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IMPACTS OF PHYSICOCHEMICAL–BIOLOGICAL INTERACTIONS ON METAL AND METALLOID TRANSFORMATIONS IN SOILS: AN OVERVIEW

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Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments,
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1.1. INTRODUCTION

Soil, geoderma, is the “skin” of planet Earth and the central organizer of the terrestrial ecosystem. It is a life-sustaining material which is a structurally porous and biologically active medium that has evolved over time on continental land surfaces. This material is formed and continues to develop through weathering processes driven by geological, biogeochemical, topological, climatic, chronological, and anthropogenic influences.

Soils are complex interactive biogeochemical reactors, reservoirs of organisms (microorganisms, protozoans, and nematodes), and major compartments of the terrestrial ecosystem. Minerals, organic components, and organisms are among major solid components of soils. These components are not separate entities but rather, form a unified system whose members are constantly in association with each other in the environment (Huang and Schnitzer, 1986; Huang et al., 1995; Banfield and Nealson, 1997). The association of microorganisms with soil mineral and organic colloids is depicted in Figure 1.1. Interactions among the components have an enormous impact on the physics, chemistry, and biology of soil and surrounding ecosystems (Huang, 2002). However, physical, chemical, and biological processes are not independent but rather, interactive processes in soil environments. A fundamental understanding of physical, chemical, and biological interfacial interactions in soil is essential in restoring, enhancing, and sustaining ecosystem productivity, services, and integrity and for establishing soil’s impact on human welfare. In view of the mineral–organic component–organism interactions and interactive physical, chemical, and biological processes in the terrestrial ecosystem, a commission on Soil Physical/Chemical/Biological Interfacial Reactions was created within the structure of the International Union of Soil Sciences in 2004.

The transformation of metals and metalloids in the environment is influenced by physicochemical–biological interfacial interactions. The impact of these interactive interfacial processes on metal and metalloid transformations is especially important in the rhizosphere (Huang and Germida, 2002; Huang and Gobran, 2005) and near the decomposition of plant residues (Huang and Schnitzer, 1986), where the types and concentrations of substrates are different from those of the bulk soil because of enhanced biological activity. In the rhizosphere, root exudation leads to colonization by various populations of bacteria, fungi, protozoans, and nematodes. The distribution of microorganisms with distance from the root is illustrated in Figure 1.2. Plant–microbe interactions result in intense biological processes in the rhizosphere. These intense biological processes, in turn, affect physicochemical reactions in the rhizosphere. Physicochemical properties that can be different in the rhizosphere include acidity, concentration of complexing biomolecules, redox potential, ionic strength, moisture, and nutrient status. In the rhizosphere, it is difficult to separate the effects of microbial activity on the chemistry of metals and metalloids from the effects of plant root activity. Microorganisms act in a fashion similar to that of plant roots in that they can accumulate metals and metalloids through uptake and adsorption as well as mobilizing them through the action of microbial exudates, diffusates, and excretions.

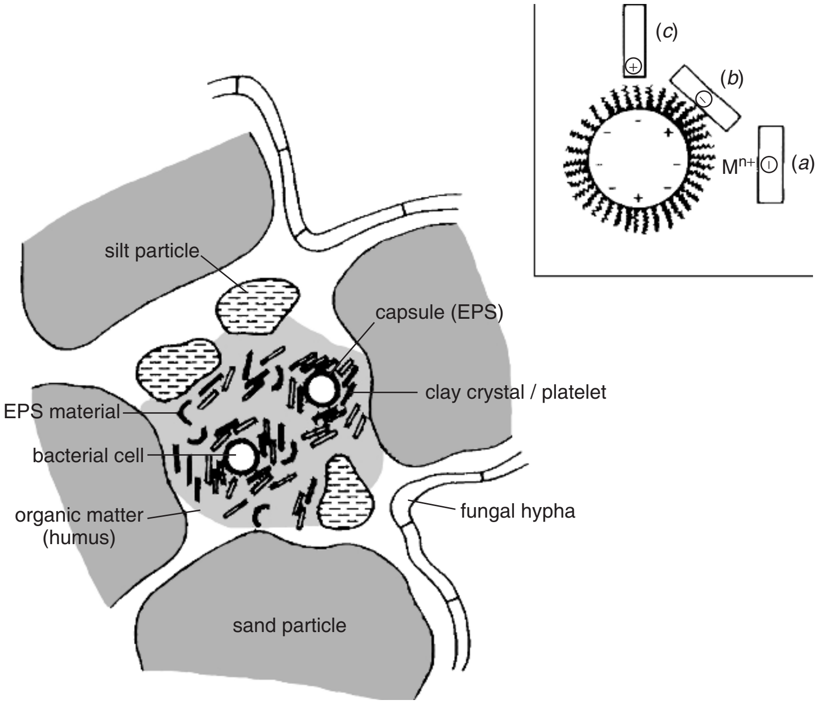


Figure 1.1. Interaction of bacteria and fungi with mineral particles in a soil aggregate. Bacterial cells with a coat of extracellular polysaccharides (EPSs) are enveloped by clay particles. The pore space where clays and bacteria interact, bounded by silt- and sand-size particles, is relatively enriched in organic matter, including EPS residues. Fungal hyphae are attached to the outside surface of an aggregate. Inset shows an enlarged view of a bacterial cell with its complement of EPS. At normal soil pH conditions, the cell has a net negative surface charge. Most clay particles adhere to the cell surface by bridging through polyvalent cations, represented by M^{n+} (*a*), although some may be attached directly by electrostatic interactions, either in face-to-face (*b*) or edge-to-face (*c*) association. (From Theng and Orchard, 1995.)

The total rhizosphere environment is governed by an interacting trinity of the soil, the plant, and the organisms associated with the root (Lynch, 1990a,b), as illustrated in Figure 1.3.

Therefore, the role of physicochemical–biological interfacial interactions in controlling the transformation, transport, fate, and toxicity of metals and metalloids in soil and surrounding environments, especially the rhizosphere, which is the bottleneck of contamination of the terrestrial food chain, deserves increasing attention. In this chapter we present an overview of this emerging and extremely important area of science, to advance our knowledge of the interface between physicochemical and biological reactions and processes in the environment.

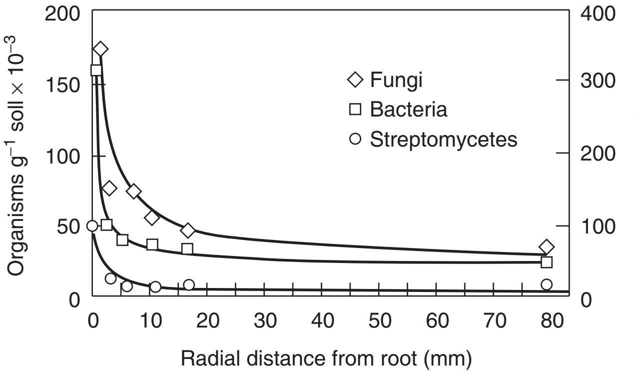


Figure 1.2. Distribution of organisms with distance from the roots of 18-day-old lupin (*Lupinus angustifolius* L.). (From Rovira and Davey, 1974.)

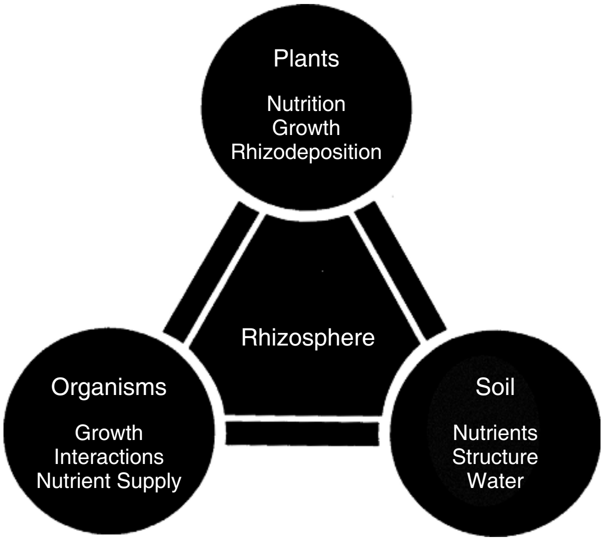


Figure 1.3. Rhizosphere trinity. The total rhizospere environment is determined by an interacting trinity of the soil, the plant, and the organism associated with the roots. (From Lynch, 1990a.)

1.2. MINERAL–ORGANIC MATTER–MICROORGANISM INTERACTIONS IN SOIL ENVIRONMENTS

Interactions of soil minerals with organic matter and microorganisms exert a vital role in the formation of short-range-ordered metal oxides, humic substances, mineral colloid–humic complexes, aggregates, and the structure and porosity of soils. These nonliving and living reactive components and the structural stability and associated nanoporosity of soils control the transformation, transport, fate, and toxicity of metals and metalloids in the environment.

1.2.1. Formation of Short-Range-Ordered Metal Oxides

Short-range-ordered Al and Fe oxides, especially nanoparticles, are indeed among the most reactive components of acidic and neutral soils (Bigham et al., 2002; Huang et al., 2002). In addition to humic substances, biomolecules, which are present in root exudates, microbial metabolites, and decomposition products of biological tissues play a very significant role in influencing the formation and transformation of these metal oxides and the resulting alteration of their surface properties pertaining to the speciation, transport, fate, and toxicity of metals and metalloids in soil environments (Huang and Violante, 1986; Schwertmann et al., 1986; Sposito, 1996, 2004; Huang and Wang, 1997; Huang et al., 2002; Violante et al., 2002; Huang, 2004). Details of this issue are treated by Violante et al., in Chapter 5.

As the third most abundant element on Earth's surface (after O and Si), Al is a major element in all mineral soils. There are only a few crystalline Al oxides, hydroxides, or oxyhydroxides, and only one, gibbsite, occurs to any great extent in soils. Aluminum, however, also forms a series of highly reactive soluble species and poorly crystalline to noncrystalline mineral colloids (Figure 1.4). The mode depicted in the figure incorporates multiple reaction paths. Reaction path I is believed to be common when systems are neutralized rapidly within seconds or hours. Under these conditions, little or no Al_{13} polynuclear species $[AlO_4Al_{12}(OH)_{24}(H_2O)_{7+}^{12}]$ forms; the formation of $Al(OH)_3$ nuclei is rapid, and gibbsite appears within days or weeks of aging. Reaction paths II and III both involve the formation of Al_{13}. Reaction path II is applicable when systems are neutralized relatively slowly compared with reaction path I. The individual Al_{13} ions can remain in solution for months to years, but eventually they transfer by one of the three pathways. If no Al_{13} nuclei are present, the soluble Al_{13} ions can slowly dissociate into Al^{3+} ions and deposit onto $Al(OH)_3$ nuclei (path IIa). These soluble Al_{13} may also aggregate and form Al_{13} nuclei (path IIb). If some Al_{13} nuclei are already present, the remaining Al_{13} ions can be deposited on them within weeks and months (path IIc). Path III is applicable when Al_{13} forms under conditions that promote the rapid formation of Al_{13} aggregates via an anion bridging mechanism (i.e., outer-sphere associations). These aggregates rearrange themselves rapidly into Al_{13} nuclei. The Al_{13} nuclei in paths IIb, IIc, and III then transform into a poorly ordered phase, microcrystalline boehmite (pseudoboehmite), which then transforms into gibbsite. The relative importance of each pathway depends greatly on reaction conditions. These soluble Al species and poorly ordered to noncrystalline Al species formed in the reaction pathways are highly reactive and thus important in influencing reactions and processes in the environment. The transformation of Al via the various pathways described above are strongly influenced by the nature and concentration of solution inorganic and organic ions and solid-state ions such as clay minerals and humic substances

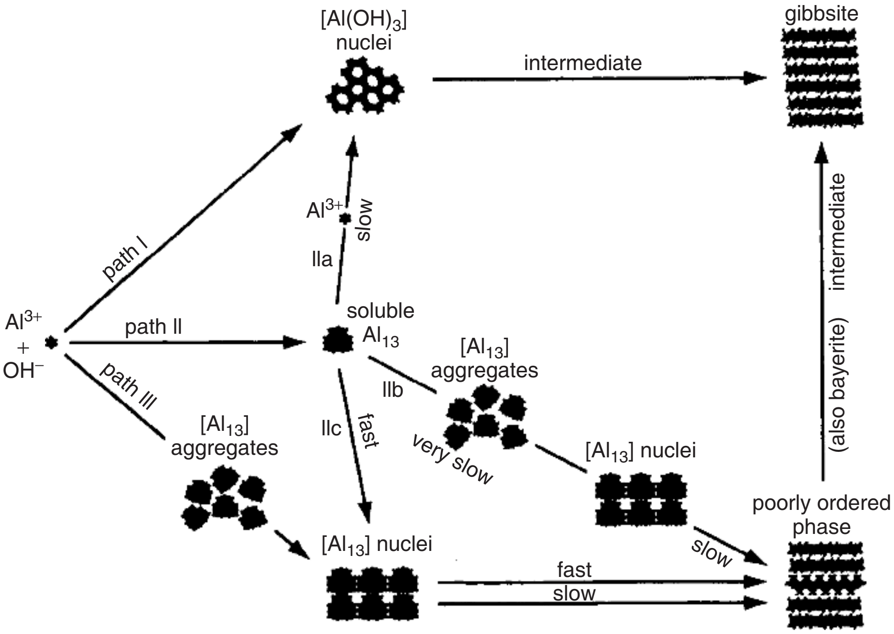


Figure 1.4. Reaction scheme proposed for Al hydroxide mineral formation from hydrolyzed Al solution. (Modified from Bertsch and Parker, 1996; Huang et al., 2002.)

(Huang and Violante, 1986, Huang, 1988; Bertsch and Parker, 1996; Krishnamurti et al., 1999, 2004; Huang et al., 2002).

Organic substances such as fulvic acid (FA) and humic acid (HA) and many low-molecular-mass organic acids (LMMOAs) form stable complexes with Al and disrupt the crystallization of Al hydroxides and thus promote the formation of short-range-ordered (SRO) Al hydroxides (Kwong and Huang, 1975, 1979a,b, 1981; Lind and Hem, 1975; Kodama and Schnitzer, 1980; Violante and Huang, 1985; Singer and Huang, 1990; Violante et al., 2002; Colombo et al., 2004). Organics greatly influence the surface properties of Al transformation products. For instance, the presence of organic acids during aging of Al hydroxide gels for 40 days increases the specific surface of the precipitation products up to 30-fold over that of the control and higher acid concentrations results in higher specific surfaces (Table 1.1). The surface charge characteristics of the precipitation products are also altered dramatically (Figure 1.5). These SRO transformation products of Al should thus exert substantial influence on the adsorption–desorption, transformation, and dynamics of metals and metalloids in the environment.

Interactions of soil minerals with organic substances and microorganisms have a great impact on the formation and transformation of SRO Fe oxides (Schwertmann et al., 1986; Cornell and Schwertmann, 2003). Microorganisms may influence Fe transformation through reduction and oxidation reactions. Soil

TABLE 1.1. **Specific Surface Area of Al Hydroxide Precipitation Products**[a]

Organic Acid	Organic Acid Concentration (mol L^{-1}) 1.0×10^{-6}	Organic Acid Concentration (mol L^{-1}) 1.0×10^{-4}
	$m^2\ g^{-1}$	
None	20	20
p-Hydroxybenzoic	22	28
Aspartic	27	587
Tannic	95	195
Malic	36	635
Citric	117	295

Source: Kwong and Huang (1981).

[a] Formed in the presence of tannic acid and selected low-molecular-weight organic acids in systems at an initial Al concentration of 1.1×10^{-3} mol L^{-1} and OH/Al molar ratios of 3.0 and aged for 40 days at room temperatures.

organic matter and microorganisms play a vital role in influencing redox cycling of Fe, hydrolytic reactions of Fe, crystallization of Fe precipitation products, and the subsequent formation of pedogenic Fe oxides (Huang and Wang, 1997). Furthermore, the fine-scale morphology, mean surface roughness, fractal dimension, specific surface, microporosity, and surface charge properties of Fe oxides are strongly influenced by biomolecules (Liu and Huang, 1999, 2003). The surface of Fe oxides is the region of their interactions with the soil solution, organic and inorganic particles, plant roots, microorganisms, and other soil biota. Surface properties of Fe oxides should have a profound impact on microaggregate formation, soil biota habitat, water flux, metal and metalloid flux, and the ability of soils to respond to management. Therefore, surface properties of Fe oxides formed under the influence of biomolecules deserve close attention in advancing our understanding of the surface chemistry pertaining to biogeochemical transformations of metals and metalloids in the terrestrial ecosystem.

1.2.2. Formation of Humic Substances and Organomineral Complexes

Humic substances are formed through biotic and abiotic processes (Stevenson, 1994; Huang, 2004). A variety of biomolecules, such as carbohydrates, phenolic compounds, and amino acids, can participate as raw materials. Soil mineral surface chemistry plays a vital role in the catalysis of abiotic formation of humic substances. The Maillard reaction (Maillard, 1913) is perceived to be a major pathway in humification because of significant similarities between humic substances and melanoidins formed through this pathway involving sugar–amino acid condensations (Ikan et al., 1996). The presence of characteristic products of the Maillard reaction (alkyl pyrazines) was detected in archaeological plant remains up to 1500 years in age (Evershed et al., 1997). The great appeal of the Maillard reaction in humification processes lies in the two types of precursors, sugars and amino acids, which are among the most abundant constituents of

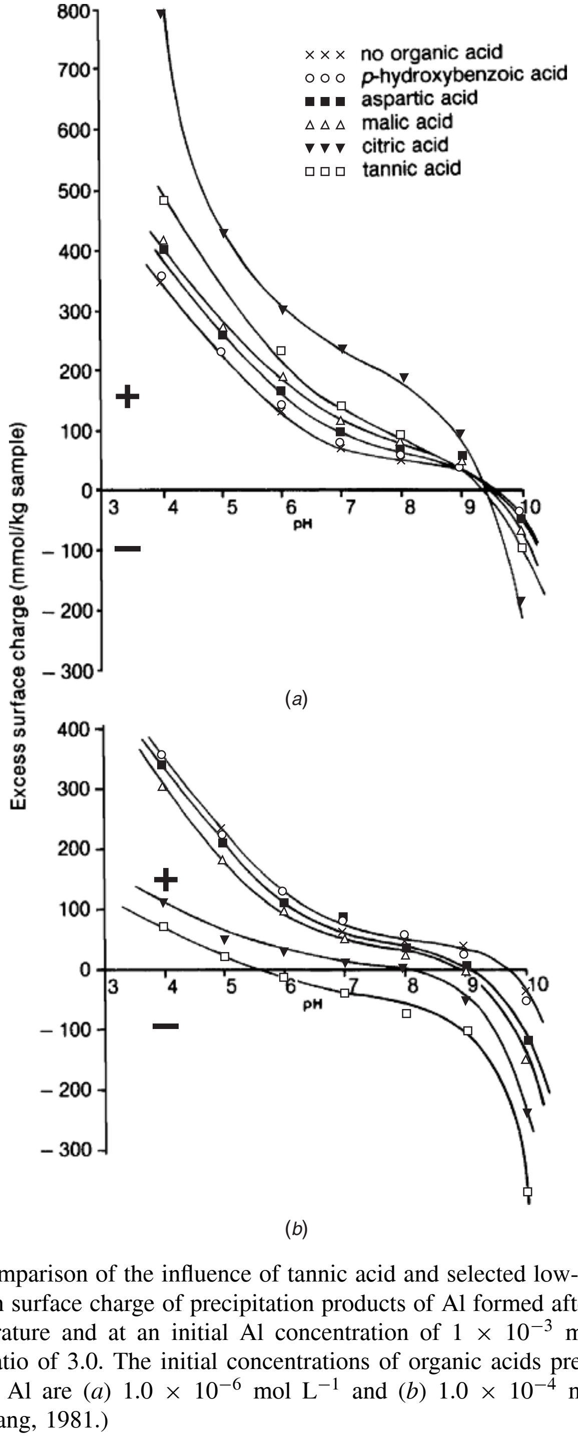


Figure 1.5. Comparison of the influence of tannic acid and selected low-molecular-mass organic acids on surface charge of precipitation products of Al formed after 40-day aging at room temperature and at an initial Al concentration of 1×10^{-3} mol L^{-1} and an OH/Al molar ratio of 3.0. The initial concentrations of organic acids present during the precipitation of Al are (*a*) 1.0×10^{-6} mol L^{-1} and (*b*) 1.0×10^{-4} mol L^{-1}. (From Kwong and Huang, 1981.)

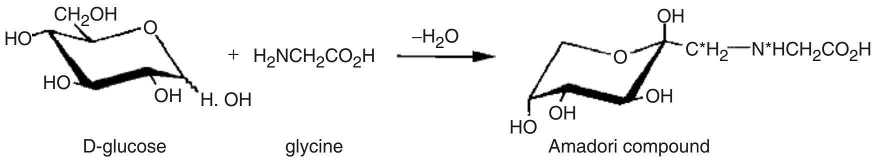


Figure 1.6. Formation of the Amadori compound from D-glucopyranose (D-glucose) and glycine. Note that a molecule of water is split off. The Amadori compound is an intermediate product in the Maillard reaction, which is perceived as one of the pathways in humification. (From Mossine et al., 1994.)

terrestrial and aquatic environments (Anderson et al., 1989). A major criticism of the Maillard reaction has been that it is very slow under ambient conditions (Hedges, 1988). To elucidate some details of the process, Jokic et al. (2001a) applied molecular topological analysis to investigate the initial reaction between D-glucose and glycine to form the Amadori compound fructosylglycine, which is an intermediate product in the Maillard reaction (Figure 1.6). Their calculations show that fructosylglycine and water and D-glucose and glycine as separate entities are very close to each other in terms of their ground-state energy. Therefore, the potential energy barrier is high and the reaction between D-glucose and glycine alone to form fructosylglycine is thus very slow at room temperature. Jokic et al. (2001b) demonstrated that the action of δ-MnO_2 under ambient environmental conditions accelerates the Maillard reaction by about two orders of magnitude, lending credence as an important abiotic pathway for the formation of humic substances in nature.

Soil minerals also play an important role in accelerating abiotic polymerization of phenolic compounds, polycondensation of phenolic compounds and amino acids, and subsequent formation of humic substances (Wang et al., 1986; Huang, 1990, 2000). Kumada and Kato (1970), Filip et al. (1977), and Wang and Li (1977) are among the pioneers in the study of browning of polyphenols catalyzed by clay-size phyllosilicates. Since the early 1980s, Huang and co-workers have investigated the sequence of catalytic ability of phyllosilicates and their reaction sites in the polymerization of phenolic compounds and subsequent formation of humic substances (Shindo and Huang, 1985a,b; Wang and Huang, 1986, 1988, 1994). Among Al, Fe, and Mn oxides, hydroxides, and oxyhydroxides, Mn oxides are the most reactive catalysts in the transformation of phenolic compounds by virtue of their high oxidation potentials, high specific surfaces, and high surface reactivity (Shindo and Huang, 1982, 1984; Wang and Huang, 2000a,b). Manganese oxides (birnessite, cryptomelane, and pyrolusite), which are common in soils, act as Lewis acids that accept electrons from phenolic compounds, resulting in the formation of semiquinones, oxidative polymerization, and the genesis of humic substances. Therefore, the catalytic power of these oxides in the formation of humic substances via abiotic processes in soil and surrounding environments merits close scrutiny.

TABLE 1.2. Visible Absorbances of Supernatants in a Series of Reaction Systems

Reaction System	Absorbance 400 nm	 600 nm
25°C, 60 days		
Glucose–glycine	0.077 ± 0.004	0.021 ± 0.001
Glucose–glycine–δ-MnO_2	0.367 ± 0.006	0.067 ± 0.002
Glucose–glycine–catechol	10.8 ± 0.6	3.8 ± 0.2
Glucose–glycine–catechol–δ-MnO_2	90.4 ± 3.8	37.6 ± 1.7
45°C, 15 days		
Glucose–glycine	0.342 ± 0.018	0.103 ± 0.006
Glucose–glycine–δ-MnO_2	14.7 ± 0.68	1.50 ± 0.10
Glucose–glycine–catechol	5.60 ± 0.35	2.13 ± 0.08
Glucose–glycine–catechol–δ-MnO_2	73.7 ± 1.3	24.7 ± 1.5

Source: Jokic et al. (2004).

The Maillard reaction and the polyphenol transformation model are considered as separate significant pathways for the formation of humic substances. In nature, however, it is likely that these two pathways do not occur separately, but rather, interact closely with each other, since sugar, amino acids, and polyphenols coexist in soil solutions and natural waters. Jokic et al. (2004) reported that soil mineral colloids such as δ-MnO_2 significantly accelerate humification processes in systems containing glucose, glycine, and catechol under ambient conditions (Table 1.2). The promoting effect of δ-MnO_2 on a system consisting of carbohydrate, amino acid, and polyphenol is a complex process involving mineral surface sorption and condensation. This points to a linking of the polyphenol and Maillard reactions in humification pathways, which is a significant advance in our understanding of the chemistry of humification and its impact on biogeochemical reactions and processes in the environment.

Humic substances are the principal organic components of soils and waters, in which they interact with metal ions, metal oxides, metal oxyhydroxides, metal hydroxides, and clay minerals to form complexes of widely differing physicochemical and biological stabilities (Senesi and Loffredo, 2005). These interaction products affect the moisture and aeration regime; the exchange capacity; the transformation, transport, and fate of metals and metalloids; and other physical, chemical, and biological reactions and processes. In soils and waters, large amounts of humic substances are adsorbed on the surfaces of hydrous metal oxides and clay minerals. The importance of metal–humic and clay–humic interactions in predominantly mineral soils, with the exception of extremely sandy ones, is illustrated by the data presented by Greenland (1965), which show that between 52 and 98% of the organic C in a wide range of soils is associated with the clay fraction. It is likely that most of the remaining organic C is linked to metal oxides, oxyhydroxides, and hydroxides (Schnitzer and Kodama, 1977). Short-range-ordered mineral colloids are especially reactive in binding and stabilizing organic matter, due to their high specific surface area and high charge density (Wada, 1995; Torn et al., 1997; Guggenberger and Haider, 2002).

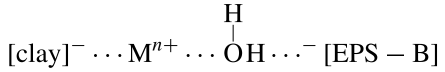
1.2.3. Formation of Aggregates and Porosity

Interactions of mineral particles with microorganisms and organic matter in the formation of aggregates and porosity of soils are depicted in Figure 1.1. Microbial cells with a coat of extracellular polysaccharides (EPSs) are enveloped by clay particles. At normal soil pH conditions, the microbial cell has a net negative surface charge. Most clay particles adhere to the microbial cell surface with a coat of EPS by bridging through polyvalent cations. Some may be attached directly by electrostatic interactions, either in face-to-face or edge-to-face association. The pore space where clays and bacteria interact, bounded by silt- and sand-size particles, is relatively enriched in organic matter, including EPS residues.

Polyvalent cation bridging may be direct [scheme (1.1)] or effected by hydrogen bonding to water molecules in the primary hydration shell of a polyvalent cation [scheme (1.2)]:

$$[\text{clay}]^- \cdots \text{M}^{n+} \cdots {}^-\,[\text{EPS} - \text{B}] \tag{1.1}$$

or



$$[\text{clay}]^- \cdots \text{M}^{n+} \cdots \overset{\text{H}}{\overset{|}{\text{O}}}\text{H} \cdots {}^-\,[\text{EPS} - \text{B}] \tag{1.2}$$

where M^{n+} denotes a polyvalent cation of valency n and B is a bacterial cell (Theng and Orchard, 1995). The predominant mechanism would depend on the nature of the polyvalent cation but even more on the hydration status of the soil. Dehydration conditions would clearly favor the mechanism shown in scheme (1.1). In addition, short-range interactions (van der Waals, hydrogen bonding) may come into play because the EPS chains are induced to make close contact with the surface, increasing the net energy of interactions.

Mineral colloids are coated with hydroxy Al (or Fe) polymers in both interlayers (Brown, 1953; Rich and Obenshain, 1955; Rich, 1960, 1968, Jackson, 1962; Barnhisel and Bertsch, 1989; Huang et al., 2002) and on the edges and external planar surfaces (Huang and Kozak, 1970; Huang et al., 2002). Furthermore, hydroxyaluminosilicate ions, which are common in soil solutions, especially in temperate and subtropical regions, can be adsorbed on the surfaces of mineral colloids (Lou and Huang, 1988). The coated mineral colloids thus behave as a positively charged species or display amphoteric characteristics. Therefore, mineral colloids can interact strongly with negatively charged microbial cells coated with EPS in soil environments. This type of bonding, which is stronger than cation bridging, is also expected to occur with discrete hydrous Al and Fe oxides in the pH range of soils. The attachment of microorganisms to SRO mineral colloids and the crystal edges of phyllosilicates through electrostatic interactions and subsequent binding to mineral surfaces would also be predicted to occur when the soil pH falls below 6 because all of these surfaces would then be largely positively charged.

In the majority of cases, minerals in top soils are partially covered with organic materials, especially humic substances (HSs), which are microbially resistant and most prevalent. The most common mode of mineral colloid–organic matter–microbe interactions may be represented by scheme (1.3). In humic-rich calcareous Mollisols, Ca would be the predominant bridging cation:

$$[\text{mineral colloid} - \text{HS}]^{-} \cdots \text{M}^{n+} \cdots {}^{-}\,[\text{EPS} - \text{B}] \tag{1.3}$$

In Andisols, Oxisols, Ultisols, and the B horizons of Spodosols, HSs occur largely as complexes with Al and Fe or their respective poorly crystalline and noncrystalline oxides (Oades et al., 1989; Theng et al., 1989). In soils with little organic matter and in subsoils, mineral colloid–microbe interactions are governed largely by the mineralogical composition and pH of the system.

Interactions between soil mineral particles, organic substances, and organisms can occur at many different size scales, as these materials have a large size range in soils (Figure 1.7). Therefore, it is important to indicate the size scale being considered when discussing soil aggregates and soil structure and the mechanisms of their stabilization, because the potential mechanisms for stabilization vary with aggregate size. The adsorption of organic molecules such as microbially derived polysaccharides and other unaltered and altered biomolecules onto mineral surfaces is important in binding together the clay microstructures and silt particles into small microaggregates with 2- to 50-μm diameters and density greater than 2.0 Mg m^{-3} (Baldock, 2002). Many microaggregates contain pieces of fungal hyphae, bacteria, or bacterial colonies coated with EPSs and clay minerals (Oades and Waters, 1991). The polysaccharides are present throughout the matrix but concentrated in pores between clay microstructure.

Particulate organic matter (POM) is an important stabilizing agent at larger size scales: large microaggregates and small macroaggregates (Jastrow and Miller, 1998). Soil structure can be stabilized by POM through two mechanisms related to its physical properties and its susceptibility to biological decomposition (Baldock, 2002). The bridging can result from a combination of binding to aggregate surfaces, penetration through aggregates, and the formation of a network capable of holding groups of aggregates together. POM also enhances the stability of soil structure by providing a substrate for microorganisms to enhance the production of fungal hyphae and microbial metabolites such as polysaccharides. Mechanisms of stabilization of soil structure can operate over larger distances to bind microaggregates together to form macroaggregates (Figure 1.7). In view of the distances involved, the stabilization of macroaggregates is related to the presence of nonliving POM capable of spanning distances greater than 100 μm or the existence of a network of fungal hyphae and plant roots that physically enmeshes microaggregates.

The formation of aggregates alters the spatial arrangement of soil particles within soil aggregates, and the pore-size distribution even more (Theng and

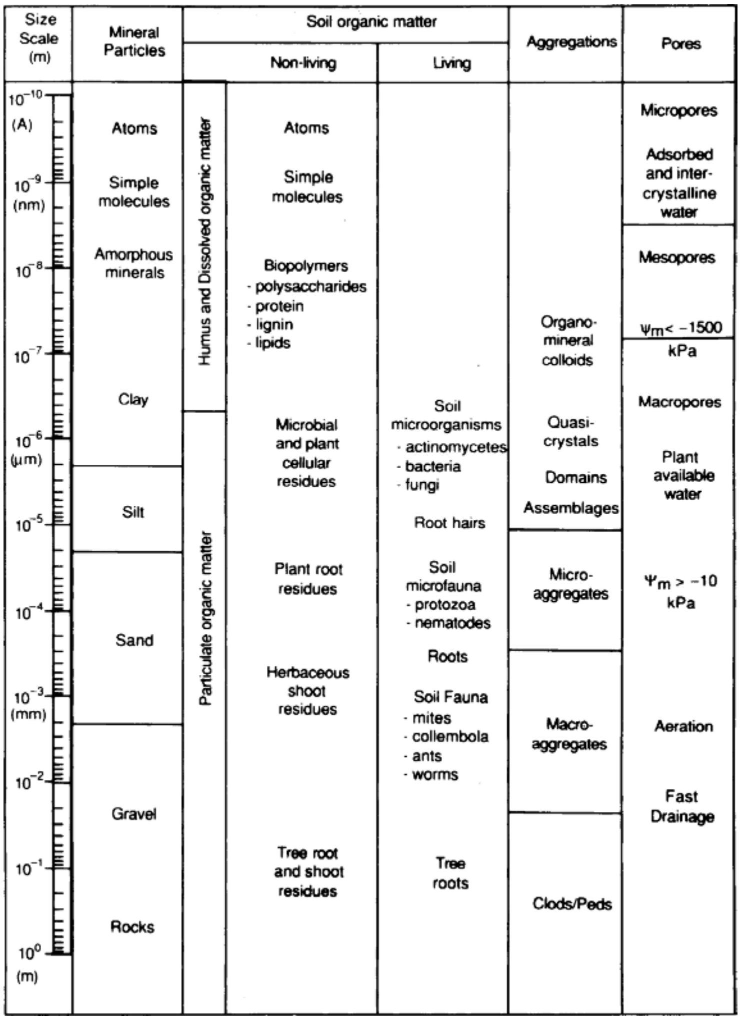


Figure 1.7. Size scales associated with soil mineral particles, organic components, pores, and aggregations of mineral and organic components. The definitions of pore size have used those developed by IUPAC (micropores, <2 nm; mesopores, 2 to 50 nm; and macropores, > 50 nm). Alternatively, the pore sizes corresponding to the lower ($\psi_m = -1500$ kPa) and upper ($\psi_m = -100$ kPa) limits of water availability to plants may be used to define the boundaries between the various classes of pore size. (From Baldock, 2002.)

Orchard, 1995). Such a modification of aggregate "architecture" results in a complex and discontinuous pattern in pore spaces of various sizes and shapes (Haider and Guggenberger, 2005) and would thus greatly influence the physical, chemical, and biological properties of soils. The dimension of pore sizes ranges from <2 nm (micropores) to 2 to 50 nm (mesopores) to >50 nm (macropores). The pore neck determines the accessibility by microbes. Microbial access to metals and metalloids adsorbed in small pores may be limited by steric factors and thus prevent microbial and biochemical transformations of these elements. Most recently, research findings show that organic substances such as tannate ligands induce the development of microporosity through structural perturbation of Al hydroxides (Yu et al., 2007). Furthermore, the kinetics of adsorption of metals such as Cd are greatly influenced by structural perturbation-induced microporosity development (Yu et al., 2006). Therefore, the impact of the formation of aggregates and porosity of various sizes and shapes through mineral–organic matter–microbe interaction on the transformation of metals and metalloids in soil environments should be an important and exciting area of research for years to come.

1.3. SOLUTION COMPLEXATION REACTIONS OF METALS

Complexation reactions in the soil solution affect metal transformation and transport in soils, especially the rhizosphere (Huang and Gobran, 2005). Metal complexation reactions with ligands in the soil solution play a significant role in controlling the chemical reactivity, bioavailability, and toxicity of metals in soil environments. The most important complexing functional groups of soil organic matter can be classified based on their affinity for hard, borderline, and soft metals (Buffle, 1988). For soft metals (e.g., Cd^{2+}, Pb^{2+}, Hg^{2+}), the order of donor atom affinity is $S > N > O$; the reverse order is true for hard cations (e.g., alkaline-earth metals Ca^{2+} and Mg^{2+}). Borderline metals, including most transition metals (e.g., Fe^{3+}, Cu^{2+}, Zn^{2+}, Mn^{2+}), have properties intermediate between hard and soft metals and thus demonstrate appreciable affinity for both hard and soft ligands. In general, the competitive reactions for a given ligand essentially involve hard and borderline metals for O sites, and borderline and soft metas for N and S sites, with competition between hard and soft metals being weak (Buffle, 1988; Senesi and Loffredo, 2005). The typical affinity sequence of soil organic matter for divalent metal ions (at pH 5) generally parallels the metal electronegativity values of Linus Pauling; however, the type, source, and concentration of soil organic matter, the amount of metal bound, and the method used to measure metal bonding and pH can affect metal binding affinity (Stevenson and Ardakani, 1972; Davies et al., 1969). Details of metal complexation reactions by humic substances are discussed by Senesi and Loffredo in Chapter 4.

Biomolecules are present in soils, especially in the rhizosphere, because of root exudates and microbial metabolites (Lynch, 1990a,b; Marschner, 1998). Furthermore, in view of the stability constants of these biomolecular ligands with metals (NIST, 2004), a substantial fraction of the soluble metal ions in soil solution may be complexed with a series of biomolecules commonly present in microbial metabolites and root exudates. The concentrations in the rhizosphere of such metals as Cu, Mn, Zn, and Co vary with the seasons and are related to the presence of complexing biomolecules (Nielson, 1976; Linehan et al., 1989). The pH of the rhizosphere soil is generally lower than that of the corresponding

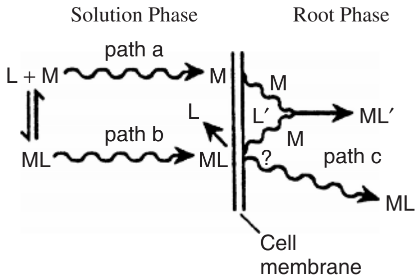


Figure 1.8. Conceptual model for potential uptake by plants of metal ions (M) complexed by organic ligands (L) (Laurie et al., 1991). (After McLaughlin et al., 1998.)

bulk soil. The cadmium availability index (CAI) values in the rhizosphere are higher, indicating that more Cd is complexed with biomolecules at the soil–root interface (Krishnamurti et al., 1996). The plant root and prolific microbial activity should result in increased amounts of biomolecules. A larger fraction of the metal contaminant will thus be in a complexed and usually soluble form in the soil–root interface than in the bulk soil.

Research on the metal speciation of the soil solution has been encouraged by the free metal ion hypothesis in environmental toxicology (Lund, 1990). This hypothesis states that the toxicity or bioavailability of a metal is related to the activity of the free aquo ion. This hypothesis is gaining popularity in studies of soil–plant relations (Parker et al., 1995). However, some evidence is now emerging that free metal ion hypothesis may not be valid in all situations (Tessier and Turner, 1995). Plant uptake of metals varies with the types of chelators present in solution at the same free metal activity. Furthermore, given the same chelate, total metal concentration in solution affects metal uptake by plants. Either kinetic limitations to dissociation of the complex or uptake of the intact complex could explain these observations (Laurie et al., 1991). The possible reactions of complexed metals at the soil–root interface and the potential uptake by plants of metal–organic complexes are depicted in Figure 1.8.

1.4. REDUCTION–OXIDATION REACTIONS OF METALS AND METALLOIDS

Changes in the oxidation state of trace metals can occur depending on the redox condition of the environment. Redox reactions are thus important in influencing the chemical speciation of a number of metals and metalloids, notably Hg, As, Se, Cr, Pu, Co, Pb, Ni, and Cu (Oscarson et al., 1981; Bartlett and James, 1993; Alloway, 1995; Myneni et al., 1997; Huang, 2000; James and Bartlett, 2000; Adriano, 2001; Sparks, 2003). Redox reactions also exert a great influence in the transformation and reactivity of Fe and Mn oxides in soils that have an enormous capacity to adsorb metals and metalloids (Huang and Germida, 2002). Furthermore, reduction of sulfate to sulfide in an anerobic environment also affects the transformation, solubility, and bioavailability of these pollutants through the formation of highly insoluble metal sulfides.

Masschelyn and Patrick (1994) have summarized the critical redox potentials for the transformation of some metal contaminants in soil environments. There has been little information on how changes in soil redox potential in the rhizosphere could affect the transformation of metal and metalloid contaminants. The generation of biomolecules through root exudation and microbial metabolism in the rhizosphere influences the redox potential. From a thermodynamic point of view, complexation of ligands with metals both on solid and solute phases has a dramatic effect on the redox potentials (Stumm and Morgan, 1996). For exemplification, Fe(II) and Fe(III) are used to illustrate the consequences of complexation on the redox potentials because (1) more data are available with this redox pair than with others, and (2) the transformations of Fe are especially important in the redox cycling of electrons in natural environments. The Fe(III)/Fe(II) redox couple can be adjusted with appropriate ligands to any redox potential within the entire range of the stability of water. As illustrated in Figure 1.9, the redox potential at pH 7, E^{o}_{H} (pH 7), decreases in the presence of most complexing ligands, especially chelates with oxygen donor atoms, such as citrate, EDTA, and salicylate, because these ligands form stronger complexes with Fe(III) than with Fe(II). Phenanthroline, which stabilizes Fe(II) more than Fe(III), is an exception. But Fe(II) complexes are usually stronger reductants than Fe^{2+}. The range of redox potentials for heme derivatives given on the right in Figure 1.9 illustrates the possibilities involved in bioinorganic systems. The principles exemplified here are applicable to other redox systems. Furthermore, when metals are complexed with ligands, the kinetics of their oxidation are substantially retarded. This complexation effect is clearly illustrated in the kinetics of Fe(II) oxidation as influenced by a series of organic ligands (Table 1.3). Therefore, the consequences of complexation on the redox potentials of soils and related environments and the impact on the transformations of metals and metalloids warrant in-depth research.

Although complexation with most complexing ligands, such as biomolecules in the rhizosphere, should decrease the redox potentials, the creation of an oxidized zone adjacent to the plant root in wetland soils has been identified as one process affecting the chemistry of Zn, Cu, and As in soils. In wetland soils, steep gradients in redox potentials develop around plant roots. This process is reflected in the precipitation of FeOOH (iron plaque) on the roots (Otte et al., 1989; Kirk and Bajita, 1995). Compared with the surrounding soil, these Fe-rich plaques on the roots of the saltmarsh plant *Aster tripolium* are enriched in Zn and Cu (Otte et al., 1989). Zinc also accumulates in the rhizosphere (*Oryza sativa* L.), which is the result of the formation of a zone of oxidation of Fe^{2+} to Fe^{3+} adjacent to the roots (Kirk and Bajita, 1995). Zinc concentration is higher in red roots (with iron plaque) than in white roots; a positive effect of the Fe concentration on the root surface, up to a certain level, on Zn uptake into the xylem fluid has been demonstrated (Otte et al., 1989). Above this level of Fe coating, Zn uptake by the plant is reduced, which is attributed to complete coating of the root surface by

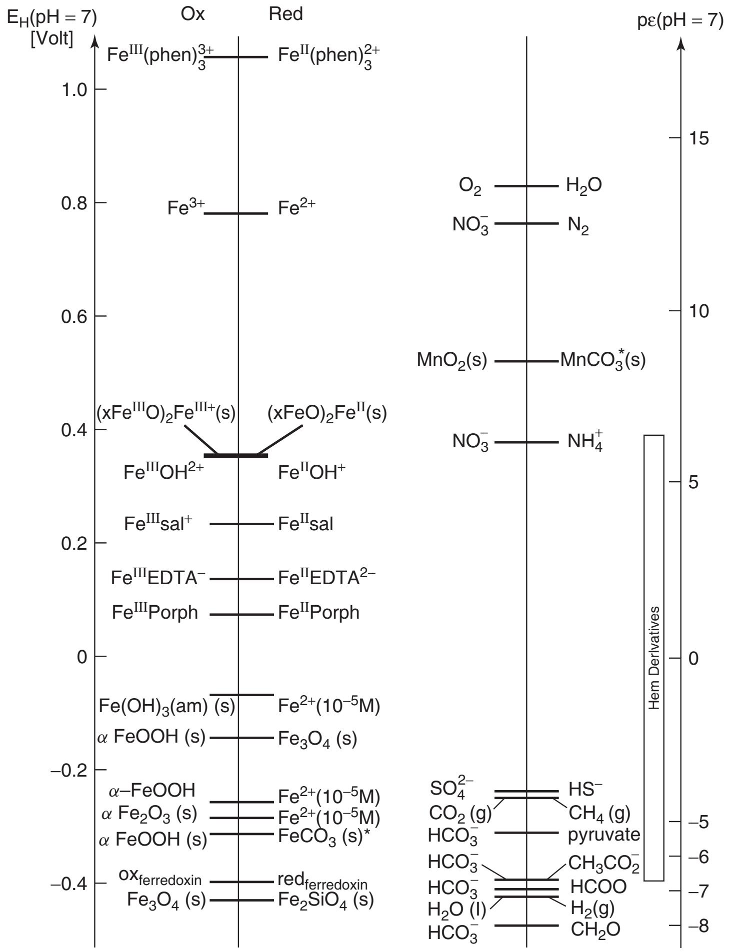


Figure 1.9. Representative Fe(II)/Fe(III) redox couples at pH 7 (phen, phenanthroline; sal, salicylate; porph, porphyrin; *, valid for $[HCO_3{}^-] = 10^{-3}$ mol L^{-1}). Complex formation with Fe(II) and Fe(III) both on solid and solute phases has a dramatic effect on the redox potentials; thus electron transfer by the Fe(II), Fe(III) system can occur at pH 7 over the entire range of the stability of water; E_H (−0.5 to 1.1 V). (= $Fe^{III}O)_2Fe^{III}$ refers to Fe^{3+} adsorbed inner spherically to a surface of a hydrous ferric oxide. The range of redox potentials for heme derivatives given on the right illustrates the possibilities involved in bioinorganic systems. (From Stumm and Morgan, 1996.)

FeOOH and blocking of absorption sites. In reduced conditions, As is mobilized as a result of reduction of Fe and Mn oxides and reduction of As(V) to As(III). However, in the rhizosphere in wetlands, As is immobilized due to oxidation of As and its adsorption onto FeOOH (Otte et al., 1991). Most of the As in the rhizosphere is probably retained on the root surface (Otte et al., 1991, 1995).

TABLE 1.3. Kinetics of Oxygenation of Fe(II)[a]

Ligand	Stability Constant (log K) of Fe–Ligand Complex[b] Fe(II)	Fe(III)	Rate Constant[c] ($\text{min}^{-1} \times 10^4$)
Oxalate	2.52	8.63	26.7 ± 1.2
Acetate	1.22	3.93	24.5 ± 1.1
Tartrate	4.85	9.00	8.6 ± 0.8
Citrate	3.86	10.69	7.6 ± 0.9

Source: Krishnamurti and Huang (1990).

[a] As 0.01 mol L^{-1} ferrous perchlorate in the absence and presence of organic complexing ligands.

[b] The log K values are for $\mu = 0.01$ and at 25°C.

[c] The rate constant was obtained at a ligand/Fe molar ratio of 0.1 at pH 6.00 and 23.5°C.

1.5. SORPTION–DESORPTION REACTIONS OF METALS AND METALLOIDS

Metals and metalloids undergo a series of reactions involving both the aqueous and solid phases, which vary in space and time. Sorption may be considered as a major process controlling the partitioning of metals and metalloids between the aqueous and solid phases in soils. It may represent the combined effects of ion exchange, nonspecific and specific adsorption, surface complexation, and (co)precipitation on the transfer of ions from the aqueous phase to the solid phase. Adsorption refers to ion exchange, nonspecific and specific adsorption, and surface complexation. When no molecular-scale data on which to base a decision as to mechanism are available, the prima facie loss of an adsorptive from aqueous solution to the solid phase can be termed sorption to avoid the implication that either adsorption or precipitation has taken place (Sposito, 2004). As a general rule, a surface precipitation mechanism is favored by high adsorptive concentrations and long reaction times in sorption processes. The reactions between adsorptive metal and metalloid ions and soil particles can be portrayed as a web of sorption processes mediated by two parameters, time scale and surface coverage (Charlet, 1994; Hayes and Katz, 1996; Sposito, 2004). Surface complexes (i.e., adsorption complexes) are the expected products of these reactions when time scales are sufficiently short and surface coverage is sufficiently low, *sufficiently* always being defined operationally in terms of conditions attendant to the sorption process (Figure 1.10). As time scales are lengthened and surface coverage increases, or as chemical conditions are altered (e.g., pH changes) for a fixed reaction time, adsorbate “islands” comprising a small number of adsorptive ions bound closely together will form. These reaction products are termed *multinuclear surface complexes* (Figure 1.10) by analogy with their counterpart in aqueous chemistry. They are more likely for adsorptive ions that readily form polymeric structures in aqueous solution. Multinuclear surface complexes may,

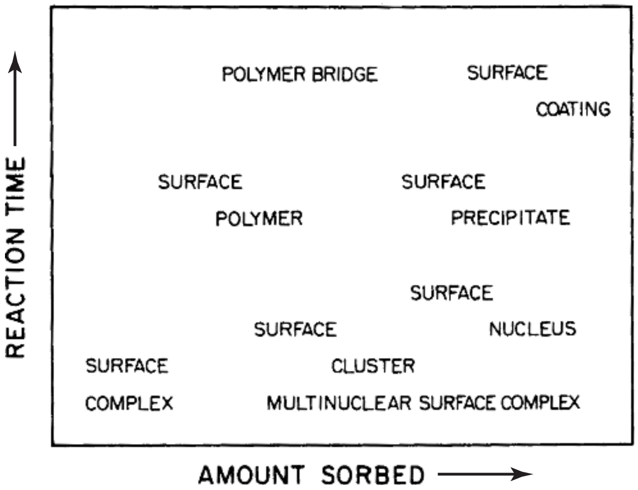


Figure 1.10. Regions of stability in a two-dimensional field defined by the quantity of sorbate and the sorption time, for the products of sorption reactions with natural particles. (From Schindler and Stumm, 1987.)

in turn, grow with time to become colloidal structures that are precursors of surface polymers, or if they are well organized on a three-dimensional lattice, of surface precipitates (Charlet, 1994).

Humic substances contain a large number of complexing sites per molecule, and thus behave as other natural "multiligand" complexing agents, such as metal oxides (Buffle, 1988). The principal molecular characteristics that govern the complexing ability of humic substances are polyfunctionality, polyelectrolyte character, hydrophobicity, and the capacity to form intermolecular associations and change molecular conformation. The major functional groups in humic substances that can bind metal ions are O-bearing groups, including carboxylic, phenolic, alcohoholic, and enolic hydroxyl groups as well as carbonyl functionalities of various types (Stevenson and Fitch, 1986; Senesi, 1992; Senesi and Loffredo, 2005). Amino groups and S- and P-bearing groups are also involved in metal binding. Two main types of complexes may be formed between metal ions and humic substances: (1) inner-sphere complexes, which result in the formation of bonds with some covalent character between the ligand atom(s) and the metal ion, both completely or partially dehydrated; and (2) outer-sphere complexes, which result in electrostatic attraction between the ligand(s) and the metal ion that remains completely hydrated. The electronic and steric environment of the ligand site, such as its chemical network, geometry, and conformation, and physical and chemical characteristics of the surrounding medium, including pH, ionic strength, and metal concentration, can exert a marked influence on the overall interaction process (Buffle, 1988). The binding of metal ions by humic substances is treated in detail by Senesi and Loffredo in Chapter 4.

The transformation of metals and metalloids is influenced significantly by adsorption–desorption reactions in soil environments. These reactions are affected by physicochemical and biological interfacial interactions, which should be especially important in the rhizosphere. Few studies have investigated the adsorption–desorption reactions as influenced by physicochemical and biological interfacial interactions. Microbial metabolites, decay products of biomass, and root exudates include a series of biomolecules which are capable of forming complexes with metal ions (Robert and Berthelin, 1986; Stevenson, 1994; Huang, 2004). There is increasing evidence showing that biomolecules may modify the transformation and dynamics of metals and metalloids (McLaughlin et al., 1998; Huang and Germida, 2002; Violante et al., Chapter 5, this volume). For example, the increase in Cd release in the presence of biomolecules is evidently due to the surface complexation of the particulate-bound Cd in soil with biomolecules, which is reflected in an increase in the release of Cd from soils with the increase in the stability constant of Cd–biomolecule complexes (Krishnamurti et al., 1997). Furthermore, the rate coefficients of the Cd release from the soils, calculated from the parabolic diffusion equation, are influenced substantially by the type of biomolecules (Table 1.4). The rate coefficients of Cd release within each ligand vary from soil to soil, which is attributable to the reactivity of the particulate-bound Cd of the soils toward biomolecules. The activity of Cd species in the soil solution of the soil–root interface governs the labile pool of soil Cd. The importance of the metal/organic complex–bound particulate Cd species in determining the bioavailability of soil Cd has been demonstrated by Krishnamurti et al. (1995a). The rate coefficients of Cd release from the soils by biomolecules (Table 1.4), which is a measure of the rate of the release of soil Cd to soil solution through complexation of soil Cd with biomolecules, follow the same sequence as that of Cd availability index (CAI) values of the soils (Krishnamurti et al., 1995b). Furthermore, the amounts of Cd released from the soils by renewal of biomolecules (Krishnamurti et al., 1997), which is an indication of the Cd sustaining power of the soils, follow the same order as the CAI values of the soils. More research should be conducted to understand the dynamics of adsorption–desorption of metals and metalloids under the influence of physicochemical and biological interactive processes.

TABLE 1.4. Overall Diffusion Coefficients of Cd Release from Soils by 10^{-2} mol L^{-1} Low-Molecular-Mass Organic Acids During a 0.25^{-} to 1-h Reaction Period

	Overall Diffusion Coefficient (μmol kg^{-1} h$^{-0.5}$)				
Soil Site	Acetic Acid	Citric Acid	Fumaric Acid	Oxalic Acid	Succinic Acid
Luseland	0.112 ± 0.010	0.200 ± 0.015	0.199 ± 0.012	0.079 ± 0.006	0.090 ± 0.005
Waitville	0.046 ± 0.004	0.049 ± 0.003	0.050 ± 0.005	0.036 ± 0.004	0.019 ± 0.003
Jedbergh	0.036 ± 0.005	0.196 ± 0.009	0.041 ± 0.003	0.026 ± 0.004	0.009 ± 0.003

Source: Krishnamurti et al. (1997).

1.6. PRECIPITATION–DISSOLUTION REACTIONS OF METALS AND METALLOIDS

Dissolution or precipitation reactions are generally slower than reactions among dissolved species, but it is quite difficult to generalize about rates of precipitation and dissolution (Stumm and Morgan, 1996). There is a lack of data concerning many geochemically important solid–solution reactions. Furthermore, there is not only a continuum between surface complexation (adsorption) and precipitation, but there is also obviously a continuum between heterogeneous nucleation and surface precipitation.

For many of the more abundant elements, such as Al, Fe, and Mn, precipitation of mineral forms is common and may greatly influence or even control their solubility. For most trace elements, direct precipitation from solution through homogeneous nucleation appears to be less likely than adsorption–desorption, by virtue of the low concentration of these metals and metalloids in soil solutions in well-aerated dryland soils. When soils become heavily polluted, metal solubility may reach a level to satisfy the solubility product to cause precipitation. Precipitation may also occur in the immediate vicinity of the phosphate fertilizer zone, where the concentration of heavy metals and metalloids present as impurities may be sufficiently high. Precipitation of trace metals as sulfides may have a significant role in metal transformation in reduced environments where the solution sulfide concentration is sufficiently high to satisfy the solubility product constants of metal sulfides (Robert and Berthelin, 1986).

In aerobic soils, although precipitation of trace metals through homogeneous nucleation is not likely, heterogeneous nucleation may play a significant role in metal transformation because of the presence of mineral, organic, and microbial surfaces that catalyze the nucleation set of crystallization (Huang and Germida, 2002). The energy barrier to nucleation is reduced or removed by surfaces. This is especially true in cases where there are crystallographic similarities between the surface and the precipitation phase. This catalytic process reduces the extent of supersaturation necessary for precipitation to occur. However, precipitation reactions are often slower than adsorption–desorption reactions in soil environments. Figure 1.11 illustrates the growth process from surface complex to surface nucleus to surface precipitate for Cr^{3+} sorbed by poorly crystalline goethite at pH 4 (Manceau et al., 1992).

Besides physicochemical reactions, metals have easy access to bacterial surfaces through diffusion. Metal sorption and precipitation on bacterial surfaces are interfacial effects. Surface metal concentrations frequently exceed the stoichiometry expected per reactive chemical sites within cell walls (Beveridge, 1989; McLean et al., 2002). The sorption of metals can be so great that precipitates can be formed, and distinct minerals are eventually formed through microbial biomineralization (i.e., the formation of minerals by microbes).

In the rhizosphere, activities of free metal ions may be decreased through uptake by plants and microbes. Metal contaminants are complexed substantially with biomolecules in the rhizosphere due to higher concentrations of complexing

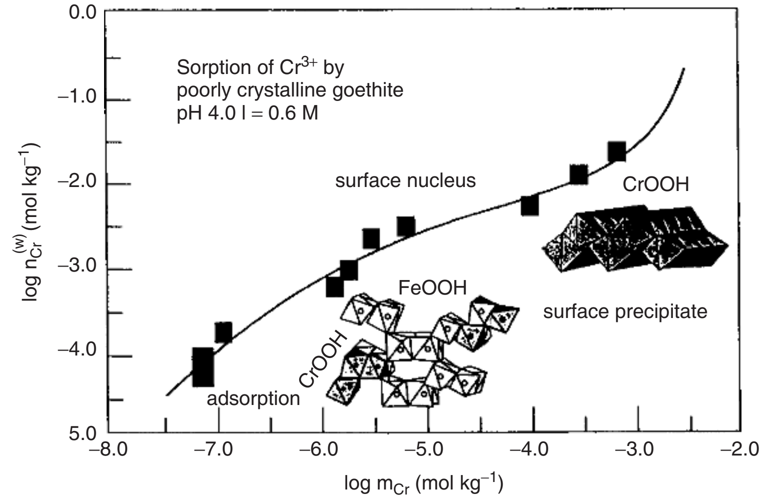


Figure 1.11. Sorption isotherm for Cr^{3+} reacted with poorly crystalline goethite (Cs = 10 kg m^{-3}), illustrating movement from lower left to upper right (Manceau et al., 1992) in the stability field of Figure 1.10 (Schindler and Stumm, 1987). (After Sposito, 2004.)

biomolecules than in bulk soils. Activities of free metal ions should thus be decreased further. Therefore, compared with bulk soils, the activities of free trace metal ions in the soil solution of the rhizosphere in aerobic dryland soils should be even less controlled by precipitation through homogeneous nucleation. In the rhizosphere, precipitation of metals through heterogeneous nucleation on microbial surfaces on the one hand and metal mobilization by biomolecules on the other hand, as a result of root exudation and intense microbial activity, warrants in-depth research for years to come.

1.7. MICROBE-MEDIATED METAL AND METALLOID RELEASE FROM SOIL PARTICLES

Soil biomass–organic matter is present as live plant (roots), animals (e.g., invertebrates), and microbial tissues. One kilogram of surface soil may contain as many as 10 billion bacteria, 2 billion actinomycetes, 120 million fungi, 25 million algae, and a faunal population in the millions (Table 1.5). Added to this biomass is the kilometer or so total length of roots from a single plant in the top meter of soils. Therefore, surface soils are teeming with dense and diverse populations of microorganisms and invertebrates. They play a myriad of important functions in the transformation of metals and metalloids in the environment (Gadd, 2001; Gadd et al., 2001; Glasauer et al., 2005; Gadd, Chapter 2, and Violante et al., Chapter 5, this volume).

TABLE 1.5. Vertical Distribution of Different Groups of Microorganisms in Soil ($\times 10^3$ g^{-1} Soil)

Depth (cm)	Aerobic Bacteria	Anaerobic Bacteria	Actinomycetes	Fungi	Algae
3–8	7800	1950	2080	119	25
20–25	1800	379	245	50	5
35–40	472	98	49	14	0.5
65–75	10	1	5	6	0.1
135–145	1	0.4	—	3	—

Source: Eijsackers (1994).

Chemical weathering of minerals as a part of the soil formation process can be enhanced by microbial activity by a factor as high as 10^6 (Kurek, 2002). Microorganisms can dissolve minerals by direct and indirect action under aerobic and anaerobic conditions (Ehrlich, 2002; Kurek, 2002). The modes of attack of minerals by microorganisms include (1) direct enzymatic oxidation or reduction of a reduced or oxidized mineral component; (2) indirect attack with a metabolically produced redox agent or inorganic and organic acids; (3) indirect attack by metabolically produced alkali, usually in the form of ammonia; (4) indirect attack by a metabolically produced ligand that forms a highly soluble product with a mineral component; and (5) indirect attack by a biopolymer. The mode of microbial attack of a mineral may involve a combination of these mechanisms. The microorganisms may be dispersed in soil solutions in some cases of attack; in others, they may grow in biofilms on the surface of susceptible minerals.

Oxidation of sulfur entities of metal sulfides to obtain energy is an example of direct dissolving action under aerobic conditions (Kurek, 2002). When oxidized metal compounds [e.g., Fe(III), Mn(IV), As(V)] act as electron acceptors, anaerobic respiration becomes an example of direct dissolving action under anaerobic conditions (Ahmann et al., 1994; Ehrlich, 2002). Volatilization of metals and metalloids or biomethylated metals and metalloid compounds from the soil into the atmosphere can be a mechanism of detoxification of toxic elements such as Hg, As, and Se for microorganisms (Gadd, 1993).

1.8. MICROBIAL SORPTION AND UPTAKE OF METALS AND METALLOIDS

All microorganisms contain biopolymers such as proteins, nucleic acids, and polysaccharides, which provide reactive sites for binding metal ions (Hughes and Poole, 1989). These binding sites include negatively charged groups such as carboxylate, thiolate, and phosphate, and groups such as amines, which coordinate to the metal center through lone pairs of electrons. Large concentrations of metals are frequently associated not only with living microbial biomass but also with dead cells (Berthelin et al., 1995), because microbial biopolymers have the ability to bind metals. Metals bind with various degrees of tenacity to the largely anionic outer surface layers of microbial cells. Metal binding by microbial cells alters cell wall composition and induces morphological, ultrastructural, and surface charge changes (Venkateswerlu et al., 1989; Collins and Stotzky, 1996). Bacterial cell walls and membranes may act as foci for the accumulation of metals in soils, since some metals are bound by cell walls and envelopes to a greater extent than by clay minerals such as kaolinite and smectite (Table 1.6).

Microorganisms have a range of metal transport systems, which are often highly specific for certain metals and capable of accumulating metals against large concentration gradients (Kurek, 2002). Certain microorganisms synthesize compounds that bind specific metals with high affinity (Lynch, 1990a,b). For example, some microorganisms make Fe-binding siderophores, which are biomolecules, usually a phenolate or hydroxamate ligand (Nielands, 1981). Some microorganisms produce biomolecules termed *metallothioneins* that are small cystine-rich proteins that strongly bind Cd, Cu, and Zn. Biomolecules of this type or related compounds are significant in influencing the transformation, transport, bioavailability, and toxicity of metals in soil environments, especially in the rhizosphere.

Bacteria and fungi have the ability to uptake and concentrate elements such as Ca, Fe, and K. For example, Weed et al. (1969) reported that fungi can adsorb K from solution and thus shift K equilibrium in suspensions of trioclahedral and dioclahedral micas and transfer them into vermiculites. Some microorganisms can promote the transformation of one mineral into another by a process termed *mineral diagenesis*, which can be an indirect effect of aerobic and anaerobic microbial metabolisms (Ehrlich, 2002; Kurek, 2002).

Most plants in natural habitats form associations with mycorrhizae. Arbuscular mycorrhizal fungi (AMF) are obligate symbionts, and infection of plant roots exerts a metabolic load on the host plant (Reid, 1990). During infection and

TABLE 1.6. Metals Bound by Native *Baccilus subtilis* Walls, *Escherichia coli* Envelopes, Kaolinite, and Smectite

	Amount of Metal Bound (μmol g^{-1}) (Oven-Dry Weight)[a]			
Metal	Walls	Envelopes	Kaolinite	Smectite
Ag	423 ± 15	176 ± 3	0.46 ± 0.02	43 ± 0.3
Cu	530 ± 13	172 ± 9	5 ± 0.03	197 ± 4
Ni	654 ± 25	190 ± 3	4 ± 0.2	173 ± 10
Cd	683 ± 19	221 ± 6	6 ± 0.2	1 ± 0.02
Pb	543 ± 11	254 ± 5	3 ± 0.2	118 ± 6
Zn	973 ± 13	529 ± 32	37 ± 1	65 ± 2
Cr	435 ± 37	102 ± 2	8 ± 0.5	39 ± 5

Source: Walker et al. (1989).

[a] The data represent the average of three to five determinations for each sample from duplicate experiments and the standard error.

colonization of host plant roots, mycorrhizal fungi produce mycelia inside root cortical cells. They may form storage structures termed *vesicles*, may also form structures called *arbuscules*, and serve as the site of ion exchange between the host plant and the mycorrhizal fungus. The fungi also form extracellular hyphae that penetrate out of the root and explore the soil in search of nutrients, including metals. Mycorrhizal infection thus expands the volume of soil that a root can penetrate. Therefore, plant uptake of metals and metalloids may be facilitated by mycorrhizae, since these elements are diffusion limited in soils. However, the effect of mycorrhizal infection on metal and metalloid uptake depends on the ability of the fungal symbiont to absorb metals and metalloids and to transfer them to the symbiotic roots through extensive vegetative mycelium. Mycorrhizal fungi release low-molecular-mass organic acids into soils to enhance the solubilization of particulate-bound metals and metalloids and thus might facilitate their uptake by plant roots. To date, there are considerable gaps in our knowledge of the mechanisms of the effect of fungi on the transformation and uptake of metals and metalloids.

1.9. BIOMINERALIZATION OF METALS AND METALLOIDS AND FINE-GRAINED MINERAL DEVELOPMENT

Microbial *biomineralization*, the formation of minerals by microorganisms, is another important activity of microorganisms (Beveridge, 1989). It involves metal and metalloid transformations and the development of fine-grained minerals of tremendous range and type (McLean et al., 2002). Most biominerals generated by microorganisms are nanoparticles (Banfield and Zhang, 2001). Research on biomineralization indicates that specific molecular interactions at inorganic–organic interfaces can result in the controlled nucleation and growth of inorganic crystals (Mann et al., 1993). A central tenet of biomineralization is that the nucleation, growth, morphology, and aggregation (assembly) of the inorganic crystals are regulated by organized assemblies of organic macromolecules, the *organic matrix*. Control over the crystallochemical properties of biominerals is achieved by specific processes involving molecular recognition at inorganic–organic interfaces. Electrostatic binding or association, geometric matching (epitaxis), and stereochemical correspondence are important in these recognitions. The subtle differences in the kinetics of these recognition processes on different crystal faces lead to specific changes in crystal morphology. Biomineralization should have global consequences in dynamics, transformation, toxicity, and the fate of metals and metalloids in the environment.

Geochemical modeling of metal speciation is only beginning to include bacteria as geochemically active surfaces. The physical and chemical characteristics of bacteria, such as their large surface area-to-volume ratio, serve to increase the metal-binding capacity of their charged surfaces, leading to precipitation and formation of mineral phases on their cell walls or surface biopolymers (McLean et al., 2002). The mechanisms by which bacteria initiate the formation of minerals in the bulk solution vary widely among species. There may be a combination of biochemical and surface-mediated reactions during the process. Bacteria surface layers may positively adsorb and indirectly serve as a nucleation template. Bacteria can also more directly initiate mineral precipitation by producing reactive compounds such as enzymes, siderophores, metallothioneins, which bind metals or catalyze their transformations. Furthermore, bacteria can instigate the spontaneous precipitation of metals by altering the chemistry of their microenvironments (Beveridge et al., 1997; Douglas and Beveridge, 1998).

Metal complexing ligands such as metallothioneins and siderophores serve to sequester metals from the environment for incorporation into cellular components (McLean et al., 2002). Reactive inorganic ligands such as sulfide and phosphate may also be produced as cellular metabolic by-products. Sulfide reacts with metals to form metal sulfides, a common reaction in anoxic environments with sulfate-reducing bacteria. Phosphate pumped out of cells can also react with metal ions to form cell-associated and extracellular precipitates. Another example of microbially mediated fine-grained mineral development is the formation of Mn oxides. Microbial oxidation of Mn(II) is a major process that can produce Mn oxide coatings on soil particles 10^5 times faster than can abiotic oxidation (Tebo et al., 1997). The microbially mediated formation of Mn oxide is illustrated in Figure 1.12. Manganese oxides are highly reactive minerals that help to restrict

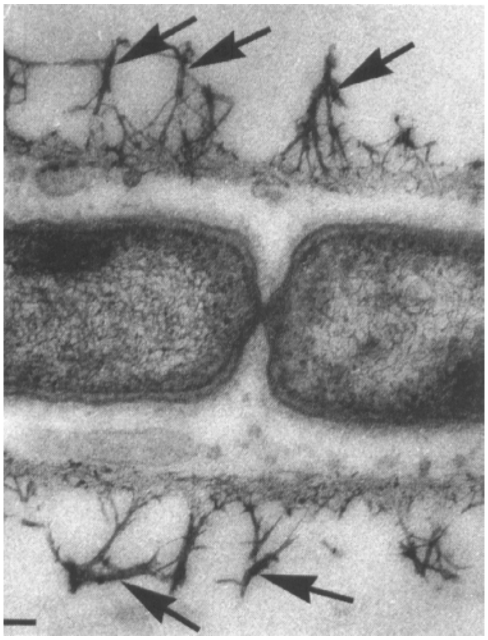


Figure 1.12. Thin section of *Leptothrix* sp., which is precipitating manganese oxide on its outermost structure, called a sheath. The arrows point to the manganese mineral phase, identified by EDS. Scale bar = 150 nm. (From McLean et al., 2002.)

the mobility of metals in soils and related environments through adsorption on their surfaces. Biogenic Mn oxides formed by *Leptothrix discophora* ss-1 have a significantly larger specific surface and higher Pb adsorption capacity than those of abiotically precipitated Mn oxides (Nelson et al., 1999). Bioformation of minerals should thus have a significant bearing on remediation of metal contamination of the environment.

1.10. IMPACTS ON THE TERRESTRIAL ECOSYSTEM

1.10.1. Global Ion Cycling

Transformations and transport of metals and metalloids are part of natural biogeochemical cycling. One of the characteristics of the cycle of metal and metalloid mobilization and deposition is that the form of the metal and metalloid is changed. This change of metal or metalloid speciation has a great effect on its fate and impact on ecosystem health (Benjamin and Honeyman, 1992; Hayes and Traina, 1998; Adriano, 2001). These trace elements are found in the environment in solid, solution, and gaseous phases, associated with thousands of different compounds. The critical processes controlling global metal and metalloid cycling are adsorption–desorption, precipitation–dissolution, complexation, oxidation–reduction, and volatilization (Benjamin and Honeyman, 1992; Hayes and Traina, 1998; Adriano, 2001; Kurek, 2002; McLean et al., 2002; Lollar, 2004). Transport in solution and aqueous suspensions is a major mechanism for metal and metalloid movement in the ecosystem. This transport process is influenced profoundly by adsorption–desorption on surfaces of minerals, organic matter, organomineral complexes and microbes; precipitation–dissolution, especially in reduced environments when sulfide concentration is sufficiently high; and a series of inorganic and organic complexation reactions in solution and particulate phases. Microorganisms can help dissolve, precipitate, complex, oxidize, or reduce metals and metalloids and can initiate the formation of fine-grained minerals, including nanoparticles.

Natural particles suspended in the air can be transported to regions far from their sources. This is important for transporting many metals and metalloids in the ecosystem. A few metals and metalloids, most notably Hg, As, and Se, can exist not only in the solid and liquid phases but also as gases in ambient environments. The loss of Hg from the aqueous phase can result from reduction of Hg^{2+} to Hg^0 and alkylation to form methyl- or dimethylmercury. Through microbial activity, the methylated forms can be converted to Hg^0, which is more volatile and less toxic. Microbial mediation can also transform several other trace elements (e.g., As, Se) to organometallic compounds (Gadd, 1993). These volatile organometallic compounds can dominate the transport of these trace elements in local environments. However, bacterial mediation of alkylation of metals such as Hg is influenced substantially by Hg speciation. Mineral colloids vary in their ability to affect the bioavailability and methylation of Hg(II) in aqueous systems

(Farrell et al., 1998). In particular, MnO_2 (birnessite) is a very effective scavenger of Hg(II) even in the presence of competing ligands and also an inhibitor of the methylation of Hg(II), due to its ability to bind Hg(II) tenaciously . Therefore, soil physicochemical–biological interfacial interactions play important roles in influencing the speciation and cycling of metals and metalloids in the environment. The role of microorganisms in influencing metal transformation and mobilization in the environment is addressed in detail by Gadd in Chapter 2.

1.10.2. Geomedical Problems

Geomedicine is the science dealing with the environmental factors that influence the geographical distribution of pathological and nutritional problems relating to human and animal health (Låg, 1980). Hunger and malnutrition are of concern for large groups of populations, especially in developing countries. In addition to prevention of starvation, promotion of better nourishment and better quality of food and feed is essential. Pollution of the environment and related health problems have increased rapidly with industrialization. Knowledge of soil science is indispensable for solutions to many geomedical problems (Låg, 1994). The effect of soil physical, chemical, and biological reactions and processes on the quality of vegetation and the food and feed produced and related geomedical problems should be investigated in depth.

The transformation and bioavailability of trace elements are profoundly influenced by soil physical, chemical, and biological interactions (Huang and Gobran, 2005). Many trace elements are of concern to animal nutrition and human health (National Academy of Sciences, 1974, 1977; Adriano, 2001). These include Se, Fe, I, Zn, Cu, Mn, Mo, Cr, F, Co, Si, V, Ni, As, and Mg. One trace element may serve in one, several, or dozens of different metalloenzymes or tissue constituents.

To facilitate fundamental understanding of the linkage of trace elements in soils with plant–animal–human–environment systems and related geomedical problems and to provide practical solutions to their deficiency and toxicity problems, it is essential to promote research on the relationship between soil physicochemical–biological interactions and the impacts on the transformation, transport, bioavailability, toxicity, and fate of trace elements in the terrestrial environment.

1.10.3. Ecotoxicological Problems

Ecotoxicology is a fairly new field of science developed from the traditional field of toxicology and environmental chemistry that gave rise to environmental toxicology. When applied to the ecosystem setting, environmental toxicology virtually becomes ecotoxicology. *Ecotoxicology* is defined as "the study of fate and effect of toxic agents in ecosystems" (Cairns and Mount, 1990). Ecotoxicology integrates several disciplines, including environmental biogeochemistry, toxicology, and ecology, dealing with mechanisms, processes, and responses. Therefore, ecotoxicological research deals with the interactions among organisms, the toxic agents (in this case metals and metalloids), and the environment.

There are several levels of biological organization in ecotoxicology research (Eijsackers, 1994; Newman, 1995): molecular level (e.g., RNA/DNA), cellular level (e.g., enzymes, hormones, ATP content, phytochelatins, metallothioneins), individual level (e.g., growth rates, organ functioning, behavioral responses), population level (e.g., lethality, reproduction, genetic drift), community level (e.g., species diversity, community structure), and ecosystem level (e.g., nutrient cycling, energy fluxes). Our present understanding of effects along the ecological spectrum of organization is depicted in Figure 1.13, which becomes poorer as the level of organization increases. The lower level of ecological organization is generally more sensitive and responds more rapidly to toxicant effects than are higher levels of organization.

Soil plays the central role as organizer of the terrestrial ecosystem (Coleman et al., 1998). It may be perceived as the center of the ecosystem, which evolves because of interactions of the lithosphere, hydrosphere, atmosphere, and biosphere. A factor of central importance of soil to ecological studies is that soils on a global scale have a range of characteristics, which enable an enormous array of microorganisms, plants, animals, and humans to coexist and thrive. Among the environmental compartments, about 90% of environmental pollutants are bound with soil particles and 9% of the pollutants are bound with aquatic sediments (Table 1.7). These soil- and sediment-bound pollutants are in dynamic equilibrium with the hydrosphere, atmosphere, and biosphere. Soil physicochemical and

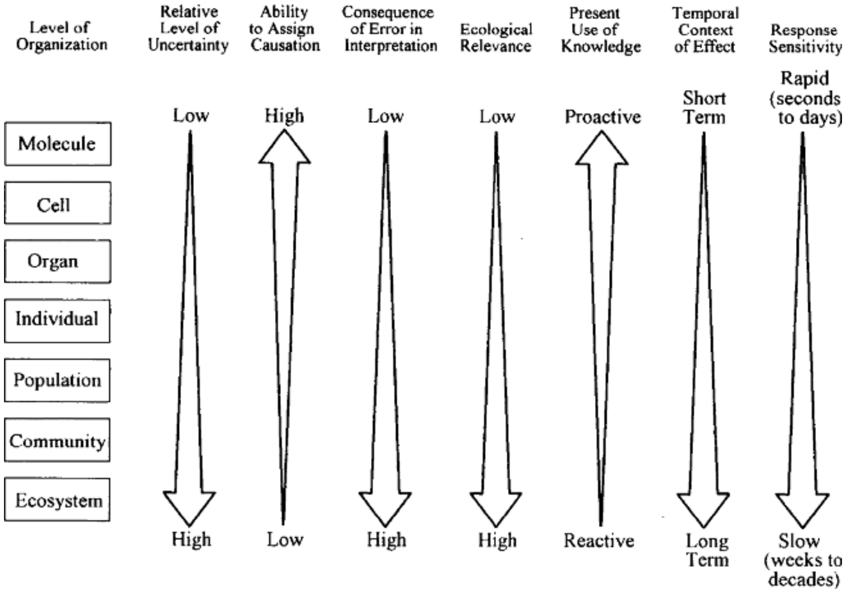


Figure 1.13. Features of ecotoxicological effects based on the level of ecological organization. (From Newman, 1995.)

TABLE 1.7. Theoretical Pollutant Distribution in the Environment at Equilibium

Compartment	Distribution in Compartment[a] (%)
Air	0.35
Water	0.01
Sediment	9.10
Soil	90.50
Aquatic biota	0.01

Source: Crosby (1982).

[a] Assumes approximately 100 kg of pollutant (MW 100) introduced into 10 km^3 of the environment.

biological interfacial interactions have vital roles in governing the transformation, speciation, transport, bioavailability, and toxicity of metals and metalloids of ecological concerns. These interactions may enhance the release of metals and metalloids from soils and sediments and thus pose a threat to ecosystem integrity, including human health.

The long-term ecological effects of metals and metalloids introduced to soils are very difficult to assess, as only a few such experiments exist. Even less is known about the adverse long-term effects of metals and metalloids on soil microorganisms than on crop growth and metal uptake. McGrath et al. (1995) summarized the evidence for the impact of metals on the growth of selected plants and on the effects of metals on soil microbial activity and soil fertility in the long term. They integrated the information from long-term controlled field experiments in the United States, the United Kingdom, Sweden, and Germany. Adverse effects of metals on soil microbial parameters may indeed be not only additive (McGrath et al., 1995) but also interactive. Furthermore, the influence of soil type, organic matter, mineral colloids, microorganisms, pH, and other relevant soil properties on the lowest observed adverse effect concentrations (LOAECs) of a metal for each parameter may be interactive. For instance, heavier soils (i.e., more clayed), near-neutral soils (i.e., higher pH), or soils having a high content of organic matter and short-range-ordered mineral colloids may be expected to reduce the detrimental effects of metals to soil microorganisms by binding the contaminants and rendering them less bioavailable, thus giving high LOAECs.

1.10.4. Biodiversity

The functioning and stability of the terrestrial ecosystem are determined by plant biodiversity and species composition (Schulze and Mooney, 1993; Tilman et al., 1996; Hooper and Vitousek, 1997). However, the ecological mechanisms by which they are regulated and maintained are not well understood. It is essential to identify these mechanisms to ensure successful management for conservation and restoration of diverse natural ecosystems.

All terrestrial ecosystems consist of above- and belowground components that interact to influence community- and ecosystem-level processes and properties (Wardle, 2002; Wardle et al., 2004). These components are closely interlinked at the community level, reinforced by a greater degree of specificity between plants and soil organisms than had previously been supposed. As such, above- and belowground communities can be powerful mutual drivers, with both positive and negative feedback.

Soil is a focal point of the terrestrial ecosystem (Odum, 1989; Coleman et al., 1998). It is the most complicated biomaterial on the planet. As with any material, physical habitat is of prime importance in determining and regulating biological activity (Young and Crawford, 2004). Therefore, soil is Earth's most important resource in sustaining biological activity in both above- and belowground ecosystems. Belowground biodiversity is a major factor contributing to the maintenance of plant biodiversity and to ecosystem functioning and stability. Floristically rich systems may display greater stability under stress (Tilman and Downing, 1994), are more likely to mitigate global problems posed by atmospheric CO_2 enrichment (Naeem et al., 1994), and are more productive (Tilman et al., 1996). However, the diversity of terrestrial vegetation systems is under stress everywhere. The present reduction in biodiversity on Earth and its potential threat to ecosystem stability and productivity are of concern (Tilman et al., 1996; van der Heijden et al., 1998). There is a need to determine how biotic relationships interact with abiotic agents to drive community and ecosystem properties and processes.

Enzymatic activity in soil has been regarded as an indication of soil microbial activity. Certain enzymatic activity (e.g., dehydrogenase enzyme) has decreased on several occasions in direct relationship with soil metal concentration (Reddy et al., 1987; Adriano, 2001). Reduced populations of actinomycetes, bacteria, and fungi in ridgetop soils contaminated with Zn, Cd, and Pb from zinc smelters in Pennsylvania were observed (Jordan and Lechevalier, 1975). Studies of litter–soil fauna indicate marked differences in the taxa of invertebrates at the contaminated sites (Table 1.8). In particular, millipedes (Diplopoda), earthworms (Annelida), and woodlice (Isopoda) were greatly decreased in population at the contaminated site. However, the influence of the speciation of metals and metalloids, which should be governed by soil physicochemical and biological interfacial interactions, on soil microbial and enzymatic activity and the taxa and activity of soil fauna remain obscure. Furthermore, subsequent impact of the reduction of belowground biodiversity on aboveground biodiversity remains to be uncovered.

1.10.5. Risk Assessment, Management, and Restoration of Soil Environments

Metal contamination of soils from anthropogenic chemicals and their transformations has become a major concern because of the critical role of soil resources in sustaining ecosystem integrity and human health and prosperity. Metal contaminants in soils may not only affect their production potential and biodiversity

TABLE 1.8. Number of Invertebrates in Litter Collected from Hallen Wood, Avonmouth, England Compared with a Relatively Uncontaminated Woodland (Wetmoor Wood) (no. kg^{-1})

	Hallen Wood (Contaminated)	Wetmoor Wood (Control)
Isopoda		
Oniscus asellus	3.9	14.8
Trichoniscus pusillus	0	112
Diplopoda		
Polydesmidae	0.6	58.5
Julidae	0	8
Glomeridae	0	15.6
Chilopoda		
Lithobiidae	7.8	86
Geophilomorpha	23	195
Arachnida		
Acari	9,034	14,370
Aranae	17.4	60
Pseudoscorpionidae	14	50
Insecta		
Collembola	1,457	6,436
Coleoptera	63	36
Coleoptera (larvae)	8.4	3
Diptera (larvae)	321.4	215.6
Annelida		
Lumbricus rubellus	2	2.2
L. terrestris	0	21.5
Aporrectodea longa	0	3
A. caliginosa	0	22
Octoclasium cyaneum	0	6.7

Source: Martin and Bullock (1994).

adversely but also compromise the quality of the food chain and the underlying groundwater. Therefore, regulatory-driven risk assessment and management are essential in restoration of soil environments.

Soil quality may be defined in relation to the functions that soils perform in ecosystems (Table 1.9). *Soil quality*, which is used interchangeably with *soil health*, can be deduced or estimated by measuring key indicators, including physical, chemical, and biological properties. Therefore, soil quality reflects the composite picture of soil physical, chemical, and biological properties and processes that interact with each other to determine its conditions. The chemical speciation, concentration, and bioavailability of metals and metalloids are important indicators for soil quality, which, in turn, is related to soil functions. Assessing exposure to metals and metalloids in soil environments includes determination of the pathways to exposure (inhalation, drinking water, food, or

TABLE 1.9. Indices for Soil Quality and Their Relationship to Soil Functions

	Soil Function			
Indicator	Promote Plant Growth	Regulate Water Flow	Buffer Environmental Changes	Promote Biodiversity
Nutrient availability	Direct	Indirect	Direct	Direct
Organic matter	Indirect	Direct	Direct	Direct
Infiltration	Direct	Direct	Indirect	Indirect
Aggregation	Direct	Direct	Indirect	Direct
pH	Direct	Direct	Indirect	Direct
Soil fauna	Indirect	Indirect	Indirect	Direct
Bulk density	Direct	Direct	Indirect	Indirect
Topsoil depth	Direct	Indirect	Indirect	Direct
Salinity	Direct	Direct	Indirect	Direct
Cation exchange capacity	Indirect	Indirect	Indirect	Indirect
Water-holding capacity	Direct	Direct	Indirect	Direct
Soil enzymes	Indirect	Indirect	Indirect	Indirect
Soil flora	Indirect	Indirect	Indirect	Direct
Heavy metal bioavailability	Direct	Indirect	Direct	Direct

Source: National Research Council (1993).

TABLE 1.10. Pathways for Human Exposure to Soilborne Contaminants[a]

Pathway	MEI
Soil → plant → human	Human lifetime plant ingestion; general population Human lifetime plant ingestion; home gardener
Soil → human	Child
Soil → plant → animal →human	Human lifetime ingestion of animals products; animals raised on forage
Soil → animals → human	Human lifetime ingestion of animals products; animals ingest soil
Soil → dust → human	Human lifetime dust inhalation
Soil → surface water → human	Human lifetime ingestion of surface water and fish
Soil → groundwater → human	Human lifetime ingestion of groundwater
Soil → air → human	Human lifetime inhalation of volatilized contaminants

Source: Logan (1998).

[a] The most exposed individual (MEI) of the population is also identified. Based on U.S. Environmental Protection Agency exposure assessment for land-applied contaminants in sewage sludge.

direct soil ingestion) (Table 1.10) and the extent of contaminant transfer from soil to the various pathway components (Logan, 1998). In environmental exposure assessment, a *transfer coefficient* must be determined for each component of the pathway: namely, the fraction of the component that is transferred from one component to another (e.g., from soil to plant, soil to air, soil to surface water, soil to groundwater). The transfer coefficient can be viewed as an *availability index*, although other terms (*extractability, solubility, accessibility, volatility*) have also been used. This will depend on the mechanisms of transfer, which should be governed by physicochemical and biological interfacial interactions in soil environments.

The cleanup of soils polluted by hazardous metal and metalloid contaminants has become a matter of urgent public concern. Nature has evolved ways of remediating problems of many contaminants without human intervention. Over a very long period of time, natural degradation might remove many of the organic contaminants in soil, but may result in an accumulation of metals and metalloids. Affordable novel technologies are needed to enhance natural remediation processes and restore healthy ecosystems. Natural remediation usually influences the extent of mobility and bioavailability of contaminants in the soil complex (Adriano et al., 2004; Bollag et al., 2005). The various natural remediation–bioavailability processes, which influence contaminant dynamics, are depicted in Figure 1.14. In the initial phase (A), the dynamics of contaminants between the aqueous and solid phases are governed by various biogeochemical processes (e.g., adsorption–desorption, precipitation–dissolution, redox reactions, and complexation). The nature of these processes determines the kinetics of natural remediation that can be parameterized by bioavailability. The role of the rhizosphere in contaminant transformation and mobility can be very important. The next phase (B, B′) involves the transport of contaminants to organisms. The contaminant can be transported in soluble, colloidal, and/or particulate form. The particulate form can play a significant role in humans and animals. For

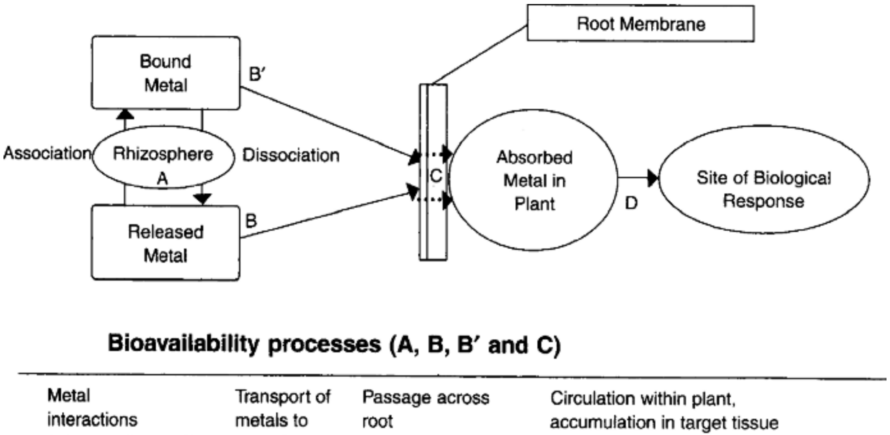


Figure 1.14. Bioavailability processes in soils. Note the delineation of the entire scheme into “natural remediation” (left) and “bioavailability” (right). (Modified from the National Research Council, 2003; Adriano et al., 2004.)

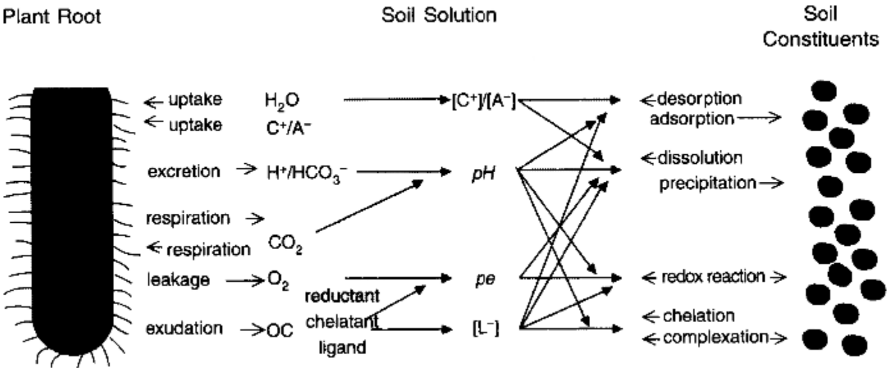


Figure 1.15. Schematic rhizosphere, showing the various exudates and how they can influence abiotic factors and mechanisms at the soil–solution interface (OC, organic carbon; C^+, cation; A^-, anion; L^-, ligand; re, redox potential.) (Modified from Hinsinger, 2001; Adriano et al., 2004.)

example, ingestion of soil particles by children is an important exposure pathway for lead; ingestion of soil particles by grazing livestock is an important exposure pathway for animals feeding on contaminated pastures. From the aqueous phase, metals and metalloids can be mobilized in either soluble or colloidal form, the latter being viewed as facilitated transport. The next phase (C) involves passing through a biological membrane, which in many instances can serve as a biofilter for contaminants. The last phase (D) involves circulation and assimilation in the metabolic machinery of the organisms, culminating in some form of biological response which refers to the endpoint of interest.

The rhizosphere, which is characterized by distinct physical, chemical, and biological conditions (Figures 1.14 and 1.15), is the focal point of the potential role of higher plants in accelerating natural remediation in contaminated soils. Rhizosphere conditions are created by the plant roots and their microbial associations. Rhizospheric biogeochemical processes are influenced substantially by soil physical, mineralogical, chemical, and biological features and also by edaphic and climatic conditions. Special tools and techniques are required to study the characteristics and processes of the rhizosphere because of its limited areal extension (Wenzel et al., 2001).

The physicochemical and biological reactions occurring in the rhizosphere play a significant role in the natural remediation and subsequent bioavailability of metals and metalloids to plants. Plant roots may change the physical, chemical, and biological conditions of the soil in the rhizosphere, which compared to bulk soil is enriched with biomolecules of plant and microbial origin, including low-molecular-mass organic acids (LMMOAs), sugars, amino acids, lipids, coumarins, flavonoids, proteins, enzymes, other aliphatics, aromatics, and carbohydrates, among others (Pomilio et al., 2000). Among these biomolecules, the LMMOAs are the most abundant and chemically very reactive with soil particles. The commonly found LMMOAs are acetic, butyric, citric, fumaric, lactic, malic, malonic, oxalic, propionic, tartaric, and succinic acids (Szmigielska et al., 1996; Koo, 2001). These LMMOAs in the rhizosphere affect the dynamics and mechanisms of the transformation of metals and metalloids in soils by their effects on acidification, complexation, precipitation–dissolution, redox reactions, microbial activity, rhizosphere physical properties, and root morphology (Huang and Germida, 2002).

The use of bioremediation technology for metals and metalloids is just becoming recognized as an efficient and effective strategy. Cadmium, lead, zinc, nickel, cobalt, and other base metals generally exist as cations in the aqueous phase, and adsorption to negatively charged sites of the surface layers of bacteria can remove those metals very effectively (Mullen et al., 1989; Volesky, 1990). Highly toxic and mobile oxyanions of uranium, chromium, arsenic, and selenium are of particular concern in many soils and groundwaters throughout the world. Their speciation in the environment and hence their reactivity, mobility, bioavailability, and toxicity are influenced significantly by microbially mediated reactions. Oxyanions such as arsenates, selenates, and chromates do not bind to the bacterial surface to any significant extent. Bioremediation of these oxyanions is based predominantly on microbially catalyzed redox conversions to insoluble forms (McLean et al., 2002). Application of bioremediation technology to decontaminate polluted sites is still a developing science. The mechanisms driving microbial activity and degradation pathways of specific pollutants should be further elucidated before successful and better controlled site-specific treatments can be applied (Bollag et al., 2005). It is of great importance to consider the fact that the growth, metabolism, and activity of soil microorganisms is strongly influenced by their interactions with mineral and organic colloids that bind organic chemicals, inorganic ions, and water films to their surfaces (Stotzky, 1986; Theng and Orchard, 1995; Huang, 2004). Recent advances in biotechnology have enabled modification of organisms at the molecular level for improved degradative performance (Bollag et al., 2005).

Besides biotic processes, abiotic processes play a very important role in remediation of metal- and metalloid-contaminated sites. Many soil ameliorants have been used to remediate contaminated soils (Table 1.11). These soil ameliorants are rather inexpensive and readily available on a global scale. Application of limestone to elevate soil pH to about 6.5 is recommended when agricultural soils are amended with sewage sludge high in metals, especially cadmium (Page et al., 1983; Pierzynski et al., 2000). The addition of certain clay minerals, such as vermiculite, to contaminated soils may be effective in immobilizing metals and radionuclides such as ^{137}Cs and ^{90}Sr (Adriano et al., 1997; Mench et al., 1997). Zeolites, which serve as molecular sieves, have been used as soil ameliorants (Gworek, 1992a,b). Application of phosphate and potash fertilizers may have some beneficial effects on certain contaminants. When mixed with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, lead of soil particles will dissolve and precipitate as hydroxypyromorphite, $Pb_{10}(PO_4)_6(OH)_2$ (Ma et al., 1993; Melamed and Ma, Chapter 15, this volume). Use of potash fertilizer is based on the similar physiological behavior of K toward Cs. As such, they compete for the same sites

TABLE 1.11. Selected Ameliorants Adapted to Metal-Contaminated Soils

Technique	Target Contaminants	Soil Processes Involved	Constraints
Limestone	Metals, radionuclides	Precipitation, sorption	Ineffective for oxyanions; certain crops (lettuce, spinach, tuber, and others); short term
Zeolite	Metals, radionuclides	Ion exchange, sorption, fixation	Insufficient data; short term
Apatite	Metals	Sorption, precipitation, complexation	Selective, insufficient data
Clay mineral	Metals, radionuclides	Ion exchange, sorption, fixation	Type of clay; short term

Source: Adriano et al. (1998).

on plant roots, causing antagonistic effects. The ameliorants listed in Table 1.11 have been applied in agricultural soils but may provide only an interim solution in stabilizing contaminants. Their efficacy over the long term remains to be studied.

Furthermore, abiotic and biotic reactions are not independent but rather, interactive processes in soil environments. Interactions of abiotic and biotic processes are thus very important in governing the dynamics and fate of metals and metalloids in soils, especially at the soil–root interface. Abiotic and biotic interactions in the rhizosphere in influencing the stabilization of contaminants and the efficacy of ameliorants need to be investigated. The impact of physical, chemical, and biological interfacial interactions on risk assessment and management of metal and metalloid contamination and restoration of ecosystem health merits close attention.

1.11. CONCLUSIONS AND FUTURE DIRECTIONS

Soil is the most diverse ecosystem and Earth's most important resource in sustaining all life in the terrestrial environment. Physical, chemical, and biological processes are not independent but rather, interactive with each other. The interactions at physical–chemical–biological interfaces govern the mechanisms of transformations, speciation, dynamics, bioavailability, toxicity, and fate of metals and metalloids in soil and related environments.

Soil particles, be they minerals, organic matter, microorganisms, protozoans, or nematodes, are constantly in close association and interaction. They play key roles in affecting physical, chemical, and biological processes in soil environments. The interactions of these soil components, mediated by soil solution and atmosphere, govern mineral weathering transformations; formation of short-range-ordered mineral colloids, humic substances, and organomineral complexes; microbial and enzymatic activity; formation and stability of soil structure and porosity of various sizes and shapes; dynamics of aggregate turnover; and subsequent impact on the biogeochemical cycling of metals and metalloids and related geomedical, ecotoxicological, and biodiversity problems.

Fundamental understanding of soil physical, chemical, and biological interfacial interactions at the molecular level is essential to understanding the behavior of metals and metalloids in the pedosphere and to restoring terrestrial ecosystem health on the global scale. Future research on this extremely important and exciting area of science should be stimulated to sustain and enhance ecosystem productivity, services, and integrity and the impact on human health and prosperity.

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