Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Retention and Release of Lead by a Silty Loam and a Fine Sandy Loam. II. Kinetics

Patrick P. E. Carriere[a]; Brian E. Reed[a]; Steve R. Cline[b]
[a] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, WEST VIRGINIA UNIVERSITY, MORGANTOWN, WEST VIRGINIA [b] MARTIN MARIETTA ENERGY SYSTEMS, INC. ENVIRONMENTAL SCIENCES DIVISION OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE

To cite this Article Carriere, Patrick P. E. , Reed, Brian E. and Cline, Steve R.(1995) 'Retention and Release of Lead by a Silty Loam and a Fine Sandy Loam. II. Kinetics', Separation Science and Technology, 30: 18, 3471 — 3487

To link to this Article: DOI: 10.1080/01496399508015130

URL: http://dx.doi.org/10.1080/01496399508015130

SEPARATION SCIENCE AND TECHNOLOGY, **30**(18), pp. 3471–3487, 1995

Retention and Release of Lead by a Silty Loam and a Fine Sandy Loam. II. Kinetics

PATRICK P. E. CARRIERE and BRIAN E. REED
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
WEST VIRGINIA UNIVERSITY
MORGANTOWN, WEST VIRGINIA 26506-6103

STEVE R. CLINE
MARTIN MARIETTA ENERGY SYSTEMS, INC.
ENVIRONMENTAL SCIENCES DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE 37381-6036

ABSTRACT

The kinetics of lead retention and release by a silty loam and a fine sandy loam was investigated. Batch experiments were conducted to assess the rate and degree of lead retention. The rate of lead sorption onto the soils was determined using lead solution with concentrations of 10, 100, and 1000 mg/L. Kinetics of lead retention was very rapid for both soils. Lead was completely removed from both the 10 and 100 mg/L solutions, but partially removed from the 1000 mg/L solutions within the first hour. It was noted that the rate of lead soption was faster for the 10 and 100 mg/L than the 1000 mg/L solutions. The slower retention kinetics for both soils at the 1000 mg/L lead contamination level can be attributed to surface precipitation effects. Batch extraction experiments were also performed using three different types of washing solutions. Lead release using the $CaCl_2$ washes was less than the release using EDTA and HCl, but the kinetics of lead release was initially rapid with most of the removal occurring within the first hour for the three washing solutions. It was observed that the lead solution concentration has no effect on lead removal during the rapid step for the HCl and EDTA washes, but has some effect for $CaCl_2$ washes.

INTRODUCTION

Heavy metals are a major concern in groundwater. Most of them arise from industrial practices and discharges from mining, metal plating, plumbing, coal, gasoline, and pesticides-related industries. Many of these metals are very toxic. Many processes take place in groundwater that are of interest when considering the fate and transport of heavy metals in the subsurface. Metals can sorb onto the soil, undergo chemical precipitation, be subjected to abiotic reactions, and be part of oxidation–reduction sequences. Sorption causes metal pollutants to move more slowly than the flowing groundwater. Sorption effects must be considered when evaluating the movement of the metal in an aquifer and designing remediation activities at hazardous-waste sites. The calculation of the kinetics of heavy metal retention and releases is necessary to predict the transport of heavy metal through the subsurface or to estimate performance of remediation technologies. The objective of this study is to determine the kinetics of retention and release of lead by a silt loam and a fine sandy loam. In a previous article, the isotherm models for retention of lead were presented (1).

BACKGROUND

Metal Retention Mechanisms

Metals in soil systems can be soluble in the soil pore water, sorbed onto the surface of soil components, fixed into the structure of the soil components, and precipitated. Sorption from the soil pore water to the soil phase is an important process controlling the behavior of metals in soils. Metals can be sorbed electrostatically in a process termed cation exchange or chemically via specific adsorption. Cation exchange is a process in which cations from the bulk soil pore water are exchanged for cations that are near the soil's surface. Metals can become fixed because of solid-state diffusion (i.e., heavy metals that specifically adsorbed onto secondary minerals may diffuse into the lattice structure of these minerals). Finally, metals may be precipitated at the soil surface or as discrete particles. More than one type of metal retention is usually operative, and while the magnitude of retention can be found experimentally, it is difficult to discern between the retention mechanisms.

Factors Affecting Retention and Release of Metals

The retention and/or release of metals depends upon multiple factors. The more important factors are: pH, initial metal concentration, ionic strength, heavy metal competition, liquid: soil ratio, differences in heavy metal properties, soil composition, and mineral age. Metal solution chemistry and soil surface chemistry are affected by pH. The pH also affects the specific adsorption and precipitation of heavy metals on soils. James and Healy (2) suggested that specific adsorption of metals onto oxides surfaces can begin once the secondary hydration spheres of the metal ions are removed. The extent of soil contamination is also directly related to the initial heavy metal concentration in the soil. If the same treatment levels are imposed, sites contaminated by small amounts of heavy metals are often just as difficult to remediate as grossly contaminated sites. This is due to the binding energies associated with low adsorption densities that are large (Langmuir behavior). Sorption of some trace metals may be limited if other metal cations are present. The sorption of Cd was reduced by 60% in the presence of 120, 300, and 1500 mg/L of Co, Ni, and Zn, respectively (3). The retention and release of heavy metals can also be altered by changes in the liquid: soil ratio that will affect the chemical equilibrium of the soil system. Alterations in the liquid will upset the chemical equilibrium of the soil system. Finally, the metal type also influences the retention. A cation with a small ionic radius can be bound tightly by specific adsorption and solid-state diffusion. Nickel and zinc are retained in greater quantities by specific adsorption and solid-state diffusion mechanisms than are cadmium and lead (4).

Kinetics of Metal Retention and Release

Many studies have shown that metal retention and release reactions are typically rapid initially, followed by a slower second step (4). Kinetics of retention and release depends on a transport and a reaction component. Heavy metal transport occurs via bulk flow (advection) and molecular diffusion, which is a function of the concentration gradient between the solid and liquid phases. Ion exchange, complexation, and precipitation are examples of reactions that affect retention and release kinetics. Most laboratory studies involving metal retention and release employ mechanical shakers so that the soil reactions will not be limited by transport to the soil surface. Therefore, lab scale kinetics is generally faster than those found in-situ where mass transport resistance is large.

Retention Kinetics

Cation exchange and specific adsorption reactions generally possess higher reaction rates than precipitation reactions, which involve the formation of intricate, three-dimensional lattice structures. The reaction rates for metal precipitation varies with reactant species. The kinetics of soil reactions is often limited by the concentration of heavy metals present and the advective transport rate through the interparticle spacings and intraparticle pores. Advective transport through low permeability soils (e.g., consolidated clays) is generally slow so that metal transport is controlled by diffusion. For a given initial metal concentration, the concentration gradient driving the sorption reactions decreases as the metal from the soil pore water reacts with the soil. Thus, additional removals from solution require progressively greater periods.

Release Kinetics

As mentioned previously, the kinetics of complexation reactions with ligands such as EDTA or exchange reactions with calcium chloride is expected to be fairly rapid. Thus the kinetics of soil metals release using such chelating and exchange reactions should also be quick. Tuin and Tels (4) fitted 0.1 N HCl extraction data from Melchior clay to two different reaction rate equations. The clay was from an actual waste site having a lead concentration of 1830 mg/kg. Initially rapid removals, most likely of metals retained via exchange, were fitted to an irreversible first-order reaction with a constant rate coefficient, $k = 2.50 \times 10^{-1}\ \text{min}^{-1}$. A much slower second step was fitted to a reversible first-order equation having a significantly smaller rate constant ($k = 6.6 \times 10^{-4}\ \text{min}^{-1}$). Reaction rates for artificially contaminated clays in the same study were at least an order of magnitude greater than that of the actual waste soil. Extraction results for a sandy soil contaminated with lead (2000 mg/kg) and other heavy metals revealed a similar two step removal processes (5) ElKhatib and Hern (6) found that desorption kinetics of potassium, although not a heavy metal, from soils is best described by the first-order reaction equation. The study involved the removal of potassium from five soils. The desorption studies lasted less than 3 hours, but over 50% of the initial potassium was removed during the first 5 minutes. Most kinetic studies have demonstrated that metal release is not a simple reversal of metal retention. If the extractions are performed in-situ, slow release kinetics may be due to the slow diffusion rates of the metals through small, interstitial spaces of the soil.

Removal kinetics can be improved by using sequential extractions rather than one long extraction period. The removal of lead (initial concentration: 1830 mg/kg) from an actual waste soil during a single 24-hour extraction using 0.1 N HCl was 79%, but removals of 86% were obtained for the same soil when subjected to three 30 minute extractions with 0.1 N HCl (3). Thus, the use of multiple extraction steps increases the kinetics of metal release by increasing the metal concentration gradient between the soil and extracting solution.

MATERIALS AND METHODS

Soil Characterization

Experimental work was performed at the West Virginia University Environmental Engineering Laboratories. Two soil samples, a silt loam and a fine sandy loam from the eastern United States, were selected for this study. These soils were chosen so that different soil characteristics and properties would be represented in the study. The soils were air-dried in the laboratory, passed through a No. 10 sieve, and stored until needed for experimental work. The soils were characterized using the parameters listed in Table 1. Titrations were also performed in order to obtain an estimate of the relative buffering capacity of each soil. Soil pH and approximations of the metal oxide content were determined since these parameters are considered to be key factors in controlling heavy metal retention. Soil digestions were performed to determine the total indigenous lead content of each soil. The cation-exchange capacity (CEC), a common soil characterization parameter, provided an estimate of the number of negatively charged surface sites that can exchange lead. The percent loss of mass upon ignition was used to determine the relative quantities of organic matter present in the soils. Particle size analyses were conducted to determine the dominant size fraction of each soil, since clays and silts are known to retain heavy metals to a greater degree than sandy soils. The hydraulic conductivity of the soils was determined in order to assess which soil could be easily flushed in-situ. Soil moisture contents were immediately determined once the samples were brought into the labora-

TABLE 1
Selected Soil Parameters and Analytical Methods

Parameter	Method	Ref.
Soil pH	1:1 Slurry	7
Indigenous Pb, Fe, Al, and Mn content	EPA Method 3050	8
Cation-exchange capacity (CEC)	EPA Method 9081	9
Total volatile solids	Standard Method 209	10
Particle size distribution	ASTM 422	11
Soil moisture content	ASTM D2216	11
Hydraulic conductivity	ASTM D2434 and D5084	11

tory so that field moisture contents could be closely approximated. Values obtained for these parameters were correlated with the sorption and desorption capacities of the soils. Lead nitrate was used as the source of lead. Each soil was contaminated at three lead concentrations. Contaminating the soils at three different lead levels allowed simulation of the various levels of lead contamination encountered at different waste sites.

Retention Kinetics Experiments

Retention kinetics experiments were conducted to assess the rate and degree of lead retention. The rate of lead sorption onto the soils was investigated using lead solution concentrations of 10, 100, and 1000 mg/L. The ionic strength of these solutions was adjusted to 0.04 using 3200 mg/L $NaNO_3$ to simulate the ionic strength of groundwater. Fifty grams of soils were added to 500 mL of lead nitrate ($Pb\text{-}NaNO_3$) solution in a 1-L beaker. The beaker was placed on a Phipps & Bird stirrer. At predetermined time intervals the pH of each of the three slurry reactors was taken and recorded. One minute after pH measurement a small aliquot (10 mL) was withdrawn from each beaker using an Oxford pipet, filtered, acidified, and analyzed for lead. The aliquots were taken at 15, 30, 45, 60, and 120 minutes. Then, after 2 hours, an Oxford pipet was used to prepare seven 25-mL samples from the completely mixed slurry reactor for each soil concentration listed above. The samples were added to 60 mL Nalgene containers and placed on a mechanical shaker. One sample was removed from the shaker at times of 4 hours, 8 hours, 1 day, 3 days, 7 days, 14 days, and 21 days. Each sample was measured for pH, filtered, acidified, and analyzed for lead. The percent lead retained by each sample was determined by substracting the fraction of the initial lead solution concentration remaining in the filtrate from 1.0.

Release Kinetics Experiments

Lead removal kinetics was determined for the soils contaminated with 100 and 1000 mg/L lead solutions. Each soil was artificially contaminated with lead. A 10:1 liquid ratio was employed in the contamination step. Solutions of lead nitrate were prepared having approximate lead concentrations of 100 and 1000 mg/L. Sodium nitrate was also added to each solution to simulate the ionic strength of groundwater. Batch extraction experiments were conducted using three different types of washing solutions: 0.1 and 1.0 N HCl, 0.01 and 0.1 M EDTA, and 0.1 and 1.0 M $CaCl_2$. A 25:1 liquid:soil ratio was used. For each soil and lead contamination level a 1-gram sample was placed into seven 60 mL Nalgene bottles in which 25 mL of washing solution was also added. Upon addition of the washing solution, the samples were immediately placed on the mechanical shaker. Lead release capacities were determined over a period of 7 days. One sample was removed from the shaker at times of 15 minutes, 30 minutes, 1 hour, 4 hours, 8 hours, 1 day, and 7 days. Approximately 10 mL of each sample was filtered through a 0.45-μm 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, and analyzed for lead. The filtrates from the nonacidic washing solutions were preserved by adding concentrated nitric acid. The lead values obtained from the filtrates were plotted against the time that the samples were taken. Lead not removed from the soils during this time was considered residual lead released over a much longer time span or upon mineral dissolution. Since lead removal is often a function of pH, the slurry pH of each sample was taken before filtration and lead analysis.

General Laboratory Practices

All chemical used were reagent grade. Solutions were prepared in nitric-acid-rinsed volumetric flasks and then stored in polyethylene containers. Measurements of pH were obtained using Orion meters and combination electrodes standardized with pH 4.0 and 7.0 buffer solutions. All samples for metals analyses were filtered through a 0.45-μm membrane filter. They were preserved by acidification with nitric acid if the pH of the filtrate was greater than 2.0. The filter assembly and the pH electrode were rinsed between samples to reduce the possibility of sample contamination.

Lead concentrations were determined using a Perkin-Elmer 2380 atomic absorption (AA) spectrophotometer equipped with a flow spoiler. The analyses were performed using an air-acetylene flame and a wavelength setting of $\lambda = 217.0$ nm. Lead calibration standards contained 5% (v/v) nitric acid. All sample dilutions for AA analysis were made in deionized distilled water and were prepared using Eppendorf and Oxford pipets. Percent recoveries were performed on approximately one per five samples to ensure that significant interferences were not present.

RESULTS AND DISCUSSIONS

Physical and Chemical Properties of the Soils

Soil pH; indigenous lead, iron, aluminum, and manganese content; CEC; total volatile solids; particle size distribution; field moisture content; and hydraulic conductivity values are presented in Table 2. The pH of the fine sandy loam soil was higher than the silt loam soil pH. The fine

TABLE 2
Soil Parameters Data

Parameter	Silt loam	Fine sandy loam
Soil pH	6.1 ± 0.10	8.0 ± 0.10
CEC, meq/100 g	23.5 ± 1.50	20.5 ± 3.20
Total volatile solids, %	4.54 ± 0.10	4.05 ± 0.20
Indigenous metal, mg/kg:		
Pb	20.3 ± 0.3	21 ± 0.5
Fe	24,800 ± 420	15,500 ± 120
Al	11,750 ± 1650	10,200 ± 325
Mn	800 ± 15	800 ± 20
Particle size distribution, % passing:		
No. 10	99.45	91.0
No. 20	86.7	77.6
No. 40	75.1	68.2
No. 60	63.5	61.6
No. 100	46.15	51.5
No. 200	28.8	24.7
Soil moisture content, %	21.9 ± 0.30	16.3 ± 0.30
Hydraulic conductivity, cm/s	9.4×10^{-5}	2.3×10^{-4}

sandy loam was collected from an agricultural site that had been amended with lime and/or fertilizers. None of the soils contained Pb in large enough quantities to be considered contaminated. The silt loam soil had the highest amount of aluminum and iron content. The amount of manganese was similar for both soils. CEC and organic matter obtained for both soils were fairly similar. As expected, the hydraulic conductivity of the fine sandy loam soil was higher than the silt loam soil. Both soils had a fairly even distribution of the medium sands, fine sands, and silts and clays. The fine sandy loam soil had a percentage of coarse sand higher than the silt loam.

Retention Kinetics

The retention kinetic data obtained for the silt loam and the fine sandy loam soils are presented in Figs. 1 to 2. The rate of lead sorption onto the soils was determined using lead solutions with concentrations of 10, 100, and 1000 mg/L. Kinetics of lead retention was very rapid for both soils. Lead was completely removed from both the 10 and 100 mg/L solutions, but partially removed from the 1000 mg/L solutions within the first hour. It was noted that the rate of lead soption was faster for the 10 and 100 mg/L than for the 1000 mg/L solutions. The slower retention kinetics

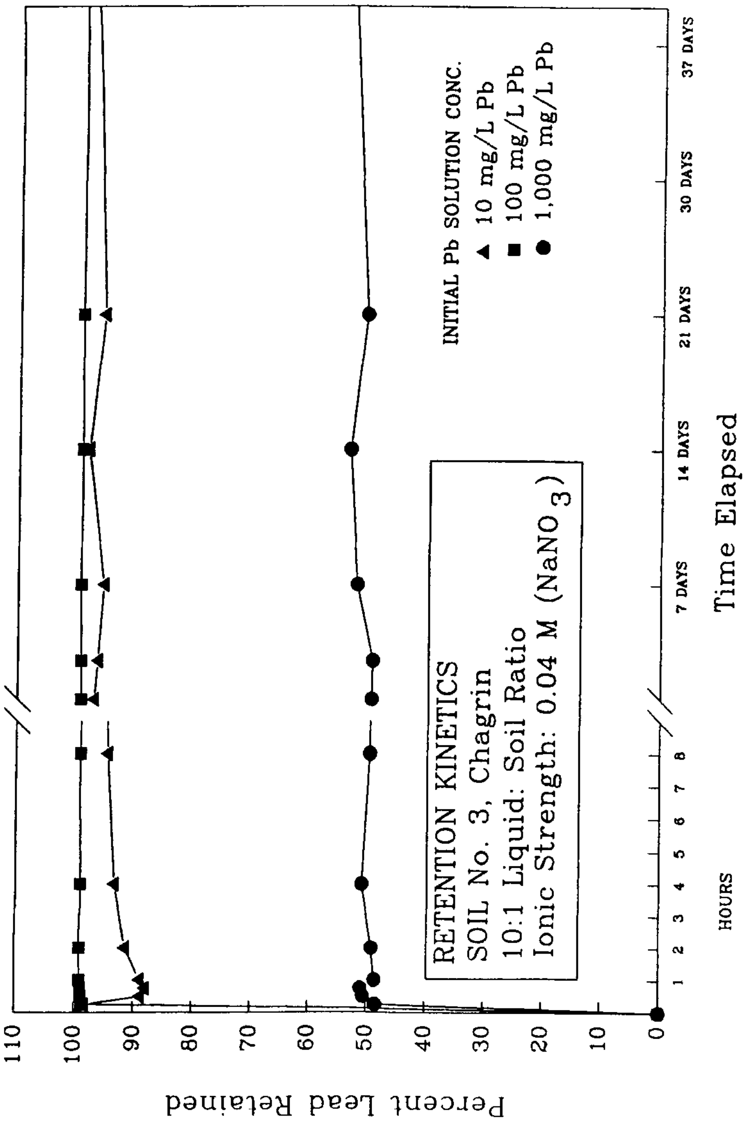

FIG. 1 Lead retention kinetics for a silty loam.

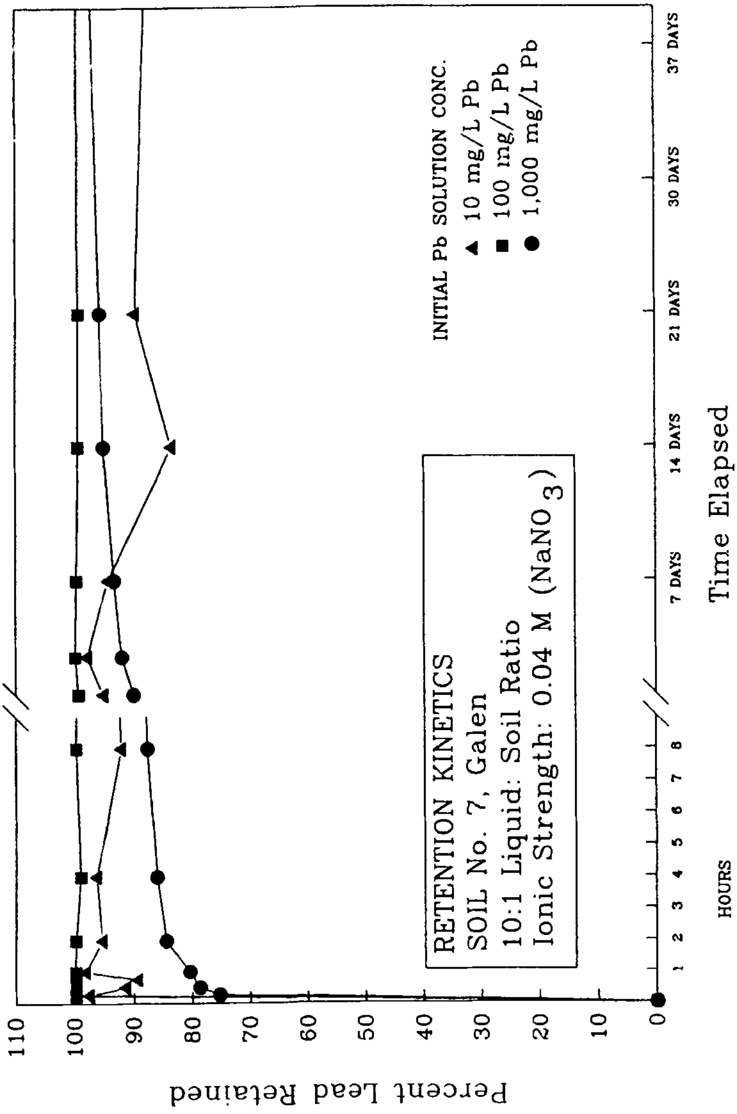

FIG. 2 Lead retention kinetics for a fine sandy loam.

for both soils at the 1000 mg/L lead contamination level can be attributed to surface precipitation effects. The maximum lead quantities retained by the soils during the kinetic testing correlated well with the percentages of lead removed from solution during artificial soil contamination. Thus, the selection of a 21-day detention time in the contamination procedure appears to provide a very good approximation of quasi-equilibrium conditions. The slower retention kinetics for the 1000 mg/L lead solutions can be attributed to surface precipitation because of the large quantities of Pb present. The precipitates are entrapped in the soil matrix or form coatings (i.e., surface precipitation).

Release Kinetics

Kinetics experiments were conducted on the contaminated samples using a 25:1 liquid:soil ratio. Three different washing solutions were selected. EDTA and HCl washing solutions achieved 92 and 89% lead removal, respectively, while $CaCl_2$ washing solutions achieved only 36%. Results from the lead release kinetic experiments are presented in Figs. 3 to 6 for both soils. The release kinetics from the 100 and 1000 mg/L lead contaminations was similar. The total lead releases obtained at the end of the 7-day testing period were generally similar to the lead release values obtained in the 24-hour batch wash experiments.

As observed by other researchers (4, 5, 12), Pb release was initially rapid with most of the lead removal occurring within the first hour. The slopes of the release curves leveled out after the rapid step. Thus, additional removal of any significance would require a very large contact time. The removal obtained during the rapid step for the HCl and EDTA washes was independent of the solution concentration. As expected, Pb release from the calcium chloride experiments was less than from either the HCl or EDTA experiments. The kinetics of Pb release using $CaCl_2$ washes was nearly as rapid as the release using HCl and EDTA washes. The Pb release using $CaCl_2$ kinetics should be expected since cation-exchange reactions are rapid and often limited by mass transport through the liquid film. The indigenous lead concentrations were low relative to the quantity of lead added to the soils. The final slury pH values ranged from 1.1 to 1.8 and from 0.1 to 0.9 for the 0.1 and 1.0 N HCl, respectively. The pH of the HCl solutions controlled the final slurry pH values since the slurry pH values were close to those of the pure HCl solutions. At these extremely low pH values, dissolution of the soil structure most likely occurred, and the lead removal appeared to be fairly independent of the soil type. Lead removals were slightly dependent on the acid concentration as shown in Figs. 3 to 6. EDTA was highly effective in removing lead from the

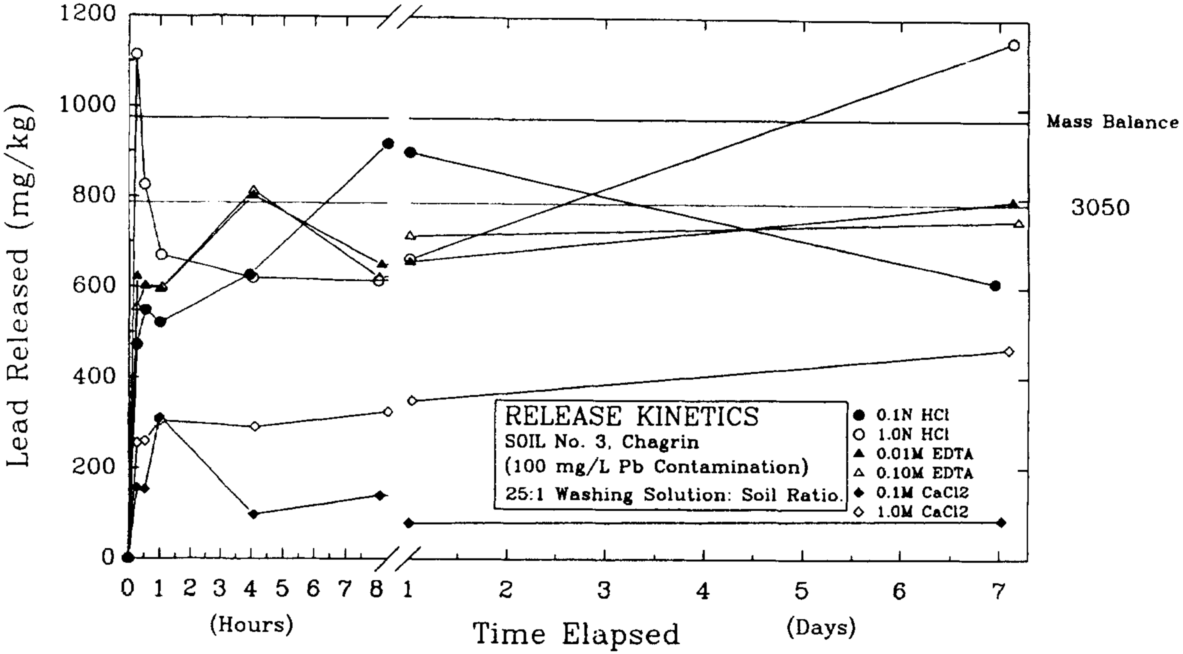

FIG. 3 Release kinetics for the 100 mg/L contamination of a silty loam.

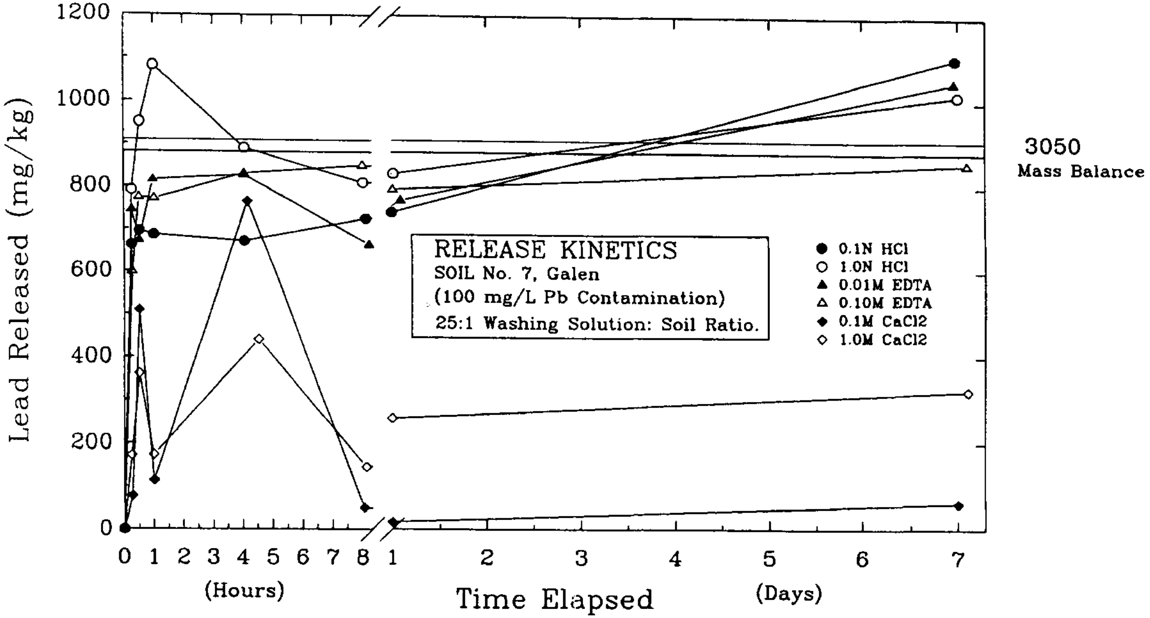

FIG. 4 Release kinetics for the 100 mg/L contamination of a fine sandy loam.

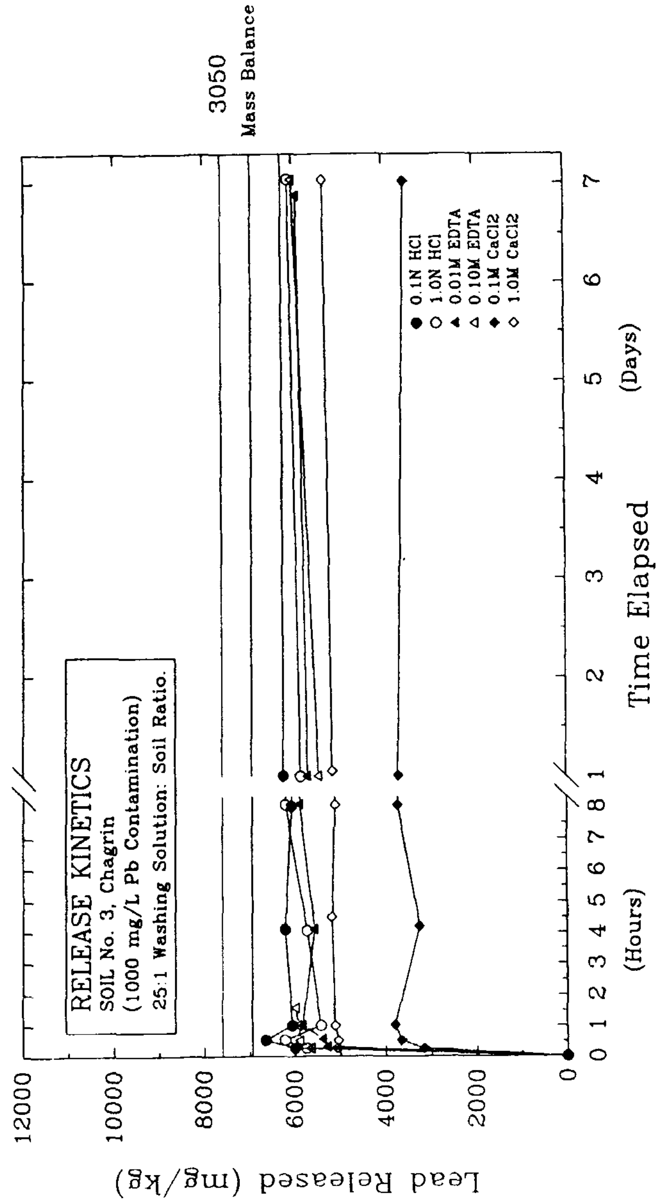

FIG. 5 Release kinetics for the 1000 mg/L contamination of a silty loam.

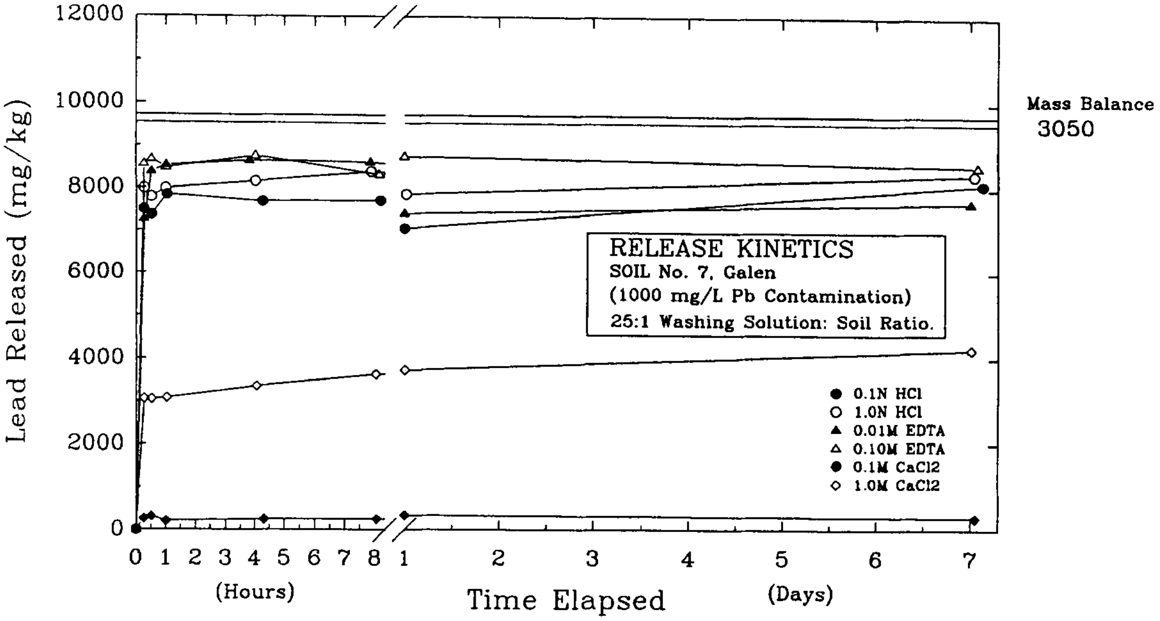

FIG. 6 Release kinetics for the 1000 mg/L contamination of a fine sandy loam.

contaminated soils. The differences between the removal efficiencies of the 0.01 and 0.1 M EDTA washing solutions were insignificant. The final slurry pH values of the EDTA samples were within the range of 4.0 to 5.4 and of 4.3 to 4.8 for the 0.01 and 0.1 M EDTA washes, respectively. The calcium chloride wash efficiencies were dependent on solution concentration. Lead removals from the 1.0 M washes were approximately two times greater than removals from the 0.1 M washes at the 100 mg/L lead contamination levels as shown in Figs. 3 and 4. As observed, the removals from the 1000 mg/L contaminations were less dependent on solution concentration.

SUMMARY AND CONCLUSIONS

The silty loam and the fine sandy loam soils selected for the study were characterized and contaminated with lead concentrations of 100, 1000, and 10,000 mg Pb/kg soil. The rate of lead sorption onto the soils was determined using lead solution with concentrations of 10, 100, and 1000 mg/L. Kinetics of lead retention was very rapid for both soils. Lead was completely removed from both the 10 and 100 mg/L solutions, but partially removed from the 1,000 mg/L solutions within the first hour. It was noted that the rate of lead soption was faster for the 10 and 100 mg/L than for the 1000 mg/L solutions. The slower retention kinetics for both soils at the 1000 mg/L lead contamination level can be attributed to surface precipitation effects. The batch extraction experiments data indicated that lead release using the $CaCl_2$ washes was less than the release using EDTA and HCl. The kinetics of lead release was initially rapid, with most of the removal occurring within the first hour for the three washing solutions. It was observed that the lead solution concentration has no effect on lead removal during the rapid step for the HCl and EDTA washes, but has some effect for $CaCl_2$ washes. The efficiency of lead release from the contaminated samples was greater for the EDTA and HCl than the $CaCl_2$ washes. Removals were generally independent of soil type. In addition, removal efficiencies for the EDTA washes appeared to be independent of EDTA solution concentration, particularly at the highest lead contamination levels.

ACKNOWLEDGMENT

The research presented in this article was conducted under USEPA Contract S009-92.

REFERENCES

1. B. E. Reed and S. Cline, *Sep. Sci. Technol.*, *29*(12), 1529 (1994).
2. R. O. James and T. W. Healy, *J. Colloid Interface Sci.*, *40*(1), 65 (1972).
3. T. H. Christensen, *Water, Air, Soil Pollut.*, *34*, 293 (1987).
4. B. J. W. Tuin and M. Tels, *Environ. Technol.*, *11*, 1039 (1990).
5. J. E. Van Benschoten, B. E. Reed, M. R. Matsumoto, and P. J. McGarvey, *Water Environ. Technol.*, *66*(2), 168 (1994).
6. E. A. ElKhatib and J. L. Hern, *J. Soil Sci.*, *145*, 11 (1988).
7. E. O. McLean, *Methods of Soil Analysis: Part 2—Chemical and Microbiological Properties*, 2nd ed. (Agronomy No. 9), American Society of Agronomy, Madison, Wisconsin, 1982, p. 199.
8. USEPA, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, 3rd ed., Washington, D.C., 1986.
9. O. P. Mehra and M. L. Jackson, *Clays and Clay Minerals, Proceedings of the Seventh National Conference* (Monograph No. 5. Earth Science Series), 1960, p. 317.
10. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Washington, D.C., 1985.
11. ASTM, *Annual Book of ASTM Standards, Soil and Rock, Dimension Stone, Geosynthetics*, Vol. 4.08, American Society of Testing and Materials, Easton, Maryland, 1991.
12. M. M. Benjamin and J. O. Leckie, *J. Colloid Interface Sci.*, *79*(1), 209 (1981).

Received by editor March 7, 1995