



Ground Water Issue

Behavior of Metals in Soils

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The Regional Superfund Ground-Water Forum is a group of scientists, representing EPA's Regional Superfund Offices, organized to exchange up-to-date information related to ground-water remediation at Superfund sites. One of the major issues of concern to the Forum is the mobility of metals in soils as related to subsurface remediation.

For the purposes of this Issue Paper, those metals most commonly found at Superfund sites will be discussed in terms of the processes affecting their behavior in soils as well as laboratory methods available to evaluate this behavior. The retention capacity of soil will also be discussed in terms of the movement of metals between the other environmental compartments including ground water, surface water, or the atmosphere. Long-term changes in soil environmental conditions, due to the effects of remediation systems or to natural weathering processes, are also discussed with respect to the enhanced mobility of metals in soils.

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Introduction

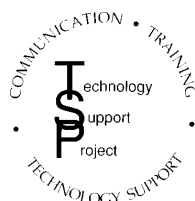
The purpose of this document is to introduce to the reader the fundamental processes that control the mobility of metals in the soil environment. This discussion will emphasize the basic chemistry of metals in soils and will provide information on laboratory methods used to evaluate the behavior of metals in soils. The metals selected for discussion in this document are the metals most commonly found at Superfund sites and will be limited to lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu), mercury (Hg), silver (Ag), and selenium (Se).

Metals are defined as any element that has a silvery luster and is a good conductor of heat and electricity. There are many terms used to describe and categorize metals, including trace metals, transition metals, micronutrients, toxic metals, heavy metals. Many of these definitions are arbitrary and these terms have been used loosely in the literature to include elements that do not strictly meet the definition of the term. Strictly speaking arsenic and selenium are not metals but are metalloids, displaying both metallic and non-metallic properties. For this paper, the term metal will be used to include all the elements under discussion.

The average concentration of select metals in soils is listed in Table 1. All soils naturally contain trace levels of metals. The presence of metals in soil is, therefore, not indicative of contamination. The concentration of metals in uncontaminated soil is primarily related to the geology of the parent material from which the soil was formed. Depending on the local geology, the concentration of metals in a soil may exceed the ranges listed in Table 1. For example, Se concentration in non-seleniferous soils in the U.S. range from 0.1 to 2 mg/Kg. In seleniferous soils, Se ranges from 1 to 80 mg/Kg, with reports of up to 1200 mg/Kg Se (McNeal and Balistrier, 1989). Use of common ranges or average concentration of trace metals in soils as an indicator of whether a soil is contaminated is not appropriate since the native concentration of metals in a specific soil may fall out of the listed ranges. Only by direct analysis of uncontaminated soils can background levels of metals be determined.

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Table 1. Content of Various Elements in Soils (Lindsay, 1979)

<i>Metal</i>	<i>Selected Average for Soils mg/kg</i>	<i>Common Range for Soils mg/kg</i>
Al	71,000	10,000-300,000
Fe	38,000	7,000-550,000
Mn	600	20-3,000
Cu	30	2-100
Cr	100	1-1000
Cd	0.06	0.01-0.70
Zn	50	10-300
As	5	1.0-50
Se	0.3	0.1-2
Ni	40	5-500
Ag	0.05	0.01-5
Pb	10	2-200
Hg	0.03	0.01-0.3

Metals associated with the aqueous phase of soils are subject to movement with soil water, and may be transported through the vadose zone to ground water. Metals, unlike the hazardous organics, cannot be degraded. Some metals, such as Cr, As, Se, and Hg, can be transformed to other oxidation states in soil, reducing their mobility and toxicity.

Immobilization of metals, by mechanisms of adsorption and precipitation, will prevent movement of the metals to ground water. Metal-soil interaction is such that when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix in question.

Fate of Metals in the Soil Environment

In soil, metals are found in one or more of several "pools" of the soil, as described by Shuman (1991):

- 1) dissolved in the soil solution;
- 2) occupying exchange sites on inorganic soil constituents;
- 3) specifically adsorbed on inorganic soil constituents;
- 4) associated with insoluble soil organic matter;
- 5) precipitated as pure or mixed solids;
- 6) present in the structure of secondary minerals; and/or
- 7) present in the structure of primary minerals.

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fraction, and those fractions in equilibrium with this fraction, i.e., the exchange fraction, are of primary

importance when considering the migration potential of metals associated with soils.

Multiphase equilibria must be considered when defining metal behavior in soils (Figure 1). Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and As. At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated.

Most studies of the behavior of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reactions are likely to occur under prescribed conditions, but do not indicate the time period involved. The kinetic aspect of oxidation/reduction, precipitation/dissolution, and adsorption/desorption reactions involving metals in soil matrix suffers from a lack of published data. Thus the kinetic component, which in many cases is critical to predict the behavior of metals in soils, cannot be assessed easily. Without the kinetic component, the current accepted approach is to assume that local equilibrium occurs in the soil profile. Equilibrium thermodynamic data can then be applied not only to predict which precipitation/dissolution, adsorption/desorption, and/or oxidation/reduction reactions are likely to occur under a given set of conditions, but also to estimate the solution composition, i.e., metal concentration in solution, at equilibrium. This approach relies heavily on the accuracy of thermodynamic data that can be found in the literature.

Soil Solution Chemistry

Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+} , Zn^{2+} , Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., CdSO_4^0 , ZnCl^+ , CdCl_3^-), or associated with mobile inorganic and organic colloidal material. A complex is defined as an unit in which a central metal ion is bonded by a number of associated atoms or molecules in a defined geometric pattern, e.g. ZnSO_4^0 , CdHCO_3^+ , $\text{Cr}(\text{OH})_4^-$. The associated atoms or molecules are termed ligands. In the above examples, SO_4^{2-} , HCO_3^- , and OH^- are ligand. The total concentration of a metal, Me_T , in the soil solution is the sum of the free ion concentration $[\text{Me}^{z+}]$, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material.

Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are SO_4^{2-} , Cl^- , OH^- , PO_4^{3-} , NO_3^- and CO_3^{2-} . Soil organic ligands include low molecular weight aliphatic, aromatic, and amino acids and soluble constituents of fulvic acids. Formation constants for various metal complexes are available in the literature (e.g., see Nordstrom and Munoz, 1985; Lindsay, 1979; Martell and Smith, 1974 -1982). Organic complexation of metals in soil is not as well defined as inorganic complexation because of the difficulty of identifying the large number of organic ligands that

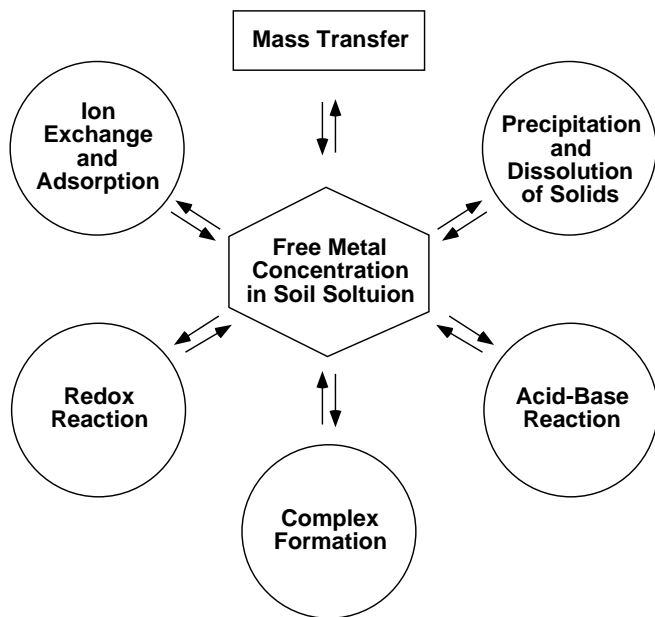


Figure 1. Principal controls on free trace metal concentrations in soils solution (Mattigod, et al., 1981).

may be present in soils. Most of the metal-organic complex species identified in the literature were generated from metal interaction with fulvic acids extracted from sewage sludges (Baham, et al., 1978; Baham and Sposito, 1986; Behel, et al., 1983; Boyd et al., 1979; Boyd et al., 1983; Dudley, et al., 1987; Lake et al., 1984; Sposito et al., 1979; Sposito et al., 1981; Sposito et al., 1982). The soluble metal organic complexes that may form in other waste systems, however, have not been identified.

The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion. With complexation, the resulting metal species may be positively or negatively charged or be electrically neutral (e.g., CdCl_3^+ , CdCl^- , CdCl_2^0). The metal complex may be only weakly adsorbed or more strongly adsorbed to soil surfaces relative to the free metal ion. A more detailed discussion on the effect complex formation has on metal mobility is given in the section: Effect of anions on adsorption and precipitation. Speciation not only affects mobility of metals but also the bioavailability and toxicity of the metal. The free metal ion is, in general, the most bioavailable and toxic form of the metal.

Several metals of environmental concern exist in soils in more than one oxidation state: arsenic, As(V) and As(III), selenium, Se(VI) and Se(IV), chromium, Cr(VI) and Cr(III), and mercury, Hg(II) and Hg(I). The oxidation state of these metals determines their relative mobility, bioavailability, and toxicity. For example, hexavalent Cr is relatively mobile in soils, being only weakly sorbed by soils. Hexavalent Cr is also extremely toxic and a known carcinogen. Trivalent Cr, on the other hand, is relatively immobile in soil, being strongly sorbed by soils and readily forming insoluble precipitates, and it is of low toxicity.

Atomic absorption spectrophotometers (AA) and inductively coupled plasma emission spectrometers (ICP) are commonly used to determine the metal concentration in soil solutions. Both techniques measure the total metal concentration in the solution without distinguishing metal speciation or oxidation state. Free metal, complexed metal ion concentrations and concentration of metals in different oxidation states can be determined using ion selective electrodes, polarography, colorimetric procedures, gas chromatography-AA, and high performance liquid chromatography-AA (see Kramer and Allen, 1988). While these specific methods are necessary for accurate measurements of metal speciation and oxidation state, these methods are not routinely performed by commercial laboratories nor are these procedure standard EPA methods.

Metal concentrations determined by AA or ICP are often used as inputs into a thermodynamic computer program, such as MINTEQA2 (USEPA, 1987). This program can be used to calculate the speciation and oxidation state of metals in soil solution of known composition. Formation constants are known for many metal complexes. There is, however, only limited information for metal-organic complexes, including formation constants for many naturally occurring ligands and those in waste disposal systems. The required input data for these models include: the concentration of the metal of interest, the inorganic and organic ligands, and the major cations and other metal ions, and pH. In specific cases the redox potential and pCO_2 also may be required. Output consists of an estimation of the concentration of free metals and complexed metals at equilibrium for the specified conditions.

Many predictive methods, based on solution and solid phase chemistry, do not adequately describe transport of metals under field conditions. Solution chemistry considers the interaction between dissolved species, dissolved being defined as substances that will pass a $0.45\mu\text{m}$ filter. However, in addition to dissolved metal complexes, metals also may associate with mobile colloidal particles. Colloidal size particles are particles with a diameter ranging from 0.01 and $10\mu\text{m}$ (Sposito, 1989). Gschwend and Reynolds (1987) reported that colloidal particles of intermediate diameter, $0.1\mu\text{m}$ to $1\mu\text{m}$, were the most mobile particles in a sandy medium. Colloidal particles include iron and manganese oxides, clay minerals, and organic matter. These surfaces have a high capacity for metal sorption. Puls et al. (1991) reported a 21 times increase in arsenate transport in the presence of colloidal material compared with dissolved arsenate. This increased transport of contaminants associated with mobile colloidal material has been termed facilitated transport.

Solid Phase Formation

Metals may precipitate to form a three dimensional solid phase in soils. These precipitates may be pure solids (e.g., CdCO_3 , $\text{Pb}(\text{OH})_2$, ZnS_2) or mixed solids (e.g., $(\text{Fe}_x\text{Cr}_{1-x})(\text{OH})_3$, $\text{Ba}(\text{CrO}_4, \text{SO}_4)$). Mixed solids are formed when various elements co-precipitate. There are several types of co-precipitation, inclusion, adsorption and solid solution formation, distinguished by the type of association between the trace element and the host mineral (Sposito, 1989). Solid solution formation occurs when the trace metal is compatible

with the element of the host mineral and thus can uniformly replace the host element throughout the mineral. An example of solid solution formation is the substitution of Cd for Ca in calcium carbonate. Cadmium and Ca have almost identical ionic radii so that Cd can readily substitute of Ca in this carbonate mineral. Mechanisms of retention, whether surface adsorption, surface precipitation, co-precipitation, and pure solid formation are often difficult to distinguish experimentally. Retention involves a progression of these processes. The term sorption is used when the actual mechanism of metal removal from the soil solution is not known.

Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and with metal concentration (or activity). The diagrams also allow some prediction of which solid phase regulates metal activity in the soil solution. Methods for constructing such diagrams is given in Sposito (1989) and Lindsay (1979). Santillan-Medrano and Jurinak (1975) used stability diagrams for predicting the formation of precipitates of Pb and Cd in a calcareous soil. The stability diagrams (Figures 2 and 3) illustrate the decrease in Pb and Cd solubility with increasing pH, which is the usual trend with cationic metals. Solution activity of Cd is consistently higher than that for Pb indicating that Cd may be more mobile in the environment. Lead phosphate compounds at lower pH and a mixed Pb compound at pH>7.5 could be the solid phases regulating Pb in solution. The authors concluded that cadmium solution activity is regulated by the formation of CdCO₃ and Cd(PO₄)₂ or a mixed Cd solid at pH<7.5. At higher pH, the system is undersaturated with respect to the Cd compounds considered.

The formation of a solid phase may not be an important mechanism compared to adsorption in native soils because of the low concentration of trace metals in these systems (Lindsay, 1979). Precipitation reactions may be of much greater importance in waste systems where the concentration of metals may be exceedingly high. McBride (1980)

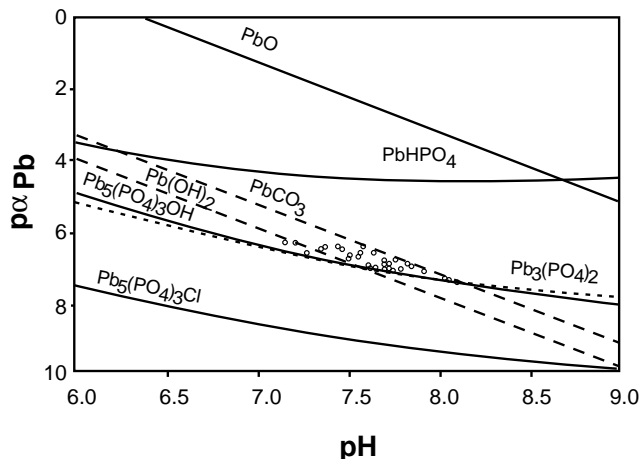


Figure 2. The solubility diagram for Pb in Nibley clay loam soil (Santillan-Medrano and Jurinak, 1975).

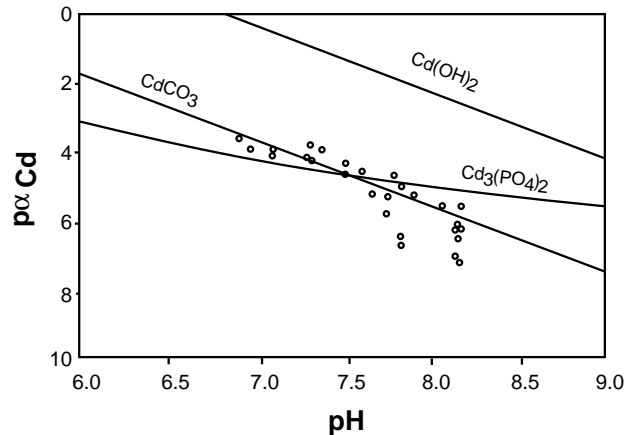


Figure 3. The solubility diagram for Cd in Nibley clay loam soil (Santillan-Medrano and Jurinak, 1975).

concluded that calcite (CaCO₃) serves as a site for adsorption of Cd²⁺ at low concentrations of Cd, while CdCO₃ precipitation, possibly as a coating on the calcite, occurs only at higher Cd concentrations.

Surface Reactions

Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption differs from precipitation in that the metal does not form a new three dimensional solid phase but is instead associated with the surfaces of existing soil particles. The soil matrix often includes organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates.

Soil organic matter consists of 1) living organisms, 2) soluble biochemicals (amino acids, proteins, carbohydrates, organic acids, polysaccharides, lignin, etc.), and 3) insoluble humic substances. The biochemicals and humic substances provide sites (acid functional groups, such as carboxylic, phenolics, alcoholic, enolic-OH and amino groups) for metal sorption. A discussion of the nature of soil organic matter and its role in the retention of metals in soil is given by Stevenson (1991) and Stevenson and Fitch (1990). The biochemicals form water soluble complexes with metals, increasing metal mobility, as discussed in a previous section. The humic substances consists of insoluble polymers of aliphatic and aromatic substances produced through microbial action. Humic substances contain a highly complex mixture of functional groups. Binding of metals to organic matter involves a continuum of reactive sites, ranging from weak forces of attraction to formation of strong chemical bonds. Soil organic matter can be the main source of soil cation exchange capacity, contributing >200meq/100 g of organic matter in surface mineral soils. Organic matter content, however, decreases with depth, so that the mineral constituents of soil will become a more important surface for sorption as the organic matter content of the soil diminishes.

There have been numerous studies of the adsorptive properties of clay minerals, in particular montmorillonite and

kaolinite, and iron and manganese oxides. Jenne (1968) concluded that Fe and Mn oxides are the principal soil surface that control the mobility of metals in soils and natural water. In arid soils, carbonate minerals may immobilize metals by providing an adsorbing and nucleating surface (Santillan-Medrano and Jurinak, 1975; Cavallaro and McBride, 1978; McBride, 1980; Jurinak and Bauer, 1956; McBride and Bouldin, 1984; Dudley et al., 1988; Dudley et al., 1991).

Soil surfaces carry either a net negative or positive charge depending on the nature of the surface and the soil pH. The permanent net negative charge on surfaces is due to charge imbalance resulting from the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layers and/or substitution of Mg^{2+} , Fe^{2+} , etc. for Al^{3+} in the octahedral layers of aluminosilicate clays. The charge on the surface is not affected by changes in soil pH and hence it is termed a permanent charged surface. pH dependent charged surfaces are associated with the edges of clay minerals, with the surfaces of oxides, hydroxides and carbonates, and with organic matter (acid functional groups). The charge arises from the association and dissociation of protons from surface functional groups. Using an iron oxide surface functional group as an example, the association of protons with the functional group results in a positive charge [$-Fe-OH_2^+$] and dissociation of protons, under more alkaline conditions, results in a negative charge [$-Fe-O^-$]. At the point of zero net proton charge (PZNPC) the functional group is neutral [$-Fe-OH^0$]. For all pH dependent charged surfaces, whether organic or inorganic, as the pH decreases, the number of negatively charged sites diminishes. Under more acidic conditions, the majority of pH dependent surfaces will be positively charged and under more alkaline conditions, the majority of sites will be negatively charged. The pH dependent charged surfaces in soils differ widely in their PZNPC.

The structural charge developed on either a permanent charged surface or a pH dependent charged surface must be balanced by ions of opposite charge at or near the surface. The cation exchange capacity is a measure of the negatively charged sites for cation adsorption and anion exchange capacity is a measure of the positively charged sites for anion adsorption. The anion capacity is, however, very small relative to the cation adsorption capacity of soils.

A surface complexation model is often used to describe adsorption behavior (Sposito, 1989). Several types of surface complexes can form between a metal and soil surface functional groups and are defined by the extent of bonding between the metal ion and the surface (Figure 4). Metals in a diffuse ion association or in an outer sphere complex are surrounded by waters of hydration and are not directly bonded to the soil surface. These ions accumulate at the interface of the charged surfaces in response to electrostatic forces. These reactions are rapid and reversible with only a weak dependence on the electron configuration of the surface group and the adsorbed ion. These two metal-surface interactions have also been termed exchange reactions because the introduction of other cations into the system, in sufficient concentration, causes the replacement or exchange of the original cations. Metals associated with exchange sites may, depending on the environment, be relatively mobile. Exchangeable metals may be the most significant reserve of potentially mobile metals in soil (Silveira and Sommers, 1977; Latterell et al., 1978).

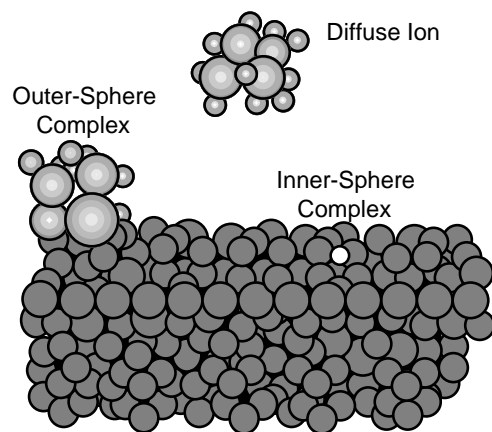


Figure 4. The three mechanisms of cation adsorption on a siloxane surface (e.g., montmorillonite). (Sposito, 1989).

With inner sphere complexation, the metal is bound directly to the soil surface, no waters of hydration are involved. It is distinguished from the exchangeable state by having ionic and/or covalent character to the binding between the metal and the surface. A much higher bonding energy is involved than in exchange reactions, and the bonding depends on the electron configuration of both the surface group and the metal. This adsorption mechanism is often termed specific adsorption. The term specific implies that there are differences in the energy of adsorption among cations, such that other ions, including major cations, Na, Ca, Mg, do not effectively compete for specific surface sites. Specifically adsorbed metal cations are relatively immobile and unaffected by high concentrations of the major cations due to large differences in their energies of adsorption.

At low concentrations, metals are adsorbed by the specific adsorption sites. These adsorbed metals are not removed by the input of major cations. With increasing concentration of the metal, the specific sites become saturated and the exchange sites are filled (Hendrickson and Corey, 1981; Lehmann and Harter, 1984; Garcia-Miragaya et al., 1986; O'Connor et al., 1984; O'Connor et al., 1983). Metals associated with these nonspecific sites are exchangeable with other metal cations and are thus potentially mobile. For example, in an adsorption study using Cd, O'Connor et al. (1984) showed two mechanisms were responsible for metal retention by soil. The authors attributed the first mechanism, active at low concentration (0.01-10mg/L added Cd), to specific adsorption. At higher concentrations (100-1000mg/L added Cd), adsorption was attributed to exchange reactions. Desorption studies showed that the added Cd at low concentration was not removed by 0.05M calcium solutions, whereas at the higher loading rates, the calcium salt removed significant amounts of the adsorbed Cd. These results indicate that the observed affinity of a metal for soil surfaces is concentration dependent. These results also emphasize the importance of using literature or laboratory generated values that cover the range of metal concentration of interest at a specific location. Use of data generated in the wrong concentration range may lead to misinterpretation of the metal binding strength of the soil.

The relative affinity of a soil surface for a free metal cation increases with the tendency of the cation to form strong bonds, i.e., inner sphere complexes, with the surface. The general order of preference for monovalent cations by montmorillonite is Cs > Rb > K = NH₄ > Na > Li. For the alkaline earth metals the order is Ba > Sr > Ca > Mg. The preference series indicates a greater attraction of the surface for the less hydrated cations that can fit closer to the clay surface. For transition metals, the size of the hydrated cation cannot be used as the only predictor of adsorption affinity since the electron configuration of a metal plays an important role in adsorption. Table 2 reports on results from various researches on the relative sorption affinity of metals onto a variety of soils and soil constituents. Although there is consistently a higher affinity of these surfaces for Pb and Cu compared with Zn or Cd, the specific order of sorption affinity depends on the properties of the metals, surface type, and experimental conditions.

Anions in the Soil Environment

Common anionic contaminants of concern include: arsenic (AsO₄³⁻ and AsO₂⁻), selenium (SeO₃²⁻ and SeO₄²⁻), and chromium in one of its oxidation states (CrO₄²⁻). Soil particles, though predominantly negatively charged, also may carry some positive charges. The oxide surfaces, notably iron, manganese, and aluminum oxides, carbonate surfaces, and insoluble organic matter can generate a significant number of positive charges as the pH decreases. The edges of clay minerals also carry pH dependent charge. These edge sites may be important sites of retention of anions at pHs below the point of zero charge (PZC).

Clay minerals, oxides, and organic matter exert a strong preference for some anions in comparison to other anions, indicating the existence of chemical bonds between the surface and the specific anion. Phosphate has been the most extensively studied anion that exhibits this specific adsorption (inner sphere complex) phenomenon. Selenite (SeO₃²⁻) and arsenate (AsO₄³⁻) are adsorbed to oxides and soils through specific binding mechanisms (Rajan, 1979; Neal, et al., 1987b). Selenite (SeO₄²⁻) and hexavalent chromium are only

weakly bound to soil surfaces and are thus easily displaced by other anions. Balistrieri and Chao (1987) found the sequence of adsorption of anions onto iron oxide to be: phosphate = silicate = arsenate > bicarbonate/carbonate > citrate = selenite > molybdate > oxalate > fluoride = selenate > sulfate. The adsorption capacity for anions is, however, small relative to cation adsorption capacity of soils.

Soil Properties Affecting Adsorption

The adsorption capacity (both exchange and specific adsorption) of a soil is determined by the number and kind of sites available. Adsorption of metal cations has been correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content. Anion adsorption has been correlated with Fe and Mn oxide content, pH, and redox potential. Adsorption processes are affected by these various soil factors, by the form of the metal added to the soil, and by the solvent introduced along with the metal. The results of these interactions may increase or decrease the movement of metals in the soil water.

Korte et al. (1976) qualitatively ranked the relative mobilities of 11 metals added to 10 soils (Table 3) to simulate movement of metals under an anaerobic landfill situation. The leachate used was generated in a septic tank, preserved under carbon dioxide and adjusted to pH of 5. Of the cationic metals studied lead and copper were the least mobile and mercury(II) was the most mobile (Figure 5). The heavier textured soils with higher pHs (Molokai, Nicholson, Mohaveca and Fanno) were effective in attenuating the metals, while sandy soils and/or soils with low pH did not retain the metals effectively. For the anionic metals, clay soils containing oxides with low pH were relatively effective in retaining the anions (Figure 6). As with the cationic metals, the light textured soils were the least effective in retaining the anions. Chromium (VI) was the most mobile of the metals studied. Griffin and Shimp (1978) found the relative mobility of nine metals through montmorillonite and kaolinite to be: Cr(VI) > Se > As(III) > As(V) > Cd > Zn > Pb > Cu > Cr(III).

Table 2. Relative affinity of metals for soils and soil constituents

Soil or Soil Constituent	Relative Order of Sorption	Reference
goethite	Cu>Pb>Zn>Co>Cd	Forbes et al., 1976
Fe oxide	Pb>Cu>Zn>Cd	Benjamin and Leckie, 1981
montmorillonite	Cd=Zn>Ni	Puls and Bohn, 1988
kaolinite	Cd>Zn>Ni	Puls and Bohn, 1988
soils	Pb>Cu>Zn>Cd>Ni	Biddappa et al., 1981
soils	Zn>Ni>Cd	Tiller et al., 1984
mineral soils	Pb>Cu>Zn>Cd	Elliott et al., 1986
organic soils	Pb>Cu>Cd>Zn	Elliott et al., 1986
soil	Pb>Cu>Zn>Ni	Harter, 1983

Table 3. Characteristics of the soils (Korte et al., 1976)

Soil	Order	pH meq/100g	CEC m2/g	Surface Area %	Free Fe oxides %	Clay	Texture
Wagram	Ultisol	4.2	2	8.0	0.6	4	loamy sand
Ava	Alfisol	4.5	19	61.5	4	31	silty clay loam
Kalkaska	Spodosol	4.7	10	8.9	1.8	5	sand
Davidson	Ultisol	6.2	9	61.3	17	61	clay
Molokai	Oxisol	6.2	14	67.3	23	52	clay silty clay
Chalmers	Mollisol	6.6	26	125.6	3.1	35	loam
Nicholson	Alfisol	6.7	37	120.5	5.6	49	silty day
Fanno	Alfisol	7	33	122.1	3.7	46	clay
Mohave	Aridisol	7.3	10	38.3	1.7	11	sandy loam
Mohave ca	Aridisol	7.8	12	127.5	2.5	40	clay loam
Anthony	Entisol	7.8	6	19.8	1.8	15	sandy loam

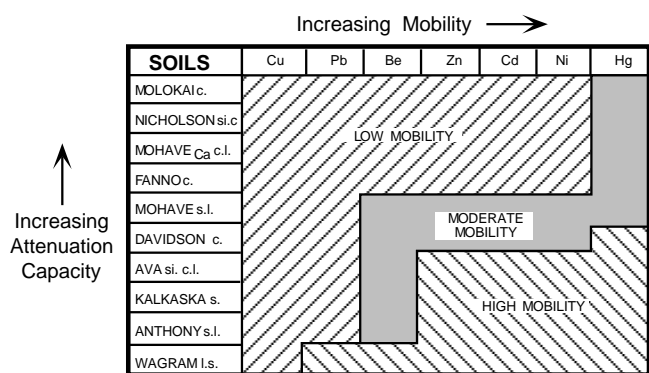


Figure 5. Relative mobility of cations through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976).

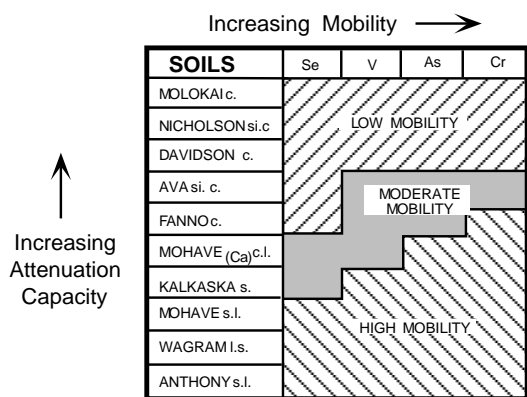


Figure 6. Relative mobility of anions through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976).

Factors Affecting Adsorption and Precipitation Reactions

Although the principles affecting sorption and precipitation are similar for cationic and anionic metals, for clarity, the following section will concentrate on a general discussion of factors affecting the behavior of cationic metals in soils. Factors affecting anion adsorption and precipitation will be discussed for each individual metal anion in a later section.

Effect of competing cations

For specific adsorption sites, trace cationic metals are preferentially adsorbed over the major cations (Na, Ca, Mg) and trace anionic metals are preferentially adsorbed over major anions (SO_4^- , NO_3^- , soluble ionized organic acids). However, when the specific adsorption sites become saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important. Cavallaro and McBride (1978) found that adsorption of Cu and Cd decreased in the presence of 0.01M $CaCl_2$. They attributed this decrease to competition with Ca for adsorption sites. Cadmium adsorption was more affected by the presence of Ca than Cu. The mobility of Cd may be greatly increased due to such competition. Likewise, Harter (1979) indicated the Ca in solution had a greater effect on Pb adsorption than on Cu. In another study, Harter (1992) added Cu, Ni and Co to calcium saturated soils. The presence of Ca, a common ion in soils with $pH > 5.6$, did not affect Cu sorption but did limit the sorption of Co and Ni. The author emphasized the importance of these results in that standard management practice for metal contaminated soils is to raise the pH to 7, often using a Ca buffered system. The addition of Ca, as low as 0.01M Ca, may increase the mobility of some metals by competing for sorption sites.

Trace metals also will compete with each other for adsorption sites. Although there have been several studies on the relative adsorption affinities of trace metals by soils and soil constituents (see Table 2), these studies have compared how much of each metal, added to the soils as individual

components, was adsorbed and not whether the adsorption of one metal will interfere with that of another. Few studies have looked directly at the competitive adsorption of metals. Kuo and Baker (1980) reported that the presence of Cu interfered with the adsorption of Zn and Cd. Adsorbed Cu was not significantly affected by added Zn but the presence of Cu, at concentrations as low as 15 µg/L, completely prevented Zn adsorption in one soil with a low cation exchange capacity (Kurdi and Doner, 1983). In contrast, McBride and Blasiak (1979) found that Cu was ineffective in competing for Zn adsorption sites over a pH range of 5-7. The inability of Cu to block Zn adsorption in this study was taken as evidence that Zn and Cu were preferentially adsorbed at different sites. Simultaneous addition of Cd and Zn to Mn oxide lowered the adsorption of both metals (Zasoski and Burau, 1988).

The presence of other cations, whether major or trace metals, can significantly effect the mobility of the metal of interest. Use of data from the literature, generation of laboratory data, or use of computer models that do not reflect the complex mixture of metals specific to a site may not be useful to understand or accurately predict metal mobility.

Effect of complex formation

Metal cations form complexes with inorganic and organic ligands. The resulting association has a lower positive charge than the free metal ion, and may be uncharged or carry a net negative charge. For example, the association of cadmium with chloride results in the following series of charged and uncharged cadmium species: Cd^{2+} , CdCl^+ , CdCl_2^0 , CdCl_3^- . Benjamin and Leckie (1982) stated that the interaction between metal ions and complexing ligands may result in either a complex that is weakly adsorbed to the soil surface or in a complex that is more strongly adsorbed relative to the free metal ion. In general, the decrease in positive charge on the complexed metal reduces adsorption to a negatively charged surface. One noted exception is the preferential adsorption of hydrolyzed metals (MeOH^+) versus the free bivalent metal (James and Healy, 1972). The actual effect of complex formation on sorption depends on the properties of the metal of interest, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox conditions, as is illustrated by the follow research results.

In the presence of the inorganic ligands Cl^- and SO_4^{2-} , the adsorption of Cd on soil and soil constituents was inhibited (O'Connor, et al., 1984; Hirsch et al., 1989; Egozy, 1980; Garcia-Miragaya and Page, 1976; Benjamin and Leckie, 1982) due to the formation of cadmium complexes that were not strongly adsorbed by the soils. Using much higher concentrations of salt than normally encountered in soil solutions (0.1 to 0.5M NaCl), Doner (1978) concluded that the increased mobility of Ni, Cu, and Cd through a soil column was due to complex formation of the metals with Cl^- . The mobility of Cd increased more than that of Ni and Cu, Ni being the least mobile. These observed mobilities are in the same order as that of the stability constants of the chloride complexes of these metals. Within normal concentration of electrolytes in soil solution, Elrashidi and O'Connor (1982) found no measurable change in Zn adsorption by alkaline soils due to complex formation of Zn with Cl^- , NO_3^{2-} , or SO_4^{2-} ions. Under these conditions (anion concentration of 0.1M), anion complex formation did not compete with the highly selective adsorption sites for Zn. Shuman (1986), using acid soils,

observed a decreased adsorption of Zn in the presence of Cl^- at the concentration of CaCl_2 used by Elrashidi and O'Connor (1982) but no effect at lower concentrations. McBride (1985), using aluminum oxide, and Cavallaro (1982), using clays, found that high levels of phosphate suppressed adsorption of Cu and Zn. Phosphate did not form strong complexes with Cu or Zn but it was strongly adsorbed to soil surfaces thus physically blocking the specific adsorption sites of Cu and Zn. Other researchers (Kuo and McNeal, 1984; Stanton and Burger, 1970; Bolland et al., 1977), using lower concentrations of added phosphate, demonstrated enhanced adsorption of Zn and Cd on oxide surfaces. At the concentration of phosphate used in these studies, the adsorption of phosphate onto the oxide surfaces increased the negative charge on the oxide surface, thus enhancing adsorption of the metal cations.

Complex formation between metals and organic ligands affects metal adsorption and hence mobility. The extent of complexation between a metal and soluble organic matter depends on the competition between the metal-binding surface sites and the soluble organic ligand for the metal. Metals that readily form stable complexes with soluble organic matter are likely to be mobile in soils. Overcash and Pal (1979) reported that the order of metal-organic complex stabilities, for the system they studied, was $\text{Hg} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Cd}$. Khan et al. (1982) showed that the mobility of metals through soil followed the order: $\text{Cu} > \text{Ni} > \text{Pb} > \text{Ag} > \text{Cd}$. The high mobility of Cu and Ni was attributed to their high complexing nature with soluble soil organic matter. Amrhein, et al. (1992) also showed the increased mobility of Cu, Ni, and Pb in the presence of dissolved organic matter. In this study, the Cd leached from the columns was not associated with dissolved organic carbon but was associated with Cl or acetate anions. Metals, such as Cd and Zn, that do not form highly stable complexes with organic matter are not as greatly affected by the presence of dissolved organic matter in the soil solution as metals that do form stable complexes, such as Cu, Pb, or Hg. Dunnivant et al. (1992) and Neal and Sposito (1986), however, demonstrated that dissolved organic matter does reduce Cd sorption due to complexation formation under their experimental conditions.

In systems where the organic ligand adsorbs to the soil surface, metal adsorption may be enhanced by the complexation of the metal to the surface-adsorbed ligand. Haas and Horowitz (1986) found that, in some cases, the presence of organic matter enhanced Cd adsorption by kaolinite. They interpreted these findings to suggest that the presence of an adsorbed layer of organic matter on the clay surface served as a site for Cd retention. Davis and Leckie (1978) found Cu adsorption to iron oxide increased in the presence of glutamic acid and 2,3 pyrazinendicarboxylic acid (2,3 PDCA) but decreased in the presence of picolinic acid. Picolinic acid complexed Cu and the resulting complex was not adsorbed by the oxide surface. The glutamic acid and 2,3 PDCA were adsorbed to the oxide surface, then complexed the added Cu. Using natural organic matter, Davis (1984) demonstrated the adsorption of Cu but not Cd to an organic coated aluminum oxide.

The effect of complexation formation on sorption is dependent on the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox. The presence of complexing ligands may increase metal retention or greatly increase metal

mobility. Use of literature or laboratory data that do not include the presence of complexing ligands, both organic and inorganic, present at the particular site of interest, may lead to significant overestimation or underestimation of metal mobility.

Effect of pH

The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. Figure 7 shows the impact of soil pH on the adsorption of Pb, Ni, Zn, and Cu by two soils adjusted to various pHs ranging from approximately 4.3 to 8.3 (Harter, 1983). As is true for all cationic metals, adsorption increased with pH. The author, however, points out that the retention of the metals did not significantly increase until the pH was greater than 7. Figure 8 illustrates the adsorption of selenite, SeO_3^{2-} , on five soils adjusted to various pHs. As is true with all oxyanions, i.e., arsenic, selenium and hexavalent chromium, sorption decreases with pH.

The pH dependence of adsorption reactions of cationic metals is due, in part, to the preferential adsorption of the hydrolyzed metal species in comparison to the free metal ion (McBride, 1977; McLauren and Crawford, 1973; Davis and Leckie, 1978; Farrah and Pickering, 1976a,b; James and Healy, 1972; McBride, 1982; Cavallaro and McBride, 1980; Harter, 1983). The proportion of hydrolyzed metal species increases with pH.

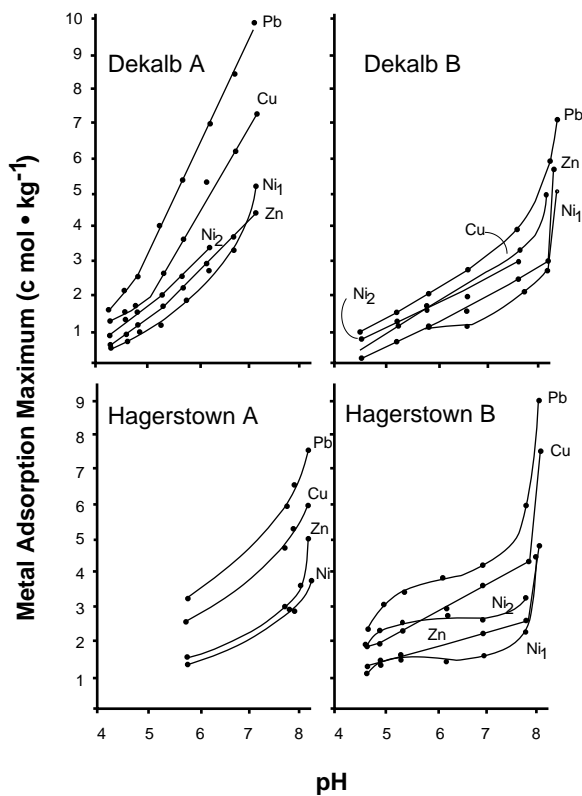


Figure 7. Effect of soil pH level on maximum Pb, Cu, Zn, and Ni retention by Dekalb and Hagerstown A and B horizons. Ni1 and Ni2 refer to two apparent sorption maxima. (Harter, 1983).

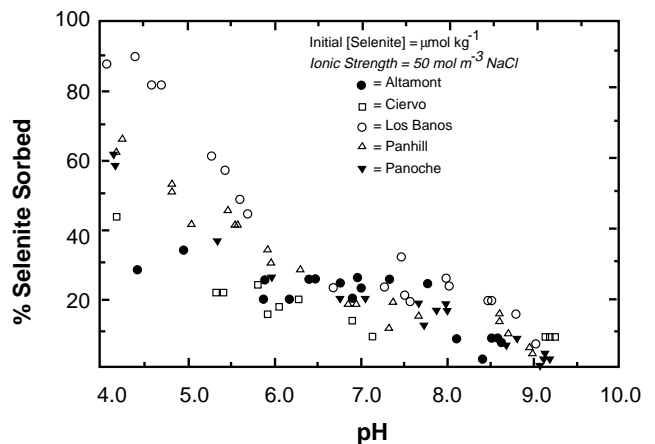


Figure 8. Selenite adsorption envelope for five alluvial soils. The initial total selenite concentration was approximately $2 \mu\text{mol kg}^{-1}$ (Neal, et al., 1987a).

Cavallaro and McBride (1980) found that copper adsorption by soils showed a stronger pH dependence than Cd. This finding is consistent with the hypothesis that hydrolysis of Cu at pH 6 increases its retention by soil, while cadmium does not hydrolyze until pH 8. Zinc was shown to be retained in an exchangeable form at low pH in four Fe and Mn oxide dominated soils but became nonexchangeable as the pH was increased above 5.5 (Stahl and James, 1991). The researchers attributed this change in mechanism of sorption as being due to the hydrolysis of Zn and the adsorption of the hydrolysis species by the oxide surfaces.

Many adsorption sites in soils are pH dependent, i.e., Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. As the pH decreases, the number of negative sites for cation adsorption diminishes while the number of sites for anion adsorption increases. Also as the pH becomes more acidic, metal cations also face competition for available permanent charged sites by Al^{3+} and H^+ .

All trace metal hydroxide, oxide, carbonate, and phosphate precipitates form only under alkaline conditions (Lindsay, 1979). The dissolution of these metal precipitates is strongly dependent on the pH of the system. Jenne (1968) stated that hydrous oxides of Fe and Mn play a principal role in the retention of metals in soils. Solubility of Fe and Mn oxides is also pH-related. Below pH 6, the oxides of Fe and Mn dissolve, releasing adsorbed metal ions to solution (Essen and El Bassam, 1981).

Work by McBride and Blasiak (1979) showed increased retention of Zn with increasing pH, as is usual for metal cations. When the pH was increased above 7.5, however, the solution concentration of Zn increased. This phenomena has been observed in other studies when acid soils were adjusted to $\text{pH} > 7$ (Kuo and Baker, 1980) and it has been attributed to

the solubilization of organic complexing ligands which effectively compete with the soil surfaces for the metal cation. Most functional groups of complexing ligands are weak acids, thus the stability of the metal complex is pH-dependent with little association in acid media. The degree of association increases with pH. Baham and Sposito (1986) and Inskeep and Baham (1983) demonstrated that the adsorption of Cu to montmorillonite, in the presence of water soluble ligands extracted from sludges and various other organic materials, decreased with increasing pH. This behavior is the opposite of the typical relationship between metal adsorption and pH. Figure 9, taken from Baham and Sposito (1986), illustrates that nearly 100% of the Cu added to the clay in the absence of the organic ligands was removed from solution at pH>7. In the presence of the organic ligands, the maximum amount of Cu removed from solution was at pH^o5.5. As the pH was increased above 5.5, adsorption of Cu decreased. The explanation for this phenomena is that at low pH, H⁺ competes with the Cu for complexation with the organic matter. As the pH increases, more of the Cu can be complexed with the organic matter and less is therefore adsorbed by the clay. This phenomena has important implications with regards to the practice of liming acid soils to raise the pH increasing metal retention. In soils with significant levels of dissolved organic matter, increasing soil pH may actually mobilize metal due to complex formation.

The pH of the soil system is a very important parameter, directly influencing sorption/desorption, precipitation/dissolution, complex formation, and oxidation-reduction reactions. In general, maximum retention of cationic metals occurs at pH>7 and maximum retention of anionic metals occurs at pH<7. Because of the complexity of the soil-waste system, with its myriad of surface types and solution composition, such a generalization may not hold true. For example, cationic metal mobility has been observed to increase with increasing pH due to the formation of metal complexes with dissolved organic matter.

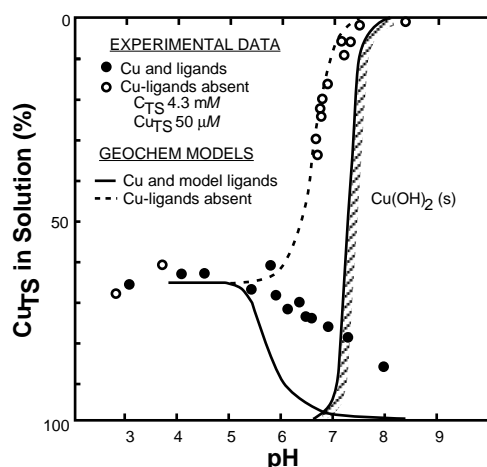


Figure 9. Adsorption of Cu [50 mmol m⁻³ (50 mM)] by Na-montmorillonite in the presence and absence of water soluble extract of sewage sludge (WSE). GEOCHEM simulations were constructed employing the "mixture model" (Baham and Sposito, 1986).

Effect of oxidation-reduction

Almost half of the metals under consideration have more than one oxidation state in the soil environment and are directly affected by changes in the oxidation-reduction (redox) potential of the soil. The redox potential of a soil system is the measure of the electrochemical potential or availability of electrons within a system. A chemical reaction in which an electron transfer takes place is called an oxidation-reduction process. Metals or elements which gain electrons and lose in valence are undergoing reduction, while those losing electrons and gaining in valence are becoming oxidized. A measure of the redox potential (electron availability) indicates whether the metals are in an oxidize or reduced state.

In soils, reducing conditions are brought about by the absence of oxygen (anaerobic). This is caused by the oxygen being utilized or consumed at a greater rate that it can be transported into the soil system. This can be caused by water-logged soils or soils contaminated with oxygen consuming compounds. The consumption could either be chemical or biological. The biological consumption of oxygen is the results of microbes utilizing the organic contaminant which have entered the soil system. Oxidizing conditions (aerobic) are normally found in well-drained soils as well as soils that have not been subjected to contamination by spills or leaks.

The degree of oxidation or reduction is indicated by the redox potential measurement. The four general ranges of redox conditions as suggested by Patrick and Mahapatra (1968) which may be encountered in soils are at pH 7, oxidized soils > +400 millivolts (mv); moderately reduced soils, from +400 to +100 mv; reduced soils, from +100 to -100 mv; highly reduced soils, -100 to -300 mv. The redox state of a soil, as discussed above, usually is closely related to the microbial activity and the type of substrate available to the organisms.

Redox reactions can greatly affect contaminant transport, in slightly acidic to alkaline environments, Fe(III) precipitates as a highly adsorptive solid phase (ferric hydroxide), while Fe(II) is very soluble and does not retain other metals. The reduction of Fe(III) to Fe(II) will bring about the release of ferrous iron to the pore waters and also any metals that were adsorbed to the ferric hydroxide surfaces. The behavior of chromium and selenium also illustrates the importance of redox conditions to metals movement in soils. Hexavalent Cr(VI) is both toxic and a relatively mobile anion while trivalent Cr(III) is far less toxic, relatively insoluble, and strongly adsorbs to surfaces. Selenate (Se(VI)) is mobile, but less toxic than selenite (Se(IV)) which is more toxic, but less mobile. In general, oxidizing conditions favor retention of metals in soils, while reducing conditions contribute to accelerated migration.

Effect of co-waste

Most soil-metal interaction studies have been performed using a specific, well characterized background solution, such as an inorganic salt solution (0.01M CaCl₂, Na₂SO₄, etc.) or a water soluble extraction of organic matter (leaf litter, sewage sludges, etc.). These studies, as reported above, have led to an understanding of the effects that metal type, metal concentration, solution composition, and soil surface type have on the retention of metals by soils. The behavior of metals associated with various industrial or mining wastes in

soil systems has not been extensively studied, however. In such wastes the metal concentration may be much greater than used in studies of native metals and metals associated with the controlled application of fertilizers and sewage sludges, and may be associated with a myriad of inorganic and organic chemicals that have not been characterized but may have a great effect on predicting metal mobility. Below are examples in which investigators have used various waste mixture for the background solution in sorption studies. In all cases, the results were highly dependent on the waste type used. These examples have been included to emphasize the importance of performing laboratory studies or using literature data that mimic the actual matrix of the waste or soils-waste system being investigated.

The retention of Cd, Cu, and Zn by two calcareous soils using a water extract of an acidic milling waste as the background solution (pH=4.0, dominant major cation was Ca and anion was sulfate) was studied by Dudley et al. (1988, 1991). The presence of carbonate minerals is known to effectively immobilize Cd and Cu by providing an adsorbing or nucleating surface and by buffering pH (Santillan-Medrano and Jurinak, 1975; Cavallaro and McBride, 1978; McBride and Bouldin, 1984). For the soil with a lower carbonate content (0.2% CaCO_3), the sorption of Cd and Zn was slow to reach equilibrium (114 hours) due to the complex set of reactions that occurred when the soil (pH 8.6) and acid milling extract (pH 4.0) were combined. The dissolution of carbonates in the acid medium controlled the rate and extent of Cd and Zn sorption. The authors concluded that Cd and Zn were retained by an exchange mechanism only after the pH of the system reached equilibrium (pH 5.5), allowing time for significant transport of these metals. Copper sorption was independent of calcite dissolution. The soil with the higher carbonate content (30%) showed a significant drop in pH (pH 9.1 to 6.6) with the addition of the acid leachate but had sufficient carbonates to buffer the system and sorbed all three metals.

Kotuby-Amacher and Gambrell (1988) studied the retention of Cd and Pb on subsurface soils using a synthetic municipal waste leachate and a synthetic acid metal waste leachate, compared with $\text{Ca}(\text{NO}_3)_2$ as the background solution. Sorption of the two metals was diminished in the presence of both synthetic leachates. The presence of competing cations and complexing organic and inorganic ligands in the synthetic wastes decreased the retention of Cd and Pb by the soils. Boyle and Fuller (1987) used soil columns packed with five different soils to evaluate the mobility of Zn in the presence of simulated municipal solid waste leachate with various amounts of total organic carbon (TOC) and total soluble salts (TSS). Zinc transport was enhanced in the presence of higher TOC and TSS. Soil properties considered important for retaining Zn in this study were surface area, CEC, and percent clay content. The authors, however, concluded that the leachate composition was more important than soil properties for determining the mobility of Zn.

Puls et al. (1991) studied the sorption of Pb and Cd on kaolinite in the presence of three organic acids, 2,4-dinitrophenol, p-hydroxybenzoic acid, and o-toluic acid. The acids were selected based on their frequent occurrence at hazardous waste sites and their persistence in soils. Sorption of Pb decreased in the presence of all the acids due to the formation of 1:2 metal-organic complex resulting in an

uncharged form of Pb. Sorption of Cd decreased in the presence of two of the acids but increased in the presence of 2,4-dinitrophenol. The authors attributed the increase in sorption as being due to either direct sorption of the acid to the clay with the subsequent sorption of Cd or to the enhanced sorption of the 1:1 complex formed between Cd and the acid.

Sheets and Fuller (1986) studied the transport of Cd through soil columns with 0 to 100% ethylene glycol or 2-propanol as the leaching solution. Soils sorbed less Cd from the ethylene glycol solutions than when the columns were leached with water. The 2-propanol increased sorption in one of the soils tested. The effect on Cd sorption was attributed to the change in soil permeability and surface characterization due to the presence of the solvents.

Metal mobility in soil-waste systems is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the concentration and type of competing ions and complexing ligands, both organic and inorganic, pH, and redox status. Generalization can only serve as rough guides of the expected behavior of metals in such systems. Use of literature or laboratory data that do not mimic the specific site soil and waste system will not be adequate to describe or predict the behavior of the metal. Data must be site specific. Long term effects also must be considered. As organic constituents of the waste matrix degrade, or as pH or redox conditions change, either through natural processes of weathering or human manipulation, the potential mobility of the metal will change as soil conditions change. Few long term studies have been reported.

Behavior of Specific Metals

Copper

Copper is retained in soils through exchange and specific adsorption mechanisms. At concentrations typically found in native soils, Cu precipitates are unstable. This may not be the case in waste-soil systems and precipitation may be an important mechanism of retention. Cavallaro and McBride (1978) suggested that a clay mineral exchange phase may serve as a sink for Cu in noncalcareous soils. In calcareous soils, specific adsorption of Cu onto CaCO_3 surfaces may control Cu concentration in solution (Cavallaro and McBride, 1978; Dudley, et al., 1988; Dudley et al., 1991; McBride and Bouldin, 1984). As reported in the adsorption sequence in Table 2, Cu is adsorbed to a greater extent by soils and soil constituents than the other metals studied, with the exception of Pb. Copper, however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils.

Zinc

Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides. Hickey and Kittrick (1984), Kuo et al. (1983), and Tessier et al. (1980) found that the greatest percent of the total Zn in polluted soils and sediments was associated with Fe and Mn oxides. Precipitation is not a major mechanism of retention of Zn in soils because of the relatively high solubility of Zn compounds. Precipitation may become a more important mechanism of Zn retention in soil-waste systems. As with all cationic metals, Zn adsorption increases with pH.

Zinc hydrolyzes at $\text{pH} > 7.7$ and these hydrolyzed species are strongly adsorbed to soil surfaces. Zinc forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface.

Cadmium

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Evidence suggests that adsorption mechanisms may be the primary source of Cd removal from soils (Dudley et al., 1988, 1991). In soils and sediments polluted with metal wastes, the greatest percentage of the total Cd was associated with the exchangeable fraction (Hickey and Kittrick, 1984; Tessier et al., 1980; Kuo et al., 1983). Cadmium concentrations have been shown to be limited by CdCO_3 in neutral and alkaline soils (Santillan-Medrano and Jurinak, 1975). As with all cationic metals, the chemistry of Cd in the soil environment is, to a great extent, controlled by pH. Under acidic conditions Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6, cadmium is adsorbed by the soil solid phase or is precipitated, and the solution concentrations of cadmium are greatly reduced. Cadmium forms soluble complexes with inorganic and organic ligands, in particular Cl^- . The formation of these complexes will increase Cd mobility in soils.

Lead

Soluble lead added to the soil reacts with clays, phosphates, sulfates, carbonates, hydroxides, and organic matter such that Pb solubility is greatly reduced. At pH values above 6, lead is either adsorbed on clay surfaces or forms lead carbonate. Of all the trace metals listed in Table 2, Pb is retained by soils and soil constituents to the greatest extent under the conditions of these studies. Most studies with Pb, however, have been performed in well defined, simple matrices, i.e., 0.01M CaCl_2 . Puls et al. (1991), and Kotuby-Amacher and Gambrell (1988) have demonstrated decrease sorption of Pb in the presence of complexing ligands and competing cations. Lead has a strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of Pb in soil.

Nickel

Nickel does not form insoluble precipitates in unpolluted soils and retention for Ni is, therefore, exclusively through adsorption mechanisms. Nickel will adsorb to clays, iron and manganese oxides, and organic matter and is thus removed from the soil solution. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils.

Silver

Published data concerning the interaction of silver with soil are rare. As a cation it will participate in adsorption and precipitation reactions. Silver is very strongly adsorbed by clay and organic matter and precipitates of silver, AgCl , Ag_2SO_4 and AgCO_3 , are highly insoluble (Lindsay, 1979). Silver is highly immobile in the soil environment.

Mercury

The distribution of mercury species in soils, elemental mercury (Hg^0), mercurous ions (Hg_2^{2+}) and mercuric ions (Hg^{2+}), is dependent on soil pH and redox potential. Both the mercurous and mercuric mercury cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption is pH dependent, increasing with increasing pH. Mercurous and mercuric mercury are also immobilized by forming various precipitates. Mercurous mercury precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of Hg commonly found in soil, only the phosphate precipitate is stable. In alkaline soils, mercuric mercury will precipitate with carbonate and hydroxide to form a stable solid phase. At lower pH and high chloride concentration, HgCl_2 is formed. Divalent mercury also will form complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility (Kinniburgh and Jackson, 1978).

Under mildly reducing conditions, both organically bound mercury and inorganic mercury compounds may be degraded to the elemental form of mercury, Hg^0 . Elemental mercury can readily be converted to methyl or ethyl mercury by biotic and abiotic processes (Roger, 1976, 1977). These are the most toxic forms of mercury. Both methyl and ethyl mercury are volatile and soluble in water. Griffin and Shimp (1978) estimated that the removal of Hg from a leachate was not due to adsorption by clays, but was due to volatilization and/or precipitation. This removal of mercury increased with pH. Rogers (1979) also found large amounts of mercury volatilized from soils. Amounts of mercury volatilized appeared to be affected by the solubility of the mercury compounds added to soil. Volatilization was also found to be inversely related to soil adsorption capacity. The form of Hg lost from the soil, whether elemental Hg or methylmercury, was not determined in this study.

Arsenic

In the soil environment arsenic exists as either arsenate, As(V) (AsO_4^{3-}), or as arsenite, As(III) (AsO_2^-). Arsenite is the more toxic form of arsenic.

The behavior of arsenate in soil is analogous to that of phosphate, because of their chemical similarity. Like phosphate, arsenate forms insoluble precipitates with iron, aluminum, and calcium. Iron in soils is most effective in controlling arsenate's mobility. Arsenite compounds are reported to be 4-10 times more soluble than arsenate compounds.

Griffin and Shimp (1978), in a study of arsenate adsorption by kaolinite and montmorillonite, found maximum adsorption of As(V) to occur at pH 5. Adsorption of arsenate by aluminum and iron oxides has shown an adsorption maximum at pH 3-4 followed by a gradual decrease in adsorption with increasing pH (Hingston et al., 1971; Anderson et al., 1976). The mechanism of adsorption has been ascribed to inner sphere complexation (specific adsorption), which is the same mechanism controlling the adsorption of phosphate by oxide surfaces (Hingston et al., 1971; Anderson et al., 1976; Anderson and Malotky, 1979).

The adsorption of arsenite, As(III) , is also strongly pH-dependent. Griffin and Shimp (1978) observed an increase in

sorption of As (III) by kaolinite and montmorillonite over a pH range of 3-9. Pierce and Moore (1980) found the maximum adsorption of As(III) by iron oxide occurred at pH 7. Elkhatib et al. (1984b) found adsorption of As(III) to be rapid and irreversible on ten soils. They determined, in this study and another study (Elkhatib et al., 1984a), that Fe oxide, redox, and pH were the most important properties in controlling arsenite adsorption by these soils.

Both pH and the redox are important in assessing the fate of arsenic in soil. At high redox levels, As(V) predominates and arsenic mobility is low. As the pH increases or the redox decreases As (III) predominates. The reduced form of arsenic is more subject to leaching because of its high solubility. The reduction kinetics are, however, slow. Formation of As (III) also may lead to the volatilization of arsine (AsH_3) and methylarsines from soils (Woolson 1977a). Under soil conditions of high organic matter, warm temperatures, adequate moisture, and other conditions conducive to microbial activity, the reaction sequence is driven towards methylation and volatilization (Woolson 1977a). Woolson's (1977b) study showed that only 1 to 2 percent of the sodium arsenate applied at a rate of 10 ppm was volatilized in 160 days. The loss of organic arsenical compounds from the soil was far greater than for the inorganic source of arsenic. Arsenite, As(III), can be oxidized to As(V). Manganese oxides are the primary electron acceptor in this oxidation (Oscarson et al., 1983).

Selenium

The behavior of selenium in soils has received great attention in recent years. Studies were stimulated by the high incidence of deformity and mortality of waterfowl at the Kesterson National Wildlife Refuge in California that resulted from the input of agricultural drainage water from the western San Joaquin Valley that was high in Se. Such studies have led to a better understanding of the distribution and movement of Se in soils and ground water.

Selenium exists in the soil environment in four oxidation states: selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). The concentration and form of Se in soil is governed by pH, redox, and soil composition. Selenate, Se(VI), is the predominant form of selenium in calcareous soils and selenite, Se(IV), is the predominant form in acid soil.

Selenite, Se (IV) binds to sesquioxides, especially to Fe oxides. Balistrieri and Chao (1987) found the removal of selenite by iron oxide to increase with decreasing pH. This study not only demonstrates the effect of pH on selenite adsorption but also the effect of concentration. The decrease in the percentage of selenite adsorbed with increasing concentration of selenite at a given pH indicated multiple sites of selenite retention. At the two lower concentrations, high energy specific adsorption sites were available. As the concentration of selenite was increased these sites became saturated and the lower energy sites were utilized. Griffin and Shimp (1978) found maximum adsorption of selenite on montmorillonite and kaolinite to occur at pH 2-3. Neal et al. (1987a) used five soils from the San Joaquin Valley and found that selenite adsorption by the soils decreased with increasing pH in the range of 4-9. Selenite adsorption to oxides and soils occurs through an inner sphere complexation (specific adsorption) mechanism (Rajan, 1979; Neal et al., 1987b).

In studies of competitive adsorption using phosphate, sulfate, and chloride (Neal, et al., 1987b) and phosphate and various organic acids (Balistrieri and Chao, 1987), selenite adsorption decreased dramatically in the presence of phosphate and the organic acids but was not affected by the presence of sulfate or chloride. Balistrieri and Chao (1987), using Fe oxide, found the sequence of adsorption to be: phosphate = silicate = arsenate > bicarbonate carbonate > citrate = selenite > molybdate > oxalate > fluoride = selenate > sulfate.

Precipitation is not a major mechanism of retention of selenite in soils. Manganese selenite may form, however, in strongly acidic environments (Elrashidi et al., 1989).

Selenate dominates under alkaline conditions. In contrast to selenite, selenate, Se(VI), is highly mobile in soils. Benjamin (1983) found that selenate was adsorbed by amorphous iron oxide as a function of pH. Maximum removal was at pH 4.5 and adsorption decreased with increasing pH. Bar-Yosef and Meek (1987) found some indication of selenate adsorption by kaolinite below pH 4. Selenate seems to be adsorbed by weak exchange mechanisms similar to sulfate (Neal and Sposito, 1989), in contrast to selenite that is specifically adsorbed by soils and soil constituents. There has been some evidence that selenate was adsorbed by alkaline soils (Singh et al., 1981), but Goldberg and Glaubig (1988) found no removal of selenate by calcareous montmorillonite. Neal and Sposito (1989), using soils from the San Joaquin Valley, showed no adsorption of added selenate over a pH range from 5.5-9.0. Fio et al. (1991) also observed no sorption of selenate by alkaline soil from the San Joaquin Valley, but did observe the rapid sorption of selenite by this soil. No stable precipitates of selenate are expected to form under the pH and redox conditions of most soils (Elrashidi, et al., 1989).

Similar to other anionic species, selenium is more mobile at higher pHs. Soil factors favoring selenium mobility, as summarized by Balistrieri and Chao (1987) are; alkaline pH, high selenium concentration, oxidizing conditions, and high concentrations of additional anions that strongly adsorb to soils, in particular phosphate.

Under reduced conditions, selenium is converted to the elemental form. This conversion can provide an effective mechanism for attenuation since mobile selenate occurs only under well aerated, alkaline conditions.

Organic forms of selenium are analogous to those of sulfur, including seleno amino acids and their derivatives. Like sulfur, selenium undergoes biomethylation forming volatile methyl selenides.

Chromium

Chromium exists in two possible oxidation states in soils: the trivalent chromium, Cr(III) and the hexavalent chromium, Cr(VI). Forms of Cr(VI) in soils are as chromate ion, HCrO_4^- predominant at pH<6.5, or CrO_4^{2-} , predominant at pH 6.5, and as dichromate, $\text{Cr}_2\text{O}_7^{2-}$ predominant at higher concentrations (>10mM) and at pH 2-6. The dichromate ions pose a greater health hazard than chromate ions. Both Cr(VI) ions are more toxic than Cr(III) ions. Reviews of the processes that control the fate of chromium in soil and the effect these processes have on remediation are given in Bartlett (1991) and Palmer and Wittbrodt (1991).

Because of the anionic nature of Cr(VI), its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH. Iron and aluminum oxide surfaces will adsorb CrO_4^{2-} at acidic and neutral pH (Davis and Leckie, 1980; Zachara et al., 1987; Ainsworth et al., 1989). Stollenwerk and Grove (1985) concluded that the adsorption of Cr(VI) by ground-water alluvium was due to the iron oxides and hydroxides coating the alluvial particles. The adsorbed Cr(VI) was, however, easily desorbed with the input of uncontaminated ground water, indicating nonspecific adsorption of Cr(VI). The presence of chloride and nitrate had little effect on Cr(VI) adsorption, whereas sulfate and phosphate inhibited adsorption (Stollenwerk and Grove, 1985). Zachara et al. (1987) and Zachara et al. (1989) found SO_4^{2-} and dissolved inorganic carbon inhibited Cr(VI) adsorption by amorphous iron oxyhydroxide and subsurface soils. The presence of sulfate, however, enhanced Cr(VI) adsorption to kaolinite (Zachara et al., 1988). Rai et al. (1988) suggested that BaCrO_4 may form in soils at chromium contaminated waste sites. No other precipitates of hexavalent compounds of chromium have been observed in a pH range of 1.0 to 9.0 (Griffin and Shimp, 1978). Hexavalent chromium is highly mobile in soils.

In a study of the relative mobilities of 11 different trace metals for a wide range of soils, Korte et al. (1976) found that clay soil, containing free iron and manganese oxides, significantly retarded Cr(VI) migration (see Figure 6). Hexavalent chromium was found to be the only metal studied that was highly mobile in alkaline soils. The parameters that correlated with Cr(VI) immobilization in the soils were free iron oxides, total manganese, and soil pH, whereas the soil properties, cation exchange capacity, surface area, and percent clay had no significant influence on Cr(VI) mobility.

Rai et al. (1987) reported that Cr(III) forms hydroxy complexes in natural water, including $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$, and $\text{Cr}(\text{OH})_4^-$. Trivalent chromium is readily adsorbed by soils. In a study of the relative mobility of metals in soils at pH 5, Cr(III) was found to be the least mobile (Griffin and Shimp, 1978). Hydroxy species of Cr(III) precipitate at pH 4.5 and complete precipitation of the hydroxy species occurs at pH 5.5.

Hexavalent chromium can be reduced to Cr(III) under normal soil pH and redox conditions. Soil organic matter has been identified as the electron donor in this reaction (Bartlett and Kimble, 1976; Bloomfield and Pruden, 1980). The reduction reaction in the presence of organic matter proceeds at a slow rate at environmental pH and temperatures (Bartlett and Kimble, 1976; James and Bartlett, 1983a,b,c). Bartlett (1991) reported that in natural soils the reduction reaction may be extremely slow, requiring years. The rate of this reduction reaction, however, increases with decreasing soil pH (Cary et al., 1977; Bloomfield and Pruden, 1980). Soil organic matter is probably the principal reducing agent in surface soils. In subsurface soils, where organic matter occurs in low concentration, Fe(II) containing minerals reduce Cr(VI) (Eary and Rai, 1991). Eary and Rai (1991), however, observed that this reaction only occurred in the subsurface soil with a pH < 5. The reduction of Cr(VI) occurred in all four subsurface soils tested by decreasing the pH to 2.5.

Bartlett and James (1979), however, demonstrated that under conditions prevalent in some soils, Cr(III) can be oxidized.

The presence of oxidized Mn, which serves as an electron acceptor, was determined as an important factor in this reaction.

Industrial use of chromium also includes organic complexed Cr(III). Chromium (III) complexed with soluble organic ligands will remain in the soil solution (James and Bartlett, 1983a). In addition to decreased Cr(III) adsorption, added organic matter also may facilitate oxidation of Cr(III) to Cr(VI).

Computer Models

Several equilibrium thermodynamic computer programs are available for modeling soil solution and solid phase chemistry by providing information on the thermodynamic possibility of certain reaction to occur. In addition to calculating the equilibrium speciation of chemical elements in the soil solution and precipitate/dissolution reactions, models such as GEOCHEM (Mattigod and Sposito, 1979) and MINTEQA2 (USEPA, 1987) provide information on cation exchange reactions and metal ion adsorption. These models are used to:

- 1) calculate the distribution of free metal ions and metal-ligand complexes in a soils solution,
- 2) predict the fate of metals added to soil by providing a listing of which precipitation and adsorption reactions are likely to be controlling the solution concentration of metals, and
- 3) provide a method for evaluating the effect that changing one or more soil solution parameters, such as pH, redox, inorganic and organic ligand concentration, or metal concentration, has on the adsorption/precipitation behavior of the metal of interest.

These models are equilibrium models and as such do not consider the kinetics of the reactions. These models are also limited by the accuracy of the thermodynamic data base available.

Analysis of Soil Samples

Total concentration of metals in soil

Measurement of the total concentration of metals in soils is useful for determining the vertical and horizontal extent of contamination and for measuring any net change (leaching to ground water, surface runoff, erosion) in soil metal concentration over time. The methods do not, however, give an indication as to the chemical form of the metal in the soil system.

The complete dissolution of all solid phase components in soils requires a rigorous digestion using either a heated mixture of nitric acid, sulfuric acid, hydrofluoric acid, and perchloric acid (Page et al., 1982) or a fusion of the soil with sodium carbonate (Page et al., 1982). Both methods require special equipment and special safety considerations. A more commonly used procedure is the hot nitric acid-hydrogen peroxide procedure outlined in SW-846 Method 3050 (USEPA, 1986). This is a partial digestion of the soil solid phase. The method probably releases metals associated

with a recent pollution source, i.e., exchangeable, specifically adsorbed to clays, oxides or organic matter, and most precipitates, but would not release metals associated within solid phases that are not dissolved by the hot nitric acid and oxidizing agent, i.e., within the structure of insoluble minerals.

Sequential extractions of metals in soils

Since the potential migration of metals in soil systems is dependent on the chemical form of the metal, extraction procedures have been developed to selectively remove metals from these various geochemical forms. While these procedures cannot be used to identify the actual form of a given metal in a soil, they are useful in categorizing the metals into several operationally defined geochemical fractions, such as exchangeable, specifically adsorbed, and metals associated with carbonates, organic matter, and/or iron and manganese oxides.

Numerous extraction procedures have been developed for metal cations (Sposito et al., 1984; Hickey and Kittrick, 1984; Tessier et al., 1979; Grove and Ellis, 1980; Kuo et al., 1983) and anions (Chao and Sanzolone, 1989; Gruebel et al., 1988). Lake et al. (1984) reviewed a number of the procedures used for cationic metal extraction. The extraction procedures consist of reacting a soil sample with increasing strengths of chemical solutions. Typically water or a salt solution (KNO_3 , CaCl_2 , etc.) is the first extractant used. These are followed by mild acids, bases, chelating agents, and oxidizing solutions. Table 4 illustrates the wide variety of extractants that have been used in the literature for metal cations.

The aqueous fraction and those fractions in equilibrium, i.e., the exchange fraction, with this fraction are of primary importance when considering the migration potential of metals in soils. In theory, mild extractants, such as salt solutions, are more likely to extract metals that could be released to the soil solution with input of water than metals associated with stronger binding mechanisms, such as specifically adsorbed or precipitated metals. Work by Silveira and Sommers (1977) and Latterell et al. (1978) suggests that salt extractable metals represent the potentially mobile portion of the total concentration of metals in soils. Harrison et al. (1981) likewise suggested that the mobility of metals decreases in the order of the extraction sequence. Rigorous evaluation, however, of the appropriateness of any extraction procedure for defining the mobile fraction of metals in soils has not been reported in the literature.

Hickey and Kittrick (1984) used a sequential extraction procedure to separate Cd, Cu, Ni, and Zn in metal polluted soils and sediments into five operationally defined geochemical fractions: exchangeable (1.0M MgCl_2), metals associated with carbonates (acetate buffer, pH 5), metals associated with Mn and Fe oxides ($0.04\text{M NH}_4\text{OH}\cdot\text{HCl}$), metals associated with organic matter ($0.02\text{M HNO}_3+\text{H}_2\text{O}_2$), and residual metals ($\text{HF}+\text{HClO}_4$). Figure 10 shows the average distribution of the metals among the defined geochemical fractions. Approximately 37% of the total Cd and a significant portion of the Zn were in the exchange fraction indicating the potential mobility of these two metals. Only a small portion of the Cu and Ni were in the exchange fraction. A significant portion of the Cu was associated with the organic fraction, in agreement with the known affinity of Cu for organic material. Nickel was mostly associated with the residual

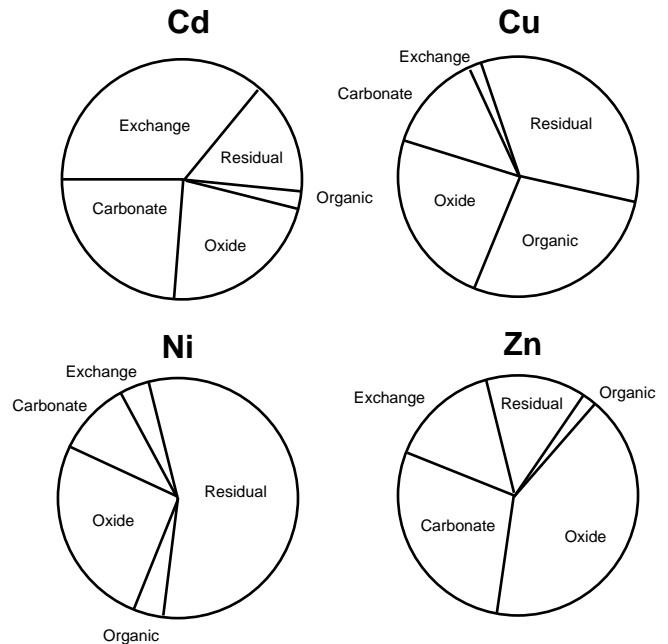


Figure 10. Proportions of Cd, Cu, Ni, and Zn in each of the operationally defined geochemical fractions of the experimental samples (Hickey and Kittrick, 1984).

fraction and significant portions of Zn and Cu were associated with the oxides. The authors concluded from this study that the relative mobility of the metals followed: $\text{Cd} > \text{Zn} > \text{Cu} = \text{Ni}$.

There has been recent criticism of these sequential extraction procedures (Miller et al., 1986; Kheboian and Bauer, 1987; Gruebel et al., 1988; Tipping et al., 1985; Rapin et al., 1986; Calvet et al., 1990). The methods are not entirely specific for a geochemical fraction of the soil and the extractant also may remove metals associated with other fractions. Secondly, re-adsorption of the extracted metals to the remaining solid phase of the soil may occur leading to artificially low concentrations of the metal being associated with that fraction. Finally, no one extraction procedure would be universally applicable for all metals and all soils. Perhaps the most suitable extractant for defining the mobile fraction of metals in soils under specific site conditions is one that simulates that soil or soil-waste solution chemistry.

TCLP

The Toxicity Characterization Leaching Procedure (TCLP) (USEPA, 1986) is a single extraction procedure, using 0.1M acetic acid, developed to simulate the leaching a waste might undergo if disposed of in a municipal landfill. This method is frequently used to determine the leaching potential of cationic metals in landfill situations where, due to microbial degradation of the waste under anaerobic conditions, acetic acid is produced. While this procedure is appropriate for demonstrating whether an excavated metal contaminated soil is defined as hazardous for disposal at a landfill, its application

Table 4. Some bibliographic data on the extraction of heavy metals present in soils and sediments (Colvet, et al., 1990)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and residual fraction
McLaren Crawford ¹¹ (1973)	0.05 N CaCl ₂	2.5% CH ₃ COOH	0.1 M (COOH) ₂ +0.175 M (COONH ₄) ₂ pH = 3.5	1 M K ₄ P ₂ O ₇	HF
Stover et al. ¹² (1976)	1 M KNO ₃ +NaF		0.1 M EDTA pH = 6.5	0.1 M Na ₄ P ₂ O ₇	1 M HNO ₃
Gatehouse et al. ¹³ (1977)		1 M CH ₃ COONH ₄ +CH ₃ COOH pH = 4.5	0.1 M NH ₂ OH +1 M CH ₃ COONH ₄ pH = 4.5	30% H ₂ O ₂	HF-HClO ₄
Filipek and Owen ¹⁴ (1979)		1 M CH ₃ COOH	0.25 M NH ₂ OH, HCl in 25% (v/v) CH ₃ COOH	Acidified 30% H ₂ O ₂	HNO ₃ -HF-HClO ₄
Tessier et al. ³ (1979)	1 M MgCl ₂ or 1 M CH ₃ COONa at pH = 8.2	1 M CH ₃ COONa + 1 M CH ₃ COOH at pH = 5.0	0.04 M NH ₂ OH, HCl in 25% (v/v) CH ₃ COOH at 96 ± 3°C or 0.3 M Na ₂ S ₂ O ₄ +0.175 M Na—citrate +0.025 M citric acid	0.02 M HNO ₃ + 30% H ₂ O ₂ , pH = 2 at 85 ± 2°C, 2 h +30% H ₂ O ₂ +HNO ₃ , pH = 2 at 85 ± 2°C, 3 h 3.2 M CH ₃ COONH ₄ in 20% HNO ₃	HF-HClO ₄
Förstner et al. ² (1979)	0.2 M BaCl ₂		0.1 M NH ₂ OH, HNO ₃ + 25% (v/v) CH ₃ COOH + HCl	30% H ₂ O ₂ + NH ₄ OH	HF-HClO ₄
Schalscha et al. ⁴ (1980)	1 M KNO ₃	0.5 M NaF pH = 6.5	0.1 M EDTA pH = 6.5 double extraction	0.1 M Na ₄ P ₂ O ₅	1 M HNO ₃
Garcia-Miragaya ¹⁵ (1981)	1 N CaCl ₂	2.5% CH ₃ COOH	0.05 M EDTA pH = 7	0.1 N Na ₄ P ₂ O ₅	HF
Badri and Aston ¹⁶ (1981)		1 M CH ₃ COONH ₄ +0.5 M (CH ₃ COO) ₂ Mg	0.25 M NH ₂ OH, HCl pH = 2	30% H ₂ O ₂ + 1 M CH ₃ COONH ₄	
Förstner et al. ¹⁷ (1981)	1 M CH ₃ COONH ₄ pH = 7		(1) 0.1 M NH ₂ OH, ClH +0.01 M HNO ₃ , pH = 2 (2) 0.2 M (COONH ₄) ₂ +0.2 M (COOH) ₂ , pH = 3	30% H ₂ O ₂ , HNO ₃ pH = 2 at 85°C extraction with 1 M CH ₃ COONH ₄	HNO ₃ at 180°C
Greffard et al. ⁶ (1981)		resin-H ⁺	(1) (COONa) ₂ (2) (COONa) ₂ + UV	30% H ₂ O ₂ at 40°C	
Sposito et al. ¹⁰	0.5 M KNO ₃		0.5 M Na ₂ EDTA	0.5 M NaOH	4 M HNO ₃ at 80°C
Dekeyser et al. ¹⁸ (1983)		1M CH ₃ COONH ₄ pH = 4.5	(1) 0.1 M NH ₂ OH, HCl (2) 0.2 M (COONH ₄) ₂ (HCOOH) ₂ , pH = 3.3 obscurité (3) Same as (2)+UV		HNO ₃ -HF-HCl
Kuo et al. ⁷ (1983)	1 M MgCl ₂		(1) (COONa) ₂ (2) Citrate dithionite bicarbonate	6% NaClO ₄ at 85°C	HNO ₃ -HClO ₄
Meguelatti et al. ⁵ (1983)	1 M BaCl ₂	1 M CH ₃ COOH +0.6 M CH ₃ COONa	0.1 M NH ₂ OH +25% (v/v) CH ₃ COOH	30% H ₂ O ₂ +0.02 M HNO ₃ +3.2 M CH ₃ COONH ₄	HF-HCl
Shuman ¹⁹ (1985)	1 M Mg(NO ₃) ₂ pH = 7		(1) 0.1 M NH ₂ OH, HCl pH = 2 (2) 0.2 M (COONH ₄) ₂ +0.2 M (COOH) ₂ , pH = 3 (3) Same as (2) + ascorbic acid	0.7 M NaOCl pH = 8.5	HF-HNO ₃ -HCl
Gibson and Farmer ²⁰ (1986)	1 M CH ₃ COONH ₄ pH = 7	1 M CH ₃ COONa pH = 5	(1) 0.1 M NH ₂ OH, ClH +0.01 M HNO ₃ (2) 1 M NH ₂ OH, ClH in 25% (v/v) CH ₃ COOH	30% H ₂ O ₂ +0.02 M HNO ₃ at 85 °C	Aqua regia + HF

for evaluating the mobility of metals under field conditions has been questioned (Dragun et al., 1990). Production of acetic acid does not commonly occur in soils. In certain soil-waste systems, leaching tests using acetic acid may be appropriate, but it is not universally representative of the leaching solution for soil-waste systems. The acetic acid leaching procedure was developed for cationic metals. The procedure is not appropriate for extraction of anionic metals. Bartlett (1991) reported that this procedure actually causes the reduction of Cr(VI) to Cr(III) leading to a false measurement of the leachability of Cr(VI) in soil. A more appropriate leaching solution would mimic the specific waste or waste-soil matrix.

Hickey and Kittrick (1984) used an acetate buffer solution in their sequential extraction scheme to remove metals associated with carbonates. This is a similar solution to the TCLP solution except that it is buffered to pH 5. This buffered solution fully dissolves the carbonate minerals in the soil. The unbuffered acetic acid solution used in the TCLP solution cannot maintain a low enough pH in calcareous soils to dissolve carbonates. The metals extracted by the TCLP solution are not related to any definable geochemical fraction and the fraction of metals extracted using this procedure have not been correlated with the mobile fraction of metals in soil.

Evaluating the Behavior of Metals in Soils

Sorption studies

Soil sorption studies are commonly performed to evaluate the extent of metal retention by a soil or soil constituent. Sorption studies are often used in an attempt to generate the equilibrium distribution coefficient (K_d), the ratio of metal sorbed to metal in solution at equilibrium, which may be utilized in transport models. Sorption studies are also used for comparison of the relative retention of several metals by a soil or the relative retention of a metal by several soils, and are used extensively in correlation studies to determine the relative importance of a soil's chemical and physical properties for metal retention. Sorption studies also can be used to evaluate the effect that changing a soil solution parameter, e.g., adjustment of pH, ionic strength, addition of competing cations, or addition of inorganic or organic ligands, has on metal retention by a soil.

In a sorption study, the soil is reacted with solutions containing varying quantities of the metal(s) of interest for a specified time period using either batch or column techniques. The concentration range used in the study should overlap the concentration of environmental concern. A background electrolyte solution also should be used to simulate normal soil's solution chemistry or the waste matrix and to equalize the ionic strength across all soils. The reaction time should approach thermodynamic equilibrium, usually determined by a preliminary kinetics experiment. After the specified time period the soil and solution are separated by centrifugation and/or filtration. The soil and/or solution phases are then analyzed by atomic absorption spectrophotometry or inductively coupled plasma emission spectrometry. With these techniques it is not possible to distinguish between true adsorption and precipitation reactions. For that reason the term sorption will be used.

Two techniques, batch and column studies, may be used to generate sorption isotherms. The batch technique involves

placing the soil and the solutions containing the various concentrations of the metals into a vessel and mixing the samples for a prescribed time period. This is the most commonly used technique because of its ease of laboratory operation and ease of data handling. The disadvantages of the technique are 1) results are sensitive to the soil:solution ratio used, 2) soil:solution ratios in actual soil systems cannot be done in batch studies, so scaling of data from batch studies to soils systems is uncertain, 3) results are sensitive to the mixing rate used, 4) separation techniques may affect results, and 5) many investigators have found that batch generated sorption coefficients are not adequate to describe the behavior of metals in flow through systems.

The column method consists of packing a glass or plastic column with soil. The solutions containing various concentrations of the metals of interest are pumped through the columns and the effluents are collected and analyzed by AA or ICP. Breakthrough occurs when the effluent concentration equals the influent concentration. The advantages of this technique are 1) low soil:solution ratios can be used, 2) separation of the soil and solution phase is not required, 3) mechanical mixing is not required and 4) column studies more closely simulate field conditions than batch methods. The disadvantages are 1) results depend on flow rates used, 2) columns are difficult to set-up and maintain, 3) uniform packing of the column is difficult often leading to channel flow, and 4) fewer columns can be operated at one time compared with the number of batch reactors.

Equilibrium sorption is described by a sorption isotherm. A sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal or, more correctly, the activity of the free metal in the soil solution. A typical sorption isotherm is shown in Figure 11. If the relationship is linear over the concentration range studied then the sorption process can be described by a single coefficient, the distribution coefficient, K_d . For metals, however, the relationship is seldom linear and other equations with two or more coefficients must be used to describe the data.

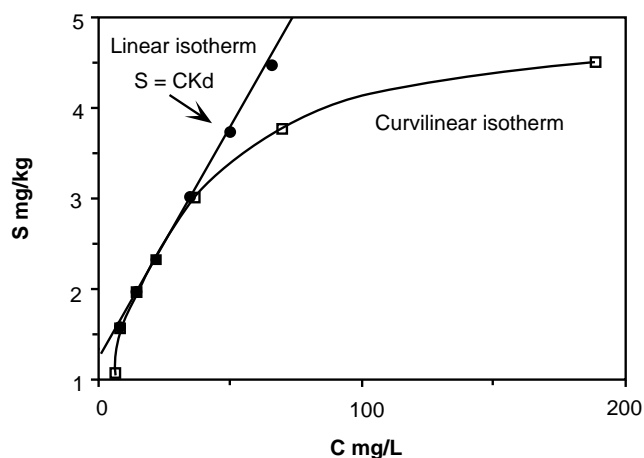


Figure 11. Sorption isotherms.

Equations most frequently used, because of their relative simplicity, to describe the curvilinear sorption behavior of metals in soil are the Langmuir and the Freundlich equations. The Langmuir equation was developed to model gas adsorption on solid surfaces. The derivation of the equation was based on the assumption that adsorption is independent of surface coverage, that there is no interaction between adsorbed ions, and that only a monolayer of adsorption occurs on the surface. These conditions are not typically met with metals sorption on soils.

The linearized form of the Langmuir equation is:

$$\frac{C}{S} = \frac{C}{M} + \frac{1}{Mb} \quad (1)$$

where C is the concentration or activity of the free metal in solution, S is the quantity of the metal ion sorbed by the soil (i.e., mg metal sorbed/Kg soil), M is the maximum sorption capacity of the soil, and b is the coefficient related to bonding energy. When C/S is plotted as a function of C, the slope is the reciprocal of the sorption capacity, M, and the intercept is 1/Mb.

The Freundlich expression is an empirically derived equation to describe the logarithmic decrease in adsorption energy with increasing surface coverage. The linearized form of the Freundlich equation is:

$$\log S = (N)\log C + \log K \quad (2)$$

where S and C have the same definition as above and N and K are constants fitted from the experimental data. When the slope, N, equals 1, the equation simplifies to:

$$S = CK_d \text{ or } K_d = S/C \quad (3)$$

where K_d is the distribution coefficient. In most studies reported in the literature for metal sorption, the slope of the Freundlich isotherm is seldom equal to 1 and the simplified expression and its single term, K_d , are not appropriate to describe the data.

Figure 12 illustrates the use of the Langmuir expression to describe Cu sorption by a soil (Cavallaro and McBride, 1978). The equation describes the behavior of Cu over all concentrations used in this study. Often, however, nonlinear behavior over the concentration range studied is observed with the use of either the Langmuir or Freundlich equations. In Figure 13, the Langmuir expression was used to describe the sorption behavior of Cd and Zn by hydrous manganese oxide (Zasoski and Burau, 1988). This non-linear behavior when using the Langmuir equation has been noted by numerous researchers using various metals and soils and soil constituents (Benjamin and Leckie, 1981; Shuman, 1975; Loganathan and Burau, 1973). Non-linearity of metal sorption using the Freundlich equation has also been noted by Zasoski and Burau (1988) Benjamin and Leckie (1981), Catts and Langmuir (1986), O'Connor et al. (1984), O'Connor et al. (1983), and Elrashdi and O'Connor (1982). This non-linear behavior has been interpreted to indicate multiple sites of sorption that have different energies of retention. The mechanisms at low concentrations have been attributed to specific adsorption, whereas the mechanisms at higher concentrations have been considered to be exchange

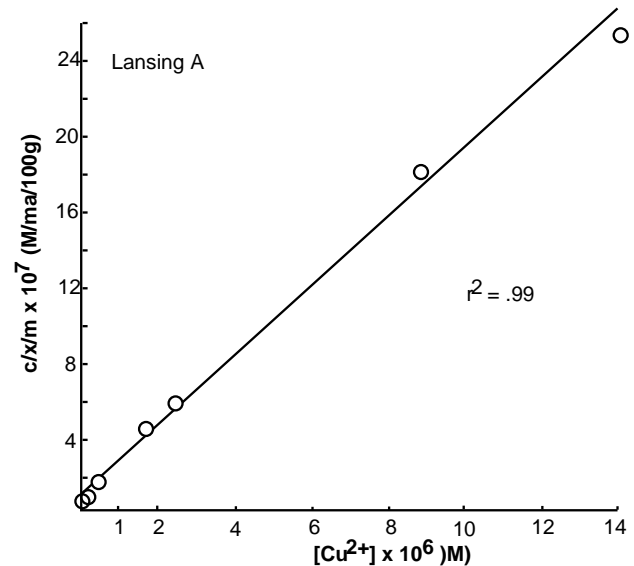


Figure 12. Langmuir adsorption isotherm for Cu²⁺ adsorption on the Lansing A soil (Cavallaro and McBride 1978).

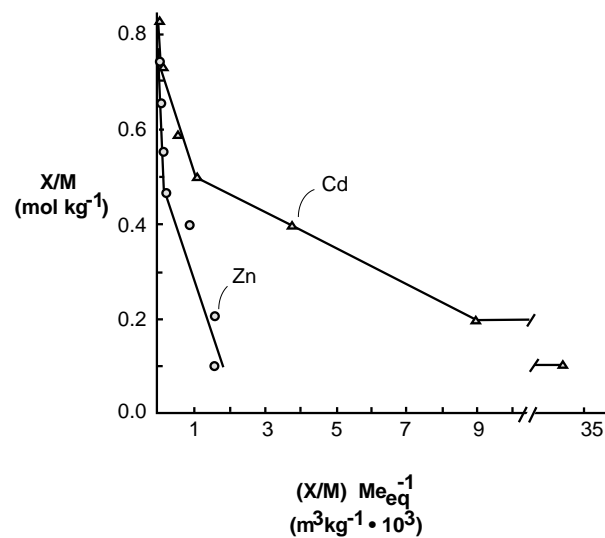


Figure 13. Langmuir plots of Cd and Zn sorbed on δ -MnO₂ for the noncompetitive pH 4 data (Zasoski and Burau, 1988).

reactions or precipitation. These results illustrate the importance of generating sorption data over the concentration range of interest for a particular application. Large error in predicting sorptive behavior may result from using data generated in one system and applied to a system with higher or lower metal concentration.

Several researchers have, however, suggested that other equations, for example the two-surface Langmuir equation (Sposito, 1982; Travis and Etnier, 1981) or the competitive Langmuir equation (Griffin and Au, 1977; Travis and Etnier,

1981), be used to describe the non-linear behavior encountered with the Langmuir equation (Sposito, 1982).

The Langmuir and Freundlich isotherm expressions have proven valuable in interpreting metal behavior in soils. The adsorption isotherm equations were, however, developed for modeling gas adsorption on solids. The sorption of metals by soils violates many of the assumptions associated with these equations. Also, the mechanism described by these equations is adsorption, but it is impossible in a soil system to distinguish between adsorption and precipitation reactions. Adsorption isotherm equations should not be used to indicate adsorption mechanisms without collaborative evidence, but they can be used for an empirical description of the data. Harter (1984) warned against over interpreting the sorption maximum and "bonding energy" determined using the Langmuir equation. The applicability of adsorption isotherm equations to the interpretation of soil chemical phenomena is a subject of controversy. For further discussion of this controversy see Elprince and Sposito (1981), Griffin and Au (1977), Veith and Sposito (1977), Sposito (1979), Harter and Baker (1977), and Harter (1984).

Desorption

Desorption studies are often performed to determine the reversibility of the sorption reactions. This gives an idea of the strength of the association of the metal with the soil surface. An example of the reversibility of a sorption reaction (Figure 14) is taken from Dudley et al. (1988). In this study, two calcareous soils were reacted with various concentrations of Cd. The soils were then desorbed with CaCl_2 . For the low carbonate soil (Kidman) virtually all of the sorbed Cd was desorbed by the Ca. Only 10-15 percent of the sorbed Cd on the highly calcareous Skumpah soil was desorbed by Ca. These results suggest that Cd was held by the Kidman soil as an exchangeable cation, whereas in the Skumpah, Cd was specifically adsorbed by the CaCO_3 .

Desorption studies are performed after completion of the sorption study. They can be carried out using either batch or

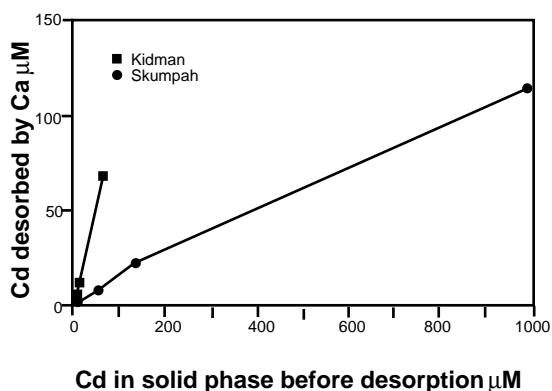


Figure 14. Desorption of Cd from Kidman and Skumpah soil by 0.01 M CaCl_2 at a soil:solution ratio of 1:25 (Dudley, et al., 1988).

column techniques. For the batch technique the soils used in the sorption are reacted with a salt solution, typically 0.01N CaCl_2 or a matrix representative of the soil-waste system being studied. Samples are shaken for a specified time period. The soil and liquid are then separated by centrifugation and/or filtration and the solution is analyzed for the metals by AA or ICP. This process is repeated several times. For a column study, the metal equilibrated soil column is flushed with an appropriate solution until the system reaches steady state conditions.

Kinetics

Attention has been mainly given in the literature to equilibrium processes in soils but soil processes are never at equilibrium. Soil systems are dynamic and are thus constantly changing. Most kinetic studies have been performed to establish the proper time interval for use in equilibrium sorption/desorption studies. Most studies assume that ion exchange processes are rapid in soils and that 16 to 24 hours mixing periods, common time periods used in sorption studies, are adequate. This assumption may not be appropriate if other reactions in addition to simple ion exchange, i.e., specific adsorption and precipitation, are involved in metals retention (Harter and Lehmann, 1983). McBride (1980) found that the initial adsorption of Cd on calcite was very rapid, while CdCO_3 precipitation of higher Cd^{2+} concentrations was slow. Lehmann and Harter (1984) used kinetics of desorption to study the strength of Cu bonding to a soil. A plot of concentration of Cu in solution versus time indicates an initial rapid release of the Cu followed by a slow reaction. They interpreted these results to indicate that Cu was held at two sites: the rapidly released Cu being loosely held on the soil surfaces and the slowly released Cu being tightly bound.

Each metal-soil system should be tested to determine the time necessary for the individual system to come to equilibrium. Figure 15 illustrates the different time periods required for equilibrium for three metals sorbed by a calcareous soil (Dudley, et al., 1988). Copper reached equilibrium within a few hours whereas Cd and Zn did not approach steady state conditions for 144 hours. Use of the time interval appropriate for Cu equilibrium for this soil would mean that only 50 percent of the Cd and Zn adsorbed under steady state conditions would have been determined.

Kinetic studies are being more widely performed because of their importance in determining the transport of metals in soil systems. Many mathematical transport models now allow a kinetic term for sorption. Equilibrium studies predict whether a reaction will occur but give no indication of the time necessary for the reaction to take place. Kinetic studies also contribute to an understanding of reaction mechanisms not discernible from thermodynamic studies (Zasoski and Burau, 1988; Harter and Smith, 1981; Sparks, 1989).

Kinetic studies are similar to sorption procedures, using either batch or column techniques, except samples are collected over time. Several equations have been used to describe the kinetics of sorption reactions of ions on soils and soil constituents. These equations include: first-order, second-order, Elovich equation, parabolic diffusion equation, and power function equation. An excellent review of kinetic processes in soil systems is given by Sparks (1989).

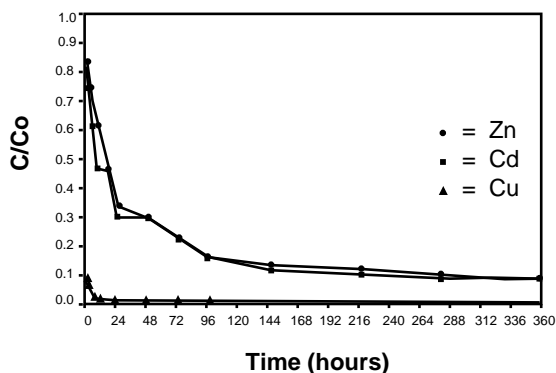


Figure 15. Change with time in reduced concentration of metals in suspensions of the Skumpah soils. C_0 was the concentration of metal ions at time = 0 (Dudley, et al., 1988).

Summary

Metals added to soil will normally be retained at the soil surface. Movement of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix.

The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with such soil properties as pH, redox potential, surface area, cation exchange capacity, organic matter content, clay content, iron and manganese oxide content, and carbonate content. Anion retention has been correlated with pH, iron and manganese oxide content, and redox potential. In addition to soil properties, consideration must be given to the type of metal and its concentration and to the presence of competing ions, complexing ligands, and the pH and redox potential of the soil-waste matrix. Transport of metals associate with various wastes may be enhanced due to (Puls et al., 1991):

1. facilitated transport caused by metal association with mobile colloidal size particles,
2. formation of metal organic and inorganic complexes that do not sorb to soil solid surfaces,
3. competition with other constituents of waste, both organic and inorganic, for sorption sites, and
4. decreased availability of surface sites caused by the presence of a complex waste matrix.

Because of the wide range of soil characteristics and various forms by which metals can be added to soil, evaluating the extent of metal retention by a soil is site/soil/waste specific. Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also

may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix.

Laboratory methods for evaluating the behavior of metals in soils are available in the literature. Thermodynamic equilibrium computer models are also available to assist with this evaluation. The advantages and disadvantages of some of the available procedures have been presented in this document.

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