

Chapter 13

Speciation of Metals in Soils

DARRYL ROBERTS, *Water and Earth Science Associates, Limited, Ottawa, Ontario, Canada*

MAARTEN NACHTEGAAL, *Paul Scherrer Institut, Villigen, Switzerland*

DONALD L. SPARKS, *University of Delaware, Newark, Delaware, USA*

The chemical, physical, and biological behavior of trace and heavy metals in soils control their movement and fate in soils. While organisms have evolved in the presence of metals in the natural environment for thousands and millions of years, it is only since industrialization that high metal concentrations are consistently being introduced to soil environments globally. This increased exposure of organisms to metals underscores the need to identify and quantify those species in soils that pose the greatest potential threat to organisms. In addition, metal species identification has use for researchers studying soil fertility (e.g., micronutrient availability to crops), land-use planning (e.g., application of metal-bearing biosolids), water quality (e.g., wastewater treatment), soil genesis and geomorphology (e.g., redoxamorphic features of Fe oxides), environmental quality (e.g., mine tailings), soil ecology (e.g., metal toxicity to microorganisms), and soil remediation (e.g., liming of smelter-impacted soils). The ubiquity of metals combined with the complexity of soils makes the study of metals one of the most important disciplines of soil chemistry.

Potentially toxic metals can be introduced to many natural systems, and evidence for this introduction can be found in freshwater bodies, marine and lacustrine sediments, soils, ice, vegetation, and animal populations. Once introduced into a particular environment, metals are not necessarily restricted to its initial host matrix as there is a dynamic cycle between all of the aforementioned phases. For instance, metals introduced to soils from industrial processes may be taken up by plants, which then can be consumed by animals, which may be consumed by other animals. Or, soils may undergo erosion, introducing metals to rivers and lakes and eventually marine environments. The speciation of metals in all of these environmentally important materials is beyond the scope of this chapter, but given the potential of soils to cycle metals between the various phases, metal speciation in soils can be used to assess regional and global metal cycling in many environmentally relevant materials.

Metals are present in soils as a result of both natural and anthropogenic processes, and separating out the two sources is often not a trivial task. Figure 13-1

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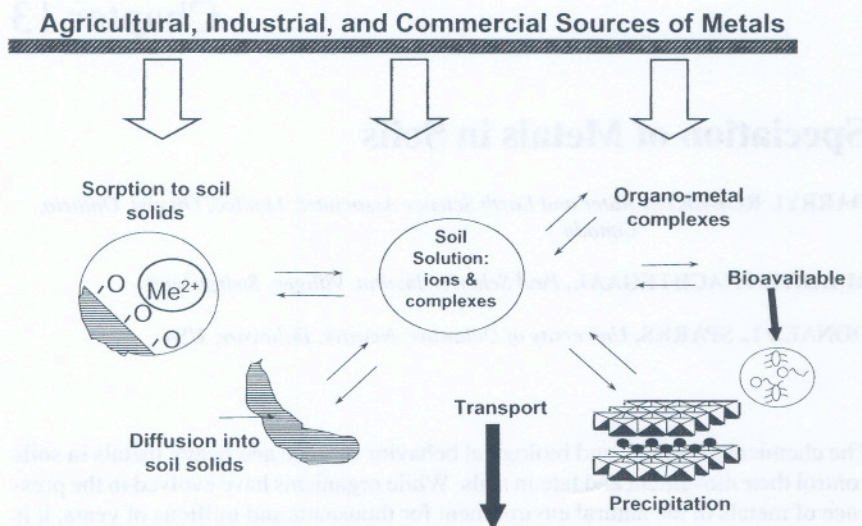


Fig. 13-1. Illustration of the various chemical and physical pathways a metal ion may encounter once introduced into the soil environment.

illustrates the fate of metals once introduced into soil environments from both natural and anthropogenic sources. Once the primary phase, be it naturally occurring or anthropogenic, is dissolved, metal ions may enter the soil solution and be subject to numerous pathways, all potentially overlapping. Each of the general pathways shown in the figure can be further divided into many more complex reactions, all with different kinetics and mechanisms. For instance, the role of colloids on metal partitioning and mobility in soils is a current research area that could keep a soil chemist occupied for decades. The soil solution may host the metal as a free ion or complexed to inorganic or organic ligands. Both the free ion and the metal-ligand complex can be exposed to one of several pathways, including: uptake by plants, mineral surfaces, and organic matter; transport through the vadose zone; precipitation as a solid phase; and diffusion into porous material. Reverse reactions also occur, making metal behavior in soils a truly dynamic process influenced by numerous physical and chemical processes. The three main pools a metal can be found in soils are (i) the soil solution, (ii) sorbed to solid phases, and (iii) as part of the structure of solid phases. The speciation of metals and trace elements in soil solutions is presented in Sauvé and Parker (2005, this publication), so the majority of this chapter will emphasize the latter two pools. Following an introduction to soil speciation and the various parameters influencing metal speciation, the various approaches and techniques that have been developed to determine metal speciation will be presented.

ORIGINS, INPUTS, AND SOURCES OF METALS IN SOILS

Before proceeding, it would be constructive to provide a definition for the broad term "metal" with respect to environmental soil chemistry and to present the

metals that are of interest to researchers in this field. Metals have traditionally been classified based on categories such as light, heavy, semimetal (metalloid), toxic, and trace, depending on several chemical and physical criteria. Density, weight, atomic number, and degree of toxicity have all been used to classify metals. The term heavy metal is commonly used to encompass those metals found in soils and sediments that are associated with contamination and toxicity, but a definition of heavy metal is not universally agreed upon and a list of metals or metalloids considered to be a heavy metal will vary between researchers (Duffus, 2002). Metals can be further classified according to their hard and soft characteristics, based on the principle of hard and soft acids and bases (Sparks, 1995). All metal ions or atoms and most cations are Lewis acids and are capable of accepting a pair of electrons from a Lewis base (anion). Further categorizing metals, most are soft or transition acids, meaning they have low positive charge and large size and form covalent bonds with ligands.

Trace metal and micronutrient are terms that are often used in soil science and agronomy as those species found in low concentrations in soils that are essential for plant growth; however, a trace metal also may be found in elevated concentrations in soils and sediments due to both natural and anthropogenic processes, thereby negating the term "trace." For the purposes of this chapter, metals will include both heavy and moderately heavy (based on atomic mass) metals found in soils in both trace amounts and elevated concentrations to the point of plant and animal toxicity in some cases. Based on these criteria, the metals that can be considered important for the remainder of this chapter include: As, Cd, Co, Cr, Cu, Ni, Pb, Se, and Zn. In addition to high concentrations of certain metals causing plant and organism (both microbial and human) toxicity, deficiency problems are an issue with elements that are considered essential nutrients. Therefore, a concentration regime exists for several metals with respect to organism health and going below or above this regime can result in deficiency or toxicity symptoms, respectively.

Establishing a metal concentration range for a normal soil (i.e., background level) compared with a contaminated soil is very difficult. The parent material and geochemical history of a soil can result in metal concentrations that would be considered polluted compared with soils with so-called "normal" background metal concentration levels. Typical concentrations for some metals found in soils that are not considered contaminated and do not have parent material that is high in these metals are: 20 mg Cu kg⁻¹ soil, 1 mg Cd kg⁻¹ soil, 50 mg Ni kg⁻¹ soil, 25 mg Pb kg⁻¹ soil, and 50 mg Zn kg⁻¹ soil (Förstner, 1995). That is not to say that metal concentrations that exceed these values can be considered polluted and pose a serious threat to organisms. As will be discussed in this chapter, it is not the total metal concentration that dictates the risk of toxicity, but rather the form the metal is in which is dependent on many chemical, physical, and biological parameters. This last statement is one of the fundamental reasons metal speciation is determined, although its acceptance is by no means universal.

One of the first things to consider when determining metal speciation in soils is the original source of the metal. Is the metal from natural weathering, industrial processing, use of metal components in commercial processes, aerial deposition of smelting materials, leaching from garbage and solid waste dumps, application of animal products to land, or some other source? These processes and more can in-

roduce all of the metals previously mentioned, often concurrently. Physical and chemical alterations to the species are unavoidable in terrestrial and geochemical settings such as soils, so identifying the source will not guarantee that the species in the soil will be identified (Förstner, 1995). In the absence of pollutants, natural levels of metals in soils are dictated by the types of elements in rocks, weathering rates, organic matter content, soil texture, and soil depth. Most of the materials added to soils for agricultural purposes such as lime, inorganic fertilizers, and manure have low trace element levels and when applied at normal rates do not affect overall concentrations of trace metals in soil. Other sources of input with respect to agriculture include herbicides, fungicides, irrigation waters, biosolid application, dredged materials, fly ash, and municipal composts (Förstner, 1995).

Often times in the soil environment, the metal of concern in terms of potential toxicity is only toxic due to the characteristics of the soil environment it is in. For example, at circum-neutral pH values most metals are in a form that makes them unavailable for direct plant uptake in the aqueous form; however, this can be disputed since the environment in the immediate vicinity of plant roots, which is not necessarily measured when the bulk pH is determined, can be several pH units lower and solubilize metals that are considered stable. Often times the source of metal pollution is also responsible for the co-contamination by addition of chemical species that are capable of altering the soil environment. For instance, acid rain deposition, acid mine drainage, and deposition of sulfate from smelting activities can all cause acidic pH values in soils and lead to mobilization of metals that were once stable as adsorbed or precipitated complexes. As will be discussed, most metals are more readily available for plant uptake at low pH values, hence the onset of severe phytotoxicity to plants at low pH values: the pH solubilizes metal ions that are normally bound in a form not available for plant uptake. Clearly, the pH of the soil is one of the most important parameters in assessing metal speciation and many consider it the master variable when it comes to many environmental processes.

METAL SPECIATION AND BIOAVAILABILITY

The term *speciation*, just like "metal," is a multi-faceted term and difficult to assign a single definition. Metal speciation includes the chemical form of the metal in the soil solution, either as a free ion or complexed to a ligand, in the gaseous phase, and distributed amongst solid phases within the soil. Therefore, for a comprehensive description and understanding of metal speciation in soils, one would address all the various phases a metal may inhabit; however, the solid phase contains the majority of metals in soils and supplies the other two phases accordingly. This chapter will primarily deal with metal speciation in the solid phase, while the speciation of metals in the solution phase is addressed in Bartlett and Ross (2005, this publication). One should note that the separation of these topics into different chapters does not indicate they are separate phenomena in the soil. To the contrary, the long-term bioavailability of metals to humans and other organisms is determined by the re-supply of the metal to the mobile pool (soil solution) from more stable phases (metals in and associated with solid species).

The quantitative speciation of metals as well as their variation with time is an important concept in environmental soil chemistry. In order to develop models capable of predicting the fate of nutrients and contaminants in soils an accurate description of the partitioning of these constituents between the solid and solution phases is necessary (Schulze and Bertsch, 1995). Before any remediation strategy is attempted it is wise to determine and understand the nature of the metal species in soils. According to Mattigod et al. (1981) "positive identification of various solid phases of a trace metal in a soil, along with knowledge of their solubility and their kinetics of dissolution and precipitation, would provide sufficient information to make reliable predictions of trace metal activities in soil solutions." Speciation encompasses both the chemical and physical form an element takes in any geochemical setting. A detailed definition of speciation includes the following components: (i) the identity of the contaminant of concern or interest, (ii) the oxidation state of the contaminant, (iii) associations and complexes to solids and dissolved species (surface complexes, metal-ligand bonds, surface precipitates), and (iv) the molecular geometry and coordination environment of the metal (Brown et al., 1999). All of the above components can be interrelated and often difficult to separate. Moreover, they all have chemical, biological, and physical considerations and for this reason metal speciation is truly a multidisciplinary endeavor. The more of these parameters that can be identified the better one can predict the potential risk of toxicity to organisms by heavy metal contaminants.

Another vague term, albeit used often, used with respect to speciation of contaminants in soils is bioavailability. There is no universally accepted definition for bioavailability and it is usually a non-quantitative concept. An essential or toxic element is bioavailable if it is in a chemical form that plants can absorb readily and if, once absorbed, it affects the life cycle of the plants (Sposito, 1989). This definition is confined to the case of plants, but the same general definition can be used for humans and soil organisms (both micro- and macro-). Moreover, bioavailability can be desirous in the case of plant uptake of the required amounts of essential nutrients, or detrimental in the case of uptake of non-essential elements or essential elements at elevated levels. Despite the uncertainty associated with the term, there is a general consensus that the form the metal takes is correlated to the bioavailability of the metal. In the case of Pb, for example, the pathway for humans is often direct ingestion into the body and dissolution of phases in gastric acid. By simulating gastric conditions (pH 1–3; $T = 278\text{--}328\text{ K}$) it was found that the nature of the Pb phases in contaminated soils influenced the Pb release and, therefore, bioavailability (Gasser et al., 1996). While bioavailability may be considered a form in which the metal can pass through a living-cell membrane, this does not necessarily mean an organism will remove it from solution. For example, bacteria and fungi are known to have mechanisms to tolerate high metal concentrations in soils including binding the metal with proteins or extracellular polymers, formation of insoluble metal sulphides, and decreased uptake (Giller et al., 1998). Considering the fact that the presence of a metal, even in a potentially available form, does not automatically mean an organism will take it up, a better definition for bioavailability is the amount or concentration of a chemical that can be absorbed by an organism thereby creating the potential for toxicity or the necessary concentration for survival (Siegel, 2002).

Determining metal speciation in soils can be quite complex as thermodynamic models may give suggestions as to the possible species to expect in a system, but metal species are usually controlled by kinetics of the reactions. In addition, many techniques used to determine speciation directly are disruptive or destructive to a sample and may alter the chemical speciation (Förstner, 1987). To alleviate some of the difficulties in determining metal speciation in soils, laboratory-based approaches are often used since most parameters can be controlled and monitored; however, simulating the conditions found in the field is quite difficult, leading to questionable findings when trying to apply to field situations. In most laboratory experiments large quantities of metals are added as soluble salts during a short period of time, rather than gradually added during a long period of time, which is more indicative of what one may find in natural settings. In addition to possible changes in metal sorption mechanisms due to this discrepancy, there also is a difference to biological communities. If added gradually over time, a metal can constitute a constant stress that can be endured, avoided or overcome whereas an immediate addition of metal leads to a drastic and sudden disturbance that does not allow for adaptation (Giller et al., 1998). Despite the shortcomings in laboratory approaches to simulate field conditions, these types of studies have paved the way to understand metal speciation in soils and, therefore, will be referred to in upcoming sections of this chapter.

METAL SPECIES AND REACTIONS IN SOILS

The general category of reactions considered the most important with respect to metal speciation in soils is sorption. Sorption is a general term that encompasses many different mechanisms and refers to the general removal of a metal ion from solution and its subsequent association with the soil solid fraction. The reverse of this process, or the removal of a metal from a solid material and introduction into the soil solution, is termed desorption. The various mechanisms of metal sorption that occur in soils are illustrated in Fig. 13-2. These mechanisms will be discussed in the following subsections. Sorption reactions of metals in soils to a large extent dictate their mobility, fate, and bioavailability and are therefore vital to understand when attempting to understand metal speciation. The removal of metals from soil solutions by inorganic and organic phases is a process by which toxic metals can be sequestered, potentially alleviating deleterious environmental effects. It is possible that several mechanisms may contribute to the removal of a metal ion from solution concurrently. One way of considering the relationship between sorption of metals on soil components and metal speciation is to think of sorption as the reaction that involves the metal ion and the speciation as the end product of this reaction; however it is important to note that just as the speciation of a metal changes over time, sorption is also a dynamic process. The speciation of a metal at any one time is merely a snapshot and it is subject to changes as the sorption mechanisms change. Figure 13-3 illustrates the time scales of many metal sorption processes in soils and demonstrates the fact that, with respect to both time and metal concentration, several mechanisms of sorption may overlap with one another.

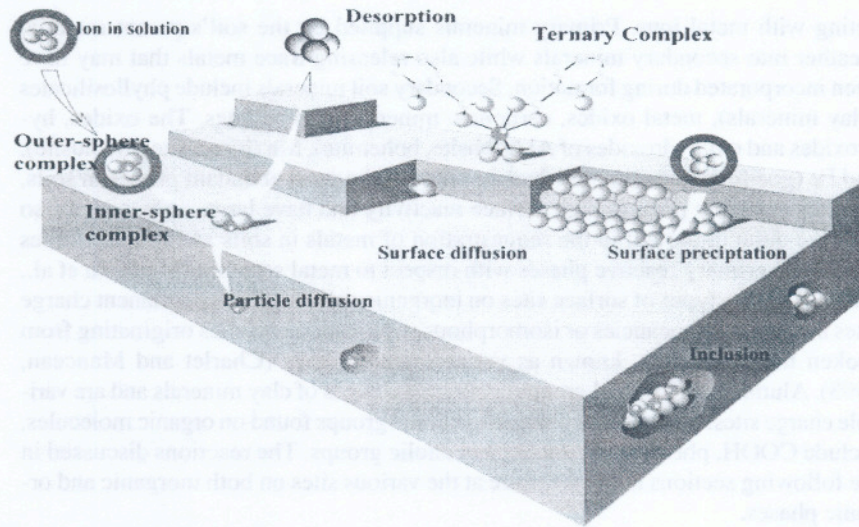


Fig. 13-2. Conceptual drawing of the various metal sorption processes that can occur on mineral surfaces (after Manceau et al., 2002).

In addition to time being a significant factor in determining metal speciation, the presence of crystalline and amorphous inorganic phases and organic material plays an important role in metal sorption and speciation. The solid fraction of a soil is a collection of non-living, living, and previously living material all capable of re-

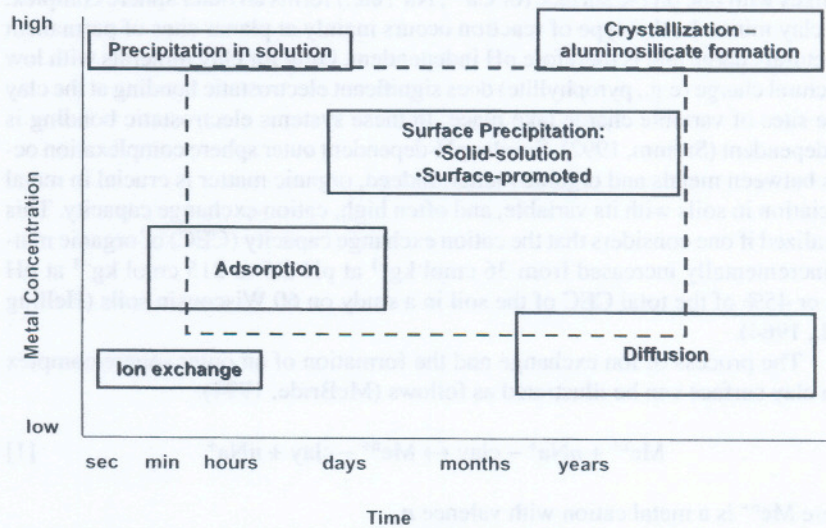


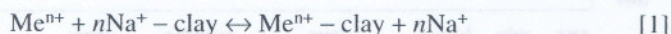
Fig. 13-3. The effect of time scales and metal concentration on various metal sorption mechanisms. The dotted line serves to connect many of the various mechanisms due to the potential continuum of processes (adapted from McBride, 1994).

acting with metal ions. Primary minerals supplied by the soil's parent material weather into secondary minerals while also releasing trace metals that may have been incorporated during formation. Secondary soil minerals include phyllosilicates (clay minerals), metal oxides, carbonate minerals, and sulfates. The oxides, hydroxides and oxyhydroxides of Al (gibbsite, bohemite), Mn (birnessite, pyrolusite), and Fe (goethite, hematite, ferrihydrite) are not the most abundant phases in soils, but they typically possess high surface reactivity and have large surface areas, so they are quite important in the sequestration of metals in soils and in many cases can be the primary reactive phases with respect to metal sorption (Manceau et al., 2002). The two types of surface sites on inorganic solids include permanent charge sites arising from vacancies or isomorphous substitution and sites originating from broken mineral lattice, known as variable charge sites (Charlet and Manceau, 1993). Aluminol and silanol groups occur on the edges of clay minerals and are variable charge sites. The variable charge functional groups found on organic molecules, include COOH, phenolic, alcoholic, and enolic groups. The reactions discussed in the following sections may take place at the various sites on both inorganic and organic phases.

Exchangeable Metal Ions (Outer-Sphere Complexes)

Both inorganic and organic solids in soils possess permanent charge sites that are often negatively charged, depending on pH. Positively charged metal cations that come into contact with these sites may form an electrostatic bond of low energy often referred to as cation exchange. In soil science, the term "cation exchange" is used to characterize the replacement of one adsorbed, readily exchangeable cation by another (Sposito, 1989). The metal cation in the soil solution that exchanges with one on the surface (or Ca^{2+} , Na^+ , etc.) forms an outer sphere complex. For clay minerals, this type of reaction occurs mainly at planar sites of permanent structural charge and is therefore pH independent. Only for clay minerals with low structural charge (e.g., pyrophyllite) does significant electrostatic bonding at the clay edge sites of variable charge take place. In these systems electrostatic bonding is pH dependent (Stumm, 1992). Similar pH-dependent outer sphere complexation occurs between metals and organic matter. Indeed, organic matter is crucial in metal speciation in soils with its variable, and often high, cation exchange capacity. This is realized if one considers that the cation exchange capacity (CEC) of organic matter incrementally increased from 36 cmol kg^{-1} at pH 2.5 to 215 cmol kg^{-1} at pH 8.0, or 45% of the total CEC of the soil in a study on 60 Wisconsin soils (Helling et al., 1964).

The process of ion exchange and the formation of an outer sphere complex on a clay surface can be illustrated as follows (McBride, 1994):



where Me^{n+} is a metal cation with valence n .

In general, multivalent cations effectively displace monovalent cations from clay exchange sites when the monovalent cation concentration is low. Studies on $\text{Na}^+ - \text{Me}^{2+}$ exchange reactions on Na^+ -saturated montmorillonite have shown that

$\text{Na}^+ - \text{Me}^{2+}$ is pH-independent below pH 6 (Inskeep and Baham, 1983). If, however, the monovalent cation concentration is high (e.g., high ionic strength), the competition for exchange sites may induce formation of adsorption complexes between the metal ion and surface. The dependence on ionic strength is one of the characteristic features of ion exchange-outer sphere complexation and is often used as a macroscopic assessment to determine if this sorption mechanism is operational.

Ion exchange reactions at surface sites exposed to solution are extremely fast and are difficult to measure by conventional methods. Cation exchange on 1:1 clays without interlayer regions (e.g., kaolinite) and 2:1 clays with expanded interlayer regions (e.g., montmorillonite) appears to be instantaneous (McBride, 1994). Kinetics of metal exchange is much slower on 2:1 interlayered minerals that may have K^+ within the interlayer region (e.g., vermiculite), since many of the exchange sites inaccessible for exchange with metal ions and the exchange process is diffusion limited (Sparks, 1995). In addition to having rapid kinetics of formation, outer sphere complexes are typically fully reversible and therefore do not represent a significantly stable metal sequestration pathway in most soil environments; however, the fact that this process is fairly rapid and energetically favorable is crucial if one considers the importance of micronutrient availability to plant roots, as ion exchange is the primary mechanism for this process. Just as the formation is fairly easy and fast, so is the reverse process. During long time scales, outer sphere complexes are not stable and will most likely convert to more stable sorption complexes.

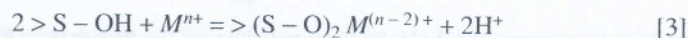
Specifically Adsorbed Metal Species (Inner Sphere Complexes)

If a metal ion forms an ionic or covalent bond directly with a surface functional group, a stable molecular entity termed an inner sphere complex forms, otherwise known as a specific adsorption complex. These types of complexes do not have a water molecule present between the surface group and metal ion, resulting in a stronger bond compared to the electrostatic interaction of an outer sphere complex. Inner sphere complexes can be further categorized as monodentate if the metal is bound to one surface oxygen and bidentate if it is bonded to two (Sparks, 1995). Inner sphere adsorption complexes have been directly observed and established as quantitatively important species in soils contaminated with Pb (Morin et al., 1999) and Zn (Roberts et al., 2002). Adsorption complexes are two-dimensional molecular arrangements and do not include the formation of three-dimensional phases or diffusion phenomena, as will be discussed further in this section.

The adsorption of a metal ion, M , on an octahedral aluminol site has the following generalized reaction (McBride, 1994):



Reaction [2] is an example of a monodentate adsorption complex since only one oxygen group has participated in the reaction. A bidentate inner sphere complex has the generalized form:



where S–OH may be either a silanol or aluminal group.

Reactions [2] and [3] have at least four features that distinguish them from cation exchange (McBride, 1994):

1. Release of H^+ ions as Me^{n+} cations are adsorbed.
2. A high degree of specificity.
3. A desorption rate that is orders of magnitude slower than the adsorption rate.
4. A change in the measured surface charge toward a more positive value.

In addition to the above observations, further generalizations regarding metal adsorption via inner sphere complexes can be made:

1. As adsorption proceeds, it will affect the speciation of trace metals and ligands that remain in solution.
2. In general, $>Al-OH$ groups are more effective at adsorbing metal ions than $>Si-OH$ groups on mineral surfaces.
3. The more electronegative a metal, the higher its preference for adsorption on a reactive site on a mineral.

Abrupt increases in divalent metal ion adsorption in soils occur over a critical pH range, often less than one unit, termed the pH edge. This tends to correspond to the point where metal ions hydrolyze to form MOH^+ (Jones and Jarvis, 1981); however, changes in reactive sites on the sorbent phase as a result of pH changes also can play a role in this observed edge. Figure 13-4 shows a typical pH edge in the case of Ni on a soil clay fraction. To obtain this edge, an experiment was conducted in which all parameters (time, temperature, metal concentration) were held constant except for pH.

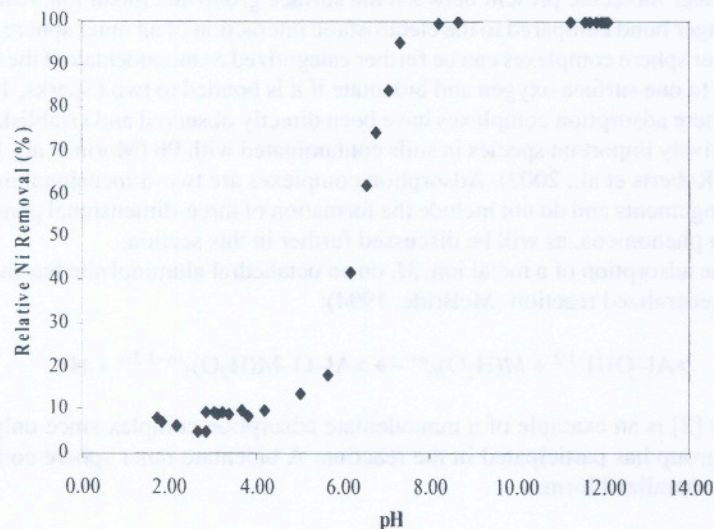


Fig. 13-4. Experimental Ni pH edge for Ni reacted with a soil clay fraction (from Roberts et al., 1999).

The methods of determining the mechanisms of metal adsorption (including inner sphere and outer sphere complexation) in soils include direct identification, macroscopic approaches, and one or both of the latter two combined with adsorption models. Direct identification methods will be discussed in the section on determining metal speciation. Macroscopically, adsorption isotherm experiments are often used to describe the relation between the equilibrium concentration of a metal ion in solution and the quantity of metal adsorbed to a solid surface. There are classically four types of isotherms based on the curve shape one gets when plotting amount of metal in solution vs. amount of metal adsorbed: S (s shaped), L (Langmuir), H (high affinity with steep slope), and C (linear) (Sparks, 1995). Often times experimentalists have assigned a particular mechanism to metal removal from solution by a solid phase based on the shape of the adsorption isotherm. Caution should be taken in making this type of assessment as these isotherms are based purely on macroscopic observations and in no way reveal any mechanistic information. Surface complexation models are further used to describe metal adsorption on soil surfaces, but again do not provide direct identification of metal species. A thorough review of surface complexation models as applied to soil chemistry can be found elsewhere (Goldberg, 1992).

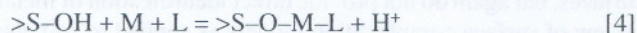
The potentially strong inner sphere complex formed between a metal cation and a sorbent phase can provide an effective way to immobilize metals in soil environments. These phases may be quite stable over time and therefore should be considered in any metal speciation assessment. It is also important to realize that outer sphere and inner sphere complexes may not be mutually exclusive, and typically one may find a continuum between the two mechanisms exists. This is the case with any of the mechanisms that remove metal ions out of the soil solution. It is merely for the sake of simplicity of explanation of concepts that the various reactions of metals in soils are separated into separate sections in this chapter. The continuum phenomenon is especially evident in the case of adsorption and precipitation, as will be discussed in a later section.

Ternary Adsorption Complexes

In soils, metals are rarely the only species found in the soil solution and are often found complexed to both organic and inorganic ligands. For this reason metal adsorption may be different from the fairly "clean" description described above. Ligands are classified as atoms or molecules capable of donating electrons in a bond. By this definition, the oxygen atoms associated with silanol and aluminol groups on soil minerals are ligands. In solution, ligands can be inorganic, such as Cl^- , CO_3^{2-} , and SO_4^{2-} , or organic such as carboxyl and phenolic sites associated dissolved organic matter (DOM) (Sparks, 1995). Most metals discussed in this chapter are capable of reacting with both types of ligands in soils. The possible scenarios encountered include metal-ligand complexes that remain in solution, precipitated metal-ligand compounds, and metal-ligand complexes that adsorb on the sorbent phase (ternary complexes). The general effects of metal-complexing ligands in the soil solution on the adsorption of metal cations to soil minerals can be classified as follows (Sposito, 1989):

1. The ligand has a low affinity for the metal and for the adsorbent.
2. The ligand has a high affinity for the metal and forms a soluble complex with it, and this complex has a low affinity for the adsorbent.
3. The ligand has a high affinity for the metal and forms a soluble complex with it, and this complex has a high affinity for the adsorbent.
4. The ligand has a high affinity for the adsorbent, and the adsorbed ligand has a low affinity for the metal.
5. The ligand has a high affinity for the adsorbent, and the adsorbed ligand has a high affinity for the metal.
6. The metal has a high affinity for the adsorbent, and the adsorbed metal has a high affinity for the ligand.

Categories 3 and 5 result directly in enhanced metal adsorption from the presence of ligands by forming metal-ligand ternary complexes. Ternary complex formation can be represented by the following equations:



or



where S-OH is the surface functional group, M is the metal, and L is the ligand.

In Reaction [4], the metal bonds to the surface functional group, and the ligand to the metal. In Reaction [5], the ligand is between the surface functional group and the metal. Due to ternary complex formation, solubilities of metals and anions in soils are lowered below those expected from either adsorption or precipitation.

Examples of ternary complex formation are quite difficult to demonstrate directly in actual soils, but in simulated laboratory systems recent advances in characterizing these reactions have been made. It has been demonstrated that in the case of U(VI) complexation to hematite in the presence of carbonate, a hematite-U(VI)-carbonate structure formed, similar to Reaction [4] (Bargar et al., 2000). Elzinga et al. (2001) demonstrated the formation of Pb-sulfate ternary complexes on the surface of goethite by probing both the sulfate and Pb with infrared spectroscopy and x-ray absorption spectroscopy, respectively. Details of these techniques will be discussed in the next section. In addition to ternary complex formation, the Pb promoted the adsorption of sulfate to goethite as a result of Pb changing the surface charge. The complexes formed in this system are presented in Fig. 13-5. In Fig. 13-5a, Pb and SO_4^{2-} complex directly to the goethite surface independently, but some interaction was still observed. In Fig. 13-5b, a similar complex as Reaction [4] above is seen. Whether the complex forms in solution prior to complexation or if the sulfate first adsorbs to the surface followed by complexation of the Pb to the sulfate was not determined. In soil environments, such ternary complexes may be more the rule than the exception, but few studies have successfully identified these complexes given the complexity of soils. The presence of ligands in an ion-sorbent complex has been shown to influence the atomic coordination environment of the ion and, therefore, may lead to differences in the stability of metal sorption complexes. One should keep in mind that both the solid and solution phases in soils are extremely

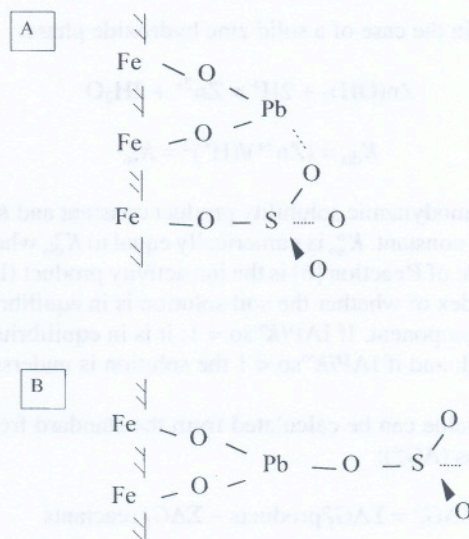


Fig. 13-5. Deduced surface complex formation for Pb and sulfate co-adsorbed on the surface of goethite. (A) Independent adsorption with some electrostatic interaction and (B) ternary complex (from Elzinga et al., 2001).

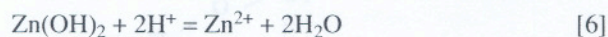
heterogeneous and competition for metals between sorption sites, ligands, and precipitated solids is commonplace.

Precipitated Metal Species

The previous two subsections have described metal species that were potentially easily bioavailable, especially if the sorption complexes had not aged and transformed to more stable entities and/or a perturbation of equilibrium induced metal release. Metal precipitates are potentially much more stable sinks for metals in soil environments and there are several pathways for their formation, both in the soil solution and on or near surfaces of solid phases in soils. In recent years, soil chemists have discovered that the occurrence of these phases in soils is probably more common than previously expected, thanks in part to the application of advanced analytical techniques (Ford et al., 1999; O'Day et al., 1994a; Roberts et al., 1999; Scheidegger and Sparks, 1996b). Prior to the application of techniques capable of directly probing metal species in soils and on soil minerals, macroscopic approaches were the main tool to decide whether or not a precipitated phase was a viable metal form.

One classical method for determining whether or not a solid precipitate is controlling the metal ions in the soil solution is the thermodynamic solubility product approach. In this approach, one compares the ion activity product (IAP) in soil solutions (assuming equilibrium) with the equilibrium ion activity products for various solid phases. The activity of any solid phase is defined as 1 if it exists in a pure form and is at standard pressure and temperature.

For example, in the case of a solid zinc hydroxide phase:



$$K_{\text{dis}} = (\text{Zn}^{2+})/(\text{H}^+)^2 = K_{\text{so}}^{\circ} \quad [7]$$

where K_{so}° = the thermodynamic solubility product constant and K_{dis}° = the thermodynamic dissolution constant. K_{so}° is numerically equal to K_{dis}° when the solid phase is pure. The right side of Reaction [6] is the ion activity product (IAP) and together with the K_{so}° is an index of whether the soil solution is in equilibrium with a given inorganic mineral component. If $\text{IAP}/K_{\text{so}}^{\circ} = 1$; it is in equilibrium. If $\text{IAP}/K_{\text{so}}^{\circ} > 1$ it is supersaturated; and if $\text{IAP}/K_{\text{so}}^{\circ} < 1$ the solution is undersaturated (Sparks, 1995).

The log K_{dis}° value can be calculated from the standard free energy accompanying the reactions (ΔG_r°):

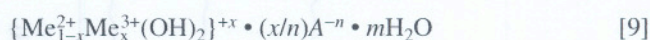
$$\Delta G_r^{\circ} = \sum \Delta G_f^{\circ} \text{products} - \sum \Delta G_f^{\circ} \text{reactants} \quad [8]$$

where ΔG_f° is the standard free energy of formation.

Published values can be found for many solid phases for which standard free energy data are known (Lindsay, 1979). The minerals whose solubility products are equal to the measured IAP are assumed to be present and hence control metal activities in the soil solution. Unfortunately, this approach has many limitations. First, thermodynamic solubility data must be known for all potential precipitates, as well as their solid-solutions. In addition to equilibrium data not being known for solid phases, the dissolution-precipitation kinetic data also is limited. Often the most less-stable, more-soluble phase will precipitate out of solution faster than a more-stable, less-soluble solid phase. Also, this approach is most successful for elements with moderate to high total concentration in soils (Al, Fe, Ca) and it does not work as well for trace elements (Cu, Zn) unless the soil is grossly contaminated with the element in question (McBride, 1994).

A major shortcoming of using the equilibrium solubility approach is that it considers the precipitation of known phases from solution without consideration of a solid surface (clay minerals, oxides, organic matter). If one considers solid surfaces when investigating the formation of metal precipitates, it becomes clear that precipitation can occur under conditions in which bulk precipitation is not anticipated. According to Ford et al. (2001), the solid surface may promote metal precipitation by (i) the sorbent changing sorbate properties to drive precipitation and (ii) the sorbent modifying the solution composition near the mineral-water interface which induces precipitation. Their review article describes four scenarios under the general term of "surface precipitation": (i) increased metal ion activity at a mineral surface leading to precipitation, (ii) increased population of metal ions near the solid surface due to a net attractive force, (iii) a two-dimensional adsorption complex incorporating into the mineral structure as it continues to grow, and (iv) an unstable mineral surface dissolving as metal ions are sorbed, yielding a mixed metal precipitate phase. The last scenario does not necessarily require that the newly formed precipitate have a structural link to the substrate. Another term for this mech-

anism of surface precipitation is dissolution-induced homogeneous precipitation (Manceau et al., 2002). Considering the fact that soils are under a continuous state of weathering and are never truly at equilibrium, it stands to reason that Scenario 4 may be quite common in contaminated soils. For example, a mixed Ni–Al layered double hydroxide phase formed when Ni was reacted with a soil at pH 7.5 that contained many Al-bearing minerals (kaolinite, vermiculite, gibbsite) (Roberts et al., 1999). The identity of this phase in a soil sample would not have been possible without earlier experiments with Ni and reference Al-bearing minerals (Scheckel and Sparks, 2000; Scheidegger et al., 1997). The general formula for these phases can be written as:



where Me^{2+} could be Co(II), Fe(II), Mg(II), Mn(II), Ni(II), or Zn(II), and Me^{3+} is Al(III), Cr(III), or Fe(III). Interlayer anions, A^{-n} , can be represented as Br^- , Cl^- , ClO_4^- , I^- , NO_3^- , or OH^- . The net positive charge, x , is counterbalanced by an equal negative charge, n . The remaining interlayer space is occupied by water molecules, m . The divalent and trivalent cations are distributed within the brucite-like octahedral hydroxide structure.

Several key observations have been made regarding the formation of solid solutions or mixed-metal surface precipitates in soil environments. In the past it was thought that most surface precipitates formed only after hours or days, but it has been seen that they can form in a matter of minutes (Elzinga and Sparks, 1999; Scheidegger et al., 1996). Over time these precipitates may become more resistant to dissolution since initial precipitates are often amorphous and have a higher free energy than crystalline phases of similar composition. The increased stability of these phases with time has been observed experimentally and in the case of Ni–Al layered double hydroxides has been attributed the gradual transformation to a precursor Ni phyllosilicate phase (Ford et al., 1999; Scheckel et al., 2000). In most cases the ionic radius of the metal must be small enough to allow it to enter octahedral sites. For this reason the relatively large Pb^{2+} ion can strongly sorb on aluminum hydroxide but it cannot substitute into the hydroxide during coprecipitation. This is a major consideration given the high toxicity level associated with Pb in soils. On the other hand, Cr^{3+} and Mn^{3+} can replace Fe^{3+} and Al^{3+} in precipitating oxides and hydroxides due to the similar ionic radii (McBride, 1994). Mn and Ni were found to be incorporated into both goethite and hematite, while Cd and Pb were not (Ford et al., 1997).

The pH of the soil also is a factor that may control the onset of surface precipitation. In experiments conducted from pH 6.0 to 7.5 it was found that Ni–Al layered double hydroxide phases only formed on a soil clay fraction above pH 6.8, regardless of reaction time. Figure 13–6 illustrates this finding, with sorption data at pH 6.0, 6.8, and 7.5 shown along with corresponding spectra from x-ray absorption fine structure (XAFS) spectroscopy in the right panel. At pH 6.0, even after several days, no sign of precipitation was found because the necessary threshold pH value was not met. The effect of this difference in sorption mechanisms influenced the release of the Ni, with the pH 6.0 sorption system releasing the greatest relative amount of Ni (Fig. 13–7).

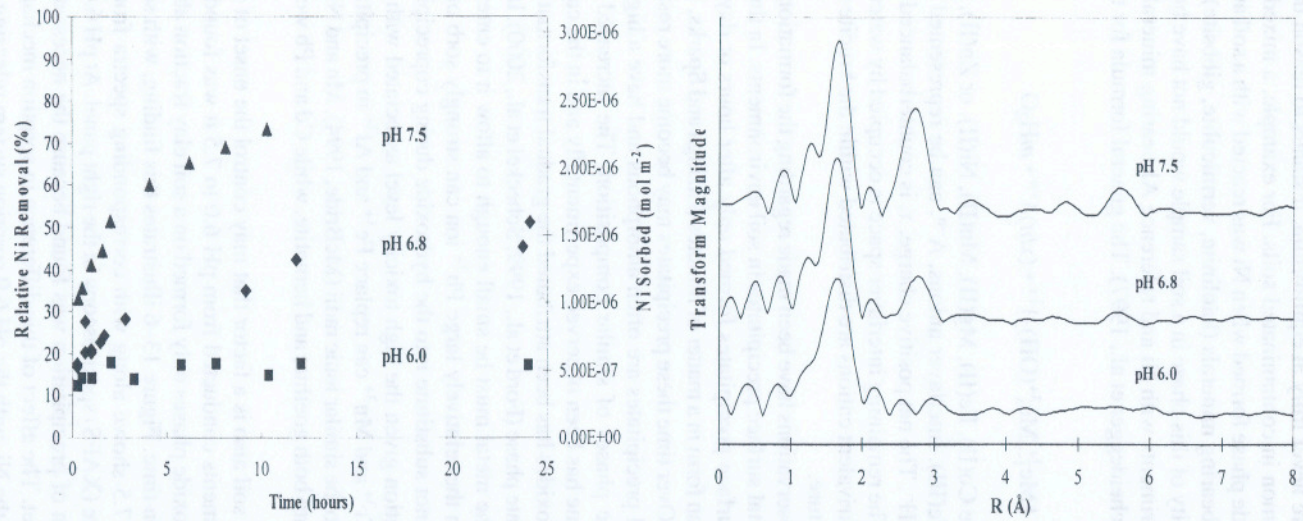


Fig. 13-6. Ni sorption kinetics on soil clay fraction at pH 6.0, 6.8, and 7.5. In the right hand panel, EXAFS radial structure functions demonstrate Ni-Al layered double hydroxide formation at pH 6.8 and 7.5, but not at pH 6.0 (from Roberts et al., 1999).

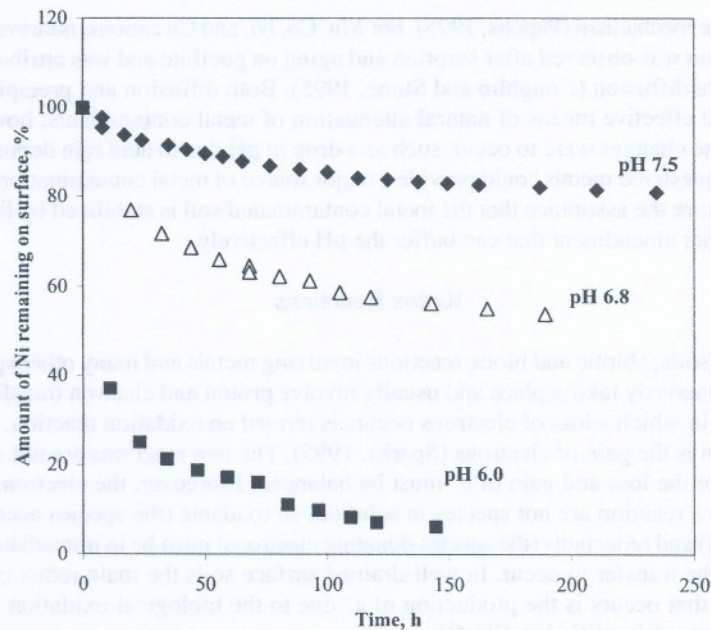


Fig. 13-7. Ni desorption-dissolution from reacted soil clay in Fig. 13-6 after reacting for several hundred hours.

Diffused Metal Species

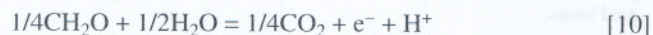
Diffusion is a physical process whereby a substance can be removed from the bathing solution around a mineral phase and therefore falls under the broad classification of sorption. Soils are porous materials consisting of both macropores (>2 nm) and micropores (<2 nm) making diffusion a major mechanism of metal sorption, especially over long time scales found in natural settings (Sparks et al., 1999). For a metal ion to reach all potential sorption sites it must be transported through the bulk solution, travel through the liquid film on the solid surface (film diffusion), traverse pores within an individual particle (intra-particle pore diffusion) or pores between particles (inter-particle pore diffusion), and penetrate into the solid matrix (Pignatello and Xing, 1996; Sparks et al., 1999). Pore diffusion and matrix diffusion are considered as probably transport-limiting processes (Sparks et al., 1999). The sorbed metal ion diffuses into the sorbent, filling vacancies or substituting for sorbent atoms. This phenomenon may be responsible for the progressive decrease of metal mobility in soils.

There are several examples in the literature that ascribe slow metal sorption and hysteretic desorption behavior to diffusion processes. Brümmer et al. (1988) monitored the kinetics of Ni, Zn, and Cd adsorption and desorption by goethite. A diffusion-dependent adsorption and fixation process of the metal cations inside the goethite structure was proposed as the reason for the observed desorption hysteresis. For Cd and Se adsorption on porous aluminum oxide, XPS results verified that adsorbate intra-particle diffusion followed by sorption was the predominant Cd and

Se uptake mechanism (Papelis, 1995). For Mn, Co, Ni, and Cu cations, nonreversible adsorption was observed after sorption and aging on goethite and was attributed to slow pore diffusion (Coughlin and Stone, 1995). Both diffusion and precipitation can yield effective means of natural attenuation of metal contaminants; however, if extreme changes were to occur, such as a drop in pH due to acid rain deposition, these sequestered metals could provide a major source of metal contamination. This may require the assurance that the metal contaminated soil is stabilized by lime or some other amendment that can buffer the pH effectively.

Redox Reactions

In soils, abiotic and biotic reactions involving metals and many other species are continuously taking place and usually involve proton and electron transfers. A reaction in which a loss of electrons occurs is termed an oxidation reaction, while reduction is the gain of electrons (Sparks, 1995). The two reactions are not exclusive since the loss and gain of e^- must be balanced. Moreover, the electrons produced in a reaction are not species in solution, so oxidants (the species accepting electrons) and reductants (the species donating electrons) must be in immediate contact for the transfer to occur. In well-drained surface soils the main redox couple reaction that occurs is the production of e^- due to the biological oxidation of organic matter (simplified as CH_2O):



The reason O_2 is the favored oxidant is that its $\log K^\circ$ value is greater than those of other potential oxidants. The sequence of oxidants in soils are usually considered (from most energetically favorable to least): $O_2 > NO_3^- > Mn(III/IV) > Fe(III) > SO_4^{2-}$. A soil under water-logged or flooded conditions may see reductive dissolution of solid Mn (IV) and Fe (III) phases, and eventually reduce SO_4^{2-} to produce sulfide minerals, such as FeS_2 (pyrite). The extent to which a soil is reduced or oxidized is generally assessed by the values Eh and pe. Eh is a redox potential and is expressed in terms of electrochemical energy (millivolts) and assumes a system is at thermodynamic equilibrium. Oxidized soils have values ranging from +400 to +700 mV while reduced soils may have values from -250 to -300 mV (Sparks, 1995). The pe is the $-\log(e^-)$ and is an index of the electron free energy level per mole of electrons. In a redox couple, the oxidant will be reduced if the pe value of its half reaction is greater than the pe value of the reductant half reaction at a particular pH. A more thorough treatment of redox behavior in soils can be found in Chapter 9 of this text or in the review chapter by Bartlett (1998).

The redox status of a soil is an important factor in considering metal speciation in soils for both direct and indirect reasons. Metals that are directly sensitive to redox changes in soils include As, Cr, Hg, and Se. They all have reduced and oxidized forms and in many cases the redox status influences their toxicity and mobility. For example, reduced Cr(III) has a low hazard associated with it while oxidized Cr(VI) can be quite toxic to organisms (Fendorf and Sparks, 1994). The

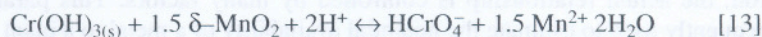
opposite holds true in the case of arsenic, with As(III), arsenite, being much more toxic to humans than As(IV), arsenate.

Perhaps the most important metals when it comes to redox reactions in soils are Fe and Mn. While we have not considered these elements as metals of interest for toxicity or deficiency purposes, the oxides and oxyhydroxides of Fe and Mn are well recognized as being indirectly involved in metal speciation due to adsorption, precipitation, and redox reactions. In oxidizing conditions, Fe(III) and Mn(III/IV) oxides are extremely common in soils and are known to retain metals given their reactivity and high surface areas. In reduced conditions, however, Fe and Mn oxides are subject to reductive dissolution and metals associated with these phases such as Cd, Ni, Pb, and Zn can have dramatic changes in their solubility and mobility in soils; however, if a soil is flooded for a long period of time, sulfide formation may ensue and immobilize the metal ions in the structure. This is the reasoning behind the construction of wetlands to sequester metals that may be toxic or mobile if not present in the sulfide fraction.

In soils, minerals such as δ -MnO₂ are present and are thermodynamically capable of oxidizing Cr(III) to Cr(VI) by the following reaction:



While one might be concerned that any Cr(III) introduced to soils containing Mn oxides would transform into the more toxic species, another reaction may compete with this one at pH values >3:



Fendorf and Zasoski (1992) used several advanced analytical techniques to show that Reaction [13] occurred at elevated pH and Cr(III) concentrations, thereby covering the δ -MnO₂ surface with Cr(OH)_{3(s)} and limiting the further oxidation of Cr(III) to Cr(VI). Given the seasonal variability of redox conditions in soils, it is important to consider redox reactions on the mobilization and sequestration of metals (Bostick et al., 2001; O'Day et al., 1998).

TECHNIQUES TO DETERMINE METAL SPECIATION IN SOILS

Metal speciation in soil continues to be a dynamic topic and of interest to soil scientists, engineers, toxicologists, and geochemists alike, as all of these disciplines do require knowledge of soil speciation to varying degrees. The accuracy and precision that is required will often dictate the approach one takes in determining metal speciation. In the case of molecular environmental science, one is often interested in obtaining the most detailed information possible, with the result being the use of advanced analytical techniques. Often, these analytical techniques have been developed in other disciplines such as surface science, solid-state physics and medical research. Soil chemistry has benefited dramatically from the application of techniques from other disciplines to study metal speciation. The combination of several techniques still remains the most prudent, practical, and comprehensive approach

to metal speciation in soils since there is no single method that is a panacea. While certain methods may have good detection limits and can speciate metals in trace amounts, they may not be ideally suited to provide structural or spatial information. Therefore, the most thorough and appropriate treatment of metal speciation methods should include a wide range of approaches, from classical methods to the cutting edge of technology.

Analytical Methods to Determine Metal Concentrations

While the majority of soil chemists agree that the total metal concentration does little to reveal information about metal speciation and gives no indication of bioavailability, it is still a necessary analytical step. For many of the methods that will be discussed, determination of metal concentration in either the solid soil matrix or in the soil solution (or extraction solution) is required. The total metal concentration of a soil has been used as a rough estimate to the degree of contamination of a soil. For instance, a partitioning coefficient, K_d , is defined as follows:

$$K_d = \frac{\text{Total Soil Metal}}{\text{Dissolved Metal}} \quad [14]$$

Total soil metal has a concentration of mg kg^{-1} and can include metals in minerals, as precipitates and as adsorption complexes. The dissolved metal is expressed as mg L^{-1} , so the units for K_d are L kg^{-1} . While a simple concept and equation, the actual relationship is controlled by many factors. This parameter is frequently used to estimate the potential availability of a metal to a plant or other organism; however, the metals in mineral phases typically are less available than the other two contributors to soil metals, so K_d values can often be overestimated. This determination alone, however, does little to reveal anything about the metal species and on its own is not a useful measure of the risk of metal bioavailability.

The soil solution contains the most mobile and potentially available metal species and are often found at very low concentrations and require sensitive analytical techniques to be measured (Walther, 1996). By measuring the metal concentration in a pristine soil solution, one would already be able to make some good predictions on the likelihood a soil poses a risk. The concentration of a particular ion in the soil solution (intensity factor) and the ability of solid components in soils to resupply an ion that is depleted from the soil solution (capacity factor) are both important properties of a given metal contaminated soil (Sparks, 1995). Water extraction and salt extractions can be used to determine the intensity factor, but the latter method may induce complexation of metals with inorganic anions. Tension-cup lysimeters can be used to collect soil solutions from the field. Metal ion concentrations of the soil solution can be done by spectrometry, chromatography, and colorimetry. To speciate the soil solution, it is necessary to apply ion association of speciation models as direct determination of all individual species is not possible.

There are several analytical techniques that can be used to measure metal concentrations in the soil solution or any solution in which the metal might be present (e.g., in extracting solutions). For soils, the solids are normally dissolved prior to

measurement in a solution strong enough to cause total dissolution of all solid phases. Solutions of this type include microwave- HNO_3 digestion, hot-plate reflux digestion with $\text{HNO}_3\text{-HCl-H}_2\text{O}_2$, aqua regia-hydrofluoric acid mixtures, and digestion in hydrofluoric acid. The solutions can then be analyzed using one of several analytical techniques including atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) spectrometry. X-ray fluorescence (XRF) also is a means of determining total metal concentration in soils and benefits from not having to use harsh chemicals for total dissolution because the analysis is done using the whole soil, but metal concentrations normally have to be upwards of 5 mg kg^{-1} . In addition, metal concentrations in solid slurries may be gleaned using ICP-MS.

Single Chemical Extraction Techniques

The use of single (one-step) extraction techniques finds the most application in soil fertility assessment in order to predict deficiencies or toxicities of trace elements. This approach to metal speciation considers several chemical pools of trace metals that share a common function (Walther, 1996). These definitions include plant available form, exchangeable cation, and labile species. Examples of solutions used to extract these chemical pools include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), acetic acid, salt solutions, and water. While water is clearly the least expensive and simplest extracting solution for soils, it is not necessarily the best extracting solution to use, since salt-free water is rarely found in natural soil waters. Dilute salt solutions with a concentration of at least 0.0001 M such as CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, KNO_3 , and NaNO_3 are routinely used. The routine use of these single extractions in soil fertility laboratories worldwide underscores their importance. This importance has led to several studies aimed at assessing extraction validity using plant uptake and crop yield studies. Alterations and adjustments to the extracting solutions have been implemented depending on the type of soils in the region of interest. Clearly, single extractions cannot estimate the amount of slowly-available metal that is released over time since extractions are carried out during a period of several hours. Moreover, the exact speciation of the metal is not gleaned using this type of approach. Despite these shortcomings, single extraction techniques will continue to be useful for both soil fertility and soil quality investigations.

Selective Sequential Extraction Techniques

A more rigorous and species-specific alternative to determining metal speciation than total metal concentration and one-step extractions is the use of selective sequential extractions. The purpose of sequential extractions is to provide detailed information on metal origin, biological and physicochemical availability, mobilization, and transport (Tessier et al., 1979). This approach to metal speciation conceptualizes soil as having several fractions that metals can be associated with, and these specific fractions can be attacked by chemicals specific to each individual fraction. Previous advances in soil chemical analysis that aimed at characterizing these fractions without the immediate goal of metal speciation were used

to develop sequential extraction methods. Typically, the first step in a sequential extraction process extracts the most labile metals, and each successive step increases in strength until the most non-labile fraction is left. The most widely cited procedure for sequential extraction is in the article by Tessier et al. (1979). This procedure was developed to speciate metals in contaminated river sediments and defined five fractions of metals: (i) exchangeable, (ii) bound to carbonates, (iii) bound to iron and manganese oxides, (iv) bound to organic matter, and (v) residual. After many studies and refinements, chemical extractions steps also are designed to selectively extract physically and chemically sorbed metal ions, metal sulfides, and metals in other fractions. Researchers have altered the technique to account for variations in soil pH, soil texture, metal concentration, redox status, and other parameters that can vary from soil to soil and regionally. The resulting extract is operationally defined based on the proposed chemical association between the extracted species and solid phases in which it is associated. Given that the extraction is operationally defined, the extracted metal may or may not represent true chemical species that it is given, so care must be taken to report the step in which it was removed rather than the phases it is associated with.

The use of sequential extractions for metal speciation is not without its limitations and pitfalls. These include (i) the incomplete dissolution of target phases, (ii) the removal of a non-target species, (iii) the incomplete removal of a dissolved species due to re-adsorption on remaining soil components or due to re-precipitation with the added reagent, and (iv) change of the valence of redox-sensitive elements (Brümmer et al., 1983; Calmano et al., 2001; Gruebel et al., 1988; La Force and Fendorf, 2000; Ostergren et al., 1999). These limitations are becoming more evident as research coupling sequential extractions with analytical techniques capable of directly determining metal speciation in soils and sediments is performed (Adamo et al., 1996; Brümmer et al., 1983; Calmano et al., 2001; Gruebel et al., 1988; Henderson et al., 1998; La Force and Fendorf, 2000; Ostergren et al., 1999).

Given the fact that sequential extractions are the most common means of determining metal speciation in soils and sediments and other geomedias, refinement and improvements of this procedure are desired. The coupling of direct speciation procedures will enable extractions to become more complete and universal, significantly improving our understanding of metal partitioning and mobility in soils. Despite the limitations of sequential extraction procedures, they will continue to be valuable for relative comparisons between contaminated sites. Moreover, these techniques are readily available, economically practical, and provide quantitative results rapidly. Combined with other speciation techniques and separation of physical phases in soils based on particle size, magnetic separation, and density gradient separation, extraction techniques can be rather robust at revealing metal speciation in soils.

Fundamentals of Spectroscopy and Microscopy

Both spectroscopy and microscopy rely on harnessing various wavelength regions on the electromagnetic spectrum and bombarding a sample in order to glean chemical and physical details. The energy that is directed at a sample results in sev-

eral potentially complicated processes, but can be generalized as a transition of an atom from a ground state to an excited state. This transition occurs at a very particular wavelength because atomic processes are quantized (O'Day, 1999). Spectroscopy and microscopy deal with the interaction of electromagnetic radiation with matter (Bertsch and Hunter, 1998). The broad energy range of the electromagnetic spectrum and the various means of measuring the various excitation phenomena that occur from the radiation bombarding the sample yield a large array of spectroscopic and microscopic techniques. Several sources provide overviews of these techniques and provide lists of acronyms (Calas and Hawthorne, 1988; Bertsch and Hunter, 1998; O'Day, 1999). The techniques useful for metal speciation in soils narrows this list down, and it can be further shortened, depending on specific interests such as in-situ requirements, cost limitations, and availability.

The two main categories of spectroscopy are defined by the interaction between the applied radiation and the sample. If the incident radiation of a particular frequency excites an internal process, this is absorption spectroscopy. Spectroscopies that fall under this category include nuclear, electronic and vibrational spectroscopies. In the other type of spectroscopy, the incoming radiation induces the emission of radiation from the sample but with a different frequency. Spectroscopies that fall in this category include energy loss spectroscopy, elastic scattering and luminescence spectroscopy (Calas and Hawthorne, 1988). The former category of spectroscopy will be the main one discussed for the remainder of this chapter. The frequency, ν of the radiation is related to the wavelength, λ by the following relation:

$$c = \nu\lambda \quad [15]$$

Where c is the velocity of propagation in vacuum (Calas and Hawthorne, 1988). The regions of the electromagnetic spectrum each have a unique associated phenomena once it comes into contact with a sample. The shorter the wavelength of the radiation, the smaller the size of the object that can be detected. For this reason, γ -rays and x-rays can provide atomic-scale resolution, while nuclear magnetic resonance (NMR) has spatial resolution corresponding to the size of a large animal. While lower energy radiation (longer wavelength) such as infrared (IR) cannot elucidate processes at the atomic level, it is able to cause vibration of bonds between atoms, giving rise to absorption spectra that can reveal information about molecules.

Electrons, like photons, are absorbed, scattered, and diffracted by matter, yielding the desired chemical and structural information (Manceau et al., 2002). Also, electrons can be focused with magnets down to the angstrom scale, like in the case of transmission electron microscopy (TEM); however, electron microscopy cannot identify structural forms of metals associated with minerals. Electron diffraction would have the best of both: good resolution and the ability to glean structures; however, electron microprobes are not both element specific and sensitive to the type and distance of neighboring atoms. With any technique one should be aware of influences the probing energy has on the sample. This is especially the case in microscopy where strong interaction of electrons with matter can induce a change in oxidation state, especially for moist soil samples that are hydrated and potential meta-stable with respect electron beams (Manceau et al., 2002).

Spectroscopic Techniques

Several analytical tools prevalent in characterization of materials in the surface sciences, chemistry, physics, and geology have been applied to direct speciation of heavy metals in soils and sediments for a number of years. The clear advantage in using direct techniques over chemical extractions is the lower risk of sample alteration and transformations of metal species from using extracting solutions. When selecting an analytical technique to speciate and quantify the form of metals in complex heterogeneous materials such as soils and sediments, a selective and non-destructive one is favorable (Manceau et al., 1996). Non-invasive, in-situ spectroscopies are those that can collect a spectrum from a sample with little alteration to the sample relative to its original state. In the case of soils this is extremely useful as soils always have some solution present, and exposing the sample to drying, heating, or pressure can substantially alter metal species (e.g., As(III) may transform to As(IV)). For laboratory-based studies designed to study single sorbent-sorbate interactions this also is necessary since experiments are performed in the hydrated state and altering the sample may alter the experimental outcome.

Spectroscopies capable of collecting data in situ include fluorescence, ultraviolet-visible (UV-vis), IR, NMR, electron spin resonance (ESR), Mössbauer, and XAFS. With the exception of the last technique that will be detailed in the next section, all of these spectroscopic methods can be found in most analytical laboratories in the field of chemistry, environmental science, surface science or solid-state physics. A good review of these techniques and others for determining metal sorption mechanisms can be found in Scheidegger and Sparks (1996a). In general, these techniques have traditionally been developed to characterize relatively clean systems, free of many of the organic and inorganic phases found in soil. Since many of the original types of experiments performed using these tools did not change significantly when dried or manipulated, sample alterations have been common in order to optimize the signal of the measurement. Unfortunately, this approach has been used for soil samples that are much more sensitive to sample alterations. In addition, the traditional experiments using these techniques rarely suffered from low element concentrations so the techniques were not optimized for metal concentrations found in most soils. This has resulted in experiments using unrealistic elevated levels of metals or other ions in order to have high surface loadings and collect high quality spectra. Fortunately, advances have been made in order to make these techniques more applicable to speciation studies of trace elements and contaminants in soils or on soil minerals. The Fourier Transform approach to IR (ATR-FTIR) and Raman (FT-Raman) spectroscopies has resulted in many experiments investigating speciation of elements at the water-mineral interface.

The principal invasive non-in-situ techniques used for soil and aquatic systems are x-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and secondary mass spectroscopy (SIMS). Each of these techniques yields detailed information about the structure and binding of minerals and bonding of minerals and the chemical species present on the mineral surfaces. The disadvantage of these techniques is that they have to be performed under ultra high vacuum, where dehydration of the sample and the particle bombardment might lead to misleading data due to experimental artifacts

(Scheidegger and Sparks, 1996a). This might especially be the case for a hydrated surface complex. Stable phases in soils that are not sensitive to invasive techniques may be well-suited for these techniques, but in the case of adsorbed complexes, amorphous precipitates or redox sensitive species, they should be avoided if possible (Bertsch and Hunter, 1998).

XPS is a surface analytical technique devised at the end of 1960s to provide chemical analyses of surfaces. X-ray spectroscopy uses x-rays as the stimulator, and photoelectrons are detected in response. For Auger spectroscopy, either x-rays or electrons can be used to generate Auger electrons whose energies are typically used for elemental identification only. Since electrons can only travel extremely short distances through solids without energy loss, these techniques are only sensitive to the near surface. The most important reason for using XPS and AES to study sorption reactions is that they are surface sensitive to most geochemically important elements. Another major advantage is that it can provide important information on the chemical state of the substrate surface before reaction, and both the substrate and chemical state of the sorbed species after reaction. Applications of XPS for determining metal speciation in soils include the study of Cr(III), Ni(II) and Cu(II) on chlorite, illite, kaolinite, and smectites; AsO_4^{3-} , CrO_4^{2-} , Zn^{2+} and Pb^{2+} sorption on ferrihydrite; and Cd and Se on corundum (Scheidegger and Sparks, 1996a).

Microscopic Techniques

Given the myriad of reactive phases in soils and their complex distribution in the soil matrix, a technique capable of providing spatial and morphological information on heavy metal speciation is desired. Microscopic techniques may resolve the different reactive sites in soil at the micron and submicron level, thus allowing for a more selective approach to speciation. Examples of these techniques include scanning electron microscopy (SEM), electron probe micro analysis (EPMA), and transmission electron microscopy (TEM). In order to glean elemental information and ratios, all the above techniques are often coupled with an energy dispersive spectrometer (EDS). While the above techniques have given insight into elemental associations and metal distributions in contaminated soils and sediments, they do have a few drawbacks. The most notable drawbacks are that EDS is only sensitive to $>0.1\%$ elemental concentration, it is insensitive to oxidation states of target elements, and it does not provide crystallographic data (La Force and Fendorf, 2000; Ostergren et al., 1999; Webb et al., 2000). A study investigating Zn speciation in contaminated sediments found that SEM coupled with x-ray EDS only provided elemental concentrations, but discerning between Zn sulfate and Zn sulfide was not possible (Webb et al., 2000). Similarly, electron microprobe analysis was unable to locate Hg grains within an Hg-contaminated sample and was unable to distinguish between polymorphs of Hg-bearing phases (cinnabar and metacinnabar) (Kim et al., 2000).

The application of scanning probe microscopy (SPM) has greatly advanced the understanding of the interaction of metals with solid phases. SPM represents a class of microscopic techniques that provide high resolution, multidimensional images of solid surfaces by monitoring the interactions between sharp tips and the surface (Bertsch and Hunter, 1998). SPM includes scanning tunneling microscopy (STM), atomic force microscopy (AFM), magnetic force microscopy (MFM) and

chemical force microscopy (CFM). AFM, CFM, and MFM are all types of scanning force microscopies (SFM). SFM techniques are advantageous in that they are relatively low in cost and the samples may be run in-situ. SFM has been used to study the kinetics of Cr(III) sorption reactions on goethite and silica using a flow cell mounted in a SFM (Fendorf et al., 1996). Scanning force micrographs revealed the formation of a Cr(III) precipitate that was distributed across the entire surface of goethite while discrete surface clusters were observed on the SiO₂ surface. High resolution tunneling electron microscopy (HRTEM) was used to observe a kaolinite surface reacted with Co for several hours (Thompson, 1998). Co was spatially associated with Al and Si, suggesting an association with kaolinite. Reactions of metals at solid-solution interfaces have become possible to monitor thanks to the development of tapping-mode SFM and the fluid cell apparatus. In tapping-mode, the tip contacts the surface at a known frequency and is useful for using on fragile surfaces and limits artifacts caused by traditional SFM. With a fluid cell, the reaction of a metal with a surface and changes that may result due to dissolution or precipitation can be monitored. For example, AFM has been used to observe the fairly rapid growth of Ni-Al precipitates on pyrophyllite (Scheckel et al., 2000).

Synchrotron-Based Methods

The use of synchrotron light sources to address environmental issues has provided insight into the reaction mechanisms of heavy metals at interfaces between sorbent phases found in soils and the soil solution. Several synchrotron facilities are operational in the USA and more exist worldwide, most of which have beamlines dedicated to environmental research. In the last decade and a half, soil chemists and other environmental and earth scientist interested in determining the atomic coordination environment of target metals in geomedias have used such facilities. To date, the most widely used technique used at synchrotron facilities by these scientists is XAFS. XAFS results from the attenuation of x-rays by atoms of a given element yielding an absorption across a narrow energy range. This narrow energy range is the absorption edge and corresponds to the production of photoelectrons due to excitation of inner-core electrons by the x-ray photons. This occurs when the incident x-ray energy, E , is approximately equal to the binding energy of the core level electron, E_b and is the reason XAFS is element-specific (Schulze and Bertsch, 1995). The term XAFS is a general term encompassing a range of energies around an absorption edge for a specific element: the pre-edge, near-edge (XANES) and extended portion (EXAFS). Each region provides specific information on an element depending on the selected energy range, making XAFS an element specific technique. Several articles provide excellent overviews on the use of this technique in environmental samples (Fendorf et al., 1994; Schulze and Bertsch, 1995). Briefly, the first region is the low-energy side of the main absorption feature and is termed the preedge region. Preedge features are common for first row transition metals and can provide information to the oxidation state of the metal. In the XANES region, electron transitions lead to absorption edge from which chemical information of the target element, such as oxidation state, can be deduced. This region is often used for fingerprinting, or comparing known compounds to unknown samples. In addition, interatomic distances from the central absorbed to surround-

ing atoms can be estimated (Schulze and Bertsch, 1995). The extended region can provide the identity of the ligands surrounding the target element, specific bond distances, and coordination numbers of first and second shell ligands (Schulze and Bertsch, 1995). This information is extremely useful in speciation of metals in soils and sediments as it provides quantitative information on the geometry, composition and mode of attachment of a metal ion at a sorbent interface (Brown et al., 1999).

The type of spectra one collects during an XAFS experiment is displayed in Fig. 13–8. As one sees, the spectra require analysis in order to get detailed atomic information, such as the identity of the first and second neighboring atoms, coordination numbers, and atomic distance (in this case, for Zn). Theoretically, one can use this information to distinguish between outer sphere complexes, inner sphere complexes, and surface precipitates. This has certainly been successfully achieved in the case of studies involving one metal ion adsorbed onto one mineral surface. While the conditions of these types of studies may not be indicative of the conditions one may encounter in a field situation, they certainly have made the transition to more complex systems possible. As a result, several recent studies have used XAFS to quantitatively speciate metals in contaminated soils (O'Day et al., 1998; Manceau et al., 2000; Calmano et al., 2001; Roberts et al., 2002).

One of the major shortcomings of several analytical techniques used to speciate metals is the limited detection limit. Given the intensity of synchrotron facilities, this technique has a detection limit down to 50 ppm. Moreover, a specific metal of interest can be targeted, potentially with little interference from other elements in the complex matrix in which it is located. Gleaning molecular scale information in-situ is not possible with any other technique. Features that have dramatically increased the use of XAFS in environmental studies include; more synchrotron facilities are becoming available, more routine data analysis due to computer-based packages, and word of mouth via professional meetings and journal articles. Although not used by the majority of scientist working to speciate metals in soils, XAFS certainly has changed the way we think about metal speciation in soils and has revealed so many things that we were otherwise unaware of.

To date, standard, bulk XAFS has been the most widely used synchrotron-based technique used to characterize heavy metals in environmental samples; however, in soils and sediments, there exist microenvironments having isolated phases in higher concentrations relative to the average of the total matrix (Schulze and Bertsch, 1995). For example, the microenvironment of oxides, minerals and microorganisms in the soil rhizosphere has been shown to have a quite different chemical environment compared to the bulk soil (Wang et al., 2002). Often these phases may be very reactive and of significance in the partitioning of heavy metals, but quantitatively they are minority phases in the overall makeup of the soil and are therefore overlooked. As previously mentioned, electron microscopy can be used to provide micro-scale speciation of a metal in soil matrices, but they cannot provide all of the atomic and structural information of XAFS. The average x-ray beam size in an XAFS experiment is several centimeters. With focusing mirrors and other devices, the x-ray beam bombarding a sample may go down to a few square microns in area, nearing the size of the most reactive species in soils, enabling one to distinguish between individual species in a heterogeneous system. These same principles can be applied to XRD and one can employ μ -XRD to attain crystallo-

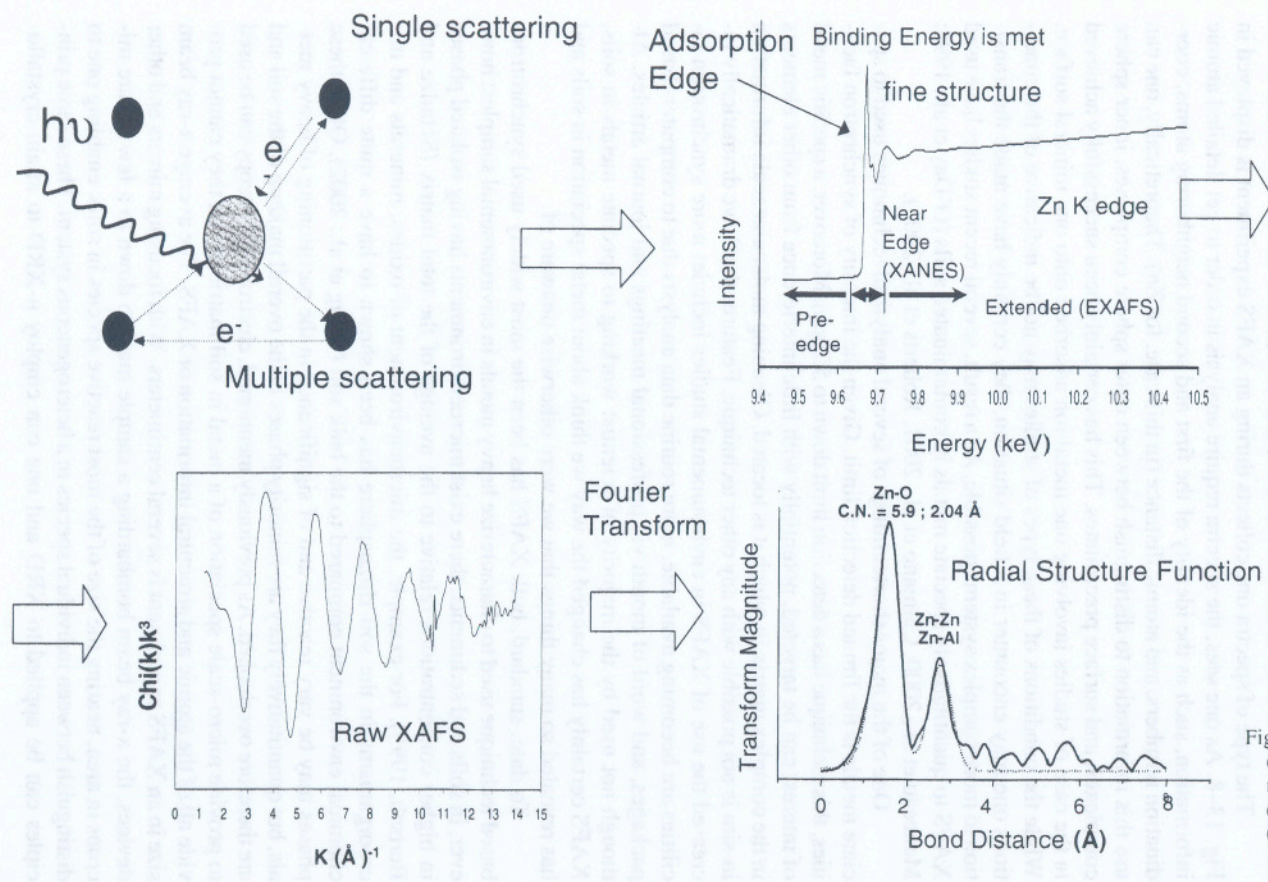


Fig. 13-8. Overview of EXAFS experiment through the data analysis step (after Fendorf et al., 1994).

graphic information on minerals that may occur in micrometer aggregates. In order to determine the exact location to place the focused x-ray beam on the sample, μ -XAFS is often combined with micro synchrotron-based XRF (μ -SXRF), allowing elemental maps to be obtained prior to analysis. While electron microprobe is often not sensitive enough to detect trace metals in soil, μ -SXRF offers sufficient sensitivity to investigate the spatial distribution of trace metals and their spatial correlation with other elements. Until recently, most studies have employed μ -XANES to determine the oxidation state of target elements in environmentally relevant samples since first and second generation light sources were not bright enough to achieve decent results for μ -EXAFS (Duff et al., 2001, 1999; Hunter and Bertsch, 1998; Manceau et al., 2000).

With the advent of brighter, third generation sources, μ -EXAFS has been used to speciate metals in soils and sediments (Isaure et al., 2002; Manceau et al., 2000; Roberts et al., 2002; Strawn et al., 2002). For example, Zn contaminated soils due to aerial deposition of smelter materials was probed using bulk EXAFS, μ -SXRF, and μ -EXAFS. The soil in question sits just below the soil surface and any Zn present is from the dissolution of Zn-bearing solid phases identified in the surface soil. Figure 13-9 presents the results of using all of these techniques. As one sees from the XRF elemental maps, Zn is spatially associated with both Fe and Mn in the sample, and also is concentrated in a region where neither element is present. The bulk XAFS reveal Zn has many second neighbor atoms, but distinguishing between them is difficult given the similar bond distances Zn shares with Fe and Mn atoms. With μ -XAFS, individual contributions from second neighbor Al, Fe, and Mn atoms can be observed and demonstrates that over an area of only a few millimeters, Zn can be adsorbed to three different phases. The results from a stirred-flow desorption experiment for the surface and subsurface soil demonstrated how a difference in speciation for Zn between the two soils influenced its release back into the soil solution. For the surface soil, Zn was in a fairly stable phase(s) and not easily dissolved. For the subsurface soil, Zn was more readily released into solution since adsorption complexes made up the majority of Zn species. A similar study by Manceau et al. (2000) use XRD, XAFS and μ -XAFS to demonstrate that upon weathering of Zn-mineral phases in soils, Zn was taken up by the formation of Zn-containing phyllosilicates and, to a lesser extent, by adsorption to Fe and Mn (oxyhydr)oxides. The major difference between the two Zn systems was the soil pH. In the former experiment, acidic pH values were operational, while in the latter study the soils were closer to neutral values. This demonstrates the influence pH has on metal speciation.

With XAFS, in order to discriminate between species and quantify them in a multi-species system, the species must have different oxidation states, or vary in atomic distances by ≥ 0.1 Å and/or coordination numbers by $\neq 1$ (O'Day et al., 1994b). Using a nonlinear-least square fit of the raw data or a shell-fitting approach of Fourier-transformed data, typically only two species may be detected within a given sample and there is a tendency to overlook soluble species with weak or missing second-shell backscattering in the presence of minerals with strong second-shell backscattering (Manceau et al., 2000). This latter point often leads to the inability to successfully detect minor metal bearing phases, even though they may be the most reactive or significant in the metal speciation. Discrimination between species has

Micro-X-Ray Fluorescence Spectroscopic Maps: Zn Associated with Fe and Mn

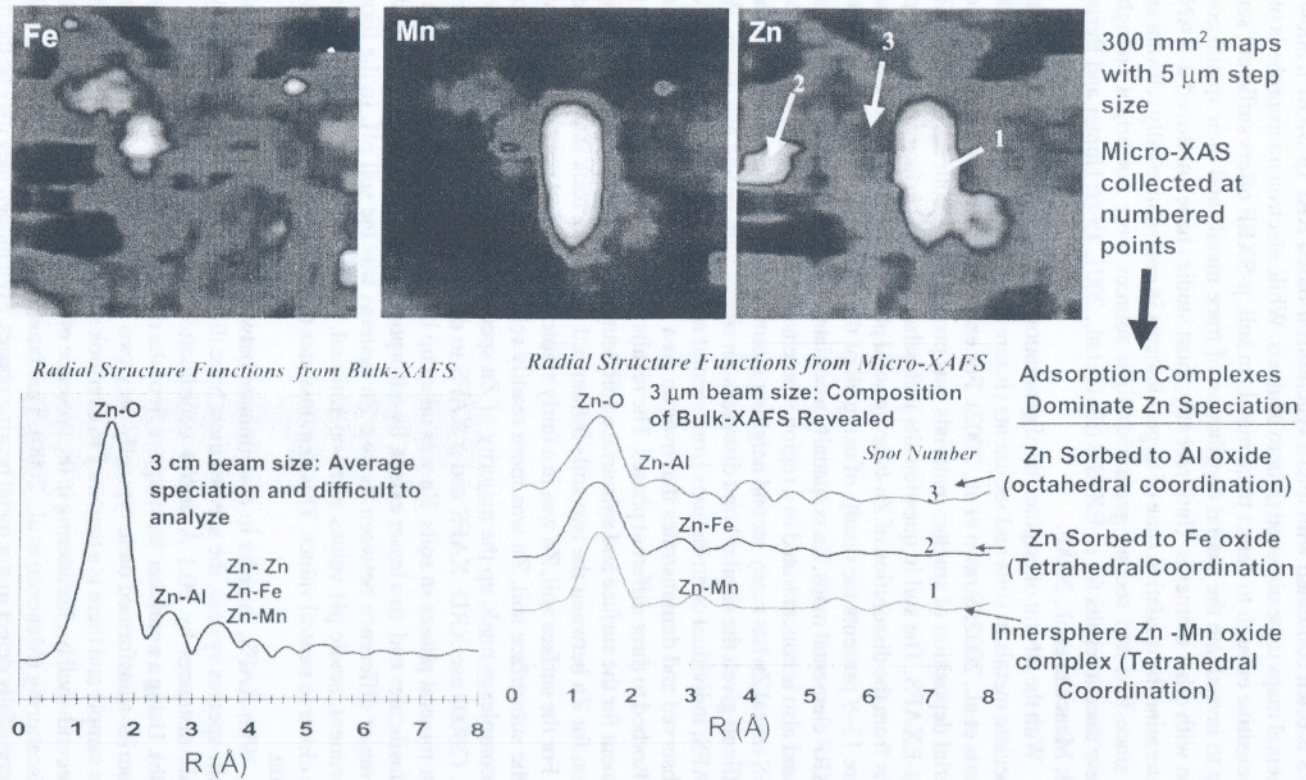


Fig. 13-9. Results from a synchrotron-based study for Zn contaminated soils combining several analytical techniques (from Roberts et al., 2001).

also been achieved using the linear combination fit (LCF) technique, where spectra of known reference species are fitted to the spectrum of the unknown sample. LCF has been successfully employed to identify and quantify up to three major species, including minerals and sorption complexes (Morin et al., 1999; Ostergren et al., 1999). The success of the speciation depends critically on a spectral database containing all the major species coexisting in the unknown sample, underscoring the need to have a thorough database of reference spectra.

Logistical drawbacks to doing synchrotron-based studies include the availability of synchrotron light sources, the increased demand for beamtime at these facilities, and the difficulty in analyzing data. Clearly, the number of metal-impacted sites requiring metal speciation information far exceeds the amount of time available at synchrotron facilities. Therefore, the combination of XAFS with more routine speciation techniques, such as sequential extractions, is important as the former technique has been able to detect artifacts and other shortcomings of the latter technique and may eventually lead to more specific and defined extraction procedures (Calmano et al., 2001; La Force and Fendorf, 2000). By combining sequential extraction techniques with XAFS, the number of species may be reduced by chemical separation prior to attempting their identification by XAFS. Moreover, the use of two independent methods for determining metal speciation in soils may provide a more reliable result than each of the methods alone.

Another shortcoming of using XAFS in metal speciation studies in soils is the requirement for sufficiently high metal concentrations, depending on the beam-line conditions. This requirement has resulted in many studies that rely on high pH values (> pH 7) and high metal concentrations in order to ensure adequate surface loading on the soil minerals. Voegelin et al. (2002) attempted to circumvent this issue by performing flow-through column experiments in combination with XAFS measurements. This approach relied on relatively low initial solution concentrations of Zn, Ni, Cd, and Co reacted with soil for a period of 42 d, leading to an accumulation of metal in the soil. Their studies showed that Zn-Al LDH precipitates formed in the soils, as well as in the case of Ni and Co sorption, though the latter two metals were relatively low in concentration and spectral analysis was difficult.

Additional Techniques for Determining Metal Speciation

For characterization of crystalline phases and minerals, XRD is extremely useful; however, metal-contaminated soils and sediments often contain the metal in a form such that it is a minority phase below the detection limit of the instrument, or the important reactive phase is amorphous and only produces a large background in the diffractogram.

Even if metal concentrations are below a reasonable level, one is still able to characterize the mineralogy of a sample that is crucial to understanding metal speciation in soils. A misconception is that only information on crystalline material can be gleaned using this technique; however, amorphous Fe and Mn oxyhydroxides and organic matter yields broad features in a diffractogram that can be exploited to reveal differences between samples. A popular method of using x-ray diffraction in metal speciation studies is to combine it with SSE, a term often called dif-

ferential XRD (dXRD). While the extracting solution may induce changes in the speciation of the metal or alter phases in an unnatural way, this approach is still useful. As stated earlier, synchrotron XRD has been developed and is being used to overcome some of the shortcomings of standard XRD instruments, namely flux and spatial resolution. Even more powerful is to combine μ -XRD with μ -XRF and XAFS so that one can glean information on both the metal species and the sorbent phase the metal may be associated with (Manceau et al., 2002).

High-resolution thermogravimetric analysis (HR-TGA) is not the first method one considers in performing metal speciation studies, but has recently been demonstrated to be quite powerful and discerning metal speciation. Using this technique a sample is gradually heated and while heated the weight loss is determined. Weight loss events are often specific to minerals in soils, and even to the surface functional groups on mineral surfaces. For example, Ford et al. (1997) was able to identify and quantify individual populations of surface OH groups on the Fe oxyhydroxide mineral goethite (FeOOH). While not directly determining metal speciation, studies of this type are still applicable to speciation studies since these surface sites can control effectively adsorb metal ions such as Pb and Ni.

Another useful spectroscopic technique used in metal-mineral studies is diffuse reflectance spectroscopy (DRS). DRS is the study of light as a function of wavelength that has been reflected or scattered from a solid, liquid, or gas (Clark et al., 1990). This technique is sensitive to elements in minerals that have unfilled electron shells. This makes DRS useful to investigate Ni precipitates since Ni²⁺ has an unfilled d orbital. This technique would not be useful in the case of identifying Zn²⁺ precipitates since this element has no unfilled electron orbital. The usefulness in using DRS to identify Ni hydroxide precipitates is due to the sensitivity of this technique to OH absorption bands. DRS is capable of distinguishing kaolinite from halloysite and montmorillonite from illite that is difficult using XRD alone (Clark et al., 1990). Scheinost et al. (1999) demonstrated the usefulness of DRS in differentiating Ni(OH)₂ from a Ni-Al layered double hydroxide phases. This task would be difficult using XAFS alone since Al is a fairly weak backscattering atom and would most likely be drowned out by the Ni signal.

Many computer models have been developed to calculate speciation of metals in soils. The advantage to this approach is its ease in execution if the proper parameters required are known. The drawbacks include, lack of proper thermodynamic data, overlooking reaction kinetics, no consideration for hysteresis, unknown identity of sorbent phases, inadequacies in describing ternary sorption systems, and overlooking the role of precipitates and solid-solutions. Regression models have been used in the literature and need to have inputs of pH, organic matter content, oxide content, CEC, metal concentration, competing ions, etc.

The more species are added to the system, the more complex the mathematics becomes. Several speciation programs with which one can calculate the speciation of a certain element in aqueous solutions are available. A comprehensive list of these programs can be found in (Sparks, 1995). Parameters in these kinds of programs are temperature, pH, I, initial concentrations, and solid phases. One should be careful not to put too much emphasis on these results. Data in the thermodynamic databases of these programs are often from different sources and sometimes insufficient.

The purpose of chemical modeling of soil systems is to obtain information on the distribution of elements within a soil between solid, aqueous, and gaseous phases at a given point in time. The modeling should be capable of predicting the types and quantities of various solids, the concentrations and distribution of exchangeable and/or adsorbed ions, the metal and ligand speciation in the aqueous phase, and the composition of the gas phase.

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