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Retention and Release of Lead by a Very Fine Sandy Loam. I. Isotherm Modeling

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ABSTRACT

The retention of lead by a very fine sandy loam was investigated. Aqueous lead concentrations between 10 and 1000 mg/L and soil concentrations ranging from 10 to 167 g/L were used. Lead retention by the soil was a strong function of pH. The width of the pH–adsorption edge decreased with increasing lead concentration. Experimental results were modeled using the Langmuir, Freundlich, and BET isotherms. Only the Langmuir and Freundlich isotherms successfully represented the experimental results. The role of surface precipitation was assumed to be small because of the failure of the BET isotherm to adequately predict metal retention. The Freundlich isotherm provided the best fit because a maximum surface concentration was usually not observed. Langmuir and Freundlich isotherms parameters varied in a way that suggested that the average binding energy and the distribution of bond strengths increased with increasing pH. The isotherm expressions determined in this study can be used as source-sink terms in the generalized mass transport model.

INTRODUCTION

The presence of heavy metals in soils is a major concern because of their toxicity and persistence. Unlike organic compounds, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end-products. Thus, unless there is a remedial response, the potential for increased exposure through groundwater transport exists. In order to model the transport of metals through the subsurface or the estimate performance of remediation technologies (e.g., in-situ soil flushing), the retention–release of metals by the soil must be quantified (i.e., the source-sink in the general mass transport equation). With this in mind, the objectives of the study were to conduct Pb retention experiments using an actual soil and to determine the extent to which several common isotherm models could represent the experimental data. Because metal retention–release is a function of pH, the retention experiments were conducted over a wide range of pH values. In a forthcoming article, the kinetics of retention and release for several soils will be presented.

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. This scenario is represented by the following formula:

$$X_{\text{Total}} = X_{\text{Soluble}} + X_{\text{Sorbed}} + X_{\text{Fixed}} + X_{\text{Precipitated}} \tag{1}$$

where $[X_i]$ represents the mass of a heavy metal found in each phase. Sorption from the soil pore water to the solid 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. Metals can become "fixed" as a result of solid-state diffusion. Finally, metals may precipitate 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 determined experimentally, it is difficult to discern between the retention mechanism(s). The types of retention mechanisms and the extent to which each mechanism is operative are discussed next.

Cation Exchange

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. Cation exchange is strictly an electrostatic phenomenon. All soil components possessing an electrostatic charge can participate in cation-exchange reactions. The magnitude of exchange is estimated by the cation-exchange capacity (CEC) of the soil. Much of a soil's CEC is associated with the clay and organic fractions. Cation exchange is a key mechanism for the retention of many alkali and alkaline earth metals (e.g., Na^+, Ca^{2+}, and Mg^{2+}) and heavy metals. Cation exchange, also referred to as nonspecific adsorption, is a form of outer sphere complexation. With cation exchange, the waters of hydration are present, preventing strong covalent bonding between the metals and the charged particles. Thus, exchanged cations are weakly held and other cations can replace those originally attracted to the charged particles. Theoretically, the exchange process is completely reversible under the appropriate conditions. Exchange reactions occur quickly and are generally mass transport limited (i.e., the diffusion of replacing ions to the exchange sites is the rate-limiting step).

Typical CEC values for selected soil components and different soil types are presented in Table 1. The high CEC values typical for 2:1 clays and the organic fraction indicate that these components have a significant number of surface sites available for cation exchange. The CEC of an actual soil will vary depending upon the relative contributions of its individual components. Also include in Table 1 is the maximum amount of lead that could possibly be retained by the different soils via cation exchange. To determine these values, it was assumed that an exchange was driven completely to the right (i.e., Soil + Me → Soil-Me). It should be noted that such an event would not be expected since many chemical interactions and other types of metal retention can occur to reduce cation exchange.

TABLE 1
Typical CECs for Selected Soil Components and Various Soil Types

Soil component or soil type	CEC (meq/100 g)	Maximum soil Pb (mg/kg)
Kaolinite (1:1 clay)	3–15[a]	3,150–15,650
Montmorillonite (2:1 clay)	80–150[a]	83,000–156,500
Oxides of Fe and Al (pH 8)	0.50–1.0	520–1,050
Allophane (amorphous)	50–100	52,000–105,000
Colloidal humus (organic matter)	150–300	156,500–313,000
Quartz (silica mineral	Less than 5[a]	<5,200
Sand	2–7	2,100–7,300
Sandy loam	2–18	2,100–19,000
Loam	8–22	8,300–23,000
Silt loam	9–27	7,300–28,000
Clay loam	4–32	4,100–33,000
Clay	5–60	5,200–62,000

[a] Reference 3.

Specific Adsorption

Specific adsorption, a form of inner sphere complexation, involves covalent bonding of metals (free or complexed) with soil surfaces and is much stronger than cation exchange. Because of specific adsorption, a larger amount of heavy metals can be retained by a soil than would be predicted by cation exchange alone. On variable charges surfaces (e.g., metal oxides and the organic fraction), specific adsorption is most important for metals that readily hydrolyze. Hydroxyl–metal complexes are adsorbed more strongly than the completely hydrated metal because the formation of an OH group on the metal reduces the free energy requirement for adsorption (1). Metal hydrolysis reduces or rearranges the waters of hydration so that soil surface groups can more easily penetrate the primary hydration sphere of the metal to form an inner sphere complex. The hydrous oxides of Al, Fe, and Mn are thought to be the chief soil components that specifically adsorb heavy metal ions (2). In particular, significant amounts of lead are held by hydrous oxides of manganese (3).

Humic materials possess a large number of functional groups (e.g., hydroxyl, phenoxyl, carboxyl, and amino groups) that can specifically adsorb heavy metals. Evans (2) summarized results of several studies suggesting that humic and fulvic acid fractions of soils retained heavy metals in the order $Hg = Fe = Pb = Al = Cr > Cd > Ni = Zn > Co > Mn$ at pH 4.7. The reaction appeared to be independent of hydrated or ionic radius, atomic weight, and atomic number.

For permanent charge sites, specific adsorption is most important for larger monovalent cations which are weakly held by exchange mechanisms (2). Thus, total metal sorption is dependent upon both pH and the affinity between the surface sites and soluble metal species.

Surface Precipitation

Metals can precipitate as oxides, hydroxides, carbonates, sulfides, or phosphates. These precipitates are entrapped in the soil matrix or form coatings on other soil components (i.e., surface precipitation). The extent of surface precipitation is dependent upon pH and the relative quantities of metal and/or anions present. Reed and Matsumoto (4) reported that surface precipitation on hydrous solids occurs at pH values less than those required for the precipitation of metal hydroxides in a pure aqueous system (4). X-ray diffraction and scanning electron microscopic (SEM) images of a soil contaminated with a lead were performed by Van Benschoten et al. (5). Silica and iron were the major soil components identified. When the SEM was magnified, a lead surface coating was detected. When x-ray diffraction of the magnified portion was performed, lead was detected but the major soil components were not.

Solid-State Diffusion

In addition to cation exchange, specific adsorption, and precipitation, heavy metals can also be retained by soils via strong fixation reactions. For example, heavy metals that specifically adsorbed onto secondary minerals such as clays and metal oxides may diffuse into the lattice structure of these minerals. The metals slowly become fixed into the pore spaces of the mineral's structure (3). This process is often referred to as solid-state diffusion. Heavy metals retained via solid-state diffusion can be removed by dissolving the soil particles in which the metals are incorporated. However, release of fixed metals can occur over time as the weathering process dissolves soil components.

Factors Affecting Retention and Release of Metals

The pH, initial metal concentration, heavy metal competition, liquid: soil ratio, type of heavy metal, soil composition, and mineral age all affect heavy metal retention and release by soils. Each factor will be discussed separately.

Soil pH

Metal solution chemistry and soil surface chemistry are affected by pH. The number of variable or "pH-dependent" surface sites that are negatively charged increase with pH. Thus, increases in pH can lead to significant increases in CEC if a soil contains a large number of pH-dependent charges. In a study involving 60 Wisconsin soils, the mean CEC for the soils at pH 2.5 was 5.8 meq/100 g. The mean CEC increased to 14.8 meq/100 g when the pH of each soil was adjusted to 8.0 (6). The pH also affects the specific adsorption and precipitation of heavy metals on soils. James and Healy (7) suggested that specific adsorption of metals onto oxide surfaces can begin once the secondary hydration spheres of the metal ions are removed. (The secondary sphere is generally shed at 1–2 pH units below that where metal hydrolysis begins.) With greater increases in pH, the metals will form precipitates with OH^-, CO_3^{2-}, and other anions. Research performed by Harter (8), indicated that lead retention increased from 3,000 to 16,000 mg/kg as the soil pH was increased from 4.3 to 7.1. The large increase in soil-bound lead was most likely due to precipitation at soil pore water pHs above 6.0. The pH range in which metal retention increases from near zero to near 100% is referred to as the pH–adsorption edge. The range of the pH–adsorption edge is dependent on the type of soil and heavy metal.

Initial Metal Concentration

The extent of soil contamination is 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 because the binding energies associated with low adsorption densities are large. Assuming that soils have multiple types of surface sites, trace quantities of metals would be preferentially adsorbed by the sites with the highest binding energies, making their subsequent release difficult. Thus, greater metal removal percentages can be obtained at a highly contaminated site (where much of the metal retention is associated with low energy binding sites). The initial metal concentrations will also influence the dominant retention mechanism(s). For example, at high initial heavy metal concentrations, a large percentage of the metals present will precipitate. Although surface precipitation leads to high metal retention, surface precipitation can also reduce the number of surface sites that participate in cation exchange or specific adsorption reactions by coating the soil particles and blocking access to the surface sites.

Competition with Other Heavy Metals

Sorption (exchange and specific adsorption) of some trace metals may be limited if other metal cations are present. Christensen (9) reported on research involving the sorption of a 40 mg/L Cd solution onto soils in the presence of Co, Ni, Zn, Cr, Cu, and Pb. Cd sorption was reduced by 60% in the presence of 120, 300, and 1500 mg/L of Co, Ni, and Zn, respectively. Competition can also be used to remediated a soil; for example, the addition of Ca^{2+} will cause the desorption of Pb (10).

Liquid:Soil Ratio

The retention and release of heavy metals can be altered by changes in the liquid:soil ratio. Alterations in the liquid:soil ratio will upset the chemical equilibrium of the soil system. For example, a contaminated soil will release more metals at high liquid:soil ratios. The presence of a large volume of "clean" solutions creates a concentration gradient which drives the release reaction until equilibrium is reached. Similarly, sorption of metals from solution will decrease as the liquid:soil ratio is increased, assuming the total mass of metal remains the same (11). While changes in the liquid : soil ratio can be observed in nature (e.g., increased groundwater flow due to rainfall), the effect of liquid:soil ratios on metal retention/release is primarily a laboratory phenomenon. Thus, the efficiency of washing or flushing agents to extract metals from the soils may be enhanced if larger volumes are used, but the additional increase in metal release is often small. Tuin and Tels (12) reported that the removal of copper from an artificially polluted soil (CEC = 23 meq/100 g and 50% clay fraction) increased from 85 to 93% as the liquid : soil ratio was changed from 5:1 to 100:1.

Heavy Metal Type

The size of both the ionic and hydrated radius of a metal cation play a role in the cation selectivity of surface sites as well as determining the operative retention mechanisms. 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 (12). The ionic radii of cadmium and lead are large enough to reduce specific adsorption and allow substitution of these metals into interior sites of layer silicates and metal oxides. Padmanabham (13) obtained similar results in retention/release studies involving copper, zinc, cobalt, and lead. The difference between the amount of copper, zinc, and cobalt that was retained and subsequently released from geothite was significant (i.e., adsorption hysteresis). Little hysteresis was observed for lead, suggesting that greater quantities of lead are held by loose retention mechanisms (i.e., ion exchange) than by more fixative mechanisms such as solid-state diffusion.

Soil Composition and Mineral Age

Sands generally have a low tendency to retain heavy metals, mainly because of the lack of large surface groups and a small surface area. Clays are very effective in immobilizing heavy metals, mainly by specific adsorption and cation-exchange reactions. Metal oxides are also very good scavengers of heavy metals, with specific adsorption of hydroxyl metal complexes being the primary retention mechanism. The large number of functional groups and high CEC values of organic matter allow for considerable retention of metals by complexation, exchange, and precipitation in spite of the relatively small quantity present in most soils.

The strength of metal sorption increases as contaminated soil particles age because of the formation of stable surface coatings with time and the diffusion and incorporation of retained metals into the crystal structure of clay minerals. Metal oxides are amorphous in nature and are commonly found as coatings on other soil components such as sands. With time, these amorphous minerals develop crystalline patterns which retain heavy metals stronger than the amorphous compounds. Hence, it is often necessary to dissolve oxide minerals in order to release specifically adsorbed metals. As should be expected, the ability of extracting agents to dissolve such minerals becomes more difficult with aging. A study by Slavek and Pickering (14) determined the amount of freshly precipitated iron oxides, oxides aged 1 month, and naturally occurring geothite that could be dissolved in 1 M HNO_3 was 95%, 60%, and <2%, respectively. Thus, soils with large metal oxide contents (generally found in areas of extreme weathering) may prove more difficult to treat for heavy metals than soils in less weathered areas where the percentage of metal oxides is generally small.

Mathematical Models of Retention and Release

Langmuir, Freundlich, and BET (Brunauer, Emmet, Teller) isotherms are used to model metal retention and release. While the exact mechanism(s) of metal retention cannot be ascertained from experimental isotherms, the magnitude of metal retention and average binding energies can be estimated.

Langmuir Isotherm

The Langmuir equation was first developed to describe the adsorption of gases unto solid surfaces but has since been used to model solute adsorption unto various absorbents, including soil. The Langmuir isotherm predicts linear adsorption at low adsorption densities and a maximum surface coverage at higher solute metal concentrations. Two familiar forms of the Langmuir isotherm are presented in the following equations:

$$\frac{X}{M} = \frac{(kbC)}{(1 + kC)} \tag{2}$$

$$\frac{C}{(X/M)} = \frac{1}{kb} + \frac{C}{b} \tag{3}$$

where X = quantity of metal adsorbed (mg)
M = weight of soil (kg)
C = equilibrium concentration of metal in solution (mg/L)
k, b = experimentally determined constants

The derivation of the Langmuir equation was based on three assumptions (6):

1. A constant adsorption energy, independent of adsorption density.
2. No interaction between sorbed metals.
3. At most, monolayer coverage of the surface by the contaminant.

The constants k and b are a measure of the binding strength and the maximum surface concentration, respectively and can be determined graphically by plotting $C/(X/M)$ versus C.

Freundlich Isotherm

The Freundlich isotherm was originally derived as an empirical relationship. Later, Sposito (15) derived the Freundlich equation for soil sorption by assuming that soil is composed of multiple types of adsorption sites (i.e., heterogeneity) and that each type is modeled by the Langmuir equation. The adsorption of metal ions is often best described by the Freundlich isotherm. Common forms of the Freundlich isotherm are

$$X/M = KC^{(1/n)} \tag{4}$$

$$\log(X/M) = \log K + (1/n)\log C \tag{5}$$

where X = quantity of metal adsorbed (mg)
M = weight of soil (kg)
C = equilibrium concentration of metal in solution (mg/L)
K, n = experimentally determined constants

Equation (4) predicts that adsorption is exponentially proportional to the solute metal concentration, C. The linearized form (Eq. 5) is used to determine the constants K and n. Unlike the Langmuir equation, the Freundlich equation does not predict a maximum removal quantity. The constants K and n are related to the strength of the adsorptive bond and the distribution of bond strengths, respectively. The greater the difference between n and 1, the wider is the distribution of bond energies. When $n > 1$, which is common for most soils, bonding energies decrease with increasing surface concentrations. This phenomenon is most likely due to the presence of several surface sites, each having different binding energies. As the surface metal concentration increases, the strongest binding sites will be filled first, followed by the weaker sites. Thus, the average binding strength will decrease. Note that the change in n and K with surface concentration must be examined at a constant pH.

The Freundlich isotherm often models sorption reactions poorly at low adsorption densities because adsorption is linear. At high solute metal concentrations the fit is better because monolayer saturation (Langmuir behavior) is usually not observed. The continuous increase in sorption is due to multilayer adsorption and surface precipitation (16).

Linear Adsorption Isotherm

The linear adsorption model is a special case of the Freundlich isotherm for $n = 1$. At $n = 1$, the energy of adsorption is not a function of surface coverage. The binding strength constant is referred to as the linear distribution coefficient, K_d. The equation for the linear adsorption model is

$$X/M = K_dC \tag{6}$$

The linear equation is generally only used over a narrow concentration range and for very low metal concentrations. Anderson and Christensen (17) reported that the value of K_d increases dramatically as metal concentrations decreases (due to selectivity of trace metals). This equation was not used to determine sorption capacities in this research because large heavy metal concentrations were used.

Brunauer, Emmett, Teller (BET) Isotherm

Several researchers have reported that as heavy metal concentrations increase, the surfaces of soil components become coated with hydroxyl metal precipitates. Surface precipitation is defined by the occurrence of a sharp increase in metal removal over a very small pH range. This sharp transition may or may not be obvious on a log-log Freundlich plot of the experimental data. While the Langmuir isotherm assumes a maximum monolayer coverage, the BET isotherm assumes that multiple layers of adsorbate can exist on the soil surface. Thus, the BET model is often used to describe metal retention when surface precipitation is suspected. Two common forms of the BET isotherm are presented in the following equations:

$$\frac{X}{M} = \frac{BC_eb}{(C_s - C_e)[1 + (B - 1)(C_e/C_s)]} \tag{7}$$

$$\frac{C_e}{(C_s - C_e)(X/M)} = \frac{1}{Bb} + \frac{(B - 1)}{Bb}(C_e/C_s) \tag{8}$$

where X = quantity of metal adsorbed (mg)
M = weight of soil (kg)
C_e = equilibrium concentration of metal in solution (mg/L)
C_s = saturation concentration (mg/L)
b = Langmuir monolayer saturation constant
B = experimentally determined constant

C_s represents the minimum adsorbate concentration at which precipitation of the metal would theoretically occur for the pH value at which the isotherm is constructed. B and b are determined by plotting Eq. (8). C_s can be found from the literature, by experimentation, or by trial and error when Eq. (8) is plotted. The BET equation reduces to the Langmuir isotherm when B is much greater than 1 and when the saturation constant is significantly greater than the equilibrium solution concentration.

MATERIALS AND METHODS

Experimental work was performed at the West Virginia University Environmental Engineering Laboratories. The study soil, a Minoa very fine sandy loam, was collected in Erie County, New York. The soil was air-dried in the laboratory, passed through a No. 10 sieve, and stored until needed for experimental work. The soil was characterized using the parameters listed in Table 2. Following characterization, pH–adsorption edges were determined. These curves were then used to construct adsorp-

TABLE 2
Selected Soil Parameters and Analytical Methods

Parameter	Value	Method (Ref.)
Soil pH	5.5 ± 0.1	1:1 Slurry (18)
Indigenous Pb, Fe, Al, and Mn, mg/kg:		EPA Method 3050 (19)
Pb	20.4 ± 1.4	
Fe	12,600 ± 3,000	
Al	6,275 ± 1,575	
Mn	112 ± 20	
Amorphous aluminum oxide, mg/kg	1,230 ± 100	Na Dithionite Extraction (20)
Amorphous manganese oxide, mg/kg	80 ± 20	AAO Extraction (21)
Amorphous iron oxide, mg/kg	1,100 ± 50	AAO Extraction (21)
Free iron oxide, mg/kg	5,300 ± 320	Na Dithionite Extraction (20)
CEC, meq/100 g soil	7.6 ± 0.40	EPA Method 9081 (19)
Total volatile solids, %	1.46 ± 0.04	Standard Methods 209 (22)
Particle size distribution, % passing:		ASTM 422 (23)
No. 10	99.9	
No. 20	77.6	
No. 40	68.2	
No. 60	61.6	
No. 100	51.5	
No. 200	24.7	
Soil moisture content, %	8.7 ± 0.2	ASTM D2216 (23)
Hydraulic conductivity, cm/s	2.5×10^{-3}	ASTM D2434 and D5084 (23)

tion isotherms as a function of pH. Lead solution concentrations of 10, 100, and 1000 mg/L were used. An aliquot of each initial solution was preserved and kept for lead analysis. Soil concentrations used for each of the lead levels are presented in Table 3. The ionic strength of the soil slurry was adjusted to 0.04 using $NaNO_3$.

Twelve 50-mL samples were prepared for each soil concentration listed above. The pH of the samples were adjusted to between 1.5 to 6.5 by using either 0.1 N HNO_3 or 0.1 N NaOH. The volume of acid or base added to each 50 mL sample was recorded in order to correct for these additions after the samples were analyzed. After pH adjustment, the samples were placed a mechanically shaker for 7 days. The pH of each sample was again determined after the samples were removed from the shaker. The sample's pH after 7 days was usually lower than the initial pH due to the exchange of Pb for H^+. Approximately 10 mL of each sample were 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 amount of lead retained was determined by subtracting the filtrate Pb concentration from the initial Pb concentration. The data were plotted against the corresponding 7-day pH value to obtain the pH–adsorption edge curves.

From the pH–adsorption edge curves, lead adsorption isotherms were determined for pH values of 1.0, 2.0, 3.0, 4.0, 4.6, 4.8, 5.0, 5.2, 5.4, and 5.6. Vertical lines were drawn on the adsorption edge curves at each of the above pH values. For a given pH value, the percent lead removed from solution for each soil concentration was determined by the intersection of each curve with the vertical line constructed at that pH value. Adsorption capacities were calculated by dividing the amount of lead removed from solution by the weight of the soil in the sample. Experimental isotherms were then constructed by plotting the X/M (mg Pb/kg soil) against the corresponding equilibrium solution lead concentrations (C_e).

TABLE 3
Soil Concentrations Used in Isotherm Experiments

Pb solution	Soil concentration (g soil/L Pb solution)
10 mg/L	10, 30, 60, 140
100 mg/L	20, 40, 70, 100, 150
1000 mg/L	50, 67, 100, 125, 167

General Laboratory Practices

All chemicals 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 metal(s) analysis were filtered through a 0.45-μm membrane filter and 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 spectrophotometer (A.A.) equipped with a flow spoiler. The analyses were performed using an air-acetylene flame and wavelength settings of $\lambda = 217.0$ nm. Lead calibration standards contained 5% (v/v) nitric acid. All sample dilutions for A.A. analysis were made in deionized distilled water and were prepared using calibrated Eppendorf and Oxford pipets. Percent recoveries were performed on approximately 1 in every 5 samples to ensure that significant interferences were not present.

RESULTS AND DISCUSSION

The results obtained during the experimental investigation are first presented in this article as pH–adsorption edges, then as Langmuir, Freundlich, and BET isotherms.

pH–Adsorption Edges

The pH–adsorption edges for the study soil are presented in Figs. 1 through 3 for 10, 100, and 1000 mg/L Pb solutions, respectively. Zero and 100% retention of the initial adsorbate lead were not achieved experimentally. The pH range over which adsorption occurred (i.e., the width of the pH–adsorption edge) decreased with increasing lead concentration. Lead retention generally increased with increasing soil concentrations if the pH was greater than 3.0. At pH values lower than 3, retention was not a function of soil concentration. The pH–adsorption edges for study soil tended to converge at low pH values; thus, at low pHs, a single lead retention value was determined by averaging the lead retention values obtained for the five soil concentrations investigated. Average lead retention values of 19 ± 3%, 6 ± 3%, and 6 ± 3% were obtained for 10, 100, and 1000 mg/L Pb, respectively, at the lowest pH values ($\cong 0.7$). The study soil retains lead in excess of the indigenous lead content (≈ 20 mg/kg). At the highest pH values, maximum percent removal of lead ranged from 88

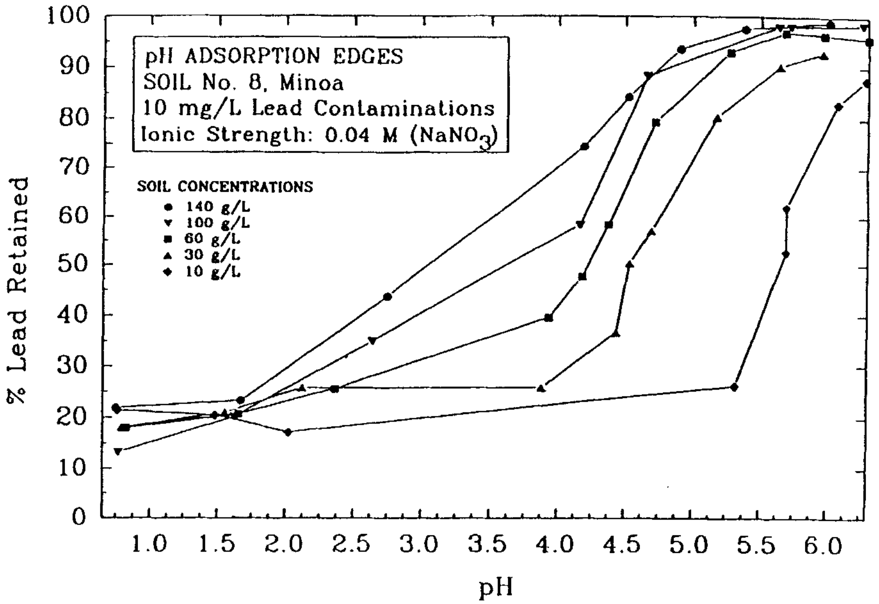

FIG. 1 pH–adsorption edges at 10 mg/L Pb.

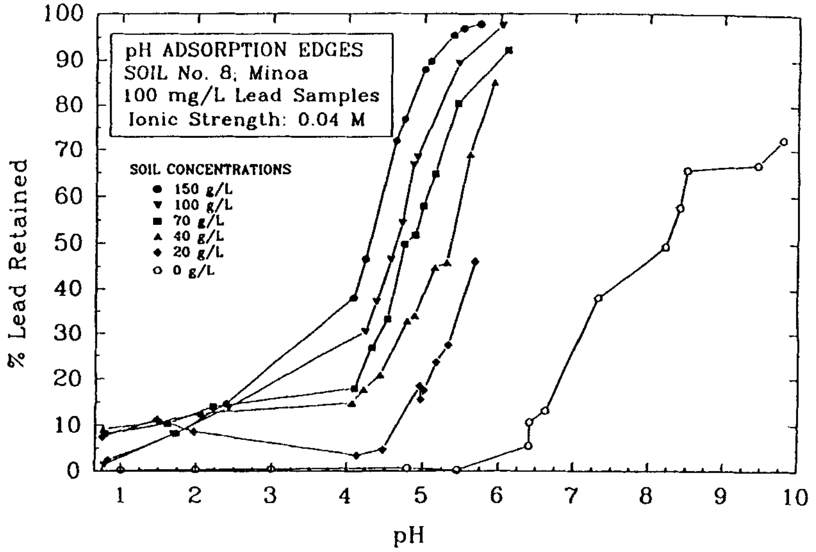

FIG. 2 pH–adsorption edges at 100 mg/L Pb.

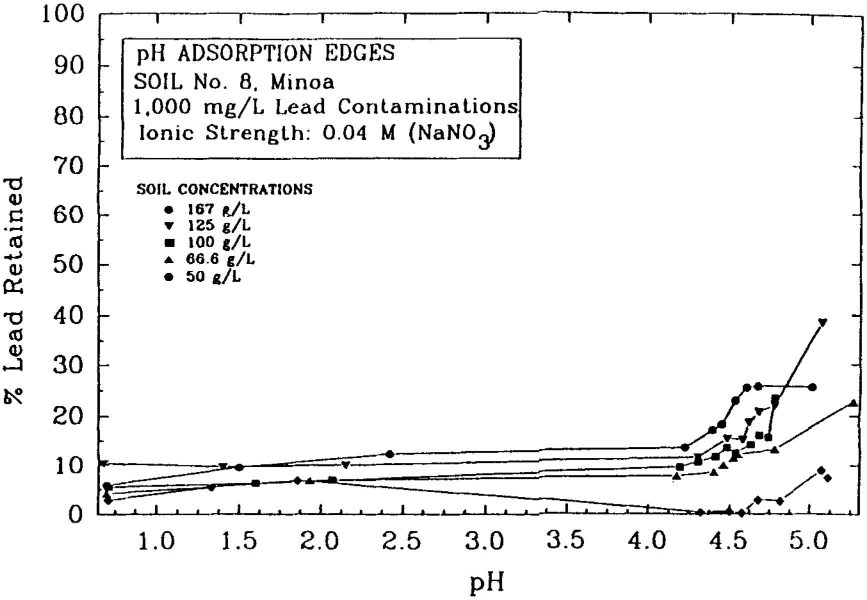

FIG. 3 pH–adsorption edges at 1000 mg/L Pb.

to 99, 46 to 98, and 8 to 38 for the 10, 100, and 1000 mg/L lead contaminations, respectively.

Adsorption Isotherms

Adsorption isotherms for the study soil were developed from the pH–adsorption edges. The experimental isotherms exhibited significant increases in retention at high Pb solution concentrations and pH, possibly due to surface precipitation. *X/M* versus C_e for 100 mg/L Pb data for pH 5.6 (the highest pH value studied) is presented in the Freundlich isotherm form in Fig. 4. The soil concentrations of the samples are also included. Retention was most likely due to sorption (ion exchange, specific adsorption) for the samples having large soil concentrations. At lower soil concentrations, the isotherm becomes vertical, indicating that retention is not a function of the number of removal sites. The precipitation of lead on the soil surface would account for this behavior. These outlying data points were not used in the construction of the Langmuir and Freundlich isotherms.

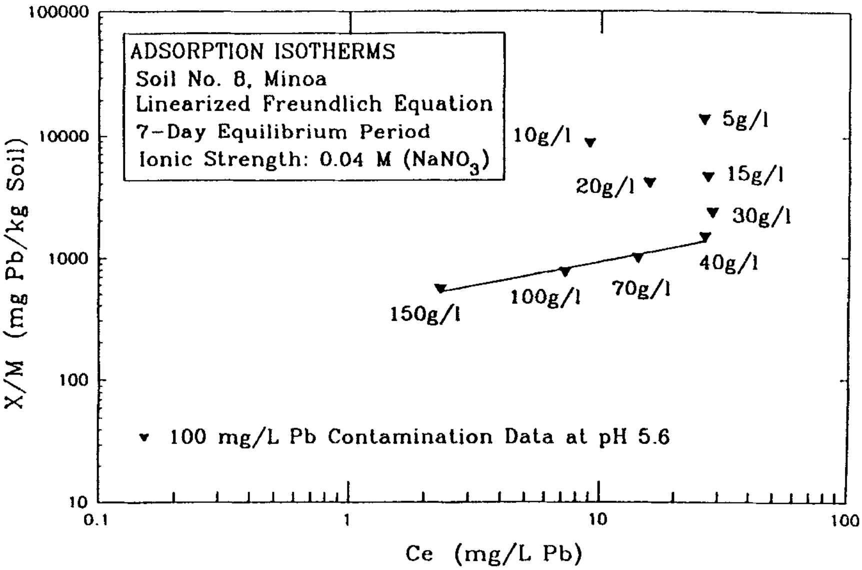

FIG. 4 Freundlich isotherm at pH 5.6 and 100 mg/L Pb.

Experimental and predicted lead soil concentrations (X/M, mg Pb/kg soil) versus the equilibrium aqueous lead concentration (C_e) for pH values of 1, 2, 3, 4, 4.6, 4.8, 5, 5.2, 5.4, and 5.6 will be presented.

Langmuir Isotherms

Langmuir isotherm constants (k and b) were determined by graphing the experimental data using the linearized form of the Langmuir isotherm (Eq. 3). In Figs. 5 and 6, $C_e/(X/M)$ is plotted versus C_e. The solid line is a best fit curve (first-order) to the data. Best fit values of k and b are presented in Table 4. The maximum surface density (b) increased with pH while the average binding constant (k) was fairly constant between pH 1 to 5 and between pH 5.2 to 5.6. Values of r^2 from the regression analysis are also presented in Table 4. The highest r^2 values were determined for the higher pH values (pH = 5.2, 5.4, and 5.6). For these pH values, a smaller range of data was used to determine the constants; thus, a better fit should result. In Figs. 7 and 8, the Langmuir predicted and experimental values of X/M are plotted versus C_e. For several pHs, the maximum Pb soil concentration was underpredicted (e.g., pH = 5, 4.8, 4.6). The Langmuir model was more successful at the higher pHs (Fig. 8).

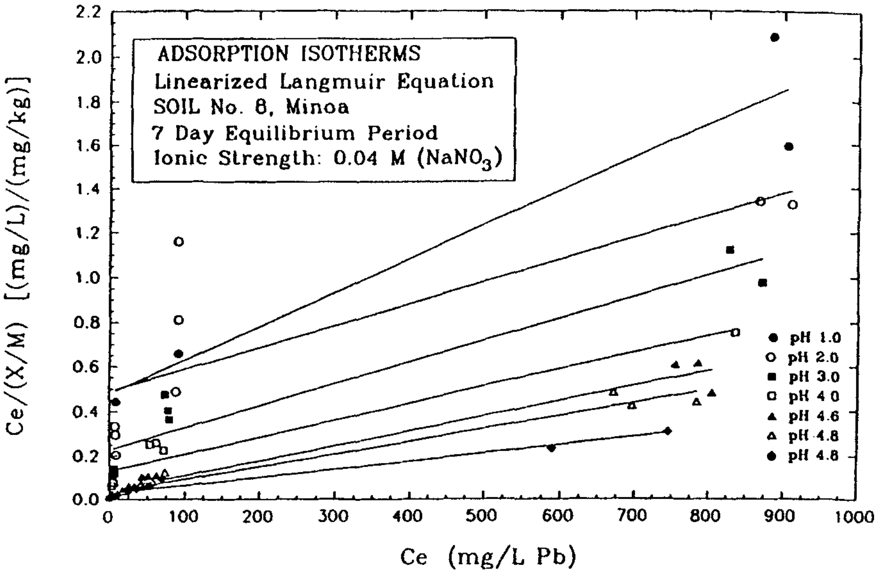

FIG. 5 Linearized Langmuir isotherms for pH values of 1, 2, 3, 4, 4.6, 4.8, and 5.0.

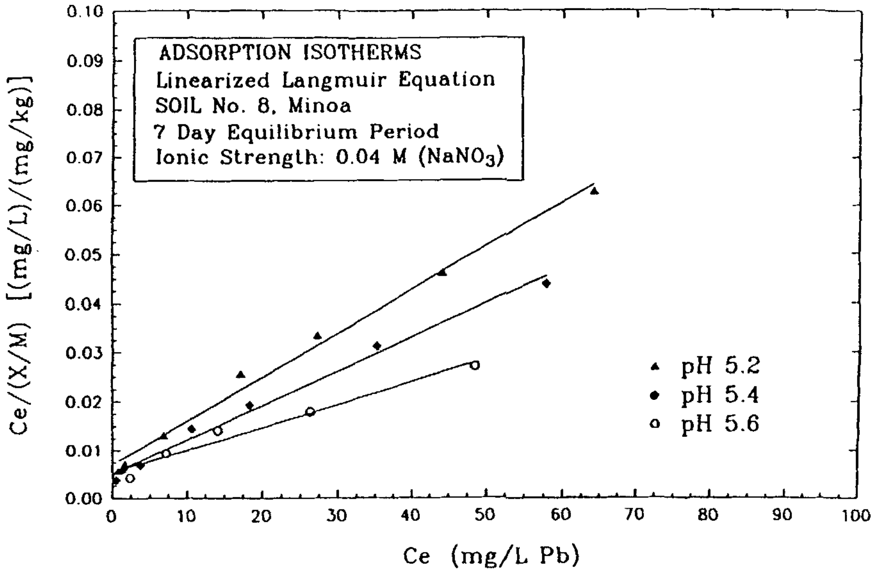

FIG. 6 Linearized Langmuir isotherms for pH values of 5.2, 5.4, and 5.6.

TABLE 4
Experimentally Determined Constants for the Langmuir Isotherm

pH	r^2	k	b (mg Pb/kg soil)
1.0	0.957	0.003	667
2.0	0.807	0.002	1000
3.0	0.955	0.004	1000
4.0	0.961	0.006	1250
4.6	0.982	0.02	1430
4.8	0.986	0.02	1670
5.0	0.982	0.01	2500
5.2	0.996	0.13[a]	1110[a]
5.4	0.994	0.13[a]	1430[a]
5.6	0.982	0.09[a]	2000[a]

[a] Constant obtained using a much smaller data range.

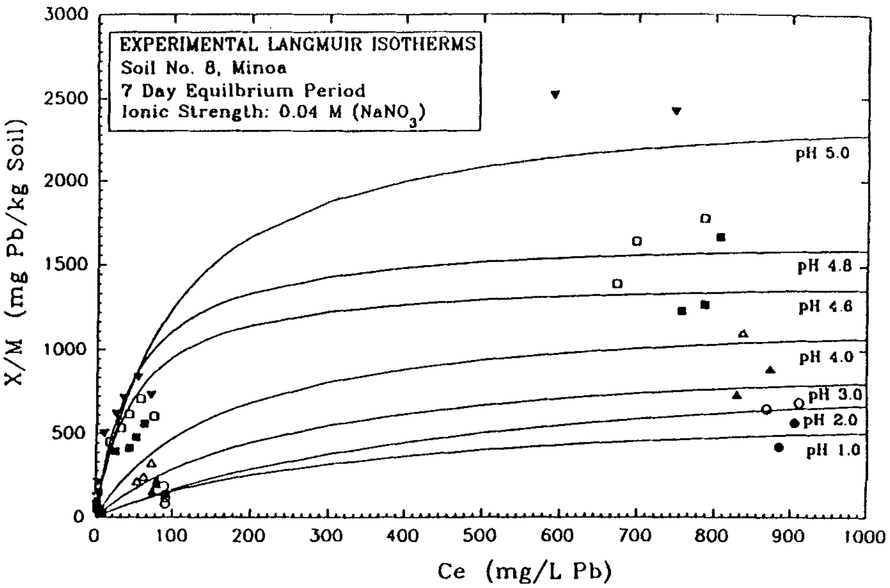

FIG. 7 Predicted and experimental Langmuir isotherms at pH values of 1, 2, 3, 4, 4.6, 4.8, and 5.

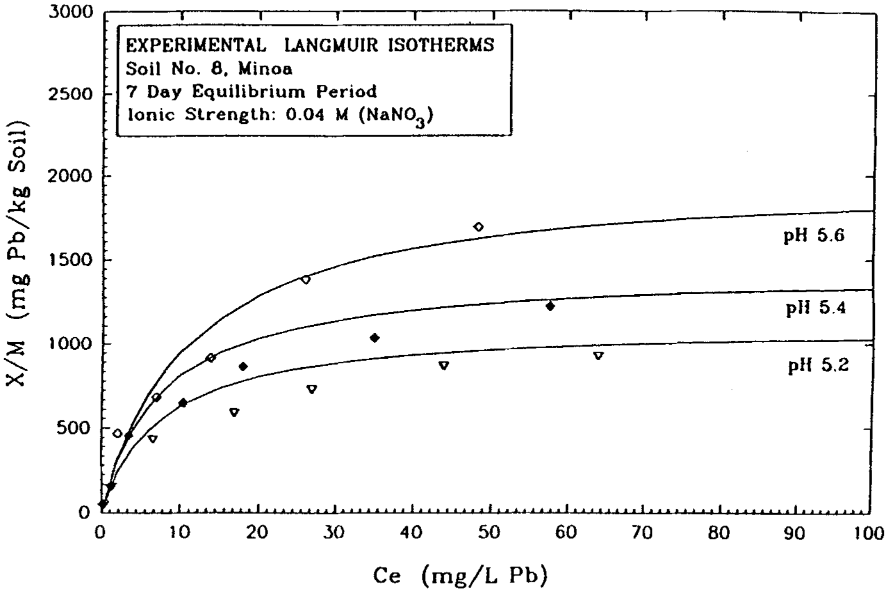

FIG. 8 Predicted and experimental Langmuir isotherms for pH values of 5.2, 5.4, and 5.61.

Freundlich Isotherms

Freundlich isotherm constants (*K* and *n*) were determined by graphing the experimental data using the linearized form of the Freundlich isotherm (Eq. 5). In Fig. 9, log *X*/*M* is plotted versus log C_e. The solid line is a best fit curve (first-order) to the data. Best fit values of *K* and *n* are presented in Table 5. *K* is an indicator of the average bond strength, and *n* is an indicator the distribution of bond strengths. The greater the difference between *n* and 1, the greater the distribution of bond energies. As the pH increased, the average binding energy and the distribution of surface sites increased with pH. Values of r^2 from the regression analysis are also presented in Table 5. The high r^2 values were due in part to the decrease in sensitivity of a log-log plot. A better indication of the fit of the Freundlich isotherm can be determined when an arithmetic scale is used. In Fig. 10, the Freundlich predicted and experimental values of *X*/*M* are plotted versus C_e. The Freundlich isotherm does not predict a maximum *X*/*M*, and it thus provides a better fit to the experimental data than does the Langmuir isotherm.

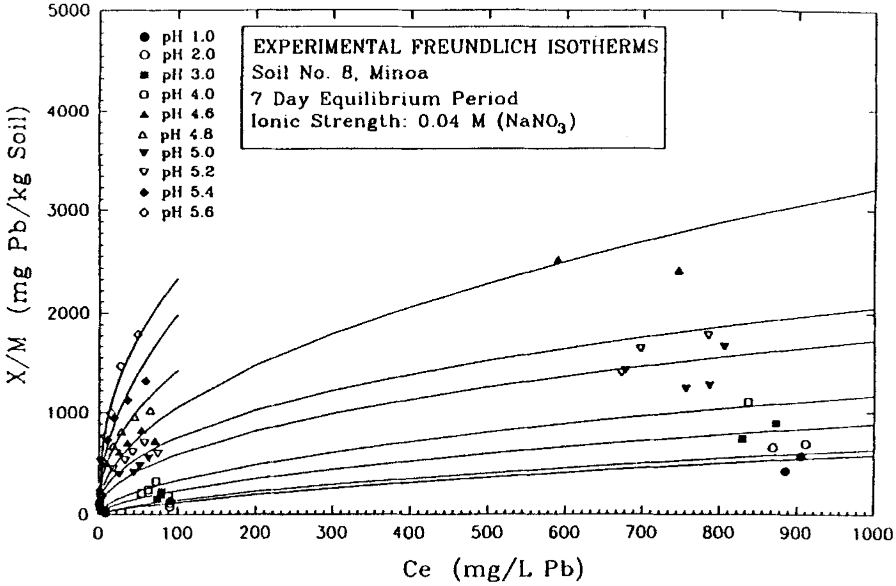

FIG. 9 Linearized Freundlich isotherms.

TABLE 5
Experimentally Determined Constants for the Freundlich Isotherm

pH	r^2	K	n
1.0	0.992	4.91	1.45
2.0	0.975	7.08	1.54
3.0	0.995	15.9	1.72
4.0	0.996	26.3	1.82
4.6	0.991	67.76	2.13
4.8	0.987	102.09	2.30
5.0	0.983	115.61	2.08
5.2	0.987	176.20	2.20
5.4	0.984	216.77	2.08
5.6	0.990	371.53	2.50

BET Isotherms

BET isotherm constants were determined by graphing the experimental data using the linearized form of the BET isotherm (Eq. 8). In Fig. 11, $C_e/(C_s - C_e)(1/b)$ is plotted versus C_e/C_s. The solid line is a best fit curve (first-order) to the data. All data points were used in the construction of

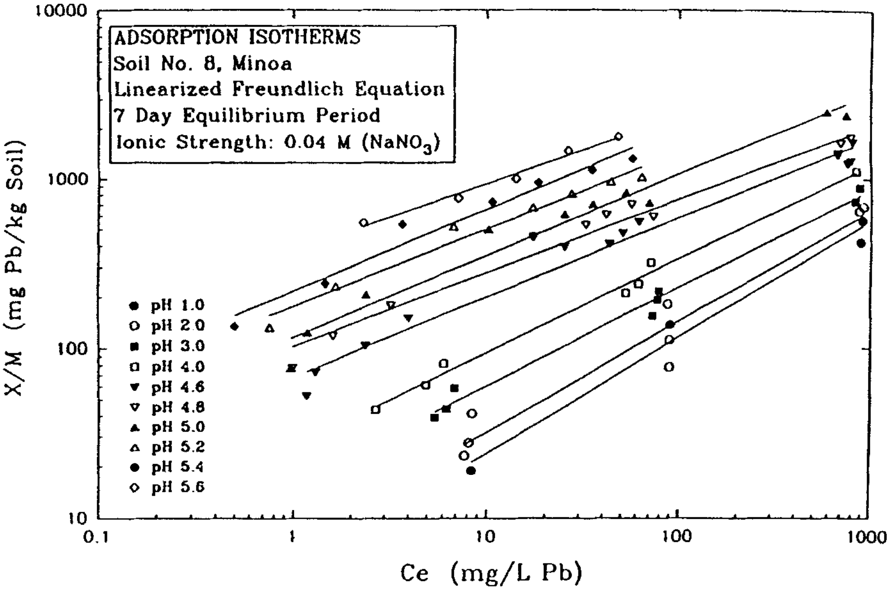

FIG. 10 Predicted and experimentally determined Freundlich isotherms.

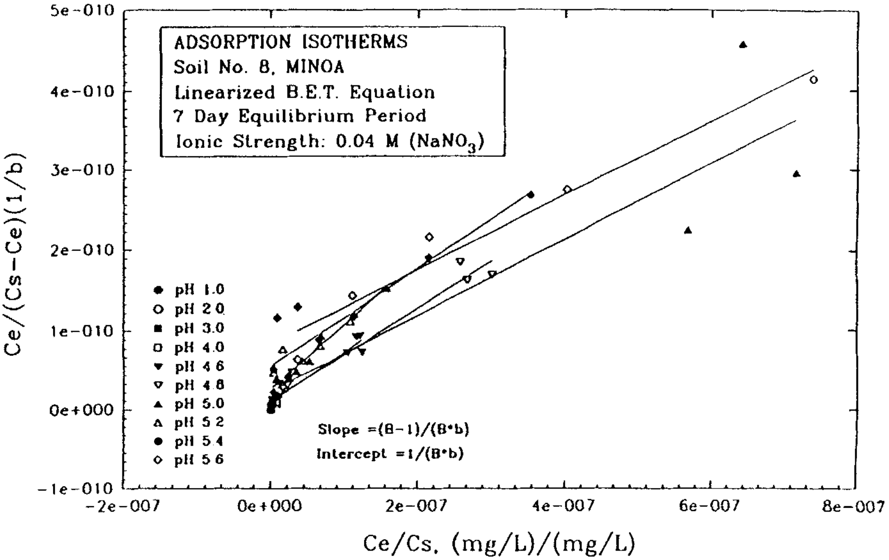

FIG. 11 Linearized BET isotherms.

the BET isotherms since surface precipitation (i.e., multilayered coverage) can be accounted for in the BET isotherm. The values used for the solution saturation variable (C_s) in Eqs. (7) and (8) were obtained from lead solubility diagrams (24). Data fit was poor for most pH values. The worst fit was obtained for pH values of 1, 2, and 5. At low pHs, the saturation value (C_s) were much greater than the equilibrium lead concentrations obtained from the adsorption experiments. Thus, the slopes of the linearized BET isotherms were nearly zero for all pH values examined, indicating that the constant B in the BET isotherm is very large. In instances where $B \gg 1$ and $C_e \ll C_s$, the BET equation theoretically reduces to the Langmuir isotherm. It appears that lead is not retained on the study soil in multiple layers.

SUMMARY AND CONCLUSIONS

The adsorption of lead by a very fine sandy loam was investigated. Aqueous lead concentrations of 10, 100, and 1000 mg/L and soil concentrations ranging from 10 to 167 g/L were used. Seven-day adsorption isotherms were conducted as a function of pH. Lead retention by the soil was a strong function of pH. The pH range over which adsorption occurred (i.e., the width of the pH–adsorption edge) decreased with increasing lead concentration. Experimental results were modeled using the Langmuir, Freundlich, and BET isotherms. Only the Langmuir and Freundlich iso-therms successfully represented the experimental results. The role of surface precipitation was assumed to be small because of the failure of the BET isotherm to adequately predict metal retention. The Freundlich iso-therm provided the best fit because a maximum surface concentration was usually not observed. Langmuir and Freundlich isotherms parameters varied in a way that suggests that the average binding energy and the distribution of bond strengths increased with increasing pH. The isotherm expressions determined in this study can be used as source-sink terms in the generalized mass transport model. The generalized mass transport model can be used to predict the fate of lead in the unremediated subsurface as well as the performance of remediation technologies (e.g., in-situ soil flushing).

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