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Heavy Metals in Soils

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ABSTRACT

For the purposes of this Issue Paper, metals most commonly found at Superfund sites will be discussed in terms of the processes affecting their behavior in soils, as well as in those of the laboratory methods available to evaluate this behavior. The retention capacity of soil will also be discussed with regard to the movement of metals between the other environmental compartments: 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 explained with respect to the enhanced mobility of metals in soils.

Keywords: heavy metals, soils

1. 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.

2. 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 associated with soils.

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. 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.

3. 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 , 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 , 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 ligands. The total concentration of a metal, M, in the soil solution is the sum of the free ion concentration $[\text{M}^{z+}]$, 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 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.

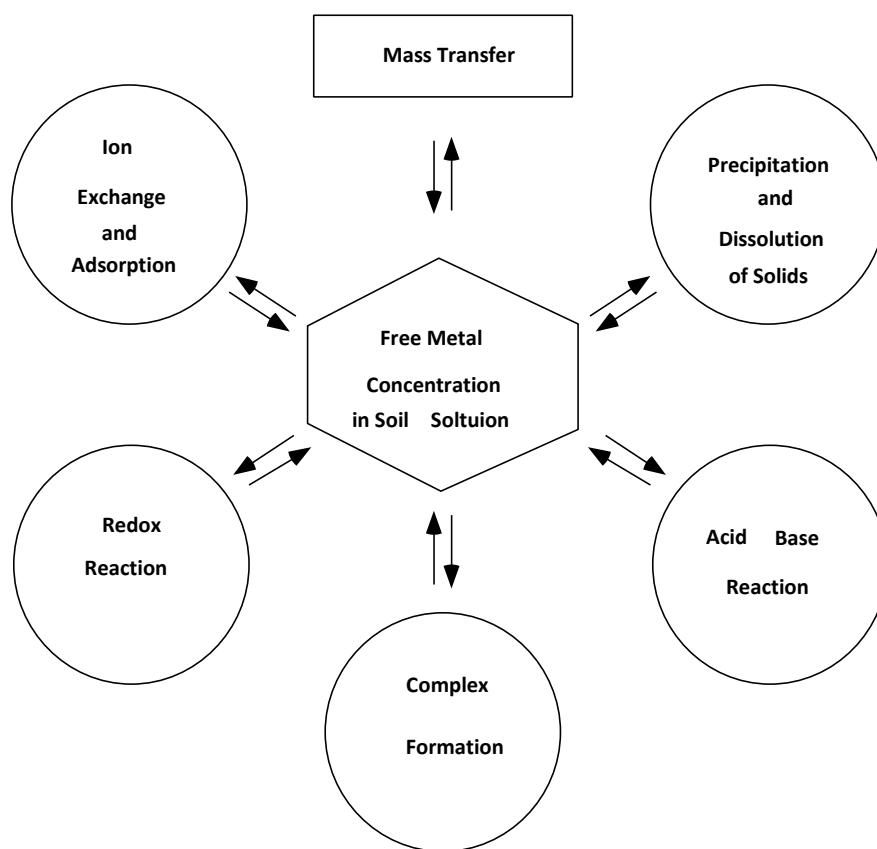


Figure 1. Principal controls on free trace metal concentrations in soils solution (Mattigod et al., 1981).

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.

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). 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.

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 μm 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 μm (Sposito, 1989). Gschwend and Reynolds (1987) reported that colloidal particles of intermediate diameter, 0.1 μm to 1 μm , 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.

4. 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 , Pb(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.

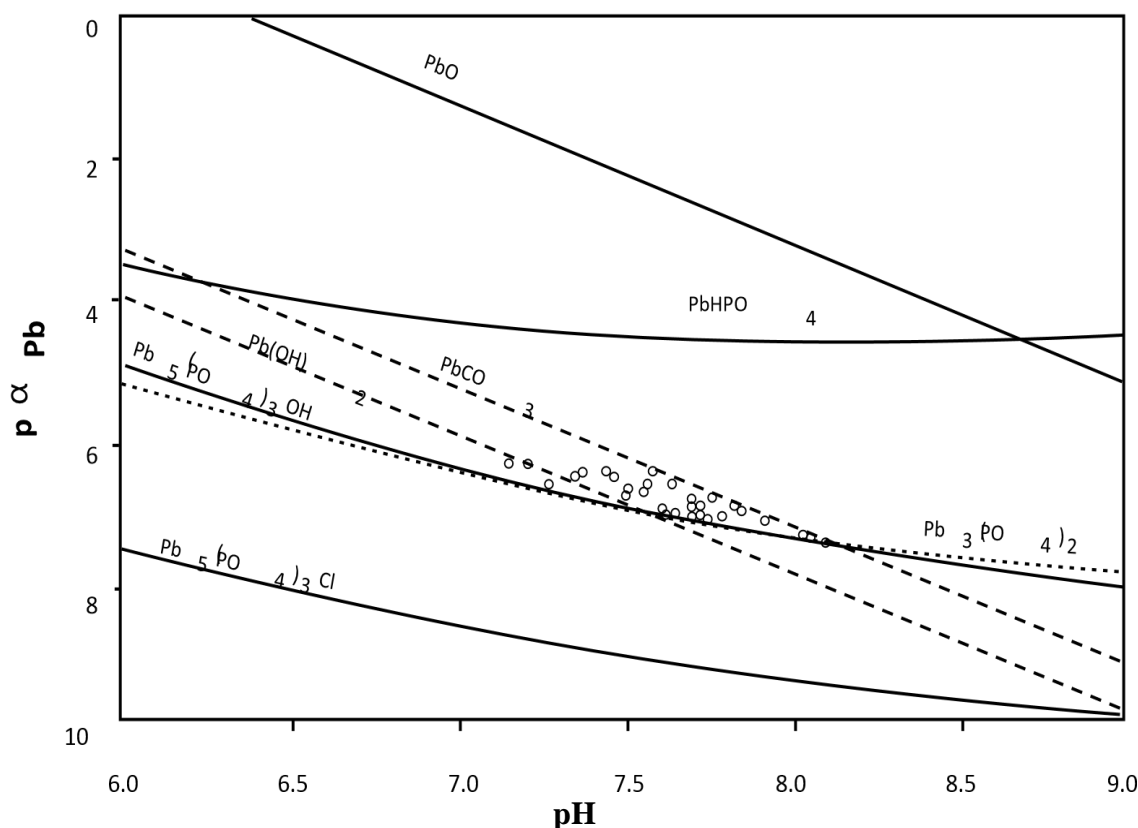


Figure 2. The solubility diagram for Pb in Nibley clay loam soil (Santillan-Medrano and Jurinak, 1975).

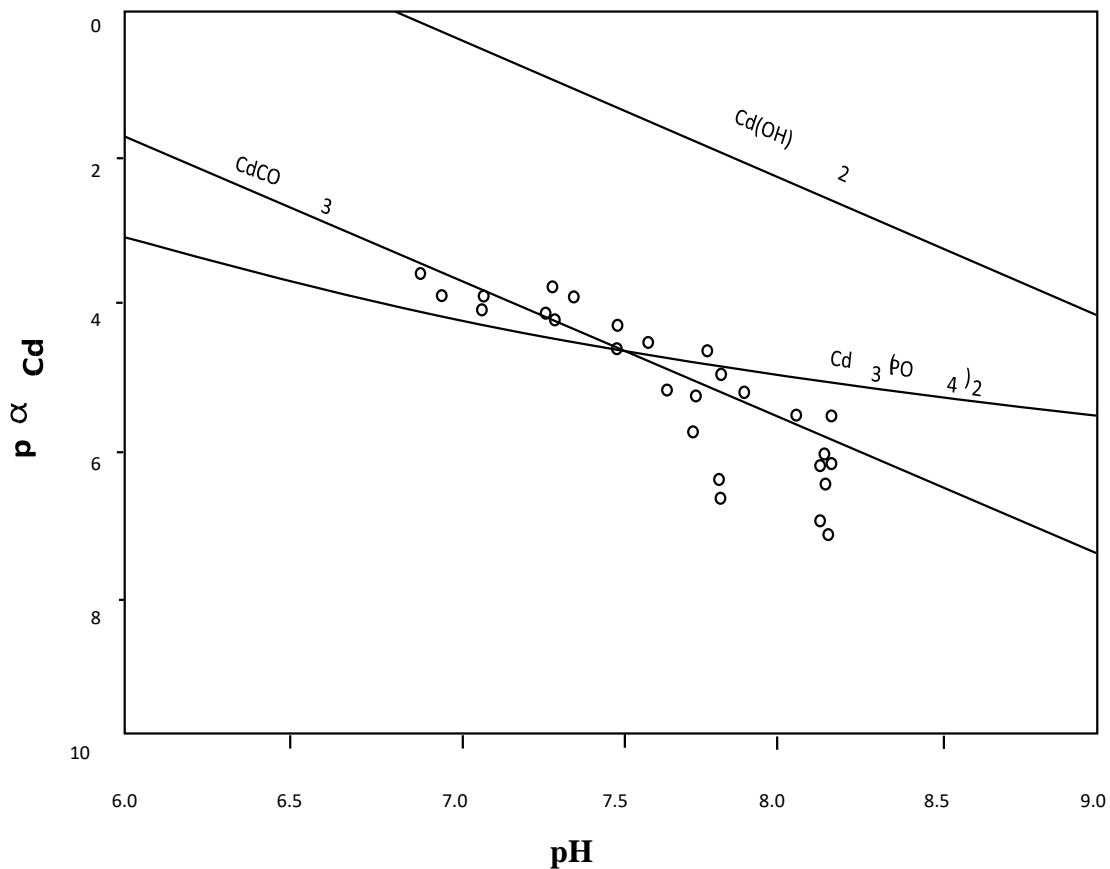


Figure 3. The solubility diagram for Cd in Nibley clay loam soil (Santillan-Medrano and Jurinak, 1975).

5. 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 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 >200 mEq/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 (SantillanMedrano 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). 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.

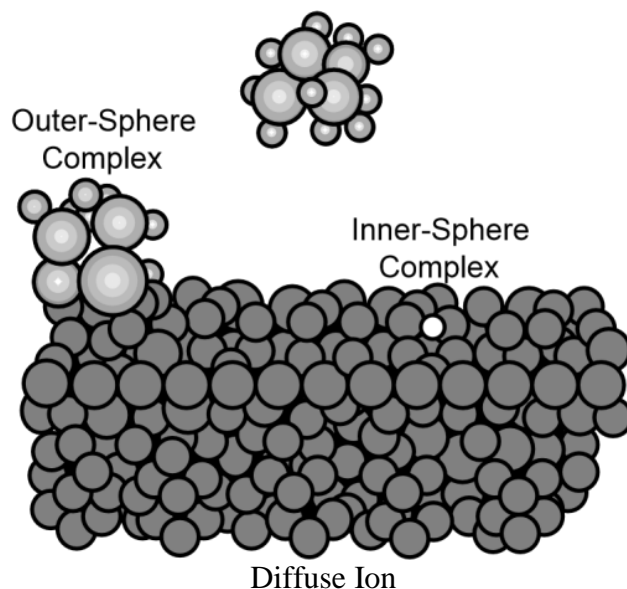


Figure 4. The three mechanisms of cation adsorption on a siloxane surface (e.g., montmorillonite), (Sposito, 1989).

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).

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 (0.01-10 mg/L added Cd), to specific adsorption. At higher concentrations (100-1000 mg/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 $Cs > Rb > K = NH_4 > Na > Li$. 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.

6. CONCLUSIONS

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