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The influence of organic ligands on the retention of lead in soil

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Abstract

Organic acids are commonly produced and exuded by plant roots and soil microorganisms. Some of these organic compounds are effective chelating agents and have the potential to enhance metal mobility. The effect of citrate and salicylate on the leaching of lead in soil was investigated in a laboratory experiment. In short-term batch experiments, adsorption of lead to soil was slightly enhanced with increasing salicylate concentration (500–5000 μM) but decreased significantly in the presence of citrate. These observations suggested that citrate may enhance Pb leaching, but this was not observed in the column study. Soluble Pb in the presence and absence citrate or salicylate (up to 5000 μM) was added to soil columns at a moderate flow rate, but no Pb was observed to emerge from the soil in any of the soil columns. Rapid biodegradation of citrate in soil eliminated potential complexing ability. Breakthrough of Pb from soil was noted only when using small columns at high flow rates (>20 pore volumes per day). Under these conditions of physical and chemical non-equilibrium, citrate was not degraded and significantly enhanced Pb mobility. As in the batch adsorption experiments, the presence of salicylate reduced Pb leaching. Considering the extreme conditions required to induce Pb leaching, it is likely that Pb will remain relatively immobile in soil even in the presence of a strong complexing agent such as citrate.

Keywords: Heavy metals; Soil; Lead; Rhizosphere; Adsorption; Redox; Transport; Leachate; Organic acids; Citrate; Salicylate

1. Introduction

Lead is a common contaminant of soil and considered to be a risk to human health when soil concentrations exceed 400–500 mg Pb/kg soil (US EPA, 2001). Lead may contaminate soil through vehicle exhausts, sewage-sludge biosolids, mining, and smelting (Abdel-saheb et al., 1994). Highly contaminated soils may have Pb concentrations >10 000 mg/kg. Toxicity from Pb-contaminated soils primarily occurs from direct ingestion. Symptoms of lead poisoning in adults include irritability, poor muscle coordination, nerve damage, increased blood pressure, hearing and vision impairment, and reproductive disorders. In children, lead poisoning can cause brain damage, mental retardation, behavioral problems, anemia, liver and kidney damage, hearing loss, hyperactivity, developmental delays, and other

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physical and mental problems (Reagan and Silbergeld, 1989; Xintaras, 1992; US EPA, 2000).

Heavy metals can be toxic to soil microorganisms if present in high concentrations. Heavy metal pollution was negatively correlated to microbial population and activity (Baath, 1989). Observed effects include reduced microbial activity, decreased litter decomposition (Tan, 1986) and reduced nitrogen transformations (Baath, 1989). Plants can tolerate and accumulate certain levels of heavy metals; however, heavy metals are generally toxic to most plants at high concentrations.

Plants have been used for decades for stabilization of disturbed and contaminated sites, and plant-based remediation technologies are receiving broad acceptance (Lasat, 2002). One of the mechanisms by which plants are able to reduce toxicity from heavy metals in soils is the exudation of organic acids. Specific organic acids can sequester heavy metals and protect the roots from toxicity effects. (Benyahya and Garnier, 1999; Jones et al., 2003; Jung et al., 2003; Liao and Xie, 2004). The concentration of organic acids in soil solution is normally less than 1 mM and variable (Robert and Berthelin, 1986; Jones et al., 2003). The most commonly reported organic acids exuded by plants are those that participate in the tricarboxylic acid cycle such as citric, succinic, malic, and *cis*-aconitic acids. Aliphatic acids including formic, acetic, propionic, butyric, oxalic, and tartaric acids; aromatic acids such as *p*-coumaric, caffeic, ferulic, gallic, salicylic, and protocatechuic acids also are present (Stevenson, 1967; Jones, 2004). Citric, malic, oxalic, succinic, vanillic, *p*-hydroxybenzoic, and *p*-coumaric acids have been identified in leachate from leaf litter (Bruckert et al., 1971). The concentration of organic acids is generally in the range of 10^{-3}–10^{-5} M (Manley and Evans, 1986; Sposito, 1989), but higher concentrations of organic acids can be found under litter (Robert and Berthelin, 1986).

Adsorption/desorption and precipitation/dissolution reactions control heavy metal accumulation in the soil profile, metal transport to the groundwater, and bioavailability for plant uptake. Quantifying sorption is a critical aspect of predicting chemical behavior of a metal in soils. Adsorption can be affected by many factors such as pH (Kuo and McNeal, 1984; Stahl and James, 1991), cation exchange capacity, insoluble organic matter and clay content (McBride and Blasiak, 1979), competition from other metal ions (Elliott et al., 1986; Covelo et al., 2004), and soluble organic and inorganic ligands (McLean and Bledsoe, 1992; Bradl, 2004). The presence of soluble organic ligands in soil may significantly influence metal adsorption through the formation of stable complexes (Chairidchai and Ritchie, 1990; McLean and Bledsoe, 1992).

In vegetated soil, the effects of soluble organic ligands on the adsorption of heavy metals to soil may be important because plant roots and soil microorganisms continually produce organic acids throughout their life cycles. Some of these organic acids are very strong complexing agents for metals, but the influence of the organic ligands on heavy metal adsorption is not completely understood. In heavy metal-contaminated soil, vegetation can significantly affect metal adsorption and hence mobility (Schwab and Banks, 1993; Shuman, 1999; Schmidt, 2003).

If a ligand strongly complexes with Pb in solution, the presence of this ligand has the potential to reduce sorption to soil and increase leaching (Benyahya and Garnier, 1999). Ligands that sorb to soil may increase ternary soil–ligand–metal complexes (Davis and Leckie, 1978; Glover et al., 2002; Schwab et al., 2004). The presence of citrate and EDTA was found to decrease the adsorption of Pb to soil minerals (Chen et al., 2003; Wu et al., 2003), although the addition of citrate increased Pb sorption to humus (Wu et al., 2003). Increasing concentrations of acetate, oxalate, tricarballylate, salicylate, humate and catechol were found to decrease Zn adsorption; this pattern was not observed for citrate (Chairidchai and Ritchie, 1990). Burckhard et al. (1995) studied the effects of formic, oxalic, succinic, and citric acids on the leaching of Zn from mine tailings and found that four naturally occurring organic acids increased zinc leaching. Of these four, citric acid was the most effective.

Organic ligands do not always reduce adsorption of heavy metals to soil (Schwab et al., 2004). Adsorption of organic anions can increase the negative charge on soil surfaces (Barrow, 1985) providing more sites for metal adsorption. In some cases, organic ligands have increased heavy metal adsorption to soils (Chairidchai and Ritchie, 1990).

The objective of this research was to quantify the impact of citrate and salicylate on Pb retention in soil. We hypothesize that high concentrations of rhizophere organic acids will increase lead mobility in soil. In addition, a batch adsorption experiment was designed to establish the initial parameters for two column experiments examining the leaching of Pb with variable citrate and salicylate concentrations.

2. Materials and methods

2.1. Soil and leaching solutions

The uncontaminated soil used in this study was selected from the southeast Kansas mining area. The 0–20 cm layer was sampled in an area mapped as Parson silt loam, with 0–2% slopes (fine, mixed, thermic Mollic Albaqualfs) in Labette County, Kansas. The soil sample was air-dried and passed through a 2 mm sieve before use. The soil texture was analyzed by the hydrometer method (Sheldrick, 1986), and consisted of 35% sand,