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The Effect of Contaminant Aging Upon Soil Washing Removal Efficiencies for Lead Contaminated Soils

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INTRODUCTION

Soil washing has recently become a popular *ex-situ* technique for remediating sites contaminated with heavy metals. This research focused on lead contamination, since lead is one of the most common heavy metals at Superfund sites across the nation.¹ Lead is commonly found at sites where past industrial activities include battery breaking and recycling, oil refining, paint manufacturing, metal molding and plating, and smelting. Lead pollution from the automobile industry is also extensive. The objective of this research was to investigate lead removal efficiencies from various soils using a variety of washing solutions. Most soil types have a strong affinity for lead. Thus, it is plausible to expect washing solutions that are capable of removing lead could also remove other divalent heavy metals.

Like most bench scale soil washing studies, the soils used here were artificially contaminated with lead. Spiking soils in such a manner can often reduce the heterogeneity in initial contamination levels often observed in soils from actual contaminated sites. As with any experimental work, lab conditions cannot perfectly mimic natural conditions. Soils that have been contacted with heavy metals in nature are often more difficult to remediate than soils spiked in the laboratory, for the stronger retention mechanisms (*i.e.*, specific adsorption, solid state diffusion and precipitation) occur slowly over a period of many years.² For example, metal oxides in nature are often initially amorphous and found as coatings on other soil components such as sands. With time, however, these amorphous minerals will develop crystalline patterns which retain heavy metals very tightly. In a kinetic release study, lead release was observed to be a two step process, with the initially rapid removals being associated with weak retention mechanisms such as cation exchange. The second phase of lead release, most likely of the stronger bound lead, occurred at a much slower rate. Reaction rates obtained for artificially contaminated soils in the same study were at least an order of magnitude greater than that of the naturally contaminated soil.³

Four (4) soil samples from the eastern United States were collected and characterized for this study. The study soils were then spiked to approximate lead concentrations of 1,000, and 10,000 mg Pb/kg soil. The efficiencies of six washing solutions in removing lead from the contaminated soils were then investigated via lab-scale batch washing experiments. Unlike current field-scale soil washing practices, all particle size fractions were washed and recovered in these experiments. (Solutions investigated include: tap water, HCl, EDTA, HNO₃, CH₃COOH, and CaCl₂). In order to examine the effect of aging upon soil washing efficiencies, some of the spiked soils were washed a second time after an aging period of nearly 2 years.

MATERIALS AND METHODS

Experimental work was performed at the WVU Environmental Engineering laboratories. All chemicals used were reagent grade. Solutions were prepared in nitric acid rinsed volumetric flasks then stored in polyethylene containers. To minimize chemical biodegradation, organic reagents, such as EDTA or acetic acid were refrigerated prior to use. Measurements of pH were obtained using Orion™ meters and combination electrodes. All samples for lead analysis were filtered through a 0.45µm membrane filter and were preserved by acidification with nitric acid if the pH of the filtrate was greater than 2.0. All wash experiments were conducted in triplicate. The filter assembly and the pH electrode were rinsed between triplicates in order to reduce the possibility of sample contamination. Lead concentrations were determined using a Perkin Elmer 2380™ atomic absorption spectrophotometer (A A) equipped with a flow spoiler. The analyses were performed using an air-acetylene flame and wavelength settings of λ = 217.0 nm. Percent recoveries were performed on approximately 1 in every 5 samples to ensure that significant interferences were not present.

Soil Spiking Procedure

Each study soil was spiked with lead at two (2) different concentrations. If complete adsorption of lead from solution were to occur, this contamination procedure would yield soil concentrations of 1,000 and 10,000 mg/kg Pb above indigenous soil lead concentrations. A 10:1 liquid:soil ratio was employed in the contamination step. Solutions of lead nitrate [Pb(NO₃)₂] were prepared having approximate lead concentrations 100 and 1,000 mg/L. Sodium nitrate (NaNO₃) was also added to each solution to simulate the ionic strength (µ) of groundwater. As a result, all lead solutions were prepared with a NaNO₃ concentration of 3,200 mg/L (µ = 0.04 Moles/L).

One hundred fifty grams of air-dried, No. 10 sieved, soil was placed in a 2 liter Nalgene™ container with 1.5 liters of the appropriate Pb-NaNO₃ solution. An aliquot of each Pb-NaNO₃ solution, taken prior to the addition of soil, was acidified and kept for lead analysis. Initial slurry pH's were taken, and the samples were placed on mechanical shakers for twenty one (21) days. To reduce the possibility of lead precipitation, the 1,000 mg/L Pb contaminating solution was pH adjusted to 4.8 with nitric acid (HNO₃) before being mixed with the soil. At the end of the contact period, the samples were not disturbed for 24 hours in order to provide adequate time for the colloidal clay particles to settle. The supernatant was then decanted off in a graduated cylinder, and the volume removed was recorded for subsequent mass balance calculations. A small aliquot of the supernatant was taken, 0.45 µm filtered, and preserved for lead analysis. The remaining soil was then air dried and crushed to pass through an ASTM No. 10 sieve. Two methods were used to determine the final contamination levels. The first method was based upon mass balance principles. It was assumed all lead removed from solution was retained by the soils. Hence, the amount of lead retained by the soil was determined via the difference between the lead concentrations of the initial Pb-NaNO₃ solution and supernatant solution according to the following equation:

$$\text{Soil Pb} = \{[\text{Pb}_o \cdot V_o] - [\text{Pb}_f \cdot V_f]\} / [W_s] \quad (1)$$

Where:

- Pb_o = Initial Pb Concentration.
- Pb_f = Final Pb Concentration
- V_o = Initial Volume Pb Solution.
- V_f = Supernatant Volume.
- W_s = Weight Soil Added

As a check, a second method was used where the contaminated soils were digested in triplicate for total metal content using EPA Method 3050.⁴ The average of these two values was used as the initial lead value during the washing experiments unless otherwise noted.

Laboratory Washing Experiments

The study soils, contaminated with two concentrations of lead, were washed in triplicate with the solutions listed in Table 1. In these batch experiments, 25 mL of each washing solution was delivered (via a wide-mouth volumetric pipette) into a 60 mL Nalgene™ bottle that contained 1.0 ± 0.02 grams of contaminated soil. The samples were then placed on mechanical shakers for 24 hours. At the end of the 24 hour period, the pH of the each sample slurry was measured and recorded. Approximately 10 mL of each sample was then vacuum filtered through a 0.45µm membrane filter. The remaining portion of the sample was rinsed from the sample bottle and discarded in a waste container. The resulting filtrate was placed back into the same bottle, preserved if required, and kept for lead

analysis Atomic absorption results represented the quantity of lead removed from the contaminated soils and was divided by the initial lead mass on each soil (determined earlier via both acid digestion and the mass balance approach described above) to obtain soil washing efficiencies. The portion of each spiked soil not used in the first wash was stored in sealed containers and allowed to age. To investigate the effects of aging, the soils were then washed in the same manner as the original washes described above.

RESULTS AND DISCUSSION

Characterization data determined for the study soils used in the aging experiments are presented in Table 2. Soils 1 is sandy in nature while Soils 2 is much finer grained. Subsequently, Soil 2 possesses a greater CEC value and a higher organic content, typically of finer grained soils. It was thought that the selection of these soils would not only provide insight into the effect of aging but might also provide data illustrating the effect of soil type upon washing efficiencies.

The batch soil washing experiments were first conducted 2 months after the soils were artificially contaminated with lead. Additionally, wash experiments were conducted on a second sample of each contaminated soil 20 months after soil spiking. The wash results for Soil 1 are presented in Figures 1 and 2 for the low and high lead spiking levels, respectively. Similarly, Figures 3 and 4 present the wash results for Soil 2 at the low and high lead contamination level. The initial lead contamination level (as discussed in

previous section) is also provided on each plot. The values plotted in these figures represent the average of triplicate washes. Reproducibility among triplicate samples were generally very good. One notable exception was for the 0.1N HNO₃ wash of Soil 1 (see Figure 1), where the triplicate samples yielded a range of lead removals from 61 to 144 percent. The results of the tap water washes are included in Figures 1-4 to illustrate that the lead was not readily removed from any of the soils even though a soluble lead source was used in the spiking procedure.

As expected, the greatest removals were obtained from the acid washes (HCl and HNO₃) and the EDTA washes. A more detailed discussion of the HCl and EDTA washes performed as part of this study can be found elsewhere.⁵ Considerably lower removals were obtained by the acetic acid and calcium chloride washes. Removals achieved by strong acid solutions are likely due to dissolution of some of the soil components, thereby releasing lead was originally bound by cation exchange, specific adsorption, and other stronger retention mechanisms. Although some chloride ions may complex with soil bound lead, cation exchange is most likely the dominant removal mechanism that is operative during the CaCl₂ washes. (The excess Ca²⁺ cations invoke a concentration gradient that forces the exchange of Pb²⁺ ions for Ca²⁺ ions on the soil surface sites.) The concentration of the washing solutions also had an effect upon the CH₃COOH and CaCl₂ samples, where removal efficiencies increased markedly with increases in washing solution strength.

Figures 1-4 present the data from both washes of each soil. It is evident that removal efficiencies decreased for many of the samples as a result of the "aging" process. This phenomenon was the greatest for the HCl and EDTA washes where the average removal were 8 percent less for the samples aged 20 months than for the soils aged 2 only months. In addition, the effect of aging is more pronounced for the samples spiked at the lower lead level than at the higher lead level for both study soils. (The effect of initial contamination level upon removals will be discussed later.)

For each soil and lead contamination level, the removal efficiencies obtained for the acetic acid washes appear to be essentially identical for the 2 month and 20 month washes (See Figures 1-4).

Results of other research indicate that the ability of acetic acid to decrease heavy metal retention by soils is limited. By definition, acetic acid is not a chelating agent, but acetic acid can form weak complexes with heavy metals. Cadmium-adsorption experiments using a silt loam (1125 mg/kg Cd) with characteristics similar to Soil 2 were performed in the presence of 2.0×10^{-2} N acetic acid and then in the presence of 5.0×10^{-6} M EDTA. In the pH range of 3.5-8, the maximum reduction in cadmium retention (as compared to controls samples with no complexing ligands present) was found to be 50% for EDTA but only 5% for the acetic acid experiments.⁶

Even though acetic acid is a weak complexing agent, it most likely mobilizes soil bound lead via its ability to lower the pH of a soil system. Acetic acid is a weak acid which dissociates at pH 4.75 (pK_a value). The un-ionized form dominates at pH's below the pK_a value. The slurry pH values taken at the end of the wash experiments (prior to filtering) were all below the pK_a value. Thus, the neutrally charged species (CH₃COOH) may have been adsorbed by the soils, thereby lowering the system pH and reducing the number of surface sites available for heavy metal retention. The observation that the acetic acid removals were seemingly not affected by soil aging could possibly be explained by the fact that the slurry pH reduction induced by acetic acid was not great enough to release any more lead from the "newly" spiked samples than it was capable of releasing from the aged soils.

In contrast to all other washing solutions investigated, nearly all calcium chloride removals were greater for the aged samples, in fact, the average removals from the 20 month samples were 13 percent greater than from the samples aged only 2 months. It is suspected that this situation is caused by the pH values of the CaCl₂ slurries. Unlike the other washes which typically had slurry pH values less than 4.0, pH values for the CaCl₂ slurries were generally in the range of 5.5-6.2. At such high pH values, surface precipitation reactions may be occurring that increase enhance lead retention. In experiments involving an aqueous solution of 100 mg/L Pb with ionic strength used in the contaminating slurries ($\mu=0.04$ M), significant quantities of lead began to be removed from solution at a pH of 6.⁷ In addition, the presence of a solid phase typically decreases the pH at which lead is removed from solution (via precipitation and other adsorption reactions). The CaCl₂ solutions prepared for the 20 month experiments had slightly lower initial pH values than those prepared for the washes conducted 2 months after spiking. This anomaly resulted in slurry pH values after the 24 hour wash period to be approximately 0.2-0.4 pH units less for the 20 month samples than for the 2 month samples. Such a small decrease in pH can lead to drastic increases in lead mobility in situations where conditions, as predicted here, are conducive to surface precipitation reactions.

The soil washing data presented here also illustrated other factors in addition to contaminant aging that affected removal efficiencies. It has been known that lead is less tightly bound to soils when present at high initial concentrations, for lead cations are preferentially retained by the high energy binding sites (reactive surface sites) when lead is present in trace quantities. As more lead is added to the soil, the average binding strength of the available sites decreases and the selectivity coefficient decreases because the high energy sites have already been filled.⁸ Such a trend was observed in this study. The average removal efficiency for Soil 1 in Figure 1 (average of all wash solutions except tap water) was 66 percent, while the average lead removal from the samples spiked at the higher lead level (Figure 2) was 82 percent (16% greater). The difference between removal efficiencies was slightly less for Soil 2. The average removal efficiency for Soil 2 in Figure 3 was also 66 percent, while the average lead removal from the samples spiked at the higher lead level was 71 percent (5% greater). The effect of initial concentration, however, would not be expected to be as great for Soil 2. Due to its larger organic content and greater abundance of clay particles (*i.e.*, reactive sites), Soil 2 likely has a larger average binding strength than Soil 1. Note, however, that the lower removal efficiency of Soil 2 compared to Soil 1 at the higher lead

contamination level (71% vs. 82%) could also be due to the fact that the initial lead concentration of Soil 2 is much larger than that of Soil 1 (9110 mg/kg vs. 2680 mg/kg) whose lead retention capacity was probably not reached during the 21 day contamination period. (Retention kinetic studies have suggested that surface precipitation, which is a slower retention mechanism than cation exchange, etc., may have been the dominant retention mechanism for Soil 1.)⁹

CONCLUSIONS

Although the aging study did not yield enough data to support a thorough statistical analysis, the results obtained do illustrate the effect that several factors have upon the effectiveness of soil washing to remediate lead and possibly other heavy metal contaminated soils. These factors include: contaminant aging; washing solution type and concentration, soil type; and initial contaminant concentration. Of the washing solutions investigated, the effect of aging was most apparent for the HCl, EDTA, and HNO₃ washes, particularly for the samples contaminated at the lower lead level ($\approx$ 1,000 mg/kg). In addition, removals via the acetic acid and calcium chloride washes were generally low, similar or increased removals being obtained for the aged soil samples. Such an occurrence is suspected to be due to the characteristics/properties of these washing solutions, rather than a true reduction in the strength of lead retention to these soils after a 20 month period of aging.

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Table 1. Washing Solutions Investigated

Washing Solutions	Concentrations
Tap Water (H ₂ O)	Not Applicable
Hydrochloric Acid (HCl)	0.1 N and 1.0 N
Nitric Acid (HNO ₃)	0.1 N and 1.0 N
EDTA (Na ₂ C ₁₀ H ₁₄ O ₈ N ₂ ·2H ₂ O)	0.01 M and 0.1 M
Acetic Acid (CH ₃ COOH)	0.1 N and 1.0 N
Calcium Chloride (CaCl ₂)	0.1 M and 1.0 M

Table 2. Selected Properties of the Study Soils.

Parameter	Soil No. 1	Soil No. 2
Soil pH ⁴	6.2±0.20	7.0±0.10
% Passing No. 200 Sieve ¹⁰	1.7	37.2
Indigenous Pb(mg/kg) ⁴	6.3±1.3	19±1.5
CEC (meq/100g) ⁴	6.4±0.60	20.5±2.0
Total Volatile Solids (Wt %) ¹¹	1.60±0.10	4.37±0.20
Fe _{AAO} (mg/kg) ¹²	1350±80	5000±200
Al _D (mg/kg) ¹³	600±50	2110±120
Mn _{AAO} (mg/kg) ¹²	52	515±10

Figure 1. Soil Washing Results for Soil 1 Spiked at the Low Lead Concentration Level.

Figure 1 Soil Washing Results for Soil 1 Spiked at the High Lead Concentration Level

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Figure 1 Soil Washing Results for Soil 2 Spiked at the Low Lead Concentration Level

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Figure 1. Soil Washing Results for Soil 2 Spiked at the High Lead Concentration Level