Effects of Soil Organic Matter on the Kinetics and Mechanisms of Pb(II) Sorption and Desorption in Soil

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ABSTRACT

To improve predictions of the toxicity and threat from Pb contaminated soil, it is critical that time-dependent sorption and desorption behavior be understood. In this paper, the sorption and desorption behavior (pH = 5.50, I = 0.05 M) of Pb in a Matapeake silt loam soil (Typic Hapludult) were studied by stirred-flow and batch experiments. In addition, we studied the effects of soil organic matter (SOM) on sorption and desorption behavior by treating the soil with sodium hypochlorite to remove the SOM fraction, and using a soil with six times as much SOM (St. Johns loamy sand [Typic Haplaquods]) as the Matapeake soil. Lead sorption consisted of a fast initial reaction in which all of the Pb added to the stirred-flow chamber was sorbed. Following this initial fast reaction, sorption continued and appears to be rate limited (indicated by a decrease in the outflow concentration when the flow rate was decreased, or when the flow was stopped). The total amount of Pb sorbed was 102, 44, and 27 mmol kg^{-1} for the St. Johns soil and the untreated and treated Matapeake soils, respectively. Desorption experiments were conducted on the soils with the background electrolyte as the eluent in the stirred-flow chamber. In the St. Johns soil only, 32% of the total sorbed Pb was desorbed, while 47 and 76% of the sorbed Pb was released from the untreated and treated Matapeake soil, respectively. The correlation between SOM in the soils, and the percentage Pb desorbed from the soils suggests that SOM plays an important role in slow desorption reactions of Pb from soil materials. Aging experiments in which sorbed Pb was incubated for 1, 10, and 32 d showed that sorption incubation time had no effect on Pb desorption behavior. Analysis of the treated and untreated Matapeake soils by x-ray absorption fine structure (XAFS) spectroscopy revealed that the local atomic structure of sorbed Pb is distinctly different in the two samples. In the soil treated to remove SOM, the data were well represented by theoretical models using O, Si, and Pb backscattering atoms. In the untreated soil, the XAFS data were best described by O and C backscatterers. These XAFS results confirm that the sorption mechanisms in the two systems are different.

To PREDICT the fate and transport of contaminants such as Pb in the environment, scientists and engineers commonly rely on distribution coefficients and maximum adsorption levels that are obtained from experiments in which it is assumed that the reaction is at equilibrium. However, reactions in the environment are rarely at equilibrium, but instead are in a state of continuous change because of the dynamic processes occurring (Sposito, 1989; Sparks, 1995). Another discrepancy that causes errors in predicting the potential toxicity of a contaminant is that researchers often neglect desorption behavior, which is an important process controlling metal bioavailability in the environment. Thus, in order to improve remediation strategies, risk assessments, and make better predictions about the mobility of contaminants, it is critical that time-dependent metal sorption and desorption behavior on soil be understood, as well as the mechanism of the sorption–desorption reactions.

Lead sorption behavior is often initially fast, followed by a slow reaction (Benjamin et al., 1981; Hayes et al., 1986; Strawn et al., 1998). The fast reaction is most likely adsorption via electrostatic attraction, and/or inner-sphere complexation with functional groups present on the soil components. There are several possible reasons for the slow sorption steps, such as: slow interparticle diffusion in porous minerals and organic matter, formation of precipitates on surfaces which can sometimes be slower than typical sorption, and adsorption onto sites that have relatively large activation energies (Fuller et al.,1993; Papelis et al., 1995; Loehr et al., 1996; Scheidegger et al., 1998). It is possible that multiple slow reaction mechanisms are responsible for the slow sorption reactions in soils.

There are three main processes that control the fate and bioavailability of metals in soils: (i) removal of metals from the soil solution by sorption onto soil particles, (ii) release of the metal from the soil particle to the soil solution (desorption), and (iii) precipitation–dissolution of the metal as an independent phase in the soil matrix. Less is known about the desorption behavior of metals from soils than the other two processes. This is unfortunate since once a soil is contaminated desorption is an important process that controls the bioavailability of the contaminant. If accurate assessments of the fate of metals in soils are to be gained, it is critical that desorption behavior be studied as well as sorption behavior.

It is often observed that desorption reactions are slower than sorption reactions. Smith and Comans (1996) predicted that adsorption half-lives for Cs sorption on sediments were between 50 and 125 d, while desorption half-lives were on the order of 10 yr. Failure to include the slow desorption reaction in transport models severely underestimated the remobilization potential of Cs. Slow desorption reactions have also been observed for metals (Kuo and Mikkelsen, 1980; McKenzie, 1980; Schultz et al., 1987; Ainsworth et al., 1994; Scheidegger et al., 1996). A possible reason that desorption reactions are slower than sorption reactions is because the sorbate undergoes a transformation from one state to another, for example: conversion from an adsorbed species to a surface precipitate. In addition, desorption reactions often require large activation energies, which cause the reaction to proceed slowly (McBride, 1994).

The rates of Pb sorption and desorption on mineral

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Abbreviations: CV, chamber volume; SOM, soil organic matter; XAFS, x-ray absorption fine structure.

surfaces have been observed to be similar (Ainsworth et al., 1994; Gunneriusson et al., 1994; Strawn et al., 1998). However, in some cases desorption from soils is much slower than sorption. This could be due to the presence of SOM and/or the formation of Pb multinuclear complexes with carbonates, phosphates, and sulfates present in the soil. Bunzl et al. (1976) found that the desorption rate of Pb from SOM was significantly slower than the adsorption rate. Similar trends were found for Pb adsorption and desorption on activated carbon (Wilczak et al., 1993).

Soil organic matter is an important component of the soil since it has a high surface area, and has functional groups that are Lewis bases (e.g., carboxyl and phenol groups) that metals can form chemical bonds with (Sparks, 1995). It has been observed that Pb forms strong complexes with SOM, and that it can out compete most other metals for adsorption sites on SOM (Kendorff and Schnitzer, 1980; Elliot et al., 1986; Jin et al., 1996; Suave et al., 1998). Thus, it is important that a better understanding of Pb desorption behavior from the SOM be gained.

Kinetic studies are most often conducted by means of batch reactors. While valuable information has been obtained from these experiments, the batch technique is not ideal in desorption studies since readsorption of the sorbate and accumulation in solution can hinder desorption (Sparks, 1989). One of the most beneficial uses of stirred-flow reactors is to study desorption reactions since the desorbed products are continuously removed from solution. There are several other reasons that stirred-flow reactors are advantageous for studying sorption and desorption reactions: relatively fast reactions can be measured compared with batch methods; carbon dioxide can be easily removed from the system; sorption and desorption kinetics can be measured in a single experiment; and the system is well mixed, which aids in elimination of film diffusion and calculation of the dilution occurring in the reaction chamber (Sparks, 1989; Amacher, 1991; Yin et al., 1997).

The objectives of this study are to characterize sorption and desorption behavior of Pb on soil, and to determine the importance of SOM on sorption and desorption. To accomplish these objectives, we used both batch and stirred-flow studies and soils with three different amounts of SOM. Information obtained from this study will give insights to scientists and engineers that may lead to improved remediation strategies, disposal practices, and risk assessments. Such information is critical, since Pb is used in a variety of industrial and manufactur-

ing processes and is one of the most common contaminants found at hazardous waste sites (Reed et al., 1996).

METHODS AND MATERIALS

The A horizons (~0–20 cm) of a Matapeake silt loam (Typic Hapludult) and a St. Johns loamy sand (Typic Haplaquods) from Delaware were used in this study. The physicochemical and mineralogical properties of the soils were determined by standard methods (Sparks, 1996), and are reported in Table 1. Studies were also conducted on a Matapeake soil that was treated to remove organic matter by the following procedure: 30 g of soil were suspended in ~50 mL of sodium hypochlorite (pH = 9.5) (Na-hypochlorite is an effective oxidant for SOM, and is less invasive than other SOM removal procedures [Lavkulich and Wiens, 1970]); the suspension was heated to 338 K and allowed to react for 20 min; the samples were then centrifuged, decanted, and treated with additional Na-hypochlorite. This procedure was repeated four times. Following oxidation of the organic matter the soil was washed repeatedly with a 1 M NaNO$_3$ solution to Na saturate. The Na-saturated soil was then washed with deionized water to remove excess NaNO$_3$. The resulting soil had 0.1% SOM remaining, as determined by the Walkley Black method (Nelson and Sommers, 1996). Analysis of the soils for total carbon by loss on emissions resulted in 1.38% for the untreated Matapeake soil, and 0.18% for the treated Matapeake soil.

In all of the soils used in this research, the <2-mm fraction was separated by sieving. In order to eliminate fine colloids that are difficult to separate, and can pass through the filter membranes, the soils were preconditioned by the following procedure: the soils were suspended in 0.01 M NaNO$_3$ and shaken at 160 rpm for 16 h, and the samples were centrifuged at 7800 g for 10 min and the supernatant was discarded, thus eliminating any fine colloids that did not settle during centrifugation. This procedure was repeated three times; in the third treatment, deionized water rather than NaNO$_3$ was used to resuspend the soil. The final paste was washed with deionized water and filtered to separate the soil.

All solutions were made with ACS reagent grade chemicals and distilled deionized water. Carbon dioxide was eliminated from all experiments by working under an N$_2$ atmosphere. The temperature of all experiments was maintained at 298 K.

Batch Experiments

To gain insight into the overall sorption behavior, and make comparisons to the results from the stirred-flow experiments, batch isotherm and kinetic studies were conducted on the Matapeake soil. One gram of soil was preequilibrated for 24 h in background solution adjusted to pH = 5.50. The background solution consisted of a mixture of NaNO$_3$ and 0.05 M MES (buffer, [2-(N-morpholino) ethane sulfonic acid]). The buffer was necessary to control pH during the adsorption experiments since initial experiments revealed that Pb sorp-

Table 1. Physicochemical and mineralogical characteristics of the soils used in this study.

Soil type	Subgroup	pH	Cation-exchange capacity†	Organic matter‡	Sand/silt/clay fractions	Mineralogy of <2 μm clay fraction
			cmol + kg^{-1}	%		
Matapeake silt loam	Typic Hapludult	5.3	13.4	2.1	42/54/5	kaolinite~vermiculite>quartz>mica
Treated Matapeake silt loam	–	–	11.9	0.1	–	–
St. Johns loamy sand	Typic Haplaquods	3.6	23.3	13	70/24/5	mica>kaolinite>montmorillonite>gibbsite>quartz

† pH = 7.
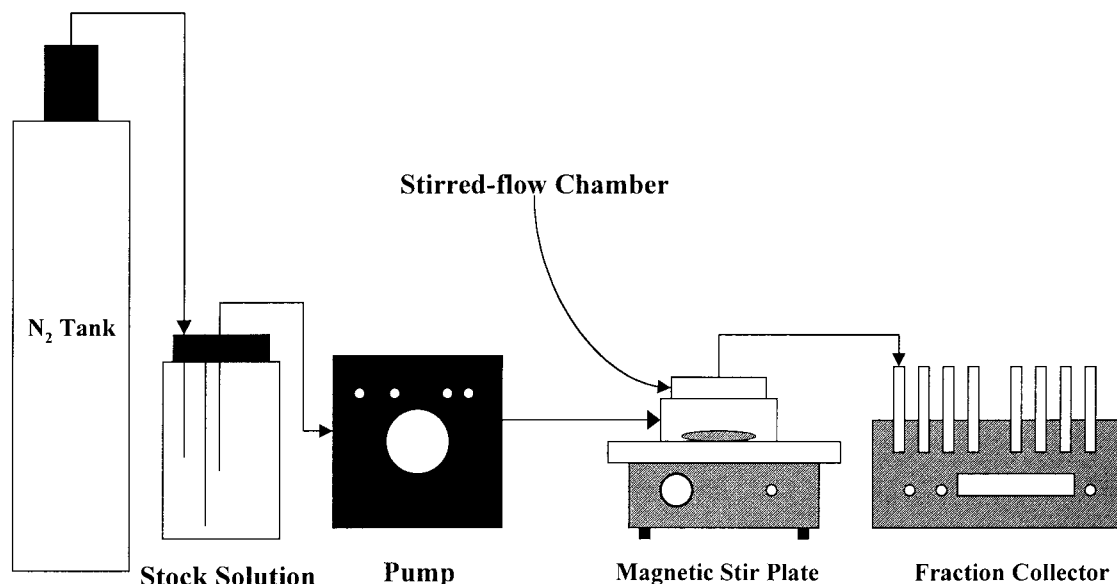‡ Walkley-Black method (Nelson, 1986).

Fig. 1. Schematic illustrating the experimental design of the stirred-flow experiments.

tion and desorption involve proton exchange reactions. Titration experiments with this buffer in solutions of Pb confirmed the results of others (Good et al., 1966; Baeyens and Bradbury, 1997); no detectable complexation reactions occur between Pb and the MES buffer. The concentration of $NaNO_3$ used in the experiments was adjusted to make the total $I = 0.05$ M (including the MES and the Pb solution).

In the isotherm experiment, the initial Pb concentrations ranged from 1 to 12 mM. Samples with no soil present were prepared by identical procedures as the sorption samples to determine the exact initial concentration of the sorption samples. The solid concentration of the samples was 100 g L^{-1}. Following the addition of the Pb solution the pH of the samples was adjusted to pH = 5.50. After 24 h, the samples incubated at the highest concentrations required minor pH adjustments. The samples were incubated for a total of 48 h on an end-over-end shaker operating at 20 rpm. At the end of the incubation period, the samples were centrifuged at 7800 g for 10 min. The supernatant was filtered through a 0.2-μm filter and diluted 2:3 with 1 M HNO_3. The solution was then analyzed for total Pb with an ICP spectrometer.

At the start of the kinetic experiment, 3.5 mL of a Pb stock solution [Pb] = 12.25 mM was added to 1.5 mL of suspension (0.50 g soil). The pH of the suspension was maintained at 5.50 throughout the experiment with the MES buffer. Minor pH adjustments were made throughout the experiment by addition of NaOH. Periodically (8 min–800 h) samples were removed from incubation and processed by the same procedures as mentioned above. The total amount of Pb adsorbed in the kinetic and the isotherm experiments was calculated from the difference between the initial and final Pb concentrations.

Stirred-Flow Experiments

The reaction chamber used for these experiments was similar in design to the reaction chamber used in the experiments of Bar-Tal et al. (1990). The setup of the stirred-flow experiment is illustrated in Fig. 1. The pump used in these experiments was a piston displacement pump designed for use in an HPLC system. The experiment was started by placing 0.75 g of pretreated soil in the reaction chamber and filling the chamber with background electrolyte ($I = 0.05$ M [MES and $NaNO_3$] and pH = 5.50). A 25-mm-diam filter membrane with a 0.2-

μm-pore size was used in the reaction chamber. Upon sealing the reaction chamber, CO_2 free background electrolyte solution was flowed through the chamber for 10 min at 1 mL min^{-1} and the suspension was allowed to sit (no flow) for 20 min to preequilibrate. The reactor had an approximate volume of 8 mL. The suspension in the reaction chamber was stirred by a magnetic stir bar (12.7 mm long and 3 mm in diameter) at 400 rpm. To initiate the experiment a Pb solution ([Pb] = 2.32 mM, $I = 0.05$ M) was pumped into the chamber. The effluent was collected with a fraction collector set to collect 2 mL of solution per tube. The fraction collector was started when the first drop of solution exited the outflow tube. The flow rate in the experiments was either 0.4 mL min^{-1} or 4 mL min^{-1}. The flow rate was monitored and found to be stable within ±3% throughout the experiment.

The desorption experiment was initiated when the concentration of Pb in the outflow was equal to the concentration of Pb in the inflow. The desorption reaction was started by purging the tubing before and after the stirred-flow chamber with background electrolyte (desorptive solution). In all of the desorption experiments, the pH and ionic strength of the inflow solution was the same as in the sorption experiments; in other words, the desorption and sorption solutions were identical except for the presence of Pb. Thus, the desorption reaction was promoted by driving the adsorption reaction backward via removal of the Pb from solution.

To determine if the sorption and desorption reactions were rate limited, the flow was stopped during the experiment for 30 min. If the reaction were not at equilibrium when the flow was stopped, then sorption would continue (Bar-Tal et al., 1990). This would result in a drop in the [Pb] in the chamber, which can be detected in the outflow when the flow resumes.

The effects of aging on desorption were measured on the Matapeake soil by first adsorbing Pb by the batch incubation procedures described above, and then transferring the soil to the stirred-flow chamber for desorption. In these experiments, the initial sorptive in the chamber was a 2.32 mM Pb solution, which is the same concentration present in the chamber at the start of the desorption experiments conducted directly after the stirred-flow sorption experiments. The outflow from all of the experiments was acidified and analyzed with an ICP spectrometer for total Pb.

The data from the stirred-flow experiments were plotted as a function of chamber volumes (CV), which was calculated by multiplying the flow rate and the time and dividing by the volume of the chamber. This was useful for comparisons of data obtained from experiments conducted at different flow rates since it normalized the data relative to the flow rate. Thus, any differences between the data obtained at the different flow rates were the result of changes in the extent of the surface reactions.

To analyze accurately the results from stirred-flow experiments, it was necessary to calculate the effective volume of the chamber (V_{ce}). To accomplish this, tracer experiments at several different flow rates and no soil present in the chamber were conducted. From these data V_{ce} was calculated by fitting the outflow concentration using Eq. [1] ($dq/dt = 0$) and subtracting the volume of the soil. The resulting V_{ce} for $Q = 0.4$, 2.0, and 4.0 mL min^{-1} are 7.98, 8.10, 8.32 mL, respectively (a maximum difference of ~ 4%). Use of the effective volume of the chamber (V_{ce}) instead of the actual volume to calculate CV allowed data obtained at different flow rates to be compared. Thus, in all of the adsorption and desorption experiments presented in this study the flow rate dependent values of V_{ce} were used to calculate CV.

Data Analysis

One of the limitations of stirred-flow analysis is that the amount of sorbate being sorbed at any given time cannot be measured directly. Instead, it is necessary to use models to derive the adsorption behavior. A common approach to modeling reactions in a stirred-flow system utilizes a mass balance equation (Bar-Tal et al., 1990). The mass balance equation for a stirred-flow reactor is as follows:

$$\frac{dC_{chamber}}{dt} \times V_c = [(C_{in} - C_{out}) \times Q] - \left(m \times \frac{dq}{dt}\right) \quad [1]$$

Where $C_{chamber}$ is the [Pb] in the chamber (mmol L^{-1}), t is time (min), V_c is the volume of solution in the chamber (L), C_{in} is the [Pb] that is being pumped into the chamber (mmol L^{-1}), C_{out} is the [Pb] leaving the chamber (mmol L^{-1}), Q is the flow rate (L min^{-1}), q is the amount of Pb sorbed (mmol kg^{-1}), and m is the mass of soil (kg). Since in the stirred-flow chamber the solution is well mixed, the [Pb] in the chamber equals [Pb] leaving the chamber ($C_{chamber} = C_{out}$). If there is no soil in the chamber, or there is no reaction occurring, then $dq/dt = 0$, and the equation can be integrated to find C_{out} as a function of time, which is equivalent to the outflow concentration of a non-sorbing tracer.

Within the mass balance equation the rate of the reaction on the surface is represented by the reaction term dq/dt. The mass balance equation can be solved for dq/dt only in limited cases (Skopp and McCallister, 1986; Sparks, 1989; Bar-Tal et al., 1990). Some of the equations that have been used to describe sorption behavior (dq/dt) in a stirred-flow reactor are first-order, fractional-order, elovich, and parabolic diffusion (Skopp and McCallister, 1986; Sparks, 1989; Bar-Tal et al., 1990). However, on the basis of the Pb sorption behavior observed in this study, these equations are not appropriate since the sorption behavior consist of a fast and slow reaction phase. A better model to describe the Pb sorption data would include a fast equilibrium reaction, and a slow rate-limited secondary reaction. Several different multireaction models have been developed to describe metal sorption and desorption in soils (Amacher et al., 1988; Selim et al., 1989; Smith et al., 1996). In this study, these equations were not used.

For the desorption study, to make relative comparisons, it is useful to normalize the data by the total amount of Pb sorbed. To do this, we estimated the amount of Pb desorbed at a given time from the difference in the areas under the curves of the tracer, and the outflow concentration when desorption is conducted. The total amount of Pb sorbed can be estimated by a similar approach, i.e., when the outflow concentration is the same as the inflow concentration the difference between the blank and the sorption curve represents the total amount of Pb removed from solution. The amount of Pb sorbed or desorbed is then calculated by multiplying the area by the flow rate and dividing by the mass of soil. To calculate the areas under the curves, the integral of a cubic-spline interpolated from $C_{out}(t)$ was calculated. These calculations were made by the algorithms in the computer program Scientist (MicroMath Research, Salt Lake City, UT).

XAFS Experiments

Treated (SOM removed) and untreated soil samples were analyzed by XAFS to determine the local atomic structure surrounding the sorbed Pb in the presence and absence of SOM. The samples were incubated using the same procedures described above. For XAFS analysis, the wet pastes were loaded into Teflon sample cell holders in the glovebox and sealed with Kapton Tape.

XAFS data acquisition of the L$_{III}$-edge (13055 eV) was conducted at beamline X-11A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY. Details of the XAFS data collection procedures and data analysis are described in Strawn et al. (1998). In this study, three to five scans were merged, the data were normalized, and the background was removed by fitting three knots at unequal distances. The data were then converted to k-space, windowed, and fourier filtered to convert to R-space. Fitting of the RSF was attempted by theoretical paths for Pb, O, Si, and C backscatterer atoms generated from model compounds using FEFF 6.0. Estimations of the errors associated with the coordination numbers (N), bond distances (R) and Debye-Waller factors (σ^2) were made from the confidence limits of the least squares non-linear fitting procedure. Previous data analysis (Strawn et al., 1998) has shown that these values are usually larger than the absolute errors associated with fitting model compounds.

RESULTS AND DISCUSSION

Batch Experiments

The adsorption isotherm for the Matapeake soil is presented in Fig. 2. This isotherm represents the sorption behavior as a function of concentration after incubating for 48 h. In the next section, the sorption kinetics reveal that a significant amount of sorption can occur after 48 h. Thus the isotherm presented in Fig. 2 is not necessarily an equilibrium sorption isotherm, but nevertheless gives an indication of the sorption behavior. In addition, this discrepancy highlights the importance of incubating samples for times longer than the traditional 24 or 48 h. The solid line in Fig. 2 represents the best fit of the data to the Freundlich adsorption isotherm equation:

$$q = K_d \times C^{1/n} \quad [2]$$

Where K_d is the Freundlich distribution coefficient and n is a correction factor (Sparks, 1995). For the Matapeake soil, $K_d = 53.83$ and $n = 4.64$. When the initial concentration of Pb is low, most of the Pb is sorbed by the soil. This is characteristic of a strong affinity of the
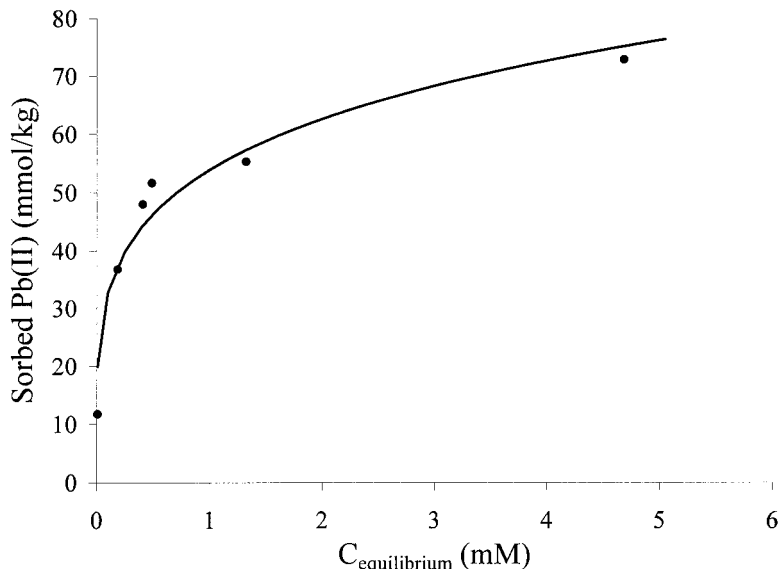
Fig. 2. Sorption isotherm on the untreated Matapeake soil. The solid line is the best fit to the Freundlich equation (Eq. [2]).

soil for Pb. As the initial concentration of Pb increases, the slope of the sorption isotherm levels off, indicating that the soil is reaching a sorption maximum. The sorption behavior displayed by the Matapeake soil is typical L-type sorption behavior which is commonly observed for metal sorption by soils (Sparks, 1995).

The results of the batch sorption kinetic experiments are presented in Fig. 3. Within the first 8 min (first sampling time), a very fast reaction occurred, accounting for 78% of the total sorbed Pb. Following the initial fast reaction, the sorption reaction continued for ~100 h. At times longer than 100 h, only a small amount of additional sorption occurred. After 800 h, ~79% of

the Pb initially added to the suspension had been removed. Since a majority of the Pb is sorbed prior to the first sample (78% of the total Pb sorbed occurred within 8 min), and the rest of the sorption occurs within 100 h, it is hypothesized that there are two distinct reactions occurring: one fast reaction and one slow reaction. The slow data were modeled using a reversible first-order reaction:

$$\frac{dq}{dt} = k \times (q_{max} - q) \qquad [3]$$

Where q_{max} is the maximum amount of sorption at equilibrium (mmol kg^{-1}), and k is the overall rate coefficient
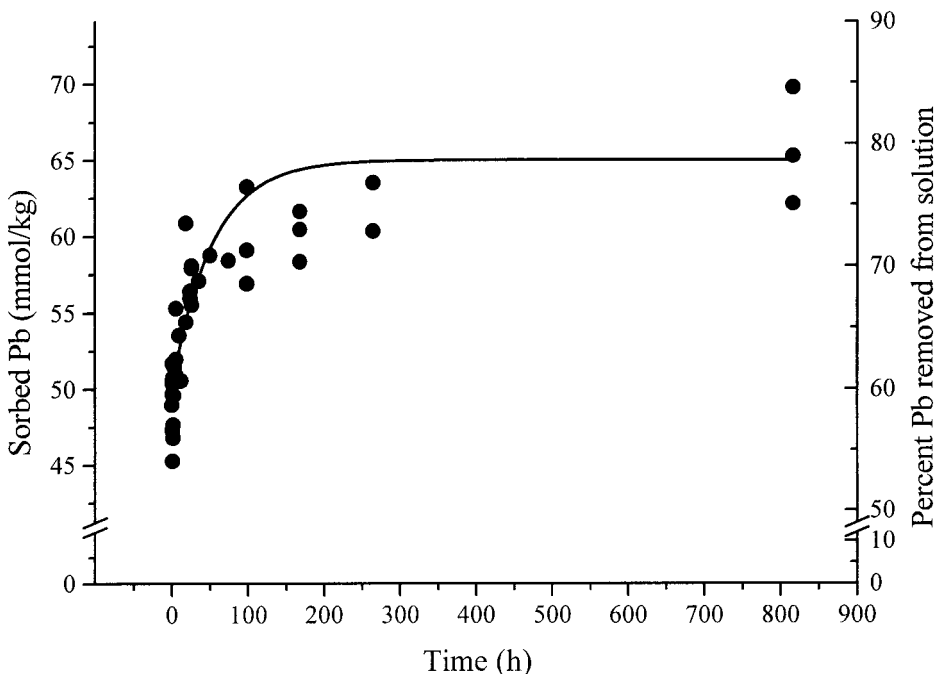

Fig. 3. Sorption kinetics on Matapeake soil measured by the batch method. The solid line is the best fit to the first-order reversible equation, Eq. [3].
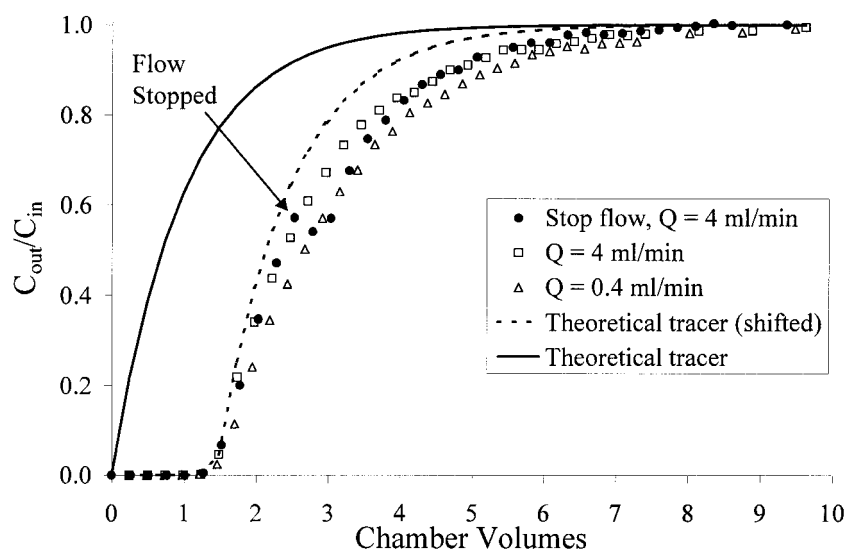
Fig. 4. Results of sorption experiment conducted on Matapeake soil in the stirred-flow chamber, and theoretical tracers calculated by Eq. [1].

(t^{-1}). This equation was chosen since reactions in soils are often observed to follow apparent first-order reaction kinetics (Sparks, 1989; Amacher, 1991). Use of this equation does not suggest any mechanistic information, but simply implies that the sorption behavior can be represented by a first-order equation that is dependent on surface loading. The initial conditions used to fit the data were $t = 0.13$ h, $q = 50$ mmol kg^{-1}, and $q_{max} = 65.0$ mmol kg^{-1}. The overall apparent rate constant obtained from the fit of the data was $k = 0.012$ min^{-1}. As determined by this value, the half life for the slow reaction was calculated to be 58 h.

The two stage time-dependent Pb sorption behavior is similar to the results observed on pure components and soils obtained by other researchers. Carriere et al. (1995) found that Pb sorption on soil was fast at low initial Pb concentrations, but at higher concentrations the reaction became much slower, taking several days to reach a steady state. From these results, Carriere et al. (1995) suggested that precipitation reactions were responsible for the slow sorption reaction since they were most noticeable at the higher [Pb]. Hayes and Leckie (1986) and Benjamin and Leckie (1981) found that sorption of Pb on iron hydroxides (common minerals in soils) was initially fast, followed by a much slower reaction. Similar results were found by Strawn et al. (1998) for Pb adsorption on aluminum oxide. Slow Pb adsorption has also been observed on pure organic materials (Wilczak et al., 1993). Since soil is a mixture of organic and inorganic components, and it contains several different types of sorption sites, it is likely that several mechanisms are responsible for the slow sorption reactions. These may include diffusion, precipitation, and/or sorption reactions on sites that have a higher activation energy than the fast sorption sites.

Stirred-Flow Experiments

The data from the stirred-flow sorption experiments on the untreated Matapeake soil are presented in Fig. 4. Five different data sets are presented in Fig. 4: data

from experiments conducted at two flow rates, data from a stopped-flow experiment, and two sets of theoretical tracer data. When the flow rate is increased from 0.4 to 4 mL min^{-1}, there is a shift in the midpoint ($\frac{1}{2} \times C_{out}/C_{in}$) of the breakthrough from 2.7 to 2.4 CVs, respectively. This shift is a result of changes in the reaction occurring in the chamber. The average time the solute spends in the reactor vessel (τ) is a function of the CV and the flow rate ($\tau = V_{ce}/Q$) (Brezonik, 1994). For the experiment in which $Q = 4$ mL min^{-1}, $\tau = 2$ min, while for the experiment conducted at $Q = 0.4$ mL min^{-1}, $\tau = 21$ min. In a system where the reaction occurring is slower than the solute residence time (τ), the outflow concentration would be expected to increase as the flow rate increases. This is the behavior observed in Fig. 4 for Pb sorption on the Matapeake soil, suggesting that sorption kinetics are being measured.

The results of the stopped-flow experiment are presented in Fig. 4. After 2.5 CV of Pb solution had flowed through the chamber, the flow was stopped for 30 min. The [Pb] in the outflow solution dropped by ~6%. This is a significant drop giving additional evidence that the reaction is rate limited. Thus, it can be concluded from the experiments in which the flow rate is changed, and the stopped-flow experiment, that the reactions in the stirred-flow reactor at 4 mL min^{-1} are rate limited. Although not shown, data from 2 mL min^{-1} also show a shift in the outflow concentration that is intermediate between the 0.4 and 4 mL min^{-1} experiments, suggesting that at this flow rate the reaction is also rate limited.

The solid line in Fig. 4 is the theoretical tracer calculated from Eq. [1], when $dq/dt = 0$. The midpoint of the breakthrough for this data is 0.75 CVs. The midpoint for the sorption experiment conducted at 4 mL min^{-1} occurs at 2.4 CV, this is shifted 1.65 CVs from the midpoint of the breakthrough in the tracer. This retardation shows that the soil is adsorbing significant amounts of Pb. One of the distinctive characteristics present in the stirred-flow experiments is that initially all of the Pb input into the chamber is sorbed, resulting in the outflow
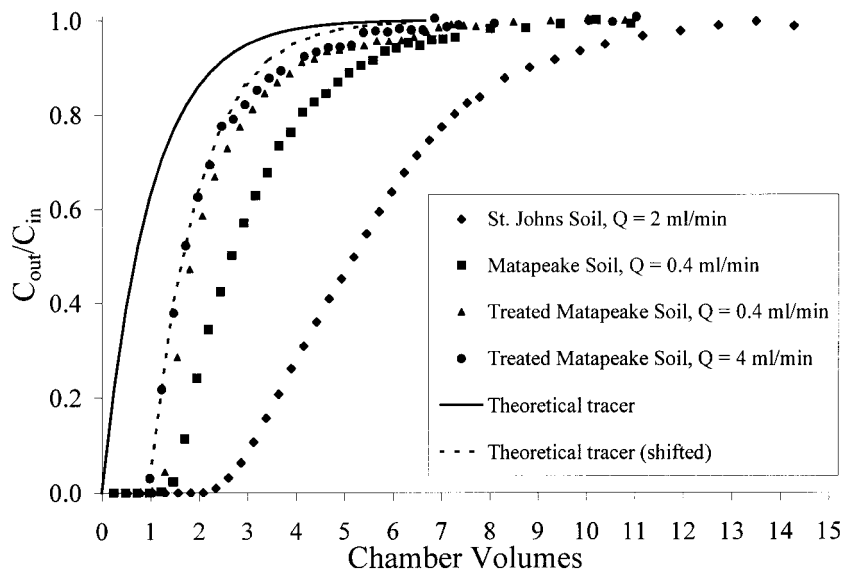
Fig. 5. Breakthrough curves for sorption on treated and untreated Matapeake soils, the St. Johns soil, and theoretical tracers.

[Pb] being zero until ~1.2 CV. The initial adsorption accounts for ~65% of the total sorption that occurred on the soil. Since in this experiment $\tau = 2$ min (Q = 4 mL min^{-1}), the fast reaction occurring on the soil must have a half life <2 min. Fast adsorption reactions for Pb on oxides have been studied by pressure-jump relaxation (Hayes et al., 1986; Yasunaga and Ikeda, 1986). Results from these studies suggest that the fast adsorption reaction is primarily due to the formation of bonds with functional groups that are readily available on surfaces, and that the reaction occurs within seconds. These types of adsorption reactions are too fast to be measured by the stirred-flow reactor.

After ~1.2 CV, the Pb concentration in the outflow becomes >0 (Fig. 4). This suggests that Pb sorption is either slowing down, or that the soil has reached its maximum sorption capacity. If the soil were to sorb no additional Pb from solution, then the breakthrough would follow the dashed line (a shifted theoretical tracer data set) in Fig. 4. However, the [Pb] in the outflow is retarded compared with the tracer, indicating that sorption is continuing at these longer times. The stopped-flow and variable flow rate experiments indicate that the sorption reaction occurring after 1.2 CV is rate limited. The slow reaction could be due to sorption on sites which are less readily available than those in which fast sorption occurred (diffusion limited), or a result of secondary sorption mechanisms such as precipitation or sorption on sites with larger activation energies.

Sorption on the Matapeake soil reached a steady state after about 8 to 9 CV ($C_{out}/C_{in} = 1$). At this point, the total sorption on the soil was 44 mmol kg^{-1}. This value is only 68% of the total sorption that occurred in the batch kinetic experiment that was allowed to equilibrate for 800 h. The difference between the total sorption measured by batch and stirred-flow methods is most likely due to the fact that the slow reaction is occurring too slowly ($t_{1/2} = 58$ h) to detect any noticeable change

in the [Pb] in the outflow solution in this series of experiments.

The effect of SOM on Pb sorption is shown in Fig. 5. In the treated Matapeake soil (0.1% SOM), the midpoint of the breakthrough arrives ~0.95 CV earlier than in the untreated soil. The total amount of Pb sorbed in the treated soil was 27 mmol kg^{-1}. This is a 40% decrease compared with the untreated Matapeake soil. If the difference in Pb sorption between the treated and untreated soil is due to the presence of SOM, then the amount of Pb sorbed on the SOM under these conditions is at least 810 mmol kg^{-1} (1620 mmol charge (kg SOM)$^{-1}$). Since the very slow sorption reaction is not included in the stirred-flow measurement, the true sorption capacity may be higher. The measured SOM sorption capacity is very high, and demonstrates the importance of SOM for Pb sorption in soils. The CEC range for SOM that is reported in the literature is 1500 to 3000 mmol charge (kg SOM)$^{-1}$, depending on the pH of the soil solution (Sparks, 1995).

Changing the flow rate had only a small effect on C_{out}/C_{in}(CV) for sorption in the treated soil (Fig. 5), suggesting that the reaction being measured in these experiments is not necessarily rate limited. In addition, following the initial fast reaction the shape of the breakthrough curve is nearly identical to the tracer (dashed line). The similarities between the tracer and the data indicate that very little additional sorption occurred following the initial fast reaction, which is contrary to what was observed for the untreated soil where a slower sorption reaction continued after the initial fast reaction. The lack of a slow reaction in the soil in which the SOM was removed suggests that the slow sorption reaction in the soil is a result of sorption on SOM. Since SOM consists of large polymers (Sparks, 1995), it is likely that slow diffusion to sites on the interior of the SOM molecule is the rate-limiting sorption process.

The midpoint of the breakthrough for the St. Johns soil occurred after 5.1 CV (Fig. 5). This is 2.4 CV later
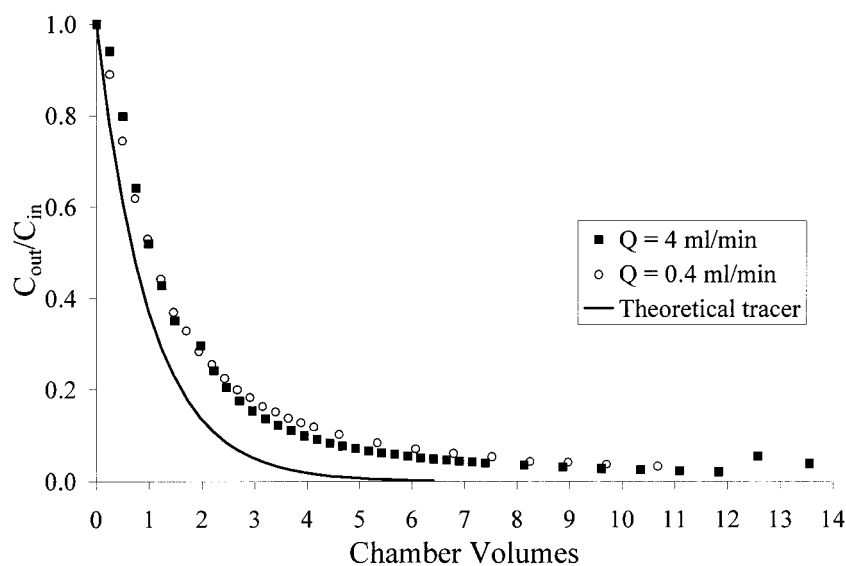
Fig. 6. Breakthrough curves for desorption from the untreated Matapeake soil and theoretical tracer.

than the breakthrough from the untreated Matapeake soil. In addition, the slope of C_{out}/C_{in} (CV) is significantly smaller than it is for the Matapeake soil, and much different than the tracer. These differences imply that sorption is continuing after the initial fast reaction. The total sorption on the St. Johns soil is 102 mmol kg^{-1}. This is 2.3 times the sorption occurring in the Matapeake soil. Since the clay contents in the Matapeake and the St. Johns soils are similar (Table 1), but the St. Johns soil has ~6 times more SOM, the most likely reason for the increased Pb sorption is the increase in sorption sites existing on the SOM. As determined by the sorption capacity calculated for the SOM in the Matapeake soil [810 mmol (kg SOM)$^{-1}$], the predicted amount of Pb sorbed on the SOM fraction in the St. Johns soil (13% SOM) is 105 mmol (kg whole soil)$^{-1}$, which is close to the observed value of total Pb sorbed in the St. Johns soil (102 mmol kg^{-1}). Thus, from the stirred-flow experiments, it is clear that SOM is an important factor for Pb sorption in the environment.

The results obtained from the desorption experiments on the untreated Matapeake soil are shown in Fig. 6. Since a much smaller amount of Pb is recovered in the desorption experiment than was removed from solution in the sorption experiment the desorption reaction is not complete. This can be considered as an apparent hysteresis (DiVincenzo and Sparks, 1997) since the reaction will most likely be reversible if given enough time. Changing the flow rate from 0.4 to 4 mL min^{-1} had insignificant effects on C_{out}/C_{in} (CV). If desorption was fast and reversible within the time frame of the experiment, then all of the sorbed Pb would be recovered from the soil, and there would be no change in the desorption breakthrough curves. However, only a fraction of the total sorbed Pb was recovered, indicating that the reaction is not at equilibrium. From the sorption isotherm, it was observed that at low equilibrium concentrations the slope of the isotherm is steep (high surface loadings and low solution concentration); this would cause a significant amount of tailing in the desorp-

tion measured in the stirred-flow reactor, particularly if the release of Pb from the soil is slow. Since the desorption behavior is clearly much different than sorption behavior, and the desorption breakthrough curves are nearly identical, it can be concluded that the desorption kinetics are too slow to measure by the stirred-flow reactor at flow rates of 0.4 mL min^{-1}.

The total amount of Pb desorbed at the end of the desorption experiment can be determined from the difference in the areas under the breakthrough curves with and without soil in Fig. 6. The total amount of Pb sorbed, and then desorbed for the treated and untreated Matapeake soil, as well as the St. Johns soil are listed in Table 2. In order to make comparisons, the desorption data were converted to percentage Pb desorbed by dividing by the total amount of Pb sorbed. These data are presented in Fig. 7. Since the area under the breakthrough curves does not include desorbed Pb that is present in the solution in the chamber, the values of the percentage desorbed as a function of CV underestimate the percentage desorption at the early times (when [Pb] is large). However, since the amount of Pb in the chamber towards the end of the experiment is small, the percentage desorbed at later times is fairly accurate. In all soils, desorption was incomplete within the time scales of these experiments (apparent hysteresis). In the treated and untreated Matapeake soils, the total amount of Pb desorbed varied only slightly, even though there were dramatic differences in the amount of Pb sorbed. In the St. Johns soil, only 35.6% of the sorbed Pb was

Table 2. Comparison of total Pb sorbed and desorbed in stirred-flow reactor for the soil samples after 12 chamber volumes (CV).

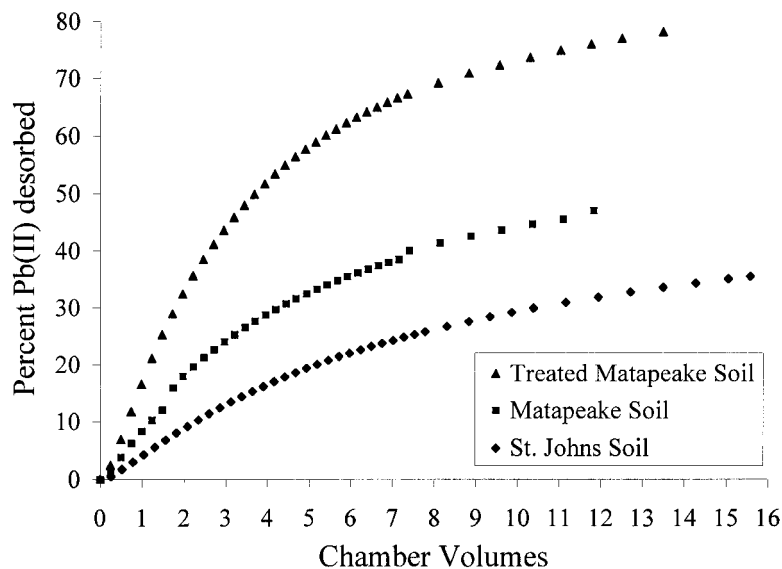| Sample	Sorbed	Desorbed after 12 CV	Percentage desorbed
	——— mmol kg^{-1} ———		
Untreated Matapeake soil	44.0	20.7	47.0
Treated Matapeake soil	26.8	20.4	76.1
St. Johns soil	102	32.6	32.0

Fig. 7. Percentage Pb desorbed from treated and untreated Matapeake and St. Johns soils.

desorbed. From these observations, it appears that the amount of Pb able to be desorbed is decreasing as the amount of SOM increases, suggesting that the difference in sorption and desorption in the soils is due to slow desorption from the SOM fraction. This behavior agrees with the trend observed in the sorption experiments; as the percentage SOM present in the soil increased, slow sorption was more noticeable. Yin et al. (1997) found similar results for sorption and desorption of Hg from soil; an inverse relationship between the rate constant and the percentage SOM present in four soils. Strawn et al. (1998) found that desorption of Pb from Al_2O_3 is completely reversible within ~3 d. Similar results were found by Ainsworth et al. (1994) and Guneriusson et al. (1994) for Pb desorption on iron oxides. Desorption experiments conducted on montmorillonite (Strawn, 1998) have revealed that the time scales for Pb sorption and desorption are similar. Thus, it appears that Pb sorption on oxides and clays is reversible. However, on the basis of the results of this study, desorption from whole soils is not completely reversible within the time scales of these experiments, and the amount of Pb desorbed is directly correlated to the percentage SOM present in the soils. From these observations, it can be concluded that Pb desorption from the SOM fraction of soils is slow. The most likely reason for this behavior is that the type of complex that forms between the Pb and the SOM is stronger than the complex forming on the surface of the mineral. On the surfaces of minerals,

the only type of Lewis bases for Pb to sorb are hydroxyls, which are considered to be hard bases (low polarizability) (Sparks, 1995). The functional groups on SOM include carboxyls, phenols, amines, and several sulfur containing functional groups which are soft bases (Sparks, 1995). Since soft acids prefer soft bases, the complexation of Pb by the functional groups on the SOM would be preferential to the hard acid hydroxyl ligands present on the mineral surface (Sparks, 1995).

It is often observed that increasing incubation time leads to a decrease in the amount of sorbate that can be desorbed (Kuo et al., 1980; Schultz et al., 1987; Backes et al., 1995). The effects of sorption incubation time on the total amount of Pb desorbed are presented in Table 3. Increasing the incubation time from 1 to 32 d resulted in an increase of ~11% in adsorption. Despite increasing the sorption incubation time from 1 to 32 d, the percentage of Pb desorbed decreased only slightly. This result shows that the complexes formed during Pb sorption are stable within 32 d of incubation, and do not convert into phases that are less readily desorbed.

From the stirred-flow experiments five important conclusions can be made: (i) Pb sorption consists of a fast and a slow reaction, (ii) Pb sorption increases with increasing SOM, (iii) desorption is not reversible within the time frame of these experiments, (iv) longer sorption incubation times have little impact on the amount of Pb that can be desorbed, and (v) apparent hysteresis increases as the percentage SOM in the soil increases. In addition, the experiments discussed in this section have demonstrated the utility, and limitations, of using the stirred-flow reactor for studying reactions on surfaces. One of the unique aspects of this set of experiments was that desorption was studied using the same background as the sorption experiments. Often researchers conduct desorption experiments using organic chelators such as ethylenediaminetetraacetic acid to prevent readsorption of the metal; however, in many cases, the chelate is actually promoting desorption by interacting with the sorbed metal, and the measured

Table 3. Effect of residence time on Pb desorption from the Matapeake soil using the stirred-flow reactor for desorption.

Sorption incubation time†	Sorbed	Desorbed	Percentage desorbed
d		mmol kg^{-1}	
1	54.9	27.9	50.8
10	60.0	28.7	47.8
32	66.1	30.5	46.1

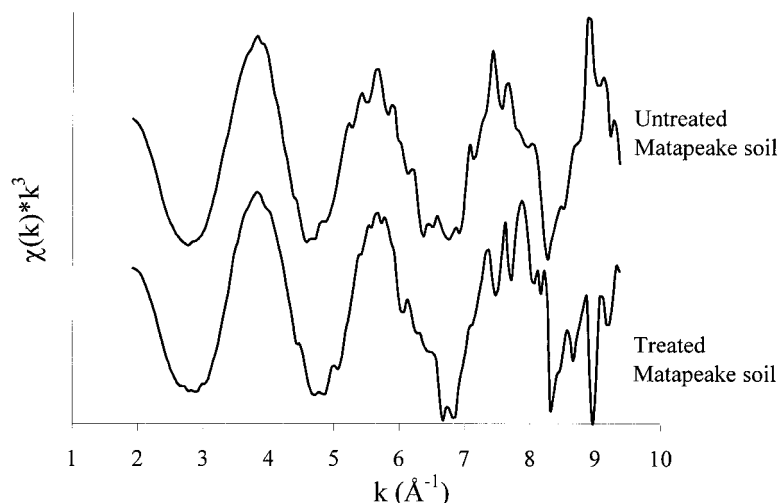† Sorption studies were conducted using a batch reactor.

Fig. 8. k^3 **Weighted normalized χ-functions from XAFS experiments for Pb sorption on the treated and untreated Matapeake soil.**

desorption rate is actually a ligand promoted desorption rate. Another method often used to study desorption is to lower the pH of the desorbing solution (proton promoted desorption). While both of these desorption methods provide important information, they do not describe the desorption behavior in terms of a reversible reaction in which the desorption conditions are the same as sorption. The experiments presented in this study demonstrate the utility of the stirred-flow reactor for measuring desorption behavior without promoting the reaction by adding another reactant.

XAFS Experiments

Figure 8 shows the background subtracted k^3 weighted χ functions for the treated and untreated Matapeake soil samples. The χ structures are distinctly different in phase, wavelength, and shape, particularly at higher k. The uniqueness of the χ structures is due to differences in backscattering from the atoms residing in the first and second coordination shells surrounding the sorbed Pb.

The radial structure functions for the two soil samples ($\Delta k = 2.2$–8.9 Å^{-1}) are presented in Fig. 9. The first major peaks that occur in the RSF are located at ~1.60 and 1.75 Å in the treated and untreated Matapeake soil, respectively. In the untreated Matapeake soil, a large peak is observed at ~2.4 Å. This peak is noticeably smaller and shifted in the treated sample. The identity of the atoms surrounding the sorbed Pb can be determined by fitting the data to the theoretical model created using the backscattering simulation program FEFF 6.0. As described in the Methods and Materials, the fits of the samples were made by means of theoretical pathways from Pb, O, Si, and C as the backscattering atoms. In SOM, there also exists N and S containing functional groups that can form complexes with Pb (Sparks, 1995). Analysis of the total N and S in the Matapeake soil revealed that in the untreated Matapeake soil there was only 0.016% total S, and 0.2% total N. In the treated Matapeake soil, S and N were not detected. The total C in the untreated Matapeake soil was 1.38% (7 and 87 times the total N and S, respectively). Thus, contributions to the XAFS from N and S
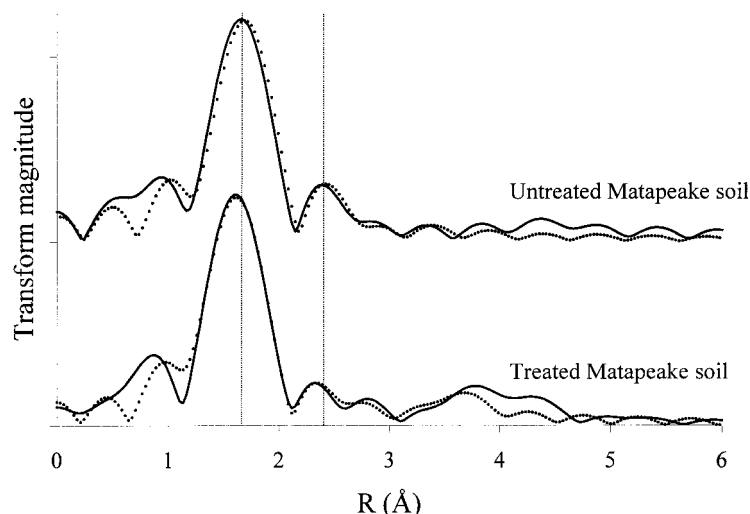

Fig. 9. Fourier transforms (RSF) of the χ-functions in Fig. 8 (solid line), and results from multi-shell fits using theoretical backscattering phase and amplitude functions (dotted line). Vertical dotted lines are aligned at the center of the two peaks used for fitting in the untreated Matapeake soil.

Table 4. Structural parameters derived from the XAFS experimental data using theoretical phase shift and amplitude functions for Pb sorption on treated and untreated Matapeake soil samples.

Sample	Pb-O shell			Pb-C or -Si shell			Pb-Pb shell			E₀ (eV)‡‡
	R (Å)†‡	N§¶	σ^2 (Å²)#	R (Å)‡	N††	σ^2 (Å²)	R (Å)‡	N#	σ^2 (Å²)	
Untreated Matapeake soil	2.29	1.55	0.006	3.06 C atom	1.21	0.004				11.5
Treated Matapeake soil	2.25	1.72	0.007	3.24 Si atom	0.86	0.01§§	3.72	1.28	0.01§§	16.1

† Interatomic distance.
§ Coordination Number.
# Debye-Waller factor.
‡‡ Phase shift.
Fit quality confidence limits:
‡ 1%, ¶ 10%, †† 25%.
§§ Fixed.

are not likely to be large unless the Pb is only forming complexes with these functional groups. Manceau et al. (1996) used XAFS to speciate Pb contaminated soil. They found that the XAFS spectra from the soil were best modeled by a linear combination of Pb–salicylate and Pb–catechol reference compounds, suggesting that the Pb is complexed to these types of functional groups in the SOM. Xia et al. (1997) also found that Pb adsorption on humic acids isolated from SOM was best described by fitting first shell O atoms and second shell C atoms. Thus, in this study, S and N were not considered as second shell backscattering atoms (note: because of the similar atomic size of N and C, isolating the individual contributions from these atoms to the EXAFS is difficult). The best fits of the data ($R = 1–3$ Å) are represented by the dashed lines in Fig. 9, and the resulting values for N, R, and σ^2 are presented in Table 4. In both soils, the fits represented the data very well.

The bond distances and coordination numbers for the treated Matapeake soil are similar to those found by Strawn et al. (1998) and Bargar et al. (1997) for Pb adsorption on Al_2O_3. In these cases, Pb was adsorbed as inner-sphere complexes on the edges of octahedrally coordinated Al atoms. On the basis of R_{Pb-O}, and R_{Pb-Si} in the treated Matapeake soil, it can be concluded that sorption on the mineral particles of the soil consists of primarily inner-sphere complexes, similar to those that form on aluminum oxide. Some Pb backscattering was observed for this sample, suggesting that some multinuclear complexation is also occurring.

The EXAFS of the untreated Matapeake soil was best described by fitting O and C atoms as the backscattering atoms present in the local atomic structure of sorbed Pb. Attempts to fit Si and or Pb in the second shell of the sorbed Pb were unsuccessful. The predicted bond distance between the Pb and O (2.29 Å) is distinctly longer than the R_{Pb-O} in the treated Matapeake soil (R_{Pb-O} = 2.24 Å). The bond distance observed between the Pb and C atoms is 3.05 Å. This distance is shorter than the distance predicted by Xia et al. (1997) (3.26 Å) for Pb sorption on humic acid, but too long for Pb-O (O and C cannot be distinguished by XAFS because of their similar size). The shorter bond distance can result from a decrease in the Pb-O-C bond angle occurring in the sample, or coordination to different ligands than were present in the humic acid sample. Manceau et al. (1996) used XAFS to predict that the speciation of Pb in a contaminated soil was 60% Pb–salicylate complexes and 40% Pb–catechol complexes. These complexes involve the formation of a five-membered chelate complex between the phenol functional groups of the catechol, and a six membered chelate complex formed between the phenol and carboxyl functional groups of the salicylate.

The differences in the RSF reveal that the local atomic structure surrounding the sorbed Pb atom is different in the two samples. In the treated soil, C was not detected in the local atomic structure of the sorbed Pb, while in the untreated soil, the dominant backscatterers were O and C. Figure 10 illustrates the sorption mecha-
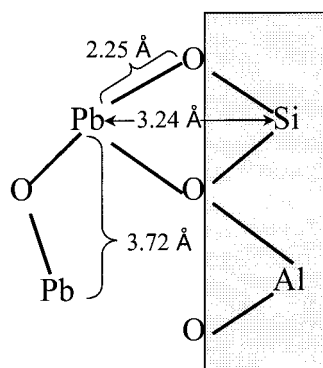
Treated Matapeake soil   Untreated Matapeake soil
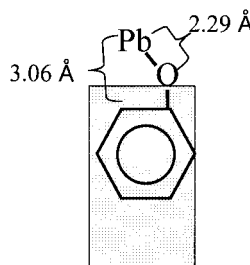

Fig. 10. Examples of sorption complexes illustrating possible molecular environments for Pb sorbed onto functional groups on a soil mineral (Treated Matapeake Soil) and soil organic matter (Untreated Matapeake Soil) based on the fit results of the XAFS data.

nisms predicted from the XAFS results using a clay mineral surface and a phenol functional group from SOM as the sorbents for the Pb (these models are only examples of the bonding environments, the actual bonding environment in the soil involves several different types of sorbents). The XAFS results confirm that the sorption mechanisms in the two soils are different. Since in the untreated sample no Pb or Si backscatterers were detected, most of the Pb must be sorbed onto the SOM, suggesting that the SOM is outcompeting, or blocking, the mineral surfaces from sorbing available Pb.

SUMMARY

The results of this study provide evidence that Pb sorption and desorption behavior on soil cannot be characterized by batch equilibrium sorption isotherms alone, but factors such as reaction time, percentage organic matter, and desorption behavior must also be considered to make accurate assessments of the fate of Pb in the soil. Results from the isotherm experiment showed that soil has a strong affinity for Pb. Batch sorption kinetic experiments revealed that Pb sorption behavior involves fast and slow sorption reactions. The fast reaction accounted for 78% of the total sorption within 8 min (the first sampling time). From the stirred-flow experiments the half life of the fast reaction was estimated to be less than 2 min. The slow reaction was fit by means of a first-order reversible equation. The half life for the slow reaction was estimated to be 58 h by the overall rate constant.

Measurement of sorption kinetics using the stirred-flow reactor revealed that the extent of the fast and slow reactions occurring in the soil is directly dependent on the amount of SOM present. Specifically, with increasing SOM content the rate of Pb sorption decreases. The Pb sorption capacity of the SOM is estimated to be at least 810 mmol kg^{-1}. Desorption experiments conducted using the stirred-flow reactor revealed that Pb desorption is hysteretic within the time frame of these experiments. The fraction of Pb that was desorbed from the soil decreased as the amount of SOM present in the soil increased. This indicates that the slow desorption reaction is primarily related to the SOM fraction of the soil. XAFS results from this study confirm that the types of complexes forming in the soil with SOM and the soil without SOM are different, and help explain the macroscopic Pb sorption–desorption behavior.

The information presented in this study shows the importance of not only measuring sorption equilibrium to predict the behavior of Pb in soil, but also measuring time-dependent sorption and desorption reactions. This additional information will allow scientists and engineers to make better predictions about the transport, bioavailability, and sorption and desorption behavior of Pb in soil. Such information is critical for protecting natural resources, developing improved remediation strategies, and making better risk assessments.

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