MECHANISMS AND PATHWAYS OF TRACE ELEMENT MOBILITY IN SOILS

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ABBREVIATIONS

TE	Trace Elements
EPA	Environmental Protection Agency
CEC	Cation Exchange Capacity
DOM	Dissolved Organic Matter
OM	Organic Matter
EDTA	Ethylenediamine Tetracetic Acid
NTA	Nitrilotriacetate

I. INTRODUCTION

Trace elements, hereafter referred to as TEs, are a major group of contaminants worldwide arising from natural and anthropogenic sources. In the modern era, the anthropogenic sources arising primarily from industrialization have assumed paramount importance in the quality and sustainability of ecosystems (Adriano, 2001). The main anthropogenic sources include mining and smelting of metallic ores, combustion of coal and other fossil fuels, use of pesticides in agriculture and timber industry, manufacturing, landfills, and so on.

While certain TEs have essential biological functions in plant, animal, and human nutrition (such as the essential micronutrients Fe, Zn, Cu, Mn, Mo, and B in plant nutrition and Se, $Cr_{(III)}$, Ni, and so on in animal and human nutrition), others (such as Cd, Hg, Pb, and to a large extent As) have no known biological functions whatsoever (Adriano *et al.*, 2004). In fact, Cd, Hg, Pb, and As are on the EPA's list of priority pollutants because of their widespread and intense occurrence at waste sites and their known detrimental effects on ecological and human receptors (EPA, 1995).

The importance of TEs in soils depends largely on their fraction that has immediate biological function, that is, the fraction of the total soil burden that is soluble, mobile, and bioavailable. The nature and extent of mobility and bioavailability underlines the integrity and sustainability of a particular environment and in particular, the role of TEs in the functioning and well-being of an ecological endpoint (Allen, 2002; NRC, 2003). In an impacted ecosystem, the potential risks of TEs to ecological and human receptors largely depends on several factors, which primarily include site and waste characteristics, source term and chemical properties of the contaminants including chemical speciation, geo-hydrological characteristics of the site, diversity of ecological receptors, and climate. These factors, to a large extent, influence the magnitude and intensity of solubility, mobility, and bioavailability of TEs. Thus predicting mobility and bioavailability of TEs in the soil environment is critical yet quite complicated. Generally, a TE in soil has to be mobile before it can become bioavailable to plants and other soil biota.

As indicated earlier, contaminants, such as TEs, need to be mobile and bioaccessible to organisms to be beneficial or detrimental, they would also need to be mobilized to eventually reach a surface body of water or to be leached to underlying ground water. It then appears that, generally speaking, to be of any consequence to ecological receptors, a TE should have a distinct characteristic of being mobile first and secondly of being bioaccessible and/or bioavailable to organisms (Semple *et al.*, 2004). These processes and their associated mechanisms underline the thrust of biogeochemical cycling of TEs in the environment.

This chapter covers the basic mechanisms in the solubility and mobility of the TEs in the soil, including their movement in the soil profile, the entire vadose zone and the eventual leaching to the ground water. In essence the mechanisms influencing the extent of TE partitioning between the soil's solid and aqueous phases are elucidated in Section II. This leads to the various transport pathways (Section III) in soil responsible for disseminating TEs in the form of gaseous (volatilization), aqueous (soluble solute), colloids, and particulate matter. Then the most pertinent factors influencing the partitioning and movement of TEs are discussed. And finally, transport modeling of the most environmentally important TEs (Section V) and their applications (Section VI) typified by field case studies are illustrated. Transport modeling in the vadose zone is emphasized.

II. MECHANISMS OF TRACE ELEMENT MOBILITY

There are basic physical, chemical, and biological processes that control mobility of TEs in soils. The first major group can be lumped into physicochemical processes (see in a later section) that promote and regulate mechanisms such as solubility and precipitation, adsorption, complexation, and occlusion/encapsulation. The processes that sequester TEs can be grossly termed sorption which, to a large extent, determines the partitioning between the solid and solution phase. These processes can be expected to predominate in severely metal-contaminated soils as biological processes could be limited by the toxicity of the metals of concern.

A. Physicochemical Processes

The majority of TEs in soils usually occur in association with the solid phase, where they can be bound to the surface of the soil's solids, or they can be precipitated as various minerals or simply be coprecipitated within various forms. For most TEs, only a small portion is dissolved in the soil solution; most of the dissolved TE is bound to organic acids in the soil solution, the remainder being distributed as inorganic ion pairs and free ions. This free ion pool is usually quite small relative to the other TE pools, but it is the most reactive, chemically and biologically. Thus it is critical in understanding the mobility, transport, and fate of TEs in soils.

Figure 1 illustrates the implications of fractionation and speciation of Cd in a hypothetical soil contaminated with 1 mg Cd per kilogram dry soil with a pH of 5. The proportion of Cd atoms is correctly scaled to represent the relative importance of the various metal pools. The actual occurrence of Cd associated with the solid phase is clearly predominant (◇). Furthermore, the importance of complexation with organic ligands (▲) or the formation of inorganic ion-pairs (□) shows that a tiny proportion of the Cd in this soil actually occurs as free Cd^{2+} in solution (★) while most of it is not very reactive. This figure illustrates vividly that the proportion of the TE bound to the solid phase predominates in this system. When the pH is elevated from 5 to 7 there would be about 100-fold more Cd on the solid phase. If Pb, generally an immobile TE, is substituted for Cd, a relatively mobile TE, the binding to the solid phase would also be about a 100-fold stronger (cumulative with any pH effects, e.g., $\sim 10^4$ times stronger binding by changing Cd in Fig. 1 to Pb at pH 7).

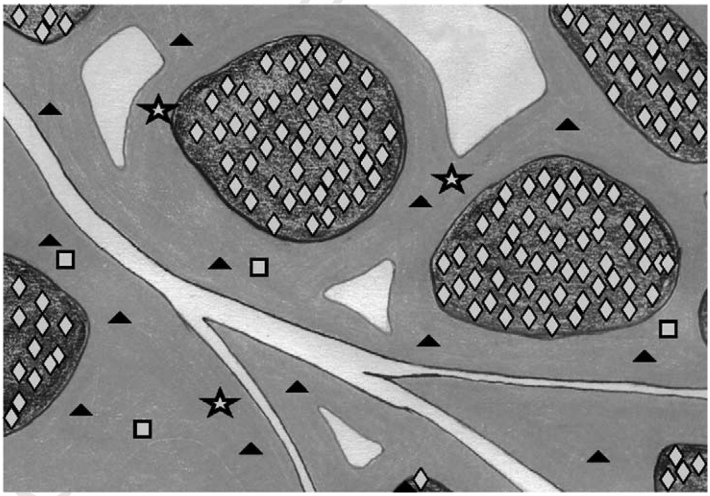

Figure 1 Fractionation and speciation of Cd in a hypothetical soil contaminated with 1 mg Cd kg^{-1} dry soil at pH 5. The distribution of Cd atoms is proportionally scaled to represent the relative importance of the various metal pools; bound to the solid phase (◇), complexed with organic ligands (▲), associated with inorganic ion-pairs (□), or occurring as free Cd^{2+} in solution (★). Adapted from Sauvé (2003a).

The diagram (Fig. 1) illustrates the effect of solution pH and type of the element on the chemical speciation of the TE in question, providing some insight as to the potential mobility of that element.

1. Mineral Solubility and Precipitation

Soils can be viewed as a mixture of discrete aluminosilicate minerals, precipitated minerals, and partially decomposed and transformed organic matter residues. Within the soil solution phase, anytime a chemical element exceeds its solubility for a given compound, this mineral could precipitate. Likewise, when the solution concentration of a given component of the mineral phase is below its chemical equilibrium concentration, it could dissolve until the concentration increases to attain this equilibrium concentration. The dissolution–precipitation process, depending on a myriad of factors, can be expected to be slow in most cases.

It is not uncommon for minerals to first precipitate as amorphous materials, then undergoing slow transformation to a more crystalline form. Coprecipitation of TEs can easily occur within the newly formed matrix of common soil components such as carbonates, hydroxides, phosphates, metal (Fe, Mn, and Al) oxides, and others. These reactions can be expected to occur commonly in soils and can be considered as major mechanisms to sequester TEs, limiting their mobility and bioavailability to biota. For example, in alkaline, calcareous soils, TEs can be occluded in the carbonate phase (Adriano, 2001); in highly fertilized agricultural soils, TEs can be sequestered when they coprecipitate with phosphates; and in highly weathered oxidic soils, TEs can be immobilized by the metal oxides. Combined, these sequestration processes could induce an attenuation of metals to levels considered acceptable by regulatory standards by virtue of decreased risk (Adriano, 2001). However, in heavily contaminated soils significant proportions of the total TE mass can be solubilized and eventually mobilized, or simply occur as TE-based mineral phase. A classic example is the occurrence of Pb pyromorphite, a highly stable, immobile mineral in soils heavily contaminated with Pb in the presence of phosphate (see also Section IV.D).

The solubility of standard mineral forms is much easier to evaluate and predict than the interaction with coprecipitating minerals. The data needed to evaluate the solubility of TEs are, for the most part, available in the literature and the principal mineral forms for some often-observed TEs are compiled in Table I. It is easy to use these compiled constants in evaluating the extent of solubility of the mineral forms of a given TE in a contaminated soil.

Figure 2 illustrates this for Cd, Cu, and Pb where the dots represent experimentally measured free metal ion activities and the lines the equilibrium concentrations for various TE minerals in an oxidic soil. For the Cd-contaminated soils in this figure, in all cases, the free Cd^{2+} activities in the

Table I
Selected Chemical Equilibrium Constants for Various Cd, Cu, and Pb Minerals[a]

Equilibrium reactions	log *K*
Cd minerals	
$\beta - \mathrm{Cd(OH)_2}(c) + 2\mathrm{H^+} \Leftrightarrow \mathrm{Cd^{2+}} + 2\mathrm{H_2O}$	13.74
$\mathrm{CdCO_3(octavite)} \Leftrightarrow \mathrm{Cd^{2+}} + \mathrm{CO_2}(g) + \mathrm{H_2O}$	6.16
$\mathrm{CdO(monteponite)} + 2\mathrm{H^+} \Leftrightarrow \mathrm{Cd^{2+}} + \mathrm{H_2O}$	15.14
$\mathrm{CdSO_4}(c) \Leftrightarrow \mathrm{Cd^{2+}} + \mathrm{SO_4^{2-}}$	−0.11
$\mathrm{CdSO_4} \cdot 2\mathrm{Cd(OH)_2}(c) + 4\mathrm{H^+} \Leftrightarrow 3\mathrm{Cd^{2+}} + \mathrm{SO_4^{2-}} + 4\mathrm{H_2O}$	22.65
$\mathrm{Cd_3(PO_4)_2}(c) + 4\mathrm{H^+} \Leftrightarrow 3\mathrm{Cd^{2+}} + 2\mathrm{H_2PO_4^-}$	1.00
$\mathrm{CdSiO_3}(c) + 2\mathrm{H^+} + \mathrm{H_2O} \Leftrightarrow \mathrm{Cd^{2+}} + \mathrm{H_4SiO_4^0}$	7.63
Cu minerals	
$\mathrm{Cu(OH)_2}(c) + 2\mathrm{H^+} \Leftrightarrow \mathrm{Cu^{2+}} + 2\mathrm{H_2O}$	8.68
$\mathrm{CuCO_3}(c) + 2\mathrm{H^+} \Leftrightarrow \mathrm{Cu^{2+}} + \mathrm{CO_2}(g) + \mathrm{H_2O}$	8.52
$\mathrm{Cu_2(OH)_2CO_3(malachite)} + 4\mathrm{H^+} \Leftrightarrow 2\mathrm{Cu^{2+}} + \mathrm{CO_2}(g) + 3\mathrm{H_2O}$	12.99
$\mathrm{Cu_3(OH)_2(CO_3)_2(azurite)} + 6\mathrm{H^+} \Leftrightarrow 3\mathrm{Cu^{2+}} + 2\mathrm{CO_2}(g) + 4\mathrm{H_2O}$	19.59
$\mathrm{CuO(tenorite)} + 2\mathrm{H^+} \Leftrightarrow \mathrm{Cu^{2+}} + \mathrm{H_2O}$	7.66
$\mathrm{Cu_4(OH)_6SO_4(bronchantite)} + 6\mathrm{H^+} \Leftrightarrow 4\mathrm{Cu^{2+}} + \mathrm{SO_4^{2-}} + 6\mathrm{H_2O}$	15.35
$\mathrm{Cu_3(PO_4)_2} \cdot \mathrm{H_2O}(c) + 4\mathrm{H^+} \Leftrightarrow 3\mathrm{Cu^{2+}} + 2\mathrm{H_2PO_4^-} + 2\mathrm{H_2O}$	0.34
Pb minerals	
$\mathrm{Pb(OH)_2}(c) + 2\mathrm{H^+} \Leftrightarrow \mathrm{Pb^{2+}} + 2\mathrm{H_2O}$	8.16
$\mathrm{PbCO_3(cerussite)} + 2\mathrm{H^+} \Leftrightarrow \mathrm{Pb^{2+}} + \mathrm{CO_2}(g) + \mathrm{H_2O}$	4.65
$\mathrm{Pb_2(CO_3)_2(OH)_2(hydrocerussite)} + 6\mathrm{H^+} \Leftrightarrow 3\mathrm{Pb^{2+}} + 2\mathrm{CO_2(g)} + 4\mathrm{H_2O}$	17.51
$\mathrm{PbO(red)} + 2\mathrm{H^+} \Leftrightarrow \mathrm{Pb^{2+}} + \mathrm{H_2O}$	12.72
$\mathrm{PbSO_4(anglesite)} \Leftrightarrow \mathrm{Pb^{2+}} + \mathrm{SO_4^{2-}}$	−7.79
$\mathrm{PbHPO_4}(c) + \mathrm{H^+} \Leftrightarrow \mathrm{Pb^{2+}} + \mathrm{H_2PO_4^-}$	−4.25
$\mathrm{Pb_5(PO_4)_3OH(hydroxypyromorphite)} + 7\mathrm{H^+} \Leftrightarrow 5\mathrm{Pb^{2+}} + 3\mathrm{H_2PO_4^-} + \mathrm{H_2O}$	−4.14
$\mathrm{Pb_5(PO_4)_3Cl(chloropyromorphite)} + 6\mathrm{H^+} \Leftrightarrow 5\mathrm{Pb^{2+}} + 3\mathrm{H_2PO_4^-} + \mathrm{Cl^-}$	−25.05

[a] Sources: Carroll *et al.*, 1998; Lindsay, 1979.

soil solution are much below the potential chemical equilibrium; thus it is clear that the solubility and mobility of Cd in soils is not controlled by chemical solubility equilibrium with a mineral phase. Rather the various sorption or coprecipitation mechanisms could control the solubility of Cd. The case for Cu is somewhat intermediate, with most of the soil data well below the solubility equilibrium of potential mineral phase, except for the most critically contaminated soils where few samples close or above the least soluble mineral form are represented by a set of soils contaminated with more than 10,000 mg Cu kg^{-1} dry soil. It indicates that only in the case of an extreme contamination is a mineral phase likely to control Cu solubility. In the case for Pb, quite a few points are clustered around the solubility line for chloropyromorphite ($\mathrm{PO_5(PO_4)_3Cl}$) given that some of these soils are contaminated with only 1000 mg Pb kg^{-1} dry soil. This implies that mineral solubility could, in some situations, control the solubility of Pb in contaminated soils. Indeed, chloropyromorphite formation has been observed in contaminated soils (Ryan *et al.*, 2004) and can actually be used to limit

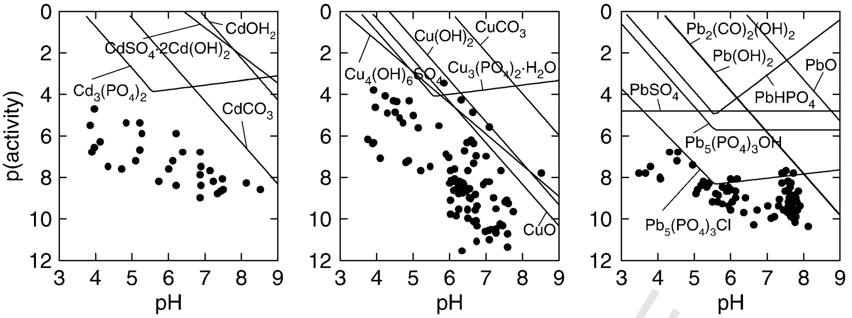

Figure 2 Soil solution mineral solubility equilibria for Cd, Cu, and Pb. The solid lines represent the theoretical free-metal ion activity maintained at equilibrium by various mineral phases. The computations assume 0.005 M Cl^-, 0.001 M SO_4^{2-} and NO_3^-, atmospheric CO_2, 0.01 M Ca and PO_4^{3-} solubility controlled by $FePO_4$ below pH 5.6 and by $Ca(PO_4)_3OH$ at higher pH values. The dots represent actual electrochemical speciation measurements in field-collected contaminated soils (Sauvé, 1999; Sauvé *et al.*, 1997a,b, 2000b). Reproduced from Sauvé (2003b) pending permission.

mobility and bioavailability of Pb in soils (Berti and Ryan, 2003; Ryan *et al.*, 2004).

In other words, when soils become heavily contaminated with metals, metal solubility may reach a level to cause precipitation. In addition, precipitation may occur in the vicinity of phosphate fertilizer zone or in the vicinity of carbonates and/or alkaline waste by-products. In reducing environments where the sulfide concentration is sufficiently high, precipitation of TEs as sulfides may have a significant role in metal dynamics.

2. Partitioning

The simplest means to represent partitioning of TEs between the solid–liquid phases in soils is to use a K_d coefficient. This is a gross expression of TE interactions between phases. In other words, it is a result of the degree of association or dissociation of the TE from the solid phase. The coefficient is usually expressed as the ratio of the sorbed metal on the solid phase relative to the amount of dissolved metal present; therefore, the higher the K_d values the higher the sorption to the solid phase and the lower the solubility.

$$K_d = \left(\frac{\text{sorbed metal}}{\text{dissolved metal}}\right) \tag{1}$$

where sorbed metal is usually given in mg·kg^{-1} and dissolved metal in mg liter^{-1}, hence the units for K_d's are in liter kg^{-1}. Standard sorption experiments that model metal sorption using a single-value K_d approach presume that the sorption capacity of a material is relatively independent of soil physicochemical properties. However, the dependence of K_d's on soil texture and soil organic matter content is well recognized (Buchter *et al.*, 1989; Sauvé *et al.*, 2000b, 2003) and attempts have been made to delineate data into various soil textural categories (Sheppard and Thibault, 1990). Although some default values are available for a large number of elements (Anderson and Christensen, 1988; Buchter *et al.*, 1989; Gooddy *et al.*, 1995; Sauvé *et al.*, 2000b, 2003; Sheppard and Thibault, 1990), many values had to be estimated from plant/soil/solution relationships which rely on simplified assumptions (Sheppard and Evenden, 1988; Sheppard and Thibault, 1990). Furthermore, there is ample evidence that single-value K_d's are not appropriate to represent metal solubility in soil chemistry models (Jopony and Young, 1994; Sauvé *et al.*, 2000b, 2003) and some considerations for chemical properties, such as pH (Fig. 3) (see more detailed discussion in Section IV.A), organic matter, and total metal burden, need to be considered (Janssen *et al.*, 1997; Jopony and Young, 1994; Sauvé *et al.*, 2000b, 2003).

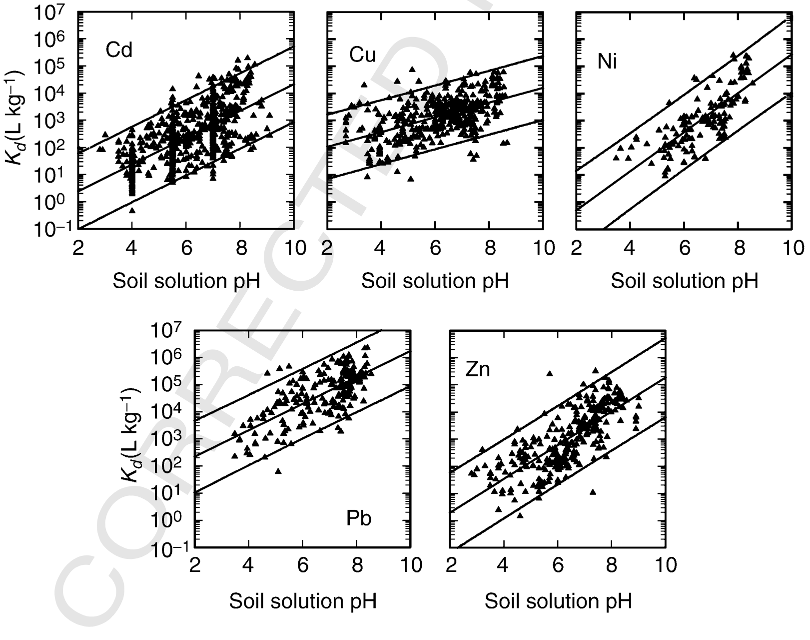

Figure 3 The partitioning coefficient (K_d) as a function of soil solution pH for Cd, Cu, Ni, Pb, and Zn data. Results were calculated from the compilation of Sauvé *et al.* (2000b). The upper and lower lines represent the 95% prediction intervals. Reproduced from Environmental Science and Technology 2000, 34:1125–1131, *pending* permission from the American Chemical Society.

a. The Freundlich Isotherm. The Freundlich isotherm considers the effects of saturation of sorbing surfaces. Relative to the single-value K_d approach, an n parameter is introduced to allow for variations in the K_d values according to the relative saturation of the sorbing surfaces. Hence, as the solution concentration of the metal increases, the ratio adsorbed on the solids will vary. The Freundlich equation takes the form:

$$(\text{Sorbed metal}) = K_d(\text{dissolved metal})^n \tag{2}$$

where the units are the same as in (1) in the case where the value of the constant, n, is 1. The relationship between adsorbed and dissolved metal is illustrated in Fig. 3. Also, Buchter *et al.* (1989) have measured Freundlich parameters (K_d and n) for 11 different soils and 15 TEs. They also explored the correlation of the Freundlich parameters with selected soil properties and found that the pH, cation-exchange capacity (CEC) and Fe/Al oxide contents were the most important factors for correlation with the partitioning coefficients. Buchter *et al.* (1989) observed the following results.

1. pH is the most important soil property that affects K_d and n.
2. Cation-exchange capacity substantially influences K_d for cation species.
3. The amounts of amorphous Fe and Al oxides, and amorphous materials in soils influence both cation and anion retention parameters.
4. Except for Cu and Hg, transition metal (Co and Ni) and group IIB cations (Zn and Cd) have similar K_d and n values for a given soil.
5. Significant relationships between soil properties and retention parameters exist even in a group of soils with greatly different characteristics.

Corroborations by other recent studies (Anderson and Christensen, 1988; Gooddy *et al.*, 1995; Janssen *et al.*, 1997; Jopony and Young, 1994; Lee *et al.*, 1996; McBride *et al.*, 1997b; Sauvé *et al.*, 2000b, 2003) suggest that metal partitioning between the solution and the solid phase in contaminated soils could be, at least to some extent, predicted from common soil properties.

Buchter *et al.* (1989) suggested that certain groups of TEs could have similar sorption properties in a certain soil. They also found that the Freundlich parameter n varied experimentally from ~0.4 to ~1.5 for 15 different chemical elements, indicating that different elements have different sorption properties. For example, comparing the behavior of Pb and Zn, higher concentrations of Pb in solution could promote its adsorption, increasing the apparent K_d (case of $n > 1$). For Zn on the other hand, higher solution concentrations could decrease the apparent K_d, reflecting lower affinity of the solid phase for Zn as it moves toward saturation ($n < 1$). Thus it is not advisable to use K_d values derived under low-contamination levels and use them for risk assessment modeling of contaminated conditions (or reverse).

Most of the elements studied by Buchter *et al.* (1989) have an *n* parameter below 1, and should therefore react qualitatively like Zn (except for Pb and possibly Hg).

The comparison of the K_d values derived from mineral soils are also quite different from that of organic soils (Sauvé *et al.*, 2003). If one intends to use a K_d approach for estimating metal mobility or transfer in the environment, corrections for pH and organic matter content could be critical and coefficients derived from a given dataset could only be appropriate for interpolation within the physicochemical parameters of that dataset but should not be extrapolated outside those parameters.

3. Complexation

Complexation of TEs is ubiquitous in both aquatic and terrestrial systems, especially for trace metals (e.g., Pb, Zn, Cd, Hg, Cu, and so on). In most situations, a significant proportion of the soluble metals occur in association with dissolved natural organic matter (DOM). This DOM is composed of an heterogeneous mixture of fulvic and humic acids (Stevenson, 1994). Given that these natural ligands occur at rather large concentrations in soils and have variable chemical composition and structure, complexation with natural organic acids is rather difficult to model.

Complexation can be subdivided among weakly bound ion pairs (an example of outer-sphere complex formation), complexes (an example of inner-sphere complex) and strong ligands. Ion pairs often refer to electrostatic interaction of a metal with an inorganic anion where, for the most part, the hydration shells of the ions are largely unaffected. With complexation, some of the bonding is covalent and the hydration shells of the ions are reduced. Whereas with chelate ligands metals usually posses more than a single binding site and with little, if any, of the hydration shell retained. Weak ion-pairs with inorganic anions are rather easier to model, so is binding with strong ligands having clear and definitive structure. Overall modeling of complexation with DOM is quite challenging because of the heterogeneity and variable chemical composition of the organic substance.

A further complication is that chemical equilibrium models can indeed be used to calculate the complexation of metals with natural organic ligands, given that one has the appropriate stability constants for the metal binding affinity of the natural organic matter actually present in the matrix under study. Various computer models are available to calculate the solution speciation of metals (e.g., GEOCHEM, SOILCHEM, HYDROQL, ECOSAT, MINTEQ2, WHAM, PHREEQC, and so on). Inasmuch as these models are used to calculate the speciation or partitioning among inorganic chemical species, which model is applied has very little influence on the end result.

In modeling metal complexation by DOM, the actual stability constants used and model assumptions can have a larger influence on the results. Unfortunately, a majority of the data available for those constants are derived from titration data where large metal concentrations are added to purified organic acids of mostly aquatic origin. The purification protocol, which is desired to produce consistent experimental results transforms the properties of the fulvic and humic acids. Furthermore removing cations not included in the study can render the results unrealistic, misrepresenting DOM occurrence under field conditions. However, recently various chemical models, called surface complexation models, have been used to describe B adsorption, in which molecular features, specific surface complexation, chemical reactions and charge balances are considered. The prediction of adsorption on the soil using such models has been successful for B, Mo, Mn, and As (Goldberg, 2004, 2005; Goldberg and Forster, 1998; Goldberg *et al*., 2002).

Even more difficult to integrate in those chemical *equilibrium* models is that by definition, they fail to account for the slow kinetics of some of these reactions and this is an area of research that needs to be further expanded, especially in soil environments where complexation of a particular TE may be slowed and hindered by the need to displace cations, such as calcium or magnesium, from the ligands before complexation can take place. Many factors need to be considered when trying to model and predict complexation of TEs in soils and those are further discussed in Section IV.

B. Biological Processes

In typical, uncontaminated soils, biological processes are usually mediated by microbes, invertebrates, and plant roots. However, in severely contaminated soils the metal toxicity limits the importance of biological organisms. Thus, it is not uncommon to find derelict old mining sites largely nonvegetated with less biodiversity in soil microbes (González Chavez *et al*., 2005) and invertebrates such as worms, nematodes, and so on. However, once soil amendments are added to soils to create a more favorable growth environment to these organisms, biological processes can assume major importance in the attenuation of metals. In typical soils, biological processes are more predominant in the top soil since the majority of the microbial and invertebrate biomass is confined in this layer (Adriano, 2001). In agricultural and grassland soils, this active biological zone corresponds to the plow layer or to the layer where roots are most dense. For soils where phreatophytic (groundwater-using) species are grown, the rhizospheric zone increases, because of the bigger root exploration volume down the soil profile; as a result changes in TEs availability can occur. The introduction of active roots in anoxic sediments can influence oxidation and drying through increasing evaporation and aeration of the root zone, and the availability of some TEs such as Cd, Cu, and Zn (Vervaeke *et al.*, 2004).

Plant roots can play a vital role in the transformation and chemical speciation of TEs in soils (Koo *et al.*, 2005). Three mechanisms can be influenced by plant roots: modification of the soil environment in the rhizosphere, transformation of chemical form of TEs, and biosorption. Roots exude plant metabolites including several forms of carbohydrates and organic acids that can serve as energy source for soil microbes. These low-molecular-weight organic acids can complex metal ions rendering them potentially more mobile and bioavailable. Soil microbes can carry out important biotic redox reactions for some TEs in soils (Mahimairaja *et al.*, 2005). This includes the transformations of multivalence anionic TEs, such as As, Cr, and Se, altering their oxidation state and chemical species. For example, *Alcaligenes faecalis* was found to oxidize $As_{(III)}$ to $As_{(V)}$ (Osborne and Ehrlich, 1976). Bacteria, fungi, and algae could also reduce $As_{(V)}$ to $As_{(III)}$ (Frankenberger and Losi, 1995).

Soil microbes and invertebrates can promote temporary immobilization of metal ions by biological accumulation. Such accumulation is facilitated by biosorption by microbial biomass and its byproducts and physiological uptake by organisms through metabolically active and passive processes (Mahimairaja *et al.*, 2005). Microbes can dissolve minerals by direct or indirect action under aerobic and anaerobic conditions (Kurek, 2002). When oxidized metal compounds, such as $Fe_{(III)}$, $Mn_{(IV)}$, or $As_{(V)}$, act as terminal electron acceptors, anaerobic respiration becomes an example of direct dissolving action under anaerobic conditions. Oxidation of ferrous Fe or sulfur entities of metal sulfides to obtain energy is an example of direct dissolving action under aerobic conditions. Indirect dissolution of minerals can be the result of microbial activity connected with the production of organic and inorganic acids, and oxidizing agents which can influence soil conditions including changes in pH and Eh. Metals can also be mobilized from minerals by complexation with biomolecules of microbial metabolites. Organisms have developed two major strategies of internal sequestration of TEs: formation of inclusion bodies for instance in vacuoles (Clemens *et al.*, 1999) and binding of metals to heat-stable proteins, such as phytochelatins and metallothioneins, and stable molecules such as ferrihydrite (Hall, 2002; Hansel and Fendorf, 2001).

C. *IN SITU* STABILIZATION

In situ stabilization, also coined ‘‘inert inactivation,’’ aims to modify the mobility and bioavailability of a chemical pollutant to reduce its potential risk and thus transform a toxic pollutant to a contaminant which is still present in the matrix but unable to reach or intoxicate the target organisms (Adriano *et al.*, 2004; Berti and Ryan, 2003). This is practically a remediation process to sequester metal contaminants in soil, accomplished by adding soil amendments to precipitate and/or sorb the metals in question, thus the term "inert inactivation." In this approach, the total metal content is not altered but the solubility and mobility are drastically reduced. The most studied and demonstrated amendment materials to induce metal stabilization include phosphate, Fe, and Mn oxide, and alkaline, stabilized biosolids (Adriano *et al.*, 2004). The mechanisms of this stabilization have not been conclusively established, but many processes can decrease metal mobility by, for example, increasing the CEC, or inducing precipitation of hydroxides or carbonates, or TEs migration into micropores.

Because hydroxyapatite is an abundant and inexpensive natural mineral, it has been used and promoted to inactivate metals, especially Pb as metal pyromorphite, a fairly stable precipitate over a wide range of pH (Ma *et al.*, 1993, 1994). It has also been used to stabilize Zn, Cd, and other trace metals in soils (Chlopecka and Adriano, 1996). The abundance and reactive nature of metal (Fe, Mn, and Al) oxides with most TEs in most soils enhance their use as metal inactivators. Commercial by-products, such as the "steel shot" or zero valence Fe, could be used in soil remediation for both cationic and anionic TEs such as As (Mahimairaja *et al.*, 2005) because once applied into the soils, the metallic Fe is oxidized and becomes more reactive. The heterogeneous and variable chemical nature of organic matter, more specifically biosolids, renders its use as a metal inactivator somewhat tenuous. Although the use of alkaline, stabilized biosolids has proven effective in immobilizing metal ions via adsorption, the capacity of DOM to complex and mobilize most metal ions renders it much less interesting to use in sequestering metals. This evolves around the possibility of advanced oxidation/transformation of organic matter, further complicating its role as an inactivator.

A nice example of *in situ* stabilization is the work done in Joplin, Missouri where Pb-contaminated soils in an urban area were amended with various phosphate treatments, which significantly reduced Pb transfer to plants, and even decreased its gastrointestinal availability in experimental animals (Berti and Ryan, 2003; Ryan *et al.*, 2004). These field trials and live animal tests, clearly demonstrated this technique's remediation potential.

In situ stabilization is a clear case of solubility–precipitation phenomena in soils where a process is induced by introducing foreign materials into the soils to foster high K_{d}. In essence, *in situ* stabilization induces attenuation of metals rendering them less threatening to the environment and biota. Since the inactivator materials are rather abundant, some found in nature, and inexpensive, they can offer a viable cost-effective remediation strategy for heavily metal-contaminated sites. However, data demonstrating their long term efficacy under field conditions are still lacking.

III. TRACE ELEMENT TRANSPORT PATHWAYS

The major mechanisms and transport vectors and pathways of TEs in terrestrial systems are exhibited in Fig. 4. Although the surface soil is emphasized in Fig. 4, most of the reactions are valid in the rest of the soil profile and the vadose zone as well. Atmospheric deposition, fertilizer applications, and soil amendments represent the major input sources into the soil. In pristine natural environments, aerial deposition is the most important source especially for TEs such as Hg, Pb, and As. Erosion is considered a very important pathway in arable lands, derelict mining sites, and other nonvegetated landscapes. The usual vertical transport pathway (i.e., mass flow and diffusion) can be complimented by preferential flow in macroporous and/or

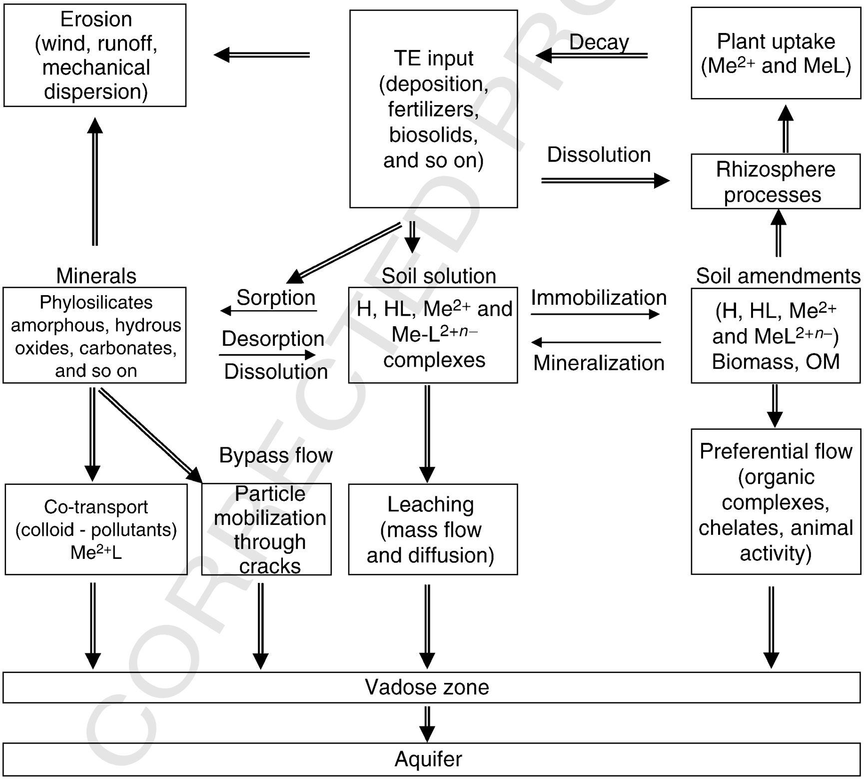

Figure 4 Possible mechanisms and pathways of trace element movement in soils. Me represents trace element ion or atom, H hydrogen ion or atom, L ligand or other substance that combines with Me.

cracked soils and facilitated transport due to TEs mobilization with colloids. Volatilization, as discussed in the text, is not included in Fig. 4, as it is usually more important in aquatic systems and applies to only certain elements.

Figure 4 presents an overview of possible mechanisms of TE movement in soils. Significant TE movement in soils after sewage sludge or wastewater application, or residues deposition has been observed (Lund *et al*., 1976). Dispersion of these elements above the soil surface could be caused by soil erosion or by limited volatilization in the case for Se and Hg. While TE distribution in the top soil layer (0.3 m) can result from tillage operations, the vertical movement below this depth is likely due to other mechanisms. Although TEs movement in sewage-amended soils has been explained as a result of pH reduction caused by organic compounds (Robertson *et al*., 1982), element transport has been observed even after an increase in pH. Transport of soluble chelate complexes with organic matter has been suggested as a possible explanation (Darmony *et al*., 1983). Application of sewage sludge or C-rich residues can increase DOM (dissolved organic matter), promoting the formation of soluble TE-organic complexes, which can then reduce metal adsorption. Trace element movement in structured soils, through desiccation cracks, has been reported to be likely enhanced by preferential flow (Richards *et al*., 1998). Movement of TEs from the application or deposition zone downward through the soil profile could occur by: (1) diffusion (either as free ions or as complexes), (2) movement of metal-laden particulates through soil macropores, (3) movement through soil cracks during the wetting–drying cycle, and (4) bioturbation (i.e., mixing by soil fauna) (Dowdy and Volk, 1983).

TE mobility depends on the soil particle distribution. Mobility is lower in fine textured soils as compared with coarse textured soils. While the flow rate affected the mobility of some TEs such as Be, Cr, and Fe, it had little effect on the mobility of Cd, Ni, and Zn at low concentrations (<97 mg liter^{-1}) in repacked soil columns. Leaching of these elements was in direct proportion to their concentrations (Alesii *et al*., 1980). The slow water movement through soil columns apparently allowed the element adsorption onto soil surfaces, because TEs could diffuse into the soil aggregates where is a higher chance of adsorption. In addition, other adsorption processes, such as physical exclusion (molecules of TEs are unable to penetrate the inner layer of the minerals) or competitive sorption between target cations and cations present in the system, can affect TE transport in the soil.

While more than one transport mechanism is often simultaneously involved, the contribution of each mechanism varies depending on metal properties (Tam and Wong, 1996), soil conditions, and soil management (Murray *et al*., 2004).

A. DIFFUSION AND DISPERSION

Diffusion is a transport mechanism that is active when a chemical moves between two locations, with the direction dependent on the concentration gradient. The random motion of chemical molecules is called molecular diffusion while the random motion of water containing dissolved chemicals is the turbulent diffusion (Hemond and Fechnor, 1994). This random molecular motion of molecules is called diffusive transport, contrary to the dispersive transport that is caused by the uneven distribution of velocities within and between various soil pores. Both these transport processes are described by Fick's law. The distance traveled by a solute during a particular time interval due to the Fickian transport is often much shorter than the distance traveled due to the mass flow. Krishna and Wesseling (1997) argued that the Maxwell Stefan formulation provides a better description of diffusion of trace metals than Fick's law. Diffusion of TEs is apparently relatively low in soils, with a possible exception of sandy acid soils that typically have low-adsorption capacities (Delolme *et al.*, 2004).

The dispersivity of a solute in a porous medium is defined as the increase of the spatial variance of its distribution with distance traveled (Rose, 1973). The dispersivity of elements such as Cd is much greater than that of nonreactive solutes due to the high rate of adsorption and due to the heterogeneous distribution of adsorption sites along pores (Gerritse, 1996). Different metal concentrations inside and outside of soil aggregates have been observed, apparently due to adsorption effecting the metal diffusion (Wilcke *et al.*, 1999). However, this local heterogeneity apparently also depends on the metal solubility, since Pb and Cu were observed to be lower in aggregate interiors than exteriors, but only small or no differences were observed for Cd concentrations.

In structured soils, metals can move with sludge-borne particles or colloids. Although metals have been detected in higher concentrations on ped surfaces, the binding of metals to water soluble organic ligands of the sludge may, apparently, depress metal adsorption on the clay-rich ped surfaces (Chubin and Street, 1981) and allow metal redistribution within the ped (Dowdy *et al.*, 1991). Therefore, the release of colloids is a diffusion-limited process (Schelde *et al.*, 2002) (see also Section II.A).

B. PREFERENTIAL FLOW

Movement of heavy metals with flowing water requires that TEs are in the soluble phase or associated with mobile particulates. The naturally occurring soil structure contains pores of different diameters, cracks formed by soil shrinking during drying and wetting cycles, and various macropores and conduits created by soil fauna and plant roots. Liquid, suspended mobile colloids, and suspended particles can move vertically down the soil profile through these channels or cracks without interacting with the soil matrix. This preferential/nonequilibrium flow and transport is a recognized way for mobilizing contaminants in macroporous soils (Camobreco *et al.*, 1996; McCarthy and Zachara, 1989).

Since macropores in structured soils can conduct water rapidly to deeper soil horizons, while bypassing the denser, less permeable soil matrix (Jarvis *et al.*, 1999), an application of polluted residues with TEs during the dry season can cause rapid contaminant (pollutant) transport. Mineral surfaces in preferential pathways and matrix are often quite different, being coated in the flow paths with organic matter (OM) that can sorb specifically TEs (Bundt *et al.*, 2001). It has been proposed that TEs move down the soil profile through these preferential flow pathways after application of sewage sludge, waste water, or smelter residues. Sterckeman *et al.* (2000) reported that concentrations of Cd, Pb, and Zn increased down to a 2-m depth in soils near smelters. They suggested that earthworm galleries were the main pathways for accelerated particulate metal migration.

Soils receiving heavy sludge applications during a period of 15 years showed considerably increased concentrations of Hg and Cu below the application site (McBride *et al.*, 1997a). The authors suggested that downward transport via organic complexes and preferential flow are the main factors responsible for the increased element mobility (see also discussion on Fig. 4 of this section). Maeda and Bergström (2000) found that Zn leaching was enhanced by preferential flow, while Cu transport was negligible. Apparently, only insignificant interactions between the solid phase and metals in the soil solution occur when the soil structure and/or incoming water allow for preferential flow. Consequently, metals can move to much greater depths.

Preferential flow mechanisms in structured soils have been studied at both field and laboratory conditions. However, laboratory studies have several limitations due to difficulties in excavating and transporting undisturbed soil samples to the lab (Morris and Mooney, 2004). One of the difficulties of soil column studies is that the process of packing the column tends to destroy or reduce soil aggregation and the resulting exposure of much greater surfaces on the soil solids increases tremendously the potential for sorption onto the solid phase. In addition, the type of experimental method used for studying the preferential flow processes at the laboratory scale can also influence the TE transport. However, more attention should be given to studying these processes since Flury *et al.* (1994) reported that the majority of water flow can use less than 10% of the pore space and move preferentially much faster and to much greater depths than uniform flow.

C. COLLOIDAL TRANSPORT

Trace elements generally have high affinity for sorbing substances, which are mainly associated with the solid phase, and thus the amount in the soil solution is relatively small (see also Section II.A). Colloidal particles can act as TEs carriers, since they are highly reactive, have low bulk density, are lighter than water, and can thus be easily suspended (Totsche and Kügel-Knabner, 2004). The activities of Mn, Co, Sb, Cs, Ce, and Cu in groundwater samples collected from underground nuclear test cavities at the Nevada Test Site were associated with colloidal particles (Buddemeier and Hunt, 1988). Zhang *et al.* (2003) observed TEs were transported to surface water through runoff attached in the fine fractions: the <53-μm fractions contained 13–19% and the 0.125- to 0.053-mm fraction contained 28–38% of the total Cu, Cd, Cr, Co, Pb, Ni, and Zn. Oxyanions of eluted Cr and As were associated mainly with Fe and Mn oxides (Sandhu and Mills, 1987). Also As-organic compounds complexes have a neutral charge and move faster than the dissolved anionic arsenate (Kaplan *et al.*, 1993). Grolimund *et al.* (1996) observed the movement of Pb bound to colloids and concluded that colloid-facilitated transport is an important process especially for strongly sorbing contaminants. They also noted that colloid-facilitated transport is a very complex process since the release of colloid-carrying contaminants is kinetically limited, and thus the flow rate significantly affects the transport.

Application of certain organic residues to structured soils could cause movement of TEs by particulate transport. In soils with undisturbed structure, macropores can act as rapid flow conduits and particulates and contaminants associated with organic (particulate) matter can move rapidly through them to subsurface soil layers (Oygarden *et al.*, 1997). Keller *et al.* (2002) found in a lysimeter experiment that particulate matter in drainage water accounted for, on average, 20% of trace metals leaching from a sludge-amended soil.

The role of colloids in facilitating the TEs transport is moderated by the element and colloid type, by concentration of the TE, and by soil properties. It has been observed that the increase in the colloid surface area, the charge of the colloids, pH, and the organic compounds in solution can facilitate transport of colloids and TEs. In contrast, TEs associated with large colloids have lower movement. Also the increase in the element concentration affects coagulation, flocculation, flow retardation, and pore clogging (Karathanasis, 1999) through cation–colloid association, which then decrease solubility. Apparently, the solid phase dispersion increases at the low ionic strength and thus the colloid migration is more likely to occur (Schelde *et al.*, 2002). For example, Zn will move faster in the leachate from an acidic sandy soil column when the column is leached with deionized water than when leached

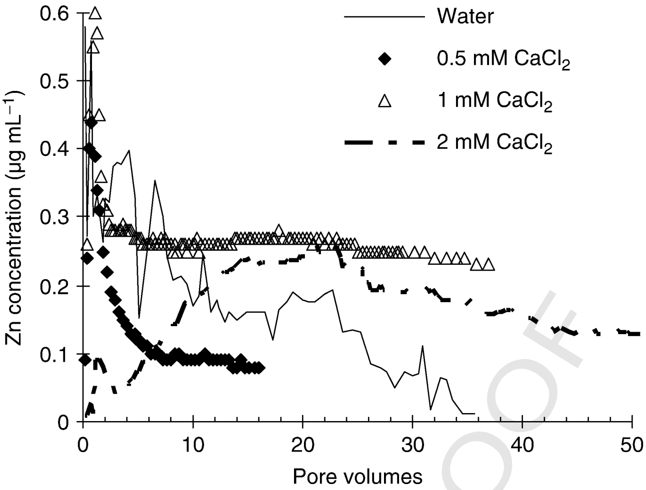

Figure 5 Zn breakthrough after leaching soil columns with deionized water, and 0.5 or 2 mM $CaCl_2$ solutions through an acid sandy soil (Carrillo-González, 2000).

with 0.5 or 2 mM $CaCl_2$ solutions and this is believed to be due to dispersion of organic colloids (Fig. 5) (Carrillo-Gonzalez, 2000).

The adsorption of dissolved organic molecules and humic substances can modify the surface charge of colloids, increasing their stability and mobility. For example, colloids composed of oxides, layer silicates, and calcium carbonate and those coated with humic substances can develop a negative charge and remain in the solution (Harter and Naidu, 1995). Adsorption of some organic compounds is partially irreversible (Weigand and Totsche, 1998), which affects the specific surface, and therefore could modify the retention of TEs. For instance Fe and Zn adsorption decreased with the presence of natural organic matter at pH 5, but changes were also observed at pH 7 (Schmitt *et al.*, 2002).

D. Soluble Metal Complexes Transport

Organic compounds in the soil that may form complexes with metal ions may be grouped into three main classes (Senesi, 1992): (1) naturally occurring molecules derived from soil biota and having known structure and chemical properties (polysaccharides, amino acids, polyphenols, and aliphatic acids), (2) xenobiotic organic chemicals derived from human, agricultural, industrial and urban activities, and (3) humic substances that include humic and fulvic acids, and humin. Fulvic acids represent a significant proportion of organic carbon. They form complexes that bind TEs (e.g., Cu, Fe, Cd, Zn, V, and Ni) mainly on carboxylic and phenolic functional groups (Saar and Weber, 1982) and on organic molecules derived from chemicals used in agriculture, industrial activities, and urban residues.

Cations tend to form stable complexes with organic ligands (see also Section II.A). DOM forms stronger complexes with Cu and Cd than those formed with Pb and Zn. More than 50% of Cd was bound in the organic matter (Karapanagiotis *et al.*, 1991), and specifically humic and fulvic acids derived from sludge play a significant role in the chemical speciation of metals. Senesi *et al.* (1989) suggested that the humic acid fraction of sludge-amended soil shows selectivity in binding trace metal ions (Cu^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, Cr^{6+}), whereas more labile metal ions are desorbed and replaced (Mn^{2+}, V, Ti, Mo).

It is expected that xenobiotic organic molecules discussed earlier could also form complexes with metals. For example, the following chelating ligands can be found in wastes (sewage sludge and wastewater): nitrilotriacetate (NTA), hydroxyethyliminodiacetate (HIDA), dihydroxyethyl glycine (DHG), triethanolamine (TEA), hydroxyethylenthylen diaminotriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), CDTA (*trans*-1,2-cyclohexyl-diamine-*N,N,N′,N′*tetraacetate), ethylene-bis-oxyethylenenitrilo-tetraacetate (EDDHA), HBED (*N,N*-bis (2-hydroxybenzyl) ethylenediamine-*N-N′*-diacetate), oxalic acid, gluconic acid, and citric acid (Lasat, 2002; Martell, 1975; Russel *et al.*, 1998). These substances have been detected in rivers (Hoffman *et al.*, 1981) and the vadose zone (Jardine *et al.*, 1989). It has been observed that trace metals, such as Cd, Cu, and Pb, were associated with low and intermediate (1000–10,000) molecular weight organics, which passed through 0.4-μm membrane filters.

Element–ligand (organic) formation from hydrated elements can be represented as follows:

$$M^{a+}_{(aq)} + xH_2O \Leftrightarrow M(H_2O)^{a+}_{x(aq)} \tag{3}$$

$$M(H_2O)^{a+}_{x(aq)} + L^{b-}_{(aq)} \Leftrightarrow ML^{a-b}_{(aq)} + xH_2O \tag{4}$$

where M is the trace element ion and L is the ligand; the number of trace elements and ligands could change depending on the chemistry of both reactants.

The stability of these complexes depends on the equilibrium constants, which provide an indication of the affinity of the ion for ligand, and for bi- and polydentate ligands. Each successive interaction has its own equilibrium constant and the product of successive values gives the net stability constant. The successive interactions depend on the association of the ligand and the H^+

$$\beta_i = \frac{[\mathrm{ML}]}{[\mathrm{L}^{b-}] \cdot [\mathrm{M(H_2O)}_x^{a+}]} \qquad (5)$$

where β is the stability constant for the *i* association.

The conditional stability constants for TEs and fulvic acid vary widely as a function of the nature of the original organic matter, from which fulvic acids are derived, and pH (apparently increasing with pH). Stability constants for TE–organic acid complexes increase with the molecular weight. Chelating ligands form very stable associations with TEs and are able to extract them even if they are bound to the organic matter. This increases the likelihood of TE migration from the deposition site if synthetic organic ligands, such as ethylenediamine tetracetic acid (EDTA) or NTA, are present in the applied residues.

Strong ligands, such as EDTA, show almost no adsorption on the soil surface and have been reported to increase TEs concentration in the soil profile (Kent *et al.*, 2002). In addition, they may exhibit a low rate of degradation, and thus could modify the behavior of TEs. For example, Wu *et al.* (2003) showed that a significant increase in Cu and Pb mobility (but not Zn and Cd) was achieved when a polluted paddy soil was leached with EDTA. While Ni and Zn were displaced with the EDTA solution from a quartz sand aquifer, Al and Fe dissolved from the sediments competed with Zn and Cd to form metal–EDTA complexes (Kent *et al.*, 2002). Apparently, there is a competition among metal ions during leaching with the EDTA solution. Cu was leached slightly faster than Zn and Cd, while Pb moved even slower. However, the rate of mobility of Pb increased after more mobile elements were displaced (Sun *et al.*, 2001). The vertical movement of Cu, Ni, and Zn in calcareous soils in the form of mobile metal organic complexes in the soil solution was also reported by Kaschl *et al.* (2002).

Novillo *et al.* (2002) observed that Zn applied in solution to the top of the soil column and leached with dissolved organic ligands, migrates at different rates in acid, neutral, and calcareous soils. The retention of TEs depends on the type of metal complexes formed. Zn–EDTA complexes are very stable and can migrate to larger distances than other complexes such as Zn-lignosulfonate or 2-hydroxyl-1,2,3 propanotricarboxylate. The addition of EDTA, citric or oxalic acids increased Cr mobility more than 200-fold (Shahandeh and Hossner, 2000).

E. Leaching and Runoff

Leaching of TEs from soils has resulted from intensified use of fungicides, application of sewage sludge, spilling timber treatment solution, and acid mine wastes. There are contrasting reports about leaching of TEs from fertilized soils. While some authors found negligible movement of TEs (Singh and Myhr, 1997), others reported substantial losses (Williams and David, 1976). Transport is likely to occur in acid, sandy soils, where the adsorption process is relatively insignificant, and where the water fluxes vary from moderate to high (the hydraulic conductivity ranges from 3 to >300 mm h^{-1}). It may also occur in subsoil (below the 0.3-m depth) where organic matter content and metal retention decreases. The probability of movement of TEs also increases with their concentration. Migration of TEs may take place when their concentrations exceed the capacity of the soil to retain them, that is, especially in stabilized soils. The metal loss from application sites is usually low, but varies significantly among elements.

Leaching is strongly affected by soil pH (see also Section IV.A). While low-metal leachability at high-pH values is the norm, potential leaching from dredged sediments at pH 4 has been estimated to be as high as 61% for Zn, 60% for Cd, 53% for Mn, 27% for Co, 26% for Ni, 14% for As, 4% for Cu, and 2% for Pb (Singh *et al.*, 2000). Formation of ion-pairs with inorganic anion can also increase mobility. Doner (1978) was the first to suggest that an anion index of the leaching solution could play an important role in the displacement of TEs in sandy soils. He observed that Cd moved four times faster when Cl^- was present in the solution instead of $ClO_4{}^-$.

TEs can be leached in the soil profile as hydrated cations, oxyanions, and organic or inorganic complexes. Darmony *et al.* (1983) took soil samples to a depth of 150 cm (in 25-cm increments) from a sludge-treated silt loam soil and observed that Zn was translocated to the 75-cm depth, with a gradual decline in concentration with depth. They concluded that the transfer of soil in desiccation cracks accounted for the metal distribution. Giusquiani *et al.* (1992) leached soil columns amended with fresh compost (90 t ha^{-1}) with 0.01 M $CaCl_2$ and observed that the total concentration of complexed TEs increased significantly in the organic matter that passed through the soil column. Fraction of leached metals from a sludge amended soils (sand and sandy loam) ranged from 10% to 41%, 1.8% to 25%, 21% to 51%, and 6.8% to 41% for Zn, Cu, Pb, and Ni, respectively. No differences were observed between dry or fresh sludge applications (Gove *et al.*, 2001). Legret *et al.* (1988) observed an increase in exchangeable Cd and Pb in deep layers (0.4–0.6 m) of the sandy soil profiles after application of sewage sludge. Apparently, cations in solution can displace exchangeable Cd and Pb from the upper layers and move down. They concluded that exchangeable forms of TEs can play an important role under certain soil conditions. Also, the dominant anion in the solution has an important effect on the element leaching apparently due to two processes: (1) soluble metal-ligand formation, which can increase TEs in solution, and (2) ligand adsorption, which can modify surface adsorption and aggregation behavior of the particles.

Some TEs can move in the soil profile not only as hydrated cations, but as inorganic complexes. For instance, Zn can form with Cl^- the following complexes depending on chloride concentration and pH of the solution: $ZnCl^+$, $ZnCl_2^0$, $ZnCl_3^-$, and $ZnCl_4^{2-}$. Theoretically, elements with high values of the stability constant, such as Cd and Hg chloride complexes, are more stables in the solution and are more likely to migrate. However, the retention of these complexes on the soil surfaces can affect their mobility.

Soil erosion and surface water runoff are other mechanisms that can mobilize TEs in different environments. These mechanisms of TE dispersion are considered to be diffuse pollution because most of the suspended sediments carried with water during heavy rainfalls have a low density and can remain suspended. Barrel *et al.* (1993) reported that runoff from selected highways contained about 45–798 mg liter^{-1} of suspended solids, 0.073–1.78 mg liter^{-1} of Pb, and 0.113–0.998 mg liter^{-1} of P. Cr, Fe, Mn, Cu, Ni, Pb, and Cd have also been detected in street and highway sediments (Barbosa and Hvitved-Jacobsen, 1999; Rietzler *et al.*, 2001). The highest concentrations were detected during the first rainfalls after the dry season (Jiries *et al.*, 2001) and they varied depending on the nature of the element. While concentrations of Fe and Cu increased as the water flow increased, Zn, Cr, and Mn concentrations decreased. The dilution effect due to the input of sediments with low concentrations of these elements and the presence of iron oxides apparently caused the displacement among these TEs (Carvalho *et al.*, 1999).

Increases of TE concentrations in runoff from agricultural soils, after repeated pesticide applications, has been reported (Moore *et al.*, 1998; Quilbé *et al.*, 2004). However, He *et al.* (2004) found that dissolved TE concentrations in runoff from vegetable and citrus fields were usually below drinking water standards and that the TE concentrations were affected by soils TE accumulation, rainfall intensity, volume of runoff, soil properties and agricultural practices.

Release of metals from abandoned mining areas can occur due to acid mine drainage and erosion of waste dumps and tailing deposits. Presence or absence of vegetation, topographical characteristics and rainfall patterns can strongly affect the erosion processes (Clark *et al.*, 2001; Lee *et al.*, 2001). Birch *et al.* (2001) linked metal contents (easily exchangeable phase) in fluvial sediments to the coal mining activities. Ongley *et al.* (2003) observed high concentrations (from 10 to 100 mg kg^{-1}) of As, Cu, Pb, and Zn as far as 6 km away from piles of mining residues containing high concentrations of As (32,000 mg kg^{-1}), Pb (41,000 mg kg^{-1}), and Zn (17,000 mg kg^{-1}). Heavy rainfall storms during short time intervals after long dry seasons were the main cause for the elevated metal concentrations. Fine clay minerals contribute to TE migration because of the observed close relationship between some elements, such as Hg in sediments and Al from silicates, and other biogeochemical parameters related to aluminosilicates (Roulet *et al.*, 2000). These sediments contribute to soil, water, and sediment pollution that can eventually modify the biogeochemical cycles.

F. VOLATILIZATION

Volatilization of certain TEs occurs through microbial transformation of metals/metalloids to their respective metallic, hydride, or methylated form. These forms have low-boiling points and/or high-vapor pressure, hence are subject to volatilization. Methylation is considered to be the major process of volatilizing As, Hg, and Se in soils and sediments, resulting in the release of poisonous methyl gas such as alkylarsines (Frankenberger and Benson, 1994; Wood, 1974). Arsenic forms volatilized from soil or water are $AS_{(III)}$ and $AS_{(V)}$, di- and trimethylarsine. However, these two alkylarsines could be adsorbed onto iron oxides. Most scientists accept that Hg volatilization requires three steps: reduction of $Hg_{(II)}$ to $Hg_{(0)}$, diffusion or mass transport of $Hg_{(0)}$ to the soil surface and then transport to the atmosphere by diffusion or mass flow (Bizily *et al.*, 2002; Grigal, 2002). Hg reduction may involve abiotic processes, but there is also an enzymatic reduction of bivalent ions to the elemental form which are subsequently volatilized (Essa *et al.*, 2002). The concentration of Hg volatilized from soil could lead to air concentrations ranging from 1.5 to 3.7 ng m^{-3} (Kim *et al.*, 1995). Similarly to arsenic, selenium can be oxidized and then transformed by microorganisms to dimethyl-selenide a volatile compound. Soil organic matter can also contribute to enhance Se volatilization.

Volatilization through methylation is thought to be a protective mechanism, that is, a detoxification process used by organisms such as microorganisms in seleniferous environments (Frankenberger and Losi, 1995). Volatilization is affected by soil pH, OM and iron oxides content, temperature, and colloids content (Grigal, 2002). Thus the loss of TEs in gaseous form from the soil is basically limited to those that can be biologically methylated such as As and Se, and to $Hg_{(0)}$.

IV. FACTORS AFFECTING TRACE ELEMENT MOBILITY AND TRANSPORT

TE mobility in soils depends on their interactions between the solid and liquid phases, which determine their partitioning. The underlying mechanisms regulating the partitioning of these TEs include physicochemical and biological processes (discussed in Section II), which in turn are controlled by several factors. As discussed earlier TE solubility and partitioning between the solid and liquid phases is the starting point for understanding their fate and transport in soils (Adriano, 2001; McBride, 1989; Ross, 1994).

A. Soil pH

It is generally viewed that pH is the main variable controlling the solubility (see also Section II.A.1), mobility and transport of TEs, as it controls metal hydroxide, carbonate and phosphate solubility. Soil solution pH also affects ion pair and complex formation, surface charge, and organic matter solubility (Appel and Ma, 2001; Huang *et al.*, 2005; Lebourg *et al.*, 1998).

TE solubility could be strongly affected by small changes in pH values. Metal solubility and their ion activity decrease with higher pH. The release of TE from freshwater sediments after gradual reduction of pH was Ca $\cong$ Mn >Fe > Ni > Zn > Cd > Al > Pb > Cu, which depend on the solid compound that held the TEs (Buyks *et al.*, 2002). Soil pH controls the movement of TEs from one soil compartment to another, since TEs can be held in the lattice of secondary minerals (1:1 and 2:1 clay minerals), adsorbed on Fe and Mn oxides, and carbonates, or precipitated as carbonates. For instance, Maskall and Thornton (1998) found increases in the proportion of readily mobile form of Pb and Zn as pH fell below 5. Cattlet *et al.* (2002) observed a decrease of the Zn^{2+} activity in the soil solution as pH increased. They concluded that the organic matter adsorption and the formation of franklinite accounted for this trend.

Soil pH affects many soil processes including TE sorption. Boekhold *et al.* (1993) observed that Cd sorption doubled for each 0.5 increase in pH from 3.8 to 4.9. In sandy soils, a unit increase in pH produced a 2- to 10-fold increase in ion sorption. The type and concentration of electrolyte and the substrate control this change (Barrow and Whelan, 1998; Harter and Naidu, 2001). Nickel removal from the soil solution by pyrophyllite increased strongly when pH went from 6 to 7.5, or even higher (Scheidegger *et al.*, 1996). While the retention and release varied little for various cationic elements, they manifested large differences for those TEs that form anionic chemical species such as As, Cr, or Se. The concentration of arsenate in solution, that is, the predominant inorganic species of As decreased at low pH because of its adsorption (Manning and Goldberg, 1996). Tyler and Olsson (2001) observed an increase in the concentrations of As, Se, Mo, Cr, Sb, and U in soil solutions with increasing pH.

A direct relation has been found between Cu, Zn, Cd, and Pb activities ($pM = -\log M_T$) and pH, organic matter content, and total metal content (M_T), resulting in a general equation $pM = a + b\ pH - c \log (M_T\ OM^{-1})$ (McBride *et al.*, 1997b). Likewise the variation of Cd leached from allophanic soils can be explained by a regression model involving, as independent variables, leachate pH and total drainage (Gray *et al.*, 2003).

$$\mathrm{Cd}_{\mathrm{leached}}(\mathrm{g\ ha}^{-1}) = 3.5 - 0.591\ \mathrm{pH}_{(\mathrm{leachate})} + 0.003\ \text{total drainage (mL)} \quad (6)$$

While the solubility of naturally occurring Cd and Zn from mineral soils depends upon pH, in some situations dissolved concentrations of Cd, Cu, and other elements, such as Pb, may not follow a single relationship with pH for polluted soils. In some cases we can even observe that the concentration of dissolved metal is better predicted simply as a function of total soil metal burden (Sauvé *et al.*, 1997b for Cu).

Radiolabile Cd and Zn in topsoils, extracted with 0.01 M $CaCl_2$, increased as the soil pH decreased (Adams and Sanders, 1985; Degryse *et al.*, 2003). High proportions of metal ions in the soil solution is unlikely to occur at pH values higher than 6.5 (Plant and Raiswell, 1983), because the predominant form is hydroxo-complexes. However, the soluble Pb hydroxo-complexes may contribute poorly (about 12%) to the total dissolved Pb (Lindsay, 1979). The apparently large TE retention at pH values larger than 6 is partially due to ionization of surface OH and COOH groups, which involves complex formation on high-selectivity sites (Abd-Elfattah and Wada, 1981).

Still, as a general model, useful empirical regressions can be used to predict concentration of trace metals in soil solution. One possible model is given as Eq. (7):

$$\begin{aligned}\mathrm{Log}_{10}(\text{dissolved metal}) = a + b\ \mathrm{pH} + c\,\mathrm{Log10}(\text{total soil metal})\\ +d(\text{soil organic matter})\end{aligned} \quad (7)$$

Coefficients for those regressions or similar ones are available from various reviews (Sauvé, 2002; Sauvé *et al.*, 2000a, Tipping *et al.*, 2003). Albeit soil organic matter is often a significant parameter (except for Pb), most of the variability is usually explained by soil pH and total metal content.

B. CHEMICAL SPECIATION

Although the total TE content largely determines the extent of elemental partitioning between the aqueous and solid phases in soils, the chemical speciation is likely one of the most important factors that influences TE availability, solubility, and mobility. TE ions can combine with organic and inorganic ligands or substances in soil solution or in the rhizosphere. The ligands can be hydroxyl, carbonates, sulfate, nitrate, chloride, DOM, or chelating agents. The distribution of metal ion species is apparently governed by redox reactions, pH, and solubility of hydroxides, carbonates, oxides, and sulfides. Three kinds of soluble complexes can be formed between metal ions and ligands: ion pairs, soluble metal–organic ligand complexes, and chelation (Gao *et al.*, 2003). While the first type is a weak electrostatic association, the second is a strong association that includes covalent bonding.

The proportion of free hydrated cations and OH complexes changes as the pH value changes:

$$\mathrm{M}^{2+} + n\mathrm{OH}^{-} \Leftrightarrow [\mathrm{MOH}_{n}]^{2+n-} \qquad (8)$$

where n can have values from 1 to n. The number of OH^- associated with M^{2+} increases as the OH^- concentration increases. Presence of $\mathrm{Pb(OH)}^+$ and $\mathrm{Pb(OH)}_2^0$ has been used to explain Pb extractability at high-pH values. When other anions are present in the solution such as Cl^-, NO_3^-, SO_4^{2-}, HCO_3^{2-}, or CO_3^{2-}, a new equilibrium takes place and more than one type of complexes is present:

$$\mathrm{M}^{2+} + n\mathrm{OH}^{-} + \mathrm{mL}^{\mathrm{m}-} \Leftrightarrow [\mathrm{MOH}_{n}]^{2+n-} + [\mathrm{ML}_{\mathrm{m}}]^{2+\mathrm{m}-} \qquad (9)$$

Since some of them can form soluble complexes, a wide range of chemical species can be present in the solution at the same time depending on ion concentrations. Lebourg *et al.* (1998) found in seven soils from the Calais region in France that Pb^{2+} predominated at pH lower than 6.5, but carbonate complexes became important at higher pH. Zn^{2+} and Cd^{2+} were dominant forms of Zn and Cd at low pH, but the speciation was a function of pH. Ion pairs behave as monovalent ions and can be adsorbed on hydroxyl surface complexes (Gier and John, 2000).

The soluble nature of CdCl^+ complexes caused substantial leaching of Cd from a soil column (Doner, 1978), reduction of Cd adsorption on a montmorillonite (Hirsh *et al.*, 1989), and Cd bioavailability to plants in soils (McLaughlin and Tiller, 1994) (see also Section VI.B). $\mathrm{CdCl_2}{}^0$, $\mathrm{CdCl_3}{}^-$, or $\mathrm{CdCl_4}{}^{2+}$ complexes could be formed at high-chlorine concentrations (Khalid, 1980), but are unlikely to occur at natural soil conditions.

TE mobility is strongly restricted by carbonates in calcareous soils, likely due to chemisorption or precipitation (Papadopoulos and Rowell, 1988). However, the presence of humic acids increases Cd, Co, Cu, and Zn adsorption even at low pH, while at high pH they reduced the precipitation of TEs, apparently due to the formation of metal humate species (Sparks *et al.*, 1997a,b).

The stability of the metal–organic matter complexes is affected by pH. Copper, Pb, and Cr form stable complexes, while Cu complexes dissociate at low pH. The association of TEs to ligands in the soil is controlled by pH, with the ligand species ionic concentration increasing with higher pH.

C. Soil Organic Matter

Organic matter (OM) can play a dual role in TEs solubility. Particulate OM, by virtue of its high CEC, can effectively adsorb TEs (Adriano, 2001). High-molecular-weight organic compounds can also bind and strip TEs from the solution, because they can be insoluble and therefore semi-immobile (Schmitt *et al.*, 2002; Sparks *et al.*, 1997a). It has been reported that humic acids can increase Cd retention on kaolinite four times (Taylor and Theng, 1995) and the formation of stable organo metallic complexes can lead to relatively lower mobility of Cu, Pb, Ni, Zn, and Cd (Karapanagiotis *et al.*, 1991).

It has also been observed that insoluble organic molecules decreased the availability of some elements, such as Cu or Pb, by the formation of insoluble complexes (Bataillard *et al.*, 2003; Sauvé *et al.*, 1998). In contrast, Temminghoff *et al.* (1998) found that humic acids enhanced Cu mobility, but the process was strongly affected by Ca concentration and pH of the soil solution. In general however, low-molecular-weight compounds, such as fulvic acids, could remain in the soil solution and thus increase the mobility of bound metals (Christensen *et al.*, 1996; Chubin and Street, 1981; Naidu and Harter, 1998). Some authors have found that the naturally occurring DOM can increase the mobility of some elements such as Cd (Dunnivant *et al.*, 1992; Lasat, 2002). OM may also limit the precipitation of chloropyromorphite ($Pb_5(PO_4)_3Cl$), because DOM inhibits crystal growth (Lang and Kaupenjohann, 2003). Also organic ligands could affect crystallization of secondary minerals; organic coatings around the crystal seeds may inhibit or retard crystallization (Holm *et al.*, 1996; Ma, 1996).

Christensen *et al.* (1996) concluded from sorption experiments with aquifer material that DOM present in landfill leachates formed soluble complexes with Cd, Ni, and Zn, which migrated at low speed (less than 1–2% of the water migration velocity). The contribution of DOM to Cd, Ni, and Zn migration in an aquifer is directly proportional to the complex formation constant and ligand concentration, and inversely proportional to the distribution coefficient on the aquifer suspension. OM reduced Zn, Pb, and Fe adsorption onto kaolinite and montmorillonite at pH 5 and 7, possibly due to metal-complexes formation (Schmitt *et al.*, 2002).

The adsorption of organic compounds on soil minerals and the interaction among organic molecules and TEs are affected by the soil pH. At low pH, cations compete with H^+ for the functional groups (Balcke *et al.*, 2002; Weigand and Totsche, 1998). The OM content also affects of TE complexes sorption (Carrillo-Gonzalez *et al.*, 2005). Because of the hydrophobic character of organic compounds, the solid phase with the high-OM content can adsorb more organic compounds than the soil with lower OM content; application of OM increased acidity (Strobel *et al.*, 2004). Strawn and

Sparks (2000) conducted Pb desorption experiments using stirred-flow reactors and observed that the amount of Pb desorbed decreased as the OM increased in the medium.

Preferential flow paths can adsorb certain TEs due to the higher OM content compared to the soil matrix (Bundt *et al.*, 2001). In contrast, the soluble OM may increase the amount of TEs in the soil solution by the formation of soluble organo metallic complexes (Naidu and Harter, 1998). It has been suggested that OM may limit the ability of phosphate to immobilize Pb (Lang and Kaupenjohann, 2003).

D. FERTILIZERS AND SOIL AMENDMENTS

Although fertilizers have been identified as a source of TEs (Adriano, 2001; Gimeno-Garcia *et al.*, 1996; Jeng and Singh, 1995), the amounts of TEs derived from fertilizers typically do not significantly increase TE uptake by plants. The main exception are possibly phosphate fertilizers. He *et al.* (2005) reported that phosphate rocks contain on average 11, 25, 188, 32, 10, and 239 mg kg^{-1} of As, Cd, Cr, Cu, Pb, and Zn, respectively. Cadmium is probably the main element of concern in this case since it can vary from near zero to more than 150 mg Cd kg^{-1} in some phosphate fertilizers (Mortvedt and Osborn, 1982). Cd is the most susceptible to be of concern in terms of crop accumulation from fertilizers and soil amendments (McLaughlin *et al.*, 1999).

Moreover, application of fertilizers can further affect soil properties related to metal availability. Ammoniacal nitrogen fertilization has been shown to decrease soil pH in the rhizosphere, which could modify TEs (Zn, Cu, and Mn) availability (Mench, 1998). In addition, formation of metal complexes with NH_3 could affect TE availability due to its high-stability constants for Cd, Co, Cu, Ni, and Zn (Ringbom, 1963).

Metal phosphate minerals (see also Section II.C) control metal solubility in the soil suspension and induce formation of metal phosphate precipitates. It has been observed that addition of hydroxyapatite decreased the solubility of Pb^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Sr^{2+}, or U (Seaman *et al.*, 2001). Soluble phosphate, a rock phosphate, fertilizers such as monoammonium phosphate and diammonium phosphate decrease Cd, Pb, and Zn mobility, probably due to formation of metal minerals (McGowen *et al.*, 2001) (see also Section VI.B). Also phosphatic clay minerals, which characteristically have a high content of apatite $[Ca_{10}(PO_4)_6(OH,F,Cl)_2]$, are effective metal adsorbents (Singh *et al.*, 2001). However, DOM present in the solution can coat the phosphate surfaces and thus inhibit the sorption on phosphate compounds, reducing the amount and rate at which phosphate becomes available for precipitation.

Application of limestone and alkaline waste by-products such as beringite, a modified aluminosilicate produced from the fluidized bed burning of coal refuse, to the soil has increased pH and precipitated metals, Beringite depresses TEs (Adriano *et al.*, 2004) mobility, apparently by precipitation, ion exchange and crystal growth. Zeolites have reduced TEs solubility by changing the soil pH and, to some extent, by binding metals to their surfaces (Mench *et al.*, 1998; Wingenfelder *et al.*, 2005). Synthetic zeolites tend to be more efficient than natural zeolites. Ferric hydrous oxide also is known to retard metal mobility (Kukier and Chaney, 2001).

Applications of OM and biosolids to soils increase DOC pool, which could form complexes with TEs; more than 90% of Cu, Zn, and Pb were complexed with DOC and mineral colloids (Al-Wabel *et al.*, 2002). Planquart *et al.* (1999) found migration of Cu and Pb within the profile as a result of the application of biosolids, probably due to the release of soluble organic compounds. However, although soluble TEs increased with long term application of biosolids, an increase in metal adsorption and hence decreased bioavailability has been reported due to enhanced adsorptive phase (Chubin and Street, 1981; Li *et al.*, 2001).

E. Redox Potential

Redox processes are controlled by the aqueous free electron activity (Sposito, 1983), but certain microorganisms can modify and mediate most redox reactions in aquatic and terrestrial environments (Motelica-Heino *et al.*, 2003). Several elements, such as As, Cr, Mn, Fe, V, Mo, and Se, manifest different oxidation states in the environment. Arsenic is found in −3, 0, +3, and +5 oxidation states. At the soil surface, oxidizing conditions are favored, so it allows the formation of either $As_{(V)}$ or $As_{(III)}$. However, microbial activity could promote methylation, demethylation, or change in the oxidation state, while the presence of clay minerals, Fe, Al, Mn oxides, and OM can also modify the oxidation state (O'Neill, 1995). The most stable As chemical species are H_3AsO_4 up to pH 2.2, $H_2AsO_4^-$ in the pH range approximately between 2 and 7, and $HAsO_4^{2-}$ above pH 7. It has been reported that more than 90% of the total As present in the soil was arsenate (Matera *et al.*, 2003). Furthermore, As was shown to move to groundwaters 180-m deep, being released from minerals such as adamite [$Zn_2(AsO_4)OH$], arsenopyrite ($FeAsS$), lolingite (Fe_2As), mimetite [$Pb_5(AsO_4)\cdot Cl$], olivinite [$Cu_2(AsO_4)OH$], hidalgoite [$PbAl_3(AsO_4)SO_4OH_6$], and tennantite [$(CuFe)_{12}As_4S_{13}$] (Armienta *et al.*, 1997).

Chromium, Hg, Se, and Mn occur in more than one oxidation state, with their solubility in the soil depending on pH and mineral content. $Cr_{(III)}$ is an essential nutrient, it has a low solubility, it is mainly trivalent, it is specifically sorbed by Fe, Mn, and clay minerals, and its concentration in solution decreases with increasing pH and soil OM content (Bartlett and Kimble, 1976). $Cr_{(VI)}$ on the other hand is anionic, relatively soluble and represents a very mobile ion. Combined with its toxicity and carcinogenicity, this element certainly warrants careful speciation to differentiate trivalent from hexavalent chromium. The mobile and reactive chemical species of mercury are Hg^0, $(CH_3)_2Hg$. Hg^{2+} and $HgX_n{}^{2+n-}$, where X could be OH^-, Cl^-, Br^-, or organic ligands, hence more than one oxidation state could be present in the same environmental matrix. Selenate $Se_{(VI)}$ ($HSeO_4{}^-$) is the most mobile form of Se that can be leached to groundwaters. But, it is unlikely that selenate could migrate to deeper groundwaters underlying acid soils (Neal, 1995).

Manganese occurs in two oxidation states: $Mn_{(IV)}$, which is the most stable in neutral to slightly alkaline conditions, and $Mn_{(II)}$, which is stable in reducing conditions. The solubility of Mn is highly sensitive to redox conditions; under oxidizing conditions Mn is precipitated as nodules or concretions of Mn oxides, but reduction of Mn oxides increases Mn solubility (Sposito, 1989). TEs such as Cu, Co, Cr, Ni, Pb, and Zn associate to Mn oxides through coprecipitation and substitution (Green *et al.*, 2003; Liu *et al.*, 2002; Negra *et al.*, 2005), so when Mn is reduced the solubility of Pb, Zn, Cu, and Ni increases. Under experimental conditions, a reduction of 300 mV in Eh was enough to increase Cu, Ni, and Zn solubility fourfold (Green *et al.*, 2003).

Vanadium may occur in +2, +3, +4, and +5 oxidations states, from which $V_{(IV)}$ and $V_{(V)}$ are the dominant and more soluble species in moderately reducing and aerobic conditions. Reduction to $V_{(V)}$ decreases V mobility (Fox and Doner, 2002). Molybdenum may exist in nature in −4, −6 valence states, with $Mo_{(VI)}$ being the dominant species in oxic conditions.

In anoxic materials such as sediments, TEs are typically associated with OM, sulfides and, to a smaller extent, carbonates and other mineral fractions (Cantwell *et al.*, 2002). When reduced humic materials or sediments are exposed to oxidizing conditions for a long period, certain organic compounds and TEs such as Cd are released (Gambrell *et al.*, 1980; Motelica-Heino *et al.*, 2003). This happens because TE ions can form complexes with oxidized radicals, as documented for Cu^{2+}, Mn^{2+}, $Mo_{(V)}$, $Mo_{(III)}$, Cr^{3+}, $(VO)^{2+}$, and Fe^{3+} ions (Schnitzer, 2000). TEs are released also when sulfide precipitates (from slag tailing residues) are exposed to aerobic environment. Under anoxic conditions sulfides can effectively bind Zn and Cd (Lu and Chen, 1977). Oxidation of sulfide to sulfate in anaerobic dredged sediments results in the release of Cd, Ni, Pb, Zn, Fe, and Mn (Brooks *et al.*, 1968; Patrick *et al.*, 1977). When redox potential of polluted soils is changed to −60 mV, dissolved concentrations of Cd and Pb decreased between pH 5 and 6 (Davranche and Bollinger, 2001).

F. Clay Content and Soil Structure

Clay-rich soils generally have higher retention capacity than soils with little or no clay (Murray *et al.*, 2004). Cation sorption on clay minerals varies depending on clay nature and cation properties. Vermiculites adsorbed twice as much Cs than illite and 20 times more than kaolinite in a single cation suspension (Tamura, 1972). The Pb and Cu adsorption was higher than Zn, Ni, and Cd adsorption on illite, beidellite, and montmorillonite. Desorption followed the trend $\text{Pb} > \text{Cd} \gg \text{Cu} > \text{Ni} > \text{Zn}$ for beidellite and $\text{Pb} > \text{Cd} = \text{Cu} > \text{Ni} > \text{Zn}$ for illite and montmorillonite (Rybicka *et al.*, 1995). Tiller *et al.* (1984) found a Pellustert (containing montmorillonite and kaolinite) adsorbed more Cd, Zn, and Ni than a Haplohumox or an Udalf (containing illite, kaolinite, chlorite, and quartz) at low pH value (4.5), while at high-pH values (>6.5) Cd and Ni adsorption capacity of Udalf was higher.

Selectivity of TE cation adsorption varies with clay minerals. Vermiculite is very effective for adsorbing Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Ni, and the selectivity is greater than in montmorillonite, apparently due to more specific adsorption sites (Malla, 2002). But selectivity changes with cations, as Brigatti *et al.* (2004) found that montmorillonite adsorbed greater amount of Hg than vermiculite. Tiller *et al.* (1984) identified three reaction types, each having different affinities for cations: (1) those associated with iron oxides, which appeared to be controlled by metal ion hydrolysis; (2) those associated with organic colloids; and (3) those associated with 2:1 clay minerals with lower sensitivity to pH.

Proportion of nonspecifically sorbed elements is low in soils containing iron oxides. The sequence of metal cation selectivity is affected by the aging (weathering) of the soil, with younger soils, such as alfisol and ultisol, adsorbing more cations than older soils, such as Oxisol (Gomes *et al.*, 2001). Such affinity could be linked to the mineral composition. Abd-Elfattah and Wada (1981) observed the following selective adsorption:

$$\begin{aligned}\text{Pb}: {} & \text{Fe-oxides}, \text{Ht}_{(\text{halloysite})}\text{A-Im}_{(\text{imogolite})}, \text{A}_{(\text{allophane})} > \\ & \text{Humus}, \text{Kt}_{(\text{kaolinite})} > \text{Mt}_{(\text{montmorillonite})}\end{aligned}$$

$$\text{Cu}: \text{Fe-oxides}, \text{Ht A-Im} > \text{Humus}, \text{Kt}, \text{A} > \text{Mt}$$

$$\text{Zn}: \text{Fe-oxides}, \text{Ht}, \text{A-Im} > \text{Kt} > \text{A}, \text{Humus} > \text{Mt}$$

$$\text{Cd}: \text{Fe-oxides} > \text{A-Im} > \text{A}, \text{Kt} > \text{Ht}, \text{Mt}$$

Surface complexation of metal cations at aluminol or silanol sites of allophane and imogolite depends on pH. The affinity sequence for cation adsorption on aluminol and silanol groups is still incomplete, but from the order of decreasing affinity it can be viewed that the selectivity sequence depends on the molar Si/Al ratio (Harsh *et al*., 2002).

Formation of clay–hydroxide complexes affects metal clay retention. Even at low pH, clay–Al hydroxide polymer complexes play an important role in metal binding, because the metal binding affinity for these complexes is greater than for pure Al hydroxides (Barnhisel and Bertsch, 1989; Janssen *et al*., 2003; Keizer and Bruggenwert, 1991). Hydroxyaluminum and hydroxylaluminosilicate montmorillonite complexes are common in acid to slightly acid soils. These complexes adsorb much more Cd, Zn, and Pb than the single montmorillonite (Saha *et al*., 2002). Elements such as $Cr_{(VI)}$ are adsorbed on Fe, Mn, and Al oxides, kaolinite and montmorillonite with hydroxyl groups on their surface (Davis and Lackie, 1980). However, small minerals such as lepidocrocite (γ-FeOOH) particles with adsorbed TEs can be mobilized with the drainage water (Roussel *et al*., 2000).

Leaching experiments in lysimeters with repacked soils may underestimate metals transport, because they do not replicate well the natural pore structure and do not involve preferential flow through macropores, root channels, and cracks (Carey *et al*., 1996). Any alteration of the soil structure may affect the hydraulic conductivity and the contact time between the soil and solute, before it is leached out of the soil profile. In structured soils the interaction between solid and solute is reduced, and the probability of TEs bypassing the soil matrix increases. Since the disturbance of the soil structure changes the connectivity of pores and the apparent water dispersion, the mobile water content in homogenized soils, as well as the water volume to displace the solute, increases (Cassel *et al*., 1974).

Main factors affecting mobility or bioavailability of TEs in soils are summarized in Table II. The most important factors affecting TEs release from soil are pH, OM including DOM, and chemical speciation, while clay content and redox potential are less important.

V. TRANSPORT MODELING

Model development, its parameterization and validation for simulating transport of TEs is important for environmental impact assessment studies, as well as for research and teaching purposes. A large number of models of varying degree of complexity and dimensionality have been developed during the past several decades to quantify the basic physical and chemical processes affecting water flow and transport of TEs in the unsaturated zone (Šimůnek, 2005). Modeling approaches range from relatively simple analytical (Šimůnek *et al*., 1999b; Toride *et al*., 1995) and semianalytical solutions, to more complex numerical codes that permit consideration of a

Table II
Effects of Soil Factors on Trace Metal Mobility and/or Bioavailability[a]

Soil factor	Affected process	Effect on process
Low pH	Decreasing sorption of cations onto oxides of Fe and Mn	Increase
	Increasing sorption of anions onto oxides of Fe and Mn	Decrease
High pH	Increasing precipitation of cations as carbonates and hydroxides	Decrease
	Increasing sorption of cations onto oxides of Fe and Mn	Decrease
	Increasing complexation of certain cations by dissolved ligands	Increase
	Increasing sorption of cations onto (solid) humus material	Decrease
	Decreasing sorption of anions	Increase
High-clay content	Increasing ion exchange for trace cations (at all pH)	Decrease
High-swelling clays	Forming structured soils, which allow bypass flow	Increase
High OM (solid)	Increasing sorption of cations onto humus material	Increase
High-(soluble) humus content	Increasing complexation for most trace cations	Decrease/ increase
Competing ions	Increasing competition for sorption sites	Increase
Dissolved inorganic ligands	Increasing trace metal solubility	Increase
Fe and Mn oxides	Increasing sorption of trace cations with increasing pH	Decrease
	Increasing sorption of trace anions with decreasing pH	Decrease
Low redox	Decreasing solubility at low Eh as metal sulfides	Decrease
	Decreasing solution complexation with lower Eh	Increase/ decrease

[a] Adapted from Adriano (2001).

large number of simultaneous nonlinear processes for one (Šimůnek *et al.*, 1999a, 2005; Yeh *et al.*, 1992) or multiple (Jacques and Šimůnek, 2005; Steefel, 2000; Yeh and Cheng, 1999) solutes. While analytical and semianalytical solutions are still popular for some applications, the ever-increasing power of personal computers, and the development of more accurate and numerically stable solution techniques have motivated the much wider use of numerical codes in recent decades. The wide use of numerical models is also significantly enhanced by their availability in both the public and commercial domains, and by the development of sophisticated graphic-based interfaces that can substantially simplify their use (Šimůnek *et al.*, 1999a).

Although a large number of models exists, there are no models that consider all complex processes affecting transport of TEs. Soils often contain micro- and macropores, in which water moves preferentially in macropores and is stagnant in micropores, and in which there is no significant interaction between the soil solution and the immobile phase. Structured soils may develop compacted peds and/or temporal cracks depending on the moisture conditions. Trace elements are affected by a multitude of complex, interactive physical, chemical and biological processes (Sections II.A and B). The transport and transformation of many TEs is further mediated by subsurface aerobic or anaerobic bacteria. Simulating these and related processes requires coupled reactive transport codes that integrate the physical processes of nonequilibrium/preferential variably saturated water flow and advective–dispersive solute transport with a range of biogeochemical processes. Models still need to be developed that would describe all these complex interactions.

A. VARIABLY SATURATED WATER FLOW

1. Uniform Flow

Predictions of water movement in the vadose zone are traditionally made using the Richards equation for variably saturated water flow. For a one-dimensional soil profile this equation is given by

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} - K(h)\right] - S \tag{10}$$

where θ is the volumetric water content (L^3L^{-3}), h is the soil water pressure head (L), t is time (T), z is distance from the soil surface downward (L), K is the hydraulic conductivity (LT^{-1}) as a function of h or θ, and S (T^{-1}) is the sink term accounting for root water uptake. Since Eq. (10) is a highly nonlinear partial differential equation, it is typically solved for specified initial and boundary conditions numerically, using finite differences or finite elements methods. Nonlinearity of the Richards equation is due to the nonlinearity in the soil hydraulic properties, which are characterized by the retention curve, $\theta(h)$, and the hydraulic conductivity function, $K(h)$. The soil hydraulic properties in numerical models are usually represented by two analytical functions, such as those developed by Brooks and Corey (1964), van Genuchten (1980), or Durner (1994).

2. Preferential Flow

Preferential flow in structured media (macroporous soils) can be described using a variety of dual-porosity, dual-permeability, multiporosity, and/or multipermeability models (Bodvarsson *et al.*, 2003; Gerke and van Genuchten, 1993; Jarvis, 1994; Šimůnek *et al.*, 2003). Dual-porosity and dual-permeability models both assume that the porous medium consists of two interacting regions, one associated with the inter-aggregate, macropore, or fracture system, and the other one comprising micropores (or intra-aggregate pores) inside soil aggregates or the rock matrix. While dual-porosity models assume that water in the matrix is stagnant, dual-permeability models allow for water flow in the matrix as well.

Equation (10) can be extended for dual-porosity system as follows (Šimůnek *et al.*, 2003):

$$\begin{aligned} \theta &= \theta_{\mathrm{m}} + \theta_{\mathrm{im}} \\ \frac{\partial \theta_{\mathrm{m}}}{\partial t} &= \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} - 1\right)\right] - S_{\mathrm{m}} - \Gamma_{\mathrm{w}} \\ \frac{\partial \theta_{\mathrm{im}}}{\partial t} &= -S_{\mathrm{im}} + \Gamma_{\mathrm{w}} \end{aligned} \tag{11}$$

where θ_{m} is the mobile (flowing) water content representing macropores or inter-aggregate pores ($\mathrm{L}^3\mathrm{L}^{-3}$), θ_{im} is the immobile (stagnant) water content representing micropores (matrix) or intra-aggregate regions ($\mathrm{L}^3\mathrm{L}^{-3}$), S_{m} and S_{im} are sink terms for both regions (T^{-1}), and Γ_{w} is the transfer rate for water from the inter- to the intra-aggregate pores (T^{-1}).

Available dual-permeability models differ mainly in how they implement water flow in and between the two pore regions. Approaches to calculating water flow in macropores or inter-aggregate pores range from those invoking Poiseuille's equation (Ahuja and Hebson, 1992), the Green and Ampt or Philip infiltration models (Ahuja and Hebson, 1992; Chen and Wagenet, 1992), the kinematic wave equation (Germann and Beven, 1985; Jarvis, 1994), and the Richards equation (Gerke and van Genuchten, 1993). Gerke and van Genuchten (1993) applied Richards equations to each of two pore regions. The flow equations for the macropore (fracture) (subscript f) and matrix (subscript m) pore systems in their approach are given by

$$\begin{aligned} \theta &= w\theta_{\mathrm{f}} + (1 - w)\theta_{\mathrm{m}} \\ \frac{\partial \theta_{\mathrm{f}}(h_{\mathrm{f}})}{\partial t} &= \frac{\partial}{\partial z}\left[K_{\mathrm{f}}(h_{\mathrm{f}})\left(\frac{\partial h_{\mathrm{f}}}{\partial z} - 1\right)\right] - S_{\mathrm{f}}\ (h_{\mathrm{f}}) - \frac{\Gamma_{\mathrm{w}}}{w} \\ \frac{\partial \theta_{\mathrm{m}}(h_{\mathrm{m}})}{\partial t} &= \frac{\partial}{\partial z}\left[K_{\mathrm{m}}(h_{\mathrm{m}})\left(\frac{\partial h_{\mathrm{m}}}{\partial z} - 1\right)\right] - S_{\mathrm{m}}\ (h_{\mathrm{m}}) + \frac{\Gamma_{\mathrm{w}}}{1 - w} \end{aligned} \tag{12}$$

respectively, where *w* is the ratio of the volumes of the macropore (or fracture or inter-aggregrate) domain and the total soil system (–). This approach is relatively complicated in that the model requires characterization of water retention and hydraulic conductivity functions (potentially of different form) for both pore regions, as well as the hydraulic conductivity function of the fracture–matrix interface. Note that the water contents θ_f and θ_m in (12) have different meanings than in (11) where they represented water contents of the total pore space (i.e., $\theta = \theta_m + \theta_{im}$), while here they refer to water contents of the two separate (fracture or matrix) pore domains (i.e., $\theta = w\theta_f + (1-w)\theta_m$).

Multiporosity and/or multipermeability models are based on the same concept as dual-porosity and dual-permeability models, but include additional interacting pore regions (Gwo *et al.*, 1995; Hutson and Wagenet, 1995). For a recent comprehensive review of various modeling approaches used to simulate preferential flow see Šimůnek *et al.* (2003).

B. Solute Transport

1. Convection–Dispersion Equation

Under ideal soil conditions the convection–dispersion equation for reactive solutes can be used for modeling solute transport under unsaturated conditions:

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \theta c}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z} - qc\right) - \phi \tag{13}$$

where s is the solute concentration associated with the solid phase of the soil (MM^{-1}, e.g., mol kg^{-1}), c is the solute concentration in the liquid phase (ML^{-3}, e.g., mol m^{-3}), ρ is the soil bulk density (ML^{-3}), θ is the volumetric water content (L^{3}L^{-3}), D is the solute dispersion coefficient (L^{2}T^{-1}) accounting for molecular diffusion and hydrodynamic dispersion, q is the volumetric fluid flux density (LT^{-1}) given by Darcy's law, and ϕ (ML^{-3}T^{-1}) is the reaction term representing sinks or sources for solutes. The element reactivity processes, such as ion exchange, precipitation–dissolution, and root solute uptake can be coupled to this equation through a reaction term ϕ (Hinz and Selim, 1994; Vogeler, 2001).

The governing transport Eq. (13) can be reformulated for volatile solutes residing and being transported also in the gaseous phase as follows:

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \theta c}{\partial t} + \frac{\partial a c_g}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z} - qc\right) + \frac{\partial}{\partial z}\left(a D_g \frac{\partial c_g}{\partial z}\right) - \phi \tag{14}$$

where a is the air content (–), c_g is the concentration in the gaseous phase (ML^{-3}), and D_g is the diffusion coefficient (L^2T^{-1}) accounting for molecular diffusion in the gaseous phase. The liquid and gaseous concentrations are usually related using Henry's law.

2. Sorption

Soil can be viewed as a mixture of pure mineral substances, which together form a heterogeneous soil system. Adsorption of chemicals on these mixtures is commonly described with empirical models, since chemically meaningful models are difficult to apply (see Section II.A.2). The adsorption isotherm for TEs usually has a nonlinear shape. Linear adsorption isotherms could be expected for acid soil conditions and low concentrations. However, as the metal concentration increases the slope of the adsorption curve changes and thus the distribution K_d coefficient changes as well. Adsorption is usually very high in soils with pH higher than 6.5 and only traces of the element could remain in the solution (Section IV.A). In addition, desorption process can be very slow and therefore only negligible release of the TE to the soil solution is often observed. Adsorption–desorption process is often hysteretic, and thus a set of desorption isotherms can be obtained depending on the initial element concentration (Fig. 6) (Carrillo-Gonzalez, 2000). Desorption is often not completely reversible as a result of specific adsorption, precipitation, and/or occlusion reactions in the solid phase, and thus the activity of the TE in the soil solution can be easily overestimated. Since simpler models assume that solute adsorption is reversible, the amount of mobile TE can be overestimated and predicted concentrations can be higher than those observed.

Providing that the sorption of solute onto the solid phase is an instantaneous process, it can be described using empirical adsorption isotherms. Many numerical models use either the Freundlich (see also (2))

$$s = K_d c^n \tag{15}$$

or Langmuir isotherms

$$s = \frac{s_{\max}\omega c}{1 + \omega c} \tag{16}$$

where K_d (L^3M^{-1}), n (–), and ω (L^3M^{-1}) are the empirical coefficients, and $s_{\max}$ is the adsorption maximum (MM^{-1}). General formulation that encompasses both Freundlich and Langmuir isotherms can also be used (Šimůnek *et al.*, 1999a):

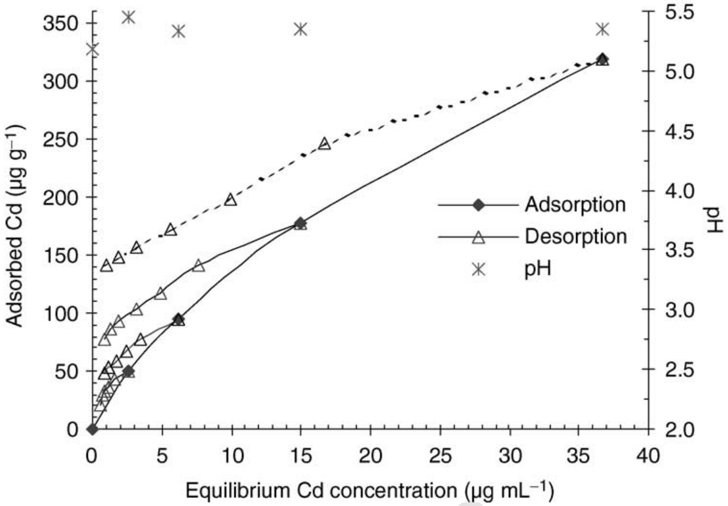

Figure 6 Adsorption–desorption isotherms of Cd in an agricultural sandy soil with 10 mM $CaCl_2$ as an electrolyte background (Carrillo-González, 2000).

$$s = \frac{K_d c^n}{1 + \omega c^n} \tag{17}$$

When $n = 1$, Eq. (17) becomes the Langmuir equation, when $\omega = 0$, Eq. (17) becomes the Freundlich equation, and when both $n = 1$ and $\omega = 0$, Eq. (17) leads to a linear adsorption isotherm (Šimůnek *et al.*, 1999a). Solute transport without adsorption is described with $K_d = 0$. Instantaneous sorption leads to the retardation of the solute transport that is characterized by the retardation factor R defined as:

$$R = 1 + \frac{\rho}{\theta}\frac{\mathrm{d}s}{\mathrm{d}c}\left(= 1 + \frac{\rho K_d}{\theta} \text{ for linear sorption}\right) \tag{18}$$

Kinetic nonequilibrium adsorption–desorption reactions are usually implemented using the concept of two-site sorption (Selim *et al.*, 1987; van Genuchten and Wagenet, 1989) that assumes that the sorption sites can be divided into two fractions. Sorption on one fraction of the sites (f, the type-1 sites) is assumed to be instantaneous, while sorption on the remaining (type-2) sites is considered to be time dependent. Sorption on the type-2 nonequilibrium sites is often assumed to be a first-order kinetic rate process.

$$\frac{\partial s_k}{\partial t} = \omega_k[(1-f)s_e - s_k] - \phi_k \tag{19}$$

where f is the fraction of exchange sites assumed to be in equilibrium with the solution phase (–), ω_k is the first-order rate constant (T^{-1}), s_k is the sorption concentration on type-2 sites (MM^{-1}), s_e is the sorption concentration on type-2 sites at equilibrium (MM^{-1}), and ϕ_k is the reaction term for kinetic sorption sites ($MM^{-1}T^{-1}$). Depending on the value of the f parameter the two-site sorption model simplifies to either a fully kinetic ($f = 0$), or fully instantaneous ($f = 1$) sorption model.

Models based on the sorption isotherms are not sufficiently general to account for variations in sorption with pH, multiple oxidation states, electrostatic forces, and other factors. For these more complex conditions, surface complexation models, such as the constant capacitance, diffuse double layer, and triple layer models (Mattigod and Zachara, 1996), must be used. The various surface complexation models differ in their depiction of the interfacial region surrounding an adsorbent, that is, the number of considered planes and the charge-potential relationships.

Although many adsorption processes are more accurately described by more sophisticated surface complexation models, isotherm models have been successfully applied to the environmentally significant classes of neutral, relatively nonpolar organic compounds, such as chlorinated hydrocarbons and pesticides (Šimůnek and Valocchi, 2002), or As (Decker *et al.*, 2006a,b). In soils with significant fractions of organic carbon, these compounds adsorb primarily to solid-phase organic matter as a result of hydrophobic interactions, and the K_d of these compounds is often found to correlate directly with the organic carbon content of the soil.

3. Cation Exchange

In addition to sorption, TEs can be retarded due to additional chemical reactions, such as precipitation–dissolution, exchange of cations between those adsorbed on the soil surfaces and colloids, and those in the soil solution. Retention of TE (Me^{2+}) in soil (S) and under acid conditions can be described as a cation-exchange process. The exchange of any cation (Ca^{2+}) by a TE cation can be written as:

$$\mathrm{CaS}_x + \mathrm{Me}^{2+} \Leftrightarrow \mathrm{MeS}_x + \mathrm{Ca}^{2+} \tag{20}$$

with the corresponding exchange coefficient K_{MeCa}:

$$K_{\mathrm{MeCa}} = \frac{q_{\mathrm{Me}}\alpha_{\mathrm{Ca}}}{q_{\mathrm{Ca}}\alpha_{\mathrm{Me}}} \tag{21}$$

where q is the adsorbed element and α is the activity of the free element in the solution. This exchange coefficient is derived for a binary system. It can be scaled to account for effects of various soil factors such as pH, background cation concentration, and the nature of the soil material. White and Zelazny (1986) provide a review of other general forms for cation selectivity coefficients, such as Gapon and Vanselow equations, that are commonly used to describe cation exchange.

4. Precipitation–Dissolution

Precipitation–dissolution process can be similarly considered as either instantaneous or kinetic (see also Section II.A). Equations describing precipitation–dissolution reactions are also obtained using the law of mass action, but contrary to the other processes, they are represented by inequalities rather than equalities, as follows (Šimůnek and Valocchi, 2002):

$$K_\mathrm{p} \geq Q_\mathrm{p} = \prod_{k=1}^{N_\mathrm{a}} (\alpha_k)^{a_k^\mathrm{p}} \tag{22}$$

where K_p is the thermodynamic equilibrium constant of the precipitated species, that is, the solubility product equilibrium constant, Q_p is the ion activity product of the precipitated species, a_k^p is the stoichiometric coefficient of the kth aqueous component in the precipitated species, α_k is the activity of the kth aqueous component, and N_a is the number of aqueous components. The inequality in (22) means that a particular precipitate is formed only when the solution is supersaturated with respect to its aqueous components; if the solution is undersaturated then the precipitated species (if it exists) will dissolve in order to reach equilibrium conditions. Equation (22) assumes that the activity of the precipitated species is equal to unity.

Precipitation–dissolution reactions are often orders of magnitude slower than other chemical reactions, while rates of dissolution of different minerals can also differ by orders of magnitude. Therefore, precipitation–dissolution reactions usually have to be considered as kinetic, rather than equilibrium reactions (e.g., Šimůnek and Valocchi, 2002). It is commonly assumed that the rate of precipitation–dissolution process is proportional to the disequilibrium of the system. Lichtner (1996) provided an excellent discussion of kinetics and related issues (the surface area, a moving boundary problem, a boundary layer, quasi-stationary states, and so on). Numerical models that account for cation exchange or precipitation–dissolution can not consider single solutes, but need to simulate simultaneous transport of multiple species that affect these processes.

5. Preferential Transport

Similarly as for water flow, preferential solute transport is usually described using dual-porosity (van Genuchten and Wagenet, 1989) and dual-permeability (Gerke and van Genuchten, 1993) models. The dual-porosity formulation is based on the convection–dispersion and mass balance equations as follows (van Genuchten and Wagenet, 1989):

$$\begin{aligned} \frac{\partial \theta_{\mathrm{m}} c_{\mathrm{m}}}{\partial t} + \frac{\partial f \rho s_{\mathrm{m}}}{\partial t} &= \frac{\partial}{\partial z}\left(\theta_{\mathrm{m}} D_{\mathrm{m}} \frac{\partial c_{\mathrm{m}}}{\partial z}\right) - \frac{\partial q c_{\mathrm{m}}}{\partial z} - \phi_{\mathrm{m}} - \Gamma_{\mathrm{s}} \\ \frac{\partial \theta_{\mathrm{im}} c_{\mathrm{im}}}{\partial t} + \frac{\partial (1-f) \rho s_{\mathrm{im}}}{\partial t} &= -\phi_{\mathrm{im}} + \Gamma_{\mathrm{s}} \end{aligned} \tag{23}$$

for the macropores (subscript m) and matrix (subscript im), respectively, where f is the dimensionless fraction of sorption sites in contact with the macropores (mobile water), and Γ_s is the solute transfer rate between the two regions ($ML^{-3}T^{-1}$).

Analogous to equations (12) for water flow, the dual-permeability formulation for solute transport can be based on advection–dispersion type equations for transport in both the fracture and matrix regions as follows (Gerke and van Genuchten, 1993):

$$\begin{aligned} \frac{\partial \theta_{\mathrm{f}} c_{\mathrm{f}}}{\partial t} + \frac{\partial \rho s_{\mathrm{f}}}{\partial t} &= \frac{\partial}{\partial z}\left(\theta_{\mathrm{f}} D_{\mathrm{f}} \frac{\partial c_{\mathrm{f}}}{\partial z}\right) - \frac{\partial q_{\mathrm{f}} c_{\mathrm{f}}}{\partial z} - \phi_{\mathrm{f}} - \frac{\Gamma_{\mathrm{s}}}{w} \\ \frac{\partial \theta_{\mathrm{m}} c_{\mathrm{m}}}{\partial t} + \frac{\partial \rho s_{\mathrm{m}}}{\partial t} &= \frac{\partial}{\partial z}\left(\theta_{\mathrm{m}} D_{\mathrm{m}} \frac{\partial c_{\mathrm{m}}}{\partial z}\right) - \frac{\partial q_{\mathrm{m}} c_{\mathrm{m}}}{\partial z} - \phi_{\mathrm{m}} + \frac{\Gamma_{\mathrm{s}}}{1-w} \end{aligned} \tag{24}$$

where the subscript f and m refer to the macroporous (fracture) and matrix pore systems, respectively; ϕ_f and ϕ_m represent sources or sinks in the macroporous and matrix domains ($ML^{-3}T^{-1}$), respectively; and w is the ratio of the volumes of the macropore domain (inter-aggregate) and the total soil systems (–). Equation (24) assumes complete advective–dispersive type transport descriptions for both the fractures and the matrix. Several authors simplified transport in the macropore domain, for example by considering only piston displacement of solutes (Ahuja and Hebson, 1992; Jarvis, 1994).

C. Colloid Transport and Colloid-Facilitated Solute Transport

Colloid-facilitated transport is a complex process that requires knowledge of colloid transport, dissolved contaminant transport, and colloid-facilitated contaminant transport. Colloids are inorganic and/or organic constituents that are generally chemically reactive. Inorganic colloids are primarily fine-sized mineral soil constituents, while organic colloids are organic matter based (Adriano, 2001). Transport equations must be formulated for both colloids and contaminants, in all their forms. Equations must be therefore written for the total contaminants, for contaminants sorbed kinetically or instantaneously to the solid phase, and for contaminants sorbed to mobile colloids, to colloids attached to the soil solid phase, and to colloids accumulating at the air–water interface. Presentation of all these equations is beyond the scope of this manuscript. Below we will give only selected equations (for colloid attachment–detachment, and total contaminant) from the total set of equations for colloid-facilitated transport that were recently incorporated in the HYDRUS software packages (Šimůnek *et al.*, 2006b; van Genuchten and Šimůnek, 2004). We refer readers to other literature for a complete description of the colloid-facilitated transport (Corapcioglu and Choi, 1996; Hornberger *et al.*, 1992; van Genuchten and Šimůnek, 2004).

Colloids are subject to the same subsurface fate and transport processes as chemical compounds, while additionally being subject to their own unique complexities (van Genuchten and Šimůnek, 2004). For example, many colloids are negatively charged so that they are electrostatically repelled by negatively charged solid surfaces. This phenomenon may lead to an anion exclusion process causing slightly enhanced transport relative to fluid flow. Size exclusion may similarly enhance the advective transport of colloids by limiting their presence and mobility to the larger pores (Bradford *et al.*, 2003). In addition, the transport of colloids is affected by filtration and straining in the porous matrix, which is a function of the size of the colloid, the water-filled pore size distribution, and the pore water velocity (Bradford *et al.*, 2003).

Colloid fate and transport models are commonly based on some form of the advection–dispersion equation [e.g., Eq. (13)], but modified to account for colloid filtration (Harvey and Garabedian, 1991) and the colloid accessibility of the pore space. The colloid mass transfer term between the aqueous and solid phases is traditionally given as:

$$\rho\frac{\partial s_c}{\partial t} = \rho\frac{\partial\left(s_c^{att} + s_c^{str}\right)}{\partial t} = \theta_w k_{ac}\psi_s c_c - \rho k_{dc} s_c^{att} + \theta_w k_{str}\psi_{str} c_c \tag{25}$$

in which c_c is the colloid concentration in the aqueous phase (nL^{-3}), s_c is the solid phase colloid concentration (nM^{-1}), ${s_c}^{att}$ and ${s_c}^{str}$ are the solid phase colloid concentrations (nM^{-1}) due to colloid filtration and straining, respectively; θ_w is the volumetric water content accessible to colloids (L^3L^{-3}) (due to ion or size exclusion, θ_w may be smaller than the total volumetric water content θ, k_{ac}, k_{dc}, and k_{str} are first-order colloid attachment, detachment, and straining coefficients (T^{-1}), respectively, and ψ_s and ψ_{str} are a dimensionless colloid retention functions (–). The attachment coefficient is generally calculated using filtration theory (Logan *et al.*, 1995). To simulate reductions in the attachment coefficient due to filling of favorable sorption sites, ψ_s is sometimes assumed to decrease with increasing colloid mass retention.

At the same time, in addition to being subject to adsorption–desorption process at solid surfaces and straining in the porous matrix (Bradford *et al.*, 2003), colloids may accumulate at air–water interfaces (Thompson and Yates, 1999; Wan and Tokunaga, 2002; Wan and Wilson, 1994). A model similar to Eq. (25) may be used to describe the partitioning of colloids to the air–water interface

$$\frac{\partial A_{aw}\Gamma_c}{\partial t} = \theta_w \psi_{aca} k_{aca} c_c - A_{aw} k_{dca} \Gamma_c \tag{26}$$

where Γ_c is the colloid concentration adsorbed to the air–water interface (nL^{-2}), A_{aw} is the air–water interfacial area per unit volume (L^2L^{-3}), ψ_{aca} is a dimensionless colloid retention function for the air–water interface (–) similarly as used in Eq. (25), and k_{aca} and k_{dca} are the first-order colloid attachment and detachment coefficients to/from the air–water interface (T^{-1}), respectively.

The mass balance equation for the total contaminant, that is, the combined dissolved and colloid-facilitated contaminant transport equation (in one dimension) is given by (Šimůnek *et al.*, 2006b; van Genuchten and Šimůnek, 2004):

$$\frac{\partial \theta c}{\partial t} + \rho\frac{\partial s_e}{\partial t} + \rho\frac{\partial s_k}{\partial t} + \frac{\partial \theta_w s_c s_{mc}}{\partial t} + \rho\frac{\partial s_c s_{ic}}{\partial t} + \frac{\partial A_{aw}\Gamma_c s_{ac}}{\partial t} = \\ \frac{\partial}{\partial z}\left(\theta D\frac{\partial c}{\partial z}\right) - \frac{\partial qc}{\partial z} + \frac{\partial}{\partial z}\left(\theta_w s_{mc} D_c \frac{\partial c_c}{\partial z}\right) - \frac{\partial q_c c_c S_{mc}}{\partial z} - \phi \tag{27}$$

where θ is the volumetric water content (L^3L^{-3}) (note that we use the entire water content for the contaminant), c is the dissolved contaminant concentration in the aqueous phase (ML^{-3}), s_e and s_k are contaminant concentrations sorbed instantaneously and kinetically, respectively, to the solid phase (MM^{-1}); s_{mc}, s_{ic}, and s_{ac} are contaminant concentrations sorbed to mobile and immobile (attached to solid and air–water interface) colloids (Mn^{-1}), respectively; D is the dispersion coefficient for contaminants in solution (L^2T^{-1}), q is the volumetric water flux density for the contaminant (LT^{-1}), D_c is the dispersion coefficient for colloids (L^2T^{-1}), and q_c is the volumetric water flux density for colloids (LT^{-1}), and ϕ represents various chemical and biological reactions, such as degradation and production ($ML^{-3}T^{-1}$). Note that the left side sums up the mass of contaminant associated with the different phases (contaminant in the liquid phase, contaminant sorbed instantaneously and kinetically to the solid phase, and contaminant sorbed to mobile and immobile (attached to solid phase or air–water interface) colloids), while the right side considers various spatial mass fluxes (dispersion and advective transport of the dissolved contaminant, and dispersion and advective transport of contaminant sorbed to mobile colloids) and reactions. Additional partial differential equations need to be formulated to describe: (1) kinetic sorption of contaminant to the solid phase, (2) contaminant sorbed to mobile colloids, and (3) contaminant sorbed to immobile (attached to solid and air–water interface) colloids (Šimůnek *et al.*, 2006b; van Genuchten and Šimůnek, 2004).

VI. MODEL APPLICATIONS AND CASE STUDIES

Since there has already been a very large number of applications of model of varying degree of complexity reported in the literature, we give below only selected examples of these applications. We divided them into two main groups. Single-component models, that is, models that consider transport of single solutes without considering implicitly simultaneous transport of other solutes and their mutual interactions, represent the first group of applications. Multicomponent models, that is, models that simulate simultaneous transport and interactions of multiple solutes, represent the second group.

A. Single-Component Models

Simons used successfully a simple model for describing salts movement in soils (Rowell, 1994). In this model the soil is divided into a number of layers, while each layer is assumed to be spatially homogeneous with the constant concentration. The simulations were carried out using a single distribution constant, but could be improved when the adsorption behavior was properly modeled. Černík *et al.* (1994) used convection–dispersion and stochastic convection models (both linear) to explain the Cu and Zn concentrations in the soil profile, deposited from metal smelter. Carey *et al.* (1996) proposed to describe a nonsymmetrical sigmoidal shape of the breakthrough curves using the double exponential biomass growth model, known as the Gompertz equation. Petersen and Petrie (1999) developed a transport reaction model for heap leaching, in which kinetic and equilibrium reactions of the trace elements can be incorporated. In this model the soil column is divided into a number of layers, in which the bulk concentration is assumed spatially constant. They suggested that this is a good model for environmental risk assessment studies. Vogeler *et al.* (2001) used a model based on the numerical solution of the Richards and convection–dispersion equations (see Section V) to reliably predict movements of copper and bromide through the soil, into which a chelating agent (EDTA) had been added to increase the solubility of TEs for plant uptake during phytoremediation. Seuntjens *et al.* (2001) used water flow and solute transport numerical model HYDRUS-1D (Šimůnek *et al.*, 1998) to evaluate effects of aging on cadmium transport in undisturbed contaminated sandy soil columns. Similarly, Bahaminyakamwe *et al.* (2006) used HYDRUS-1D to simulate copper mobility in soils as affected by sewage sludge and low molecular weight organic acids.

Models simulating leaching of solutes through porous media are often based on the convection–dispersion equation and usually have significant limitations for application to natural soil conditions. Convection–dispersion-equation based models are well suited to homogeneous repacked soils, fully saturated, steady-state flow conditions, and a simple pulse injection of contaminants (Jarvis *et al.*, 1999). However, it is often reported that mass flow in the soil matrix provides only a minor contribution to element transport and that preferential transport through macropores and cracks dominates the trace element transport. Modeling of these phenomena still represents an important challenge.

Most computer programs modeling the transport of TEs have described adsorption using the distribution coefficient. But the sorption process is often different from the desorption process, and the concentration of the TE in the solution is also directly determined by the rate of desorption. Zachara *et al.* (1993) modeled the Cd leaching using the K_d value calculated from desorption isotherms. In steady-state flow experiments, Tran *et al.* (1998) observed an anomalous increase of the Cd concentration in the solution during interruption of the flow. This indicated that Cd was desorbed kinetically during the interruption period.

Considering the distribution coefficient to be constant for all soil layers may lead to an improper evaluation of the sorption phenomena and to serious errors in predicting contaminant transport through unsaturated soils (Elzahabi and Yong, 2001). In order to properly simulate movement of TEs in soils, it is necessary to consider different adsorption coefficients and rates for different soil layers. Competition between TEs for sorption sites may also affect the retardation of some elements. Since there is not enough information available about this process, more research about the interaction and competition among TEs during transport is needed.

Models simulating solute movement in structured soils must provide at least two essential features. They must describe effects of naturally occurring particles on the TE transport and simulate water flow and particle transport in structural macropores (White, 1985). Models should also be able to describe transient water flow and solute transport in layered, subsurface drained, macroporous soil (Jarvis, 1994). MACRO is one of such models that provide majority of required features and that was applied successfully to describe pesticide transport at the field scale (Besien *et al.*, 1997). The latest version of HYDRUS-1D (Šimůnek *et al.*, 2005) also provides several different approaches to simulate preferential flow and transport using various dual-porosity and dual-permeability concepts (Pot *et al.*, 2005; Šimůnek *et al.*, 2003), as well as modules to simulate colloid transport and colloid facilitated solute transport (Šimůnek *et al.*, 2006b; van Genuchten and Šimůnek, 2004).

B. Multicomponent Models

Contrary to single-component models that consider transport of only one solute and thus can not dynamically adjust behavior of this solute in response to other solutes present, multicomponent models simultaneously simulate transport of multiple solutes, and thus behavior of one solute can react to the presence of other solutes. Multiple solutes can mutually compete for sorption sites, can create various aqueous complexes, and can precipitate or dissolve depending on actual conditions in the soil profile.

Many environmental applications of reactive multispecies solute transport models appeared in the literature during the last two decades. For example, water leaching from various tailing piles (such as from uranium mills) often contains many trace metals including molybdenum, selenium, arsenic, and chromium (Brookins, 1984). Using the HYDROGEOCHEM model, Yeh and Tripathi (1991) simulated the release of trace metals and acidity from an acidic uranium mill tailings pile. Narasimhan *et al.* (1986) used the DYNAMIX model to study groundwater contamination from an inactive uranium mill tailings pile. Walter *et al.* (1994), Lichtner (1996), and Gerke *et al.* (1998) carried out similar studies. Another significant challenge is to design and evaluate facilities for a safe disposal and long term isolation of radioactive waste, especially high-level nuclear waste. The migration of neptunium between the repository and the ground water table after a hypothetical repository breach at the potential high-level nuclear waste repository at Yucca Mountain, Nevada, was studied using a multicomponent solute transport model by Viswanathan *et al.* (1998). Fate of metal-organic mixed wastes was studied by Rittmann and VanBriesen (1996) and VanBriesen (1998). An example of a biogeochemical multicomponent model is PHREEQC (Parkhurst and Appelo, 1999) that was, for example, used to simulate Cd and Zn transport by Voegelin and Kretzschmar (2003). Significant limitation of the PHREEQC and many other models, however, is that they can consider only one-dimensional or steady-state water flow conditions.

The more general geochemical transport modeling approach was used recently in several codes that coupled transient unsaturated flow to general biogeochemistry models. These include 3DHYDROGEOCHEM (Yeh and Cheng, 1999), CORE^{2D} (Samper *et al.*, 2000), MIN3P (Mayer *et al.*, 2002), RETRASO (Saaltink *et al.*, 2004) and HP1 (Jacques and Šimůnek, 2005). In the multicomponent transport model of Jacques and Šimůnek (2005) the HYDRUS-1D water flow and solute transport model (Šimůnek *et al.*, 1998) was coupled with the PHREEQC geochemical speciation model (Parkhurst and Appelo, 1999). PHREEQC considers a variety of chemical reactions, such as aqueous speciation; gas, aqueous, and mineral equilibrium; oxidation–reduction reactions; and solid-solution, surface-complexation, ion-exchange, and kinetic reactions, while HYDRUS-1D considers transient variably saturated water flow and heat and solute transport for both homogeneous and heterogeneous soil profiles. The combined HYDRUS1D-PHREEQC model, HP1 (Jacques and Šimunek, 2005) permits simultaneous simulations of variably saturated transient water flow, multicomponent solute transport, and speciation and other geochemical processes, including a broad range of mixed equilibrium and kinetic reactions.

Jacques *et al.* (2002, 2003) and Šimunek *et al.* (2006a) presented several examples that illustrate the potential power and versatility of the coupled multicomponent geochemical modeling approach used in HP1. The first example solved the hypothetical problem dealing with the multicomponent transport of major cations (Al, Ca, K, Na, and Mg), anions (Cl and Br), and three trace metals (Cd, Pb, and Zn) in a saturated short soil column. In this example, a fully saturated 8-cm long vertical soil column having an initial solution defined as "Initial" aqueous solution in Table III and its ion-exchange complex in equilibrium with this solution was considered. This problem simulates leaching of Cd, Pb, and Zn from an initially contaminated soil core using Ca-rich leaching water. Removal of trace metals from the solid phase was calculated by ion exchange with Ca, and to a lesser degree with Mg. Water was applied to the top of the column at a steady rate of 2 cm day^{-1} and having a chemical composition as given by "Boundary" aqueous solution in Table III. Dispersivity was considered to be 0.2 cm, and CEC equal to 11 mmol per cell. Resulting outflow concentrations at the outlet are shown in Fig. 7.

The second example simulated trace metal transport in a multilayered soil profile assuming steady-state water flow and pH-dependent cation-exchange

Table III
Main Components, Complex Species, and Exchange Species (X Refers to Ion Exchanger) Considered in the HP1 Simulation of the Leaching of Trace Metals from a Short Laboratory Column (Jacques *et al.*, 2002)

		Aqueous solutions (mmol liter^{-1})	
Components	Species	Boundary	Initial
Al	Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$	0.1	0.5
Br	Br^-	3.7	11.9
Cl	Cl^- (and Cd, Pb, and Zn-species)	10	0.0
Ca	Ca^{2+}, $Ca(OH)^+$	5	0.0
K	K^+, KOH	0	2
Na	Na^+, NaOH	0	6
Mg	Mg^{2+}, $Mg(OH)^+$	1	0.75
Cd	Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, $CdCl^+$, $CdCl_2$, $CdCl_3^-$	0	0.09
Pb	Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, $PbCl^+$, $PbCl_2$, $PbCl_3^-$, $PbCl_4^{2-}$	0	0.1
Zn	Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_2$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$, $ZnCl_4^{2-}$	0	0.25
X	AlX_3, $AlOHX_2$, CaX_2, CdX_2, KX, NaX, MgX_2, PbX_2, ZnX_2 (mmol)	0	11.0

Aqueous solutions initially in the soil profile (Initial) and applied as the boundary condition (Boundary).

capacities. The third example extended the analysis to variably saturated flow by simulating the long-term fate and transport of trace metals under transient field conditions. This example demonstrated that transient simulations resulted in dramatically different predictions than those based on steady-state water flow. Total concentrations were up to one order of magnitude higher than those obtained assuming steady-state flow. This was mainly caused by fluctuating pH in the transient case that caused significantly different mobility of trace metals throughout the year and resulted in significantly more leaching compared to the case of steady-state flow. All three examples were limited to aqueous speciation and equilibrium ion-exchange reactions. Yet another problem simulated based on a study of Adler (2001) the intrusion of a high-pH solution (pH 13) into a compacted clay core leading to kinetic dissolution of primary minerals (kaolinite, illite, quartz, calcite, dolomite, and gypsum) and precipitation of secondary minerals (sepiolite and hydrotalcite).

The effect of inorganic ligands (Cl) in the soil solution on the Cd transport has been demonstrated by Jacques *et al.* (2004), who investigated undisturbed 1-m long, 0.8-m wide lysimeter experiments under quasi steady-state flow conditions. During leaching with 0.005 M $CaCl_2$, a 1-day pulse

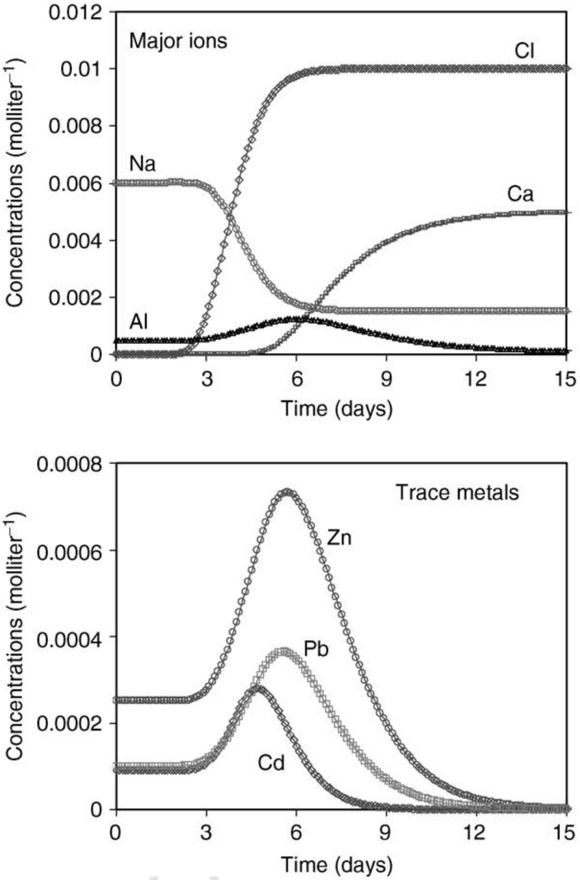

Figure 7 Outflow concentrations of selected major cations (left) and heavy metals (right) calculated using HP1 during steady-state saturated flow.

of 0.05 M $CaCl_2$ was given to mobilize Cd. The inflow of Cl-rich water clearly enhanced the leaching of Cd due to exchange with Ca and a mere mobile inorganic complex forming with chloride. A coupled reactive transport model for unsaturated transient flow conditions HP1 (Jacques and Šimůnek, 2005) was used to describe the experiments. Adsorption of Cd, some other trace metals (Cu, Pb, Zn) and major cations (Mg, Ca, Na, K) was described with a (multisite) cation-exchange complex model. Outflow concentrations of these components were modeled for a series of Cl-poor and Cl-rich water applications.

In yet another example, Jacques *et al.* (2005) evaluated the impact of long-term applications of mineral fertilizers ((super)phosphates) containing small amounts of ^{238}U and ^{230}Th to agricultural soils. Field soils that receive P-fertilizers accumulate U and Th and their daughter nuclides, which may eventually leach to groundwater. They used the HP1 code that accounted for interactions between U and organic matter, phosphate, and carbonate, considered surface complexation as the major solid phase interaction, and coupled all geochemical processes with transient soil water flow. Jacques *et al*. (2005) carried out calculations using a semisynthetic 200-year long time series of climatological data for Belgium and evaluated U fluxes into the groundwater. These examples show that the coupling of HYDRUS-1D and PHREEQC leads to a potentially very powerful tool for simulating a broad range of interacting physical, chemical and biological processes affecting the transport of TEs in soils.

Although the HP1 model can consider a broad range of interactions, it can not simulate preferential flow and transport or colloid-facilitated transport. Although individual models do exist that can simulate either: (1) preferential flow and transport, (2) colloid-facilitated transport, or (3) a broad range of interacting physical, chemical and biological processes, there is, to the best of our knowledge, at present not a single model that could consider all these processes and interactions simultaneously.

VII. SUMMARY AND CONCLUSIONS

In this chapter, we portrayed soils as a heterogeneous mixture of biotic (i.e., organic matter, organic residues including biosolids, xenobiotics, and pesticides, plant roots and debris, soil animals including invertebrates, microbes and microbial metabolites, and so on.) and abiotic (i.e., clay minerals, other aluminosilicate minerals, salts, precipitates, miscellaneous inorganic materials such as metals, coal residues, and mining residues, and so on) materials. In turn, TE dynamics in soils is governed by biotic and abiotic processes, the latter including complexation, adsorption–desorption, precipitation–dissolution, redox reactions, and catalysis. In other words, soil is a dynamic system in which continuous interaction takes place between soil minerals, organic matter, and organisms. Each of these soil components influences the physicochemical and biological properties of the terrestrial systems.

We then viewed the soil as a physicobiogeochemical filter of contaminants either in a solute, particulate or colloidal form. Mechanisms moderating biogeochemical sequestration of TEs indicate that sorption–desorption reactions, especially in severely contaminated soils, largely regulate the extent of partitioning, typically measured as Kd, in the soil-solution matrix. Sorption in this case includes precipitation, occlusion, and adsorption while desorption includes dissolution. These mechanisms are, in turn, moderated by certain factors, the most important of which include pH, OM, and chemical speciation of the element. Biological processes augment the processes above especially in typical surface soils and rhizosphere but may be limited in severely contaminated environments due to biotoxicity to organisms. The rhizosphere represents a microenvironment in soils where biological processes, by virtue of root activity, root exudates and prolific microbial consortia can assume an important role in TE dynamics. Microbes may bioaccumulate and promote biosorption of TEs, with certain microorganisms mediating redox transformation of multivalence elements such as Cr, As, Se, Fe, Mn, and so on. In general, TE partitioning in soils is dependent on the element type, chemical speciation of the element, and soil properties and conditions. Thus the extent of partitioning in soils is rather difficult to predict. However, limited success in predicting adsorption on soil for B, Mo, Mn, and As has been accomplished using surface complexation models.

When the capacity of the soil components to sequester TEs has become limited, substantial amounts of these TEs can be desorbed, mobilized and eventually transported through the soil profile, the vadose zone and ground waters. Both organic (e.g., low-molecular-weight organic acids, such as fulvic acids, and other organic acids from root exudates, decay of plant, animal, and microbial tissues, microbial metabolites, and high-molecular-weight organic acids such as humic acids) and inorganic (e.g., chlorides, sulfates, nitrates, phosphates, and so on) ligands could promote TE dissolution/desorption and serve as transport vectors thereby enhancing leaching through mass flow and diffusion. These ligands form soluble, stable TE–ligand complexes that render them more mobile and bioavailable. Although leaching plays only a minor role in the vertical transport of cationic elements, it represents an important transport vector for anionic elements such as Se, Cr, and As. Cationic elements move to significant vertical distances only under rare, specific soil conditions such as acidic sandy soils or in association with reactive, mobile colloids. Facilitated solute transport can occur in the presence of highly reactive colloids of either organic, that is, OM based, and inorganic (e.g., clay minerals, and so on) forms. In general, transport of solutes, colloids, and particulates is enhanced under field, structured soils with macropores or in cracked soils.

While there are models applicable to preferential and nonequilibrium water flow and solute transport in structured soils and fractured rocks, models dealing with the colloid transport and colloid-facilitated solute transport that consider complex reactions between colloids and the soil solid phase, and the air–water interface, as well as between contaminant and colloids in different states (mobile and/or immobile), are being actively developed. Also significant efforts to combine variably saturated flow and transport models with biogeochemical models (e.g., coupled HYDRUS-1D–PHREEQC) that can take into account various interacting geochemical and biological reactions under variable conditions are underway. To the best of our knowledge, there are no models available at present that address all these interactive processes in their full complexity. Additionally, further integration of various types of models is necessary to address practical problems in the transport of TEs in the subsurface environment. However, advanced methodologies and techniques should precede such efforts in order to simplify and understand these complex processes and how they behave in inherently heterogeneous subsurface environment and the stochastic nature of boundary conditions in these systems.

In summary, understanding various physicobiogeochemical processes and how they are affected by certain factors such as pH, OM, and so on, is necessary to predict TE partitioning in soils. Such more accurate prediction of the TE behavior in the soil-solution phase is vital to more accurately predict the subsequent mobility and transport of these substances in the soil profile and the subsurface environment. Advances in this field have become imminent by virtue of the efforts to couple the conventional variably saturated flow and transport models with biogeochemical models with the desire to address interactive, complex processes in heterogeneous systems.

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REFERENCES

Abd-Elfattah, A., and Wada, K. (1981). Adsorption of lead, copper, zinc cobalt, and cadmium by soils that differ in cation exchange materials. *J. Soil Sci.* **32**, 271–283.

Adams, T., and Sanders, J. R. (1985). The effect of incubation on the composition of soil solution displacement from 4 soils treated with zinc, sopper or nickel-loaded sewage sludge. *In* "Chemical Methods for Assessing Bio-Available Metals in Sludge and Soils" (R. Leshbar and R. D. Davis, Eds.), pp. 68–81. Elsevier Applied Science, New York.

Adler, M. (2001). Interaction of claystone and hyperalkaline solutions at 30°C: A combined experimental and modeling study, p. 120. Ph.D Dissertation, Universität Bern.

Adriano, D. C. (2001). "Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals," 2nd edn., p. 860. Springer, New York.

Adriano, D. C., Wenzel, W. W., Vangronsveld, J., and Bolan, N. S. (2004). Role of assisted natural remediation in environmental cleanup. *Geoderma* **122**, 121–142.

Ahuja, L. R., and Hebson, C. (1992). "Root Zone Water Quality Model." GPSR Tech. Rep. No. 2, USDA, ARS, Fort Collins, CO.

Alesii, B. A., Fuller, W. H., and Boyle, M. V. (1980). Effect of leachate flow rate on metal migration through soil. *J. Environ. Qual.* **9**, 119–126.

Allen, H. E. (Ed.) (2002). "Bioavailability of Metals in Terrestrial Ecosystems: Importance of Partitioning for Bioavailability to Invertebrates Microbes and Plants." *Soc. Environ. Toxicol. Chem.* (SETAC), Pensacola, FL.

Al-Wabel, M. A., Heil, D. M., Westfalland, D. G., and Barbarick, K. A. (2002). Solution chemistry influence on metal mobility in biosolids amended soils. *J. Environ. Qual.* **31**, 1157–1165.

Anderson, P. R., and Christensen, T. H. (1988). Distribution coefficients of Cd, Co, Ni, and Zn in soils. *J. Soil Sci.* **39**, 15–22.

Appel, C., and Ma, L. (2001). Concentration, pH and surface charge effect on cadmium and lead sorption in three tropical soils. *J. Environ. Qual.* **31**, 581–589.

Armienta, M. A., Rodriguez, R., Aguayo, A., Ceniceros, N., Villaseñor, G., and Cruz, O. (1997). Arsenic contamination of groundwater at Zimpan, México. *Hydrogeol. J.* **5**, 39–46.

Bahaminyakamwe, L., Šimůnek, J., Dane, J., Adams, J. F., and Odom, J. W. (2006). Copper mobility in soils as affected by sewage sludge and low molecular weight organic acids. *Soil Sci.* **171**(1), 29–38.

Balcke, G. U., Kulikova, N. A., Hesse, S., Kopinke, F. D., Perminova, I. V., and Frimmel, F. H. (2002). Adsorption of humic substances onto kaolin clay related to their structural features. *Soil Sci. Soc. Am. J.* **66**, 1805–1812.

Barbosa, A. E., and Hvitved-Jacobsen, T. (1999). Highway runoff and potential for removal of heavy metals in an infiltration pond in Portugal. *Sci. Total Environ.* **235**, 151–159.

Barnhisel, R. I., and Bertsch, P. M. (1989). Chloride and hydroxy interlayered vermiculite and smectite. *In* "Minerals in Soil Environments" (J. B. Dixon and S. B. Weed, Eds.), 2nd edn., pp. 729–788. *Soil Sci. Soc. Am.*, Madison, WI.

Barrel, M. S., Zuber, R. D., Collins, R. D., Malina, J. F., Charbeneau, R. J., and Ward, G. H. (1993). A review and evaluation of literature pertaining to quality and control of pollution from highway runoff and construction. Centre of Research in water resources. Bureaus of Engineering Research. University of Texas, Austin. CRWR 239.

Barrow, N. J., and Whelan, B. R. (1998). Comparing the effect of pH on the sorption of metals by soil and by goethite, and on uptake by plants. *Eur. J. Soil Sci.* **49**, 683–692.

Bartlett, R. J., and Kimble, J. M. (1976). Behavior of chromium in soils: I Trivalent forums. *J. Environ. Qual.* **5**, 383–386.

Bataillard, P., Cambier, P., and Picot, C. (2003). Short-term transformations of lead and cadmium compounds in soil after contamination. *Eur. J. Soil Sci.* **54**, 365–376.

Berti, W. R., and Ryan, J. A. (2003). Inplace inactivation and natural ecological restoration technologies (IINERT). *In* "Bioavailability, Toxicity and Risk Relationships in Ecosystems" (R. Naidu, W. S. R. Gupta, S. Rogers, R. S. Kookana, N. S. Bolan, and D. C. Adriano, Eds.), pp. 253–269. Science Publishers, Inc, Enfield, NH, USA.

Besien, T. J., Jarvis, N. J., and Williams, R. J. (1997). Simulation of water movement and isoproturon behaviour in a heavy clay soil using the MACRO model. *Hydrol. Earth Sci.* **1**, 845–852.

Birch, G., Siaka, M., and Owens, C. (2001). The source of anthropogenic heavy metals in fluvial sediments of a rural catchment: Coxs river, Autralia. *Water Air Soil Poll.* **126**, 13–35.

Bizily, S. P., Rugh, C. L., and Meagher, R. B. (2002). Phytodestoxification of hazardous organomercurials by genetically engineered plants. *Nat. Biotechnol.* **18**, 213–217.

Bodvarsson, G. S., Ho, C. K., and Robinson, B. A. (Eds.) (2003). Yucca Mountain Project, Special issue, *J. Contam. Hydrol.* **62–63**, 1–750.

Boekhold, A. E., Temminghoff, E. J. M., and Vanderzee, S. E. A. T. M. (1993). Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *J. Soil. Sci.* **44**, 85–96.

Bradford, S. A., Šimůnek, J., Bettahar, M., van Genuchten, M. Th., and Yates, S. R. (2003). Modeling colloid attachment, straining, and exclusion in saturated porous media. *Environ. Sci. Technol.* **37**, 2242–2250.

Brigatti, M. F., Colonna, S., Malferrari, D., Medici, L., and Poppil, L. (2004). Mercury adsorption by montmotillonite and vermiculite: A combined XRD, TG-MS, and EXAFS study. *Appl. Clay Sci.* **28**, 1–8.

Brookins, D. G. (1984). "Geochemical Aspects of Radioactive Waste Disposal." Springer-Verlag, New York.

Brooks, B. B., Presley, J. J., and Kaplan, I. R. (1968). Trace elements in the interstitial water of marine sediments. *Eochim. Cosmochim. Acta* **32**, 397–414.

Brooks, R. H., and Corey, A. T. (1964). "Hydraulic Properties of Porous Media," p. 27. Colorado State University, Hydrology Paper No. 3.

Buchter, B., Davidoff, B., Amacher, M. C., Hinz, C., Iskandar, I. K., and Selim, H. M. (1989). Correlation of Freundlich K_d and n retention parameters with soils and elements. *Soil Sci.* **148**, 370–379.

Buddemeier, R. W., and Hunt, J. R. (1988). Transport of colloidal contaminants in ground water: Redionuclides migration at the Nevada Test Site. *Appl. Geochem.* **3**, 535–548.

Bundt, M., Zimmermann, S., Blaster, P., and Hagedorn, F. (2001). Sorption and transport of metals in preferential flow paths and soil matrix after the addition of wood ash. *Eur. J. Soil Sci.* **52**, 423–431.

Buyks, S. E. J., van de Hoop, M. A. G. T., and Loch, J. P. G. (2002). Dissolution kinetics of heavy metals in Dutch carbonate and sulfide-rich freshwater sediments. *J. Environ. Qual.* **31**, 573–580.

Camobreco, V. J., Richards, B. K., Steenhuis, T. S., Peverly, J. H., and McBride, M. B. (1996). Movement of heavy metals throgh undisturved and homogenized soil columns. *Soil Sci.* **161**, 740–750.

Cantwell, M., Burgess, R. M., and Kester, D. R. (2002). Release and phase partitioning of metals from anoxic estuarine sediments during perios of simulated resuspension. *Environ. Sci. Technol.* **36**, 5328–5334.

Carey, P. L., McLaren, R. G., Cameron, K. C., and Sedcole, J. R. (1996). Leaching of copper, chromium, and arsenic through some free draining New Zaland soils. *J. Soil Res.* **34**, 583–597.

Carrillo-Gonzalez, R. (2000). Transporte de Zn en el suelo: Simulación y factores que lo afectan. *In* "La edafología y sus perspectivas al siglo XXI" (R. Quintero-Lizaola, T. Reyna-Trujillo, L. Corlay_Chee, A. Ibáñez-Huerta y, and N. E. García Calderón, Eds.), pp. 213–223. CP, UNAM, UACH, México.

Carrillo-Gonzalez, R., Rowell, D. J., and Alloway, B. J. (2005). Displacement of through a light textured soil. *Geoderma* **124**, 335–348.

Carroll, S. A., O'Day, P. A., and Piechowsky, M. (1998). Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-State mining district. 2. Geochemical interpretation. *Environ. Sci. Technol.* **32**, 956–965.

Carvalho, C. E. V., Ovalle, A. R. C., Rezende, C. E., Molisani, M. M., Salomâo, M. S. M. B., and Lacerda, L. D. (1999). Seasonal variation of particulate heavy metals in the lower Paraiba do Sul River, R. J. Brazil. *Environ. Geol.* **37**, 297–302.

Cassel, D. K., Krueger, T. H., Schroer, F. W., and Norum, E. B. (1974). Solute movement through disturbed and disturbed soil cores. *Soil Sci. Soc. Am. Proc.* **38**, 36–40.

Cattlet, K.M, Heil, D. M., Linday, W. L., and Ebinger, M. H. (2002). Soil chemical properties controlling Zn^{2+} activity in 18 Colorado soils. *Soc. Soil Am. J.* **66**, 1182–1189.

Černík, M., Federer, P., Borkovec, M., and Sticher, H. (1994). Modelling of heavy metals transport in a contaminated soil. *J. Environ. Qual.* **23**, 1239–1248.

Chen, C., and Wagenet, R. J. (1992). Simulation of water and chemicals in macropore soils. Part 1. Representation of the equivalent macropore influence and its effect on soil water flow. *J. Hydrol.* **130**, 105–126.

Chlopecka, A., and Adriano, D. C. (1996). Mimicked in situ stabilization of metals in a cropped soil: Bioavailability and chemical forms of zinc. *Environ. Sci. Technol.* **30**, 3294–3303.

Christensen, J. B., Jensen, D. L., and Christensen, T. H. (1996). Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. *Water Res.* **30**, 3037–3049.

Chubin, R. G., and Street, J. J. (1981). Adsorption of cadmium on soil constituents in the presence of complexing ligands. *J. Environ. Qual.* **10**, 225–228.

Clark, M. W., Walsh, S. R., and Smith, J. V. (2001). The distribution of heavy metals in a abandoned mining areas; a case study if Strauss Pit, the Drake mining area Australia: Implications for the environmental management of mine sites. *Environ. Geol.* **40**, 655–663.

Clemens, S., Kim, E. J., Neumann, D., and Schroeder, J. I. (1999). Tolerance to toxic metals by a gene family of phytochelatin synthases from plants and yeast. *EMBO J.* **18**, 3325–3333.

Corapcioglu, M. Y., and Choi, H. (1996). Modeling colloid transport in unsaturated porous media and validation with laboratory column data. *Water Resour. Res.* **32**, 3437–3449.

Darmony, R. G., Foss, J. E., Intosh, M. Mc., and Wofl, D. C. (1983). Municipal sewage sludge compost amended soils: Some spatio temporal treatment effects. *J. Environ. Qual.* **12**, 231–236.

Davranche, M., and Bollinger, J. C. (2001). A desorption dissolution model for metal release from polluted soil under reductive conditions. *J. Environ. Qual.* **30**, 1581–1586.

Davis, J. A., and Lackie, J. O. (1980). Surface ionization and complexation at the oxide/water interfase 3. Adsorption of anions. *J. Colloid Interface Sci.* **74**, 32–43.

Decker, D. L., Papelis, Ch., Tyler, S. W., Logsdon, M., and Šimůnek, J. (2006a). Arsenate and arsenite sorption on carbonate hosted precious metals ore. *Vadose Zone J.* **5**, 419–429.

Decker, D. L., Šimůnek, J., Tyler, S. W., Papelis, Ch., and Logsdon, M. (2006b). Variably saturated reactive transport of arsenic in heap leach facilities. *Vadose Zone J.* **5**, 430–444.

Degryse, F., Buekers, J., and Smolders, E. (2003). Radio-labile cadmium and zinc in soils as affected by pH and source of contamination. *Eur. J. Soil Sci.* **55**, 113–121.

Delolme, C., Hebrard-Labit, C., Spadini, L., and Gaudet, J. P. (2004). Experimental study and modeling of the transfer of zinc in a low reactive sand column in the presence of acetate. *J. Contam. Hydrol.* **70**, 205–224.

Doner, H. E. (1978). Chloride as a factor in mobilities of $Ni_{(II)}$, $Cu_{(II)}$, and $Cd_{(II)}$ in soil. *Soil Sci. Soc. Am. J.* **42**, 882–885.

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, D. M. Kral, and S. L. Hawkins, Eds.), pp. 229–240. Spec. Publ. 11. ASA and SSSA Madison, WISSSA.

Dowdy, R. H., Latterell, J. J., Hinesly, T. D., Grossman, R. B., and Sullivan, D. L. (1991). Trace metals movement in an Aeric ochraqualf following 14 years of annual sludge applications. *J. Environ. Qual.* **20**, 119–123.

Dunnivant, F. M., Jardine, P. M., Taylor, D. L., and McCharty, J. F. (1992). Cotransportation of cadmium and exachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. *Environ. Sci. Technol.* **26**, 360–368.

Durner, W. (1994). Hydraulic conductivity estimation for soils with heterogeneous pore structure. *Water Resour. Res.* **30**, 211–233.

Elzahabi, M., and Yong, R. N. (2001). pH influence on sorption characteristics of heavy metals in the vadose zone. *Eng. Geol.* **60**, 61–68.

Environmental Protection Agency (EPA). (1995). *In* "Contaminants and Remedial Options at Selected Metal-contaminated Sites." U. S.-E. P. A. 540. R-95/512. Washington, D.C.

Essa, M. M. A., Macaskie, L. E., and Brown, N. L. (2002). Mechanisms of mercury bioremediation. *Biochem. Soc. Transac.* **30**, 672–674.

Flury, M., Flühler, H., Jury, W. A., and Levenberger, J. (1994). Susceptibility of soils to preferential flow of water: A field study. *Water Resour. Res.* **30**, 1945–1954.

Fox, P., and Doner, H. E. (2002). Trace element retention and release on mineral and soil in a constructed wetland. *J. Environ. Qual.* **31**, 331–338.

Frankenberger, W. T., and Benson, S. (Eds.) (1994). "Selenium in the Environment." Marcel Dekker, New York.

Frankenberger, W. T., and Losi, M. E. (1995). Applications of bioremediation in the cleanup of heavy metals and metalloids. *In* "Bioremediation: Science and Applications" (H. D. Skipper and R. F. Turco, Eds.), pp. 173–210. *Soil Sci. Soc. Am. Spec.* Publ. no. 43, Madison, WI.

Gambrell, R. P., Collard, V., and Patrick, W. H., Jr. (1980). Cadmium uptake by marsh plants as affected by sediment physicochemical conditions. *In* "Contaminants and Sediments" (R. A. Baker, Ed.), Vol. 2, pp. 425–443. Publishers, Inc., Ann Arbor, MI.

Gaskin, J. W., Brobst, R. B., Miller, W. P., and Tollner, E. W. (2003). Long-term biosolids application effects on metal concentration in soil and Bermudagrass forage. *J. Environ. Qual.* **32**, 146–152.

Gao, Y., Kan, A. T., and Tomson, M. B. (2003). Critical evaluation of desorpion phenomena of heavy metals from natural sediments. *Environ. Sci. Technol.* **37**, 5566–5573.

Gerke, H. H., and van Genuchten, M., Th. (1993). A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resour. Res.* **29**, 305–319.

Gerke, H. H., Molson, J. W., and Frind, E. O. (1998). Modelling the effect of chemical heterogeneity on acidification and solute leaching in overburden mine spoils. *J. Hydrol.* **209**, 166–185.

Germann, P. F., and Beven, K. (1985). Kinematic wave approximation to infiltration into soils with sorbing macropores. *Water Resour. Res.* **21**(7), 990–996.

Gerritse, R. G. (1996). Dispersion of cadmium in columns of saturated soil. *J. Environ. Qual.* **25**, 1344–1349.

Gier, S., and John, W. D. (2000). Heavy metal adsorption on micas and photoelectron spectroscopy. *Appl. Clay Sci.* **16**, 289–299.

Gimeno-Garcia, E., Andreu, V., and Boluda, R. (1996). Heavy metal incidence in the application of inorganic fertilizers and pesticides to rice farming soils. *Environ. Pollut.* **92**, 19–25.

Giusquiani, P. L., Gigliotti, G., and Businelli, O. (1992). Mobility and plant uptake of heavy metals in amended soils. *J. Environ. Qual.* **21**, 330–335.

Goldberg, S. (2004). Modeling boron adsorption isotherms and envelopes using the constant capacitance model. *Vadose Zone J.* **3**, 676–680.

Goldberg, S. (2005). Predicting arsenate adsorption by soils using soil chemistry parameters in the constant capacitance model. *Soil Sci. Soc. Am. J.* **69**, 1389–1398.

Goldberg, S., and Forster, H. S. (1998). Factors affecting molybdenum adsorption by soils and minerals. *Soil Sci.* **163**, 109–114.

Goldberg, S., Lesch, S. M., and Suarez, D. L. (2002). Predicting molybdenum adsorption by soils using soil chemical parameters in the constant capacitance model. *Soil Sci. Soc. Am. J.* **66**, 1836–1842.

Gomes, P. C., Fontes, P. F., da Silva, A. G., Mendonca, E. S., and Netto, A. R. (2001). Selectivity sequence and competitive adsorption of heavy metals by brazilian soils. *Soil Sci. Soc. Am. J.* **65**, 1115–1121.

González, Chávez, Pérez Moreno, J., and C. González, R. (2005). "El systema planta microorganismo suelo en áreas contaminadas con residuos de minas," pp. 61–80, 109–125. Colegio de Postgraduados, México.

Gooddy, D. C., Shand, P., Kinniburgh, D. G., and van Riemdsjik, W. H. (1995). Field-based partition coefficients for trace elements in soil solutions. *Eur. J. Soil Sci.* **46**, 265–285.

Gove, L., Cooke, C. M., Nicholson, F. A., and Beck, A. J. (2001). Movement of water and heavy metals (Zn, Cu, Pb and Ni) through sand and sandy loam amended wit biosolids under steady-state hydrological conditions. *Bioresource Technol.* **78**, 171–179.

Gray, C. W., McLaren, R. G., and Roberts, A. H. (2003). Cadmium leaching from some New Zealand pasture soils. *Eur. J. Soil. Sci.* **54**, 159–166.

Green, C.H, Heil, D.M, Cardon, G. E., Butters, G. L., and Kelly, E. F. (2003). Solubiliozation of manganese and trace metals in soils affected by acid mine runoff. *J. Environ. Qual.* **32**, 1323–1334.

Grigal, D. F. (2002). Inputs and outputs of mercury from terrestrial watersheds: A review. *Environ. Rev.* **10**, 1–39.

Grolimund, D., Borkovec, M., Barmettler, K., and Sticher, H. (1996). Colloid facilitated transport of strongly sorbing contaminants in natural porous media: A laboratory column study. *Environ. Sci. Tech.* **30**, 3118–3123.

Gwo, J. P., Jardine, P. M., Wilson, G. V., and Yeh, G. T. (1995). A multiple-pore-region concept to modeling mass transfer in subsurface media. *J. Hydrol.* **164**, 217–237.

Hall, J. L. (2002). Cellular mechanism for metal detoxification and tolerance. *J. Exp. Bot.* **53**, 1–11.

Hansel, C. M., and Fendorf, S. (2001). Characterization of Fe plaque and associated metals on the roots of mine-waste impacted aquatic plants. *Environ. Sci. Technol.* **35**, 3863–3868.

Harsh, J., Chorover, J., and Nizeyimana, E. (2002). Allophane and imogolite. *In* "Soil Mineralogy with Environmental Applications" (J. B. Dixon and D. G. Schulze, Eds.), chapter 9. SSSA Book series, no. 7. WI. pp. 291–322.

Harter, R. D., and Naidu, R. (1995). Role of metal organic complexation in metal sorption by soils. *Adv. Agron.* **55**, 219–263.

Harter, R. D., and Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace-metal sorption by soils. *Soil Sci. Soc. Am. J.* **65**, 597–612.

Harvey, R. W., and Garabedian, S. P. (1991). Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer. *Environ. Sci. Technol.* **25**, 178–185.

He, Z. L., Zhang, M. K., Calvert, D. V., Stoffella, X. P., Yang, X. E., and Yu, S. (2004). Transport of heavy metals in surface runoff from vegetable and citrus fields. *Soil Sci. Soc. Am. J.* **68**, 1662–1667.

He, Z. L., Yang, X. E., and Stoffella, P. J. (2005). Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.* **19**, 125–140.

Hemond, H. F., and Fechnor, E. L. (1994). "Chemical Fate and Transport in the Environment." Academic Press, London.

Hinz, C., and Selim, H. M. (1994). Transport of zinc and cadmium in soils: Experimental evidence and modeling approaches. *Soil Sci. Soc. Am. J.* **58**, 1316–1327.

Hirsh, D., Nir, S., and Banin, A. (1989). Prediction of cadmium complexation in solution and adsorption to montmorillonite. *Soil Sci. Soc. Am. J.* **53**, 716–721.

Hoffman, M. R., Yost, E. C., Eisenrich, S. J., and Maier, W. J. (1981). Characterization of soluble and colloidal phase metal complexes in river water by ultrafiltration: A mass balance approach. *Environ. Sci. Tech.* **15**, 655–661.

Holm, P. E., Andersen, B. B. H., and Christensen, T. H. (1996). Cadmium solubility in aerobic soils. *Soil Sci. Soc. Am. J.* **60**, 775–780.

Hornberger, G. M., Mills, A. L., and Herman, J. S. (1992). Bacterial transport in porous media: Evaluation of a model using laboratory observations. *Water Resour. Res.* **28**, 915–938.

Huang, P. M., Violante, A., Bollag, J. M., and Vityakon, P. (2005). "Soil abiotic and biotic interactions and impact on the terrestrial ecosystem and human welfare." Science Publishers, Plymouth, UK.

Hutson, J. L., and Wagenet, R. J. (1995). A multiregion model describing water flow and solute transport in heterogeneous soils. *Soil Sci. Soc. Am. J.* **59**, 743–751.

Jacques, D., and Šimůnek, J. (2005). "User Manual of the Multicomponent Variably-Saturated Flow and Transport Model HP1, Description, Verification and Examples," Version 1.0, *SCK●CEN-BLG-998,* Waste and Disposal, SCK●CEN, Mol, Belgium, p. 79.

Jacques, D., Šimůnek, J., Mallants, D., and van Genuchten, M. Th. (2002). Multicomponent transport model for variably-saturated porous media: Application to the transport of heavy metals in soils. *In* "Computational Methods in Water Resources" (S. M. Hassanizadeh, R. J. Schotting, W. G. Gray, and G. F. Pinder, Eds.), XIVth International Conference on Computational Methods in Water Resources, June 23–28, Delft, The Netherlands. Elsevier, *Dev. Water Sci.* **47**, pp. 555–562.

Jacques, D., Šimůnek, J., Mallants, D., and van Genuchten, M. Th. (2003). The HYDRUS-PHREEQC multicomponent transport model for variably-saturated porous media: Code verification and application. "MODFLOW and More 2003: Understanding through Modeling," Conference Proceedings (E. Poeter, Ch. Zheng, M. Hill, and J. Doherty, Eds.). International Ground Water Modeling Center, Colorado School of Mines, 23–27.

Jacques, D., Seuntjens, P., Šimůnek, J., Mallants, D., and van Genuchten, M. Th. (2004)."Effect of Increased Salt Concentration on Cadmium Leaching in Acid Sandy Soils, European Geosciences Union, Geophysical Research Abstracts, Volume 6, EGU first General Assembly 2004, Nice, France, 25–30, 1607-7962/gra/EGU04-A-02979.

Jacques, D., Šimůnek, J., Mallants, D., and van Genuchten, M. Th. (2005). "Long term uranium migration in agricultural field soils following mineral P-fertilization," Proceedings Of "The 10th International Conference on Environ. Remediation and Radioactive Waste Management, September 4–8, 2005. Scottish Exhibition & Conference Center, Glasgow, Scotland, UK.

Janssen, R. P. T., Peijnenburg, W. J. G. M., Postuma, R., and van den Hoop, M. A. G. T. (1997). Equilibrium partitioning of heavy metals in Dutch field soils. I. Relationship between metal partition coefficients and soil characteristics. *Environ. Tox. Chem.* **16**, 2470–2478.

Janssen, R. P. T., Bruggenwert, M. G. M., and Van Riemsdijk, W. H. (2003). Zinc ion adsorption on montmorillonite Al hydroxide polymer systems. *Eur. J. Soil Sci.* **54**, 347–355.

Jardine, P. M., Wilson, G. V., Luxmore, R. J., and McCarthy, J. F. (1989). Transport of inorganic and natural organic traces through an isolated pedon in a forest watershed. *Soil Sci. Soc. Am. J.* **53**, 317–323.

Jarvis, N. J. (1994). The MACRO model (Version 3.1), Technical description and sample simulations. Reports and Dissertations 19. Department of Soil Science, Swedish University of Agricultural Science, Uppsala, Sweden, p. 51.

Jarvis, N. J., Villholth, K. G., and Ulén, B. (1999). Modelling particles mobilization and leaching in macroporous soil. *Eur. J. Soil Sci.* **50**, 621–632.

Jeng, A. S., and Singh, B. R. (1995). Cadmium status of soils and plants from a long term fertility experiment in sotheast Norway. *Plant Soil* **175**, 67–74.

Jiries, A. G., Hussein, H. H., and Halaseh, Z. (2001). The quality of water and sediments of street runoff in Amman. *Jordan. Hydrol. Proc.* **15**, 815–824.

Jopony, M., and Young, S. D. (1994). The solid solution equilibria of lead and cadmium in polluted soils. *Eur. J. Soil Sci.* **45**, 59–70.

Kaplan, D. I., Bertsch, P. M., Adriano, D. C., and Miller, W. P. (1993). Soil-borne mobile colloids as influence by water flow and organic carbon. *Environ. Sci. Technol.* **27**, 1193–1200.

Karapanagiotis, N. K., Sterritt, R. M., and Lester, J. N. (1991). Heavy metals complexation in sludge amended soil. The role of organic matter in metals retention. *Environ. Technol.* **12**, 1107–1116.

Karathanasis, A. D. (1999). Subsurface migration of copper and zinc mediated by soil. *Soil Sci. Soc. Am. J.* **63**, 830–838.

Kaschl, A., Römheld, V., and Chen, Y. (2002). The influence of soluble organic matter from municipal solid waste compost on trace metal leaching in calcareous soils. *Sci. Total Environ.* **291**, 45–57.

Keizer, M. G., and Bruggenwert, M. G. M. (1991). Adsorption of heavy metals by clay aluminum hydroxide complexes. *In* "Interactions at the Soil Colloid Soil Solution Interface" (G. H. Bolt, M. F. De Boodt, M. H. B. Hayes, and M. B. McBride, Eds.), pp. 177–203. Kluwer Academic Publisher, Dordrecht.

Keller, C., McGrath, S. P., and Dunham, S. J. (2002). Trace metal leaching through a soil-grassland system after sewage sludge application. *J. Environ. Qual.* **31**, 1550–1560.

Kent, D. B., Davis, J. A., Anderson, L. C. D., Rea, B. A., and Coston, J. A. (2002). Effect of the adsorbed metal ions on the transport of Zn and Ni-EDTA complexes in a sand and gravel aquifer. *Geoch. Cosmoch. Acta* **66**, 3017–3036.

Khalid, R. S. (1980). Chemical mobility of cadmium in sediment-water systems. *In* "Cadmium in the Environment" (O. Nriagu, Ed.). Part 1. John Wiley & Sons. Inc.

Kim, K. M., Lindberg, S. C., and Meyer, T. P. (1995). Micrometeorological measurements of mercury vapor fluxes over background forest soils in Eastern Tennessee. *Atmos. Environ.* **29**, 267–282.

Koo, B. J., Adriano, D. C., Bolan, N. S., and Barton, C. (2005). Plant root exudates. *In* "Encyclopedia of Soils in the Environment" (D. Hillel, Ed.). Elsevier, Amsterdam, Netherlands.

Krishna, R., and Wesseling, J. A. (1997). The Maxwell-Stefan approach to mass transfer. *Chem. Eng. Sci.* **52**, 861–911.

Kukier, U., and Chaney, R. L. (2001). Amelioration of nickel phytotoxicity in much and mineral soils. *J. Environ. Qual.* **30**, 1949–1960.

Kurek, E. (2002). Microbial mobilization of metals from soil minerals under aerobic conditions. *In* "Interactions Between Soil Particles and Microorganisms" (P. M. Huang, J.-M. Bollag, and N. Senesi, Eds.). Wiley and Sons, Chichester, UK.

Lang, F., and Kaupenjohann, M. (2003). Effect of dissolved organic matter on the precipitation and mobility of the lead compound chloropyromorphite in solution. *Eur. J. Soil Sci.* **54**, 139–147.

Lasat, M. M. (2002). Phytoextraction of toxic metals: A review of biological mechanisms. *J. Environ. Qual.* **31**, 109–120.

Lebourg, A., Sterckeman, T., Ciesielski, H., and Proix, N. (1998). Trace metal speciation in three unbuffered salt solutions used to assess their bioavailability in soil. *J. Environ. Qual.* **27**, 584–590.

Lee, S.-Z., Allen, H. E., Huang, C. P., Sparks, D. L., Sanders, P. F., and Peijnenburg, W. J. G. M. (1996). Predicting soil-water partition coefficients for cadmium. *Environ. Sci. Technol.* **30**, 3418–3424.

Lee, C. G., Chon, H. T., and Jung, M. C. (2001). Heavy metal contamination in the vicinity of the Daduk Au-Ag-Pb-Zn mine in Korea. *Appl. Geochem.* **16**, 1377–1386.

Legret, M., Divet, L., and Juste, C. (1988). Migration et speciation des metaux lourds dans un sol soumis a des epandages de boues de station d'epuration a tres forte charge en Cd et Ni. *Water Res.* **22**, 953–959.

Li, Z., Ryan, J. A., Chen, J. L., and Al-Abed, S. R. (2001). Adsorption of cadmium on biosolids-amended soils. *J. Environ. Qual.* **30**, 903–911.

Lichtner, P. C. (1996). Continuum formulation of multicomponent-multiphase reactive transport. *In* "Reactive Transport in Porous Media, Reviews in Mineralogy" (P. C. Lichtner, C. I. Steefel, and E. H. Oelkers, Eds.), Chapter 1, Vol. 34, pp. 1–81. Mineralogical Society of America.

Lindsay, W. L. (1979). "Chemical Equilibria in Soils," John Wiley and Sons, New York, NY.

Liu, F., Colombo, C., Adamo, P., He, J. Z., and Violante, A. (2002). Trace elements in manganese iron nodules from a chinese alfisol. *Soil Sci. Soc. Am. J.* **66**, 661–670.

Logan, B. E., Jewett, D. G., Arnold, R. G., Bouwer, E. J., and O'Melia, C. R. (1995). Clarification of clean-bed filtration models. *J. Environ. Eng.* **121**, 869–873.

Lu, C. S. J., and Chen, K. Y. (1977). Migration of trace metals in interfase of seawater and polluted surficial sediments. *Environ. Sci. Technol.* **11**, 174–182.

Lund, L. J., Page, A. L., and Nelson, C. O. (1976). Movement of heavy metals below sewage disposal ponds. *J. Environ. Qual.* **5**, 330–334.

Ma, L. Q. Y. (1996). Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. *J. Environ. Qual.* **25**, 1420–1429.

Ma, Q. Y., Traina, S. J., Logan, T. J., and Ryan, J. A. (1993). In situ lead immobilization by apatite. *Environ. Sci. Technol.* **27**, 1803–1810.

Ma, Q. Y., Traina, S. J., Logan, T. J., and Ryan, J. A. (1994). Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environ. Sci. Tech.* **28**, 1219–1228.

Maeda, M., and Bergström, L. F. (2000). Leaching patterns of heavy metals and nitrogen evaluated with a modified tanks in series model. *J. Contam. Hydr.* **43**, 165–185.

Mahimairaja, S., Bolan, N. S., Adriano, D. C., and Robinson, R. (2005). Arsenic contamination and its risk and management in complex environmental settings. *Adv. Agron.* **86**, 1–82.

Malla, P. B. (2002). Vermiculites. *In* "Soil Mineralogy with Environmental Applications" (J. B. Dixon and D. G. Schulze, Eds.), pp. 501–529. SSSA Chapter 16. Book series, no. 7. WI.

Manning, B. A., and Goldberg, S. (1996). Modelling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci. Soc. Am. J.* **60**, 121–131.

Matera, V., Le Hecho, I., Laboudigue, A., Tellierd, S., and Astruc, M. (2003). A methodological approach for the identification of arsenic bearing phases in polluted soils. *Environ. Pollut.* **126**, 51–64.

Martell, A. E. (1975). The influence of natural and synthetic ligands on the transport and function of metal ions in the environment. *Pure Appl. Chem.* **44**, 81–113.

Maskall, J. E., and Thornton, I. (1998). Chemical partitioning of heavy metals in soils, clays and rocks at historical lead smelting sites. *Water, Air Soil Pollut.* **108**, 391–409.

Mattigod, S. V., and Zachara, J. M. (1996). Equilibrium modeling in soil chemistry. *In* "Methods of Soil Analysis: Chemical Methods, Part 3," Chapter 44 (D. L. Sparks, A. L. Page, P. A. Helmke, R. H. Loeppert, P. N. Soltanpour, M. Tabatabai, C. T. Johnson, and M. E. Sumner, Eds.), pp. 1309–1358. SSSA Book Series no. 5.

Mayer, K. U., Frind, E. O., and Blowes, D. W. (2002). Multicomponent reactive transport modeling in variably saturated media using a generalized formulation for kinetically controlled reactions. *Water Resour. Res.,* doi:10.1029-/2001WR000682.

McBride, M. (1989). Reactions controlling heavy metals solubility in soils. *Adv. Soil Sci.* **10**, 1–56.

McBride, M. B., Richards, B. K., Stenhuis, T. S., Russo, J. J., and Sauvé, S. (1997a). Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Sci.* **162**, 487–500.

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

McCarthy, J. F., and Zachara, J. M. (1989). Subsurface transport of contaminants mobile colloids in the subsurface environment may alter transport of contaminants. *Environ. Sci. Technol.* **23**, 496–504.

McGowen, S. L., Basta, N. T., and Brown, G. O. (2001). Use of diammonium phosphate to reduce heavy metals soplubility and transport in smelter contaminated soil. *J. Environ. Qual.* **30**, 493–500.

McLaughlin, M. J., and Tiller, K. G. (1994). Soil salinity causes elevated cadmium concentration in field grow potatoes. *J. Environ. Qual.* **23**, 1013–1018.

McLaughlin, M. J., Parker, D. R., and Clarke, J. M. (1999). Metals and micronutrients: Food safety issues. *Field Crops Res.* **60**, 143–163.

Mench, M. J. (1998). Cadmium availability to plants in relation to major long term changes in agronomy systems. *Agric. Ecos. Environ.* **67**, 175–187.

Mench, M., Vangronsveld, C. H. M., Lepp, N. W., and Edwards, R. (1998). Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. *In* "Metal Contaminated Soils: *In situ* inactivation and phytorestoration" (J. C. H. M. Vangronsveld, S. D. Cunningham, N. W. Lepp, and M. Mench, Eds.), pp. 151–182. R. G. Landes Company, Georgetown, TX. USA.

Moore, P. A., Jr., Daniel, T. C., Gilmour, J. T., Shreve, B. R., Edwards, D. R., and Wood, B. H. (1998). Decreasing metal runoff from poultry litter with aluminium sulfate. *J. Environ. Qual.* **27**, 92–99.

Morris, C., and Mooney, S. J. (2004). A high-resolution system for the quantification of preferential flow in undisturbed soil using observations of traces. *Geoderma* **118**, 133–143.

Mortvedt, J. J., and Osborn, G. (1982). Studies on the chemical form of cadmium contaminants in phosphate fertilizers. *Soil Sci.* **134**, 185–192.

Motelica-Heino, M., Naylor, C., Zhang, H., and Davison, W. (2003). Simultaneous release of metals and sulfide in lacustrine sediment. *Environ. Sci. Technol.* **37**, 4374–4381.

Murray, K. S., Rogers, D. T., and Kaufman, M. M. (2004). Heavy metals in an urban watershed in Southeastern Michigan. *J. Environ. Qual.* **33**, 163–172.

Naidu, R., and Harter, R. D. (1998). Effect of different organic ligands on cadmium sorption by and extractability from soils. *Soil Sci. Soc. Am. J.* **62**, 644–650.

Narasimhan, T. N., White, A. F., and Tokunaga, T. (1986). Groundwater contamination from an inactive uranium mill tailings pile, 2. Application of a dynamic mixing model. *Water Resour. Res.* **22**(13), 1820–1834.

National Research Council (NRC). (2003). Bioavailability of Contaminants in Soils and Sediments: Processes, Tools and Applications. Com. on Bioavailability of Contaminants in Soils ad Sediments, p. 240 Natl. Academy Press, Washington, D.C.

Neal, R. H. (1995). Selenium. *In* "Heavy Metals in Soils" (B. J. Alloway, Ed.), pp. 260–283. Blackie Academic & Professional, London.

Negra, C., Ross, D. S., and Lanzirotti, A. (2005). Soil manganese oxides and trace metals competitive sorption and microfocused synchrotron X-ray fluorescence mapping. *Soil Sci. Soc. Am. J.* **69**, 353–361.

Novillo, J., Obrador, A., Lopez Valdivia, L. M., and Alvarez, J. M. (2002). Mobility and distribution of zinc forms in columns of an acid, a neutral, and a calcareous soil treated with three organic zinc complexes under laboratory conditions. *Aus. J. Soil. Res.* **40**, 791–803.

O'Neill, P. (1995). Arsenic. *In* "Heavy Metals in Soils" (B. J. Alloway, Ed.), pp. 105–121. Blackie Academic & Professional, London.

Ongley, L. K., Armienta, A., and Mango, A. (2003). Concentration of heavy metals in soil, Zimapan, Mexico. *J. Phys.* **107**, 983–986.

Osborne, F. H., and Ehrlich, H. L. (1976). Oxidation of arsenite by a soil isolate of alcaligens. *J. Appl. Bacteriol.* **41**, 295–305.

Oygarden, L., Kvaerner, J., and Jenssen, P. D. (1997). Soil erosion via preferential flow to drainage systems in clay soils. *Geoderma* **76**, 65–86.

Papadopoulos, P., and Rowell, D. L. (1988). The reactions of cadmium with calcite surfaces. *J. Soil Sci.* **43**, 23–36.

Parkhurst, D. L., and Appelo, C. A. J. (1999). User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations, p. 312. Water-Resources Investigations, Report 99-4259, Denver, CO, USA.

Patrick, W. H., Gambrell, R. P., and Khalid, R. A. (1977). Physicochemical factors regulating solubility and bioavailability of toxic heavy metals in contaminated dredged sediments. *J. Environ. Sci. Health* **A12**(9), 475–492.

Petersen, J., and Petrie, J. G. (1999). Modelling heavy metal mobilization in solid waste deposits—A predictive tool for environmental risk assessment. *Water Sci. Technol.* **39**, 193–196.

Planquart, P., Bonin, G., Prone, A., and Massiani, C. (1999). Distribution, movement and plant availability of trace metals in soils amended with sewage sludge compost: Application to low metal loadings. *Sci. Total Environ.* **241**, 161–179.

Plant, J. A., and Raiswell, R. (1983). Principles of environmental geochemistry. *In* "Applied Environmental Geochemistry" (I. Thornton, Ed.). Academic Press, London.

Pot, V., Šimůnek, J., Benoit, P., Coquet, Y., Yra, A., and Martínez-Cordón, M.-J. (2005). Impact of rainfall intensity on the transport of two herbicides in undisturbed grassed filter strip soil cores. *J. Contam. Hydrol.* **81**, 63–88.

Quilbé, R., Pieri, I., Wicherek, S., Dugas, N., Tasteyre, A., Thomas, Y., and Oudinet, J. P. (2004). Combinatory chemical and biological approaces to investigate metal elements in agricultural runoff water. *J. Environ. Qual.* **33**(1), 149–153.

Richards, B. K., Steenhuis, T. S., Peverly, J. H., and Mc Bride, M. B. (1998). Metal mobility at an old, heavily-loaded sludge application site. *Environ. Pollut.* **99**, 365–377.

Rietzler, A. C., Fonseca, A. L., and Lopes, G. P. (2001). Heavy metals in tributaries of Pampulha reservoir, Minas Gerais. *Braz. J. Biol.* **61**, 370–373.

Ringbom, A. (1963)."Complexation in Analytical Chemistry." Interscience Publishers. John Wiley & Sons, London.

Rittmann, B. E., and VanBriesen, J. M. (1996). Microbiological processes in reactive modeling. *In* "Reactive Transport in Porous Media, Reviews in Mineralogy" (P. C. Lichtner, C. I. Steefel, and E. H. Oelkers, Eds.), Chapter 7, Vol. 34, pp. 311–334. Mineralogical Society of America.

Robertson, W. K., Lutrick, M. C., and Yuan, T. L. (1982). Heavy applications of liquid digested sludge on three Ultisols: I. Effects of soil chemistry. *J. Environ. Qual.* **11**, 278–282.

Rose, D. A. (1973). Some aspects of the hydrodynamic dispersion of solutes in porous materials. *J. Soil Sci.* **24**, 284–295.

Ross, S. M. (1994). Retention, transformation and mobility of toxic metals in soils. *In* "Toxic metals in soil-plant systems" (S. M. Ross, Ed.), p. 63. John Wiley & Sons Ltd.

Rowell, L. D. (1994). "Soil Science. Methods and Applications," p. 350. Longman Group, Essex, UK.

Roulet, M., Lucotte, M., Canuel, N., Farella, N., Courcelles, M., Guimãraes, J. R. D., Mergler, D., and Amorim, M. (2000). Increase in mercury contamination recorded in lacustrine sediments following deforestation in the central Amazon. *Chem. Geol.* **165**, 243–266.

Roussel, C., Bril, H., and Fernandez, A. (2000). Arsenic speciation: Involvement in evaluation of environmental impact caused by mine wastes. *J. Environ. Qual.* **29**, 182–188.

Russel, A. P. T., Lawlor, K., Bailey, M., and Macaskie, L. E. (1998). Bioldegradation of metal-EDTA complexes by an enriched microbial population. *Appl. Environ. Microbiol.* **64**, 1319–1322.

Ryan, J., Scheckel, K. G., Berti, W. R., Brown, S. L., Casteel, S. W., Chaney, R. L., Hallfrisch, J., Doolan, M., Grevatt, P., Maddaloni, M., and Mosby, D. (2004). Reducing children's risks from lead in soil. *Environ. Sci. Technol.* **38**, 19A–24A.

Rybicka, E.H, Calmano, W., and Breeger, A. (1995). Heavy metals sorption/desorption on competing clay minerals and experimental study. *Appl. Clay Sci.* **9**, 369–381.

Saaltink, M. W., Battle, F., Ayora, C., Carrera, J., and Olivella, S. (2004). RETRASO, a code for modeling reactive transport in saturated and unsaturated porous media. *Geologica Acta* **2**, 235–251.

Saar, R. A., and Weber, J. H. (1982). Fulvic acid: Modifier of metal ion chemistry. *Environ. Sci. Technol.* **16**, 510–517.

Saha, U. K., Taniguchi, S., and Sakurai, K. (2002). Simultaneous adsorption of cadmium, zinc and lead on hydroxyaluminum and hydroxyaluminosilicate-montnorillonite complexes. *Soil Sci. Soc. Am. J.* **66**, 117–128.

Samper, J., Juncosa, R., Delgado, J., and Montenegro, L. (2000). CORE^{2D}: A code for non-isothermal water flow and reactive solute transport, p. 131. User manual version 2. ENRESA Technical Publication 06/2000.

Sandhu, S. S., and Mills, G. I. (1987). Kinetics and mechanisms of the release of trace inorganic contaminants to ground water from coal ash basins on the Savannah River Plant. Savannah River Ecology Lab., Aiken, SCD. OE/SR/15170-1.

Sauvé, S. (1999). Chemical speciation, solubility and bioavailability of lead, copper and cadmium in contaminated soils, p. 174. Ph.D Dissertation, Cornell University, Ithaca, NY, USA.

Sauvé, S. (2002). Speciation of metals in soils. *In* "Bioavailability of Metals in Terrestrial Ecosystems: Importance of Partitioning for Bioavailability to Invertebrates, Microbes and Plants" (H. E. Allen, Ed.), Chapter 2, pp. 7–37. Society for Environmental Toxicology and Chemistry, Pensacola, FL.

Sauvé, S., McBride, M. B., and Hendershot, W. H. (1997a). Speciation of lead in contaminated soils. *Environ. Pollut.* **98**, 149–155.

Sauvé, S., McBride, M., Norvell, W. A., and Hendershot, W. (1997b). Copper solubility and speciation of *in situ* contaminated soils: Effects of copper level, pH and organic matter. *Water Air Soil Pollut.* **100**, 133–149.

Sauvé, S., McBride, M. B., and Hendershot, W. (1998). Soil solution speciation of lead (II): Effect of organic matter and pH. *Soil Sci. Soc. Am. J.* **62**, 618–621.

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

Sauvé, S., Norvell, W. A., McBride, M., and Hendershot, W. (2000b). Speciation and complexation of cadmium in extracted soil solutions. *Environ. Sci. Technol.* **34**, 291–296.

Sauvé, S., Manna, S., Turmel, M.-C., Roy, A. G., and Courchesne, F. (2003). Solid-solution partitioning of Cd, Cu, Ni, Pb, and Zn in the organic horizons of a forest soil. *Environ. Sci. Technol.* **37**, 5191–5196.

Scheidegger, A. M., Fendorf, M., and Sparks, D. L. (1996). Mechanisms of nickel sorption on pyrophyllite: Macroscopic and microscopic approaches. *Soil Sci. Soc. Am. J.* **60**, 1763–1772.

Schelde, K., Moldrup, P., Jacobsen, O. H., de Jonge, H., de Jonge, L. W., and Komatsu, T. (2002). Diffusion-limited mobilization and transport of natural colloids in macroporous soil. *Vadose Zone J.* **1**, 125–136.

Schmitt, D., Taylor, H. E., Aiken, G. R., Roth, D. A., and Frimmel, F. H. (2002). Influence of natural organic matter on the adsorption of metal ions onto clay minerals. *Environ. Sci. Technol.* **36**, 2932–2938.

Schnitzer, M. (2000). A lifetime perspective on the chemistry of soil organic matter. *Adv. Agron.* **68**, 1–58.

Seaman, J. C., Arey, J. S., and Bertsch, P. M. (2001). Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. *J. Environ. Qual.* **30**, 460–469.

Selim, H. M., Schulin, R., and Flühler, H. (1987). Transport and ion exchange of calcium and magnesium in an aggregated soil. *Soil Sci. Soc. Am. J.* **51**(4), 876–884.

Semple, K. T., Doick, K. J., Jones, K. C., Burauel, P., Craven, A., and Harms, H. (2004). Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environ. Sci. Technol.* **38**, 228A–231A.

Senesi, N. (1992). Metal-humic substance complexes in the environment. Molecular and mechanistic aspects by multiple spectroscopic approach. *In* "Biogeochemistry of trace metals" (D. C. Adriano, Ed.), p. 429. Lewis Publishers, Boca Raton, FL.

Senesi, N., Sposito, G., Yoltzclan, K. M., and Bradford, G. B. (1989). Chemical properties of metal humic acid fractions of a sewage sludge amended aridisol. *J. Environ. Qual.* **18**, 186–194.

Seuntjens, P., Tirez, K., Šimůnek, J., van Genuchten, M., Th., Cornelis, C., and Geuzens, P. (2001). Aging effects on cadmium transport in undisturbed contaminated sandy soil columns. *J. Environ. Qual* **30**, 1040–1050.

Shahandeh, H., and Hossner, L. R. (2000). Enhancement of Cr (III) phytoaccumulation. *Int. J. Phytol.* **2**, 269–286.

Sheppard, S. C., and Evenden, W. G. (1988). The assumption of linearity in soil and plant concentration ratios: An experimental evaluation. *J. Environ. Radioact.* **7**, 221–247.

Sheppard, M. I., and Thibault, D. H. (1990). Default soil solid/liquid partition coefficients, K_ds, for four major soil types: A compendium. *Health Physics* **59**, 471–482.

Šimůnek, J. (2005). Models of water flow and solute transport in the unsaturated zone. *In* "The Encyclopedia of Hydrological Sciences" (M. G. Anderson and J. J. McDonell, Eds.), pp. 1171–1180. John Wiley & Sons, Ltd., Chichester, UK (in press).

Šimůnek, J., and Valocchi, A. J. (2002). Geochemical Transport. *In* "*M*ethods of Soil Analysis, Part 1, Physical Methods" (J. H. Dane and G. C. Topp, Eds.), Chapter 6.9, 3rd edn., pp. 1511–1536. SSSA, Madison, WI.

Šimůnek, J., Šejna, M., and van Genuchten, M. Th. (1998). "The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media," p. 202. Version 2.0, IGWMC-TPS-70, Int., Ground Water Modeling Center, Colorado School of Mines, Golden Colorado.

Šimůnek, J., Šejna, M., and van Genuchten, M. Th. (1999a). "The HYDRUS-2D software package for simulating two-dimensional movement of water, heat, and multiple solutes in variably saturated media," p. 251. Version 2.0, *IGWMC -TPS -53,* International Ground Water Modeling Center, Colorado School of Mines, Golden Colorado.

Šimůnek, J., van Genuchten, M. Th., Sejna, M., Toride, N., and Leij, F. J. (1999b). "The STANMOD Computer Software for Evaluating Solute Transport in Porous Media Using Analytical Solutions of Convection-Dispersion Equation," Versions 1.0 and 2.0, U.S. Salinity Laboratory, USDA, ARS Riverside, CA.

Šimůnek, J., Jarvis, N. J., van Genuchten, M. Th., and Gärdenäs, A. (2003). Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. *J. Hydrol.* **272**, 14–35.

Šimůnek, J., van Genuchten, M. Th., and Šejna, M. (2005). "The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media, p. 270 Version 3.0, *HYDRUS Software Series 1*, Department of Environmental Sciences, University of California Riverside, Riverside, CA.

Šimůnek, J., Jacques, D., van Genuchten, M., Th., and Mallants, D. (2006a). Multicomponent geochemical transport modeling using the HYDRUS-1D computer software package. *J. Am. Water Res. Association* (in press).

Šimůnek, J., Che, C., Pang, J. L., and Bradford, S. A. (2006b). Colloid-Facilitated Transport in Variably-Saturated Porous Media: Numerical Model and Experimental Verification. *Vadose Zone J* (in press).

Singh, B. R., and Myhr, K. (1997). Cadmium leaching from cadmium enriched fertiliser in field lysimeters. *In* "Proceeding of 4th International Conference on the Biogeochemistry of Trace Elements", (I. K. Iskander, S. E. Hardy, A. C. Chang, and G. M. Pierzynski, Eds.), pp. 105–106. International Society of Trace Elements Biogeochemistry, Berkeley, CA.

Singh, S. H., Ma, L. Q., Tack, F. M., and Verloo, M. G. (2000). Trace metal leachability of land disposed dredged sediments. *J. Environ. Qual.* **29**, 1124–1132.

Singh, S. P., Ma, I. Q., and Harris, W. G. (2001). Heavy metals interactions with phosphatic clay: Sorption and desorption behavior. *J. Environ. Qual.* **30**, 1961–1968.

Sparks, K.M, Wells, J. D., and Johnson, B. B. (1997a). Sorption of heavy metals by mineral humic acid substrates. *Aust. J. Soil Res.* **35**, 113–122.

Sparks, K. M., Wells, J. D., and Johnson, B. B. (1997b). The interaction of a humic acid with heavy metals. *Aus. J. Soil. Res.* **35**, 89–101.

Sposito, G. (1983). The chemical form of the trace metals in soils. *In* "Applied Environmental Geochemistry" (I. Thornton, Ed.). Academic Press, London.

Sposito, G. (1989). "The chemistry of soils." Oxford University Press, New York.

Steefel, C. I. (2000). New directions in hydrogeochemical transport modeling: Incorporating multiple kinetic and equilibrium reaction pathways. *In* "Computational Methods in Water Resources XIII" (L. R. Bentley, J. F. Sykes, C. A. Brebbia, W. G. Gray, and G. F. Pinder, Eds.), pp. 331–338. A.A. Balkema, Rotterdam.

Sterckeman, T., Douay, F., Proix, N., and Fourrier, H. (2000). Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. *Environ. Pollut.* **107**, 377–389.

Stevenson, F. J. (1994). "Humus Chemistry." Wiley, New York.

Strawn, D. G., and Sparks, D. L. (2000). Effects of organic matter on the kinetic and mechanisms of Pb (II) sorption and desorption in soil. *Soil Sci. Soc. Am. J.* **64**, 144–156.

Strobel, B. W., Borggaard, O. K., Hansen, H. C. B., Andersen, M. K., and Raulund-Rasmussen, K. (2004). Dissolved organic carbon and decreasing pH mobilize cadmium and copper in soil. *Eur. J. Soil Sci.* **56**, 189–196.

Sun, B., Zhao, F. J., Lombi, E., and McGrath, S. P. (2001). Leaching of heavy metals from contaminated soils using EDTA. *Environ. Pollut.* **113**, 111–120.

Tam, N. F. Y., and Wong, Y. S. (1996). Retention and distribution of heavy metals in mangrove soils receiving wastewater. *Environ. Pollut.* **94**(3), 283–291.

Tamura, T. (1972). Sorption fenomena significant in radioactive waste disposal.pp. 318–330. *In* "Underground waste management and environmental implications" (T. D. Cook, Ed.). Proc. Of Symp., Houston, TX. Memoir no 18. *Am. Assoc. Petrol. Geol.* Tulsa, OK.

Taylor, M. D., and Theng, E. K. G. (1995). Sorption of cadmium by complexes of kaolinite with humic acid. *Commun Soil Sci. Plant Anal.* **26**, 765–776.

Temminghoff, E. J. M., van Der Zee, S. E. A. T. M., and De Haan, F. A. M. (1998). Effects of dissolved organic matter on the mobility of copper in a contaminated sandy soil. *Eur. J. Soil Sci.* **49**, 617–628.

Thompson, S. S., and Yates, M. V. (1999). Bacteriophage inactivation at the air-water-solid interface in dynamic batch systems. *Appl. Environ. Microbiol.* **65**, 1186–1190.

Tiller, K. G., Gerth, J., and Brümmer, G. (1984). The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. *Geoderma* **34**, 17–35.

Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M. R., Lofts, S, Hill, M. T., Farago, M. E., and Thornton, I. (2003). The solid–solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environ. Pollut.* **125**, 213–225.

Toride, N., Leij, F. J., and van Genuchten, M. Th. (1995). "The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments." Version 2.0, Research Report No. 137, U. S. Salinity Laboratory, USDA, ARS, Riverside, CA.

Totsche, K. K., and Kügel-Knabner, I. (2004). Mobile organic sorbent affected contaminant transport in soil: Numerical case studies for enhanced and reduced mobility. *Vadose Zone J.* **3**, 352–367.

Tran, Y. T., Bajracharya, K., and Barry, D. A. (1998). Anomalous cadmium adsorption in flow interruption experiments. *Geoderma* **84**, 169–184.

Tyler, G., and Olsson, T. (2001). Concentration of 60 elements in the soil solution as related to the soil acidity. *Eur. J. Soil Sci.* **52**, 151–165.

VanBriesen, J. (1998). Modeling Coupled Biogeochemical Processes in Mixed Waste Systems. Ph.D Thesis. Civil Engineering. Northwestern University.

van Genuchten, M. Th. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* **44**, 892–898.

van Genuchten, M. Th., and Wagenet, R. J. (1989). Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* **53**, 1303–1310.

van Genuchten, M. Th., and Šimunek, J. (2004). Integrated modeling of vadose zone flow and transport processes. *In* "Unsaturated Zone Modelling: Progress, Challenges and Applications" (R. A. Feddes, G. H. de Rooij, and J. C. van Dam, Eds.), pp. 37–69. Wageningen, The Netherlands, October 3–5, 2004.

Vervaeke, P., Tack, F. M. G., Lust, N., and Verloo, M. (2004). Short and long term effects of the willow root system on metals extractability in contaminated dredged sediment. *J. Environ. Qual.* **33**, 976–983.

Viswanathan, H. S., Robinsons, B. A., Valocchi, A. J., and Triay, I. R. (1998). A reactive transport model of neptunium migration from potential repository at Yucca Mountain. *J. Hydrol.* **209**, 251–280.

Vogeler, T. (2001). Copper and calcium transport through an unsaturated soil column. *J. Environ. Qual.* **30**, 927–938.

Voegelin, A., and Kretzschmar, R. (2003). Modelling sorption and mobility of cadmium and zinc in soils with scaled exchange coefficients. *Eur. J. Soil Sci.* **54**(2), 387–400.

Vogeler, I., Green, S. R., Clothier, B. E., Kirkham, M. B., and Robinson, B. H. (2001). "Contaminant Transport in the Root Zone." p. 23. CRC Press.

Walter, A. L., Frind, E. O., Blowes, D. W., Ptacek, C. J., and Molson, J. W. (1994). Modeling of multicomponent reactive transport in groundwater 2. Metal mobility in aquifers impacted by acidic mine tailings discharge. *Water Resour. Res.* **30**(11), 3149–3158.

Wan, J., and Wilson, J. L. (1994). Visualization of the role of the gas-water interface on the fate and transport of colloids in porous media. *Water Resour. Res.* **30**, 11–23.

Wan, J. M., and Tokunaga, T. K. (2002). Partitioning of clay colloids at air-water interfaces. *J. Colloid Interface Sci.* **247**, 54–61.

Weigand, H., and Totsche, K. U. (1998). Flow and reactivity effects on dissolved organic matter transport in soil columns. *Soil Sci. Soc. Am. J.* **62**, 1268–1274.

White, N., and Zelazny, L. W. (1986). Charge properties in soil colloids. *In* "Soil physical chemistry" (D. L. Sparks, Ed.), pp. 39–81. CRC Press, Boca Raton, Florida.

White, R. E. (1985). The influence of macropores on the transport of dissolved and suspended matter through soil. *In* (B. A. Stewart, Ed.). *Adv. Soil Sci.* **3,** 95–120.

Wilcke, W., Kretzschman, S., Bundt, M., and Zech, W. (1999). Metal concentration in aggregate interiors, exteriors, whole aggregates, and bulk of Costa Rican soils. *Soil Sci. Soc. Am. J.* **63**, 1244–1249.

Williams, C. H., and David, D. J. (1976). The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. *Soil Sci.* **121**, 86–93.

Wingenfelder, U., Hansen, C., Furrer, G., and Schulin, R. (2005). Removal of heavy metals from mine waters by zeolites. *Environ. Sci. Technol.* **39**, 4606–4613.

Wood, J. M. (1974). Biological cycles for toxic elements in the environment. *Science* **183**, 1049–1052.

Wu, L. H., Luo, Y. M., Xing, X. R., and Christie, P. (2003). EDTA-enhanced phytoremediation of heavy metal contaminated soil with Indian mustard and associated potential leaching. *Agric. Ecosys. Environ.* **102**, 307–318.

Yeh, G.-T., and Cheng, H.-P. (1999). "3DHYDROGEOCHEM: A 3-dimensional model of density-dependent subsurface flow and thermal multispecies-multicomponent HYDROGEOCHEMical transport," p. 150. EPA/600/R-98/159.

Yeh, G. T., and Tripathi, V. S. (1991). A model for simulating transport of reactive multispecies components: Model development and demonstration. *Water Resour. Res.* **27**(12), 3075–3094.

Yeh, G. T., Sharp-Hansen, S., Lester, B., Strobl, R., and Scarbrough, J. (1992)."3DFEMWATER/3DLEWASTE: Numerical codes for delineating wellhead protection areas in agricultural regions based on the assimilative capacity criterion," p. 278. Office of Research and Development, Environmental Protection Agency, Athens, GA. EPA/600/R-92/223.

Zachara, J. M., Smith, S. C., McKinley, J. P., and Resch, C. R. (1993). Cadmium sorption on specimen and soil smectites in sodium and calcium electrolytes. *Soil Sci. Soc. Am. J.* **57**, 1491–1501.

Zhang, M. K., He, Z. L., Cañvert, D. V., Stoffela, P. J., Yang, X. E., and Li, Y. C. (2003). Phosphorus and heavy metals attachment and release in sandy soil aggregate fractions. *Soil Sci. Soc. Am. J.* **67**, 1158–1167.