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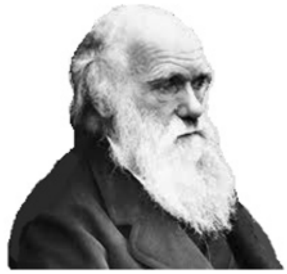

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Effect of pH and soil environment

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ABSTRACT

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 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.

***Keywords*:** pH, soil environment

pH AND SOIL ENVIRONMENT

The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. Figure 1 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 2 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.

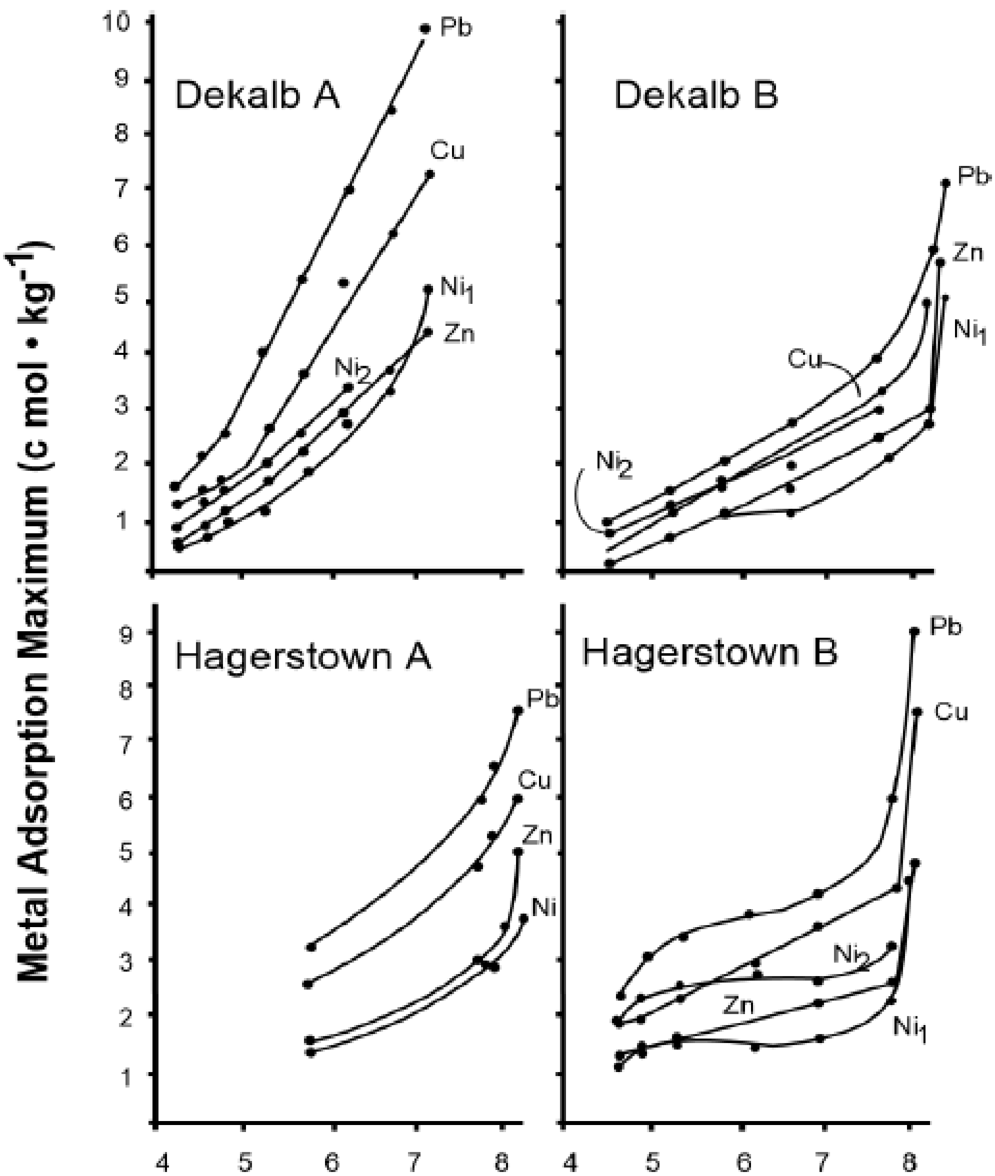

Figure 1. Effect of soil pH level on maximum Pb, Cu, Zn, and Ni retention by Dekalb and Hagerstown A and B horizons. Ni1 and Ni2 refer to two apparent sorption maxima. (Harter, 1983).

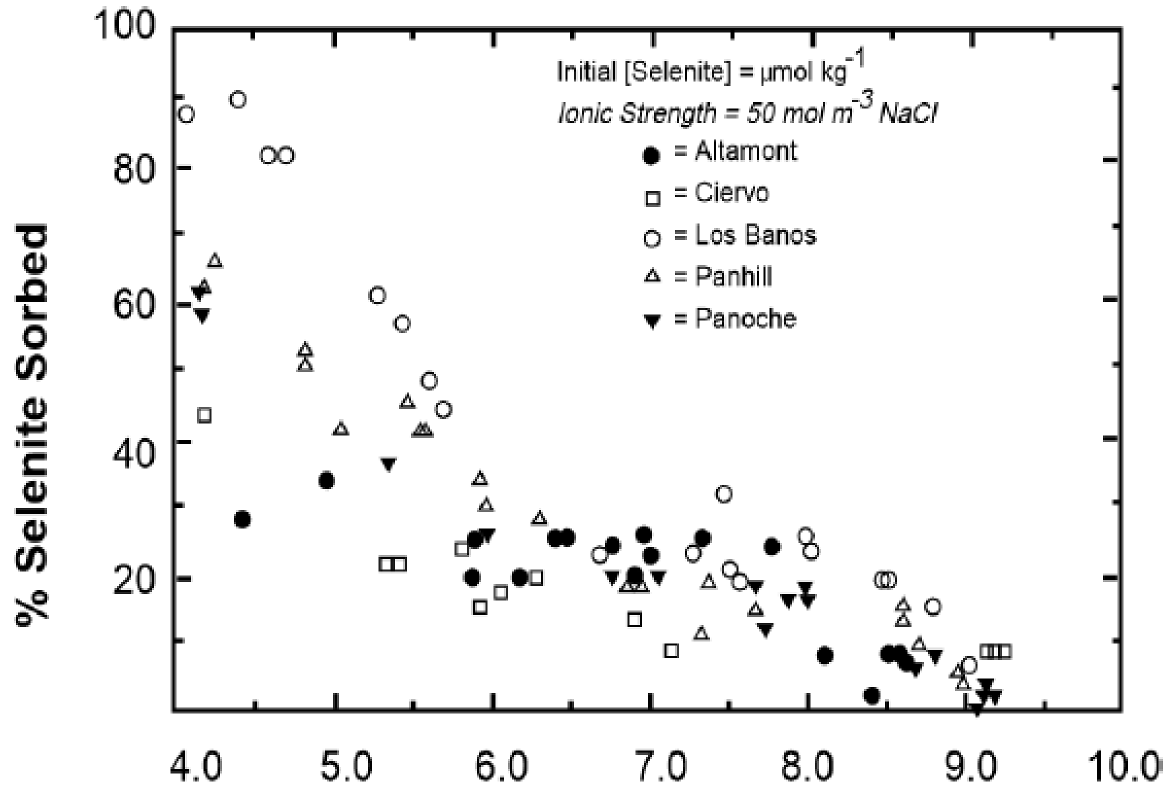

Figure 2. Selenite adsorption envelope for five alluvial soils. The intitial total selenite concentration was approximately 2 μmol kg^{-1} (Neal, et al., 1987a).

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 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 3, 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 pH³ 5.5. As the pH was increased above 5.5, adsorption of Cu decreased.

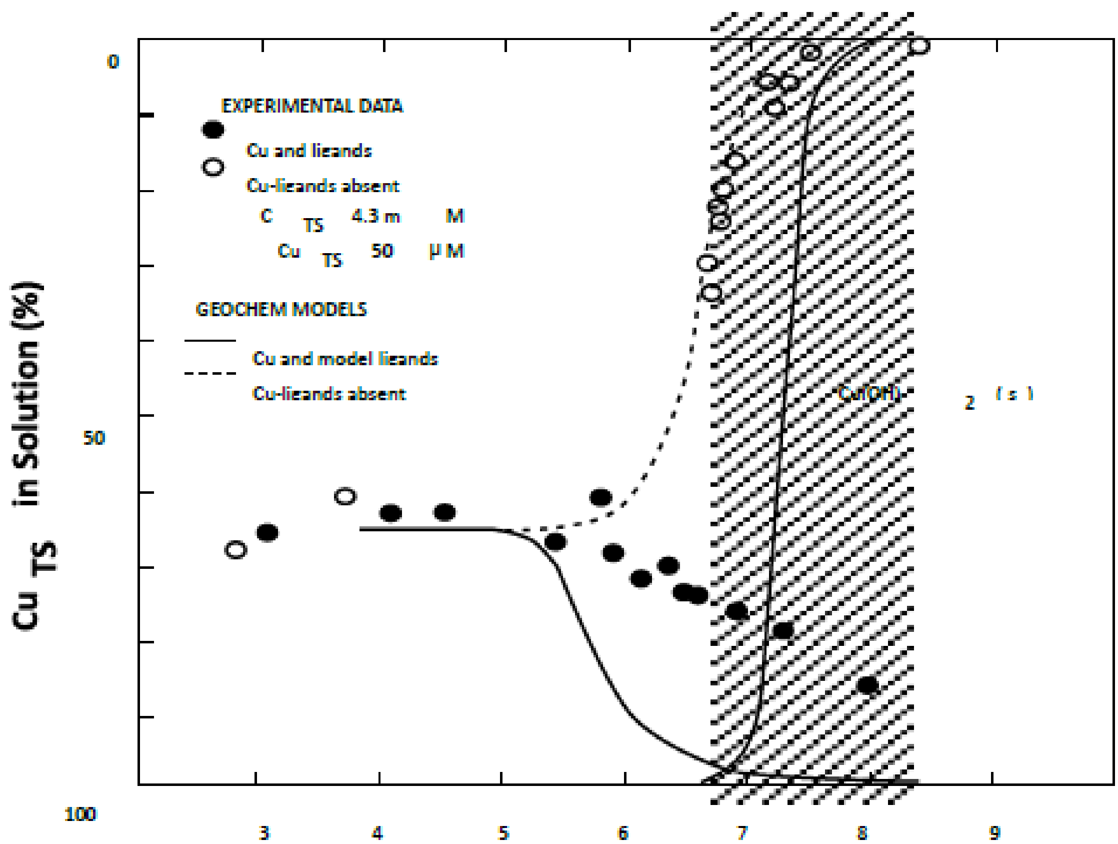

Figure 3. Adsorption of Cu [50 mmol m^{-3} (50 mM)] by Na montmorillonite in the presence and absence of water soluble extract of sewage sludge (WSE). GEOCHEM simulations were constructed employing the "mixture model" (Baham and Sposito, 1986).

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.

CONCLUSION

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.

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