Chemistry of Trace Elements in Soils and Groundwater

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CHAPTER 4

CHEMISTRY OF TRACE ELEMENTS IN SOILS AND GROUNDWATER

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INTRODUCTION

High concentrations of inorganic trace elements in irrigated soils and shallow groundwater pose a threat to agricultural production and the health of humans and animals. They do so in three ways: (1) trace elements can accumulate in plants to levels that cause phytotoxicity; (2) trace elements in plants can adversely affect humans and animals that consume those plants; and (3) trace elements can migrate with seepage through the rootzone and into groundwater, possibly re-emerging with subsurface drainage in surface waters, thereby affecting wildlife, or with groundwater pumped for domestic use, thereby threatening the health of humans.

The objective of this chapter is to provide a framework for understanding trace element chemistry in soils and groundwater: the processes that affect trace element concentrations in soils, the biochemical behavior of trace elements in soils, and the methods for evaluating pollution potential in soils in irrigated agricultural areas. Problematically high concentrations of trace elements in soils and groundwater in irrigated areas can occur concomitant with soil and groundwater salinity and can be affected by similar processes that affect soil and groundwater salinity. Problematically high trace element concentrations may also occur independent of salinity. We will describe processes that affect the mobility of trace elements.

We have focused on elements designated by the U.S. Environmental Protection Agency (EPA) as priority pollutants (EPA 1986) and on elements that have been documented as pollutants associated with irrigated agriculture. We have divided the trace elements into four categories: (1) alkali and alkaline-earth metals [barium (Ba) and lithium (Li)]; (2) transition metals [chromium (Cr), molybdenum (Mo), and vanadium (V)]; (3) metalloids

[arsenic (As) and boron (B)] and the nonmetal selenium (Se); and (4) informally denoted heavy metals [cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn)].

PROCESSES AFFECTING TRACE ELEMENT CONCENTRATIONS

Precipitation and Dissolution

Mineral precipitation and dissolution reactions often govern the activities of trace elements in soil solutions. These reactions generally are described by a solubility product relation in which the solid dissolves to form soluble constituents. For example, the solubility of solid barite, $BaSO_4(s)$, may control the activity of Ba^{2+} in the soil solution of arid-zone soils and groundwaters (Hem 1985). At constant temperature and pressure, a solution in equilibrium with $BaSO_4(s)$ is described by the following equation:

$$BaSO_4 (s) \leftrightharpoons Ba^{2+} + SO_4^{2-} \tag{4-1}$$
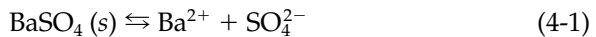
The reduced thermodynamic equilibrium constant expression for this reaction is:

$$K_{so} = (Ba^{2+}) \cdot (SO_4^{2-}) \tag{4-2}$$

where ( ) denotes activities, the solubility product constant K_{so} has a value of about 10^{-10} at 25 °C and 1 atmosphere pressure (Hem 1985), and H_2O and $BaSO_4(s)$ are assumed to be in their standard states with activities equal to unity.

Mineral phases affecting the activities of some trace elements in soil solutions and groundwaters can be assessed by calculating mineral saturation indices. The mineral saturation index (SI) is equal to the logarithm value for the quotient of the ion-activity product (IAP) and mineral solubility product constant, or SI = log (IAP/K_{so}). Negative saturation-index values indicate mineral undersaturation, while positive values indicate supersaturation. Values approaching zero indicate possible thermodynamic mineral equilibrium.

Supersaturation often indicates that kinetic constraints are preventing precipitation. The result of this evaluation alone, however, does not constitute proof that a particular mineral phase is present and affecting trace element concentrations, nor that it is absent and not a factor in a water's trace element chemistry. Mineralogical data can be collected to identify the presence of suspected minerals, thereby providing evidence to support the results of SI calculations.

Evaluation of SIs is limited by the availability and accuracy of mineral thermodynamic data that affect trace element concentrations. Several computer models calculate SIs based on currently available thermodynamic data. Nordstrom et al. (1979b) and Nordstrom and Ball (1984) reviewed a number of these codes. All codes assume that pure solid phases at their standard states are either present or will precipitate. Solid phases with unit activities probably are rare in natural systems (Corey 1981).

The evaluation of mineral SIs assumes equilibrium. This may be invalid in some natural systems. In general, the use of equilibrium calculations in mineral aqueous systems is valid only when the residence time of the water greatly exceeds the reaction half-life (Langmuir and Mahoney 1984).

For the case of mineral dissolution (mineral-water equilibria) and crystallization, equilibrium conditions may not be present in many natural systems, depending on the specific reactions and residence times. In contrast, the use of equilibrium calculations for solute-solute or solute-water interactions, such as complexation or acid-base reactions, generally will be valid because of the relatively rapid reaction rates, as long as the solution-theory model is adequate to describe the solution considered and the thermodynamic parameters are known with reasonable accuracy.

Solution-Phase Speciation of Trace Elements

The total (analytical) concentration of any given trace element in the aqueous phase depends on the ionic strength of the solution and the concentrations of other ions with which the trace element forms complexes. For example, the total aqueous concentration of Cd consists of the sum of the concentrations of uncomplexed Cd^{2+} and all of the possible complexes formed in solution. This may be expressed mathematically by the following mass-balance equation:

$$[Cd]_{total} = [Cd^{2+}] + [CdSO_4^0] + [CdNO_3^+] + [CdCl^+] + [CdCl_2^0] + [Cd\text{-}Org] + \ldots \qquad (4\text{-}3)$$

where [ ] represents molar or molal concentration and Cd-Org represents cadmium complexed by dissolved organic matter.

At constant temperature and pressure, the formation of a soluble complex, for example, $CdCl^+$, can be described by the following mass action equation:

$$Cd^{2+} + Cl^- \leftrightarrows CdCl^+ \qquad (4\text{-}4)$$

The reduced thermodynamic stability constant expression for this reaction is

$$K_s = \frac{(CdCl^+)}{(Cd^{2+})(Cl^-)} \qquad (4\text{-}5)$$

where ( ) denotes activities and H_2O is assumed to be at unit activity. Values of stability constants for inorganic complexes involving trace elements or free energy values from which the stability constants can be calculated are published extensively in the literature (see Nordstrom et al. 1979b). For Cd and other metals, pH plays an important role in determining the predominant species in soil solutions and groundwater. For example, at pH values below 7.0, Cd^{+2} is the predominant dissolved Cd species representing 70% to 99%. At pH values above 7.0 in a typical calcareous soil, $CdCO_3$ is the predominant species, representing more than 80% at pH values above 8.5 (Adriano 2001).

The activity of a single ion can be expressed as $a_i = m_i y_i$, where a_i = the activity of ion i, m_i = the molal (or, in dilute solutions, molar) concentration of species i, and y_i is the activity coefficient of species i. For extremely dilute solutions (i.e., approaching infinite dilution), activities are approximated by molar concentrations for all species and y_i equals unity. As the concentrations of charged dissolved constituents increase, y_i decreases. This decrease represents the degree of departure from ideality of the ionic properties of species i. Individual ion-activity coefficients can be calculated in different ways, depending on the ionic strength of the solution. See Chapter 3 for a complete discussion of calculation of ionic strength and ionic-activity coefficients.

Adsorption

Activities of trace elements in soil solutions and natural waters frequently are too low to be controlled by precipitation and dissolution of pure solid phases. Additionally, slow precipitation kinetics result in supersaturation with respect to many oxide, hydroxide, and carbonate minerals. Therefore, adsorption reactions occurring at the solid–liquid interface are significant mechanisms controlling trace element activities in many natural waters (Jenne 1977).

Adsorption reactions occur mainly in the clay mineral size fraction of the soil and aquifer material at the surfaces of layered aluminosilicate minerals. The reactive surfaces include amorphous oxides and hydroxides of Fe, Mn, and Al; organic matter containing weak-acid functional groups; and metal carbonates, such as calcite, $CaCO_3(s)$, and dolomite, $CaMg(CO_3)_2(s)$ (Jenne 1977). These soil components have the highest surface area and, therefore, the greatest contact with soil water. Even though

their total concentrations may be relatively low, amorphous oxides, hydroxides, and organic matter occur as coatings on clay-mineral surfaces, thereby exerting considerable control on activities of trace elements in natural waters. In contrast, colloidal-size ($<1\ \mu m$) calcite is often found in the clay mineral fraction of arid and semiarid soils. Calcite is an important adsorptive surface for metals. It buffers the soil pH in the alkaline range and decreases metal activities. Jenne (1977) presented an excellent review of these topics.

Adsorption of trace elements can be nonspecific, involving simple electrostatic attractions, or specific, involving coordinate covalent bonding. Trace element adsorption occurs at surfaces where the nature of the surface charge affects the extent of the reaction. The permanent negative surface charge of 2:1 layered silicates arises from isomorphous substitution of Al^{3+} for silicon (Si^{4+}), substitution of a divalent cation for a trivalent cation (e.g., Mg^{2+} for Al^{3+}), or substitution of a monovalent cation for a divalent cation (e.g., Li^+ for Mg^{2+}) (Bohn et al. 1979).

The permanent negative charge of layered silicate minerals is balanced by a diffuse cloud of cations. The cations, or counter ions, are electrostatically attracted to the negative surface, thereby increasing their concentration near the surface. This creates a concentration gradient favoring diffusion away from the surface. The opposite is true for anions. The balancing of these two opposing processes determines the distribution of cations and anions near the permanent charge surface, often referred to as the diffuse or electric double layer (van Olphen 1977). The simplest interpretation of adsorption selectivity of cations is that constant charge surfaces favor higher valence cations (stronger coulombic attraction) and smaller hydrated radii (closer approach to the surface).

In contrast to permanent charge sites, charge sites that are pH-dependent exist on broken edges of layered silicate minerals, hydroxylated surfaces of metal oxides and hydroxides, and weak-acid functional groups of organic material. Adsorption reactions at pH-dependent charge sites require the formation of surface complexes and some degree of coordinate covalent bonding, which results in the specificity of the adsorption reactions. Figure 4-1 depicts reactions that may take place at the hydroxylated surfaces of metal oxides, as suggested by Schindler (1981).

Figure 4-1a shows the weak-acid nature of the surface hydroxyls. At low pH, the surface hydroxyl will be protonated and positively charged, giving rise to some anion exchange capacity. At higher pH, the surface is negatively charged and can contribute to the soil's cation exchange capacity.

Figure 4-1b shows reactions for a dissolved trace metal cation (e.g., Cd^{2+} or Zn^{2+}) forming a surface complex by covalent bonding to the surface, displacing protons. Similarly, ligands can exchange with surface hydroxyls (Fig. 4-1c). The adsorption of a dissolved metal ion also can
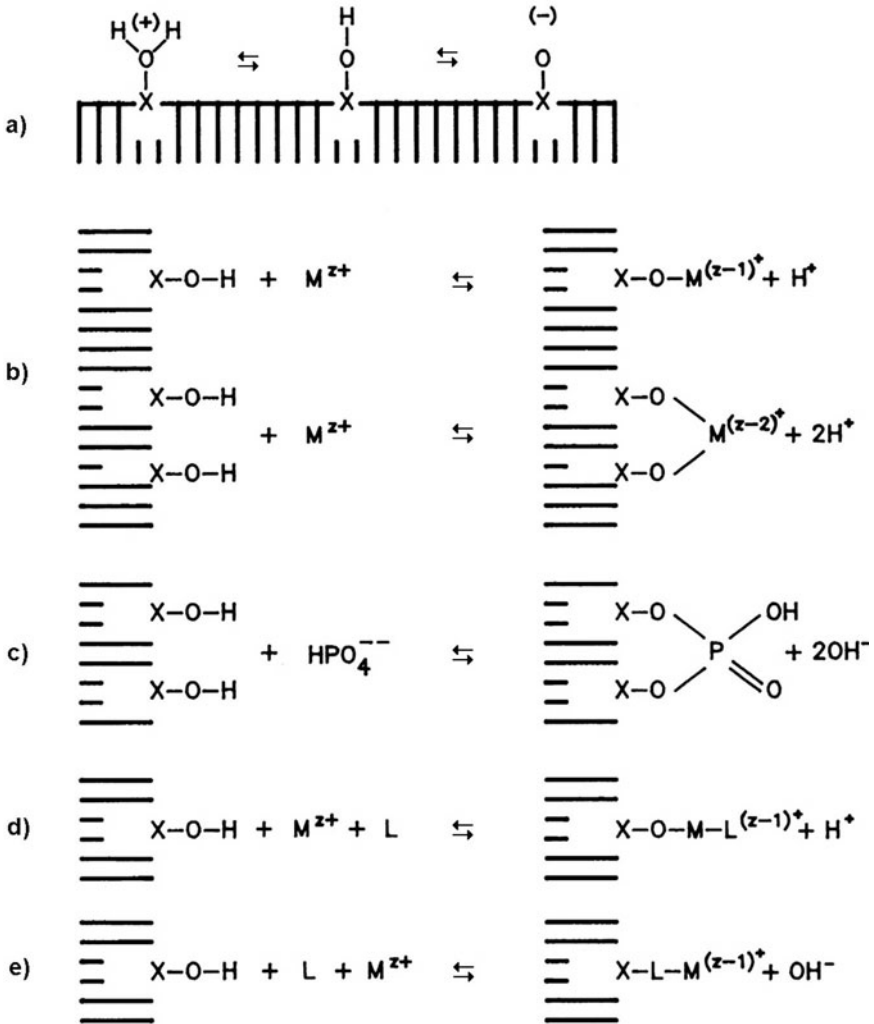
FIGURE 4-1. *Coordination phenomena at oxide–water interfaces: (a) acid-base reactions at surface hydroxyl groups; (b) deprotonated surface hydroxyls coordinate with dissolved metal ions; (c) surface hydroxyls are replaced by dissolved ligands; (d) dissolved metal ion coordinates with both deprotonated surface hydroxyls and dissolved ligands; (e) dissolved multidentate ligand coordinates with both x and the dissolved metal ion M. From Schindler (1981) with permission.*

coordinate a dissolved ligand (Fig. 4-1d), and adsorption of a dissolved ligand can coordinate a dissolved metal ion (Fig. 4-1e). Similar reactions occur at edges of layered silicate minerals (e.g., kaolinite edges) and at weak-acid functional groups attached to organic material (e.g., carboxylic acid functional groups).

Hendrickson and Corey (1981) demonstrated the dependence of Cd selectivity on adsorption site coverage for a variety of solids. A continuum of different types of sites exists in natural systems, ranging from extremely specific sites at low trace element concentrations to nonspecific, cation-exchange-type sites at high concentrations. In natural systems where a small proportion of total site coverage by trace metals or trace element oxyanions is expected, specific adsorption is usually the dominant process controlling the concentrations of many trace metals and trace element oxyanions.

Trace metals compete with each other for adsorption on minerals and soils. Kinniburgh et al. (1976) showed that the selectivity sequence for iron oxide gel was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Sr^{2+} > Mg^{2+}$. For Al oxide gel, the sequence was $Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Mg^{2+} > Sr^{2+}$. Forbes et al. (1976) found trace metal affinities for goethite to be $Cu^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$. Kuo and Mikkelsen (1979) compared Zn^{2+} competition with other trace metals for adsorption on two alkaline soils. They found the adsorption selectivities relative to Zn^{2+} to be: $Hg^{2+} > Cu^{2+} > Fe^{2+} > Mn^{2+}$.

Ligand exchange of anions for surface hydroxyls is the predominant process affecting the specific adsorption of oxyanions on goethite (e.g., Goldberg 1985; Hingston 1981) and soils (Fujii et al. 1988; Goldberg et al. 2000, 2002, 2005a,b, 2007, 2008; Neal et al. 1987a,b). Hingston et al. (1968) showed that affinity for anion adsorption on goethite followed the order phosphate > silicate > selenite > fluoride.

Describing Adsorption Data

Adsorption isotherms describe the relation between the mass of a substance adsorbed (adsorbate) by the solid (adsorbent) and the equilibrium solution concentration (or, more appropriately, activity) supported by the adsorbed phase. These data usually are fit to a model from which adsorption mechanisms may be inferred. Adsorption equations have been incorporated into solute transport models to estimate the retention and release of adsorbing species during transport (e.g., Lewis et al. 1986).

One common model used to describe trace element adsorption data is the Freundlich equation:

$$\frac{x}{m} = KC^{1/n} \tag{4-6}$$

where x = the mass of trace element adsorbed; m = the mass of solid phase adsorbent; C = the equilibrium concentration of adsorbate in solution; and K and n are empirically determined constants. Many researchers have applied the Freundlich adsorption equation to describe adsorption

of trace metals onto soils and soil minerals (e.g., Bowman et al. 1981; Garcia-Miragaya and Page 1976).

Another model commonly used to describe trace element adsorption is the Langmuir equation, which Langmuir (1918) originally developed for adsorption of gases onto solids. When applied to minerals, soils, and sediments, the equation can take the form

$$\frac{x}{m} = \frac{kbC}{(1 + kC)} \qquad (4\text{-}7)$$

where k = a parameter related to the affinity of the adsorbent for the adsorbate; and b = the adsorption maximum. A linearized form of the equation typically is used to describe sorption data as follows:

$$\frac{C}{x/m} = \left(\frac{1}{kb}\right) + \left(\frac{C}{b}\right) \qquad (4\text{-}8)$$

From a plot of $C/x/m$ versus C, the b and k terms can be estimated from the slope and intercept, respectively.

The original derivation of the Langmuir model assumes that only one type of adsorption site exists and that it has constant binding energy (homogeneous surface). However, minerals, soils, and sediments contain surface sites of varying specificity or binding energies. Syers et al. (1973) addressed this problem by using a two-site Langmuir model (high-energy and low-energy sites) to describe the sorption of phosphate by soils. Harter and Baker (1977) and Sposito (1984) addressed other problems associated with using the Langmuir model, such as precipitation of the adsorbate and competition from other adsorbates.

Surface complexation models provide molecular descriptions of trace element adsorption using an equilibrium approach that defines surface species, chemical reactions, mass balances, and charge balances. Examples of surface complexation models of the solid–solution interface are: the constant-capacitance model (Stumm et al. 1980), the diffuse-layer model (Dzombak and Morel 1990), the triple-layer model (Davis et al. 1978), and the charge distribution multisite surface complexation (CD-MUSIC) model (Hiemstra and van Riemsdijk 1996).

The constant-capacitance model assumes that adsorbing ions form tightly bound inner-sphere complexes. The mechanism of adsorption of anionic trace elements is ligand exchange with surface hydroxyls on oxides and clay minerals. The model has been applied to the adsorption of trace elements including B, Mo, arsenate, selenite, chromate, Cd, Cu, Pb, Ni, Zn, and Hg (Goldberg 1985, 1986; Goldberg and Glaubig 1985; Goldberg et al. 1996; Grossl et al. 1997; Gu and Evans 2007; Gunneriusson

and Sjöberg 1993). The model has also been used to describe B, Mo, arsenate, and selenite adsorption by soils (Goldberg and Glaubig 1986a; Goldberg et al. 2000, 2002, 2005a,b, 2007, 2008; Sposito et al. 1988).

In the diffuse-layer model, adsorbing trace elements also form inner-sphere surface complexes with anion adsorption proceeding via a ligand exchange mechanism. This model, as its name implies, also includes a diffuse layer formed by the background electrolyte ions. The model has been applied to the adsorption of the trace elements: Cr, V, B, Mo, As, Se, Cd, Cu, Pb, Ni, Zn, and Hg on oxides (Dzombak and Morel 1990; Gustafsson 2003; Peacock and Sherman 2004). The model has not yet been applied to adsorption by soils.

In the triple-layer model, adsorption can occur as inner-sphere surface complexation or via an outer-sphere adsorption mechanism that results in the formation of weaker surface complexes containing at least one water molecule between the adsorbing ion and the surface functional group. The model has been applied to the adsorption of the trace elements: Cr, V, B, As, Se, Cd, Cu, Pb, Zn, and Hg on oxides (Balistrieri and Chao 1990; Balistrieri and Murray 1982; Blesa et al. 1984; Davis and Leckie 1978, 1980; Peacock and Sherman 2004; Sarkar et al. 1999) and Hg adsorption on the clay mineral kaolinite (Sarkar et al. 2000). The model has been used to describe chromate (Zachara et al. 1989) and molybdate (Goldberg et al. 1998) adsorption by soils.

The CD-MUSIC model considers various types of reactive surface groups: singly, doubly, and triply coordinated hydroxyl groups. The charge of the central ion in the surface complexes is distributed over the coordinating ligands. Inner- and outer-sphere surface complexes are possible. The model has been applied to the adsorption of the trace elements: Cr, Mo, As, Se, Cd, Cu, Pb, and Zn on oxide minerals (Bourikas et al 2001; Hiemstra and van Riemsdijk 1999; Ponthieu et al. 2006; Stachowicz et al. 2006; Venema et al. 1996; Weerasooriya and Tobschall 2000). The model has been used to describe adsorption of arsenate by soil (Gustafsson 2001).

Oxidation-Reduction Processes

Many trace elements exist in more than one oxidation state (e.g., V, Cr, Se, As), and are therefore affected by electron transfer or oxidation-reduction (redox) reactions. Comprehensive reviews of redox reactions in natural systems are presented by Ponnamperuma (1972), Sposito (1981), and Stumm and Morgan (1981).

Most unsaturated soils contain enough oxygen (O_2) to maintain oxidizing conditions. In poorly aerated soils where the supply of O_2 is limited by the rate of diffusion, anoxic microsites can develop. Under water-saturated conditions, the O_2 supply rate may be slower than the O_2

demand, and anaerobic or reducing conditions may develop (Reddy and Patrick 1983).

The potential for a substance to accept or donate electrons under equilibrium conditions is represented by standard electrode potentials of reduction half-reactions (*Eh*) relative to the half-reaction for the hydrogen electrode. These reactions involve the transfer of electrons and depend on the activity of electrons in solution, represented by *pE*, the negative logarithm of the aqueous electron activity.

A major electron-donating process in soils is the microbial oxidation of reduced organic carbon. Oxygen is the primary electron acceptor for this reaction. In the absence of O_2, other soil constituents act as the electron acceptor and are reduced. Bohn et al. (1979) lists the principal electron acceptors in soils in the order of their tendency to be reduced, as indicated by the equilibrium potentials of the half-reactions at pH 7: $O_2 > NO_3^- > MnO_2 > FeOOH > SO_4^{2-} > H^+ > (CH_2O)_n$.

Within the range of redox potentials reported for soils (Baas-Becking et al. 1960), changes in oxidation states for many trace elements are expected. The reduction reactions can increase or decrease the concentration of trace elements. For example, reduction of Mn(III) or Mn(IV) to Mn(II) increases the concentration of Mn because Mn^{2+} is more soluble. In contrast, reduction of SeO_4^{2-} to the much less soluble elemental Se decreases Se concentration. Selenate reduction may be the major mechanism immobilizing Se in sediments and preventing its transport to the groundwater at the Kesterson National Wildlife Refuge on the west side of the San Joaquin Valley, California. The refuge was formerly an impoundment for agricultural drain water with high concentrations of selenium (e.g., White et al. 1991).

Minerals, such as MnO_2 and $Fe(OH)_3$, act as sorbents for trace elements; hence, dissolution of these solid phases also can release adsorbed trace elements. During an investigation of As mobility in groundwater, Gulens et al. (1979) found decreased adsorption of As by hydrated ferric oxide under reducing conditions. They attributed this to reduction of Fe(III) to the more soluble Fe(II) and subsequent release of As. Conversely, Reddy and Patrick (1977) reported that water-soluble Pb concentrations decreased (from 45 to 22 μg/L at pH 5) with increases in redox potential due to the probable formation of Fe and Mn oxyhydroxides under oxidized conditions, with subsequent adsorption of Pb.

Under sufficiently reducing conditions, sulfate is reduced to sulfide and trace metal sulfides precipitate (Lindsay 1979). For example, Bingham et al. (1976) and Reddy and Patrick (1977) reported a decrease in Cd mobility under reducing conditions due to precipitation of cadmium sulfide.

Considerable effort has been expended to visually represent stability or predominance fields for minerals and dissolved constituents in natural

systems, as a function of Eh (or pE) and pH (e.g., Drever 1988; Garrels and Christ 1965; Hem 1985; Lindsay 1979). Their diagrams represent equilibrium systems and provide critical information on possible equilibrium assemblages of minerals and coexisting water compositions. They also help identify disequilibrium assemblages of minerals and aqueous redox couples (Thorstensen 1984).

Redox reactions in natural systems generally are considered to be at only partial equilibrium because the kinetics usually are slow; therefore, equilibrium is not achieved, owing to lack of effective coupling of redox reactions (Sposito 1983; Thorstensen 1984). The platinum (Pt) electrode has been used extensively for the measurement of redox potential in field situations. However, Pt-electrode measurements do not necessarily represent the redox potential of the system; they may be the result of a single electroactive redox couple or may represent mixed potentials at the electrode surface. Thus, in natural systems, Pt-electrode measurements should be interpreted with great caution (Lindberg and Runnells 1984; Thorstensen 1984).

In natural systems, kinetically limited redox reactions are commonly mediated by microbial organisms. Therefore, the appropriate microbial population must be present to effect a particular reaction. Organisms generally affect only the kinetics of the reaction and do not alter the thermodynamic constraints (Sposito 1983). However, some reactions and species occur that would not be predicted by the overall redox status of the soil due to the presence of microenvironments and microbial populations. Selenium, for example, can be present in oxidized and reduced forms in different microenvironments of the same system.

In spite of the problems discussed, environments exist where dominant redox couples are effectively catalyzed and thermodynamic interpretations may be applied. In flooded soils, for example, reduction of Fe and Mn minerals produces high concentrations of Fe^{2+} and Mn^{2+}, which can dominate the redox potentials of the system and, thus, allow a quantitative thermodynamic description of redox-active ion activities (Bohn et al. 1979; Ponnamperuma 1972; Sposito 1983). Other investigators have reported Nernstian behavior between measured Eh and various redox-sensitive elements (e.g., Nordstrom et al. 1979a).

BIOGEOCHEMICAL BEHAVIOR AND DISTRIBUTION OF TRACE ELEMENTS IN SOILS AND GROUNDWATER

The relative importance of biogeochemical processes discussed in the preceding sections is determined by an individual element's mode of occurrence. An element's mode of occurrence is, in turn, determined primarily by the pH and redox status of soil solutions and groundwaters, and by the solid phase controlling solubility and distribution. A review of

the distribution, sources, and behavior of individual trace elements in the near-earth-surface environment is presented here to provide a framework for evaluating potential trace element pollution problems associated with irrigated agriculture.

Sedimentary rocks and soils are the solid-earth materials that most affect and determine the trace element chemistry of groundwaters (Hem 1985). Sedimentary rocks can be divided into four groups, based on their resistance to weathering: resistates, hydrolyzates, precipitates, and evaporites. Resistates are rocks composed primarily of residual aluminosilicate minerals that are not easily altered chemically by the weathering of parent rock. Hydrolyzates are composed primarily of insoluble metal oxide and aluminosilicate minerals derived from the weathering of parent rock. Precipitates are rocks that are a result of direct precipitation of mineral matter from aqueous solution. Evaporites are rocks composed of minerals deposited during evaporation.

Evaporites affect the composition of some soil solutions and groundwaters associated with irrigated agriculture. However, little is known about their trace element concentrations (Hem 1985). Trace element concentrations generally are higher in hydrolyzates than in resistates and precipitates. This is especially true for those elements that adsorb strongly to metal oxide minerals, such as Zn, Ni, Hg, Pb, Cu, Cr, Ba, and As.

Regional assessment of groundwater and drainage-water quality in relation to regional-scale geohydrologic and geochemical processes are common goals of groundwater investigations of trace elements in irrigated areas. Spatial and statistical analysis of data collected over large geographic areas can provide information about the distribution of trace elements and insights about processes affecting their distribution and mobility. Multivariate statistical and spatial analyses can be useful tools for this endeavor. For example, Deverel (1989) used a combination of geostatisitcal analysis (kriging) and principal component analysis integrated using a geographic information system (GIS, Arc/Info) to assess the distribution of principal component scores in the San Joaquin Valley, California. This provided a way of assessing relations among constituents for a large number of samples analyzed for more than 20 chemical constituents. Analysis of the principal component scores in relation to geomorphology elucidated constituent sources and regional processes affecting trace element mobility. Deverel and Galanthine (1989) also successfully utilized spatial analysis using GIS and kriging to assess the relation of soil and groundwater salinity and selenium concentrations in the western San Joaquin Valley.

By way of another example, in the western United States during the 1980s and 1990s the U.S. Department of the Interior conducted studies related to Se and other trace elements in soils, drainage waters, surface waters, and biota in major irrigation projects (Engberg et al. 1998; Presser

et al. 1994). Naftz (1996) attempted to summarize and synthesize the data for the 23 projects where studies had been conducted throughout the western United States. He used a combination of geochemical modeling and simple salt calculations for 1,962 samples collected from the 23 study areas using calculation of the normative salt assemblage with the program *SNORM* (Bodine and Jones 1986) and pattern recognition modeling to assess selenium–hydrochemical facies associations. The normative salt assemblage can lead to a unique characterization of the sample chemical composition providing information about solute sources and can be visualized as the solid residuum that coexists with the last vestige of water upon evaporation.

Naftz's (1996) analysis demonstrated three distinct hydrochemical facies. Facies 1, which showed an absence of calcium carbonate and elevated concentrations of Na, Ca, and Mg sulfate salts, was positively correlated with hazardous levels of Se. His results are consistent with data collected in the San Joaquin Valley and other areas that point to Se–sulfur associations in primary and secondary minerals as geologic sources for Se in soils, groundwater, and drainage water (Presser and Swain 1990).

Alkali and Alkaline Earth Metals

Barium

Barium is a priority pollutant, and aquatic life and drinking-water criteria have been established (EPA 1986). Mineralogical sources of Ba include aluminosilicate mineral structures, such as feldspars and micas, where Ba substitutes for K and Ca. Barium, which is present in the +2 valence state, also substitutes for Ca in secondary minerals, such as calcite and apatite. In weathering environments, Ba solubility seems to be primarily controlled by reactions with mineral surfaces and by the precipitation and dissolution of barite ($BaSO_4$) and witherite ($BaCO_3$) (Rai and Zachara 1984).

The interaction of Ba with mineral surfaces is important in controlling aqueous concentrations. Nonspecific adsorption on constant-charge surfaces exerts substantial control on aqueous Ba concentrations (e.g., Elprince et al. 1980). Barium is also specifically adsorbed onto silicate and Al, Mn, Ti, and Fe oxide minerals (Kinniburgh et al. 1976; Posselt et al. 1978). We found no documentation of high Ba levels in saline environments. The available evidence for marine environments indicates that Ba concentrations are limited by the solubilities of the sulfate and carbonate minerals.

Lithium

Although typically present as a monovalent cation, lithium's small ionic and atomic size causes it to behave similarly to the divalent alkaline earth

metals, especially Mg^{2+}. Mineralogically, lithium occurs in Li-halogen and Li-oxygen bonds, primarily in silicate, phosphate, and halide minerals.

Released from these primary minerals during weathering, Li^+ commonly is removed from solution by incorporation into clays. Among monovalent cations, Li is the most weakly bonded of all the alkali metals. In soils and groundwater in which Na and K are present at high concentrations, Li may remain in solution and behave conservatively. Deverel and Millard (1988) found that Li concentrations greater than 100 µg/L were associated with groundwater salinity in $NaSO_4^-$ dominated shallow groundwater beneath the western San Joaquin Valley, California.

The environmental toxicity of Li is not well documented; however, it is apparently toxic to plants at concentrations of less than 100 µg/L in irrigation water. Bradford (1963) reported that citrus trees may be damaged by irrigation water containing 60 to 100 µg/L of Li.

Transition Metals

Chromium

Chromium exists primarily in the trivalent (Cr(III)) and hexavalent (Cr(VI)) forms. The hexavalent form is substantially more toxic than the trivalent form (EPA 1986). Reduced plant growth (James and Bartlett 1984; Turner and Rust 1971) and soil microbial activity (Ross et al. 1981) were reported due to high concentrations of Cr in soil.

Anthropogenic inputs in the form of sewage sludges, waste water, industrial metal processing, and wood preservation and mining activities are the primary sources of high Cr concentrations in soils and groundwaters. Chromium is second to Pb in frequency of occurrence at U.S. Superfund sites (Tiesta 2005). Robertson (1975) reported naturally occurring Cr(VI) concentrations as high as 200 µg/L in Arizona, owing to the dissolution and oxidation of Cr(III)-bearing minerals. Oze et al. (2007) summarized data for other locations where high naturally occurring Cr(VI) concentrations have been identified, including Italy, Mexico, and California. Chromite in mafic and serpentinic rocks and sediments occurring at convergent plate margins is the primary source of hexavalent chromium. Oze et al. (2007) demonstrated accelerated chromite oxidation in the presence of birnessite, a common Mn mineral. This natural oxidation can lead to Cr(VI) concentrations that exceed the World Health Organization maximum drinking water contaminant level of 50 µg/L.

Ball and Izbicki (2004) assessed the processes affecting the natural occurrence of Cr in 200 groundwater samples collected in the Mojave Desert in California. Concentrations ranged from less than 0.1 to 60 mg/L; almost all in the hexavalent form in groundwater samples collected in sediments derived from mafic rock. Close to recharge areas

where near-oxygen-saturated groundwater pH values were near neutral, Cr concentrations were low. Concentrations increased downgradient as long as oxygen was present. Trivalent Cr was present in groundwater discharge areas where oxygen was below 1 mg/L. Concentrations varied by geologic material. Higher concentrations were associated with mafic rocks, and lower concentrations were associated with alluvial materials derived from mixed volcanic, granitic, and mafic sources. The results of this study indicated that geologic origin of aquifer materials and groundwater redox status are the primary factors affecting Cr species and concentration in groundwater.

In Hinkley, California, in the Mojave Desert, where cooling water from an industrial facility containing Cr as a corrosion inhibitor entered the groundwater, there was some evidence for reduction of Cr(VI) to Cr(III) (Andrews and Neville 2003), and pH and *Eh* data pointed to Cr(III) as the stable species. However, the long-term persistence of Cr(VI) in the upper aquifer indicated that electron donors for reduction of Cr(VI) were limited. In contrast, in the oxic and ferruginous Trinity aquifer in Odessa, Texas, Henderson (1994) presented substantial evidence of adsorption, reduction by iron minerals and immobilization of Cr(VI) at a Superfund site. Trivalent Cr is the thermodynamically stable chemical form in these and most environments (Barnhart 1997).

Laboratory studies and modeling by Friedly et al. (1995) and Anderson et al. (1994) demonstrated the importance of reduction of Cr(VI) by ferrous iron in aquifer materials and along groundwater flow paths. However, the time scale for disappearance of Cr(VI) in the field was limited by diffusion resistance. In the model of the field experiments, the reducing agents [Fe(II)-bearing minerals] were heterogeneously distributed in thin strata located between larger nonreducing sand lenses that comprised the bulk of the aquifer solids. The authors identified reducing strata of the order of centimeters thick that were sufficient to contribute enough diffusion resistance to cause the long observed timescales for Cr(VI) reduction in the field relative to laboratory experiments. This reduction process has been identified as a mechanism for Cr(VI) removal along a groundwater flow path underlying and downgradient of a land fill (Loyaux-Lawniczak et al. 2001). Extremely reducing and polluting conditions, such as those identified by Davis et al. (1994) in groundwater underlying and downgradient of a tannery in Woburn, Massachusetts, increased solubility and mobility of Cr(III) due to its association with hydrophilic acids.

Manganese also affects the fate and transport of Cr(VI) (Stanin 2005). Oxidation of trivalent chromium by MnO_2 is likely to occur in three steps: sorption of trivalent chromium to MnO_2 surface sites, subsequent oxidation to hexavalent chromium by Mn(IV), and desorption of Cr(VI). The interaction of Cr and Mn is important in groundwater fate and transport

as they often show opposing tendencies (Stanin 2005). For example, in the San Joaquin Valley, California, Deverel and Millard (1988) observed high Cr and low Mn concentrations in the upgradient alluvial fan groundwater and the opposite in the more reducing downgradient basin-trough groundwater. Their results indicate that soluble Mn serves as an electron donor for reduction of Cr(VI) to Cr(III).

The solubility of Cr(III) in soil solution and groundwater is affected primarily by its interaction with mineral surfaces and co-precipitation with iron-oxide-type minerals. Chromite ($FeCr_2O_4$) is stable at low temperatures for most of the water stability region and could be formed as an admixture or co-precipitate with ferrous hydroxide (Hem 1977). Rai and Zachara (1986) identified the solid solution $Cr_xFe_{1-x}(OH)_3$ and $Cr(OH)_3$ (chromium hydroxide) as the solid phase exercising the predominant solubility control on Cr(III) in geologic systems. The amount of Cr(III) adsorbed by a Typic Fragiorthod soil increased with pH increasing to 4 (Bartlett and Kimble 1976). Trivalent Cr was also complexed by organic compounds in soil (Bartlett and Kimble 1976).

Trivalent Cr oxidizes to the hexavalent form under conditions prevalent in some field soils (Bartlett and James 1979). Organic material and manganese oxides (Bartlett and James 1979; Rai and Zachara 1986) are important electron acceptors for this reaction. The hexavalent form can be reduced to Cr(III) in soils (James and Bartlett 1983) and in water samples acidified for preservation (Stollenwerk and Grove 1985b).

The mobility of Cr(VI) in soil solutions and groundwaters is controlled by adsorption/desorption reactions at mineral surfaces and redox reactions. Amorphous iron oxide has a high capacity for adsorption of Cr(VI) (Leckie et al. 1980). Stollenwerk and Grove (1985a) and Weng et al. (1997) used Langmuir isotherms to describe adsorption of Cr(VI) onto aquifer materials and titanium oxide. Ionic-strength-dependent Cr(VI) adsorption as a function of pH was well described on amorphous iron oxide using the triple-layer model (Davis and Leckie 1980) and on goethite using the diffuse-layer model (Mesuere and Fish 1992). The diffuse-layer model was also used to successfully describe Cr(III) adsorption on silica and aluminum oxide (Csoban and Joo 1999). Adsorption of CrO_4^{2-} by goethite (Grossl et al. 1997) and titanium oxide (Weng et al. 1997) has been successfully described using the constant-capacitance model. The CD-MUSIC model was able to describe Cr(VI) adsorption by goethite as a function of pH and equilibrium CrO_4^{-2} concentration (Weerasooriya and Tobschall 2000). These approaches underscore the need to consider the supporting electrolyte and competing ions in describing adsorption of Cr(VI). Zachara et al. (1989) described chromate adsorption by soils as a function of pH using the triple-layer model. These authors assumed that the adsorption sites for chromate in these soils were the iron sites of aluminum substituted goethite.

Molybdenum

Molybdenum occurs in oxidation states from +3 to +6. Under acidic reducing conditions, the Mo(IV) oxidation state dominates and usually precipitates as a sulfide. Under oxidized conditions, the Mo(VI) oxidation state dominates, primarily as MoO_4^{-2}. Because of its oxyanion form, it commonly behaves conservatively in alkaline, oxidized environments. Consistently, in western San Joaquin Valley shallow groundwater (Deverel and Millard 1988), specific conductance explained 58% to 85% of the variance in Mo concentrations. Molybdenum can substitute for Al, Fe, and Ti in aluminosilicates or metal oxides, and is often associated with organic materials in sedimentary rocks and soils.

Little evidence exists of human Mo toxicity from drinking water, and few data are available on chronic Mo toxicity. Ruminants grazing in some parts of the San Joaquin Valley of California were found to be adversely affected by elevated Mo content, especially in legumes and mainly on alkaline soils (Barshad 1948). Unlike legumes, most grasses and grains tend not to accumulate Mo to toxic levels (O'Connor et al. 2001).

Mineral surface reactions and interactions with organic matter are the predominant processes controlling the mobility of Mo in soils and groundwaters (Jarrell et al. 1980). Adsorption and incorporation into Mn, Fe, and Al oxides are predominant mechanisms controlling Mo solubility in oxidized environments at low pH (Hem 1977; Reyes and Jurinak 1967). Co-precipitation and adsorption of Mo with and onto manganese and iron oxides decreases with increasing pH greater than 5 (Chan and Riley 1966; Reyes and Jurinak 1967).

Molybdenum adsorption has been described on Al and Fe oxides (Goldberg et al. 1996), Ti oxide (Saripalli et al. 2002), and clay minerals (Manning and Goldberg 1996; Motta and Miranda 1989) using the constant-capacitance model. The CD-MUSIC model was used to describe Mo adsorption on titanium oxide as a function of solution Mo concentration and pH (Bourikas et al. 2001). Gustafsson (2003) found the diffuse-layer model to be superior to the CD-MUSIC model in describing molybdate adsorption by amorphous iron oxide. The triple-layer model was able to describe Mo adsorption on Al and Fe oxides, clay minerals, and soils as a function of solution pH and ionic strength (Goldberg et al. 1998, 2008).

A new approach for predicting Mo adsorption used a general regression model to predict constant-capacitance model (Goldberg et al. 2002) and triple-layer model (Goldberg et al. 2008) parameters from easily measured soil chemical properties: cation exchange capacity, organic carbon content, inorganic carbon content, and iron oxide content. This approach provides a completely independent model evaluation and was well able to predict Mo adsorption on soils of diverse orders having a wide range of chemical characteristics, as indicated in Fig. 4-2.
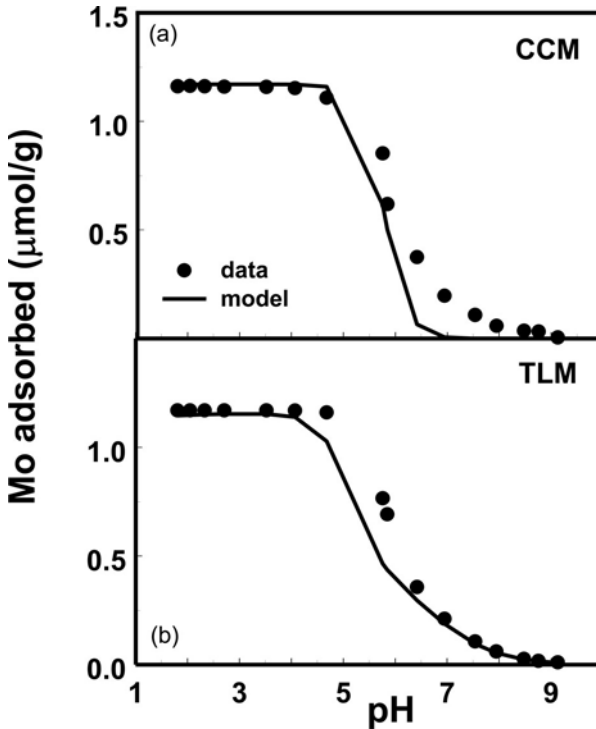
FIGURE 4-2. *Prediction of Mo adsorption on Wyo soil: (a) constant-capacitance model; (b) triple-layer model. Circles represent experimental data; model predictions are represented by solid lines. Adapted from Goldberg et al. (2008).*

Vanadium

Vanadium (V) exists in four different geochemical environments: sulfide deposits, oxidized sulfide ores, aluminosilicates, and iron-oxide deposits (Wedepohl 1972). Vanadium can exist in three oxidation states: $+3$, $+4$, and $+5$ (Hem 1977). The trivalent form of V is incorporated into sulfide minerals, and it often replaces Al in aluminosilicate structures and Fe in iron oxide minerals (Schwertmann and Pfab 1996).

In oxidized deposits, V is present in the tri-, tetra- and pentavalent forms. Evans and Garrels (1958) identified a V mineral weathering sequence spanning the valence states from $+3$ to $+5$ and associated with oxidized uranium deposits in the Colorado Plateau. Hem (1977) presented evidence that ferric and ferrous vanadates may control the solubility of V in natural waters. The vanadyl ion, VO^{2+}, is dominant under reducing environments and is strongly complexed by organic matter (Wehrli and Stumm 1989). A large pool of adsorbed V exists in salt-

affected Kesterson Reservoir evaporation pond soils that may be mobilized under reducing conditions (Amrhein et al. 1993).

Interactions with mineral surfaces substantially influence aqueous V activities in acidic environments. McBride (1979) and Taylor and Giles (1970) described the adsorption of V on montmorillonite and Mn- and Fe^{3+}-oxides. Both the vanadyl, VO^{2+} (Wehrli and Stumm 1989), and the vanadate, HVO_4^{2-} (Peacock and Sherman 2004), species are strongly adsorbed on oxide surfaces. Both the diffuse-layer model and the triple-layer model were successful in describing vanadate adsorption onto goethite (Peacock and Sherman 2004).

Because it tends to exist in oxyanion forms, V commonly is mobile in alkaline, oxidized aqueous environments. Consistently, Deverel and Millard (1988) reported V concentrations to be significantly correlated with specific conductance data in shallow groundwater in the San Joaquin Valley, California. Anthropogenic sources of V in soils and groundwater include industrial wastes, sewage sludge, fossil fuel by-products, and mine spoils (Mattigod and Page 1983; National Academy of Sciences 1974). Because of its mobility in oxidized environments, V from these sources may represent a potential pollution hazard. Although tolerance levels for aquatic life have not been established, incidences of industrial V toxicosis, primarily from airborne V, have been documented (National Academy of Sciences 1974).

Metalloids and Nonmetals

Arsenic

Because of its carcinogenic effects on human health, detectable concentrations (μg/L levels) of arsenic (As) in water consumed by humans are undesirable (EPA 1986). In recognition of the hazards arsenic poses to humans and domestic animals, the EPA recently lowered the drinking water standard from 50 to 10 μg/L. The predominant factors governing As levels in natural waters are the redox state of the water, aqueous–mineral interactions, and biochemical transformations (Welch et al. 2000). At higher soil redox (500–200 mV), As solubility is low and is predominantly present as As(V) in solution; under moderately reducing conditions (0–100 mV), As solubility is controlled by the dissolution of iron oxides (Masscheleyn et al. 1991).

Arsenic exists in several oxidation states. In the tri- and pentavalent forms, it can be incorporated into aluminosilicates and titanium and iron oxide minerals. In the more reduced −3 valence state, As forms sulfides, such as arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3). Welch et al. (1988) described geochemical environments in the western United States where As may be present in groundwaters. High As concentrations

are found in groundwaters in alluvial basins derived from neutral to acidic extrusive and volcanic rocks. Groundwaters in gold mining areas and geothermal areas where arsenosulfide minerals are present generally have high As concentrations. The application of arsenical pesticides is another source of As pollution in groundwaters and soils (Hem 1985).

Biogeochemical transformations of arsenic include biomethylation to produce soluble methylated arsenic compounds and mono- or dimethyl arsine gases (Faust et al. 1983; Lemmo et al. 1983; Welch et al. 1988). Volatilization rates of As as arsines are influenced by As form, As concentration, soil moisture, soil temperature, and organic amendment (Gao and Burau 1997).

Adsorption and co-precipitation of As by clay minerals and metal oxides are the predominant solubility controls in oxidized environments (Hem 1977; Leckie et al. 1980; Pierce and Moore 1980). Leckie et al. (1980) demonstrated that arsenate adsorption on amorphous iron oxyhydroxide, $Fe(OH)_3$, decreased at pH values greater than 8. Both arsenate, As(V), and arsenite, As(III), are adsorbed on oxide minerals. The adsorption behavior is pH-dependent; at low pH arsenate is adsorbed to a greater extent, while arsenite is adsorbed more at high pH (Raven et al. 1998).

Arsenic adsorption has been described on Al and Fe oxides (Gao and Mucci 2001, 2003; Goldberg and Johnston 2001) and clay minerals (Manning and Goldberg 1996) using the constant-capacitance model. The diffuse-layer model (Dixit and Hering 2003; Dzombak and Morel 1990) and the triple-layer model (Benjamin and Bloom 1981; Goldberg and Johnston 2001; Hsia et al. 1992) have been used to describe the adsorption of arsenate and arsenite on iron oxides. Arsenate and arsenite adsorption has been described using the CD-MUSIC model for gibbsite (Weerasooriya et al. 2003, 2004), goethite (Stachowicz et al. 2006), and an allophanic soil (Gustafsson 2001).

Similar to the approach for Mo, arsenate adsorption was predicted using a general regression model to predict constant-capacitance-model parameters from easily measured soil chemical properties: cation exchange capacity, inorganic carbon content, organic carbon content, iron oxide content, and surface area (Goldberg et al. 2005b). This approach provided a completely independent model evaluation and was well able to predict As(V) adsorption on many soils from both the southwestern and midwestern United States having a wide range of chemical characteristics, as indicated in Fig. 4-3.

Boron

Boron generally behaves conservatively in natural waters. It occurs primarily as the undissociated acid H_3BO_3 at pH < 9 and as the $B(OH)_4^-$ anion at pH > 9. Primary and secondary aluminosilicate minerals often
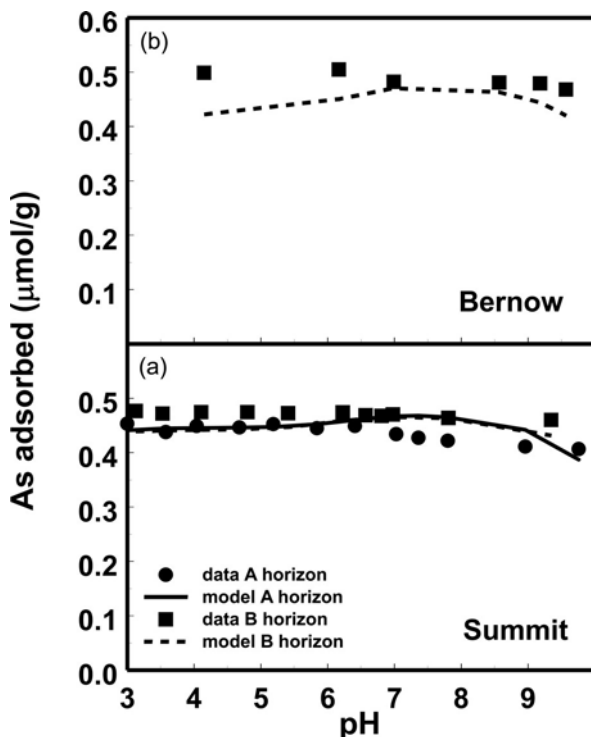
FIGURE 4-3. Prediction of As adsorption on soils using the constant-capacitance model: (a) Bernow soil; (b) Summit soil. Experimental data are represented by circles for the A horizon and squares for the B horizons. Model predictions are represented by solid lines for the A horizon and dashed lines for the B horizons. Adapted from Goldberg et al. (2005a).

contain B, as it substitutes for silica and Al. In semiarid, and arid environments, B may substantially threaten irrigated agriculture due to its phytotoxic effects and conservative behavior. Soil minerals can attenuate potentially phytotoxic soil-solution B concentrations because plants respond only to B in solution (Keren et al. 1985). Evidence exists that bioaccumulation to levels toxic to waterfowl can occur (Smith and Anders 1989; Hoffman et al. 1990). Deverel and Millard (1988) reported B concentrations that were highly correlated with shallow groundwater salinity in the San Joaquin Valley, California. Boron concentrations can be affected substantially by interaction with mineral surfaces. Most researchers have described the B–soil association as one of adsorption or desorption. Goldberg (1997) and Rai and Zachara (1984) have summarized research in this area.

Elrashidi and O'Connor (1982) used the Langmuir and Freundlich equations to describe B adsorption. The change in adsorptive behavior with changing pH cannot be accurately described using this approach. Boron adsorption onto various minerals and soils is strongly pH-dependent, exhibiting maximum adsorption from pH 7 to 10.

Keren et al. (1981) successfully modeled the pH dependence of B adsorption on soils and montmorillonite. Goldberg and Glaubig (1985, 1986a, 1986b) and Goldberg et al. (2000) applied the constant-capacitance model to B adsorption on soils and various minerals from pH 3 to 12. The diffuse-layer model has been applied to B adsorption by amorphous iron oxide (Dzombak and Morel 1990). The triple-layer model was used to describe B adsorption by oxide minerals (Blesa et al. 1984) and kaolinite (Singh and Mattigod 1992).

Similar to the approach for Mo and As(V), B adsorption was predicted using a general regression model to predict constant-capacitance-model parameters from easily measured soil chemical properties: surface area, inorganic carbon content, organic carbon content, and Al oxide content (Goldberg et al. 2000, 2004, 2005a). This approach provided a completely independent model evaluation and was well able to predict B adsorption on soils of diverse orders having a wide range of chemical characteristics, as depicted in Fig. 4-4. The prediction equations, developed from B adsorption as a function of pH on a set of soils from the southwestern United States, were able to predict B adsorption as a function of solution B concentration on a set of soils from the midwestern United States, indicating wide predictive capability (Goldberg et al. 2004).

The soluble B in irrigated soils may regenerate or increase in concentration after reaching a constant low concentration. Peryea et al. (1985) concluded that slow release of B from adsorption sites and diffusion of B from small pores to large pores are the mechanisms responsible for the regeneration of B in the soil solution. Weathering of soils with a high amount of structural B may release phytotoxic levels of B within a few years of reclamation unless leaching is maintained (Su and Suarez 2004). (See Chapter 19 for a discussion on B reclamation in soils.) Corwin et al. (1999) evaluated five different approaches for predicting B–surface interactions and transport in large lysimeters using the *TETrans* solute transport model. They concluded that the pH-dependent Keren equation was the best-performing chemical adsorption model. Their results suggest that pH and ionic strength were the most influential chemical factors, followed by temperature and kinetics for B transport.

Selenium

Selenium generally is similar to sulfur in its chemical behavior (Lakin 1973). Substantial evidence exists that suggests Se is associated primarily with sulfide minerals present in sedimentary environments (Sindeeva
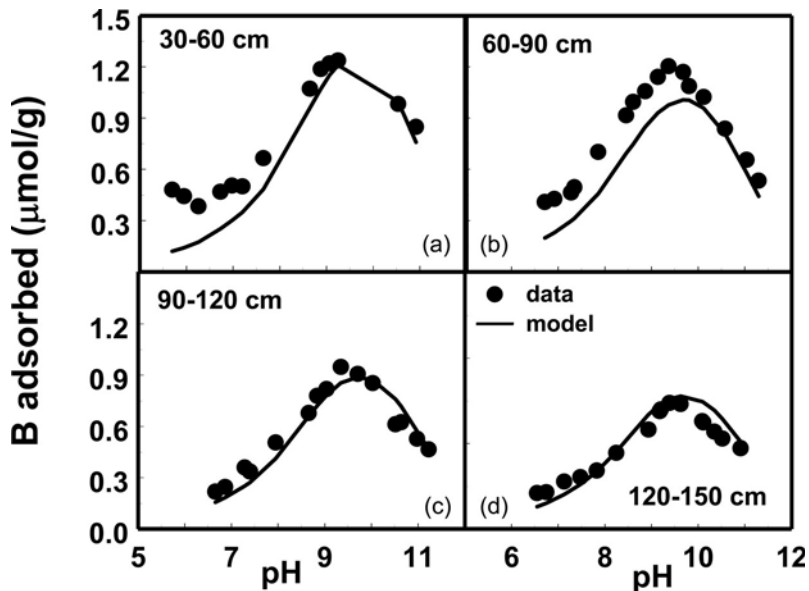
FIGURE 4-4. Prediction of B adsorption on various depths of a soil profile using the constant-capacitance model: (a) 30–60-cm depth; (b) 60–90-cm depth; (c) 90–120-cm depth; (d) 120–150-cm depth. Circles represent experimental data; model predictions are represented by solid lines. Adapted from Goldberg et al. (2005b).

1964). The mobility of Se in the aqueous phase depends on aqueous complex formation, redox speciation, and reactions at mineral surfaces. High concentrations of Se in groundwaters and agricultural drain waters in several western U.S. states primarily result from the high mobility of the SeO_4^{-2} (selenate) ion, the predominant species in alkaline, oxidized environments (Crist 1974; Deverel and Millard 1988; Sylvester et al. 1988).

Selenate (SeO_4^{2-}), although it adsorbs on oxide surfaces (Peak and Sparks 2002), generally is nonadsorptive in soils (Neal and Sposito 1989), especially in the presence of high concentrations of sulfate. Selenite (SeO_3^{2-}), in contrast, generally adsorbs strongly onto mineral surfaces (Balistrieri and Chao 1987; Ryden et al. 1987) and soils (Neal et al. 1987a,b).

Selenite adsorption has been described on iron oxide minerals using the constant-capacitance model (Goldberg 1985; Duc et al. 2006) and the diffuse-layer model (Dzombak and Morel 1990). The triple-layer model described selenite adsorption on iron and manganese oxide (Balistrieri and Chao 1990). By describing selenite adsorption using inner-sphere surface complexes and Se(VI) adsorption using outer-sphere surface complexes, the triple-layer model (Hayes et al. 1988) and the CD-MUSIC

model (Hiemstra and van Riemsdijk 1999; Rietra et al. 2001) correctly accounted for the differing strength of adsorption of these ions.

Selenite adsorption on four California soils was qualitatively predicted using the surface complexation constants obtained by applying the constant-capacitance model to one other California soil (Sposito et al. 1988). Similar to the approach for Mo, As(V), and B, Se(IV) adsorption was predicted using a general regression model to predict constant-capacitance-model parameters from easily measured soil chemical properties: inorganic carbon content, organic carbon content, Al oxide content, Fe oxide content, and surface area (Goldberg et al. 2007). This approach provided a completely independent model evaluation and was well able to predict Se(IV) adsorption on many soils from both the southwestern and midwestern United States having a wide range of chemical characteristics, as depicted in Fig. 4-5.

Fio et al. (1991) evaluated the mobility of selenite and selenate in San Joaquin Valley irrigated and nonirrigated soils. They conducted sorption studies of selenite and selenate and incorporated the results into a one-dimensional solute transport model to simulate changes in soluble and adsorbed Se and to evaluate the potential for leaching of Se to groundwater. Model results showed that selenite can represent a potential long-term source of Se to the groundwater. In contrast, selenate behaves conservatively under the alkaline and oxidized conditions in the western San Joaquin Valley and is easily leached from the soil.
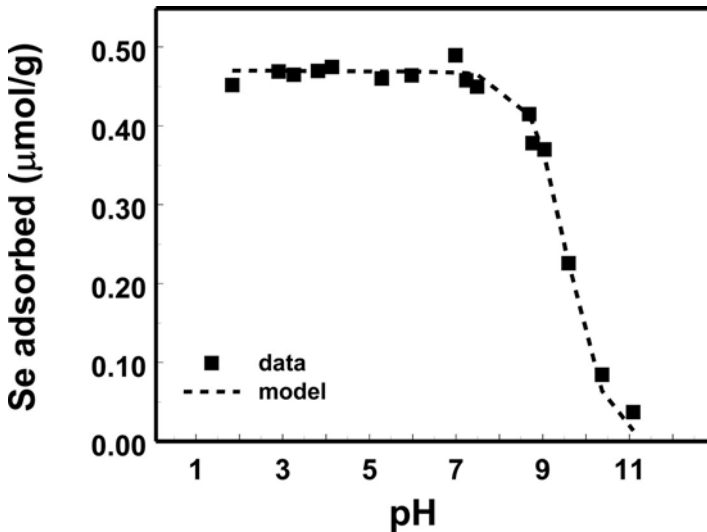

FIGURE 4-5. Prediction of Se adsorption on the B horizon of Dennis soil using the constant-capacitance model. Circles represent experimental data; model predictions are represented by solid lines. Adapted from Goldberg et al. (2007).

Selenium toxicity in waterfowl at Kesterson Reservoir in the San Joaquin Valley, California, resulted from high concentrations of SeO_4^{2-} in shallow groundwater (e.g., Presser and Ohlendorf 1987). This Se contamination of the groundwater results from irrigation of soils derived from cretaceous and tertiary geologic materials in the California coast range. The semiarid climate resulted in the formation of naturally saline soils in many areas. Irrigation of these soils resulted in the movement of soluble salts, including Se, into the groundwater. Partial evaporation of a shallow water table in low-lying areas resulted in even higher salinity and Se concentrations (Deverel and Fujii 1988). Farm drainage systems remove this high Se groundwater in some areas. Drain water in some areas is mixed with nonsaline water and reused for irrigation. In other areas, drain water is mixed with surface runoff and irrigation water and discharged to adjacent wetlands and the San Joaquin River.

Metals: Cadmium, Copper, Lead, Nickel, and Zinc

The biogeochemical behaviors these metals are similar; therefore, they will be discussed as a group. In oxidized sedimentary and secondary mineral environments, the solubility, mobility, and distribution of these metals is primarily affected by adsorption onto and co-precipitation with iron and manganese oxides and oxyhydroxides, pH and interactions with solid- and dissolved-phase organic matter (e.g., Adriano, 2001; Gibbs 1976; Jenne 1968; Kinniburgh et al. 1976; Quirk and Posner 1976). Sewage sludge, animal manures, pesticides, and fertilizers are significant sources of Cd, Cu, Pb, Ni, and Zn in agricultural soils. Mattigod and Page (1983), Alloway (1995) and Adriano (2001) have extensively reviewed the sources and mobility of these metals in soils. Fertilizers and sewage sludge are Cd sources, swine manure and pesticides are Cu sources, and sewage sludge and pesticides are Pb and Zn sources (Adriano, 2001). Sewage sludge is the primary anthropogenic source of Ni. The primary sources of these constituents in agricultural soils are sewage sludge and fertilizers. Pesticides, mining, and smelting activities also contribute these elements to some agricultural soils. Non-anthropogenic sources can also contribute soil concentrations that cause lowered crop productivity and phytotoxicity. For example, Ni concentrations in serpentine-derived soils can be problematically high for some plant growth.

Sewage sludge application is a significant source of Cd, Cu, Pb, Ni, and Zn to soils worldwide. There has been some long-term research on the behavior of these elements in sludge-amended agricultural soils as interest in applying sewage sludge to soils has increased substantially during the last two decades. Adriano (2001) summarized results of field experiments that spanned more than 10 years. Data from the United States and Europe indicated Zn as having the highest input rate (usually by an order of magnitude) to sludge-amended soils. The high Zn inputs

can in turn affect the mobility and bioavailability of other trace metals of concern (Cu, Cd, Ni, and Pb). Incorporation of sewage sludge has led to marked increase in Cd, Cu, Pb, Ni, and Zn concentrations in the upper 30 cm of receiving soils. Field studies generally showed no significant concentration differences between soils with and without sludge application below 30 cm (Adriano 2001; Berti and Jacobs 1998; Dowdy and Volk 1983). However, some studies point to the mobility of these metals to deeper depths (Dowdy et al. 1991; Steehuis et al. 1999). The increased mobility of Cd, Cu, Pb, Ni, and Zn in sludge-amended soils can be attributed to the formation of metal-organic compounds and preferential flow in the unsaturated zone.

There are also soil ecological effects of application of sewage sludge as plant growth, soil microbial activity, and fertility can be affected. McGrath et al. (1995) summarized the evidence for effects of metals applied in sewage sludge on soil microbial activity and fertility in long-term for studies conducted in the United States and Europe. Although reduced plant yields were documented in some cases, these were not due to decreased fertility but, rather, to adverse effects on nitrogen-fixing microbes. There was also evidence for reduced total soil microbial mass. Effects on microbes and plants were reduced by increased pH, clay content, and percent organic matter content which enhanced metal sequestration. Notably, effects on the microbial community were observed at soil metal levels below European maximum allowable levels.

Application of animal manures (primarily poultry, swine, and bovine) represents a significant source of Cu and Zn in soils. These metals are often added to animal feeds in excessive amounts relative to animal needs and significant amounts are passed through to feces. Sistani and Novak (2006) recently summarized research on trace-metal accumulation in manure amended soils. There is little evidence for movement of these elements past the upper 30 cm of soil. However, there is evidence for Cu and Zn concentrations in surface runoff in the southeastern United States that are toxic to aquatic life. Also, soil concentrations can build up to levels high enough to result in yield reductions and phytotoxicity.

Phosphate fertilizers derived from sedimentary phosphates may contain high levels of Cd, although concentrations and amounts of Cd applied to soils are highly variable (Adriano 2001). In contrast, phosphate fertilizers derived from magmatic sources generally contain negligible amounts of Cd. Pesticides, such as copper sulfate, are sources of Cu in many agricultural soils, and there is evidence that application of pesticides and Cu fertilizers has resulted in high soil concentrations that can lead to adverse effects on plants or the microbial community. In tropical areas, long-term continuous application of Cu pesticides and fertilizers has resulted in high crop concentrations and soil residues and occurrence of phytotoxicity symptoms in tropical crops, such as coffee, tea, cocoa, and bananas (Adriano 2001). Application of lead arsenate pesticides prior

to the 1960s in deciduous fruit tree orchards has led to accumulation of Pb (and As) in orchard surface soils (Peryea and Creger 1994). Atmospheric deposition of Pb from its use in gasoline has resulted in high Pb concentrations in soils in highly industrialized areas.

Numerous studies have demonstrated high soil concentrations of Cd, Pb, and Zn and phytotoxicity resulting from atmospheric deposition near Pb, Zn, and battery smelting facilities (Adriano 2001). The phytotoxicity of Cd, Cu, Ni, Pb, and Zn corresponds to their electronegativity (Cd > Cu > Ni > Zn > Pb).

Even though there is little evidence for significant movement of Cd, Cu, Pb, Ni, and Zn to groundwater, organic complexation and soil-water and groundwater pH, salinity and redox potential need to be considered when evaluating the mobility, solubility, and bioavailability of these elements in soils and groundwaters. Mobility and bioavailability of metals in soils are generally reduced by increasing pH, organic matter content, cation exchange capacity, and redox potential. Adding lime to soils with high metal concentrations and sludged soils has been shown to reduce plant uptake of Cd, Cu, Pb, Ni, and Zn. These metal species in soil are dependent on pH, as illustrated previously for Cd. The most phytotoxic cationic form predominates at pH values below 7.0, whereas metal hydroxide or carbonate complexed species predominate above pH 7.0. Solubilities of metals are reduced at higher pH values (above 6.5 to 7.0) due to formation of metal phosphates and carbonates. For Cd, Cu, Pb, Ni, and Zn, increasing pH is the predominant factor affecting bioavailability to plants. Low pH (below 4.0) and low redox potential values that favor solubilization of iron minerals facilitate movement in soils and may result in groundwater contamination. This has been observed at industrial hazardous waste sites in which other pollutants have greatly altered subsurface redox and pH. Low redox and pH conditions favor solubilization of metal hydroxides and oxy-hydroxides, thus increasing metal solubility. However, reducing conditions that favor sulfate reduction result in formation of metal sulfides and reduced metal solubility.

Cadmium, Cu, Pb, Ni, and Zn strongly adsorb on organic matter in oxic sediments through ion exchange and chelation. Zinc and Ni form insoluble organic complexes and adsorb onto soil organic matter. (Addition of organic matter and/or lime is a common practice for reducing Ni availability in the reclamation of serpentine soils.) For sludge-amended soils, numerous investigators have reported that variable proportions of Cd, Cu, Pb, Ni, and Zn are present in organically bound forms. For example, Hickey and Kittrick (1984) used selective extraction techniques to determine that organically bound heavy metals represented significant proportions of the total metal present in the soil. Other studies with sludge-amended soils also demonstrated that Cu is organically complexed to a greater degree than the other metals (e.g., Emmerich et al. 1982). Paradoxically, metal-organic complexes in soil can enhance aqueous solubility.

Modeling and quantitative estimation of organically complexed metals in natural waters has traditionally been limited by lack of information on the chemical composition of the dissolved organic matter and the appropriate thermodynamic constants. Lerman and Childs (1973), Stumm and Morgan (1981), Davis (1984), Davis and Leckie (1978), and others attempted to quantify the effect of organic ligands on the aquatic solubility and mobility of various metals. Several authors have documented the use of empirical, semi-empirical, and statistical models for estimating metal–organic interactions (e.g., Elzinga et al. 1999; Guy and Chakrabarti 1976; McBride et al. 1997).

Several authors have examined the effects of varying salinity on metal mobility and bioavailability. Cadmium mobility and availability for plant uptake generally increased with increasing salinity and Cl concentrations. For example, Amini et al. (2005) assessed the spatial variability of diethylenetriaminepentaacetic acid (DPTA) extractable Cd in Iranian soils and identified a positive and significant correlation with soil electrical conductivity. Similarly, Khoshgoftar et al. (2004) and Norvell et al. (2000) found that NaCl salinity mobilized soil Cd and increased its phytoavailability. In contrast, Zn availability and mobility was generally not affected by moderate salinity levels due to its propensity to adsorb or precipitate independently of soil salinity. Khoshgoftarmanesh et al. (2006) obtained similar results. Their study and other studies (e.g., McLaughlin et al. 1997; Weggler et al. 2004) included the analysis of Zn and Cd species in solution. With increasing salinity, Cd increasingly forms chloride complexes, which increases total solution concentrations and Cd availability to plants. Cadmium-chloride complex formation also results in displacement of Cd from exchange sites. Although we were unable to find studies of effects on groundwater quality, based on these results of these studies, we expect that increasing salinity may increase Cd movement to groundwater.

We identified three studies of salinity effects on the bioavailability and mobility of other metals. Preeda et al. (2002) evaluated the effect on DPTA extractable Zn, Cu, Ni, Pb, Cd, and Cr in Thailand sludge-amended soils at different salinity levels ranging from a nonsaline control and 2 to 42dS/m. DPTA-extractable Zn, Cu, and Pb concentrations were higher than the control in the 2 and 4 dS/m treatments, and concentrations were lower in the 8, 19, 31, and 42 dS/m treatments. DPTA-extractable Ni concentrations were unaffected by salinity below 8 dS/m but concentrations were lower at higher salinities.

Usman et al. (2005) assessed the effect of metal immobilizing substances (Na-bentonite, Ca-bentonite, zeolite, iron oxides and phosphate fertilizers) and NaCl salinity (1,800 mg/L versus a deionized-water control) on the availability of heavy metals: Zn, Cd, Cu, Ni, and Pb to wheat. The largest reduction in metal bioavailability was found for bentonites.

Irrigation with saline water (1,600 mg L^{-1} NaCl) resulted in a significant increase in metal chloride species (MCl^+ and MCl^{+2}). The highest metal complexation with Cl occurred for Cd, which was about 53% of its total soil-solution concentration. The total concentration of Cd in soil solution increased by 1.6- to 2.8-fold in saline water. The NaCl salinity caused a significant increase in uptake and shoot concentration of Cd for two harvests, and small but significant increase in shoot Pb concentration. Saline water increased the availability of Cd and Pb to wheat and decreased the efficiency of bentonites to immobilize soluble Cd. Zinc, Cu, and Ni levels in wheat were not different for the nonsaline and saline treatments, presumably due to the relatively low propensity to form chloride complexes.

Keshavarz et al. (2006) assessed the mobility of native-soil Zn under different NaCl salinities in calcareous soils. Their results indicate that the partitioning of soil Zn changed with increasing salinity to 20 dS/m. These authors concluded that increased salinity redistributed nitric-acid-extracted Zn to the soluble and exchangeable and organic forms of Zn and became more available to plants with increasing salinity.

Mercury

Mercury exists in the mercurous (+1), mercuric (+2), and metallic (0) forms in soils and groundwater (Hem 1970). Mercury readily forms aqueous organic complexes and commonly is present in methylated forms derived from biological metabolism (Jensen and Jernolov 1969). Chronic toxicity of Hg is a dominant environmental issue (EPA 1986), and methyl mercury is of primary concern in surface and subsurface drainage in agricultural soils, especially soils flooded for rice or wetlands.

Sources of Hg in soils and groundwater include sewage sludges, mining wastes, atmospheric deposition, soil parent materials, pesticides, fungicides, and fertilizers. Phosphorous fertilizers in particular are reported to have high Hg concentrations—4 $\mu g/g$ to 100 $\mu g/g$ (Anderson 1979). Organic-rich shales, sedimentary clays, and sulfides are the major geologic sources of Hg (Fleischer 1970).

The fluxes and forms of Hg in soils and groundwater depend on several factors, including temperature, moisture content, and oxidation and reduction state (e.g., Benes and Havlik 1979; Hem 1985). Soil atmospheric flux can be considerable, with volatilization of inorganic forms and release of methylated forms predominant. Although Hg sometimes can move through the soil profile to shallow groundwater and drain water, it usually is substantially removed from solution by adsorption or incorporation into organic matter (Anderson 1979).

In oxidized solutions, the Hg^{2+} ion predominates. The divalent form complexes with Cl^- ion, so that aqueous $HgCl_2^0$ will be the predominant

dissolved inorganic form in most oxidized waters (Benes and Havlik 1979). Under reducing conditions, Hg exists in the relatively insoluble elemental or sulfide forms, $Hg(SH)_2$ and HgS_2^{2-}. Dismutation of the mercurous form, Hg_2^{2+}, to $HgO + Hg^{2+}$ also increases volatility and solubility (Hem 1970).

Organic Hg complexes, including methylated and phenylated forms (Benes and Havlik 1979) comprise a significant portion of soluble Hg in soil solutions and groundwater. These complexes generally are unstable and easily decomposed or volatilized. Adsorption of Hg^{2+} removes Hg from solution. Adsorption of Hg^{2+} onto Mn oxides (Jenne 1970), Fe oxides (Anderson 1979), and soils and sediments (Benes and Havlik 1979) controls the fate of Hg in aqueous environments.

Mercury adsorption has been described using various surface complexation models. The constant-capacitance model was used to describe Hg(II) adsorption by goethite (Gunneriusson and Sjöberg 1993; Gunneriusson et al. 1995). Mercury(II) adsorption by Fe oxides and silicas was described using inner-sphere surface complexes in the diffuse-layer model (Bonnissel-Gissinger et al. 1999; Dzombak and Morel 1990; Tiffreau et al. 1995). A combination of inner-sphere and outer-sphere surface complexes were used to describe Hg(II) adsorption on quartz, gibbsite (Sarkar et al. 1999), and kaolinite (Sarkar et al. 2000).

Caution must be exercised in the collection and preservation of samples for Hg analysis. Sources of Hg contamination are ubiquitous and the ultraclean sampling methods (see Olsen and deWild 1999; USGS 2011) should be used for groundwater and surface-water sample collection. Adsorption to container walls can be prevented by acidification. Reduction to elemental Hg, which is easily volatilized, can be prevented by the addition of an oxidizing agent, such as potassium dichromate or potassium manganate.

EVALUATION OF POLLUTION POTENTIAL IN SOILS

Evaluation of soil quality relative to inorganic trace element concentrations involves general consideration of the soil's capacity to perform its function within the ecosystem. This historically has been defined as plant productivity and plant uptake and concentration [see Adriano (2001) for more in-depth discussion of assessment of soil quality]. However, other factors requiring consideration include potential leaching to groundwater or drain water and potential movement of trace elements within eroded soils or in surface runoff. Evaluation of uptake by plants requires comparison of trace element concentrations in the soil with levels known to be associated with harmful levels of plant uptake. Evaluation of all considerations requires that the mode of occurrence of the element or elements be

determined and the effects of the various biogeochemical and physical processes be identified.

Soil chemical extractants have generally been used successfully to predict plant uptake, especially under controlled conditions. However, the use of chemical extractants may be ineffective for predicting plant uptake in uncultivated soils and among native species (Gough et al. 1979). Soil chemical extraction procedures theoretically dissolve specific phases and minerals in a soil sample. Chao (1984) wrote a comprehensive review of selective dissolution techniques. The partitioning of elements, such as Se and As, which typically are present as anions and undergo oxidation and reduction reactions in soils, may not be effectively characterized by these procedures (Gruebel et al. 1988). Less destructive techniques, such as scanning electron microscopy, electron-microprobe energy-dispersive x-ray analysis, and x-ray photoelectron spectroscopy, can provide information about the mode of occurrence of trace elements in soils, but their utility is typically limited by high detection limits.

Models can be used to evaluate the potential for soils to leach trace elements to the groundwater. The Fio et al. (1991) study cited in the Selenium subsection is one example. Those researchers used a one-dimensional model of Se transport in the unsaturated zone to provide information about future movement to groundwater.

Evaluating the spatial distribution of the total concentrations of trace elements in soils in relation to morphological features and hydrologic processes can provide insight about sources, transport processes, and mobility. For example, Tidball et al. (1986a) spatially interpolated the results of the analyses of more than 700 samples collected in the western San Joaquin Valley, California. These samples were analyzed for more than 30 trace elements. Mobile elements, such as Se, were concentrated in areas where there was less leaching of alluvial material or evapoconcentration from a shallow water table. They also found that less-mobile elements, such as Hg and As, tended to be concentrated near the source of the alluvial deposits.

Factor analysis provides a way of examining the results from chemical analyses of a large number of samples containing trace elements (Joreskog et al. 1976) by simplifying large quantities of data into associations with master variables. Controversy arises because of the subjectivity involved in identifying master variables and assigning physical and chemical meaning to them. Tidball et al. (1986b) used factor analysis to evaluate the results of the sampling described by plotting the spatially interpolated factor scores. McNeal et al. (1985) determined the mode of occurrence of various trace metals in uncultivated soils of the northern Great Plains by combining partial dissolution techniques (Chao 1984) and factor analysis.

Another method of understanding the areal distribution and spatial variability of soil trace element concentrations is the low-density, hierarchical,

analysis-of-variance approach extensively used by the U.S. Geological Survey Branch of Regional Geochemistry (Tourtelot and Miesch 1975). Geochemical differences among regional subgroups are identified by determining the proportion of the total variability among all samples represented by the subgroups. This division also allows for evaluation of the proportion of the variance attributable to sampling and analytical error.

Geographic information systems (GIS) are used extensively for mapping soil trace element concentrations in soils relative to factors that may affect concentrations and transport to groundwater. Of specific interest is the possibility of using GIS coupled with transport modeling to predict potential groundwater contamination. Corwin and colleagues at the USDA-ARS U.S. Salinity Laboratory in Riverside, California, developed GIS for this use (e.g., Corwin 1996; Corwin and Wagenet 1996). Coupling of GIS to transport models for assessing nonpoint source pollution presents numerous challenges resulting primarily from limitations in the mathematical representations of complex transport processes, heterogeneous media, data availability, and difficulties in parameter estimation. To date, applications have included primarily salt, pesticides, and nitrates. GIS linked to deterministic or stochastic transport models offer promise for characterizing the spatially variable nature of groundwater contamination potential due to nonpoint sources of trace elements.

Soils are generally considered contaminated if the concentrations exceed background levels unaffected by human activities. However, there are numerous examples of high naturally occurring soil trace element concentrations. For example, Ni concentrations in serpentine-derived soils can be toxic to plants and animals. Sampling methodology and soil clay and organic matter content also affect soil concentrations as trace elements accumulate in these soil fractions. The comparison of soil trace element concentrations with background and/or established acceptable levels needs to be conducted in conjunction with assessment of an element's mode of occurrence, mobility, and relevant soil physical and chemical characteristics.

Several sources of trace element background values are available (Alloway 1995; Bowen 1979; Kabata-Pendias and Pendias 1992). Adriano (2001) provided a comparison of values for several investigators, including Bowen (1979) who compiled the concentration ranges and median values of trace elements shown in Fig. 4-6. Values of total concentrations higher than those listed may indicate that a problem exists. However, because of spatial variability and factors affecting concentrations, it is difficult to assign single values for background concentrations. Also, the mode of occurrence and mobility of an element in the soil needs to be evaluated before drawing conclusions about potential harmful effects to plants or animals or movement to surface or groundwater.
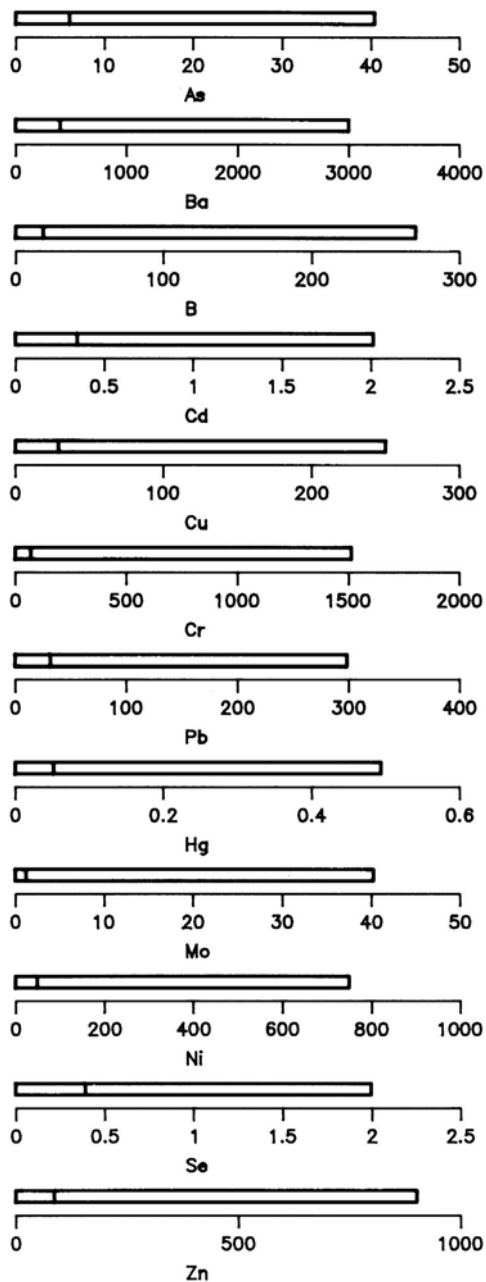
FIGURE 4-6. *Ranges of concentrations of trace elements in soils in mg/kg (Bowen 1979). The rectangle represents the middle 50% of the data, and vertical lines represent the median.*

During the last 20 years, various agencies have developed environmental standards for soils by determining potential health effects related to levels and duration of exposure to trace elements. Values vary depending on assumptions about exposure scenarios. Relevant to this chapter, standards for trace elements have been established for application of sewage sludge to agricultural soils. Adriano (2001) described the critical levels used throughout Europe.

SUMMARY

The dominant processes that affect trace elements in soils and groundwater are (1) precipitation and dissolution, (2) surface interactions and adsorption, and (3) oxidation-reduction reactions. For each element or group of elements, we provided a review of mode of occurrence, sources, and relevant biogeochemical processes affecting mobility and plant health, and trace element uptake. Last, we presented a discussion of considerations of evaluation for pollution potential in soils. Salient general conclusions follow.

- Because of their tendency to form oxyanions, the transition metals, metalloids, and nonmetals (As, B, Cr, Se, V) are often mobile in soils and groundwater. Mobility depends primarily on redox potential and pH and secondarily on surface interactions. Depending on geologic sources, high concentrations of these elements are often observed in arid and semiarid areas because of the typically oxidized and alkaline conditions.
- The informally named heavy metals (Cd, Cu, Pb, Ni, and Zn) are generally unlikely to be mobile in soils due to their strong potential to adsorb to soil minerals and soil organic matter, and to precipitate as carbonates and phosphates. There is typically little potential for leaching to groundwater at near-neutral pH and above. Long-term application of sewage sludge, manures, and pesticides can cause high soil concentrations that may affect plant productivity and affect the soil microbial community. Low pH, high salinity, and formation of soluble organic complexes and preferential flow can result in increased mobility and leaching to deeper soil horizons. Cadmium and Pb form soluble chloride complexes in saline soils, which increases their availability to plants and may increase the potential for leaching to groundwater.
- Mercury is an important contaminant in many locations throughout the world. It is subject to a complex series of biogeochemical processes that affect its mobility and toxicity.

- Evaluation of the pollution potential of soils requires evaluation of multiple factors and criteria. These include (1) spatial variability of soil trace element concentrations and the processes affecting concentrations, (2) background concentrations unaffected by anthropogenic activity, and (3) the forms of constituents of concern. In evaluating pollution potential, it is important to consider the following:
  – To effectively compare soil trace element concentrations with background levels requires collection of sufficient numbers of samples to effectively represent measures of central tendency and variance, which necessitates analysis of spatial variability relative to possible sources.
  – Use of multivariate statistical methods, such as factor and principal component analysis, can provide insight into geochemical associations and processes affecting distribution and mobility and provide a framework for analyzing large amounts of trace element data.
  – Geographic information systems (GIS) can be an effective tool for regional and subregional assessment of the distribution and mobility of soil and groundwater trace element concentrations and the potential for movement of trace elements to groundwater.
  – Soil extractants can provide useful information about how trace elements are partitioned in soils, especially relative to plant uptake. However, for some elements, such as As, these selective extraction techniques are ineffective.
- Trace element adsorption in soils is a key factor for understanding mobility of many trace elements and can be quantified in different ways. These include surface complexation, constant-capacitance, diffuse-layer, and triple-layer models, which have been applied successfully in a variety of systems and to numerous trace elements.

REFERENCES

Adriano, D. (2001). *Trace elements in terrestrial environments*, Springer, New York.

Alloway, B. J. (1995). *Heavy metals in soils*, Chapman and Hall, London.

Amini, M., Khademi, H., Afyuni, M., and Abbaspour, K. C. (2005). "Variability of available cadmium in relation to soil properties and land use in an arid region in central Iran." *Water, Air, and Soil Poll.*, 162, 205–218.

Amrhein, C., Mosher, P. A., and Brown, A. D. (1993). "The effects of redox on Mo, U, B, V, and As solubility in evaporation pond soils." *Soil Sci.*, 155, 249–255.

Anderson, A. (1979). "Mercury in soils," in *The biogeochemistry of mercury in the environment*, J. O. Nriagu, ed., Elsevier, Amsterdam, 79–110.

Anderson, L. D., Kent, D., and Davis, J. A. (1994). "Batch experiments characterizing the reduction of Cr(VI) using suboxic material from a mildly reducing sand and gravel aquifer." *Environ. Sci. Technol.*, 28, 178–185.

Andrews, C. B. and Neville, C. J. (2003). "Groundwater flow in a desert basin: Challenges for simulating transport of dissolved chromium." *Groundwater,* 41, 219–226.

Baas-Becking, L. G. M., Kaplan, I. R., and Moore, D. (1960). "Limits of natural environment in terms of pH and oxidation-reduction potentials." *J. Geol.*, 68, 243–284.

Balistrieri, L. S., and Chao, T. T. (1987). "Selenium adsorption by goethite." *Soil Sci. Soc. Am. J.*, 51, 1145–1151.

———. (1990). "Adsorption of selenium by amorphous iron oxyhydroxide and manganese oxide." *Geochim. Cosmochim. Acta*, 54, 739–751.

Balistrieri, L. S., and Murray, J. W. (1982). "The adsorption of Cu, Pb, Zn, and Cd on goethite from major ion seawater." *Geochim. Cosmochim. Acta*, 46, 1253–1265.

Ball, J. W., and Izbicki, J. A. (2004). "Occurrence of hexavalent chromium in groundwater in the western Mojave Desert, California." *Appl. Geochem.*, 19, 1123–1135.

Barnhart, J. (1997). "Chromium chemistry and implications for environmental fate and toxicity." *J. Soil. Contamination,* 6, 561–568.

Barshad, I. (1948). "Molybdenum content of pasture plants in relation to toxicity to cattle." *Soil Sci.*, 66, 187–191.

Bartlett, R. J., and James, B. (1979). "Behavior of chromium in soils: III. Oxidation." *J. Environ. Qual.*, 8, 31–35.

Bartlett, R. J., and Kimble, J. M. (1976). "Behavior of chromium in soils: I. Trivalent forms." *J. Environ. Qual.*, 5, 379–383.

Benes, F., and Havlik, B. (1979). "Speciation of mercury in natural waters," in *Biogeochemistry of mercury in the environment,* J. O. Nriagu, ed. Elsevier, Amsterdam, 175–202.

Benjamin, M. M., and Bloom, N. S. (1981). "Effects of strong binding of anionic adsorbates on adsorption of trace metals on amorphous iron oxyhydroxide," in *Adsorption from aqueous solutions,* P. H. Tewari, ed., Plenum Publishing, New York, 41–60.

Berti, W. R., and Jacobs, L. W. (1998). "Distribution of trace elements in soil from repeated sewage sludge applications." *J. Environ. Qual.,* 27, 1280–1286.

Biggar, J. W., and Fireman, M. (1960). "Boron adsorption and release by soils." *Soil Sci. Soc. Am. Proc.*, 24, 115–119.

Bingham, F. T., Page, A. L., Mahler, R.J ., and Ganje, T. J. (1976). "Cadmium availability to rice in sludge-amended soil under 'flood' and 'nonflood' culture." *Soil Sci. Soc. Am. J.*, 40, 715–719.

Blesa, M. A., Maroto, A. J. G., and Regazzoni, A. E. (1984). "Boric acid adsorption on magnetite and zirconium dioxide." *J. Colloid Interface Sci.*, 99, 32–40.

Bodine, M. W., and Jones, B. F. (1986). *The salt norm: A quantitative chemical-mineralogical characterization of natural waters*, U.S. Geological Survey Water Resource Investigative Report 86-4086, U.S. Geological Survey, Washington, D.C.

Bohn, H. L., McNeal, B. L., and O'Connor, G. A. (1979). *Soil chemistry,* John Wiley and Sons, New York.

Bonnissel-Gissinger, P., Alnot, M., Lickes, S.-P., Ehrhardt, J.-J., and Behra, P. (1999). "Modeling the adsorption of mercury(II) on (hydr)oxides. II: α-FeOOH (goethite) and amorphous silica." *J. Colloid Interface Sci.*, 215, 313–322.

Bourikas, K., Hiemstra, T., and van Riemsdijk, W. H. (2001). "Adsorption of molybdate monomers and polymers on titania with a multisite approach." *J. Phys. Chem. B*, 105, 2393–2403.

Bowen, H. J. M. (1979). *Environmental chemistry of the elements,* Academic Press, London, 32–46.

Bowman, R. S., Essington, M. E., and O'Connor, G. A. (1981). "Soil sorption of nickel: Influence of solution composition." *Soil Sci. Soc. Am. J.*, 45, 860–865.

Bradford, G. R. (1963). "Lithium survey of California's water resources." *Soil Sci.*, 96, 77–81.

Chan, K. M., and Riley, J. P. (1966). "The determination of molybdenum in natural waters, silicates and biological materials." *Anal. Chim. Acta*, 36, 220–229.

Chao, T. T. (1984). "Use of partial dissolution techniques in geochemical exploration." *J. Geochem. Explor.*, 20, 101–135.

Corey, R. B. (1981). "Adsorption vs. precipitation," in *Adsorption of inorganics at solid-liquid interfaces,* M. A. Anderson and A. J. Rubin, eds., Ann Arbor Science Publishers, Ann Arbor, Mich., 161–182.

Corwin, D. L. (1996). "GIS applications of deterministic solute transport models for regional-scale assessment of non-point source pollutants in the vadose zone," in *Application of GIS to the modeling of non-point source pollutants in the vadose zone,* D. L. Corwin and K. Loague, eds., SSSA Special Publication 48, Soil Science Society of America, Madison, Wisc.

Corwin, D. L., Goldberg, S., and David, A. (1999). "Evaluation of a functional model for simulating boron transport in soil." *Soil Sci.*, 164, 697–717.

Corwin, D. L., and Wagenet, R. J. (1996). "Application of GIS to the modeling of non-point source pollutants in the vadose zone: A conference summary." *J. Environ. Qual.*, 25, 403–411.

Crist, M. A. (1974). *Selenium in waters in and adjacent to the Kendrick project*, *Natrona County, Wyo*, U.S. Geological Survey Water-Supply Paper 2023, U.S. Geological Survey, Washington, D.C.

Csoban, K., and Joo, P. (1999). "Sorption of Cr(III) on silica and aluminium oxide: Experiments and modeling." *Colloids Surf. A: Physicochem. Eng. Aspects*, 151, 97–112.

Davis, J. A. (1984). "Complexation of trace metals by adsorbed natural organic matter." *Geochim. Cosmochim. Acta*, 48, 679–691.

Davis, J. A., James, R. O., and Leckie, J. O. (1978). "Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions." *J. Colloid Interface Sci.*, 67, 90–107.

Davis, A., Kempton, H., and Nicholson, A. (1994). "Groundwater transport of arsenic and chromium at a historical tannery, Woburn, Massachusetts, U.S.A." *Appl. Geochem.*, 9, 569–582.

Davis, J. A., and Leckie, J. O. (1978). "Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides." *Environ. Sci. Technol.*, 12, 1309–1315.

———. (1980). "Surface ionization and complexation at the oxide/water interface. 3. Adsorption of anions." *J. Colloid Interface Sci.*, 74, 32–43.

Deverel, S. J. (1989). "Geostatistical and principal component analysis of ground-water chemistry and soil salinity data, San Joaquin Valley, California, in *Regional Characterization of Water Quality,* Stephen Ragone, ed., Publication No. 182, International Association of Hydrological Sciences, IAHS Press, Centre for Ecology and Hydrology, Wallingford, UK.

Deverel, S. J., and Gallanthine, S. K. (1989). "Distribution of salinity and selenium in relation to hydrologic and geochemical processes, San Joaquin Valley, California." *J. Hydrol.*, 109, 125–149.

Deverel, S. J., and Fujii, R. (1988). "Processes affecting the distribution of selenium in shallow ground water of agricultural areas, western San Joaquin Valley, Calif." *Water Resour. Res.*, 24, 516–524.

Deverel, S. J., and Millard, S. P. (1988). "Distribution and mobility of selenium and other trace elements in shallow ground water of the western San Joaquin Valley, Calif." *Environ. Sci. Technol.*, 22, 697–702.

Dixit, S., and Hering, J. G. (2003). "Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility." *Environ. Sci. Technol.*, 37, 4182–4189.

Dowdy, R. H., Latterell, J. J., Hinesly, T. D., and Grossman, R. B. (1991). "Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge application." *J. Environ. Qual.* 20, 119–123.

Dowdy, R. H., and Volk, V. V. (1983). "Movement of heavy metals in soils," in *Chemical mobility and reactivity in soil systems,* D. W. Nelson, ed., SSSA Publication 11, Soil Science Society of America, Madison, Wisc.

Drever, J. I. (1988). *The geochemistry of natural waters,* 2nd ed., Prentice Hall, Upper Saddle River, N.J.

Duc, M., Lefevre, G., and Fedoroff, M. (2006). "Sorption of selenite ions on hematite." *J. Colloid Interface Sci.*, 298, 556–563.

Dzombak, D. A., and Morel, F. M. M. (1990). *Surface complexation modeling: Hydrous ferric oxide*, John Wiley and Sons, New York.

Elprince, A. M., Vanselow, A. D., and Sposito, G. (1980). "Heterovalent ternary cation exchange equilibria: NH_4^+–Ba^{+2}–La^{+3} exchange on montmorillonite." *Soil Sci. Soc. Am. J.*, 44, 964–969.

Elrashidi, M. A., and O'Connor, G. A. (1982). "Boron sorption and desorption in soils." *Soil Sci. Soc. Am. J.*, 46, 27–31.

Elzinga, E. J., Van Grinsven, J. J. M., and Swartjes, F. A. (1999). "General purpose Freundlich isotherms for cadmium, copper and zinc in soils." *Eur. J. Soil Sci.*, 50, 139–149.

Emmerich, W. E., Lund, L. J., Page, A. L., and Chang, A. C. (1982). "Solid phase forms of heavy metals on sewage sludge-treated soils." *J. Environ. Qual.*, 11, 178–181.

Engberg, R. A., Westcott, D. A., Delamore, M., and Hotz, D. D. (1998). "Federal and state perspective on regulation and remediation of irrigation induced selenium problems," in *Environmental chemistry of selenium*, W. T. Frankenburger and R. A. Engberg, eds., Marcel Dekker, Inc., New York, 1–26.

Evans, H. T. and Garrels, R. M. (1958). "Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits." *Geochim. Cosmochim. Acta*, 15, 131–149.

Faust, S. D., Winka, A., Belton, T., and Tucker, R. (1983). "Assessment of the chemical and biological significance of arsenical compounds in a heavily contami-

nated watershed. Part II. Analysis and distribution of several arsenical species." *J. Environ. Sci. Health*, 18, 389–411.

Fio, J. L., Fujii, R., and Deverel, S. J. (1991). "Selenium mobility and distribution in irrigated and nonirrigated alluvial soils." *Soil Sci. Soc. Am. J.*, 55, 1313–1320.

Fleischer, M. (1970). "Summary of the literature on the inorganic geochemistry of mercury," in *Mercury in the environment,* U.S. Geological Survey Professional Paper 713, U.S. Geological Survey, Washington, D.C.

Forbes, E. A., Posner, A. M., and Quirk, J. P. (1976). "The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite." *J. Soil Sci.*, 27, 154–166.

Friedly, J. C., Davis, J. A., Kent, D. B. (1995). "Modeling hexavalent chromium reduction in groundwater in field-scale transport and laboratory batch experiments." *Water Resources Res.*, 31, 2783–2794.

Fujii, R., Deverel, S. J., and Hatfield, D. B. (1988). "Distribution of selenium in soils of agricultural fields, western San Joaquin Valley, Calif." *Soil Sci. Soc. Am. J.*, 52, 1274–1283.

Gao, S., and Burau, R. G. (1997). "Environmental factors affecting rates of arsine evolution from and mineralization of arsenicals in soil." *J. Environ. Qual.*, 26, 753–763.

Gao, Y., and Mucci, A. (2001). "Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7 M NaCl solution." *Geochim. Cosmochim. Acta,* 65, 2361–2378.

———. (2003). "Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater." *Chem. Geol.*, 199, 91–109.

Garcia-Miragaya, J., and Page, A. L. (1976). "Influence of ionic strength and inorganic complex formation of the sorption of trace amounts of Cd by montmorillonite." *Soil Sci. Soc. Am. J.*, 40, 658–663.

Garrels, R. M., and Christ, C. L. (1965). *Solutions, minerals and equilibria,* Harper and Row, New York.

Gibbs, R. J. (1976). "Transport phases of transition metals in the Amazon and Yukon Rivers." *Geol. Soc. Am. Bull.*, 88, 829–843.

Goldberg, S. (1985). "Chemical modeling of anion competition on goethite using the constant capacitance model." *Soil Sci. Soc. Am. J.*, 49, 851–856.

———. (1986). "Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals." *Soil Sci. Soc. Amer. J.*, 50, 1154–1157.

———. (1997). "Reactions of boron with soils." *Plant Soil*, 193, 35–48.

Goldberg, S., Forster, H. S., and Godfrey, C. L. (1996). "Molybdenum adsorption on oxides, clay minerals, and soils." *Soil Sci. Soc. Am. J.*, 60, 425–432.

Goldberg, S., and Glaubig, R. A. (1985). "Boron adsorption on aluminum and iron oxide minerals." *Soil Sci. Soc. Am. J.*, 49, 1374–1379.

———. (1986a). "Boron adsorption on California soils." *Soil Sci. Soc. Am. J.*, 50, 1173–1176.

———. (1986b). "Boron adsorption and silicon release by the clay minerals kaolinite, montmorillonite, and illite." *Soil Sci. Soc. Am. J.*, 50, 1442–1448.

Goldberg, S., Corwin, D. L., Shouse, P. J., and Suarez, D. L. (2005a). "Prediction of boron adsorption by field samples of diverse textures." *Soil Sci. Soc. Am. J.*, 69, 1379–1388.

Goldberg, S., and Johnston, C. T. (2001). "Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling." *J. Colloid Interface Sci.*, 234, 204–216.

Goldberg, S., Johnston, C. T., Suarez, D. L., and Lesch, S. M. (2008). "Mechanism of molybdenum adsorption on soils and soil minerals evaluated using vibrational spectroscopy and surface complexation modeling," in *Adsorption of metals by geomedia II: Variables, mechanisms, and model applications,* M. O. Barnett and D. B. Kent, eds., Developments in Earth and Environmental Sciences 7, Elsevier, Amsterdam, 235–266.

Goldberg, S., Lesch, S. M., and Suarez, D. L. (2000). "Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model." *Soil Sci. Soc. Am. J.*, 64, 1356–1363.

———. (2002). "Predicting molybdenum adsorption by soils using soil chemical parameters in the constant capacitance model." *Soil Sci. Soc. Am. J.*, 66, 1836–1842.

———. (2007). "Predicting selenite adsorption by soils using soil chemical parameters in the constant capacitance model." *Geochim. Cosmochim. Acta*, 71, 5750–5762.

Goldberg, S., Lesch, S. M., Suarez, D. L., and Basta, N. T. (2005b). "Predicting arsenate adsorption by soils using soil chemical parameters in the constant capacitance model." *Soil Sci. Soc. Am. J.*, 69, 1389–1398.

Goldberg, S., Su, C., and Forster, H. S. (1998). "Sorption of molybdenum on oxides, clay minerals, and soils: Mechanisms and models," in *Adsorption of metals by geomedia: Variables, mechanisms, and model applications,* E. A. Jenne, ed., Proc., American Chemical Society Symposium, Academic Press, San Diego, 401–426.

Goldberg, S., Suarez, D. L., Basta, N. T., and Lesch, S. M. (2004). "Predicting boron adsorption isotherms by midwestern soils using the constant capacitance model." *Soil Sci. Soc. Am. J.*, 68, 795–801.

Gough, L. P., Severson, R. C., and McNeal, J. M. (1979). "Extractable and total-soil element concentrations favorable for native plant growth in the northern Great Plains," in *Ecology and coal resource development,* vol. 2., M. K. Wali, ed., Pergamon Press, New York, 859–869.

Grossl, P. R., Eick, M., Sparks, D. L., Goldberg, S., and Ainsworth, C. C. (1997). "Arsenate and chromate retention mechanisms on goethite. II. Kinetic evaluation using a pressure-jump relaxation technique." *Environ. Sci. Technol.*, 31, 321–326.

Gruebel, K. A., Davis, J. A., and Leckie, J. O. (1988). "The feasibility of using sequential extraction techniques for As and Se in soils and sediments." *Soil Sci. Soc. Am. J.*, 52, 390–397.

Gu, X., and Evans, L. J. (2007). "Modelling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto Fithian illite." *J. Colloid Interface Sci.*, 307, 317–325.

Gulens, J., Champ, D. R., and Jackson, R. E. (1979). "Influence of redox environments on mobility of arsenic in ground water," in *Chemical modeling in aqueous systems,* E. A. Jenne, ed., American Chemical Society, Washington, D.C., 81–95.

Gunneriusson, L., Baxter, D., and Emteborg, H. (1995). "Complexation at low concentrations of methyl and inorganic mercury(II) to a hydrous goethite (α-FeOOH) surface." *J. Colloid Interface Sci.*, 169, 262–266.

Gunneriusson, L., and Sjöberg, S. (1993). "Surface complexation in the H$^+$-goethite (αFeOOH)-Hg(II)-chloride system." *J. Colloid Interface Sci.*, 156, 121–128.

Gustafsson, J. P. (2001). "Modelling competitive anion adsorption on oxide minerals and an allophane-containing soil." *Europ. J. Soil Sci.*, 52, 639–653.

———. (2003). "Modelling molybdate and tungstate adsorption to ferrihydrite." *Chem. Geol.*, 200, 105–115.

Guy, R. D., and Chakrabarti, C. L. (1976). "Studies of metal–organic interactions in model systems pertaining to natural waters." C*an. J. Chem./Rev. Can. Chim.*, 54, 2600–2611.

Harter, R. D., and Baker, D. E. (1977). "Application and misapplication of the Langmuir equation to soil adsorption phenomena." *Soil Sci. Soc. Am. J.*, 41, 1077–1080.

Hayes, K. F., Papelis, C., and Leckie, J. O. (1988). "Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces." *J. Colloid Interface Sci.*, 125, 717–726.

Hem, J. D. (1970). "Chemical behavior of mercury in aqueous media," in *Mercury in the environment,* U.S. Geological Survey Professional Paper 713, U.S. Geological Survey, Washington, D.C.

———. (1977). "Reactions of metal ions at surfaces of hydrous iron oxide." *Geochim. Cosmochim. Acta*, 41, 527–538.

———. (1985). *Study and interpretation of the chemical characteristics of natural water*, U.S. Geological Survey Water Supply Paper 2254, U.S. Geological Survey, Washington, D.C.

Henderson, T. (1994). "Geochemical reduction of hexavalent chromium in the Trinity Sand Aquifer." *Groundwater,* 32, 477–486.

Hendrickson, L. L., and Corey, R. B. (1981). "Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes." *Soil Sci.*, 131, 163–171.

Hickey, M. G., and Kittrick, J. A. (1984). "Chemical partitioning of cadmium, copper, nickel, and zinc on soils and sediments containing high levels of heavy metals." *J. Environ. Qual.*, 13, 372–376.

Hiemstra, T., and van Riemsdijk, W. H. (1996). "A surface structural approach to ion adsorption: The charge distribution (CD) model." *J. Colloid Interface Sci.*, 179, 488–508.

———. (1999). "Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (hydr)oxides." *J. Colloid Interface Sci.*, 210, 182–193.

Hingston, F. J. (1981). "A review of anion adsorption," in *Adsorption of inorganics at solid–liquid interfaces*, M. A. Anderson and A. J. Rubin, eds., Ann Arbor Science Press, Ann Arbor, Mich., 51–90.

Hingston, F. J., Posner, A. M., and Quirk, J. P. (1968). "Adsorption of selenite by goethite," in *Adsorption from aqueous solution*, R. F. Gould, ed., Advances in Chemistry Series, No. 79, American Chemical Society, Washington, D.C., 82–90.

Hoffman, D. J., Camardese, M. B., Lecaptain, L. J., and Pendleton, G. W. (1990). "Effects of boron on growth and physiology of mallard ducklings." *Environ. Toxicol. Chem.* 9, 335–346.

Hsia, T. H., Lo, S. L., and Lin, C. F. (1992). "As(V) adsorption on amorphous iron oxide: Triple layer modeling." *Chemosphere*, 25, 1825–1837.

James, B. R., and Bartlett, R. J. (1983). "Behavior of chromium in soils. VI. Interactions between oxidation-reduction and organic complexation." *J. Environ. Qual.*, 12, 173–176.

———. (1984). "Plant–soil interactions of chromium." *J. Environ Qual.*, 13, 67–70.

Jarrell, W. M., Page, A. L., and Elseewi, A. A. (1980). "Molybdenum in the environment." *Residue Rev.*, 74, 1–43.

Jenne, E. A. 1968. "Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides." *Adv. Chem.*, 73, 337–387.

———. (1970). "Atmospheric and fluvial transport of mercury," in *Mercury in the environment,* U.S. Geological Survey Professional Paper 713, U.S. Geological Survey, Washington, D.C.

———. (1977). "Trace element sorption by sediments and soils—sites and processes," in *Symposium on molybdenum in the environment,* Vol. 2, W. Chappell, and K. Peterson, eds., Marcel-Dekker, Inc., New York, 425–553.

Jensen, S., and Jernolov, A. (1969). "Biological methylation of mercury in aquatic organisms." *Nature*, 223, 753–754.

Joreskog, K. G., Klovan, J. E., and Reyment, R. A. (1976). *Geological factor analysis,* Elsevier Scientific Publishing, New York.

Kabata-Pendias, A. and Pendias, D. C. (1992). *Trace elements in soils and plants*, CRC Press, Boca Raton, Fla.

Keren, R., Bingham, F. T., and Rhoades, J. D. (1985). "Plant uptake of boron as affected by boron distribution between liquid and solid phases in soil." *Soil Sci. Soc. Am. J.*, 49, 297–302.

Keren, R., Gast, R. G., and Bar-Yosef, B. (1981). "pH-dependent boron adsorption by Na-montmorillonite." *Soil Sci. Soc. Am. J.*, 45, 45–48.

Keshavarz, P., Malakouti, M. J., Karimian, N., Fotovat, A. (2006). "The effects of salinity on extractability and chemical fractions of zinc in selected calcareous soils of Iran." *J. Agric. Sci. Technol.*, 8, 181–190.

Khoshgoftar, A. H., Shariatmadari, H., Karimian, N., Kalbasi, M., van der Zee, S. E. A. T. M., and Parker, D. R. (2004). "Salinity and zinc application effects on phytoavailability of cadmium and zinc." *Soil Sci. Soc. Am. J.*, 68, 1885–1889.

Khoshgoftarmanesh, A. H., Shariatmadari, H., Karimian, N., Kalbasi, M., van der Zee, S. E. A. T. M. (2006). "Cadmium and zinc in saline soil solutions and their concentrations in wheat." *Soil Sci. Soc. Am. J.*, 70, 582–589.

Kinniburgh, D. G., Jackson, M. L., and Syers, J. K. (1976). "Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum." *Soil Sci. Soc. Am. J.*, 40, 796–799.

Kuo, S., and Mikkelsen, D. S. (1979). "Zinc adsorption by two alkaline soils." *Soil Sci.*, 128, 274–279.

Lakin, H. W. (1973). "Selenium in our environment," in *Trace elements in the environment*, E. L. Kothy, ed., Advances in Chemistry Series 123, American Chemical Society, Washington, D.C., 96–111.

Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica, and platinum." *J. Am. Chem. Soc.*, 40, 1361–1403.

Langmuir, D., and Mahoney, J. (1984). "Chemical equilibrium and kinetics of geochemical processes in ground water studies," in *First Canadian/American conference on hydrogeology,* B. Hitchon and E. I. Wallick, eds., National Water Well Association, Worthington, Ohio, 69–95.

Leckie, J. O., Benjamin, M. M., Hayes, K., Kaufman, G., and Altmann, S. (1980). *Adsorption/coprecipitation of trace elements from water with iron oxy-hydroxide,*

Electric Power Research Institute Report CS-1513, Stanford University, Stanford, Calif.

Lemmo, N. V., Faust, S. D., Belton, T., and Tucker, R. (1983). "Assessment of the chemical and biological significance of arsenical compounds in a heavily contaminated watershed. Part I. The fate and speciation of arsenical compounds in aquatic environments: A literature review." *J. Environ. Sci. Health*, 18, 335–387.

Lerman, A., and Childs, C. W. (1973). "Metal-organic complexes on natural waters," in *Trace metals and metal-organic interactions in natural waters,* P. C. Singer, ed., Ann Arbor Science Press, Ann Arbor, Mich., 201–235.

Lewis, F. M., Voss, C. I., and Rubin, J. (1986). *Numerical simulation of advective-dispersive multisolute transport with sorption, ion-exchange, and equilibrium chemistry*, U.S. Geological Survey, Water-Resources Investigations Report 86-4022, U.S. Geological Survey, Washington, D.C.

Lindberg, R. D., and Runnells, D. D. (1984). "Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling." *Science*, 225, 925–927.

Lindsay, W. L. (1979). *Chemical equilibria in soils,* Wiley-Interscience, New York.

Loyaux-Lawniczak, S., Lecomte, P., Ehrhardt, J.-J. (2001). "Behavior of hexavalent chromium in a polluted groundwater: Redox processes and immobilization in soils." *Environ. Sci. Technol.*, 35, 1350–1357.

Manning, B. A., and Goldberg, S. (1996). "Modeling arsenate competitive adsorption on kaolinite, montmorillonite, and illite." *Clays Clay Miner.*, 44, 609–623.

Masscheleyn, P. H., Delaune, R. D., and Patrick, W. H. (1991). "Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil." *Environ. Sci. Technol.*, 25, 1414–1419.

Mattigod S. V., and Page, A. L. (1983). "Assessment of metal pollution in soils," in *Applied environmental geochemistry*, I. Thornton, ed., Academic Press, London, 355–391.

McBride, M. B. (1979). "Mobility and reactions of VO^{2+} on hydrated smectite surfaces." *Clays Clay Miner.*, 27, 91–96.

McBride, M., Sauvé, S., and Hendershot, W. (1997). "Solubility control of Cu, Zn, Cd and Pb in contaminated soils." *Eur. Soil Sci.*, 48, 337–346.

McGrath, S. P., Chaudri, A. M., and Gille, K .E. (1995). "Long-term effects of metals in sewage sludge on soils, microorganisms and plants." *J. Ind. Microbiol.*, 14, 94–104.

McLaughlin, M. J., Tiller, K. G., Smart, M. K. (1997). "Speciation of cadmium in soil solutions of saline/sodic soils and relationship with cadmium concentrations in potato tubers (*Solanum tuberosum* L.)." *Aust. J. Soil Res.*, 35, 183–198.

McNeal, J. M., Severson, R. C., and Gough, L. P. (1985). "The occurrence of extractable elements in soils from the Northern Great Plains." *Soil Sci. Soc. Am. J.*, 49, 873–881.

Mesuere, K., and Fish, W. (1992). "Chromate and oxalate adsorption on goethite. 1. Calibration of surface complexation models." *Environ. Sci. Technol.*, 28, 2357–2364.

Motta, M. M., and Miranda, C. F. (1989). "Molybdate adsorption on kaolinite, montmorillonite, and illite: Constant capacitance modeling." *Soil Sci. Soc. Am. J.*, 53, 380–385.

Naftz, D. L. (1996). "Pattern recognition analysis and classification modeling of selenium-producing areas." *J. Chemometrics*, 10, 309–324.

National Academy of Sciences. (1974). *Vanadium,* National Research Council, Washington, D.C.

Neal, R. H., and Sposito, G. (1989). "Selenate adsorption on alluvial soils." *Soil Sci. Soc. Am. J.*, 53, 70–74.

Neal, R. H., Sposito, G., Holtzclaw, K. M. and Traina, S. J. (1987a). "Selenite adsorption on alluvial soils: I. Soil composition and pH effects." *Soil Sci. Soc. Am. J.*, 51, 1161–1165.

———. (1987b). "Selenite adsorption on alluvial soils: II. Solution composition effects." *Soil Sci. Soc. Am. J.*, 51, 1165–1169.

Nordstrom, D. K., and Ball, J. W. (1984). "Chemical models, computer programs and metal complexation in natural waters," in *Complexation of trace metals in natural waters*, C. J. M. Kramer and J. C. Duinker, eds., Martinus and Nijoff/W. Jurk, The Hague.

Nordstrom, D. K., Jenne, E. A., and Ball, J. W. (1979a). "Redox equilibria of iron in acid mine waters," in *Chemical modeling in aqueous systems,* E. A. Jenne, ed., American Chemical Society, Washington, D.C., 51–79.

Nordstrom, D. K., Plummer, L. N., Wigley, T. M. L., Wolery, T. J., Ball, J. W., Jenne, E. A., Bassett, R. L., Crerar, D. A., Florence, T. M., Fritz, B., Hoffman, M., Holdren, Jr, G. R., Lafon, G. M., Mattigod, S. V., McDuff, R. E., Morel, F., Reddy, M. M., Sposito, G., and Thraikill, J. (1979b). "A comparison of computerized chemical models for equilibrium calculations in aqueous systems," in *Chemical modeling in aqueous systems,* E. A. Jenne, ed., American Chemical Society, Washington, D.C., 857–892.

Norvell, W. A., Wu, J., Hopkins, D. G., and Welch, R. M. (2000). "Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium." *Soil Sci. Soc. Am. J.*, 64, 2162–2168.

O'Connor, G. A., Brobst, R. B., Chaney, R. L., Kincaid, R. L., McDowell, L. R., Pierzynski, G. M., Rubin, A., and Van Riper, G. G. (2001). "A modified risk assessment to establish molybdenum standards for land application of biosolids." *J. Environ. Qual.*, 30, 1490–1507.

Olson, M. L., and DeWild, J. F. (1999). *Techniques for the collection and species-specific analysis of low levels of mercury in water, sediment, and biota*, U.S. Geological Survey Water Resources Investigations Report 99-4018-B, U.S. Geological Survey, Washington, D.C.

Oze, C., Bird, D. K., and Fendorf, S. (2007). "Genesis of hexavalent chromium from natural sources in soils and groundwater." *Proc., Nat. Acad. Sci. USA*, 104, 6544–6549.

Peacock, C. L., and Sherman, D. M. (2004). "Vanadium(V) adsorption onto goethite (α-FeOOH) at pH 1.5 to 12: A surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy." *Geochim. Cosmochim. Acta*, 68, 1723–1733.

Peak, D., and Sparks, D. L. (2002). "Mechanisms of selenate adsorption on iron oxides and hydroxides." *Environ. Sci. Technol.*, 36, 1460–1466.

Peryea, F. J., Bingham, F. T., and Rhoades, J. D. (1985). "Mechanisms of boron regeneration." *Soil Sci. Soc. Am. J.*, 49, 840–843.

Peryea, F. J., and Creger, T. L. (1994). "Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues." *Water, Air Soil Pollut.*, 78, 297–306.

Pierce, M. L., and Moore, C. B. (1980). "Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution." *Environ. Sci. Technol.,* 14, 214–216.

Ponnamperuma, F. N. (1972). "The chemistry of submerged soils." *Advan. Agron.*, 24, 29–96.

Ponthieu, M., Juillot, F., Hiemstra, T., van Riemsdijk, W. H., and Benedetti, M. F. (2006). "Metal binding to iron oxides." *Geochim. Cosmochim. Acta*, 70, 2679–2698.

Posselt, H. S., Anderson, F. J., and Weber, W. J. (1978). "Cation sorption on colloidal hydrous manganese dioxide." *Environ. Sci. Technol.*, 2, 1087–1093.

Preeda, P., Leong, S. T., Laortanakul, P., Torotoro, J. L. (2002). "Influence of salinity and acidity on bioavailability of sludge-borne heavy metals. A case study of Bangkok municipal sludge." *Water, Air, Soil Pollut.*, 139, 43–60.

Presser, T. S., and Ohlendorf, H. M. (1987). "Biogeochemical cycling of selenium in the San Joaquin Valley, California." *Environ. Mgmt.*, 11, 805–821.

Presser, T. S. and Swain, W. C. (1990). "Geochemical evidence for selenium mobilization by weathering of pyretic shale, San Joaquin Valley, California, USA." *Appl. Geochem.*, 5, 703–717.

Presser, T. S., Sylvester, M. A., and Low, W. H. (1994). "Bioaccumulation of selenium from natural geologic sources in western states and its potential consequences." *Environ. Mgmt.*, 18, 423–436.

Quirk, J. P., and Posner, A. M. (1976). "Trace element adsorption by soil minerals," in *Trace elements in soil-plant-animal systems*, D. J. D. Nicholas and A. R. Egan, eds., Academic Press, New York.

Rai, D., and Zachara, J. M. (1984). *Chemical attenuation rates, coefficients, and constants in leachate migration, a critical review*, Electric Power Research Institute Report, EA-3356, Volume 1, Electric Power Research Institute, Palo Alto, Calif.

———. (1986). *Geochemical behavior of chromium species*, Electric Power Research Institute Report EA-4544, Electric Power Research Institute, Palo Alto, Calif.

Raven, K. P., Jain, A., and Loeppert, R. H. (1998). "Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes." *Environ. Sci. Technol.*, 32, 344–349.

Reddy, C. N., and Patrick, W. H. (1977). "Effect of redox potential on the stability of zinc and copper chelates in flooded soils." *Soil Sci. Soc. Am. J.*, 41, 729–732.

Reddy, K. R., and Patrick, W. H. (1983). "Effect of aeration on reactivity and mobility of soil constituents," in *Chemical mobility and reactivity in soil systems*, D. W. Nelson et al., eds., Soil Science Society America, Madison, Wisc., 11–13.

Reyes, E. D., and Jurinak, J. J. (1967). "A mechanism of molybdate adsorption in Fe_2O_3. *Soil Sci. Soc. Am. Proc.*, 31, 637–641.

Rietra, R. P. J. J., Hiemstra, T., and van Riemsdijk, W. H. (2001). "Comparison of selenate and sulfate adsorption on goethite." *J. Colloid Interface Sci.*, 240, 384–390.

Robertson, F. N. (1975). "Hexavalent chromium in the ground water in Paradise Valley, Maricopa County, Arizona." *Ground Water,* 13, 516–527.

Ross, D. S., Sjogren, R. E., and Bartlett, R. J. (1981). "Behavior of chromium in soils: IV. Toxicity to microorganisms." *J. Environ. Qual.*, 10, 145–148.

Ryden, J. C., Syers, J. K., and Tillman, R. W. (1987). "Inorganic anion sorption and interaction with phosphate sorption by hydrous ferric oxide gel." *J. Soil Sci.*, 38, 211–217.

Saripalli, K. P., McGrail, B. P., and Girvin, D. C. (2002). "Adsorption of molybdenum on to anatase from dilute aqueous solutions." *Appl. Geochem.*, 17, 649–656.

Sarkar, D., Essington, M. E., and Misra, K. C. (1999). "Adsorption of mercury(II) by variable charge surfaces of quartz and gibbsite." *Soil Sci. Soc. Am. J*, 63, 1626–1636.

———. (2000). "Adsorption of mercury(II) on kaolinite." *Soil Sci. Soc. Am. J.*, 64, 1968–1975.

Sauvé, S., Hendershot, W., and Allen, H. E. (2000). "Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter." *Environ. Sci. Technol.*, 34, 1125–1131.

Schindler, P. W. (1981). "Surface complexes at oxide-water interfaces," in *Adsorption of inorganics at solid–liquid interfaces*. M. A. Anderson and A. J. Rubin, eds., Ann Arbor Science Press, Ann Arbor, Mich., 1–50.

Schwertmann, U., and Pfab, G. (1996). "Structural vanadium and chromium in lateritic iron oxides: Genetic implications." *Geochim. Cosmochim. Acta*, 60, 4279–4283.

Sindeeva, N. D. (1964). *Mineralogy and types of deposits of selenium and tellurium,* Wiley-Interscience, New York.

Singh, S. P. N., and Mattigod, S. V. (1992). "Modeling boron adsorption on kaolinite." *Clays Clay Miner.*, 40, 192–205.

Sistani, K. R. and Novak, J. M. (2006). "Trace metal accumulation, movement, and remediation in soils receiving animal manure," in *Trace elements in the environment,* M. N. V. Prasad, K. S. Sajwan, and R. Naidu, eds., CRC Press, Boca Raton, Fla.

Smith, G. J., and Anders, V. P. (1989). "Toxic effects of boron on mallard reproduction." *Environ. Toxicol. Chem.*, 8, 943–950.

Sposito, G. (1981). *The thermodynamics of soil solutions,* Oxford University Press, New York.

———. (1983). "The chemical forms of trace metals in soils," in *Applied environmental geochemistry*, I. Thornton, ed., Academic Press, London, 123–170.

———. (1984). *The surface chemistry of soils,* Oxford University Press, New York.

Sposito G., de Wit, J. C. M., and Neal, R. H. (1988). "Selenite adsorption on alluvial soils: III. Chemical modeling." *Soil Sci. Soc. Am. J.*, 52, 947–950.

Stachowicz, M., Hiemstra, T., and van Riemsdijk, W. H. (2006). "Surface speciation of As(III) and As(V) in relation to charge distribution." *J. Colloid Interface Sci.*, 302, 62–75.

Stanin, F. T. (2005). "The transport and fate of chromium (VI) in the environment," in *Chromium (VI) handbook,* J. Guertin, J. A. Jacobs, and C. P. Avakian, eds., CRC Press, Boca Raton, Fla.

Steenhuis, T. S., McBride, M. B., Richards, B. K., and Harrison, E. (1999). "Trace metal retention in the incorporation zone of land-applied sludge." *Environ. Sci. Technol.*, 33, 1171–1174.

Stollenwerk, K. G., and Grove, D. B. (1985a). "Adsorption and desorption of hexavalent chromium in an alluvial aquifer near Telluride, Colorado." *J. Environ. Qual.*, 14, 150–155.

———. (1985b). "Reduction of hexavalent chromium in water samples acidified for preservation." *J. Environ. Qual.*, 14, 396–399.

Stumm, W., Kummert, R., and Sigg, L. (1980). "A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces." *Croatica Chem. Acta*, 53, 291–312.

Stumm, W., and Morgan, J. J. (1981). *Aquatic chemistry,* 2nd ed., John Wiley and Sons, Inc., New York.

Su, C., and Suarez, D. L. (2004). "Boron release from weathering of illites, serpentine, shales, and illitic/palygorskitic soils." *Soil Sci. Soc. Am. J.*, 68, 96–105.

Syers, J. K., Browman, M. G., Smillie, G. W., and Corey, R. B. (1973). "Phosphate sorption by soils evaluated by the Langmuir adsorption equation." *Soil Sci. Soc. Amer. Proc.*, 37, 358–363.

Sylvester, M. A., Deason, J. P., Feltz, H. R., and Engber, R. A. (1988). "Preliminary results of the Department of the Interior irrigation drainage studies." *Proc. on Planning Now for Irrigation and Drainage*, *Irrigation and Drainage Div., ASCE, Lincoln, Nebraska, August 1988*, ASCE, Reston, Va.

Taylor, R. M., and Giles, J. B. (1970). "The association of vanadium and molybdenum with iron oxides in soils." *J. Soil Sci.*, 21, 203–215.

Thorstensen, D. C. (1984). *The concept of electron activity and its relation to redox potentials in aqueous geochemical systems*, U.S. Geological Survey Open-File Report 84–072, U.S. Geological Survey, Washington, D.C.

Tidball, R. R., Grundy, W. D., and Swatzky, D. L. (1986a). "Kriging techniques applied to element distribution in soils of the San Joaquin Valley, California." *Proc., HAZTECH International Conference, Denver, Colorado, August 1986*, Haztech International, Englewood, Colo., 992–1009.

Tidball, R. R., Severson, R. C., Gent, C. A. and Riddle, G. O. (1986b). *Element associations in soils of the San Joaquin Valley, California*, U.S. Geological Survey Open-File Report, 86-583, U.S. Geological Survey, Washington, D.C.

Tiesta, S. M. (2005). "Sources of chromium contamination in soil and groundwater," in *Chromium (VI) handbook,* J. Guertin, J. A. Jacobs, and C. P. Avakian, eds., CRC Press, Boca Raton, Fla.

Tiffreau, C., Lützenkirchen, J., and Behra, P. (1995). "Modeling the adsorption of mercury(II) on (hydr)oxides. I. Amorphous iron oxide and α-quartz." *J. Colloid Interface Sci.*, 172, 82–93.

Tourtelot, H. A., and Miesch, A. T. (1975). "Sampling designs in environmental geochemistry." *Geol. Soc. Amer. Spec. Paper*, 155, 107–118.

Turner, M. A., and Rust, R. H. (1971). "Effect of chromium on growth and mineral nutrition of soybeans." *Soil Sci. Soc. Am. Proc.* 35, 755–758.

U.S. Environmental Protection Agency (EPA). (1986). *Quality criteria for water*, 440/5-86-001, U.S. EPA, Washington, D.C.

U.S. Geological Survey (USGS). (2011). "USGS Mercury Research Lab," http://infotrek.er.usgs.gov/doc/mercury/methods.html, accessed January 15, 2011.

Usman, A. R. A., Kuzyakov, Y., Stahr, K. (2005). "Effect of immobilizing substances and salinity on heavy metals availability to wheat grown on sewage sludge-contaminated soil." *Soil and Sed. Contam. Int. J.*, 14, 329–344.

van Olphen, H. (1977). *An introduction to clay colloid chemistry*, John Wiley and Sons, New York.

Venema, P., Hiemstra, T., and van Riemsdijk, W. H. (1996). "Multisite adsorption of cadmium on goethite." *J. Colloid Interface Sci.*, 183, 515–527.

Wedepohl, K. H. (1972). "Vanadium," in *Handbook of geochemistry*, K. H. Wedepohl, ed., Springer-Verlag, Berlin, 23-A-1 to 23-O-1.

Weerasooriya, R., and Tobschall, H. J. (2000). "Mechanistic modeling of chromate adsorption onto goethite." *Colloids Surf. A: Physicochem. Eng. Aspects*, 162, 167–175.

Weerasooriya, R., Tobschall, H. J., Wijesekara, H. K. D. K., Arachchige, E. K. I. A. U. K., and Pathirathne, K. A. S. (2003). "On the mechanistic modeling of As(III) adsorption on gibbsite." *Chemosphere*, 51, 1001–1013.

Weerasooriya, R., Tobschall, H. J., Wijesekara, and Bandara, A. (2004). "Macroscopic and vibration spectroscopic evidence for specific bonding of arsenate on gibbsite." *Chemosphere*, 55, 1259–1270.

Weggler, K., McLaughlin, M. J., Graham, R. D. (2004). "Effect of chloride in soil solution on the plant availability of biosolid-borne cadmium." *J. Environ. Qual.*, 33, 496–504.

Wehrli, B., and Stumm, W. (1989). "Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation." *Geochim. Cosmochim. Acta*, 53, 69–77.

Welch, A. H., Lico, M. S., and Hughes, J. L. (1988). "Arsenic in ground water of the western United States." *Ground Water*, 26, 333–347.

Welch, A. H., Westjohn, D. B., Helsel, D. R., and Wanty, R. B. (2000). "Arsenic in ground water of the United States: Occurrence and geochemistry." *Ground Water*, 38, 589–604.

Weng, C. H., Wang, J. H., and Huang, C. P. (1997). "Adsorption of Cr(VI) onto TiO_2 from dilute aqueous solutions." *Water Sci. Tech.*, 35, 55–62.

White, A. F., Benson, S. M., Yee, A. W., Wallenberg, H. A., Flexser, S. (1991). "Groundwater contamination at the Kesterson Reservoir, California: 2. Geochemical parameters influencing selenium mobility" *Water Resour. Res.*, 27, 1085–1098.

Zachara, J. M., Ainsworth, C. C., Cowan, C. E., and Resch, C. T. (1989). "Adsorption of chromate by subsurface soil horizons." *Soil Sci. Soc. Am. J.*, 53, 418–428.

NOTATION

a_i = activity of ion i

b = adsorption maximum

C = equilibrium concentration of adsorbate

IAP = ion-activity product

k = parameter that reflects affinity of adsorbent for adsorbate

K, n = constants (empirically evaluated)

K_s = stability constant

K_{so} = solubility product constant

m = mass of solid phase adsorbent
m_i = molal concentration of species i
SI = saturation index
x = mass of trace element adsorbed
γ_i = activity coefficient of species i