

Mobilization of Lead from Highly Weathered Porous Material by Extracting Agents

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Batch and dynamic leaching experiments were conducted to evaluate the influence of clay mineralogy and soil organic matter (SOM) present in two highly weathered, surface and subsurface soil materials on Pb sorption and subsequent extraction using ethylenediaminetetraacetic acid (EDTA) and carboxymethyl β -cyclodextrin (CMCD). Saturated soil columns were leached with an acidic Pb solution to simulate a contamination event, followed by injection of artificial groundwater (AGW) at constant velocity. Greater Pb retardation was observed within the surface soil compared to the subsurface soil material, and a significant increase in effluent turbidity was observed coincident with the Pb breakthrough in the subsurface soil material. Electrophoretic, thermo-gravimetric, and X-ray diffraction analysis of the resulting suspension suggested that the presence of strongly adsorbing Pb^{2+} and excess H^+ increased the positive charge on amphoteric mineral surfaces and reduced the negative charge on clay minerals, which induced selective dispersion and transport of Fe oxides. In contrast, no increase in turbidity was observed for the surface soil following Pb injection. While only 30% of adsorbed Pb was mobilized from contaminated subsurface soil material, less than 10% of adsorbed Pb was extracted from surface soil when Pb-contaminated soil columns were flushed with AGW. Following leaching with AGW, extraction solutions containing either 0.37 g L^{-1} (1 mM) EDTA or 10 g L^{-1} CMCD were applied to extract the residual bound Pb. Nearly 100% of residual Pb was extracted from the surface soil by EDTA as compared to about 56% removal by CMCD under similar conditions. About 80% of residual Pb was removed by EDTA from the Pb-contaminated subsurface material, but less than 2% of residual Pb was extracted by CMCD under similar conditions.

1. Introduction

Transport and fate of heavy metal contaminants commonly encountered in subsurfaces are strongly dependent on factors such as the relative abundance and type of reactive binding surfaces (e.g., oxide minerals, soil organic matter, etc.) (1, 2). In addition, solute composition (e.g., pH, ionic strength, soluble organic matter, etc.) strongly affects the binding characteristics of contaminants, with various reactive phases differing in their affinity for a given contaminant (3). For example, cationic contaminants such as Pb^{2+} or Cd^{2+} adsorb

differently on a fixed-charged surface common to montmorillonites at any pH as compared to their adsorption to goethite (FeOOH) at different pHs. Constant charged minerals, as the description indicates, maintain constant overall charge at most pHs that are of environmental concern, while the variably charged minerals protonate or deprotonate as a function of pH, thereby affecting the adsorption of both cations and anions (4, 5).

The highly weathered soils and sediments of the Southeastern Atlantic Coastal Plain typically consist of assemblages of quartz sand and kaolinite coated with variably charged Fe-oxides (6, 7). The surface soils are typically enriched in soil organic matter (SOM) and relatively depleted in Fe-oxides with respect to the subsurface soil material.

Organic and inorganic, surface and subsurface contamination has occurred as a result of various activities at the Department of Energy's Savannah River Site located near Aiken, SC. While the presence of clay lenses or tiny pores in the soil aggregates can limit the physical movement of contaminants, chemical properties such as distribution coefficients (ratio of adsorbed versus solution concentration) and sorption kinetics tend to play a major role in controlling contaminant movement. Capturing groundwater plumes down-gradient from the contamination source for treatment often requires time scales on the order of several decades to meet regulatory limits (8). To enhance contaminant extraction, reactive chemicals which have a strong affinity for the target contaminant are required. Ideally an extractant chemical would (i) interact very weakly with the soil/aquifer matrix as compared to the target contaminant itself, (ii) increase the mobility of the target contaminant, and (iii) be generally nontoxic and biodegradable. However, such desirable characteristics are almost impossible to find in any single extractant.

The most accepted in-situ treatment method for metal contaminated soils involves washing with chelating agents, such as citric acid, nitrilotriacetic acid, and ethylenediaminetetraacetic acid (EDTA) (9, 10). However, chelating agents may complex strongly with soil components such as Fe-oxides and Al-oxides instead of the targeted heavy metal such as Pb^{2+} or Cd^{2+} (11). Therefore, substantial amounts of complexing agents must be added to enhance contaminant extraction. In addition to leaching the target metals, substantial amounts of Fe, Al, and other metals may be mobilized, significantly altering the soil/aquifer matrix. Application of such large concentrations of complexing agents may also pose problems due to their long-term persistence in the environment (12). In addition, enhanced transport of radionuclides over large distances in subsurface environments due to the presence of such complexing agents is widely reported (13–15).

Recently, a carboxymethylated form of β -cyclodextrin (CD) has been employed to treat soils contaminated with a variety of organic and metal contaminants, with considerable success in laboratory studies (16–18). Cyclodextrins, derived by simple enzymatic conversion from starch, are widely utilized in many industrial processes and analytical methods (19). The compound consists of carboxymethyl (CH_2COO^-) substitutions made at the outer rim of the β -CD molecule resulting in a neutral charge at low pHs. In previous studies (17, 18), it was reported that CD did not interact to a measurable degree with soils, while at the same time it increased the leachability of several low polarity organic contaminants (anthracene, trichlorobenzene, biphenyl, and DDT) and a heavy metal (Cd). It was speculated that heavy metals and organic compounds are complexed on the outer

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TABLE 1. Physical and Chemical Characteristics of Soil Materials Used in Experiments

	Tobacco Rd. formation (subsurface soil material)	Orangeburg series (surface soil)
depth	12 m	0–15 cm
pH _{KCl} ^a	4.4	3.9
pH _{H₂O} ^a	5.4	4.6
EC, ^b μ S/cm	5.86	53.93
Particle Size Distribution, ^c %		
sand (50–2000 μ m)	94.9	85.5
silt (2–50 μ m)	0.8	7.8
clay (<2 μ m)	4.3	6.6
clay mineralogy ^d	k, m, g	k, HIV, gibb
total organic carbon, ^e %	0.02	0.76
Extractable Fe, g Fe/100 g		
CDB ^f	0.74	0.19
ammonium oxalate	0.01	0.03

^a 1:2 soil:solution in deionized water or 1 M KCl. ^b 1:2 soil:solution in deionized water. ^c Micropipet method (45). ^d Determined by X-ray diffraction, k = kaolinite, m = mica, g = goethite, HIV = hydroxy-interlayered vermiculite, gibb = gibbsite (6). ^e Dry combustion method. ^f Citrate-dithionite-bicarbonate extraction (46).

rim and inside the cavity (as an inclusion complex) of the CMCD molecule, respectively, thereby enhancing simultaneous solubilization of metal and organic contaminants. Overall, carboxymethyl β -cyclodextrin (CMCD) displayed several characteristics desirable of any ideal metal extractant. In those studies, the heavy metals were present in the soils in combination with the organic contaminants. In addition, the soils tested were only mildly weathered at near neutral pHs. It is also not known how CMCD interacts with metals complexed in the highly weathered, acidic soils and sediments common to the Southeastern Atlantic Coastal Plain and how it compares with a more commonly used extractant, EDTA.

The objective of this study was to evaluate the influence of SOM and Fe oxide content Pb sorption and its subsequent extraction by CMCD and EDTA using batch and dynamic flow techniques. Two soil materials, a surface soil and a subsurface soil material, representative of the Southeastern Atlantic Coastal Plain were chosen for the study. These materials differ only slightly in their physical and chemical properties. They are both sandy and acidic, and the clay mineralogy is dominated by kaolinite; they differ slightly in their Fe-oxide and SOM content.

2. Materials and Methods

2.1. Materials. Experiments were performed using two uncontaminated, coarse textured, sandy soil materials from the Department of Energy's Savannah River Site (SRS) in Aiken, SC: (i) a surface soil (Ap horizon) of the Orangeburg Series collected from a coniferous/deciduous forested area and (ii) a subsurface material typical of the Tobacco Road formation collected from a deep subsurface exposure approximately 12 m below the original land surface (Table 1). Both soil materials have similar parent materials (i.e., weathered Coastal Plain Sediments). Although the subsurface material is actually a vadose zone sediment, it will be referred to in the text as the subsurface soil material. This material is typical of the coarse textured materials found within the deeper horizons of the soil pedon, the vadose zone, and within the water-table and first confined aquifer on the SRS. The subsurface soil material was uniform in texture and did not need any further treatment. The field-moist surface soil was homogenized to remove pebbles, roots, and dried leaves and stored at 4 °C in a plastic bag.

All chemicals used in the study were of analytical grade except for CMCD which was purchased from Cerestar USA, Inc. (98% reported purity). The average molecular weight reported is 1375 g mol⁻¹. All solutions including the metal containing treatments and extractant solutions were prepared in "artificial groundwater" (AGW) whose chemical composition is representative of the groundwater composition found in this region (20). The recipe for preparing AGW is 0.1095 g of CaCl₂·6H₂O, 0.0214 g of NaSO₄, 0.0618 g of MgCl₂·6H₂O, 0.008 g of KCl, and 0.0622 g of NaCl mixed to 20 L of deionized water.

2.2. Experimental Procedures. The reactivity of CMCD and EDTA to the two soils was measured in batch experiments by applying 30 mL of solution containing a known concentration of the CMCD or EDTA to 2 g of soil in Oak Ridge polyethylene centrifuge tubes. After shaking for 24 ± 2 h, the tubes were centrifuged at 10⁴ g for 30 min at 20 °C, filtered (0.22 μ m polycarbonate), and analyzed for nonpurgable organic carbon (NPOC) (Shimadzu, Inc.); NPOC was used as an indirect measure for the amount of CMCD or EDTA present in solution. Sorption isotherms were constructed based on the initial and final concentrations of CMCD and EDTA. Lead sorption experiments were conducted similarly in both soil materials as a function of solution pH. Known amounts of HNO₃ or NaOH were added to a series of centrifuge tubes containing 2 g of soil and 30 mL of Pb solution at a known concentration. Following equilibration (24 ± 2 h), the solutions were separated from the soil material by centrifugation and filtration as described above; the extracts were analyzed for Pb and pH. Lead in the solutions was analyzed using atomic absorption spectrometry or inductively coupled plasma mass spectrometry (Perkin-Elmer, Inc.).

Column experiments were performed in 1.0 cm ID, 30 cm long glass chromatography columns equipped with Teflon end pieces. The columns were packed in small incremental steps with the field moist soil to obtain a uniform bulk density. The ends of the soil columns were packed with small quantities of clean filter sand to uniformly distribute solutes into and out of the column. The depth of sand was varied depending on the length of the required soil column. Preliminary experiments indicated negligible sand interaction with Pb and the extractants. The soil columns were oriented vertically and slowly saturated in an upflow direction with AGW at a Darcy's velocity of 4.2 m/day. The column pore volume and porosity were determined gravimetrically and confirmed using a conservative tracer (³H₂O). A typical bulk density of 1.29 (± 0.05) and 1.43 (± 0.05) g cm⁻³ was obtained for the surface soil and subsurface soil material, respectively, which corresponded to a porosity of 0.51 (± 0.02) and 0.46 (± 0.02), respectively. The effluents collected in a fraction collector were analyzed for metal or NPOC concentrations as previously described.

The soil columns were initially flushed with AGW until equilibrium was established (~100 pore volumes) based on pH and conductivity of the effluent. Following AGW equilibration, the soil columns were leached with a solution containing 10 mg L⁻¹ of Pb(NO₃)₂ adjusted to pH 3.5 with 1.0 M HNO₃ until the influent and effluent Pb concentrations were equal. Following Pb saturation, the influent solution was switched to AGW to leach sorbed Pb from the soil column. When Pb concentration in the column effluent remained relatively uniform for several pore volumes, the influent solution was switched to either 10 g L⁻¹ CMCD or 0.37 g L⁻¹ (1 mM) EDTA and leached for several pore volumes before switching back to AGW. The concentrations of all elements of interest (Pb, Fe, Al, and other major cations) along with pH and turbidity (NTU) were monitored throughout the course of the experiments. The full sequence of all column experiments is listed in Table 2.

TABLE 2. Description of Input Solution Sequence for Column Experiments Presented in This Study^a

Exp.	soil material	solution 1 (inj. time)	solution 2 (inj. time)	solution 3 (inj. time)	solution 4 (inj. time)
1a	TR/OS	0.1 g L ⁻¹ CMCD	AGW		
1b	TR/OS	1.0 g L ⁻¹ CMCD	AGW		
1c	TR/OS	10 g L ⁻¹ CMCD (0–10)	AGW		
2a	TR/OS	0.37 g L ⁻¹ EDTA	AGW		
2b	TR/OS	3.7 g L ⁻¹ (0–10)	AGW		
3a	TR	10 mg L ⁻¹ Pb(NO ₃) ₂	AGW	10 g L ⁻¹ CMCD	AGW
3b	TR	10 mg L ⁻¹ Pb(NO ₃) ₂ (0–150)	AGW (150–188)	0.37 g L ⁻¹ EDTA (188–218)	AGW
4a	OS	10 mg L ⁻¹ Pb(NO ₃) ₂	AGW	10 g L ⁻¹ CMCD	AGW
4b	OS	10 mg L ⁻¹ Pb(NO ₃) ₂ (0–1065)	AGW (1065–1232)	0.37 g L ⁻¹ EDTA (1232–1305)	AGW
5a	TR	10 mg L ⁻¹ Pb(NO ₃) ₂	AGW		
5b	TR	pH 3.5, AGW (0–150)	AGW		

^a Pb(NO₃)₂ solution was adjusted to a pH of 3.5 in Exp. 3 and 4, while pH was not adjusted in Exp. 5a. Injection times are in pore volumes. Acronyms: TR is Tobacco Road formation subsurface soil material, OS is Orangeburg series surface soil, and AGW is artificial groundwater at pH 6 unless otherwise indicated.

Excessively turbid samples were digested according to EPA method 3010A (21), and the total concentration of Pb was measured along with other elemental concentrations using ICP-MS. The digestion method was modified to accommodate small fractions collected in the experiments. Solution-phase Pb was also determined by removing colloid-sized particles (<0.22 μm) using filtration. The colloid fractions were isolated by freeze-drying and analyzed for their clay composition using high resolution thermo-gravimetric analysis (TGA, TA Instruments) and X-ray diffraction (XRD, Scintag, Inc.). The electrophoretic mobility of selected colloidal suspensions produced in the column experiments was determined by laser doppler velocimetry (Delsa 440, Coulter Electronics).

3. Results and Discussion

The two soil materials evaluated in this study differ in the amount and type of reactive chemical components (Table 1). While the subsurface soil material contains large amounts of Fe-oxides and negligible quantities of SOM, the surface soil contained relatively higher amounts of SOM and reactive clays and smaller quantities of Fe-oxides. Hence, Fe-oxides account for most of the reactive surfaces on the subsurface soil material, while the SOM and the reactive clays account for a significant proportion of reactive surfaces in the surface soil. Regardless, the overall surface charge is pH-dependent in both materials.

3.1. Sorption and Transport of CMCD and EDTA. Based on batch data (data not shown) it was evident that CMCD sorbed more strongly to the subsurface soil material compared to the surface soil at near-neutral pH. In both soil materials, the sorption isotherms were nonlinear, and CMCD retention was inversely proportional to applied concentration. EDTA did not sorb significantly to either material. The total NPOC measured in the surface soil extracts following completion of the experiments was considerably higher than the NPOC content present in the extracting EDTA solutions indicating a release of soil organic matter. Chelating agents such as EDTA are known to extract humic substances from some soils (22, 23). As EDTA is able to complex strongly with most major cations present in soils (11), the soil-EDTA extracts also contained large quantities of Fe and Al.

Columns packed with either the surface soil or the subsurface soil material were flushed with solutions containing different concentrations of CMCD or EDTA to evaluate

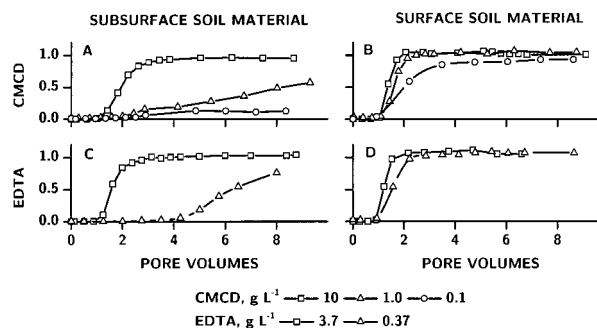


FIGURE 1. CMCD and EDTA sorption fronts measured as a function of applied concentration in columns packed with subsurface (A, C) and surface (B, D) soil materials. Notes: See description for Exp. 1 and 2 in Table 2 for the sequence of input solutions. The concentration scale on Y-axis has been normalized to the influent concentration.

extractant sorption (Exp. 1 and 2 in Table 2). Consistent with batch observations, CMCD and EDTA were nearly unretarded in surface soil at high concentrations and were only slightly retarded at lower concentrations (Figure 1). Retardation in transport processes is denoted by $R = 1 + \rho K_d$, where ρ is the soil bulk density and K_d is the slope of the adsorption isotherm. The retardation observed is consistent with the convex-shaped adsorption isotherms; retardation was inversely proportional to the applied solute concentration. This is clearly evident in both CMCD and EDTA breakthrough curves, although the effect is more prominent in the case of CMCD. Both CMCD and EDTA were significantly retarded in the subsurface soil material (Figure 1), again with retardation increasing as the influent concentration decreased.

Relatively higher quantities of Fe-oxides present in the subsurface soil material seemed to provide a more effective reactive surface for CMCD sorption. CMCD exhibits predominantly neutral or mildly negative charge at acidic pHs due to the presence of carboxylic functional groups. In addition, goethite minerals exhibit a point of zero net charge (PZNC) in the range of pH 7, i.e., a net positive charge below pH 7. Therefore, CMCD may sorb by ion exchange to a degree on Fe-oxide minerals at or below pH 7. The fact that CMCD sorbed strongly to the subsurface soil material suggests that CMCD interacts via surface complex formation at the Fe-

oxide–water interface. The surface soil, which contains less Fe-oxides compared to the subsurface soil material, sorbed less CMCD; this fact indicated the importance of Fe-oxides as the major reactive component for CMCD. Soil organic matter is often reported to exhibit PZNC in the range of pH 3 (23). However, the predominantly negative charge exhibited by SOM did not enhance CMCD sorption on to surface soil. In comparison to the subsurface soil material, little sorption was observed for the surface soil.

The effluent samples were noticeably colored following the application of EDTA to the subsurface soil material, indicating Fe dissolution. Some effluent turbidity was observed in the surface soil following the application of EDTA. Humic substances, which commonly make up SOM, are generally considered strong coagulating or soil stabilizing agents (24, 25). Hence, extraction of these humic substances disturbs the integrity of soils where SOM is a major component. In addition, EDTA dissolves the cementation agents such as Al and Fe oxides, leading to soil dispersion.

Following flushing of columns packed with subsurface soil material with CMCD, the influent solutions were switched to AGW. This resulted in a large turbidity front, the magnitude of which was directly proportional to the concentration of CMCD injected previously. The charge at the shear plane of these colloid particles generated as determined by electrophoresis was $-1.98 \pm 0.10 \mu\text{m cm V}^{-1} \text{s}^{-1}$. This phenomenon was not observed when EDTA was used instead of CMCD. We will address this issue in greater detail in the following sections.

3.2. Adsorption and Transport of Lead. pH-dependent sorption of Pb at a given concentration of Pb (C_{pb}) and a fixed soil-to-solution ratio was measured for several low C_{pb} (data not shown). Sorption in both soil materials was a strong function of solution pH with sorption edges appearing at a lower pH in the case of surface soil. The adsorption isotherms indicate that at any given pH, Pb adsorbs more strongly in the surface soil compared to the subsurface soil material. Therefore increased Pb retardation was expected in surface soil during transport. The adsorption isotherms were non-linear and convex-shaped for both soil materials indicating that sorption was strongly dependent on initial C_{pb} . Soil organic matter and reactive clays such as hydroxy-interlayered vermiculite (HIV) found in the surface soil are known to specifically bind with heavy metals such as Pb (26, 27). Batch experiments indicate that Pb sorption was more affected by SOM and HIV present in surface soil than by Fe-oxides present in subsurface soil material. In addition, extraction of Pb at low C_{pb} may be severely limited due to strong kinetically inhibited reactions.

A column packed with the subsurface soil material and equilibrated with AGW was subjected to a step increase in influent Pb concentration (C_{pb}) of 10 mg L^{-1} at pH 3.5 (Exp. 3 in Table 2). A normalized Pb concentration (C/C_0) of 0.5 was measured in the column effluents at $15 (\pm 0.5)$ pore volumes in two independent experiments. Effluent C_{pb} reached the maximum concentration from background levels within 3 pore volumes starting at 15 pore volumes (Figure 2). Effluent C_{pb} increased to a value greater than the influent concentration (C_0) up to a maximum C/C_0 of 1.3 after approximately 20 pore volumes. The effluent C_{pb} then reduced to C_0 within a few pore volumes. Upon switching the influent solution to AGW after 150 pore volumes, C_{pb} in the effluent gradually decreased to a C/C_0 of 0.1 after 165 pore volumes.

A significant increase in effluent turbidity was observed when the column influent was initially switched from AGW to acidified Pb solution (Figure 2), which was also accompanied by a decrease in effluent solution pH. The decrease in pH was gradual and displayed a self-broadening pattern indicative of exchange between strongly bound H^+

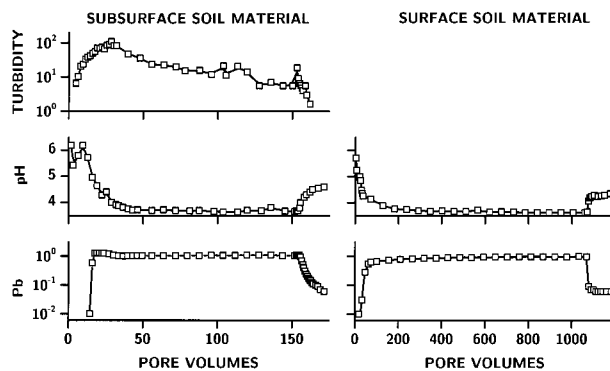


FIGURE 2. Lead sorption, turbidity, and pH fronts in columns packed with subsurface soil material and surface soil following application of an acidic Pb solution (10 mg L^{-1} , 3.5 pH). No turbidity was observed in case of column packed with surface soil. Notes: Lead and turbidity are expressed as C/C_0 and NTU, respectively. See description for Exp. 3 and 4 in Table 2 for the sequence of input solutions.

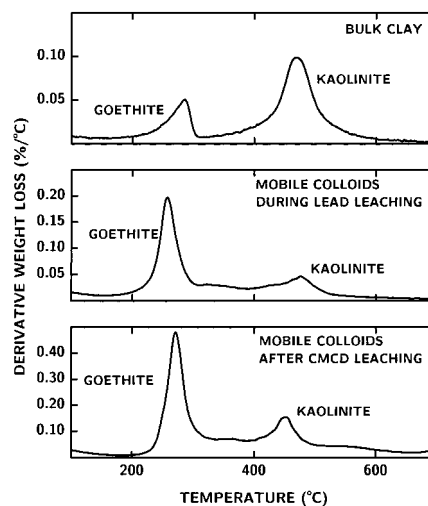


FIGURE 3. Derivative weight loss (%/°C) as a function of temperature (°C) for bulk clay and two types of mobile colloids generated in columns packed with subsurface soil material.

and Pb^{2+} at the soil surface. Following the initial increase, turbidity gradually decreased during the course of Pb leaching, and the pH remained constant after reaching the influent solution pH at about 40 pore volumes. Only a small fraction ($\sim 15\%$) of total Pb measured in digested solutions was associated with colloid-sized particles ($>0.22 \mu\text{m}$). The rise in effluent C_{pb} to a value greater than C_0 was attributed to the release of Pb associated with these colloids.

The mobile clay-sized colloid particles were isolated and analyzed using TGA to determine the clay mineralogy (Figure 3) and confirmed by XRD analysis. The mobile clay particles primarily consisted of goethite with relatively small amounts of kaolinite. This was in contrast to the larger ratio of kaolinite compared to goethite in bulk clay (Figure 3). This suggests that Pb is associated primarily with nonmobile phases, such as kaolinite, present in the soil than with goethite. This may be further corroborated with advanced spectroscopic techniques such as EXAFS. The charge at the shear plane of the colloid particles as determined by electrophoresis was $+1.98 \pm 0.10 \mu\text{m cm V}^{-1} \text{s}^{-1}$.

When the influent solution was switched back to AGW, a small increase in the effluent turbidity was followed by a sharp decrease until the effluent solutions were clear. These turbidity increases are probably the result of ionic strength changes. The decrease in turbidity was coincident with the

decrease in effluent C_{pb} and an increase in effluent pH. A self-sharpening H^+ adsorption front is not evident due to slow desorption kinetics of Pb^{2+} from the soil surface. This decrease or increase in pH as a result of corresponding increase or decrease in C_{pb} is typical of surface chemical reactions associated with specific sorption.

Adsorption of strongly sorbing cations can increase repulsive forces and hence the surface potentials between variably charged Fe-oxide coatings and negatively charged kaolinite causing a reversal of surface charge (7, 28). Consequently, repulsion between similarly charged surfaces due to Pb^{2+} and H^+ adsorption resulted in colloid mobilization. Considering the fact that at low pH, the concentration of H^+ is several orders greater than the concentration of Pb^{2+} , the soil dispersion may simply be the result of protonation of surface sites. This was verified by independently leaching columns packed with subsurface soil material with either unadjusted Pb solution or an acidified AGW solution (Exp. 5 in Table 2). While Pb was retarded for several pore volumes in the first case, no colloids were generated; a significant increase in turbidity was observed following the injection of acidified AGW (data not shown). Therefore, H^+ sorption reduced the net charge on negatively charged clay surfaces while increasing the positive charge on the iron oxide particles resulting in repulsion of iron oxide coatings on clay minerals. A similar effect may be observed if Pb were present in significantly higher concentrations in the leaching solution (29, 30).

Numerical integration of the area above the breakthrough curve ($\int_0^1 (1 - C/C_0)$) on the adsorption front yielded approximately $63 \mu\text{g}$ of Pb per g of soil. Upon switching the influent solution to AGW and integrating the area under the elution/desorption curve ($\int_0^1 (C/C_0)$) for desorbed Pb, about 31% of the adsorbed Pb was estimated to have been released during the 40 pore volumes sampled (see Table 2). This implies that flushing with several hundred pore volumes of Pb-free groundwater may be required to reach acceptable regulatory standards in field situations despite the limited residence time (e.g., aging) within the column.

Lead breakthrough curves obtained from a soil column packed with the surface soil displayed a contrasting behavior compared to the subsurface soil material (Exp. 4 in Table 2). Lead was more strongly retarded in the soil column; a C/C_0 of 0.5 was measured in the effluents after 62 pore volumes in two independent experiments (Figure 2). In addition, two characteristic features can be observed from the asymmetric shape of the breakthrough curves, where the slope of the breakthrough curves changes at different rates. Initially, C_{pb} (C/C_0) in the effluent solution increased sharply from 0 to 0.63 after 70 pore volumes. Following the sharp increase, C_{pb} increased gradually to about C/C_0 of 0.90 after nearly 800 pore volumes. However, the effluent solution concentration never reached the influent concentration within the time sampled (~1065 pore volumes). When the influent solution was switched to AGW, C_{pb} in the effluent decreased to less than 0.1 C/C_0 within 10 pore volumes. The effluent C_{pb} remained constant at about 0.07 C/C_0 for several pore volumes until the influent solution was switched again to CMCD/EDTA (see Table 2). This low recovery indicates extremely slow desorption kinetics.

The distinct shape of the breakthrough curve is indicative of the presence of two major reactive phases in surface soil. While fast sorption-desorption reactions occur in one phase, a second phase participates in much slower adsorption/desorption reactions. The shape of the adsorption front is also indicative of a partially self-sharpening and self-broadening front; similar but opposite trends can be observed in the desorption front. This shape is typical of sigmoidal-shaped nonlinear sorption isotherms (31-33). However, the effect of changes in pH on Pb sorption and the presence of

hydrodynamic dispersion makes it difficult to interpret the shape of an adsorption isotherm in such soil material.

The pH fronts measured from the column effluents strongly reflect the Pb sorption behavior. As can be seen in Figure 2, the decrease in pH following the application of acidic Pb solution is initially rapid followed by a slower decrease reflecting the Pb breakthrough patterns. Similarly, following the application of AGW, pH rises rather sharply followed by a much slower increase reflecting the Pb desorption front. It is widely reported that complexation with various organic functional groups is by far the most common metal retention mechanism compared to exchange (27). In addition, the fate of any given metal complex in a soil depends on the relative stability of the metal-organic complexes. Soil organic matter is also widely reported to complex fairly strongly with most heavy metals due to the presence of highly reactive carboxylic functional groups (23). The release in H^+ following sorption appears to occur as a result of their displacement from the carboxylic functional groups. The reverse mechanism occurs upon desorption of Pb from the SOM.

No effluent turbidity was observed during either the Pb sorption or desorption fronts in the surface soil column. The presence of relatively larger amounts of SOM and Al-oxides kept the soil matrices intact under mild to extreme chemical stresses (7, 25).

About $650 \mu\text{g}$ of Pb per g of soil was estimated to be sorbed upon integrating the area under the Pb breakthrough curves obtained from the surface soil columns. This is in sharp contrast to $63 \mu\text{g}$ of Pb sorbed per g of subsurface soil material. However, less than a tenth (9%) of the adsorbed Pb was recovered when the column was leached with Pb-free solution for 160 pore volumes, indicating that conventional pumping and treating of such contaminated sediments may require several decades to achieve effluent concentrations below acceptable standards.

3.3. Lead Extraction Experiments. In experiments 3 and 4 (see Table 2 for description), large amounts of Pb remained strongly bound to the soil materials. Leaching solutions containing either 0.37 g L^{-1} EDTA or 10 g L^{-1} CMCD were applied to the Pb-contaminated soil columns following application of AGW. The extractant concentrations were selected based on preliminary transport experiments involving CMCD and EDTA (Figure 3) and from concentrations commonly used in remediation strategies (18, 34).

Only a small amount of Pb was extracted by CMCD from the Pb-contaminated subsurface soil material; EDTA extracted larger amounts of Pb from similarly contaminated subsurface soil material (see data following the break in X-axis of Figure 4). Within two pore volumes of the application of EDTA, C_{pb} in the effluent peaked at C/C_0 of 2.4. However, the effluent C_{pb} reduced sharply within the next 10 pore volumes. An estimated 6.4 g of adsorbed Pb per g of soil was extracted by EDTA which corresponds to nearly 80% of the residual Pb estimated to be remaining in the soil columns following the Pb-free influent phase. No significant extraction of Pb was observed from the CMCD under similar conditions.

On switching the influent solution to AGW following the CMCD extraction solution, a second turbidity front appeared, similar to the one observed following injection of Pb. Turbidity rose sharply to as high as 720 NTU and dropped to background levels in the following 10 pore volumes of injected AGW. This may be attributed to the charge reversal caused by CMCD coatings on Fe-oxides or to the large decrease in the solution ionic strength. As was the case in the injection of CMCD in soil column not containing Pb, the charge at the shear plane of these colloid particles was $-1.98 \pm 0.10 \mu\text{m cm V}^{-1} \text{ s}^{-1}$. This is in sharp contrast to the positive charge measured on the colloid particles mobilized following Pb application indicating that the surface charge in Fe-oxide

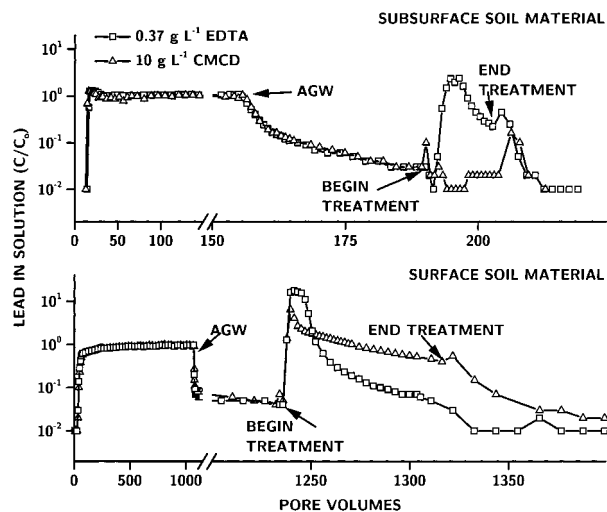


FIGURE 4. Extraction of Pb from Pb-contaminated subsurface soil material and surface soil using either 10 g L⁻¹ CMCD or 0.37 g L⁻¹ (1 mM) EDTA. Notes: Following break in the X-axis, a different scale is used to magnify some features of the breakthrough curves. See description for Exp. 3 and 4 in Table 2 for the sequence of input solutions. AGW is artificial groundwater.

dominated subsurface soil material was indeed modified by CMCD. Only minor amounts of Pb were associated with this fraction of colloidal particles. These colloids predominantly consisted of goethite, based on TGA (Figure 3C) and verified using XRD analyses (not shown). They display similar mineralogical characteristics as the ones generated during Pb injection. It did not come as a surprise to find that only negligible amounts of Pb were associated with these colloids. Similar behavior was not observed in case of EDTA.

A significant portion of the residual Pb (following application of AGW) was extracted by both EDTA and CMCD from the Pb-contaminated surface soil (see data following the break in X-axis in Figure 4). Within two pore volumes of EDTA application, the effluent C_{Pb} (C/C_0) rose sharply to as high as 18.5 before a sharp reduction in concentration within the next 10 pore volumes. When CMCD was injected into a Pb-contaminated surface soil column, the effluent C_{Pb} (C/C_0) only rose to about 6 followed by a more gradual decrease in concentration. During the time sampled, CMCD was still able to extract Pb from the contaminated soil. Nearly 100% of the residual Pb was extracted by EDTA in contrast to 56% of residual Pb extracted by CMCD under similar conditions.

Overall, CMCD was ineffective in the subsurface soil material system and more effective in the surface soil system. Based on the extraction data, it appears that the Pb–Soil complexes are stronger than Pb–CMCD complexes in the subsurface soil material, while this was not the case in the surface soil. This is due to the nature of Pb–Soil complexes formed as a result of changes in soil composition; the major difference being the relative amounts of Fe-oxides, SOM, and reactive clays present. Compared to its extraction of Pb from contaminated surface soil, EDTA was relatively less effective in the contaminated subsurface soil material. Hence, Pb–EDTA complexes may be moderate to extremely strong compared to Pb–Soil complexes in both soil materials.

Lead extraction efficiency in each of these materials is dictated by the availability of CMCD or EDTA. Earlier it was shown that CMCD and EDTA strongly sorb to the subsurface soil material at low solute concentrations (cf. Figure 1). In addition, EDTA complexes more strongly with Fe³⁺ and Al³⁺ compared with Pb²⁺ (11) and, hence, is not available to extract residual Pb from the contaminated subsurface soil material. Recently Davis et al. (35) have shown that Pb–EDTA complexes could dissociate despite strong thermodynamic

stability of such complexes. They hypothesize that strong preference of Pb²⁺ to natural aquifer sediments could result in the dissociation. Even though no thermodynamic stability constants involving CMCD and the cations of interest were available during this study, a similar phenomena is proposed to occur based on strong sorption of CMCD in subsurface soil material (cf. Figure 1). Overall, Pb seemed to form stronger complexes with EDTA compared with CMCD, thereby resulting in greater extraction of Pb by EDTA from the contaminated soil materials. In addition, EDTA was observed to extract SOM from surface soil and hence indirectly extracting SOM-bound Pb which further enhanced Pb extraction in the surface soil. McBride et al. (22) have shown that EDTA, while dissolving and dispersing substantial amounts of high molecular weight organic matter, also displaced bound metals such as Cu²⁺ from organic complexation sites by chelating the metal.

Based on these laboratory experiments, conventional treatment (pump and treat) for Pb reclamation with Pb-free water was ineffective in either soil material. The application of EDTA or CMCD to these contaminated materials greatly enhanced Pb removal in surface soil, while only EDTA was effective in the subsurface soil material. Although CMCD was relatively less effective in extracting residual Pb, it exhibits properties that may be used to great advantage depending on specific applications.

Desorption of CMCD from subsurface soil material resulted in generation of negatively charged soil colloids regardless of whether Pb was initially present on the sediments or not. This modification to surface charging behavior has several implications, especially when targeting specific fractions of a soil material that are associated with heavy metals or other contaminants. In ex-situ or controlled in-situ remediation operations, heavy metals associated with the colloid fractions can be harvested for further treatment (36–38).

Either extractant may be less effective when applied to aged contaminated sediments due to possible formation of stable contaminant mineral phases that resist treatment (22, 39–41). In addition, problems associated with mobilization of colloids hinders the application of extracting agents such as CMCD in subsurfaces.

Using advanced analytical tools such as Fourier transform ion-cyclotron resonance mass spectrometry (42–44), one may be able to determine thermodynamic stability data involving chelating agents such as CMCD that are required for reliable estimates of metal transport and extraction.

Nomenclature

AGW	artificial groundwater
CMCD	carboxymethyl β -cyclodextrin
EDTA	ethylenediaminetetraacetic acid
HIV	hydroxy-interlayered vermicullite
NPOC	nonpurgable organic carbon
PZNC	point of zero net charge

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Literature Cited

- (1) Brusseau, M. L. *Rev. Geophys.* **1994**, *32*, 285–313.
- (2) *Reactive Transport in Porous Media*; Lichtner, P. C., Steefel, C. L., Oelkers, E. H., Eds.; Mineral. Society of America: Washington, DC, 1996.
- (3) *Adsorption of Metals by Geomedia: Variables, Mechanisms, and Model Applications*; Jenne, E. A., Ed.; Academic Press: San Diego, CA, 1998.
- (4) van Olphen, H. *Clay Colloid Chemistry: For Clay Technologists, Geologists, and Soil Scientists*, 2nd ed.; Krieger Publ. Co.: Malabar, FL, 1991.
- (5) Sparks, D. L. *Environmental Soil Chemistry*; Academic Press: San Diego, CA, 1995.
- (6) Seaman, J. C.; Bertsch, P. M.; Korom, S. F.; Miller, W. P. *Ground Water* **1996**, *34*(5), 778–783.
- (7) Bertsch, P. M.; Seaman, J. C. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 3350–3357.
- (8) National Research Council. *Alternatives for Ground Water Cleanup*; National Academy Press: Washington, DC, 1994.
- (9) Palmer, C. D.; Fish, W. *Chemical Enhancements to Pump-and-treat Remediation*; Technical Report EPA/540/S-90/OOI; U.S. EPA: 1992; EPA Issue Paper.
- (10) United States Environmental Protection Agency. *A Literature Review Summary of Metals Extraction Processes used to Remove Lead from Soils*; Project Summary EPA/600/SR-94/006; Risk Reduction Engineering Laboratory, U.S. EPA: 1994.
- (11) Martell, A. E.; Smith, R. M. *Amino Acids; volume 1 of Critical Stability Constants*; Plenum Press: New York, 1974.
- (12) Means, J. L.; Kucak, T.; Crerar, D. A. *Environ. Pollut. (Ser. B)* **1980**, *1*, 45–60.
- (13) Means, J. L.; Crerar, D. A.; Duguid, J. O. *Science* **1978**, *200*, 1477–1481.
- (14) Killey, R. W.; McHugh, J. O.; Champ, D. R.; Cooper, E. L.; Young, J. L. *Environ. Sci. Technol.* **1984**, *18*, 148–157.
- (15) Brooks, S. C.; Taylor, D. L.; Jardine, P. M. *Geochim. Cosmochim. Acta* **1996**, *60*(11), 1899–1908.
- (16) Brusseau, M. L.; Wang, X.; Hu, Q. *Environ. Sci. Technol.* **1994**, *28*(5), 952–956.
- (17) Wang, X.; Brusseau, M. L. *Environ. Sci. Technol.* **1995**, *29*(10), 2632–2635.
- (18) Brusseau, M. L.; Wang, X.; Wang, W. *Environ. Sci. Technol.* **1997**, *31*(4), 1087–1092.
- (19) Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743–1753.
- (20) Strom, R.; Kaback, D. *SRP Baseline Hydrogeologic Investigation: Aquifer Characterization Groundwater Geochemistry of the Savannah River Site and Vicinity*; Technical Report WSRC-RP-92-450; Environmental Sciences Section, Department of Energy; Savannah River Site: Aiken, SC, 1992.
- (21) United States Environmental Protection Agency. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846 online): 3010A. Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy*; Technical Report <http://www.epa.gov/sw-846/sw846.htm>; U.S. EPA: 1992.
- (22) McBride, M.; Martinez, C.; Sauve, S. *Soil Sci. Soc. Am. J.* **1998**, *62*, 1542–1548.
- (23) Senesi, N.; Loffredo, E. In *Soil Physical Chemistry*, 2nd ed.; Sparks, D. L., Ed.; CRC Press: Boca Raton, FL, 1999; pp 239–370.
- (24) O'Melia, C. R.; Tiller, C. L. In *Environmental Particles*; Buffle, J., van Leeuwen, H. P., Eds.; Lewis Publishers: Boca Raton, FL, 1993; Vol. 2, pp 353–386.
- (25) Baldock, J. A.; Nelson, P. N. In *Handbook of Soil Science*; Sumner, M. E., Ed.; CRC Press: Boca Raton, FL, 1999; pp B25–B84.
- (26) McBride, M. B. In *Interactions at the Soil Colloid-Soil Solution Interface*; McBride, M. B., Bolt, G. H., de Boodt, M. F., Hayes, M. H. B., Eds.; Dordrecht, The Netherlands, 1991; pp 149–175.
- (27) Harter, R. D.; Naidu, R. *Adv. Soil Sci.* **1996**, *55*, 219–263.
- (28) Ryan, J. N.; Elimelech, M. *Colloids Surf. A. Physicochem. Eng. Aspects* **1996**, *107*, 1–56.
- (29) Ryan, J. N.; Gschwend, P. M. *Environ. Sci. Technol.* **1994**, *28*, 1717–1726.
- (30) Seaman, J. C.; Bertsch, P. M.; Strom, R. N. *Environ. Sci. Technol.* **1997**, *31*, 2782–2790.
- (31) Bolt, G. H. In *Soil Chemistry. B. Physico-Chemical Models*; Bolt, G. H., Ed.; Elsevier Scientific Publ.: Amsterdam, The Netherlands, 1979; pp 285–348.
- (32) Schweich, D.; Sardin, M. *J. Hydrol.* **1981**, *50*, 1–33.
- (33) Scheidegger, A.; Bürgisser, C. S.; Borkovec, M.; Sticher, H.; Meeussen, H.; van Riemsdijk, W. *Water Resour. Res.* **1994**, *30*, 2937–2944.
- (34) Anderson, W. C. *Soil Washing/Soil Flushing; volume 3 of Innovative Site Remediation Technology*; American Academy of Environmental Engineers: 1993.
- (35) Davis, J. A.; Kent, D. B.; Coston, J. A.; Hess, K. M.; Joye, J. L. *Water Resour. Res.* **2000**, *36*, 119–134.
- (36) McCarthy, J. F.; Zachara, J. M. *Environ. Sci. Technol.* **1989**, *23*(5), 496–502.
- (37) Grolimund, D.; Borkovec, M.; Barmettler, K.; Sticher, H. *Environ. Sci. Technol.* **1996**, *30*, 3118–3123.
- (38) Seaman, J. C.; Bertsch, P. M. *Environ. Sci. Technol.* **2000**, *34*, 3749–3755.
- (39) Lothenbach, B.; Furrer, G.; Scharli, H.; Schulin, R. *Environ. Sci. Technol.* **1999**, *33*(17), 2945–2952.
- (40) Martinez, C. E.; McBride, M. B. *Environ. Sci. Technol.* **1999**, *33*(5), 745–750.
- (41) Martinez, C.; Sauve, S.; Jacobson, A.; McBride, M. *Environ. Sci. Technol.* **1999**, *33*, 2016–2020.
- (42) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64–71.
- (43) Agnes, R. G.; Steward, I. I.; Horlick, G. *Appl. Spectrosc.* **1994**, *48*, 1347–1359.
- (44) Brown, T. L. Rice, J. A. *Anal. Chem.* **2000**, *72*(2), 384–390.
- (45) Miller, W. P.; Miller, D. M. *Commun. Soil Plant Anal.* **1987**, *1*–15.
- (46) Jackson, M.; Lin, C.; Zelazny, L. In *Methods of Soil Analysis: Part 1, Physical and Mineralogical Methods*, 2nd ed.; Klute, A., Ed.; American Society of Agronomy, Inc.: Madison, WI, 1986; pp 101–150.

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