, glutamine is further metabolized to asparagine in temperate leguminous plant species and into ureides, allantoin,

and allantoic acid in tropical species. These solutes are the principal forms of N translocated from the nodules through the xylem (Atkins, 1987). At least six genera of diazotrophic (N_2 -fixing) bacteria have been isolated from the roots of grasses and cereals of agricultural importance (Boddey and Döbereiner, 1988). In 1984, experimentation conducted with nonleguminous plants, specifically wheat, has shown that inoculation of wheat roots with *Bacillus* C-11-25 resulted in 23.9% of the N absorbed by the crop was derived from the atmosphere (Rennie and Thomas, 1987). Besides legumes that are nodulated by *Rhizobium* species, about 200 plant species covering 8 families and at least 17 genera in the tropics and subtropics are nodulated by N_2 -fixing actinomycetes of the genus *Frankia* (Peoples and Craswell, 1992). Nonsymbiotic nitrogen fixation is another aspect of the interaction of organic matter and mineral nutrients near the root surface. *Clostridium pasteurianum*, isolated in 1893, *Azotobacter choococcum*, *Azomonas agilis*, and other free-living microorganisms, including some blue-green algae and yeasts, can convert atmospheric nitrogen to ammonia, which is then available to plants. Bacteria of the genera *Beijerinckia*, *Azotobacter*, and *Clostridium* comprise the major groups of free-living, nitrogen-fixing bacteria that can make nitrogen available for uptake by plant roots (Curl and Truelove, 1986). Bacteria of the genus *Azospirillum*, also aerobic, can inhabit the cortical layers of root tissue and utilize the root exudate energy source as they benefit the plant by fixing substantial quantities of atmospheric nitrogen (Atlas and Bartha, 1981).

Plant growth-promoting rhizobacteria (PGPR) are about 2%–5% of rhizobacteria (Kloepper and Schroth, 1978). While all PGPR are free-living bacteria, some of them invade tissues of living plants and cause unapparent and asymptomatic infections (Sturz and Nowak, 2000). PGPR may induce plant growth promotion by direct or indirect modes of action (Beauchamp, 1993; Kloepper, 1993; Kapulnik, 1996; Lazarovits and Nowak, 1997). Direct modes of action include production of stimulatory bacterial volatile compounds and phytohormones, lowering of the ethylene level in the plant, improvement of the plant nutrient status (liberation of phosphates and micronutrients from insoluble sources, and nonsymbiotic nitrogen fixation), and stimulation of disease-resistance mechanisms. Indirect effects originate in cases such as when PGPR act like biocontrol agents reducing diseases and when they stimulate xenobiotics in inhibitory contaminated soils (Jacobsen, 1997). PGPR have been classified as biofertilizers (increasing the availability of nutrients to plants), phytostimulators (plant growth promoting, usually by the production of phytohormones), rhizoremediators (degrading organic pollutants), and biopesticides (controlling diseases mainly by the production of antibiotics and antifungal metabolites) (Somers et al., 2004). Among the PGPR, *Azospirillum* species head the list of bacterial biofertilizer products, yet except those formulated with *Azospirillum*, all bacterial biofertilizer products are applied as biopesticides or as biocontrol agents (Burdman et al., 2000; Lucy et al., 2004). To develop PGPR biofertilizers, the strain(s), inoculum production, and, in general, development of appropriate formulations and strategies of field experimentation are fundamental conditions for a successful application of PGPR species, at least in the case of *Azospirillum* inoculants (Fuentes-Ramirez and Caballero-Mellado, 2006).

Root exudates include carbohydrates, amino acids, organic acids, nucleotides, flavonones, enzymes, and miscellaneous compounds, among which are hydrocyanic acid, glycosides, and saponins, which are toxic to microorganisms. Root exudates can stimulate or inhibit the growth of soil microorganisms (Rovira, 1965). Organic acids have a prominent role in cell metabolism, and they affect soil pH and soil microbial activity. Moreover, organic acids are good metal-chelating compounds, and they play an important role in the absorption and translocation of mineral nutrients (Curl and Truelove, 1986).

Hunt et al. (1986) have identified five classes of chemical bonds in humic substances (C–C, N–C, S–C, S–O–C, and P–O–C). Microorganisms oxidizing carbon provide energy to mineralize the compounds characterized by the first three types of bonds. Compounds with sulfur and phosphorus atoms present as esters can be mineralized by the action of extracellular hydrolases, according to the need of the element (McGill and Cole, 1981).

18.5 INTERACTION OF MINERAL NUTRIENTS AND ORGANIC SUBSTANCES AT THE LEAF

Materials such as urea, antibiotics, and herbicides applied to plant foliage may, depending upon the plant species and the nature of the chemical compound, be translocated to the roots from which either the compound or a by-product may be released to the rhizosphere where it can affect microbes (Curl and Truelove, 1986). The "skin" of plant leaves is known as the cuticle, a continuous extracellular membrane made of highly recalcitrant material that can easily resist decay for millions of years under favorable conditions (Edwards et al., 1996; Ewbank et al., 1996). The major functions of the plant cuticle include transpiration control, control of loss and uptake of polar solutes, controlling the exchange of gases and vapors, transport of lipophilic substances, water and particle repellence, attenuation of photosynthetically active radiation and UV radiation, mechanical containment, separating agent in plant development, and serving as an interface for biotic interactions (Riederer, 2006).

Penetration of the cuticle of leaves by nonpolar compounds and polar compounds, such as inorganic ions and charged organic compounds like organic acids or amino acids, occurs via different paths in the cuticle (Schreiber, 2006). The lipophilic transport path is composed of lipophilic cutin and wax domains, and a polar transport path is presumed to be composed of polar aqueous pores (Schreiber et al., 2001; Schönherr and Schreiber, 2004; Schlegel et al., 2005). While the chemical nature of polar domains in cuticles is still being determined, neither the size nor the chemical nature of the postulated paths of transport was known in 2006. Nonetheless, plant cuticles are known to contain polar functional groups that may account for polar aqueous pores. One hypothesis is that nonesterified carboxyl and/or hydroxyl groups of cutin monomers or wax molecules could contribute to the formation of polar transport paths. Another hypothesis is that polar carbohydrates known to be associated with isolated cuticles could form the basis for polar transport paths, possibly extending through the lipophilic cuticle from the epidermal cells to the outer surface of the cuticle, forming sites where polar compounds such as inorganic nutrients or organic acids could diffuse through the cuticle to the cells contained by the epidermal cell membranes (Schreiber, 2006).

One factor in the absorption of mineral nutrients in leaves is the presence of ectodesmata, which are plasmodesmata in the outer walls of epidermal cells. Ectodesmata are microscopic channels in the walls of plant cells, allowing movement of solutes between them. Leaves of *Plantago major* and *Helxine soleirolii* were examined in connection with foliar absorption, and leaf structures such as guard cells, conical hairs, anticlinal walls, and the epidermal cells adjacent to the leaf veins were shown to consistently contain large numbers of ectodesmata, while in neighboring cells ectodesmata were low in number or lacking. The ectodesmata were explained by the investigator to be a means by which mineral nutrients could enter the leaves from their surface (Franke, 1961).

Cuticular membranes, the first barriers in nutrient uptake by leaves, appear highly permeable to monovalent and divalent cations and anions. Yamada et al. (1964) in experiments with $\text{Ca}^{45}\text{Cl}_2$, Rb^{86}Cl , $\text{FeS}^{35}\text{O}_4$, or RbCl^{36} and green onion leaf cuticles and tomato fruit cuticles found that penetration of the inorganic cations and anions studied occurred equally well through cuticles from plant surfaces with or without stomata. These investigators found that absorption (penetration from the outside surface inward) occurred more readily than leaching (penetration from the inside surface outward), and they surmised that uptake dominates loss of nutrients through foliar surfaces.

Active uptake of phosphorus, and rubidium, an analogue of potassium, into leaf tissue has been measured in primary leaves of bean seedlings. Criteria for active uptake included time-course analysis, temperature, oxygen, energy dependence, sensitivity to metabolic inhibitors, accumulation against a concentration gradient, irreversibility, and pH dependence. The results suggest that the overall process of foliar absorption of rubidium and phosphate by bean leaves, beginning with zero time and extending over a 24 h period, is metabolic. The investigators proposed that carriers play an important role in uptake and that they are proteinaceous (Jyung and Wittwer, 1964).

Urea, ammonium, and nitrate are common forms used for foliar application of nitrogen to fertilize crops. Norway spruce shoots that included both needles and twigs absorbed ammonium ions,

and there was no evidence that ammonium uptake was accompanied by exchange for base cations such as calcium (Wilson, 1992). Pathways for the absorption of solutes are known to exist in the region of radial rays across the twig bark (Klemm, 1989). Neither spruce nor pine shoots absorbed nitrate (Wilson, 1992). The fact that ammonium was absorbed by the stems of spruce and pine, but nitrate was not, suggests that the form of nitrogen used for foliar fertilization may be important in determining the efficiency of foliar nitrogen fertilizers. Uptake of urea by foliar application can be toxic to plants. Leaf-tip necrosis often observed after foliar fertilization of soybean plants with urea is usually attributed to ammonia formed through hydrolysis of urea by plant urease. Research using a urease inhibitor demonstrated that although addition of this urease inhibitor to foliar-applied urea increased the urea content and decreased the ammonia content and urease activity of soybean (*Glycine max.* (L.) Merr.) leaves fertilized with urea, it increased the leaf-tip necrosis observed after fertilization. The investigators concluded that this necrosis resulted from accumulation of toxic amounts of urea rather than from formation of toxic amounts of ammonia (Krogmeier et al., 1989). Ammonium was absorbed more rapidly than was nitrate by *Ricinus* through the stomates and cuticle around the stomates, although the rates of uptake of both were slow (Peuke et al., 1998).

Salicylic acid and zinc, when applied to the leaves of mungbean (*Vigna radiata* L. Wilczek), were found to significantly ($p \leq 0.05$) increase plant height, number of branches/plant, number of pods/plant, number of seeds/pod, 1000 seeds weight, seed weight/plant, and seed yield/ha as compared with control (untreated plants), and the superiority was due to the high salicylic acid concentration (150 ppm). Significant ($p \leq 0.05$) increases in all the earlier-mentioned traits occurred with foliar application of zinc, as compared to untreated plants. Based on the experimental results, the investigators recommended foliar application of salicylic acid and zinc to mungbeans, using salicylic acid and zinc at concentrations of 150 and 400 ppm, respectively (Ali and Mahmoud, 2013).

The size of the hydrated ion is a major factor affecting foliar absorption of mineral nutrients. Mandair and Harris (2003) investigating foliar application of N, P, K, Na, and glucose with *Prosopis chilensis* found that the most important factor affecting foliar mineral uptake was the size of the hydrated ion. They note that it is well established that the cuticular penetration rates of mineral nutrients are inversely related to the radius of the hydrated ion (Swietlik and Faust, 1984; Kannan, 1986), an observation with which their results concurred. Of the four mineral nutrients examined, K had the smallest hydrated ionic radius at 1.88 Å and was most readily absorbed. K uptake was followed in descending order by Ca, NO₃⁻, and PO₄³⁻ ions, which exhibit successively larger hydrated ionic radii. As early as 1969, Kannan (1969) reported that for ¹⁴C-labeled molecules, rates of penetration of the cuticular membranes enzymatically isolated from tomato fruit were higher for smaller molecules. A negative correlation between molecular weights of the organic solutes and their rates of penetration was obtained by regression analysis. Higher correlation was obtained for penetration through cuticles from the stomatous surfaces than for those from the astomatous surfaces.

The form of iron used to supply the element through foliar application is important, since the size of the compound containing iron affects the rate at which the element moves through the cuticle of the leaf. Experimentation with ⁵⁹Fe and intact bean leaves has shown that while specific absorption of ⁵⁹FeSO₄ and ⁵⁹FeSO₄ + urea (10 mM) was greater than that of ⁵⁹Fe-EDTA and ⁵⁹Fe-EDDHA, the percentages of the two chelated forms of iron were greater than those of the two ⁵⁹FeSO₄ forms (Wittwer et al., 1965). Kannan (1969) observed that the penetration of Fe through cuticles of tomato fruit was reduced by chelation with EDDHA, the presence of urea, or both. He speculated that the chelated form of Fe was less penetrable because of its greater molecular size. In earlier studies (Wittwer et al., 1965), uptake of Fe from FeEDDHA was also very much less than that from FeSO₄. This poor absorption of Fe from FeEDDHA by leaves of intact bean plants could be related to low permeability of cuticles to FeEDDHA, as obtained herein with isolated cuticles (Kannan, 1969).

Naturally occurring chelates such as proteins, amino acids, organic acids, flavonoids, purines, and riboflavin can facilitate the absorption of cationic plant nutrients, and the stability of metal

chelates, or the replacing power of the elements is $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, so in a solution, the ferric ion would be expected to replace other ions, if all were in equivalent amounts (by charge) (Hsu, 1986).

18.6 SOME ASPECTS OF TRANSPORT OF MINERAL NUTRIENTS IN THE PLANT

To maintain the concentration of essential metals within physiologically tolerable limits and to minimize their detrimental effects, all eukaryotes have evolved a number of mechanisms that control the uptake, accumulation, trafficking, and detoxification of metals. The main components of metal homeostasis are transport, chelation, and compartmentation (Shingles et al., 2004).

As living cells constantly exchange energy, matter, and information with their environment, the plasma membrane surrounding them cannot be impermeable and is, indeed, a selective barrier through which many solutes can be transported, sometimes against a concentration gradient. This active transport requires the plasma membrane to be energized by cation-translocating adenosine triphosphatases (ATPases) and, possibly to a lesser extent, by redox reactions. Cation-translocating ATPases reside inside the plasma membrane, and they actively pump cations against their concentration gradient. The process is powered by hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate, and inorganic phosphate (P_i) for transported cations such as H^+ , Ca^{2+} , Na^+/K^+ , and H^+/K^+ (Michelet and Boutry, 1996). In the roots, minerals are absorbed by root hair, epidermal, and cortical cells (Taiz and Zeiger, 1991), and once the mineral nutrients are in the cell, they are transported to the stele. It appears that H^+ -ATPase activity is needed not only in the cortex and epidermis of the roots for ion absorption, but also in the stele for loading ions into the conductive tissues (Parets-Soler et al., 1990; Samuels et al., 1992; Cowan et al., 1993). As an example of the ability of ATPases to transfer mineral nutrient ions against concentration gradients, the concentration of K^+ in the soil solution is often below 100 μM , and the intracellular concentration of K^+ in cells within the plant is on the order of 100 mM, 1000-fold greater than outside the plant (Maathuis and Sanders, 1993). Uptake of K^+ occurs across plasma (cell) membranes by two transport systems—low affinity and high affinity—demonstrated by Epstein et al. (1963).

During early growth of soybean, it has been shown using radioactive ^{14}C tracers that organic compounds containing nitrogen can be transferred directly from the xylem to the phloem, an indication that inorganic N compounds may also be transferred directly from the xylem to the phloem (Da Silva and Shelp, 1989–1990). Organic N compounds produced in root nodules of legumes have been shown to be mobile in both the xylem and the phloem of soybean (Shelp and Da Silva, 1990). In pea shoots, some amino acids arriving via the xylem in the mature leaves were translocated from the mature leaves to the young leaves via the phloem with relatively little metabolic conversion. Substantial amounts of another amino acid, glutamine, were converted to glutamate, which was exported (with unchanged amide) to younger leaves with little further conversion (Urquhart and Joy, 1982).

Zinc is the most common crop micronutrient deficiency, particularly in high-pH soils with low $[\text{Zn}]_{\text{pss}}$ (Graham et al., 1992; White and Zasoski, 1999; Cakmak, 2002, 2004; Alloway, 2004). Fifty percent of cultivated soils in India and Turkey, a third of cultivated soils in China, and most soils in Western Australia are classed as Zn deficient (Broadley et al., 2007). In plant cells, high Zn-status leaf epidermal cell vacuoles, cell walls, and cytoplasm can contain, respectively, 74,305, 11,577, and 3,205 $\mu\text{g Zn/g DW}$ (dry weight); lower Zn-status leaf mesophyll cell vacuoles, cell walls, and cytoplasm contain, respectively, 327, 9353, and ≤ 262 $\mu\text{g Zn/g DW}$; and root cortical vacuoles, cell walls, and cytoplasm contain, respectively, ≤ 262 , 589, and ≤ 262 $\mu\text{g Zn/g DW}$ (Freye et al., 2000). Several studies have shown no correlation between zinc efficiency and root Zn uptake, Zn translocation to shoot, or shoot Zn accumulation. While it has not been possible to conclusively link differences in leaf subcellular Zn compartmentation with zinc efficiency of plants, biochemical Zn utilization, including the ability to maintain the activity of Zn-requiring enzymes in response to Zn deficiency, may be a key component of zinc efficiency.

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