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17 Plant Nutrition

Interactions of Mineral and Organic Substances

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CONTENTS

17.1 Introduction.....	297
17.2 Properties of the Essential Plant Nutrients.....	297
17.3 Properties of Soil Organic Matter.....	298
17.4 Interaction of Mineral Nutrients and Organic Substances Near and at the Soil–Root Interface.....	301
17.4.1 Root Exudates.....	306
17.4.2 Interactions of Iron and Organic Substances.....	307
17.4.3 Aggregates of Minerals, Mineral Nutrients, and Organic Substances.....	309
17.5 Interaction of Mineral Nutrients and Organic Substances at the Leaf.....	310
17.6 Some Aspects of Transport of Mineral Nutrients in the Plant.....	312
References.....	314

17.1 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, 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 nitrogen-fixing bacteria, nitrifying bacteria, and mycorrhizae, which can increase the surface area of the root system of a plant. 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 the interaction of mineral nutrients organic substances and in plant nutrition; further, in-depth information is available via the references.

17.2 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 interactions of organic (carbon-containing) substances with mineral nutrients (elements other than carbon), it is useful to categorize the 17 essential plant nutrients as nine metals and eight non-metals. The metals are calcium, copper, iron, magnesium, manganese, molybdenum, nickel, potassium and zinc, and the non-metals are boron, carbon, chlorine, hydrogen, nitrogen, oxygen, phosphorus, and sulfur.

Of the metals, molybdenum is found principally in an anionic form (MoO_4^{2-}) in well-aerated agricultural soils with $\text{pH} > 5.0$ (Lindsay, 1972). Molybdenum is essential in ecosystem cycling of N, C, and other elements essential to life, and its most prominent role is, perhaps, its being a co-factor in the nitrogenase enzyme, which can lead to

Mo limitation of biological N_2 fixation when Mo is in short supply (Marks et al., 2015). In addition, Mo also influences nitrification, nitrate assimilation, and denitrification (Stiefel, 2002). In an ecological study of Mo in soil, bedrock, and plants across 24 forests spanning wide soil pH gradients in both basaltic and sedimentary lithologies, Marks et al. found that the oxidizable organic fraction of surface mineral soil accounted for an average of 33% of bulk soil Mo across all sites, 1.4% was associated with reducible Fe, Al, and Mn oxides, and 1.4% was in the exchangeable form. Exchangeable Mo was greatest at low soil pH, and a positive correlation of exchangeable Mo with soil carbon suggests to Marks et al. that organic matter (OM) may be a source of readily exchangeable Mo.

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), $C_i - A_i - OA \approx 0$ 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, which occurs when NH_4^+ is oxidized, producing H^+ and NO_3^- as the result of microbial processes (Loomis and Conner, 1992).

Nanoparticles of the oxides of an essential mineral nutrient, copper, ($nCuO$) and of a nonessential mineral, cerium, of the lanthanide series ($nCeO_2$), when applied to roots or leaves of *Solanum lycopersicum* (tomato), were found to significantly decrease disease infestation of the fungal pathogen *Fusarium oxysporum* f. sp. *lycopersici*. Other effects of the treatments with nanoparticles investigated were root and shoot physiological parameters, biomass, plant height, chlorophyll content, activities of the enzymes, polyphenol oxidases and catalase, total proteins, and macro- and microelement nutrients (Adisa, 2019).

At the seed germination stage, seeds of durum wheat, bread wheat, barley, and rye were exposed to 5 mL of a solution of 10 mg of 30-nm ZnO L^{-1} nanoparticles or 5 mL of 10 mg ethylenediamine disuccinic acid (EDDS) L^{-1} . In response to exposure to ZnO nanoparticles, the germination percentage of bread wheat and rye decreased, but the germination percentage of durum wheat and barley increased. Barley germination, plumule length, and seedling vigor index were all increased by both the ZnO and EDDS treatments compared to the untreated control (Doğaroğlu et al., 2019).

A US Patent Application was filed (Biswas and Ramesh, 2019) for the synthesis of nanocomposites to enhance plant nutrition. The patent application includes a disclosure

related to development of improved fertilizer for precision and sustainable agriculture. A method was developed wherein efficient NPK nanocomposite for plant nutrition was synthesized in a single step using aerosol science and technology concepts. Further, a formulation was prepared by the addition of ZnO , TiO_2 and other nanoparticles to the NPK nanocomposite. Also, an aerosol-based foliar application technique was developed for the precise delivery of nanoparticles to the plants.

17.3 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). Another way of categorizing components of SOM divides SOM into living and nonliving SOM pools, according to their decomposition rates, with the living SOM pool being called microbial biomass and nonliving pools being divided into dissolved organic matter (DOM), particulate organic matter (POM), and stable/recalcitrant organic matter (Dinakaran and Rao, 2019). Humic substances in soils comprise most of SOM, and they decompose slowly under natural conditions.

Piccolo (2016) presents a brief overview of the evolution of various concepts of humic substances and the importance of analytical methods to the changing concepts of humic substances. He notes that the current understanding of the humic substances as supramolecular structures has advanced since the time that they were understood as high-molecular-weight polyelectrolytes synthesized de novo in soil. In addition to intermolecular forces such as weak H-bonds, van der Waals forces, entanglement, and metal bridging complexes, moderate and strong H-bonding contribute to the formation of the metachemical supermolecular structure of natural organic matter (NOM, Wells, 2009).

In a comprehensive review of more than 200 years of extraction and characterization of NOM, Olk et al. (2019a) explain that SOM is composed of two major components, or humic substances: humic acid (HA, solubilized by alkali but insoluble in subsequent

acidification), and fulvic acid (FA, historically defined as soluble in both alkali and acid). The International Humic Substances Society (IHSS) has more recently defined FA as the material soluble in both alkali and acid and that will adsorb to a nonionic resin, distinguishing it from a NOM fraction that is very hydrophilic even at low pH and does not adsorb on the resin (Swift, 1996; IHSS, 2018). In addition to a general justification for alkali extractions of humic fractions, Olk et al. (2019a) specifically address major issues raised by critics about the suitability of HA and FA for use in environmental and agricultural research. They also present case studies regarding (1) reactions between persistent organic pollutants and humic fractions in DOM, (2) modeling of metal ion binding in soils, (3) pesticide sorption in soils, (4) humic acid as an indicator of compost maturity and the capacity of compost to enhance plant growth, (5) soil humic fractions as indicators of SOM responses to organic amendments, (6) soil humic fractions as indicators of young SOM for nutrient cycling in agriculture, and (7) SOM and soil N cycling for the sustainability of monoculture paddy rice.

Two critics of HA and FA as components of humic substances (HS), Lehmann and Kleber (2015) make a case against the traditional approach to the study of OM espoused by Olk et al. (2019a) and, in contrast, propose that SOM is a continuum of progressively decomposing organic compounds. Other issues raised by Lehmann and Kleber (2015) and addressed by Olk et al. (2019a) include (1) the potential for chemical alteration during alkali extraction, (2) a presumed necessary linkage of alkali extractions to belief in a macromolecular structure of HS, and (3) an alleged lack of evidence for the occurrence of “humification” that would result in chemical structures in soil and water not inherited directly from organisms (Olk et al., 2019b).

From the standpoint of using soil to treat wastewater, positively charged phenolic and carboxylic functional groups of HS in soils can accept and release (exchange) H^+ , dissolved aluminum (Al^{3+}), sodium (Na^+), quaternary ammonium (NH_4^+) compounds used for disinfection, and cationic plant nutrients. The strength of adsorption of cations on negatively charged sites on humic substances follows the order: $Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+$ (Amador and Loomis, 2019a). The chemical composition of SOM has been estimated as 50% C, 39% O, 5% N, 5% H, 0.5% P, 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, UK, has shown that spring barley grown on soil that was amended with farmyard manure yielded more barley grain than did the same soil, which was fertilized only with mineral (NPK) fertilizers (Johnston, 1994).

In a four-year study of the effects of a 5°C increase in average soil temperature, 5 g $NH_4NO_3-N m^{-2} y^{-1}$ fertilization, or both, Pisani et al. (2015) found that an increase in soil temperature and N fertilization promoted decomposition of plant-derived aliphatic and cyclic organic compounds in the forest floor. Lignin oxidation was most pronounced in the mineral horizon, and cutin degradation and relatively higher microbial activity were observed in heated plots, compared to the control. N fertilization enhanced lignin oxidation. Both soil warming and N fertilization resulted in enrichment of plant-derived alkyl structures and OM derived from microbes.

Stimulatory effects of SOM on plant growth can be considered indirect by improving the supply of nutrients, improving soil structure, increasing soil microbial population, increasing cation exchange capacity and buffering capacity of the soil, supplying defined biochemical compounds to plant roots, and supplying humic substances, which serve as carriers of micronutrients or growth factors. Direct, stimulatory effects of humic substances on plant growth include those which 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 the following (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 ammonia (NH_3) and conversion of $NO_2^- -N$ 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; and
- Alleviation of metal ion toxicities, including Al^{3+} in acid soils.

Direct or indirect effects of OM in soil can influence the incidence of pathogenic organisms, since an abundant supply of OM 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).

SOM is present as a solid material in soils and is also present in soil solution. Humus, which 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 stepwise fractionation

of the components of supramolecules by a “humeomics” approach using various advanced analytical techniques (Nebbio and Piccolo, 2011). Particulate organic matter (POM), often used as an index of SOM, contains humic materials that are heterogenous in age and function. SOM can be categorized in pools and related fractions: Labile or active SOM with a half-life of days to a few years, slow or intermediate SOM with a half-life of a few years to decades, and recalcitrant, passive, and stable SOM with a half-life of decades to centuries (Wander, 2004). The bulk of OM in most soils occurs as stable humus (Stevenson, 1994). A conference in Hangzhou, China, was devoted to analytical and ecological aspects of NOM (Xu et al., 2012), and a partial bibliography of books regarding humic substances is available at the website of the International Humic Substances Society (IHSS, 2019).

In a study of humic extracts of hydrochar and Amazonian Dark Earth, Bento et al. (2019) characterized molecules of the humic extracts and measured effects of the extracts on maize seed germination and early growth. They found that the amphiphilic arrangement of supramolecular structures enabled interaction with other organic compounds and release of bioactive molecules. The most bioactive humic-like substance (HLS) was extracted from bagasse hydrochar, and its increased bioactivity was attributed to the presence of abundant aromatic and phenolic units that promoted growth of coleoptiles, radicles, and lateral, seminal roots.

The importance of cation exchange capacity in soils is that it serves to store essential plant nutrient cations, which can then be released to the soil solution by cation exchange with other cations, such as hydrogen ion, becoming available for uptake by plants. Soil organic matter, 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 that can dissociate from the amino ($-\text{NH}_2$), carboxyl ($-\text{COOH}$), and hydroxyl ($-\text{OH}$) groups of soil organic matter. Representative cation exchange capacity (CEC) values for clay range from 30 to 100 cmol (+) kg^{-1} ($\text{meq } 100 \text{ g}^{-1}$), while the CEC of humus may be as great as 300 cmol (+) kg^{-1} . Although humus usually has been estimated to constitute 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 “cation exchange capacity”, whereas many chemists view the same property as “acidity.”

Humus is highly colloidal and amorphous, rather than crystalline, and the adsorptive capacities of humus are greater than those of layer silicate minerals. The surface

properties of humic materials are significant. For example, the CEC of well-developed humus can range from 150 to 300 cmol (+) kg^{-1} , and surface areas of well-developed humus may be as high as 800–900 $\text{m}^2 \text{ g}^{-1}$ (Bohn et al., 1979). There are a variety of functional groups of SOM, 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 HS 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 HS, 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. Values of total CEC, or acidity, of fulvic acids (640–1420 cmol (+) kg^{-1}) are much higher than for humic acids (560–890 cmol (+) kg^{-1}), 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 the soil solution was measured in the range of 2–25 mmol (+) L^{-1} , and in 10 New York soils, organic matter in soil solution was measured in the range of 15–75 $\mu\text{mol (+) L}^{-1}$ (Hodgson et al., 1966).

Petridis et al. (2013) studied interactions of glucose (a hydrophilic organic compound) and stearic acid (an amphiphilic compound) with aluminum oxide (Al_2O_3 , a soil mineral analogue). They demonstrated that regardless of whether glucose or stearic acid was the first of the two compounds to be exposed to Al_2O_3 , when both were present in an aqueous medium, glucose was bound to Al_2O_3 , and stearic acid heads and tails alternated, resulting in a three-layered nanostructure. The BAAB repeating structure of heads (A) and tails (B) of stearic acid is shown in a model by Petridis et al. to explain how hydrophilic heads of stearic acid can interact both with water and glucose, since hydrophobic tails of stearic acid are attracted to one another. They explain that in their investigation, glucose rings were mostly not parallel to the mineral surface, in contrast to aromatic compounds that can sorb to mineral surfaces in highly parallel orientations due to $n-\pi$ interactions between nonbonding electrons at siloxane surfaces and aromatic π electrons.

Purified HA caused a significant increase in shoot growth of cucumber (*Cucumis sativus* L. cv Ashley) that was associated with enhanced root H^+ -ATPase activity and significant decreases in the concentrations of several cytokinins – principally putrescine – and polyamines in the roots (Mora et al., 2010). Application of purified HA

to the roots also increased the concentration of NO_3^- , several cytokinins and polyamines in the shoot. Mora et al. explain the root-shoot distribution of NO_3^- and increased concentration of NO_3^- in the shoot as due to the activation of root plasma membrane H⁺-ATPase activity caused by the application of HA to the roots. Changes in the root-shoot distribution of P, K, Ca, Mg, Na, S, B, Cu, Fe, Mn, and Zn in cucumber were also attributed to the influence of purified HA applied to the roots.

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 soil organic matter 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, 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 (Tan, 1986; Robert and Berthelin, 1986). Rates of adsorption of phosphate in soil affect the availability of P to plants. Bulmer et al (2019) found that pseudo-second-order kinetics described both adsorption and desorption of P. They observed that citrate directly competed with phosphate for adsorption sites in soils with reduced levels of Ca, however in soils with a high concentration of labile Ca, citrate did not desorb P. An investigation into 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).

Addition of compost to soil results in many changes in soil characteristics due to the addition of humic substances. Changes in the solubility of mineral nutrients and nutrient retention in soil can occur with chelation and bridging of components of humic substances by cationic plant nutrients (Guo et al., 2019). Composted sewage sludge (CSS) used as a soil amendment increased growth of the tree, *Populus x euramericana* "Guariento" (poplar) and during a two-year field trial, uptake of N and P were increased with increasing rate of CSS application (Guoqing et al., 2019).

Exceptional quality is a term used by the wastewater industry to describe biosolids that are treated to eliminate pathogens by processes that further reduce pathogens and vectors while lowering concentrations of pollutants (Alvarez-Campos and Evanylo, 2019). Methods to produce biosolids of exceptional quality include composting, thermal drying, pasteurization, and thermal

hydrolysis plus anaerobic digestion (Cambi process), resulting in Class A biosolids (USEPA, 2006; Abu-Orf et al., 2012).

Emerging organic pollutants are increasingly of concern, since relatively little is known about their behavior as effluent from wastewater treatment moves through the soil profile (Schaidler et al., 2017). Emerging pollutants (EPs), also referred to as emerging contaminants and organic micropollutants), in ground and surface waters originate from human activities and are transported to receiving waters in effluent from the wastewater treatment plants and septic systems. EPs include synthetic and natural compounds, from pharmaceuticals to industrial chemicals, and EPs also include nanomaterials, microplastics, and microfibers. EPs are commonly found in very low concentrations (ng L^{-1} to pg L^{-1}) and can be adsorbed on the surfaces of soil particles or be absorbed by plants. Once in the plant, EPs may be metabolized, partitioned into plant tissues, or translocated to the leaves where, if sufficiently volatile, they may be lost to the atmosphere (Amador and Loomis, 2019b).

Reactive carbon (RC), also known also as permanganate oxidizable carbon, is a fraction of SOM that is oxidizable in the presence of potassium permanganate in solution. The RC pool of SOM includes C most readily degradable by microorganisms and C in SOM bound to soil minerals. The residence time of RC is estimated to be two to five years, in contrast to recalcitrant C, such as that found in humus that has a turnover time of several hundred to thousands of years. The fractions of SOM included in RC include fresh organic material, soil microbial biomass, particulate matter, and other easily metabolized compounds such as carbohydrates, proteins, amino acids, and C loosely bound to soil minerals (USDA-NRCS, 2014).

17.4 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 which 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).

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).

Phosphorus availability was increased several-fold with long-term application of manure in addition to NPK fertilization, compared to NPK fertilization alone, in rice production in China (Ahmed et al., 2019). Long-term addition of manure with inorganic fertilizer significantly increased both rice grain yield and the labile P pool, while decreasing the non-labile P pool, compared to the check and only NPK inorganic fertilization.

In a study to determine the long-term effects of elevated concentration of N in forest soil, Bowden et al. (2019), beginning in 1993 (year 0), annually applied N at 100 kg N ha⁻¹ y⁻¹, a rate approximately 10-fold greater than ambient N deposition. They determined that reduced decomposition of litter and soil organic matter drove C increases in plots with added N, compared to control plots. Addition of N reduced soil respiration, and microbial biomass in O, A, and upper-B horizons whereas lower and soil microbial community composition was changed in plots receiving N, compared to the control plots. Available forms of K, Ca, and Mg were reduced in both O and A horizons receiving N fertilization.

About 84% of the newly added mineral N applied to temperate hardwood forest soils as ¹⁵NH₄¹⁵NO₃ (99 atom% ¹⁵N) was stored in the soil organic horizon within 26 min of deposition. The N was initially stored about evenly between labile + mineral and stable forms, with most of the labile N cycling through microbial biomass as it was lost to other pools during a 9- to 12-month period. The fraction of ¹⁵N stored in the stable form, 30%, was unchanged a year later, had a median residence time of >29 years in the organic soil horizon, and was greater in late-successional, compared to young forest stands (Lewis et al., 2014).

Biochar produced by heating apple branches at 700°C in low oxygen was used as a soil amendment to determine whether it could increase nitrogen use efficiency (NUE) of *Malus hupehensis* Rehd. (Hupeh crabapple) by altering soil properties and root growth (Cao et al., 2019). NUE was increased by biochar amendment from 6.77% to 261.53%, compared with the non-amended soil. Root

nitrate reductase activity and root activity of *M. hupehensis* were significantly increased in the presence of 1% biochar at application rates within the range of 0–300 mg NO₃⁻-N kg⁻¹. The results of the investigation of Cao et al. show that biochar amendment could decrease NO₃⁻ leaching and NO₃⁻ reduction in soil and promote NO₃⁻ absorption and reduction in the roots.

Two essential plant nutrients, hydrogen and oxygen, are present as water, a fluid that interacts with surfaces as water vapor and as liquid water. In a study of Leonardite humic acid (LHA), Cheng et al. (2019) determined, using microgravimetry and vibrational spectroscopy, that liquid-like water formed in the three-dimensional array of LHA bound to synthetic goethite [α -FeO(OH)] when present at total C/Fe ratios > ~73 mg C per g FE (26 C atoms/nm²). Based on their experimentation with goethite, Cheng et al. (2019) speculated that below those loadings, all minerals become even less hydrophilic than in the absence of LHA. They explain that the lowering of hydrophilicity was caused by the complexation of LHA water-binding sites to mineral surfaces, and possibly by conformational changes in LHA structure removing available condensation environments for water.

Acquisition of mineral N by vascular plants via arbuscular mycorrhizal fungi (AMF) most likely requires mineralization of organic sources of N by other saprotrophic or hypersymbiotic microbes, because AMF possess a particularly weak exo-enzymatic repertoire. AMF are very unlikely to mineralize soil organic nutrients on their own, although some exo-phosphatase activity has been detected in AMF hyphae (Jansa et al., 2019).

Acquisition of gaseous N₂ by rhizobia is dependent upon exudation of flavonoids by roots of leguminous plants that stimulate nod factor (nodulation factor or NF) transcription by rhizobial bacteria, resulting in the production of lipochitooligosaccharides (LCOs) by the bacteria. These nod factors account for rhizobia-host specificity and in the roots of legumes, the lysine receptor-like kinase family, also referred to as LysM, that are receptors for the LCOs. The binding of LysM to the receptor-like kinase of the NF receptor in the legume root hair epidermis triggers sets of signaling events such as cytokinin accumulation and calcium spiking, enabling root hairs to curl and rhizobial infection to occur (Olanrewaju et al., 2019).

Lipochitooligosaccharides of *Bradyrhizobium japonicum* at concentrations of 10 nM and a chitin pentamer at 100 nM promoted root growth and development of *Arabidopsis thaliana* L. – not a legume – resulting in 35% longer roots, compared to untreated plants (Khan et al., 2011). In the same study, it was found that both LCOs and the chitin pentamer increased root surface area, mean root diameter, and the number of root tips, enhancing the ability of the plants to absorb mineral nutrients.

In a meta-analysis of research on crop production and environmental quality, O'Brien and Hatfield (2019) found that when applied at rates providing comparable levels of plant-available N, dairy manure fertilizer was similar to synthetic fertilizer in crop production. Manure increased SOM but also increased soil P, suggesting a P-pollution threat to water quality, since manure is commonly applied to meet crop N needs. The meta-analysis conducted by O'Brien and Hatfield includes data from 58 research investigations conducted in Australia, Canada, China, Greece, Israel, Italy, the Netherlands, Portugal, Spain, Switzerland, and the United States with crops including alfalfa, barley, canola, corn, green pepper, oat, pasture, potato, rye, sorghum, soybean, sugarbeet, turnip, triticale, and wheat.

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.

Adsorption of organic carbon (OC) molecules on clay minerals by various mechanisms, such as electrostatic attraction, hydrophobic attraction, ligand exchange and π -bonding, can protect SOM from microbial attack. In general, soils with higher clay contents can protect OC from mineralization, or microbial conversion to CO_2 , compared to soils of lower clay contents. Allophanic minerals of the sesquioxide group that have a very high specific surface area ($700\text{--}1500\text{ m}^2\text{ g}^{-1}$) and the hydroxide/oxide minerals that also have high surface area can retain greater amounts of OM than do layer silicate clay minerals (Saidy et al., 2013; Wiseman and Püttmann, 2006). Minerals such as sesquioxides and the hydroxide/oxide minerals, by ligand exchange with SOM, can prevent microbial mineralization. Multivalent cations (e.g., Ca^{2+} , Fe^{3+}) can facilitate adsorption of OM in greater amount and more strongly than do monovalent cations (e.g., K^+ , Na^+) (Sarkar et al., 2018).

In a meta-analysis of effects of N deposition or fertilization of soil that included 1160 observations from 52 individual studies, it was found that plant lignin (+7.13%), plant protein (+25.94%), and soil lignin (+7.30%) were significantly increased by N addition, whereas plant hemicellulose (−4.39%) was significantly decreased. Plant fiber, plant cellulose, plant nonstructural carbohydrate, litter lignin, and litter cellulose were not significantly changed. The effects of N addition on C chemical

composition varied among different ecosystems, plant types, and different forms of N addition (Liu et al., 2016).

Deposition of N has been associated with acidification of temperate soils and, in some cases, with the release of phytotoxic concentrations of aluminum (Al^{3+}), manganese (Mn^{2+}), and iron (Fe^{3+}) and the commonly observed shift in grass–forb ratios. Tian et al. (2016) explain that with high rates of N addition to soils, acquisition of Fe by dicots, such as forbs, is mediated by (1) the reduction of Fe^{3+} to Fe^{2+} catalyzed by the ferric chelate reductase (FCR) in root cells (Strategy I) and (2) a metal transporter (MT) in the root-cell membrane allows influx of both Fe^{2+} and Mn^{2+} into the roots. In contrast, monocot grasses exude phytosiderophores (PS) that form chelates, or Fe^{3+} –PS complexes by an iron transporter (IT) in the root-cell membrane (Strategy II). Monocots are apparently also able to absorb Fe^{2+} and Mn^{2+} by a MT in the same way that dicots do.

Dissolved organic carbon, Ca, and Mg were found to be displaced and lost in leachate from soils treated with either liquid or granular fertilizer containing $\text{NH}_4^+\text{-N}$, compared to lesser losses from unfertilized soil (Pittaway et al., 2018).

A conceptual model of organomineral interactions in soils includes self-assembly of organic molecular fragments into zonal structures on mineral surfaces (Kleber et al., 2007). In this model, soil organic matter (SOM) is assumed to consist of a heterogeneous mixture of compounds that display a range of amphiphilic (surfactant-like) properties and are capable of self-organization in aqueous solution. The conceptual model of a contact zone is characterized by strong organomineral associations, a hydrophobic zone that includes components that may exchange more easily with the surrounding solution than those in the contact zone, and a kinetic zone, or outer region, composed of organic molecules loosely retained by cation bridging, hydrogen bonding and other interactions.

Subsequent work by Gao et al. (2019) reviews studies of mineral–organic associations (MOA) in the context of the multilayer model of soil mineral–organic interfaces proposed by Kleber et al. (2007). Gao et al. observe that the multilayer model has been extensively adopted within soil science and related fields, with many studies focusing on either adsorption of organic matter (OM) on mineral surfaces or coprecipitation of OM with nanosized, poorly crystalline minerals or hydrolyzable metals. They conclude that rigid experimental testing of the multilayer model at the molecular level is still required to be integrated into improved concepts of MOA formation and OM stabilization.

Sorptive fractionation of OM at mineral–water interfaces, by altering the composition of OM, affects

fate, transport, and bioavailability of nutrients and contaminants in both terrestrial and aquatic environments. Investigating the sorption of various moieties of OM on several minerals, Liang et al. (2019) found that alkanes, alkenes, or benzenes were sorbed most strongly to bentonite, followed by kaolinite, talc, or hematite, and Al_2O_3 or quartz, relative to water. Relative to the respective alkane moiety, partitioning to the water of a moiety with either double bond, or $-\text{OH}$, or $-\text{COOH}$, or $\text{R}-\text{COO}-\text{R}'$, or $\text{R}-\text{OR}'$, or $\text{R}-\text{COH}$, or $\text{R}-\text{CO}-\text{R}'$, or $-\text{NH}_2$ was enhanced, but the opposite was found for thiols and sulfides. Liang et al. also observed a correlation, namely that as the double bond equivalence decreases and the number of C atoms of a moiety of OM increases, the degree of sorption increases.

Oxalic acid has been shown to enhance microbial access to previously mineral-protected compounds by liberating organic compounds from protective associations with minerals in the rhizosphere. This effect was most intense from 0 to 4 mm to the root surface, diminishing as the distance from the root surface increased, and became negligible at 13–50 mm from the root surface (Keiluweit et al., 2015).

In a study of mechanisms of lithogenic element dissolution and uptake of P, K, Ca, Mg, Mn, Fe, Na, Ti, Al, and Si, Burghelea et al. (2015) determined that nutrient mobilization (chemical denudation + plant uptake) was governed by nutrient supply of the parent material, nutrient availability in pore water solution, and plant physiology. Arbuscular mycorrhiza (AM) increased shoot biomass of *Bouteloua dactyloides* (buffalo grass) in rhyolite due to increased uptake of P and increased concentrations and total uptake of lithogenic elements in plants in all rocks tested but granite. Mineral weathering and the associated release of plant nutrients were promoted by plant processes and enhanced by arbuscular mycorrhizal associations of plants with symbiotic fungi; these phenomena were more pronounced in basalt and rhyolite, compared to granite and schist.

Mineral-associated organic matter (MAOM) resulting from decomposition of plant litter is a relatively large and stable fraction of SOM (Córdova et al., 2018) and plant litter can be categorized as (1) high quality, characterized by rapid decomposition rates, low C/N ratios, and low phenol content or (2) low quality, characterized by slow decomposition rates, high C/N ratios, and high phenol content (Cotrufo et al., 2013). Analyzing MAOM-N accumulated from the decomposition of four different sources of litter in two low-C subsoils (a sandy loam and a silty loam), Córdova et al. found that less NH_4^+ -N was mineralized from a low-quality litter of maize and soybean, compared to the amount of NH_4^+ -N mineralized from a litter of oats and alfalfa. Plant-derived carbohydrates were found

in MAOM, suggesting that plant biomolecules may be important contributors to MAOM in nutrient-poor environments where microbes depolymerize large amounts of plant compounds to obtain [mineral] nutrients (Córdova et al., 2018).

Organic acids and phosphatases produced by some microorganisms can increase the solubility of soil P. Organic acids transform insoluble, mineral phosphate into soluble forms through their hydroxyl and carboxyl forms, whereas phosphatase enzymes produced by microorganisms can release organic P into the solution for plant uptake. Organic P in soils, predominantly present as phytate, can be solubilized by the action of the enzyme phytase produced by various species of the gram-negative bacterial genus, *Pseudomonas* (Calvo et al., 2014).

When volumetric soil water content was decreased in rhizoboxes in which barley plants were grown, phosphatase activity in the rhizosphere decreased less than in the bulk soil, the ratio between phosphatase activity in the rhizosphere and bulk soil being 10 when the soil was close to saturation and 63 when the soil contained 5% water (Holz et al., 2019). The study demonstrated that under conditions of drying in soils, higher retention of water in the rhizosphere maintains higher enzyme activity than in the bulk soil when there is a decrease of soil volume in which phosphatase can be effective at releasing P for plant uptake.

Protons released by roots under P deficiency can result in increases of two to three orders of magnitude in H^+ ion activity of the rhizosphere, compared to the bulk soil, and organic acids (OA), such as citrate and malate, exuded by plant roots in P-deficient soil can mobilize both organic and inorganic P from the soil by displacing phosphate from the soil matrix through ligand exchange. In addition to OA, phenolics and mucilages can be released by roots under conditions of P deficiency, also contributing to the increased availability of P for plant uptake (Elanchezhian et al., 2015).

In a study of growth enhancement of *Capsicum annuum* L. (chili) by two strains of the phosphate-solubilizing bacterium (PSB), *Pseudomonas aeruginosa*, Linu et al. (2019) determined that besides solubilizing P from rock phosphate (RP) and superphosphate (SP), the PSB also displayed various potential plant growth-promoting properties, including production of indole acetic acid and siderophores. Treatments supplemented with SP, RP, and PSB displayed higher concentrations of available P, compared to untreated control plots, and treatments with PSB inoculation significantly increased uptake of both P and N. Plants whose seeds were inoculated with PSB produced more growth and fruit, compared to the control.

In an investigation of biostimulatory effects of HA derived from three sources – composted manure

(HA-MAN), artichoke compost (HA-CYN), and municipal organic wastes (HA-MOW) – Cozzolino et al. (2015) compared growth and uptake of N and P by young maize (*Zea mays* L.) plants receiving no HA, or 0.012 g HA kg⁻¹ soil of HA-MAN, HA-CYN, or HA-MOW and 50 mg P kg⁻¹ soil of either triple superphosphate (TSP) or RP. They found that 4 weeks after sowing, with TSP addition, plants treated with HA-CYN performed better than plants of the control and HA-MAN and HA-MOW treatments in terms of growth and uptake of both N and P. Treated with RP, after 4 weeks, plants of the HA-CYN and HA-MOW treatments accumulated significantly more dry matter, N and P, compared to the plants of the control and the HA-MAN treatment.

Building on the work reported by Cozzolino et al. (2015), Monda et al. (2018) analyzed the molecular composition of the humeome, or suite of humic molecules (Nebbioso and Piccolo, 2011; Nebbioso et al., 2014; Piccolo et al., 2019) extracted from different green composts and their biostimulation on early growth of maize (*Z. mays* L.). Humic acids were isolated from green composts of artichoke (HA-CYN), artichoke/fennel (HA-CYNF), tomato (HA-TOM), and cauliflower (HA-CAV), and the extracts were characterized by solid- and liquid-state nuclear magnetic resonance (NMR) spectroscopy, infrared spectrometry, pyrolysis-gas chromatography/mass spectrometry, and elemental and thermal analyses. Effects of the extracts, applied at 25, 50, and 100 mg L⁻¹ C, on maize seedling growth (roots and shoots) and chlorophyll content of leaves were measured. All humeomes from the green composts generally favored plant growth, and HA-CYN and HA-CAV were active at small concentrations, whereas the effects of HA-TOM and HA-CYNF were evident at greater rates of application.

Collaborative action in South Asia to reverse declining organic matter in agricultural systems is being advocated (Cook et al., 2016) to diminish what is viewed as overreliance on agro-chemical inputs and declining additions of organic matter by farmers. While Clarholm et al. (2015) describe mechanisms by which mineral nutrients such as N and P can be released from SOM, Cook et al. analyze the actors and processes in organic fertilizer value chains and propose means of increasing SOM such as bringing together stakeholders, developing action plans, and building national organic fertilizer value chains, changing fertilizer policy and developing a licensing system for organic fertilizer.

Humic electron shuttling has been shown to contribute to increasing solubility of the essential mineral nutrient, Fe, and toxicity of arsenic (As) in groundwater in South and Southeast Asia (Olk et al. 2019b). In a study of effects of humic acids (HA) on uptake of toxic Cd and essential mineral micronutrients Cu, Mn, and Zn, it was found that

compared to the untreated control, 10-d exposure of radish (*Raphanus sativus* L.) plants to different concentrations of HA (0–225 mg L⁻¹) did not influence biomass, but decreased the concentration of most of the trace metals in tissues examined (Ondrasek et al., 2018). Accumulation of the four metals in the radish plants was also decreased (Cu by 73%, Cd by 39%, Mn by 22%, and Zn by 20%) by treatment with HA, compared to the untreated control. Not only did HA treatment decrease uptake of the four trace metals but it also influenced transport and distribution of the trace metals in the roots, shoots, and hypocotyls of the radish plants.

Vermicompost HA pre-treatment (80 mg L⁻¹ HA) for 48 h was shown to stimulate uptake of both NO₃⁻ and NH₄⁺ and N metabolism of rice plants after pre-exposure to HA before N was supplied as 0.2 or 2.0 mM N-NO₃⁻ or N-NH₄⁺ (Huertas Tavares et al., 2019). At both ranges of concentrations of NO₃⁻ (i.e., 0–200 μM and 0–2000 μM), values of the net influx of NO₃⁻ (g FW⁻¹ h⁻¹) were greater with HA pre-treatment, compared to the untreated control. On the other hand, from 0 to 200 μM NH₄⁺, the net influx of NH₄⁺ (μmol NH₄⁺ g FW⁻¹ h⁻¹) was greater for plants in the untreated control, compared to those receiving the HA pre-treatment, whereas from 0 to 2000 μM NH₄⁺, the net influx of NH₄⁺ (μmol NH₄⁺ g FW⁻¹ h⁻¹) was greater for plants that had received HA pre-treatment, compared to those of the untreated control.

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 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 NH₄⁺ nutrition, (c) excess cation-over-anion uptake as a consequence of symbiotic N₂ fixation, or (2) exudation of organic acids as a reaction to P-starvation (Van Diest, 1991).

Biological fixation of gaseous N (N₂) in nodules of legumes (plants in the family *Fabaceae* [identified by others as *Leguminosae*]) by N-fixing bacteria is an organic system which produces NH₃ 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 (N₂-fixing) bacteria have been isolated from the roots of grasses and cereals of agricultural importance (Boddey and Döbereiner, 1988). In 1984, experimentation conducted with non-leguminous 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 which are nodulated by *Rhizobium* species, about 200 plant species covering eight families and at least 17 genera in the tropics and subtropics are nodulated by N₂-fixing actinomycetes of the genus *Frankia* (Peoples and Craswell, 1992). Non-symbiotic nitrogen fixation is another aspect of the interaction of organic matter and mineral nutrients near the root surface. *Closteridium pasteruinmum*, isolated in 1893, *Azotobacter choococum*, *Azomonas agilis*, and other free-living microorganisms, including some blue-green algae and yeasts can convert atmospheric nitrogen to NH₃, which is then available to plants. Bacteria of the genera *Beijerinckia*, *Azotobacter*, and *Closteridium* comprise the major groups of free-living, N-fixing bacteria that can make N available for uptake by plant roots (Curl and Truelove, 1986).

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; non-symbiotic nitrogen fixation), and stimulation of disease-resistance mechanisms. Indirect effects originate in cases such as when PGPR act like biocontrol agents reducing diseases, 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, 2005).

Application of a single amino acid with a hydrophobic side chain (i.e., alanine, serine, phenylalanine, or tyrosine) at a concentration of 0.2mM in half-strength Hoagland nutrient solution increased concentrations of Ca, Cu, K, Fe, and Mn in leaves of tomato seedlings. In addition, serine and tyrosine, both of which have hydroxyl groups in their structures, increased Mg²⁺ concentration in the leaves (Garcia et al., 2011).

17.4.1 ROOT EXUDATES

In nature, plants continuously release different compounds to their surrounding media, and this process known as exudation is the release of substances in solid, liquid, or gaseous form from plant organs, including leaves, shoots, or roots. The composition of mixtures of compounds that are root exudates can be quantitatively and qualitatively affected by several physical, chemical, and biological factors. These modifications of root exudates can contribute to the health of the plant by attracting beneficial microbiota, chelating toxic compounds in the soil, changing soil pH or solubilizing mineral nutrients into soluble forms (Vives-Peris et al., 2019). Passive exudation from roots is mediated through the root membrane by diffusion, ionic channels, and vesicle transport, whereas root secretion of metabolites through an active transport mechanism is mediated by proteins located in the root plasma membrane (Baetz and Martinoia, 2014).

Root exudates are important components of the rhizosphere, since they play an active role in ecosystem functioning, and carbon fluxes to roots drive exudation, which can be lost passively. Canellas and Olivares (2017) observed a strong influence of exogenous HA in the shape and number of viable and metabolically active border cells detached from maize root caps and their effects on the survival and activity of beneficial bacteria. To better understand the exudation profile of plants treated with HA, Canellas et al. (2019) studied effects of treating maize root seedlings with HA. They found that root exudation was increased by HA in the rhizosphere, resulting in the release of many chemical compounds that they identified utilizing ¹H NMR spectra, gas chromatography (GC), and time-of-flight mass spectroscopy (TOF-MS).

In their study of sampling root exudates, Oburger and Jones (2018) begin from the premise that accurate information about the quantity, quality, and spatiotemporal dynamics of metabolite release from the plant is needed. They summarize the main analytical approaches to analyze root exudates, including liquid sample analysis, isotope tracking, and imaging techniques. Terms relating to the loss of organic carbon from roots into the soil include rhizodeposition, root exudation, seed exudation, root metabolome, root proteome, root volatilome,

root secretome, and root surfaceome. Oburger and Jones (2018) present, in graphic form, relationships between physiochemical processes, biological interaction, and biochemical processes driven or affected by root exudates and rhizodeposits, and they present a cross-section elucidating means by which root exudates can pass from vesicles through the cytoplasm and plasma membrane to the soil solution and, in some instances, reflux back into the root.

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).

Mechanisms of nutrient mobilization by plant exudates, excluding that related to the acquisition of N and P, include low-molecular-weight organic acids, phytosiderophores, enzymes, and reductants. In conditions of P deficiency, plants exude a wide range of organic and inorganic compounds to increase mobilization of P from sparingly soluble sources (Rengel, 1999). The mechanisms by which root exudates increase bioavailability of nutrients are not specific to a certain class of exudates, and each class of exudates can be involved in more than one mechanism. Besides increasing nutrient availability, root exudates can facilitate root–root communication, root–microbe interactions, and toxicity relief (Keuskamp et al., 2015).

Rhizosphere studies have, in part, focused on the exudation of organic substances from the root, 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 constantly or 18°C day/14°C night resulted in 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 with corn roots did not allow a 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 $\mu\text{mol g}^{-1} \text{h}^{-1}$, 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). Aerobic bacteria of the genus *Azospirillum* 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).

Better adaption of crop genotypes to the environment and more profitable farming can be achieved by increased genetic control of root exudation. Improving control of root exudation by the selection of superior genotypes and breeding of crop plants can result in increased tolerance to nutrient deficiencies, iron toxicity, efficiency of nodulation, and tolerance to various diseases. Root exudates play a role in acquisition of Fe, Mn, P, and Zn under conditions of deficiency of these elements. (Rengel, 2002). Transferring rye chromosomes 1R and 7R into wheat increased the tolerance of wheat to Zn deficiency (Çakmak et al., 1997), and transferring chromosomes 2R and 7R from rye to wheat increased tolerance wheat to Mn and Fe deficiency (Schlegel et al., 1997).

In response to Fe starvation of *Arabidopsis*, beneficial bacteria in the rhizosphere, have been shown to stimulate the production of scopolin and subsequent production of scopoletin, a coumarin that is exuded from the roots. The exudation of scopoletin, that is, 7-hydroxy-6-methoxy-2H-1-benzopyran-2-one, results in chelation of Fe (III) in the rhizosphere, helping to mobilize Fe for absorption by the roots, and exudation of scopoletin may also strongly suppress the growth of soil pathogens of plants, *Fusarium f. sp. raphanin* and *Verticillium dahlia* JR2 (Lundberg and Teixeira, 2018).

17.4.2 INTERACTIONS OF IRON AND ORGANIC SUBSTANCES

In aerobic soils, trivalent iron, (Fe (III) or Fe^{3+}), is very insoluble (Rendig and Taylor, 1989). To increase the

solubility of Fe (III), microbes release siderophores (Greek: “iron carriers”), and plant exudates such as phytosiderophores, organic acids, and flavonoids can bind and solubilize Fe from Fe-bearing minerals (Colombo et al., 2014). Laboratory studies by Di Iorio et al. (2019) with artificial iron oxide-humic acid precipitates investigated the effect of Fe mineral crystallinity in the presence of humic acids (HA) on the availability of Fe to *Cucumis sativus* L. (cucumber) plants. Cucumber plants grown in the presence of Fe–HA coprecipitates containing either goethite or magnetite completely recovered from Fe deficiency. Plants supplied with poorly crystalline goethite and ferrihydrite mixed phases coprecipitated with HA had a lower Fe/HA ratio and showed features more similar to those of fully recovered plants supplied with Fe-DTPA, compared to plants treated with crystalline magnetite-HA. In the presence of HA, the cucumber plants absorbed Fe from goethite and ferrihydrite mixed phases and magnetite, which are usually considered unavailable for plant nutrition when not associated with HA.

Microbial siderophores and mixtures of organic acids typical of those produced by root exudates have been demonstrated to be able to remove Fe from humic complexes (Nuzzo et al., 2018). Two humic acids extracted from a volcanic soil (HA1) and a leonardite (HA2) were used to form insoluble complexes with iron metals. To simulate the rhizospheric processes that displace iron from complexes of humic molecules and solubilize the soil humeome, the insoluble iron–humates were treated with a solution of siderophore deferroxamine mesylate (DFOM) and a mixture of citric, oxalic, tartaric and ketoglutaric acids, at different concentrations and contact times.

The Fe level in cellular components, particularly the cell wall and cytoplasm, of Scots pine (*Pinus sylvestris* L.) roots was increased by structurally different siderophores. The siderophore Fe-binding mechanism by which different siderophores affected Fe redistribution was found to operate only in cell walls and the cytoplasm. Concentrations of N, P, K, Ca, Mg, Cu, Mn, and Zn increased in root cells of *P. sylvestris* due to the application of the structurally different siderophores ferricrocin and triacetylfusarinine C, but when Fe was present within the structure of the siderophores, the levels of these elements decreased in the cell wall and cytoplasm (Mucha et al., 2019).

To determine effects of ferrihydrite on biodegradation of SOM, organomineral associations of water-extractable organic matter of a Podzol forest-floor (FFE) litter or a sulfonated lignin with ferrihydrite were incubated and an inoculum extracted from the forest floor layer under oxic conditions at pH 4.8 over 68 d (Eusterhues et al., 2014). Association with ferrihydrite stabilized the associated

organic matter, degradation of the polysaccharide-rich FFE was slowed, degradation of lignin was inhibited, and there were only small differences between the adsorbed and the coprecipitated organic matter.

Iron oxide–vermiculite mixed mineral phases affect the sorption of DOM in soil (Sodano et al., 2014). The change in surface zeta potential (ζ) with increasing Fe coverage of the negative charge of vermiculite resulted in an increase in the amount of DOC retained. In controlled experimentation, as Fe concentration was increased from 0.14 to 5.68 mol Fe/kg, ζ increased from -39 to $+8$ mV. Sodano et al. observed localized nucleation of Fe-oxides with the formation of a nonhomogeneous surface on vermiculite, and they found that with increasing DOC adsorption associated with increased Fe oxide sorption, cation exchange with positively charged organic compounds diminished, selective adsorption of carboxylic groups by ligand exchange increased, and selective adsorption of aromatic compounds increased.

The ortho–ortho isomer of the chelated form of Fe, iron (III) ethylenediamine di(*o*-hydroxyphenylacetic acid) (FeEDDHA) was found to be capable of providing sufficient Fe to plants both in nutrient solution and in calcareous soil, whereas the ortho–para isomer was able to provide sufficient Fe to plants in the nutrient solution, but not in calcareous soil (Rojas et al., 2008). Subsequent research with the row-applied solution of a commercial formulation of the ortho–ortho isomer of FeEDDHA to the soil at planting was found to be economically feasible to provide adequate Fe to two commonly grown varieties of dry beans (Hergert et al., 2019).

In their study to determine the solubility of Fe from 10 common Fe fertilizers applied to 11 North American soils, Shaddox et al. (2019) concluded that soil-applied Fe fertilizers should be limited to supplying Fe chelated by ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), or ethylenediamine-*o*-hydroxyphenylacetic acid (EDDHA). Other Fe fertilizer sources that were evaluated by Shaddox et al. in each soil 1 h after application resulted in more than 95% of the applied Fe rendered insoluble; those less efficient Fe fertilizers provided Fe as Fe sulfate, glucoheptonate, polysaccharide, humate, and oxide. In another Fe fertilizer evaluated by Shaddox et al., the natural organic chelate Fe iminodisuccinic acid (IDHA), increased Fe solubility in 3 of the 11 soils for 1 d, but soluble Fe from FeIDHA declined to that of untreated soils thereafter.

Catechols are a group of aromatic compounds containing a 1,2-benzenediol moiety, and the hydroxyl groups of the catechol ring can strongly coordinate ferric ions (De Cesare et al., 2019). Using free-standing electrospun nanofibrous polycaprolactone/

polyhydroxybutrate thin membranes loaded with catechol (CL-NMs) as an Fe-chelating agent, De Cesare's team was able to mobilize Fe from insoluble forms to provide Fe to Fe-deprived *Lemna minor* L. (duckweed) plants. The plants supplied with CL-NMs with higher catechol concentrations recovered most of the physiological and growth functions previously impaired by Fe deprivation. The absence of short-term toxicity suggests that such a method of providing Fe to plants may have a low impact on ecosystems in which such a method is used (De Cesare et al., 2019).

DOM extracted from crop residues, animal manures, and compost was added by Chase et al. (2018) to soil to determine whether, after pre-absorption onto catalysis-grade iron (oxy)hydroxide (FeOOH), it would decrease adsorption of P and whether it would increase P uptake by *Solanum lycopersicum* L. "German Johnson" (tomato). The laboratory study, including a 5-week agar-culture bioassay, indicated that pre-adsorbed DOM significantly decreased P adsorption by 19%, and the pre-adsorbed DOM did not significantly affect P uptake by tomato. Based on the results of their controlled, laboratory study, Chase et al. suggest that the initial DOM leached from crop residues and animal manures would be unlikely to affect soil P availability; however, they only considered one source of P, that is, P adsorbed on FeOOH, and did not consider other sources of soil P such as organic-P and P in sparingly soluble precipitates.

A diphenolic compound, secoisolariciresinol diglucoside (SDG), a lignan abundant in flaxseed was investigated to determine its affinity for four divalent, metallic plant nutrients (Ca^{2+} , Cu^{2+} , Ni^{2+} , and Fe^{2+}) and two other elements (Pb^{2+} and Ag^+). The SDG-metal complex equilibrium constants in aqueous solution were measured as 20.34, 5.99, 4.26, 2.77, 2.46, and 1.90, respectively and are consistent with those determined for plant phenolics. PM6 geometry optimized structures, non-coordinated water molecules removed for clarity, display differences among the uncomplexed SDG molecule and the six SDG-metal hydrated complexes (Fucassi et al., 2014).

The release by grass species of low-molecular-weight, nonproteinogenic amino acids known as phytosiderophores (PSs) is a highly efficient Fe (III) acquisition mechanism, and other micronutrients such as Co, Cu, Ni, and Zn have been found to both form stable complexes with PSs and be absorbed as a PS-metal complex. In their study of root exudation of PSs from soil-grown wheat, Oburger et al. (2014) found that PS release of the Tamaro cultivar of wheat (*Triticum aestivum* L.) and PS rhizosphere soil solution concentrations were soil-dependent, indicating that there may have been complex interactions of soil factors such as salinity or the availability of trace metals. During the experimental

period, 21–47 d after germination, PS release from the wheat seedlings initially exceeded Fe plant uptake 10-fold, but significantly declined after about 5 weeks after germination.

17.4.3 AGGREGATES OF MINERALS, MINERAL NUTRIENTS, AND ORGANIC SUBSTANCES

Aggregation of organic matter (OM) and minerals depends upon several factors such as organic molecular moiety, size, and shape as well as mineralogy and surface characteristics. Sorption is affected by chemical (e.g., functional groups such as hydroxyl, carboxyl, and amino) and physical properties (e.g., specific surface area, shape, and roughness) of both organic matter and the mineral. Six principal mechanisms involved in the sorption of organic matter to mineral surfaces include ligand exchange, exchange of both cations and anions, cation bridging, van der Waals interactions, hydrogen bonds, and hydrophobic effects (Keil and Mayer, 2014).

Investigating nutrient removal characteristics in mineral-rich aerobic granular sludge reactors, Pishgar et al. (2020) developed a mineral core theory of aerobic granulation in which bio-aggregation and growth of inorganic granules are intimately related. The process develops thusly: seed of bacterial cells changes *to* decrease in biodiversity *to* microbial colonization with extracellular polymeric substances (EPS) covering the microbes *to* calcium carbonate crystallization covering the microbes *to* the crystal-to-crystal attachment *to* crystal growth toward the center and bacterial cell multiplication in the rim *to* lifeless microbial core formation further bio-aggregation and granule growth. Pishgar et al. found heterotrophic nitrification and they determined that biologically induced precipitation of phosphorus became the dominant nutrient depletion pathways in the reactors, contributing 61–84% and 39–96% to overall NH_4^+ and P removal, respectively. They examine the relationships between calcium carbonate and calcium phosphate, as regards precipitation of the two compounds related to microbial colonization of mineral-organic aggregates.

Availability of P was evaluated, comparing a granulated organomineral fertilizer (OG), an organomineral granule mixture (abbreviated by Sakurada et al. in their paper as OM, not to be confused with OM as the abbreviation for organic matter elsewhere in this chapter), and an inorganic granule mixture (MM) containing N, P, and K applied to a Eutroferic Red Latosol clay soil (Oxisol) with low P concentration. The OG were produced by mixing ground poultry litter with soluble inorganic nutrient sources. Poultry litter was granulated with milled monoammonium phosphate (MAP or $\text{NH}_4\text{H}_2\text{PO}_4$) to obtain the final composition of 5:20:2::N:P:K for OG, and for OM, pelletized

poultry litter was mixed with MAP, potassium chloride (KCl), and Calcogran (20% Ca and 10% Mg) granules to achieve a final composition of 3:15:2::N:P:K. The MM was a 3:15:2::N:P:K mixture composed of MAP, KCl, and Calcogran granules. The granulated fertilizer (OG) had lower P solubility than the granule mixture (OM), and both organomineral fertilizers had lower solubility than the mineral mixture (MM) (Sakurada et al., 2019).

Taking into account the work of Piccolo (2001, 2002) and others, Clarholm et al. (2015) elucidated a three-step, plant-induced procedure to explain the organic-acid-induced release of NH_4^+ and H_2PO_4^- from supramolecular aggregates of soil organic matter stabilized by metals such as Ca, Fe, and Al. In the initial step, oxalate and citrate are exuded from hyphae or roots, breaking up organometal complexes to expose new surfaces. Next chitinases, proteases, and phosphatases are exuded from hyphae or bacteria, releasing N and P as bacteria metabolize organometal complexes. In the third step, N and P are absorbed by hyphae or roots. The process of release and absorption of N and P described by Clarholm et al. involves disruption of the thermodynamic stability of supramolecules of the soil organic matter (SOM) by organic acids and enzymes involving fungi, bacteria, and roots.

Modern breeding programs may have reduced the responsiveness of modern wheat cultivars to AMF (Schneider et al., 2019). In a study of 14 crop species, it was observed (Martín-Robles et al., 2017) that under low and high P conditions, wild progenitors benefited from AMF under low and high P conditions, but modern cultivars benefited only under conditions of low P availability.

In pools of SOM comprised of slowly cycling C with a mean residence time (MRT) of years to centuries, SOM is stabilized against microbial decomposition by physical protection (occlusion) within soil aggregates (Jastrow et al., 1996). Soil aggregates are formed by soil particles and by biological components such as roots, fungal hyphae, and microbial biomass and necromass (Riggs et al., 2015). In their study of effects of N addition on SOM decomposition of grassland soil, Riggs et al. found that addition of $10 \text{ g N m}^{-2} \text{ y}^{-1}$, along with P, K, and micronutrients, increased the decomposition rate of the most quickly decomposing unoccluded pool and decreased the decomposition rate of the more slowly decomposing unoccluded pool. The average fast pool MRT decreased from 9.92 to 8.53 d, and the average slow pool MRT increased from 9.30 to 10.42 y, with N addition. In contrast, in the aggregate-occluded and mineral-associated SOM pools, the proportion of C occluded within the largest aggregate fraction ($>2000 \mu\text{m}$) increased slightly with N addition, and no effects

were detected in the mineral-associated fraction that slowly cycles C with long MRT of centuries to millennia. Riggs et al. speculate that the addition of N to grassland soils may increase C storage by increasing C occlusion in large macro-aggregates.

Persistence of SOM is influenced by physical and chemical stabilization, environmental conditions, and OM composition, and, fundamentally, the stability of SOM depends on the balance of microbial bioenergetics between the input of energy needed to decompose it (i.e., activation energy; E_a) and the net energy gained (i.e., energy density; ED) from its composition (Williams et al., 2018). Chemical and physical protection mechanisms in soils require additional energies to overcome for decomposition of OM to occur. In their study of bioenergetics of soil OM density fractions, Williams et al. demonstrated distinct bioenergetic signatures between particulate, light (free and occluded) fractions (LF), compared to mineral-associated, heavy OM fractions (HF) isolated from soil samples collected at two depths of several pedons in a climosequence in the Sierra Nevada mountains, California. They found that LF were characterized by larger ED and E_a values, and HF were characterized by smaller ED and E_a values. They concluded that SOM in HF pools is probably composed of relatively simple organic compounds with long turnover rates because of chemical association with soil minerals, whereas LF pools are probably composed of more chemically complex molecules with low chemical reactivity and high E_a .

Aggregates of HA fractions of weathered coal and urea (HAU) were prepared by Zhang et al. (2019) to determine whether N could be more efficiently furnished to maize (*Zea mays* L.) plants as fertilizer by a mixture of urea (NH_2CONH_2) and HA, compared to fertilization by NH_2CONH_2 alone. The three HA fractions were obtained by pH fractionation of weathered coal (Zhang et al., 2017). At harvest, the aboveground dry biomass of plants grown with HAU was 11.50–21.33% greater, compared to plants grown with only NH_2CONH_2 . The grain yields of the HAU treatments were 5.58–18.67% higher than the yield of the NH_2CONH_2 treatment, and the uptake of fertilizer N of the HAU treatments was 11.49–29.46% greater than uptake from the NH_2CONH_2 treatment.

17.5 INTERACTION OF MINERAL NUTRIENTS AND ORGANIC SUBSTANCES AT THE LEAF

Materials such as NH_2CONH_2 , 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, repellence of water and particles, attenuation of photosynthetically active 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 non-polar 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, which 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 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 consistently to 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 radioisotopes of calcium-45 chloride ($^{45}\text{CaCl}_2$), rubidium-86 chloride ($^{86}\text{RbCl}$), iron sulfate-35 ($\text{Fe}^{35}\text{SO}_4$) or rubidium chloride-36 (Rb^{36}Cl) 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 P and Rb, an analogue of K, into leaf tissue has been measured in primary leaves of bean seedlings. Criteria for active uptake included time-course analysis, dependence upon temperature, oxygen, and energy, sensitivity to metabolic inhibitors, accumulation against a concentration gradient, irreversibility, and pH dependence. The results suggest that the overall process of foliar absorption of Rb and phosphate-P 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 the uptake and that they are proteinaceous (Jyung and Wittwer, 1964).

Urea, NH_4^+ , and NO_3^- are common forms used for foliar application of nitrogen to fertilize crops. Norway spruce shoots, which included both needles and twigs, absorbed NH_4^+ , and there was no evidence that NH_4^+ uptake was accompanied by exchange for base cations such as Ca^{2+} (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 NH_4^+ 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 NH_2CONH_2 by foliar application can be toxic to plants. Leaf-tip necrosis often observed after foliar fertilization of soybean plants with NH_2CONH_2 is usually attributed to NH_3 formed through hydrolysis of NH_2CONH_2 by plant urease. Research using a urease inhibitor demonstrated that although addition of this urease inhibitor to foliar-applied NH_2CONH_2 increased the NH_2CONH_2 content and decreased the NH_3 content and urease activity of soybean [*Glycine max* (L.) Merr.] leaves fertilized with NH_2CONH_2 , it increased the leaf-tip necrosis observed after fertilization. The investigators concluded that this necrosis resulted from the accumulation of toxic amounts of NH_2CONH_2 rather than from the formation of toxic amounts of NH_3 (Krogmeier et al., 1989). Ammonium was

absorbed more rapidly than was NO_3^- 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 Zn, 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⁻¹, number of pods plant⁻¹, number of seeds pod⁻¹, 1000 seeds weight, seed weight plant⁻¹, and seed yield ha⁻¹ 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 above-mentioned traits occurred with foliar application of Zn, as compared to untreated plants. Based on the experimental results, the investigators recommended foliar application of salicylic acid and zinc (Zn) to mungbeans, using salicylic acid and Zn at concentrations of 150 and 400 ppm, respectively (Ali and Mahmoud, 2013).

The size of the hydrated ion is a major factor affecting the foliar absorption of mineral nutrients. Mandair and Harris (2003) investigating the 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, NO_3^- , and PO_4^{3-} 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 more rapid for smaller molecules. A negative correlation between molecular weights of the organic solutes and their rates of penetration was obtained by regression analysis. A 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 the 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 + NH₂CONH₂ (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 NH₂CONH₂, or both. He speculated that the

chelated form of Fe was less able to penetrate because of its greater molecular size. In earlier studies (Wittwer et al., 1965), uptake of Fe from FeEDDHA was also very much less than 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 was demonstrated with isolated cuticles (Kannan, 1969).

Naturally occurring chelating agents, or ligands, such as proteins, amino acids, organic acids, flavonoids, purines, and riboflavin can facilitate the absorption of cationic plant nutrients, and the stability of the 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).

In their characterization of contaminant manganese (Mn) cycling in a temperate watershed, Herndon et al. (2014) found that roots, stems, and foliar tissue were dominated by organic-bound and aqueous Mn (II), but they observed that a small portion of foliar Mn was concentrated as organic-bound Mn (III) in dark spots indicating Mn toxicity. Mn taken up into plant biomass as aqueous and organic Mn(II) compounds was found to be immobilized as Mn (III)/(IV) oxides during decomposition of roots and leaves that had fallen to the soil in the autumn. Herndon et al. view Mn retained within the soil-plant system resulting from a recurrent cycle of solubilization of Mn from the solid phase of the soil, uptake into vegetation, followed by subsequent immobilization of Mn in the soil as the vegetative matter is decomposed.

Chelating agents used to treat nutrient deficiencies of plants, such as Fe and Zn deficiencies, include synthetic chelates such as EDTA and EDDHA and natural chelating agents such as amino acids, organic acids, and phenolics. Amino chelates, new formulations of fertilizers for foliar application or application to leaves, can increase nutrient use efficiency and minimize negative environmental effects of fertilization (Souri and Hatamian, 2019).

17.6 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, in all eukaryotes several mechanisms have evolved 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 the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP), and inorganic phosphate (P_i) for transported cations such as H^+ , Ca^{2+} , Na^+/K^+ , 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. Several investigations indicate 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 (Cowan et al. 1993; Parets-Soler et al., 1990; Samuels et al., 1992). 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, as demonstrated by Epstein et al. (1963).

During the 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). Organic N compounds produced in root nodules of legumes have been shown to be mobile in both the xylem and 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 a 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 (Graham et al., 1992; White & Zasoski, 1999; Çakmak, 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, under conditions of high Zn-status, leaf epidermal cell vacuoles, cell walls, and the cytoplasm contained, respectively, 74,305, 11,577, and

3205 $\mu g Zn g^{-1} DW$ (dry weight); in lower Zn-status leaf mesophyll cells, vacuoles, cell walls, and the cytoplasm contained, respectively, 327, 9353 and $\leq 262 \mu g Zn g^{-1} DW$; and root cortical vacuoles, cell walls and cytoplasm contained, respectively, ≤ 262 , 589, and $\leq 262 \mu g Zn g^{-1} DW$ (Frey et al., 2000). Several studies have shown no correlation between Zn 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 Zn 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 Zn efficiency.

In a study of effects of composted sewage sludge (CSS) as a soil amendment for poplar trees (*Populus x euramericana* “Guariento”), CSS application was beneficial to the transport of S, Ni, Mg, and P from the roots to leaves or stems. Compared to the control (no CSS), leaves of trees receiving CSS in the second year of the study displayed higher concentrations of N, Mg, Fe, Zn, Mn, Ni, and Na (Guoqing et al., 2019).

Plants that are hyperaccumulators of metal(loid) contaminants of soils, such as As, Cd, Cu, Ni, and Pb, show much higher root-to-shoot translocation efficiency than non-hyperaccumulators, and the sequestration of metal ions in root-cell vacuoles is greatly reduced in hyperaccumulators than in non-hyperaccumulators. Unlike non-hyperaccumulators, hyperaccumulating plants bind metals by weak oxygen ligands, and strong ligands are used instead for transient binding during transport to storage sites. Specific transport proteins are expressed in various tissues involved in the process, in most cases in the leaf epidermis, the main site of sequestration into vacuoles containing such enzymes as phosphatases, lipases, and proteinases that are not a target of heavy-metal toxicity. (Iqbal et al., 2015).

The chemical composition of bleeding xylem sap collected during bud breaking of five woody species (*Sorbus aucuparia* L. [rowan], *Rubus idaeus* L. [raspberry], *Ribes nigrum* L. [blackcurrant], *Vitis vinifera* L. [grape vine], and *Juglans regia* L. [walnut]) was indicative of nutritional status. The amino acid concentration was highest in members of the Rosaceae family (rowan and raspberry) and values were within the range of 3 $mmol L^{-1}$ (vine) to 18 $mmol L^{-1}$ (rowan). The highest concentration of NO_3^- was in the xylem sap of raspberry, and the NO_3^- concentration was sevenfold less in the grapevine and about 12-fold less in xylem sap samples of the other three species. The organic acid concentration in xylem sap was in the range of 0.8 $mmol L^{-1}$ (walnut) to 2.6 $mmol L^{-1}$ (grapevine), and the main organic acids were malic acid, present in all species, and citric acid present

only in the grapevine and in lower amounts in rowan and raspberry. Inorganic cationic compounds detected in the xylem saps include K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ , and inorganic anionic compounds detected were Cl^- , SO_4^{2-} , and NO_3^- (Prima-Putra and Botton, 1998).

In an investigation of biological enhancement of mineral weathering by *Pinus sylvestris* seedlings, Rosenstock et al. (2019) found that weathering of soil minerals was primarily a result of seedling uptake of nutrient cations. The majority of low-molecular-weight organic acids detected in their experiment were mono-carboxylic acids (formic, lactic, and acetic acids) and not the di- and tri-carboxylic acids, such as citric and oxalic acids that have been shown by other investigators (Neaman et al., 2006; Drever and Stillings, 1997) to strongly increase weathering rates.

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