2 Bioavailability of Trace Elements in Relation to Root Modification in the Rhizosphere

Ioannis K. Mitsios and Nicholas G. Danalatos

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2.1 INTRODUCTION

The immediate vicinity of plant roots is of particular importance for plant nutrient turnover and bioavailability. The part of the soil directly influenced by the roots is called “rhizosphere.” Because the root affects the adjacent soil, it is obviously very interesting to examine the spread out zone plainly exploited for a particular solute. If this is wide, there may be no point in emphasizing effects close to the roots; however, if it is narrow, predictions based on the behavior of the bulk soil may be made.

The effect of the root on the adjacent soil medium is mainly the release of organic and inorganic material into the soil. Predicting the bioavailability of trace elements to plants is a major agricultural and environmental issue. The prime entry of toxic elements in the food chain comprises the plants and the animals. Trace elements occur naturally in rocks and soils, but principally in forms that are nonavailable to living organisms. Large quantities of trace elements are released into the environments by anthropogenic activities — for example, industrial processes, manufacturing, and agricultural amendments.

Several metals and metalloids, such as Mn, Cu, Zn, Ni, Mo, and B, play an important role in the soil–plant system. The bioavailability of these elements is therefore of fundamental importance. A small available amount of these elements can cause deficiencies in plants. However, in the case of pollution, a large available amount of these elements and other similar nonessential elements (such as Pb, Cr, Ae, etc.) can be detrimental to plant growth. Recently, many workers [1,2] have described a range of factors and mechanisms for nutrients that implied in the transfer of elements from the soil into plant roots.

Not only the uptake of trace elements but also the acquisition of these elements encompasses chemical processes that occur at the soil–root interface and that can influence the dynamics of trace elements in the rhizosphere [2,3]. The problem arises from the fact that modification in the rhizosphere may be physical [4] and chemical through several other processes [2,5–8] or microbiological. Therefore, understanding all the mechanisms implied in the process of acquisition of elements by plant roots is a prerequisite for assessing their bioavailability. Nye and Tinker [9] reported that microbial biomass and activity occur in the rhizosphere. This depends on the flux of C from root exudation. Root exudates include organic substances, some of which are very reactive compounds that can affect the chemical characteristics of the rhizosphere.

This chapter reviews the chemical processes in the rhizosphere that affect the uptake of trace elements, their bioavailability to plants, and plant nutrition. Also, in this chapter, emphasis is given to the role of rhizosphere microorganisms in the nutrient supply to plants.

2.2 TRACE ELEMENTS IN THE SOILS

Trace elements accumulate locally in soils due to weathering of rock minerals. Because trace elements are essential for plants, animals, and human beings, it is necessary to ensure their adequate levels in agricultural products. Apart from trace elements originating in parent materials and entering the soil through chemical weathering processes, soil toxic trace elements have many anthropogenic sources. Campbell et al. [10] compared natural and anthropogenic quantities of trace metals emitted to the atmosphere and showed that around 15 times more Cd; 100 times more Pb; 13 times more Cu; and 21 times more Zn are emitted by man's activities than by natural processes.

Trace elements and their total concentrations can vary widely in different soils derived from different parent materials. Levinson [11] and Alloway [12] proposed that the more basic igneous parent materials contribute highest quantities of Cr, Mn, Co, and Ni to soils; among the sedimentary parent materials, shales potentially contribute the highest quantities of Cr, Co, Ni, Zn, and Pb. Mineral weathering rates determine the release of the elements into soil — initially, in the form of simple or complex inorganic ligands. This process depends on mineral solubility under prevailing soil pH and Eh conditions. In soils, Mn, Ni, and Cr are present in highest quantities, and Cd and Hg are present in the smallest amounts.

The concentration of trace elements such as Mn, Ni, and Cr in the soil profile depends on parent material when the parent material is the main source in the soil. Brooks [13] found that the concentration of Ni in soils developed on serpentine was as high as 100 to 7000 $\mu g\ Ni\ g^{-1}$. Because many minerals are resistant to weathering, trace elements are insoluble; higher concentrations can be found in tropical soils where the weathering process is intensive.

Large quantities of Cd are applied to agricultural soils in phosphate fertilizers; the highest concentration occurs in topsoil. Topsoil concentration is maintained by vegetation recycling, and Cd and Pb show very slow movement down the profile [14]. Colbourn and Thornton [15] calculated the relative topsoil enhancement (RTE) as the ratio of Pb concentration in topsoil (<15 cm) to the Pb concentration in subsoil (>15 cm). They reported RTE values of 1.2 to 2.0 in remote agricultural areas and values of 4 to 20 in areas contaminated by mining.

2.3 ROOT MODIFICATION OF THE RHIZOSPHERE AND BIOAVAILABILITY OF TRACE ELEMENTS

2.3.1 PH CHANGES IN THE RHIZOSPHERE AND BIOAVAILABILITY OF TRACE ELEMENTS

Without doubt, most plants growing under natural conditions cause pH to rise in the rhizosphere. As pointed out by Cunningham [16], 62 plant species contain an average of 250 meq of absorbed cations per 100 g of oven-dry shoots and 360 meq anions per 100 g of oven-dry shoots. In general, roots release HCO_3 or OH to maintain electrical neutrality in the rhizosphere: an excess of 1100 meq of HCO_3 per 100 g dry matter, rather than H^+ ion, and the soil near roots become more alkaline instead of more acid.

Some other workers have showed that, when plants are supplied with NH_4^+ rather than NO_3, the pH in the root zone falls [17–19]. Nitrate normally constitutes more than half the total absorbed anions (180 meq per 100 g dry matter). If this amount of nitrogen is taken up as NH_4^+ instead of NO_3^-, cations are 430 meq per 100 g dry matter and anions are 180 me per 100 g dry matter; this yields a net release of 250 meq/100 g dry matter. For legumes, where nitrogen is fixed symbiotically and little is taken up as NO_3^- or NH_4^+, the net effect is 70 meq H^+ released per gram of dry matter. The changes in the rhizosphere are at a maximum when the pH in soil is about 5.3 because, at this value of pH, diffusion of acidity is low [20]. The thickness of the zone influenced by the root decreases to about 1 mm. It is from this thin zone that most of the micronutrients and phosphate uptake probably occurs and in which a large microbial population exists [21].

Nye [21] proposed that at soil pH 8 changes in the pH are small because HCO_3^- concentration is high in the soil solution. The gradients in the rhizosphere will have a more significant effect on pH in alkaline soils. The release of H^+ or HCO_3^- and the production of CO_2 and the variation of soil pH depend upon the plant root. At pH values above 7 for normal inputs of H^+ or HCO_3^- by the root, the soil may have a relatively high acidity diffusion coefficient and thus pH gradients are predicted to be very small. However, the production of CO_2 by the root may have a more significant effect. The solubility of CO_2 is greater than O_2 in soil water; this means that small changes in partial pressure of CO_2 lead to relatively large concentration gradients and therefore rapid diffusion [21].

Increased buffer capacity increases the time necessary to establish a given profile, and increased water content reduces the pH changes in the rhizosphere because the ions can diffuse more rapidly. Mitsios and Powell [1] measured changes around single onion roots giving average pH values in small volumes of soil. The preceding processes result in severe pH changes in the rhizosphere, which are directly involved in the dissolution of minerals [2] such as silicates [22], carbonates [23], and phosphates in the rhizosphere [24]. In the rhizosphere, pH can also affect phosphate uptake.

If plants can induce the release of Ca from Ca-carbonates and phosphates due to release of protons by roots, this process is also likely to induce a release of trace elements from them. Hinsinger and Gilkes [24] showed an increase in Ca and P concentration in the rhizosphere of ryegrass and subclover due to release of protons by their roots. It is well known that phosphorus fertilizers are a source of input of Cd in agricultural soils due to substitution of Cd that occurs in phosphate rocks used for manufacturing phosphorus fertilizers [25].

The released proton by plant roots can cause an increased dissolution of goethite. It is known that most plant species (all but grasses) have been described as strategy I plants that respond to Fe deficiency. Marschner and Roemheld [26] concluded that the response to Fe deficiency is due to increased acidifying and reducing capacity of their roots.

Fenn and Assadian [27] showed that, in the rhizosphere of *Cynodon dactylon*, pH changes and dissolution of carbonates could mobilize Pb, Cu, and Mn in the rhizosphere and accumulate them in the leaves. Youssef and Chino [28,29] found that the mobility of Zn and Cu increased in the soil surrounding the roots because of the acidification of the rhizosphere. Neng–Chang and Huai–Man [30] studied the chemical behavior of Cd in wheat rhizosphere and concluded that the mobility of

Cd increased in the soil–root interface due to acidification of the rhizosphere. The form of nitrogen taken up by the plants was the main factor responsible for acidification process.

Some works has been done to investigate pH changes and the mobility of trace elements in the rhizosphere of hyperaccumulator species. Bernal and McGrath [31] studied the effects of pH and heavy metal concentrations in solution culture on the proton release growth and elemental composition of *Alyssum murale* and *Raphanus sativus*.

Bernal et al. [32] compared redox potential and pH changes in the rhizosphere of the Ni hyperaccumulator *Alyssum murale* and the nonhyperaccumulator *Raphanus sativus*. These workers concluded that the form of N taken up by the plants was the main factor responsible for pH changes and that the plants were able to reduce system more effectively than the hyperaccumulator. These results indicate that the hyperaccumulator mechanisms may be due to other rhizosphere processes, such as the release of chelating agents, or to differences in the number and affinity of metal root transporters. McGrath et al. [33] studied the heavy metals uptake and chemical changes in the rhizosphere of *Thlaspi caerulescens* and *Thlaspi ochroleucum* grown in contaminated soils. Knight et al. [34] investigated the Zn and Cd uptake by the hyperaccumulator *Thlaspi caerulescens* in contaminated soils and its effects on the concentration and chemical speciation of metals in soil solution. They found that the decrease in the mobile Zn fraction could explain only less than 10% of the total Zn uptake by the plants. The mobile fraction of Zn was depleted by *Thlaspi caerulescens* more than the closely related, but nonaccumulating *Thlaspi ochroleucum*.

In the rhizosphere of *Thlaspi caerulescens*, no significant differences in pH were observed. To explain these results, Knight et al. [34] suggested two possible mechanisms: *T. caerulencens* is able to mobilize Zn from the soil, or the soil studied had a large capacity to buffer the concentration of Zn in soil solution. Recently, Hamon and McLaughlin [35] showed that there is no difference in specific activity of Cd or Zn taken up by *T. caerulescens* or wheat. This indicates that the hyperaccumulator plant was able to access the same pools of metals available to the wheat plants. However, the Zn added in biosolids was highly labile, and the *T. caerulescens* in this experiment acts more as a Cd-tolerant species than as hyperaccumulator for Cd. These results show that hyperaccumulator plants seem to take up from the same phytoavailable metal pools, from which the other plants can take up metals when this pool is large enough. Mechanisms of hyperaccumulators, such as root exudation, may exist in the rhizosphere that can support metal uptake from less accessible pools.

Moving to the field conditions, where metals are returned to the soil from several sources, the soil is an easily available metal pool.

2.3.2 CONCENTRATION CHANGES OF IONS IN THE RHIZOSPHERE

The root may alter simple predictions of solute movements by release of H^+ or HCO_3^- ions; evolution of CO_2 from respiration; creation of changes in concentration of other ions and solutes; and excretion of organic substances. Change in pH-associated bicarbonate ion concentration is only one example of the disturbance near the root, which may influence diffusion of other ions. In fact, multiple ion diffusion is present and an accurate solution has not been attempted [9].

Nitrate and chlorite move towards the root from a distance. These anions are accompanied by cations — for example, calcium, because calcium is the dominant cation in a normal soil. Measurements of the diffusion coefficient of an ion require knowledge of the concentration and concentration gradients of all other ions [37]. The soil moisture level has a marked effect on the absorption of solutes by whole plants. The detailed interpretation of these effects is extremely complicated because it involves the transport of soil solutes and plant physiological responses.

Some of the effects of a single root are as follows:

- Plant effects:
    - The root absorbing power may be reduced by decreased water potential within the plant affecting plant growth.

  - The contact between root and soil may be reduced by shrinkage of soil or root.
- Soil effects:
  - The diffusion coefficient will decrease because the moisture content and the impedance factors are reduced. The impedance factor takes account primarily of the tortuous pathway followed by the solute through the pores. This has the effect of increasing the path length to be traversed and of reducing the concentration along this path length. It may also include the effect on the increase in the viscosity of water near charged surfaces, which will affect the mobility of all solutes, though it is unlikely to be significant except in dry soils.
  - Convection to a root may be reduced by decrease in rate of transpiration.
  - In drier soils, the diffusion coefficient near the root may sharply decrease because the water level decreases sharply near the surface if transpiration is still appreciable.
  - The solution concentration of nonadsorbed solutes, e.g., chloride and nitrate, will increase.
  - The concentration in solution of exchangeable cations will increase. Because the anion concentration rises, the concentration of cations will rise. If Ca and Mg are the dominant cations, their concentration will increase approximately directly with the total anion concentration. The monovalent cations, e.g., potassium, will increase so that the reduced activity ratio is maintained:

$$\text{i.e.}\frac{(\mathrm{K})^2\ \mathrm{dry}}{(\mathrm{K})^2\ \mathrm{wet}} \approx \frac{(\mathrm{Ca})\,\mathrm{dry}}{(\mathrm{Ca})\,\mathrm{wet}} \tag{2.1}$$

  - The concentration of adsorbed anions, e.g., phosphate, will tend to decrease because the activity product (Ca) $(H_2PO_4)_2$ tends to be constant and (Ca) increases according to the preceding bulleted statement.
  - The processes of mass flow and diffusion occur together and the resulting concentration profile is not the result of two independent processes. Thus, it is not possible to state that a given proportion of the total solute absorbed has “arrived” or is “taken up” by mass flow and the remaining proportion by diffusion [9]. However, it is correct to state that a given amount of solute has been brought into a zone of disturbance around the root by mass flow, assuming that the radial inflow of solution from outside it does not vary with distance from the root.

Lorenz et al. [38] found that the amount of Ca and Mg transferred toward the roots by mass flow was three- to sixfold the actual rates of uptake of these nutrients by radish roots, depending on the method used for measuring soil solution concentrations. For the elements that occur at low concentrations in the soil solution, mass flow will account for only a portion of the actual flux taken up by plant roots. This is the case for P and K among the major nutrients and of trace elements such as Zn and Cd [38].

McGrath et al. [33] found that more than 90% of the Zn taken up by the hyperaccumulator plants of the *Thlaspi* genus was originating from the nonexchangeable pool of soil Zn. Nye and Tinker [9] proposed that no simple algebraic expression can describe the spread of the disturbance zone of depletion, and the concentration is in fact asymptotic to the distance axis. In practice, measurements of concentrations are not accurate enough to detect it. The spread of the disturbance zone of phosphate and potassium depends mainly on the diffusion coefficient and time rather than root-absorbing power. When the concentration of phosphate in the soil solution in the rhizosphere is less than about 10^{-6} m, the value of root-absorbing power for young roots is high, and their uptake rate depends very largely on the rate of diffusion through the soil.

In addition to the depletion of trace elements in the rhizosphere, which has a direct effect on adsorption/desorption and precipitation-dissolution equilibria, the accumulation and depletion of major elements are also likely to interfere with the kinetics of trace elements and their bioavailability to plants.

2.3.3 ROOT ORGANIC EXUDATES, TRACE ELEMENT MOBILIZATION IN THE RHIZOSPHERE, AND THEIR BIOAVAILABILITY

The plant can play an important role in metal bioavailability through mechanisms causing release of root organic exudates. Among the root exudates released in the rhizosphere, some compounds can form strong complexes or chelates with a range of metals. This is particularly the case of aliphatic and phenolic acids, on the one hand, and of phytosiderophone, on the other hand.

Plants growing under conditions in which Fe and/or Zn are deficient can actively increase the availability of these metals, releasing specific organic compounds. Different strategies have been proposed by Marschner et al. [39] and Roemheld [40]. Among them, strategy I is active in dicotyledonous and monocotyledonous species with the exception of graminaceous species. This strategy is based on a three-component system constituting a plasma membrane-bound inducible reductase; an enhanced excretion of protons; and the release of reducing and chelating agents [26]. Strategy II (active in graminaceous plants) is based on the release of phytosiderophores in the rhizosphere and specific uptake system on the root surface.

The nature and the rate of release of phytosiderophores differ among plant species and even cultivars [26,41,42]. Treeby et al. [43] and Tagaki et al. [44] proposed that phytosiderophores form chelates not only with Fe but also with Zn, Cu, and Mn.

Wiren et al. [45] found evidence that Zn can be taken up in grasses in the form of nondissociated Zn-phytosiderophores. Bienfait [46] proposed a third strategy concerning the capacity of microorganisms to release siderophores and the possibility for the plants to take up these compounds. Also, Crowley et al. [47,48] proposed the existence of a microbial siderophore Fe transport system in oat and maize.

Hofflandy et al. [49] observed exudation of organic acids in P-deficient plants. Lundstroem [50] suggested the significance of organic acids for weathering and the podzolization process. Gahoonia and Nielsen [51] proposed mechanisms for controlling the pH at the soil–root interface. It is known that mineral weathering and dissolution of P-containing minerals can increase the mobility of metals. Plant uptake of trace elements depends on the metal availability in the rhizosphere; exudation of phytosiderophores and organic acids and changes in pH and redox potential are considered key factors controlling metal mobility in the rhizosphere.

The exudation of organic acids may also be important for increasing nutrient availability. Moghimi et al. [53] were able to isolate a-ketogluconate from the rhizosphere of wheat roots in quantities that could solubilize considerable amounts of phosphate from hydroaxyapatite. This appears to be a direct effect of organic acids on phosphate availability by lowering rhizosphere pH. However, organic acids may increase phosphate availability by desorbing phosphate from the surface of sesquioxides by anion exchange and by increasing phosphate mobilization by chelation with Fe or Al phosphate or both.

Gardner et al. [54] found that the proteoid roots of white lupine release citrate that, as they suggest, is responsible for increasing phosphate availability to the plant. The authors concluded that because the plant of white lupine has the coarse proteoid root system of low surface area, the mechanism by which citrate increases phosphate availability is to increase the rate at which phosphate reaches the root surface. These workers postulate that citrate exuded from the roots reacts in the soil to form ferric hydroxyphosphate polymers, which diffuse to the root surface. In this work, Fe^{3+} is reduced to Fe^{2+}, citrate is released, and the phosphate is taken up by the root. Citrate thus acts as a shuttle mobilizing Fe phosphate in the acquisition of P from the rhizosphere.

Jauregui and Reisenauer [55] have proposed that the MnO_2 is reduced by exudated malate. Chelation of the Mn_2^+ produced prevents reoxidation and increases the mobility of Mn_2^+ in the rhizosphere.

Mench and Martin [52] studied the mobilization of Cd and other metals from two soils by root exudates of *Zea mays* L., *Nicotiana tabacum* L., and *Nicotiana rustica* L. They found that root exudates of *Nicotiana tabacum* were able to extract more Cd from soil than those of *Nicotiana rustica* and *Zea mays*.

2.3.3.1 Function of Siderophores in the Plant Rhizosphere

Siderophores are iron chelating agents secreted by microorganisms and graminaceous plants in response to iron deficiency. The nature and the rate of release of siderophores differ among plant species and even cultivars [26,41,42].

These compounds are important for iron nutrition and are also speculated to function in the ecology of microorganisms in the plant rhizosphere. Under aerated conditions, at neutral to alkaline pH, inorganic iron is extremely insoluble. In such conditions, plants and microorganisms rely absolutely on iron uptake from organic complexes or iron that has been solubilized by siderophores and organic compounds from root exudates. Organic acids secreted by plant roots dissolve iron as a specific response to iron deficiency [26]. Graminaceous plants initially release organic acids in the rhizosphere, but as the plant becomes more iron stressed, these are followed by increased production of highly efficient chelators, called phytosiderophores, secreted in localized zones behind the root tips [56].

Recently, exchange of metals between siderophores and phytosiderophores has been proposed as a primary mechanism for plant use of microbial siderophores [57–58]. It has also been shown that microbial siderophores may strip iron from phytosiderophores [59]. The partitioning of metals between different types of siderophores and other iron complexes depends on the stability constants as well as the concentration of each chelator and the ability of the chelators to attack the surface of iron minerals and undergo exchange.

The competition for iron between plant and microorganisms involves very complex interactions that depend on a number of factors. For example, differences in the level of siderophore production by all the competing microorganisms; the chemical stabilities of various siderophores and other chelators with iron; their resistance to degradation; and the ability of different siderophores in the soil solution may interact through ligand exchange.

2.3.4 BIOAVAILABILITY OF TRACE ELEMENTS AND OXIDATION REDUCTION PROCESSES IN THE RHIZOSPHERE

2.3.4.1 Oxidation, Reduction Processes, and pH in Aerobic Conditions

It is well known that the pH of aerobic soils depends on the nature of the parent material, the degree of weathering and leaching, and the effects of any additions of amendments such as agricultural lime or fertilizers. In aerobic soils, the pH is not affected very much by the oxidation and reduction processes involved in aerobic respiration. For the glucose – pyruvic acid and oxygen – water couples protons and electrons are produced in equal numbers and are utilized in equal numbers by oxygen. This appears to be so in all oxidation steps in the breakdown of cellulose. There is no net gain or loss of protons during aerobic respiration. Although some of the steps in the respiration chain linking pyruvic acid to O_2 may not involve equal numbers of protons and electrons, the steps are cyclic and the overall reaction is balanced. However, CO_2 is produced by aerobic respiration, and an increase in partial pressure of CO_2 reduces pH via the H_2CO_3–HCO_3^-–CO_3^- system in the soil water [2]. The effects are mostly in calcareous and sodic soils. The pH of calcareous and sodic soils is close to 8 and 9, respectively; in equilibrium with the atmosphere, it is close to 7.5 and 8, respectively, when the relative pressure of CO_2 is 1%.

During the respiration process, the production of organic acids may have a slight acidifying effect. The oxidation of NH_4^+ to NO_3^- also causes a drop in pH.

2.3.4.2 Redox Processes and pH in Anaerobic Conditions

In anaerobic conditions, the couple MnO_2–Mn^{2+} causes a rise in pH, but the NO_3^-–NO_2^- and CO_2–CH_4 couples produce no change. In many soils, the $Fe(OH)_3$–Fe_2^+ couple tends to predominate, thus giving a rise in pH. The production of CO_2 tends to cause a decrease in pH; the resultant effect is that, in acid soils where the CO_2 effect is small, pH rises. In alkaline soils, where the CO_2 effect is large, pH drops.

2.3.4.3 The Significance of Redox in Rhizosphere

The supply of manganese to plants is as Mn^{2+}. Solid manganese compounds have very low solubility. When the pH of the soil is high, the plants may suffer from deficiencies and when the pH is low, toxicities may appear. Waterlogged soils would be expected to have adequate and perhaps toxic amounts of manganese. Most flooded soils contain sufficient water-soluble manganese for the growth of rice. Paddy rice has a high demand and a high tolerance for manganese.

Boron, cobalt, copper, molybdenum, and zinc are not involved in oxidation-reduction reactions in soils. However, the changes in pH in iron and manganese compounds when soils become anaerobic may affect the mobility and availability of the nutrients. Thus, the concentrations of Cu, Co, and Zn may increase in soil solution due to release from their association with ferric and manganese hydroxides when these are reduced. The organic compounds may chelate the nutrients and also increase their concentration. The net result is to increase the availability of Co and Cu but to decrease that of Zn.

In waterlogged or submerged soils, roots do not grow except for the case of flood-tolerant plants such as rice. The most obvious factor for the lack of growth is the lack of O_2 at the root surface. The concentration O_2 required at the root surface varies depending on the age and type of plant root. The bacteria seem to need about 4×10^{-6} M O_2 at their surface, although the concentration required at the site of enzyme activity may be only 2.5×10^{-8} M. Because of the longer diffusion path in plant roots, the concentration required at their surface may be larger than 4×10^{-6} M.

The leakage of O_2 from the roots, as a consequence of its transfer from the shoots through the aerenchyma, provides an adequate supply of O_2 for rice root respiration. It also enables rice plants to alleviate metal toxicities that can occur due to the ambient reducing conditions of the bulk soil and much increased solubility of Fe and Mn oxides [60]. Flessa and Fischer [61] and Begg et al. [62] found that leakage of O_2 leads to a substantial reoxidation of the rhizosphere, which can result in a precipitation of Fe and Mn oxides at the root surface or even in the root cell wall [63].

The reduction of Fe is a major mechanism involved in the acquisition of Fe by most plants, as indicated previously [26,40]. Strategy I species, in particular, have been defined as plants exhibiting an enhanced reduction activity as a response to Fe deficiency [26].

2.3.5 BIOAVAILABILITY OF TRACE ELEMENTS AS RELATED TO ROOT–MICROORGANISM INTERACTIONS IN THE RHIZOSPHERE

In natural conditions, all normal roots support the microorganisms on their external surfaces and in a thin sheath of soil immediately adjacent to the rhizosphere [64,65]. Pathogens, which cause specific diseases in roots by invading the roots, are excluded from this discussion, which is largely confined to the effects of the organisms on the nutrient supply to apparently normal plants. Organisms can cause changes in the phase equilibria of soil nutrients. These become more easily absorbed by plants or become more readily transported to the roots — e.g., complex formation or redox changes or pH changes. They also can cause changes in chemical composition of the soil such as mineralization of organic matter or decomposition of soil minerals. In symbiotic processes, nutrients are transferred directly to the plant from their organisms.

Root microorganisms in the rhizosphere play an effective role in the bioavailability of trace elements. It is well known that root exudates can cause balance between Mn-oxidizing and Mn-reducing bacteria. A large number of interactions among roots, microorganisms, and the trace elements in the rhizosphere cannot be discussed in detail in this chapter. The attention here will focus on the bioavailability of trace elements as influenced by mycorrhizae. Mycorrhizal fungi occur in soils in close association with plant roots that permit plants to acquire nutrients from the soil. These fungi may be divided into two groups: the ectotrophic and the endotrophic mycorrhizae.

The ectotrophic mycorrizal fungi or ectomycorrhizae (ECM) alter the root very clearly, even in its physical form. A mass of fungal hyphae form a sheath around the root proper; hyphae extend from this into the soil and into the intercellular spaces in the cortex. These fungi, which belong to the Basidiomycetes, depend on carbohydrates supplied by the root. The thick sheath of hyphae covering the roots favors the uptake of water and inorganic nutrients — especially phosphate because it effectively enlarges the surface area of the root in direct contact with the soil. The thin mycorrhizal hyphae, with a diameter of 2 to 4 μm, are able to penetrate soil pores not accessible to the root hairs with a diameter of about five times greater than the hyphal diameter [66].

Ectotrophic mycorrhizae are mainly found on the roots of trees and shrubs. Numerous investigations have shown that they promote the growth of trees when grown on soils low in available phosphate. It has been reported that seedlings of *Pinus* and *Picea* planted on newly drained organic soils only grew when the roots were infected with appropriate mycorrhizal fungus. Endotrophic mycorrhizae form no definite sheath around the root. The most important group is known as the arbuscular mycorrhizae (AM). These are formed by most herbaceous plants (including agricultural plants) and with the majority of trees in Mediterranean and tropical ecosystems (soils with neutral pH and low organic matter content).

The rhizosphere of mycorrhizal plants may be defined as mycorrhizosphere. The rhizosphere is modified in several respects, depending on the presence or absence of mycorrhizae. Toxicity of metals in soil depends on their bioavailability — defined as their ability to be transferred from a soil to a living organism. This is a function not only of their total concentration, but also of physicochemical (pH, Eh, organic matter, clay content, etc.) and biological factors [67].

Soil microorganisms including mycorrhizal fungi are affected by the presence of high metal concentrations in soil [68]. The organisms influence the availability of trace elements in soil directly, through alterations of pH, Eh, biosorption, or uptake, or indirectly in the rhizosphere through their effect on plant growth, root exudation, and resulting rhizosphere chemistry.

2.3.5.1 Bioavailability of Trace Elements as Related to Mycorrhizal Fungi

Mycorrhizal fungi can directly affect bioavailability of trace elements by an effect on the free metals in soil solution (immobilization by adsorption, absorption, and accumulation) and indirectly by modifying root exudation or by affecting solubilization of metal-bearing minerals. Mycorrhizae have the capacity to protect their host plants when the metal uptake is excessive. Metal uptake decreases from ericoid to ectomycorrhizae (CECM) and arbuscular mycorrhizae (AM) fungi. This is the result of pH changes in soil and thus metal availability, but it is also related to morphology and biomass of the fungal structure of mycorrhizae.

The ectomycorrhizae are exceptional in this respect because they form a dense and thick sheet of fungal tissue (the mantle) that covers the root surface completely. It seems that any ion entering the root must pass the fungal mantle. In other words, ectomycorrhizae have the ability to "filter" ions that enter the plant, which the other types of mycorrhizae do not have. Mycorrhizal fungi are part of the rhizosphere, so their metal sorption capacity is a fundamental issue to researchers concerning the fate of metals in the rhizosphere. On one hand, the contact between metal ions and the hyphae in soil is the first interaction in mycorrhizal metal transport and the processes that take place at the hyphae surface affect the fate of trace elements in the rhizosphere. On the other hand, sorption of metals on mycorrhizal mycelium may be extensive and limit the amount of metals taken up by the fungi.

In a recent work on cation exchange capacity and Pb sorption in ectomycorrhizal fungi, Marschner et al. [69] found that the electron-dense lead deposits on the surface of ectomycorrhizal fungus with the highest Pb sorption capacity contained molar equivalents of P. The sorption characteristics of a fungus may differ between fungi *in vitro* and in symbiosis with a plant; Marschner et al. have found higher sorption [64]. Colpaert and Assche [70] showed heavy metal uptake and accumulation by ectomycorrhizal fungi, using axenic cultures, where the metals were added as soluble salts. Under these conditions, the fungal-soil concentration ratios were around 200 and 80 for Cd, and 40 and 30 for Zn for nontolerant and metal-tolerant isolates of *Suillus bovines*, respectively.

Gast et al. [71] studied the heavy metals in mushrooms and their relationship with soil characteristics and they found large differences between metals with very high accumulation for Cd, exclusion for Pb, and a narrower range of concentrations for Zn and Cu. These workers suggested a regulation of uptake for essential elements and concluded that species differences — not soil factors — are the primary determinants of metal levels in fungi.

Ectomycorrhizal fungi can increase the bioavailability of heavy metals in the rhizosphere by solubilizing minerals containing metals such as rock phosphates [72]. Mycorrhizal fungi associated with plant roots in symbiosis affect plant root exudation quantitatively and modify the composition of root exudates containing carbohydrate, amino acids, and aliphatic acids [73]. Leyval and Berthelin [74] proposed that the modification of the composition of root exudates by mycorrhizal fungi influence the bioweathering of minerals in the rhizosphere and the availability of metals in the mycorrhizosphere.

2.4 CONCLUSIONS

It is generally accepted that the rhizosphere plays an important role in the bioavailability of trace elements. A range of mechanisms exists, such as excretion of H^+ or HCO_3^-; respiration and release of CO_2; exudation; desorption and adsorption of trace elements; dissolution–precipitation; redox reaction; and chelation, by which plant roots can modify the chemical conditions in the rhizosphere. These factors can affect dramatically the behavior of root in the rhizosphere and substantially the bioavailability of trace elements. The mechanisms involved in chemical modifications in the rhizosphere as well as on uptake of trace elements differ among plant species and soil conditions.

The extent to which siderophores alter the ecology of the rhizosphere is a question that remains to be investigated. Scientists need to have a better understanding of how siderophores can function in the rhizosphere and under different soil conditions rather than in laboratory experiments. Research efforts must be focused on how these compounds influence heavy metal transport and bioavailability in soils. In the future, we hope these compounds may have application and use siderophores as iron fertilizers. The ability to manipulate siderophore production in the rhizosphere to improve plant trace metal nutrition will remain a significant challenge.

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