Soil mineral–organic matter–microbe interactions: Impacts on biogeochemical processes and biodiversity in soils

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Summary

Soils are the central organizer of the terrestrial ecosystem. Their colloidal and particulate constituents, be they minerals, organic matter, and microorganisms, are not separate entities; rather, they are constantly interacting with each other. Interactions of these components control biogeochemical reactions, namely, the formation of short-range-ordered metal oxides, catalysis of humic substance formation, enzymatic stability and activity, mineral transformation, aggregate turnover, biogeochemical cycling of C, N, P, and S, and the fate and transformation of organic and inorganic pollutants. Furthermore, the impacts of mineral–organic matter–microorganism interactions and associated biogeochemical reactions and processes on biodiversity, species composition, and sustainability of the terrestrial ecosystem deserve close attention for years to come. This paper integrates the frontiers of knowledge on this subject matter, which is essential to uncovering the dynamics and mechanisms of terrestrial ecosystem processes and to developing innovative management strategies to sustain ecosystem health on the global scale.

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Introduction

Soil is a life-sustaining material, which is a structurally porous and biologically active medium that has evolved over time on the continental land surfaces on our planet Earth (Fig. 1). This material is formed and continues to develop through weathering processes driven by biogeochemical, climatic, geological, topological, and chronological influences. Soil is geoderma, namely, the skin of the planet Earth. It is the pedosphere, which overlaps
with the lithosphere, hydrosphere, atmosphere, and biosphere and is, thus, an integral part of the ecosystem. Therefore, soil physical, chemical and biological process should have a profound impact on ecosystem sustainability.

Soil is the central organizer of the terrestrial ecosystem (Odum, 1989; Coleman et al., 1998). Minerals, organic components and microorganisms are among major solid components of soils. These components are not separate entities but rather a unified system constantly in association with each other in the environment (Huang et al., 1995). The association of microorganisms with soil mineral and organic colloids is depicted in Fig. 2. Interactions among these components have enormous impacts on physics, chemistry, and biology of soil and surrounding ecosystems (Huang and Schnitzer, 1986; Huang et al., 1995). Fundamental understanding of mineral–organic matter–microorganism interactions is essential for understanding, restoring, enhancing, and sustaining ecosystem integrity on a global scale. The study of the interactions of these soil components has to be considered from the molecular level to field/landscape systems and is essential to stimulate further research to uncover the dynamics and mechanisms of soil processes and the impacts on biogeochemistry and biodiversity in the terrestrial ecosystem. In view of the continual mineral–organic component–microorganism interactions and interactive physical, chemical, and biological processes in the terrestrial ecosystem, a new Commission “Soil Physical/Chemical/Biological Interfacial Interactions” was created within the structure of the International Union of Soil Sciences in 2004.

This paper integrates the existing knowledge, especially the latest advances on the fundamentals of soil mineral–organic matter–microorganism interactions, and addresses a variety of their potential impacts on biogeochemical processes and biodiversity. It begins with the topics on the formation of short-range-ordered (SRO) metal oxides, mineral catalysis of humic substance formation, effects of soil colloids on enzymatic stability and activity, and microbial mediation of mineral transformation, because mineral and organic colloids, enzymes, and microbes exert great
control over soil physical, chemical, and biological processes. We then address the topics on dynamics of aggregate turnover, biogeochemical cycling of C, N, P, and S, the fate and transformation of organic contaminants and metals, and potential impact on biodiversity in terrestrial ecosystems. Furthermore, future prospects of major research thrusts on the subject matter are also discussed to promote research and education in this important and exciting area of science.

Formation of short-range-ordered metal oxides

Metal oxides are ubiquitous in soils and play a significant role in influencing soil behavior, and, thus, have great impacts on the ecosystem. SRO Al and Fe oxides, especially their nanoparticles are undoubtedly among the most reactive components of acidic and neutral soils (Bigham et al., 2002; Huang et al., 2002). Biomolecules exert a very significant influence on the formation and transformation of metal oxides and the resultant alteration of their surface properties pertaining to the speciation, fate and bioavailability of nutrients, toxic inorganic and organic substances, and the microbial events (Huang and Violante, 1986; Schwertmann et al., 1986; Sposito, 1996; Huang and Wang, 1997; Huang et al., 2002).

As the third most abundant element on the Earth’s surface (after O and Si), Al is a major element in all-mineral soils. There are only a few crystalline Al oxide, hydroxide, or oxyhydroxide minerals, and only one, i.e., gibbsite occurs to any great extent in soils. Aluminum, however, also forms a series of highly reactive soluble species and poorly crystalline to noncrystalline minerals and colloids (Fig. 3).

The model depicted in Fig. 3 incorporates multiple reaction paths. Reaction path I is believed to be

![Figure 3. A proposed reaction scheme for Al hydroxide mineral formation from hydrolyzed aluminum solution (Huang et al., 2002).](image)

Aluminum transformation in aqueous systems may proceed through multiple reaction paths. Reaction path I is common when systems are neutralized rapidly within seconds or hours. Reaction Paths II and III both involve the formation of Al₁₃ (AlO₄Al₁₂(OH)₂₄(H₂O)₁₂). Reaction Path II is applicable when systems are neutralized relatively slowly compared with Reaction Path I. Reaction Path III is applicable when Al₁₃ forms under conditions that promote the rapid formation of Al₁₃ aggregates through an anion bridging mechanism. These reactions result in the formation of poorly ordered and highly reactive intermediate phases and stable crystalline Al hydroxides.
common when systems are neutralized rapidly within seconds or hours. Under these conditions, little or no Al\textsubscript{13} polynuclear species (\(\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{72}^{12+}\)) forms; the formation of \(\text{Al(OH)}_3\) nuclei is rapid, and gibbsite appears within days or weeks of aging. Reaction Paths II and III both involve the formation of Al\textsubscript{13}. Reaction path II is applicable when systems are neutralized relatively slowly compared with Reaction path I. The individual Al\textsubscript{13} ions can remain in solution for months to years, but eventually they transfer by one of the three pathways. If no Al\textsubscript{13} nuclei are present, the soluble Al\textsubscript{13} ions can slowly dissociate into Al\textsuperscript{3+} ions and deposit onto Al\textsubscript{(OH)}\textsubscript{3} nuclei (Path IIa). These soluble Al\textsubscript{13} may also aggregate and form Al\textsubscript{13} nuclei (Path IIb). If some Al\textsubscript{13} ions are already present, the remaining Al\textsubscript{13} ions can be deposited on them within weeks and months (Path IIc). Path III is applicable when Al\textsubscript{13} forms under conditions that promote the rapid formation of Al\textsubscript{13} aggregates via an anion bridging mechanism, i.e., outer-sphere associations. These aggregates rapidly rearrange themselves into Al\textsubscript{13} nuclei. The Al\textsubscript{13} nuclei in paths IIb, IIc, and III then transform into a poorly ordered phases, i.e., 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 the environment. The transformation of Al via the various pathways described above are strongly influenced by the nature and concentrations of soluble inorganic and organic ions and solid state ions, such as clay minerals and humic substances (Huang and Violante, 1986; Huang, 1988; Bertsch and Parker, 1996; Krishnamurti et al., 1999, 2004; Huang et al., 2002).

The influence of organic substances has been studied most extensively on the particular Al solid phases that form (Huang et al., 2002). The influence of a particular organic acid is generally related to the stability constant of the complex that the acid forms with Al (Kwong and Huang, 1979a). Therefore, \(\text{p-hydroxybenzoic}\) acid, which forms a low stability complex with Al, does not inhibit the crystallization of Al hydroxides, whereas aspartic, malic, and citric acids increasingly retard crystallization (Fig. 4). This is because organic acids replace water molecules that would otherwise coordinate with Al\textsuperscript{3+} ions and the extent to which this occurs depends on the chemical affinity of the organic acid for the Al, i.e., the stability constant of an Al-organic complex. Humic substances such as fulvic acid (FA) and humic acid (HA) also influence the transformation of Al by promoting the formation of SRO Al hydroxides (Kodama and Schnitzer, 1980; Singer and Huang, 1990). FA and HA resemble aliphatic acids such as citric and malic acids, in that they contain COOH and aliphatic OH groups. They also resemble quercetin and tannic acid, because they contain phenolic hydroxyl and ketonic C=O groups. Through these functional groups, FA and HA form stable complexes with Al and inhibit and disrupt the crystallization of Al hydroxides.

Organics substantially enhance the specific surface area and alter surface charge characteristics of Al transformation products (Kwong and Huang, 1978, 1979c, 1981). The intermediate transformation products of Al, which include soluble mononuclear and polynuclear Al species and colloidal SRO hydroxides, are the most reactive Al species in influencing biogeochemical processes in the terrestrial ecosystem. These Al species influence environmental quality and ecosystem health by impacting acidification of the environment, formation of humic substances, development of soil structure, dynamics of organic C cycling, transformations of nutrients and pollutants, biological productivity and food chain contamination, microbial and enzymatic activity, and human and animal health (Huang et al., 2002).

Interactions of soil minerals with organic substances and microorganisms also have an enormous impact on the formation and transformation of SRO Fe oxides (Schwertmann et al., 1986; Cornell and

![Figure 4. The X-ray diffraction patterns of hydrolytic precipitation products of Al, showing how four different organic acids influence the transformation to more crystalline phases. The initial concentration was \(1.1 \times 10^{-3}\) M at an OH/Al molar ratio of 3 and the solution was aged for 40 d at room temperature in the presence of \(10^{-4}\) M organic acids (Kwong and Huang, 1979b).](Image)
Schwertmann, 2003). Microorganisms may influence Fe transformation through reduction and oxidation reactions. Soil organic matter (SOM) 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 greatly influenced by organic substances (Huang and Wang, 1997; Liu and Huang, 1999). 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 profound impacts on microaggregate formation, water flux, nutrient and pollutant flux, soil biota habitat, and the ability of soils to promote plant growth, to respond to management, and to resist degradation. Therefore, surface properties of Fe oxides formed under the influence of organic substances deserve close attention in advancing our understanding of their surface chemistry pertaining to biogeochemical processes in the terrestrial ecosystem.

Mineral catalysis of formation of humic substances

Humic substances are formed through biotic and abiotic processes. A variety of biomolecules, such as carbohydrates, phenolic compounds, and amino acids, can participate as raw materials. Soil mineral surfaces play 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). Despite the importance of the Maillard reaction, the mechanisms and rates of the Maillard reaction in nature remain vague (Ikan et al., 1996). A major appeal of the Maillard reaction in humification processes lies in the two proposed precursors, sugars and amino acids, which are among the most abundant constitutions of 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). In order 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 (Fig. 5). 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 very slow at room temperature. However, it has recently been demonstrated that the action of δ-MnO₂ under ambient environmental conditions significantly accelerates the Maillard reaction, lending credence as an important abiotic pathway for the formation of humic substances (Jokic et al., 2001b).

Besides the mineral catalysis of the Maillard reaction, soil minerals play an important role in accelerating abiotic polymerization of phenolic compounds, the polycondensation of phenolic compounds and amino acids, and the subsequent formation of humic substances (Wang et al., 1986; Huang, 2000). Kumada and Kato (1970), Wang and Li (1977), and Filip et al. (1977) are among the pioneers in the study of browning of polyphenols catalyzed by clay-size layer silicate. Since the early 1980s, Huang and co-workers have studied the sequence of catalytic power of layer silicates and their reaction sites in the polymerization of phenolic compounds and the subsequent formation

![Figure 5. Formation of the Amadori compound from d-glucopyranose (d-glucose) and glycine (Mossine et al., 1994). 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.](image-url)
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 effective catalysts in the transformation of phenolic compounds because of their high oxidation potentials, high specific surface area, and high surface reactivity (Shindo and Huang, 1982, 1984; Wang and Huang, 2000a).

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 formation of humic substances. The abiotic ring cleavage of polyphenols catalyzed by SRO oxides of Al, Fe and Mn (Wang and Huang, 2000a, b) may account, in part, for the carboxylic group contents and the origin of the aliphaticity of humic substances (Schnitzer, 1977; Preston et al., 1982). Therefore, the catalytic power of these oxides in affecting the C turnover and humic substance formation via abiotic processes in soil and related environments deserves continued close scrutiny.

Both the Maillard reaction and the polymerized polyphenol model are considered as separate significant pathways for the formation of humic polycondensates. In nature, however, it is likely that these two pathways do not occur separately, but rather closely interacting with each other, since sugars, amino acids, and polyphenols coexist in soil solutions and natural waters. Jokic et al. (2004a) recently reported that soil mineral colloids such as δ-MnO₂ significantly accelerate humification processes in systems containing glucose, glycine and catechol at ordinary temperatures and pH. The data clearly show the significant increase in browning exhibited by systems containing δ-MnO₂ in contrast to non-δ-MnO₂ containing systems (Table 1). The promotional effect of δ-MnO₂ on the system consisting of carbohydrate, amino acid, and polyphenol is a complex process involving surface mineral sorption and condensation. This points to a linking of the polyphenol and Maillard reactions in humification pathways, which is a significant advancement in the understanding of natural humification processes in the environment.

### Effects of soil colloids on enzymatic activity

Extracellular enzymes are rapidly sorbed at mineral and humic colloids in the terrestrial ecosystem. Mineral colloids have a high affinity for enzymes. However, the ability of the sorbed enzymes to retain their catalytic effectiveness is greatly influenced by the nature and properties of mineral colloids. Humic substances also have the ability to retain enzyme and influence the activity of enzymes.

Mineral colloid-enzyme interactions have been well documented (e.g., Theng, 1979; Burns, 1986; Naidja et al., 2000, 2002). Adsorption of enzymes by mineral colloids may proceed through electrostatic, ionic, covalent, hydrophobic, hydrogen bonding, and van der Waals forces. When enzymes are adsorbed on mineral colloids, changes in the tertiary structures (i.e., the folding of the helix or coil into a compact, globular molecule stabilized by interfold hydrogen bonding, van der Waals, and hydrophobic interactions) of the enzymes and their

### Table 1. Effect of birnessite on glucose and glycine solutions at an initial pH 7.00 (Jokic et al., 2004a)

<table>
<thead>
<tr>
<th>Treatmenta</th>
<th>Absorbance</th>
<th>pH</th>
<th>Dissolved Mn (µg mL⁻¹)</th>
<th>pH+pE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 nm</td>
<td>600 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose+glycine+birnessite</td>
<td>10.4±0.3</td>
<td>0.74±0.01</td>
<td>7.89±0.08</td>
<td>8286±108</td>
</tr>
<tr>
<td>Glucose+glycine</td>
<td>0.34±0.02</td>
<td>0.093±0.005</td>
<td>7.03±0.05</td>
<td>0</td>
</tr>
<tr>
<td>Glucose+birnessite</td>
<td>0.043±0.002</td>
<td>0.027±0.001</td>
<td>7.47±0.08</td>
<td>2797±75</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.038±0.002</td>
<td>0.022±0.001</td>
<td>6.69±0.04</td>
<td>0</td>
</tr>
<tr>
<td>Glycine+birnessite</td>
<td>0.021±0.001</td>
<td>Colourlessb</td>
<td>7.46±0.04</td>
<td>20.9±0.8</td>
</tr>
<tr>
<td>Glycine</td>
<td>0.020±0.001</td>
<td>Colourlessb</td>
<td>6.95±0.05</td>
<td>0</td>
</tr>
<tr>
<td>25 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose+glycine+birnessite</td>
<td>0.114±0.007</td>
<td>0.023±0.001</td>
<td>7.39±0.11</td>
<td>2341±56</td>
</tr>
<tr>
<td>Glucose+glycine</td>
<td>0.025±0.001</td>
<td>0.011±0.001</td>
<td>7.06±0.05</td>
<td>0</td>
</tr>
<tr>
<td>Glucose+birnessite</td>
<td>Colorlessb</td>
<td></td>
<td>6.85±0.09</td>
<td>1001±17</td>
</tr>
<tr>
<td>Glucose</td>
<td>Colorlessb</td>
<td></td>
<td>6.65±0.07</td>
<td>0</td>
</tr>
</tbody>
</table>

*The reaction periods were 15 and 30 days, respectively, at 45 and 25 °C.

*The supernatant was colorless with an absorbance <0.01 at the wavelengths studied.
Active sites decrease the activity of the enzyme or eliminate it altogether (Burns, 1986). However, there are notable exceptions to the adsorption-decline in activity rule. Various materials have different enzyme immobilization capabilities (Table 2). There is considerable variation in the retained activities of the two enzymes (laccase and peroxidase) on four materials (glass beads, montmorillonite, kaolinite, soil). The residual specific activities (calculated as percentages of the specific activities of the free enzyme) of laccase and peroxidase immobilized on all materials are high. Furthermore, laccase immobilized on montmorillonite shows specific activities higher than that of the free enzyme. This may be attributed to steric modification of the immobilized enzyme. Therefore, the performance of enzymes in the terrestrial ecosystem is substantially influenced by mineral colloids. The role of SRO oxides, hydroxides, and oxyhydroxides of Al, Fe, and Mn in influencing enzyme activities involved in the transformations of natural organics and xenobiotics has been well documented (Huang, 1990; Naidja et al., 1997, 2000; Huang et al., 1999; Violante and Gianfreda, 2000).

Fewer studies investigated the adsorption of enzymes to humic substances, probably because of the physicochemical and biochemical complexity and dynamic nature of SOM. Nevertheless, it has been reported that SOM can inhibit enzymes (Vuorinen and Saharinen, 1996) and enzyme activity may be reduced by adsorption on humic polymers (Gianfreda et al., 1998). Enzyme inhibition of humic substances has been well demonstrated for an oxidoreductase (Pflug, 1980; Sarkar and Bollag, 1987), a protease (Ladd and Butler, 1969), an invertase and a phosphatase (Malcolm and Vaughan, 1979). On the other hand, Kang et al. (2002) and Park et al. (2000) demonstrated that, although high concentrations of humic-like polymers tend to inhibit laccase-mediated transformation of xenobiotics (including catechol), low concentrations of HA might enhance the enzymatic transformation of phenolic compounds. Furthermore, it has been reported that enzymes can be stabilized by SOM (Conrad, 1942; Burns, 1986; Nannipieri and Gianfreda, 1999).

Mechanisms proposed to account for the stability of enzymes as influenced by SOM include ion exchange, H-bonding, covalent bonding, lipophilic reactions, and entrapment within three-dimensional micelles during organic matter genesis. However, the intrinsic mechanisms of interactions of enzymes with humic substances still remain to be established. Functional groups of enzymes implicated in covalent bonding to humic polymers include terminal and basic amino, carboxyl, sulfhydryl, phenolic, and imidazole groups. All these may be involved in the stabilization processes, provided they do not form part of the active sites of the enzymes and are not crucial to the retention of its tertiary structure.

Enzyme–humic complexes can also be bound to mineral colloids and this may further enhance
enzyme stability. Violante and Gianfreda (2000) demonstrated the enhanced stability of enzymes bound to organo-mineral complexes. Furthermore, a significant portion of immobilized enzyme in soils is associated with humic substances, not by adsorption or occlusion, but by the formation of enzyme-phenolic copolymers during soil formation (Burns, 1986; Huang, 1990). Soil minerals with different structural configuration and surface properties may play a catalytic role in the formation of enzyme-phenolic co-polymers and the subsequent impact on the activity and stability of enzymes in the terrestrial ecosystem.

Microbial mediation of soil mineral transformation

Weathering of minerals in the terrestrial ecosystem can be enhanced by microbial activity by as much as $10^6$ folds (Kurek, 2002). Microbes can dissolve minerals by direct and indirect action under aerobic and anaerobic conditions (Ehrlich, 2002; Kurek, 2002). The modes of microbial attack of minerals 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 with a metabolically produced ligand that form a highly soluble product with a mineral component, and (5) indirect attack by biopolymers. Microorganisms may be dispersed in the soil solution or grow in biofilms on the surface of the susceptible minerals. Weed et al. (1969) have shown that fungi can adsorb K from solution and thus shift K equilibrium in suspensions of micas and transfer them to vermiculites. Such process can also occur for many major and trace elements (Robert and Berthelin, 1986). Some microbes can promote the transformation of one mineral into another by diagenesis, which can be an indirect effect of aerobic and anaerobic microbial metabolism (Ehrlich, 2002; Kurek, 2002).

In view of their active surfaces, bacteria have recently been included in geochemical modeling of metal speciation and transport. The large surface area-to-volume ratio and charge characteristics of bacteria facilitate their metal-binding capacity, resulting in precipitation of mineral phases on their cell walls or other surface polymers (McLean et al., 2002). The mechanisms by which bacteria initiate the formation of minerals vary widely with species. There may be a combination of biochemical and surface-mediated reactions in the formation process of minerals. Bacteria surface layers may passively adsorb and may indirectly serve as a nucleation template. Bacteria may also directly initiate mineral precipitation by producing reactive compounds (e.g., enzymes, metallothioneins, siderophores), which bind metals or catalyze metal transformation. Moreover, bacteria can instigate the spontaneous precipitation of metals by altering the chemistry of the microenvironment (Beveridge et al., 1997; Douglas and Beveridge, 1998). For example, reactive inorganic ligands such as sulfide may be produced as a cellular metabolic by-product. Catalyzed by sulfate-reducing bacteria, sulfide reacts with metals to form metal sulfides, a common reaction in anoxic environments. 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 abiotic oxidation (Tebo et al., 1997). Manganese oxides are highly reactive minerals and help restrict the mobility of metals in soils through adsorption on their surfaces. Biogenic Mn oxides have significantly larger specific surface area and higher Pb adsorption capacity than abiotically precipitated Mn oxides (Nelson et al., 1999). Thus, bioformation of minerals can play a role in developing innovative management strategies for remediation of metal-contaminated soils.

Dynamics of aggregate turnover

Living and nonliving organic components varying in size, chemical composition, and extent of decomposition have the capacity to promote and stabilize aggregations of soil particles at size scales ranging over nine orders of magnitudes (Fig. 6). Thus, they are essential in maintaining the proper balance of components of SOM to ensure the stability of the entire soil matrix. Mechanisms of stabilization of soil structure can operate over larger distances to bind microaggregates into macroaggregates. Due to the distances involved, the stabilization of macroaggregates is related to the presence of nonliving particulate organic matter (POM) capable of spanning distances $>100\mu m$ or the existence of a network of a fungal hyphae and plant roots that physically enmeshes microaggregates (Fig. 7). The death of roots and hyphae growing within and through macroaggregates produces biochemical binding agents capable of stabilizing the structure of macroaggregates.
However, SOM responsible for the stabilization of soil structure is subject to decomposition by microbial activity. Thus, aggregation is a dynamic process in soils (Baldock, 2002). Biological activity has the potential not only to stabilize soil structures through the production of organic substances capable of binding soil particles, but also to destabilize soil structure by decomposition of organic binding agents. The balance between these two processes dictates soil structural stability. A continual addition of organic matter is essential to ensure that the contents of aggregating agents are adequate to maintain soil structural stability.

The model proposed by Golchin et al. (1997) can be used to relate the physical and chemical properties of soil organic materials and their distribution and cycling to the stabilization of soil aggregates. The major organic materials...
contributing to the structural stability of soils are perceived to be free and occluded POM fractions and the biomolecules synthesized and exuded by roots, mycorrhizal fungi, and other microorganisms in soils. The model of Golchin et al. (1997), which depicts the dynamics of soil aggregation, is most applicable to the aggregation of soils with appreciable contents of clays that protect aggregating agents from rapid decomposition (Baldock and Skjemstad, 2000). The protection mechanisms that stabilize organic binding agents from microbial attack are less effective in sandy soils, i.e., a more dynamic process. The large size of mineral particles and pores in sandy soils reduces the effectiveness of polysaccharides and other unaltered and altered biomolecules to stabilize soil structure. These biomolecules are important to the adherence of soil particles to plant roots and fungal hyphae and soil microorganism to mineral particles. However, they do not have the capacity to span the distances between the large primary particles and stabilize soil structure.

**Biogeochemical cycling of C, N, P, and S**

Soil minerals play a stabilizing role in SOM and related turnover of C, N, P, and S. The interaction of Al and Fe with organic components is of primary importance in determining the content of organic matter in tropical and temperate soils (Wada, 1995). The Al and Fe that complex and stabilize organic matter against microbial decomposition are released from soil minerals during soil formation. Their supply rates affect the content of SOM to a great extent as illustrated by the relationship between pyrophosphate-extractable C and pyrophosphate-extractable Al plus Fe (Fig. 8). Close interactions between soil mineralogy and soil organic C have also been demonstrated by Torn et al. (1997). The amount of C stabilized by noncrystalline minerals is much greater than that by crystalline minerals. A positive relationship between noncrystalline minerals and organic C exists in soils through the climate gradient. Since pyrophosphate-extractable Al and Fe are in the form of SRO minerals, the findings of Wada and Higashi (1976) and Wada (1995) are in accord with those of Torn et al. (1997). Therefore, interactions of SRO minerals with organic matter should largely control the storage and turnover of SOM and atmosphere-ecosystem carbon fluxes during long-term soil development.

More than 95% of the N and S and between 20% and 90% of the P in surface soils are present in SOM (Guggenburger and Haider, 2002). The turnover of organic C is closely associated with the dynamics of N, P, and S in soils. The stabilization and degradation of SOM and its nutrients are greatly influenced by the surface reactivity of soil mineral colloids. Interactions of minerals with SOM largely result in
the stabilization of organic substances. Some soil minerals such as birnessite (\(\delta-MnO_2\)) enhance the cycling of the organically bound nutrients by catalytic degradation of biomolecules such as amino acids (Wang and Huang, 1987) and associated humification (Wang and Huang, 1992; Jokic et al., 2001b, 2004b). The catalysis of the Maillard reaction, condensation of sugar and amino acid by \(\delta-MnO_2\) and the resultant humification and the formation of unknown N are illustrated in Fig. 9.

Under most vegetation, the mass of humus in the soil profile exceeds the combined content of organic matter in the forest floor and above ground biomass (Schlesinger, 1977, 1997). Table 3 shows a global inventory of plant detritus and SOM, totaling \(1456 \times 10^{15}\) g C. Alternative estimates based on soil groups or climatic regions are similar (Post et al., 1982; Eswaran et al., 1993; Batjes, 1996). The global estimates of SOM, divided by the estimate of global litterfall, suggests a mean residence time of about 30 years for the total pool of soil organic C, but the mean residence time varies over several orders of magnitude between the surface litter and the various humus fractions (Schlesinger, 1997). The turnover times of microbial by-products and resistant plant residues adsorbed on soil particles are in the order of years. Fulvic acids (FAs) have turnover times in the neighborhood of hundred of years, whereas humic acids (HAs) and humins are much longer, i.e., thousands of years (Paul and Van Veen, 1978). The distribution and annual transfers of C in the various fractions for a grassland Chernozem are shown in Fig. 10. Although the HAs
and humins constitute the majority of the organic C in this system, they contribute only a small proportion to the annual C cycling within the soil because of their very slow turnover rate. The undecomposed litter (Fig. 10) also includes the soil biomass and microbial metabolites. These, along with the plant residues, constitute the active fraction of organic matter that has a prominent role in the cycling of elements such as C, N, and S annually.

Jenkinson et al. (1991) estimated the additional degradation effects on SOM if the global annual mean temperature rises during the next 60 years by 3°C. According to their estimate, about 100 Gt should be additionally evolved as CO₂ from SOM (1600 Gt C). This will increase the present CO₂ concentration in the atmosphere by 14% whereas the combustion of fossil fuels (5.4 Gt C year⁻¹) would add only about 330 Gt C to the atmosphere. Furthermore, transformations of C, N, and S in soils as influenced by land management and the impact on global climatic change should not be overlooked (Lal, 1998; Guggenburger and Haider, 2002).

The release of the stored organic nutrients depends on the mean residence time of SOM associated with the mineral phases. The mean residence time of SOM varies widely with the type of the organo-mineral associations and the spatial location within the aggregate structure of soil (Table 4). Some SOM with rapid turnover is apparently microbial residues, which are often loosely bound to mineral colloids. By contrast, SOM of slow turnover is tightly bound to sesquiso-oxides by the formation of inner-sphere complexes. Primary particles (layer silicates and Al and Fe oxides, hydroxides, and/or oxyhydroxides) are clustered to larger entities, i.e., the secondary soil particles or aggregates in soil environments. The arrangement of primary and secondary particles which is defined as soil structure results in the formation of a series of pores ranging in size from nanometers to centimeters. Soil structure determines the pore-size distribution and, hence, the accessibility of substrates adsorbed on surfaces of a series of pores to exoenzymes, microbes, and faunal grazers. Pools I and II (Table 4) are generally plant fragments which may be divided into easily available cell constituents and lignocelluloses at various degrees of degradation. When these plant fragments are degraded or reduced in size, the microbially available components are exhausted and the residues are more resistant to microbial attack. Pool III includes soil biomass and rapidly available organic matter within large aggregates. The pools I to III, which on average account for 20–30% of the total C in SOM, must be renewed continuously by fresh plant residues in order to maintain a relatively constant nutrient level and release by mineralization. The balance between decay and renewal processes controls the availability of N, P, and S and is sensitive to land management. Pool IV is physically protected SOM whose stability is affected by cultivation, since physical disturbance such as ploughing destroys macroaggregates. Pool V is chemically stabilized SOM having the longest mean residence time and

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>Mean soil organic matter (kg C m⁻²)</th>
<th>World area (ha × 10⁶)</th>
<th>Total world soil organic carbon (mt C × 10⁹)</th>
<th>Amount in surface litter (mt C × 10⁹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tropical forest</td>
<td>10.4</td>
<td>24.5</td>
<td>255</td>
<td>3.6</td>
</tr>
<tr>
<td>Temperate forest</td>
<td>11.8</td>
<td>12</td>
<td>142</td>
<td>14.5</td>
</tr>
<tr>
<td>Boreal forest</td>
<td>14.9</td>
<td>12</td>
<td>179</td>
<td>24.0</td>
</tr>
<tr>
<td>Woodland and shrubland</td>
<td>6.9</td>
<td>8.5</td>
<td>59</td>
<td>2.4</td>
</tr>
<tr>
<td>Tropical savanna</td>
<td>3.7</td>
<td>15</td>
<td>56</td>
<td>1.5</td>
</tr>
<tr>
<td>Temperate grassland</td>
<td>19.2</td>
<td>9</td>
<td>173</td>
<td>1.8</td>
</tr>
<tr>
<td>Tundra and alpine</td>
<td>21.6</td>
<td>8</td>
<td>173</td>
<td>4.0</td>
</tr>
<tr>
<td>Desert scrub</td>
<td>5.6</td>
<td>18</td>
<td>101</td>
<td>0.2</td>
</tr>
<tr>
<td>Extreme desert, rock, and ice</td>
<td>0.1</td>
<td>24</td>
<td>3</td>
<td>0.02</td>
</tr>
<tr>
<td>Cultivated</td>
<td>12.7</td>
<td>14</td>
<td>178</td>
<td>0.7</td>
</tr>
<tr>
<td>Swamp and marsh</td>
<td>68.6</td>
<td>2</td>
<td>137</td>
<td>2.5</td>
</tr>
<tr>
<td>Totals</td>
<td>147</td>
<td>1456</td>
<td>1456</td>
<td>55.2</td>
</tr>
</tbody>
</table>

Table 3. Distribution of soil organic matter by ecosystem types (Schlesinger, 1977)
accounting for 50–70% of the total C in SOM and is generally considered to be little affected by land management.

**Transformation of organic contaminants**

Adsorption and desorption of organic contaminants by soils are key processes in the transformation of organic contaminants in the terrestrial ecosystem (Huang, 1990, 1994; Chiou, 2002). The availability of organic contaminants for uptake by organisms, for chemical, biochemical, and microbial transformations, and for transport in solution or in gaseous phases is affected by adsorption–desorption processes. The main factors affecting the adsorption–desorption of organic contaminants in soils are the physicochemical characteristics of organic contaminants, the nature and properties of the soil colloids, and physicochemical–biological interfacial interactions in soil environments. Soil mineral colloids, especially SRO metal oxides and silicates, and humic substances, which have large and physico-chemically active surface areas, provide a major retention sink for many organic contaminants. Furthermore, since a vast majority of humic substances are bound with soil mineral colloids, the chemistry of humus–clay complexes play an important role in adsorption–desorption reactions of organic contaminants. For example, Liu and Huang (2004) reported that the complexation of Al, Fe, and Mn oxides with humic macromolecules substantially decreases the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) by metal oxides (Table 5), which is caused by the resultant alteration of the surface properties.

The degradation of organic contaminants may decrease or diminish when they are adsorbed on soil colloids due to the lower bioavailability of chemicals involved in binding processes (Alexander, 1995). The availability of sorbed organic contaminants to microorganisms varies with the chemical

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**Figure 10.** Turnover of litter and soil organic fractions in the 0–20 cm layer of a Chernozem in a grassland soil (Schlesinger, 1977). Note that mean residence time can be calculated for each fraction from measurements of the quantity in the soil and the annual production or loss (respiration) from the fraction. Carbon pools (kg C m⁻²) and annual transfers (kg C m⁻² year⁻¹) are indicated. Total profile content of C to 20 cm is 10.4 kg C m⁻².
properties of the contaminants, the nature of the sorbent, the mechanism of sorption, and properties of degrading organisms (Guerin and Boyd, 1992). The mechanism of sorption may change with residence time of xenobiotics present in soil, altering their bioavailability (Alexander, 1995). For instance, a strain of Pseudomonas mineralized as much as 45% of phenanthrene during a 5-day incubation with the compound that was in soil for less than 1 day (Hutzinger and Alexander, 1995). When phenanthrene was aged with soil for 315 days, only 5% of the compound was subject to microbial mineralization. Phenanthrene molecules adsorbed on soil colloids in the initial fast adsorption are apparently more accessible to degradation in contrast to those adsorbed after the slow diffusion of the chemical across organic matter and its subsequent sequestration in inaccessible microsites within the soil matrix. Contaminants sorbed by soil particles may be available to certain microorganisms and unavailable to others. For example, soil-sorbed naphthalene is degraded by Pseudomonas putida strain 17,484, but it does not undergo degradation by a Gram-negative soil isolate designated NP-Alk (Guerin and Boyd, 1992; Crocker et al., 1995). Apparently, the Pseudomonas strain directly mineralizes surface-localized, labile sorbed naphthalene. By contrast, degradation of naphthalene by NP-Alk appears to be mainly controlled by the passive desorption of the surface-sorbed compound (Guerin and Boyd, 1992). Some researchers have provided evidence that biotic and abiotic interactions shuld decrease the rate of transformation of organic contaminants (Dec et al., 2002). Enhanced degradation of organic contaminants by microbes in the presence of soil colloids attributable to their increased concentration in the vicinity of the microbial cells. However, both organic and mineral colloids have the ability to enhance degradation through surface-catalyzed reactions or adsorption of sorbed organic pollutants (Huang, 1990, 2000; Senesi and Miano, 1995). Therefore, both biotic and abiotic degradation processes of organic contaminants in the terrestrial ecosystem need to be taken into consideration in studying the effects of soil colloids on microbial degradation of organic contaminants on microbial surfaces. The attachment of microorganisms to solid surfaces is a common phenomenon in soils. Microorganisms may use many different mechanisms to achieve and maintain the attachment (Dec et al., 2002). In most cases, microorganisms manage to strengthen the attachment by means of degrading organisms (Guerin and Boyd, 1992). The mechanism of sorption of xenobiotics present in soil, altering their bioavailability (Alexander, 1995). For instance, a strain of Pseudomonas mineralized as much as 45% of phenanthrene during a 5-day incubation with the compound that was in soil for less than 1 day (Hutzinger and Alexander, 1995). When phenanthrene was aged with soil for 315 days, only 5% of the compound was subject to microbial mineralization. Phenanthrene molecules adsorbed on soil colloids in the initial fast adsorption are apparently more accessible to degradation in contrast to those adsorbed after the slow diffusion of the chemical across organic matter and its subsequent sequestration in inaccessible microsites within the soil matrix.

### Table 4. Comparison of estimated mean residence times of soil organic matter in soil physical fractions (Guggenburger and Haider, 2002)

<table>
<thead>
<tr>
<th>Pool</th>
<th>Mean residence time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Decomposable plant material, 0.24</td>
<td>Decomposable plant material, 0.24</td>
</tr>
<tr>
<td>II Resistant plant material, 3.33</td>
<td>Structural plant residues, 1–5</td>
</tr>
<tr>
<td>III Soil biomass, 2.44</td>
<td>Active SOM pool, 1–5</td>
</tr>
<tr>
<td>IV Physically stabilized OM, 72</td>
<td>Slow SOM pool, 25–50</td>
</tr>
<tr>
<td>V Chemically stabilized OM, 2857</td>
<td>Passive SOM pool, 1000–1500</td>
</tr>
</tbody>
</table>

*Organic matter stored within macroaggregates but external to microaggregates; includes coarse occluded POM and microbial organic matter.

*Organic matter stored within microaggregates; includes fine occluded POM and microbial derived organic matter.
Table 5. Rate coefficients of the fast adsorption of 2,4-D by various samples based on the 1st-order equation at 298 K (Liu and Huang, 2004)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate coefficients x 10^3, h⁻¹ ¹a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al oxide</td>
<td>113.8</td>
</tr>
<tr>
<td>Fe oxide</td>
<td>133.2</td>
</tr>
<tr>
<td>Mn oxide</td>
<td>98.7</td>
</tr>
<tr>
<td>Al oxide–humic complex</td>
<td>45.6</td>
</tr>
<tr>
<td>Fe oxide–humic complex</td>
<td>43.2</td>
</tr>
<tr>
<td>Mn oxide–humic complex</td>
<td>44.6</td>
</tr>
<tr>
<td>HA</td>
<td>39.4</td>
</tr>
</tbody>
</table>

¹aStandard errors were < 6%.

of extracellular polymeric adhesives such as polysaccharides and proteins, which are frequently their own metabolic products. Both electrostatic and hydrophobic interactions are involved in microbial attachment (Fletcher, 1996). Sorption of microorganisms may be extremely extensive especially in soils with high contents of clay and organic matter. The effect of adsorption of microorganism on their ability to degrade organic contaminants is difficult to predict. The microbial degradation may be enhanced or reduced, or may remain unchanged as the cells undergo the adsorption to solid surfaces. This apparently depends on the nature and properties of solid surfaces and the kinds of microorganisms. However, the utilization of sorbed organic compounds by microorganisms that adhere to the same surfaces is a common phenomenon (Di Grazia et al., 1990; Alexander, 1999). Our current understanding of the effects of mineral and organic colloids on microbial activity under field conditions is limited (Haider, 1995), which may vary with the type of soil components and microorganism. The influence of structural configuration and surface properties of soil minerals and organic matter on microbial activity and ability to degrade organic contaminants with different structure and functionality should be a challenging area for future research.

Soil is a living system in which enzymes are present either free in solution or bound onto mineral colloids, humic substances, and humus–mineral colloid complexes. Extracellular enzymes in solution are, however, rapidly bound to those highly reactive soil colloids. This immobilization is a major factor that gauges the performance of enzymes in the degradation of organic contaminants in soils. The transformation and degradation of anthropogenic organic compounds including chlorinated phenols, detergents, pesticides, and other organic contaminants can be mediated by various enzymes (Munnecke et al., 1982; Bollag, 1992; Naidja et al., 2000). The lifetime and stability of enzymes can be increased by immobilization on soil colloids (Burns, 1986; Dec et al., 2002). Enzymes immobilized by mineral colloids can be used more efficiently with a possible longer time, higher stability, and possible reusability (Ruggiero et al., 1989; Naidja et al., 2000). However, information on the involvement of immobilized enzymes in the transformation of organic contaminants in soils is sparse (Dec et al., 2002). To cope with the problems caused by increasing amounts of agrochemical and industrial effluents disposed in soil, a fundamental understanding of enzyme–soil colloid interactions and their role in remediation of anthropogenic organic compounds in the environment is essential for the development of effective, durable, and practical treatment methods. However, the mechanisms of immobilization of enzymes on mineral colloids, humic substances, and humus–clay complexes and the resultant changes of protein conformation of enzymes remain relatively unclear. A wide range of soil minerals have yet to be investigated that may have a high capability to immobilize enzymes, adsorb substrates and reaction products and may be catalytically active in the transformation of organic pollutants. Furthermore, the role of abiotic catalysis of the minerals (Naidja and Huang, 1996) in enzyme–mineral colloid complexes is still at an emerging stage and warrants an in-depth research.

Transformation of metals and metalloids

The transformation of metals and metalloids in soils is governed by interactions of physicochemical, biochemical, and biological processes. The impacts of these interactive processes on metal transformation are especially important in the rhizosphere soil where the type and concentration of substrates are different from those of the bulk soil because of root exudation (McLaughlin et al., 1998; Huang and Germida, 2002). This results in colonization by different populations of bacteria, fungi, protozoa, and nematodes. Soil–plant–biota interactions, in turn, result in intense biological, biochemical, and physicochemical processes in the rhizosphere. Therefore, reactions and processes in the rhizosphere, which is the essential pathway of metal contamination of the terrestrial food chain, can only be understood satisfactorily with interdisciplinary collaborative research efforts. Metal transformation in soil and associated environments is governed by redox reactions, complexation,
adsorption–desorption, precipitations-dissolution, biomineralization, microbial extractions, and mycorrhizal infection.

Redox reactions are important in influencing the chemical speciation of a number of contaminant metals and metalloids, such as Cr, Pu, Co, Pb, Cu, As, and Se (Oscarson et al., 1981; Bartlett and James, 1993; Sparks, 2003). Redox reactions also are important in controlling the transformation and reactivity of Mn and Fe oxides in soils, which have enormous capacities to adsorb metal and metalloid contaminants and are major sinks of these contaminants (Huang and Germida, 2002). Several dissolved organic substances have been shown to effect the reduction of ferric and maganic oxides; polyphenolic and hydroxy/carboxylic functional groups, such as found in FAs and HAs are particularly efficient in this regards (Campbell et al., 1988). Furthermore, reduction of sulfate to sulfide in anaerobic environments also affects the transformation of metal and metalloid contaminants through the formation of highly insoluble metal sulfides (Alloway, 1995). The transformation, mobility, bioavailability, and toxicity of metals and metalloids, which exist in more than one oxidation state, are significantly influenced by redox reactions. The critical redox potentials for the transformation of some metal contaminants in soils have been summarized (Massechelyn and Patrick, 1994). However, there have been limited studies of how rhizosphere processes affect redox reactions of metals and metalloids.

A series of organic ligands occur in the rhizosphere due to root exudates and microbial metabolites (Lynch, 1990a, b; McLaughlin et al., 1998). In view of the stability constants of the complexes of metals with these ligands (NIST, 1997), a large fraction of metal ions in the solution may actually be complexed with a series of organic ligands commonly present in the rhizosphere. Although the hypothesis that the toxicity or bioavailability of a metal is related to the activity of the free aquo ion is gaining popularity in the studies of soil–plant relations (Parker et al., 1995), new evidence is now emerging that free metal ion hypothesis may not be valid in all situations (Linehan et al., 1989; Tessier and Turner, 1995). Krishnamurti et al. (1996) reported that, after 2 weeks of crop growth in a field experiment, more Cd is complexed with the low-molecular-weight organics acids (LMWOAs) at the soil–root interface, compared with the bulk soil. More recent data show that the kind and amount of root exudates vary with the level of Cd in contaminated soils (Chou et al., 2003; Wang et al., 2003) as illustrated in Table 6. Hence, metal speciation in relation to its bioavailability as influenced by physicochemical and biological interfacial interactions in the rhizosphere warrants careful research for years to come.

Metal transformation is significantly influenced by adsorption–desorption reactions in soils, which are affected by biogeochemical processes, especially in the rhizosphere. Factors influencing adsorption–desorption of metals in the rhizosphere include solution pH, LMWOAs, inorganic ligands, solution ionic strength, cation concentrations, and the nature and properties of soil particles. Little is known on the adsorption–desorption of metals in the rhizosphere. Most studies investigated these reactions in bulk soils and under modified conditions to simulate rhizosphere conditions. It has been shown that the increase in Cd release in the presence of LMWOAs can be explained by the surface complexation of the particulate-bound Cd in soil with LMWOAs, which is reflected in the increase in the release of Cd from the soils with the increase in the stability constant of Cd–LMWOAs complex (Krishnamurti et al., 1997). Also, the rate coefficients of the Cd release from the soils are substantially influenced by LMWOAs and follow the same order as that of the Cd availability index (CAI) values of the soils (Krishnamurti et al., 1995). Furthermore, amounts of Cd release from soils by renewal of LMWOAs (Fig. 11) also follow the same

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Acetic (µmol kg⁻¹ soil)</th>
<th>Lactic (µmol kg⁻¹ soil)</th>
<th>Glycolic (µmol kg⁻¹ soil)</th>
<th>Maleic (µmol kg⁻¹ soil)</th>
<th>Succinic (µmol kg⁻¹ soil)</th>
<th>Total (µmol kg⁻¹ soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻⁶</td>
<td>260.8d</td>
<td>154.3c</td>
<td>797.3c</td>
<td>503.5b</td>
<td>173.7c</td>
<td>1889.6</td>
</tr>
<tr>
<td>5</td>
<td>146.4bc</td>
<td>145.3c</td>
<td>671.3ab</td>
<td>484.5ab</td>
<td>131.6ab</td>
<td>1579.1</td>
</tr>
<tr>
<td>1</td>
<td>113.5b</td>
<td>113.1b</td>
<td>594.6a</td>
<td>429.0a</td>
<td>114.6a</td>
<td>1364.9</td>
</tr>
<tr>
<td>Control</td>
<td>59.9a</td>
<td>66.9a</td>
<td>488.5a</td>
<td>384.1a</td>
<td>98.1a</td>
<td>1097.4</td>
</tr>
<tr>
<td>LSD 0.05</td>
<td>37.3</td>
<td>27.0</td>
<td>148.3</td>
<td>103.7</td>
<td>30.4</td>
<td></td>
</tr>
</tbody>
</table>

*Cd concentration (mg Cd kg⁻¹ soil).
trend as the CAI values of the soils. More research should be conducted to uncover the dynamics of the adsorption–desorption reactions as influenced by biochemical and biological processes in soil and related environments.

For most of the trace metals, direct precipitation from solution homogeneous nucleation appears to be less likely than adsorption–desorption by virtue of the low concentrations of these metals in soil solution in well aerated drylands soils (McBride, 1989; Christensen and Huang, 1999). On the other hand, in reducing environments when the sulfide concentration is sufficiently high, precipitation of trace metals as sulfide may play a significant role in metal transformation (Robert and Berthelin, 1986). In aerobic soils, although precipitation of trace metals through homogeneous nucleation is unlikely, heterogeneous nucleation catalyzed by mineral, organic, and microbial surfaces may have a significant role in metal transformation (Huang and Germida, 2002).

All microorganisms contain biopolymers, such as proteins, nucleic acids, and polysaccharides, which provide sites for binding metal ions (Hughes and Poole, 1989). These binding sites include negatively charged groups such as carboxylate, thiolate, phosphate, and groups such as amines, which coordinate to the metal center through lone pairs of electrons. Because of the ability of these biopolymers to bind metals, large concentrations of metals are frequently associated, not only with living microbial biomass, but also with dead cells (Berthelin et al., 1995). Many metals bind with varying tenacity to the largely anionic outer surface layers of microbial cells. Binding of metals by microbial cells alter cell wall composition and induces morphological, ultrastructural and surface charge changes (Venkateswerlu et al., 1989; Collins and Stotzky, 1996). Some metals are bound by cell walls to a greater extent than by mineral colloids (Table 7). This indicates that microbial cell walls and membranes may act as

Figure 11. Time function of Cd release from the Luseland soil as influenced by selected low molecular weight organic acids (LMWOAs) (citric, fumaric, oxalic, succinic, and acetic acids) at a concentration of $10^{-2}$ M. The cumulative amount of Cd released by renewal of LMWOAs after every 2-h reaction period is shown as solid line (Krishnamurti et al., 1997).
foci for accumulation of metals in the terrestrial ecosystem.

Microbial formation of minerals, i.e., biomineralization is an important pathway of mineral formation in nature (Beveridge, 1989). 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 the biominerals is achieved by specific processes involving molecular recognition at inorganic–organic interfaces. Electrostatic binding or association, geometric matching (epitaxis), and sterochemical correspondence are important in these recognitions. Compared with other life forms, bacteria may have a greater capacity to sorb and precipitate metals from solution resulting in mineral formation as they have the highest surface area to volume ratio (Beveridge, 1989). Although in most environments, soluble metals are present in low concentrations, bacteria cells have a remarkable ability to concentrate metal ions from solutions. Therefore, the impact of biomineralization on the transformation, dynamics, toxicity, and fate of metal contaminants in the environment should not be overlooked.

Microorganisms have a range of metal transformation abilities, which are often specific for certain metals and capable of accumulating metals against large concentration gradient (Kurek, 2002). For example, some microorganisms make siderophores which are biomolecules capable of binding Fe (Nielsands, 1981). Other microorganisms produce metallothioneins that are small cysteine rich protein that strongly bind Cd, Cu, and Zn. Ligands of this type and related biomolecules are significant in influencing the transformation, transport, bioavailability, and toxicity of metals in soils, especially in the rhizosphere.

Most plants in natural habitats form association with mycorrhizae. Arbuscular mycorrhizal fungi (AMF) are obligate symbionts, and infection of plant roots exerts a metabolic load on the host plant (Reid, 1990). Mycorrhizal fungi produce mycelium inside root cortical cells during infection and colonization of host plant root. They may form storage structures termed vesicles, and may also form other structures which are referred to as arbuscules and serve as the site of ion exchange between the host plant and the mycorrhizal fungus. The fungi also form extra cellular hyphae that penetrate out of the root and expand the volume of soil the root can penetrate. The influence of mycorrhizal infection on metal uptake depends upon the ability of the fungal symbiont to absorb metals and transfer them to the symbiotic roots through extensive vegetative mycelium. Mycorrhizal fungi also release LMWOAs into soils and thus enhance the solubilization of particulate-bound metals (Huang and Germida, 2002). However, there are substantial gaps in knowledge on the mechanisms with which fungi influence the transformation and uptake of metals in the terrestrial ecosystem.

### Biodiversity in terrestrial ecosystems

Soil is a focal point of the terrestrial ecosystem (Odum, 1989; Coleman et al., 1998). Physical, chemical, and biological processes are interacting processes in the terrestrial ecosystem. The functioning and stability of the terrestrial ecosystem are determined by plant biodiversity and species composition (Schulze and Mooney, 1993; Tilman

<table>
<thead>
<tr>
<th>Metal</th>
<th>Walls</th>
<th>Envelopes</th>
<th>Kaolinite</th>
<th>Smectite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>423 ± 15</td>
<td>176 ± 3</td>
<td>0.46 ± 0.02</td>
<td>43 ± 0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>530 ± 13</td>
<td>972 ± 9</td>
<td>5 ± 0.03</td>
<td>197 ± 4</td>
</tr>
<tr>
<td>Ni</td>
<td>654 ± 25</td>
<td>190 ± 3</td>
<td>4 ± 0.2</td>
<td>173 ± 10</td>
</tr>
<tr>
<td>Cd</td>
<td>683 ± 19</td>
<td>221 ± 6</td>
<td>6 ± 0.2</td>
<td>1 ± 0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>543 ± 11</td>
<td>254 ± 5</td>
<td>3 ± 0.2</td>
<td>118 ± 6</td>
</tr>
<tr>
<td>Zn</td>
<td>973 ± 13</td>
<td>529 ± 32</td>
<td>37 ± 1</td>
<td>65 ± 2</td>
</tr>
<tr>
<td>Cr</td>
<td>435 ± 37</td>
<td>102 ± 2</td>
<td>8 ± 0.5</td>
<td>39 ± 5</td>
</tr>
</tbody>
</table>

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

*Table 7.* Metals bound by native *B. subtilis* walls, *E. coli* envelopes, kaolinite, and smectite (Walker et al., 1989)
et al., 1996; Hooper and Vitousek, 1997). However, the ecological mechanisms by which they are regulated and maintained are not well understood. Therefore, it is essential to identify these mechanisms to ensure successful management for conservation and restoration of diverse natural ecosystems.

van der Heijden et al. (1998) reported that below-ground diversity of AMF is a major factor contributing to the maintenance of plant biodiversity and to ecosystem functioning. This indicates the need to protect AMF and to consider these fungi as one of the items in future management practices to maintain diverse ecosystems. Further, they indicate that conservation of the fungal gene pool is likely to be a prerequisite for maintenance of floristic diversity in grasslands and other ecosystems such as boreal forests, where fungal web is known to affect allocation of resources between plant species. Mycorrhizal community is sensitive to perturbations, particularly those associated with cultivation and nutrient enrichment (Helgason et al., 1998). The findings of van der Heijden et al. (1998) demonstrate that biodiversity and ecosystem functions can be driven by microbial interactions.

Flouristically rich systems may display greater stability under stress (Tilman and Downing, 1994), are more likely to mitigate global problems posed by atmospheric CO2 enrichment (Naeem et al., 1994), and are more productive (Tilman et al., 1996). Van der Heijden et al. (1998) reported that microbial interactions can influence not only plant diversity but also productivity. Both the plant biodiversity, as measured by Simpson’s diversity index (Fig. 12a), and productivity above and below ground (Fig. 12b and c) increased with increasing AMF-species richness. The lowest plant productivity was found in those plots without AMF or with only a few AMF species. In contrast, plant productivity was highest when eight or 14 AMF species were present. This research indicates that plant productivity in a given ecosystem can be dependent on the diversity of symbionts. The results also indicated a mechanistic explanation for the effects of mycorrhizal-species richness on plant productivity. Increased AMF-species richness led to a significant increase in the length of mycorrhizal hyphae in the soil (Fig. 12d), to a decreased soil phosphorus concentration (Fig. 12e) and to an increased phosphorus content in plant material (Fig. 12f). Therefore, increasing AMF biodiversity results in more efficient exploitation of soil phosphorus and a better use of the resources available in the system. The loss of AMF biodiversity, which may occur in agricultural systems (Naeem et al., 1994; Steitwolf-Engel et al., 1997), could decrease ecosystem productivity.

The findings of van der Heijden et al. (1998) have clearly demonstrated the impact of the loss of below-ground biodiversity on the decrease of plant biodiversity and biological productivity of soils. This represents an understudied field of research, which requires increasing attention. A factor of central importance of soil to ecosystem functions is that soils on a global scale have a range of characteristics, which enable an enormous array of microorganisms, plants, animals, and humans to co-exist and thrive. Humans have exploited the ability of soils to provide massive amounts of food. More than 40% of the net primary production of the world are exploited by humans (Vitousek et al., 1986). The exploitation is increasing with the addition of 87.6 million people to the global population every year, with the rate addition steadily increasing (Brown and Flavin, 1996). The impact of population and the accompanying intensification of agriculture and industrialization on ecosystem functions and human health is, thus, of increasing concern.

The diversity of terrestrial vegetation systems is everywhere under stress. 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). A recognition of the significance of plant biodiversity in ecosystem stability and productivity has encouraged biologists to investigate the mechanisms that determine and affect species composition in plant communities. Future development of innovative land management strategies is essential to protect the terrestrial ecosystem and to supply food to sustain human health. Below-ground microbial diversity substantially influences plant biodiversity and ecosystem variability (van der Heijden et al., 1998). Furthermore, microbial events are, in turn, significantly affected by soil surface-reactive particles (Stotzky, 1986, 2002; Theng and Orchard, 1995). These reactive particles can influence the metabolic processes, growth, adhesion, and ecology of below-ground biological entities by interactions of their reactive surfaces with microbes. They can also indirectly affect these microbial events by modifying the spatial arrangement of soil particles especially the pore size distribution within soil aggregates as well as the physicochemical environments in which viruses, microbes, and macrobiota reside. Therefore, the effect of mineral–organic component–microorganism interactions on below-ground microbe-species richness and the impact on above-ground biodiversity and biological productivity should, thus, be an issue of intense interest for years to come.
Conclusions

Minerals, organic matter, and microorganisms have significant higher order interactions in terrestrial ecosystems. These interactions exert strong control over soil physical, chemical, and biological processes.

Organic substances and microorganisms substantially affect the formation and transformation of SRO sesquioxides. These oxides exert great influences on biogeochemical processes in the terrestrial ecosystem. Soil mineral surfaces play a vital role in the catalysis of abiotic formation of humic substances. Soil minerals, especially noncrystalline minerals have the ability to chemically stabilize SOM. Organic substances also act as binding agents to promote and stabilize aggregation. Therefore, noncrystalline minerals retard the microbial degradation of SOM, which in turn inhibits the transformation of noncrystalline mineral phases to more crystalline minerals. Hence, there are distinct interactive mechanisms between soil minerals,
organic matter, and microbes, which should have a direct influence on the stability and cycling of C, N, P, and S and global change.

To date, our understanding of the impacts of soil mineral–organic matter–microbe interactions on the transformation and degradation of anthropogenic organic compounds in soils is still relatively limited. The knowledge on detailed surface structures of the enzyme–mineral colloid and enzyme–humus complexes at the molecular level and the mechanisms of their catalysis in the transformation of organic contaminants need to be advanced. More research should examine new enzymes and new mineral composite supports to be used for catalytic degradation of a wide range of industrial and agricultural organic contaminants in soils.

Microorganisms and organics can profoundly affect the transformation of metals, metalloids and minerals in the terrestrial ecosystem. Biominalization is an important pathway of mineral formation in natural environments. More attention should be paid to environmental impact of biominalization on the fate of metals and metalloids. Furthermore, little is known on the influence of physico-chemical and microbiological interactions on the transformation, dynamics and toxicity of metals and metalloids in soil and related environments. The role of these interactions in remediation of metal- and metalloid-contaminated soils is an emerging issue in environmental protection.

To sum up, more research should be conducted to uncover the effects of physical–chemical–biological interactions on biogeochemical reactions, which, in turn, govern ecosystem biodiversity, sustainability and productivity. Use of advanced analytical instrumentation, i.e., synchrotron-based X-ray and infrared spectroscopies and atomic force microscopy and the like in this area of scientific pursuits should shed new light on the mystery of soil mineral–organic matter–microorganism interactions. Fundamental understanding of these interactions at the molecular level and the impacts on the terrestrial ecosystem would facilitate our development of innovative management strategies to regulate the behavior of the terrestrial ecosystem on a global scale. Future research on this extremely important and exciting area of science should be stimulated to restore as well as sustain the ecosystem integrity.

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