Sequential sorption of lead and cadmium in three tropical soils

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The sorption and desorption of Pb and Cd in tropical soils is strongly influenced by the order in which these metals enter the soil environment.

Abstract

It is important to examine mechanisms of Pb and Cd sorption in soils to understand their bioavailability. The ability of three tropical soils to retain Pb, Cd, and Ca was evaluated. The objectives of this study were to (1) determine the extent to which soil sorption sites are metal specific, (2) investigate the nature of reactions between metals and soil surfaces, and (3) identify how metals compete for sorption sites when they are introduced to soils sequentially or concurrently. Lead was shown to be much less exchangeable than Cd and inhibited Cd sorption. Cadmium had little effect on Pb sorption, though both Ca and Cd inhibited the adsorption of Pb at exchange sites. Lead appears to more readily undergo inner-sphere surface complexation with soil surface functional groups than either Cd or Ca. Thus, regardless of when Pb is introduced to a soil, it should be less labile than Cd.

1. Introduction

Soil contamination by Pb and Cd is of great concern because both metals are toxic to humans (US EPA, 1992). These elements are used in many industrial, urban, and agricultural applications (Kabata-Pendias and Pendias, 1992; Adriano, 2001) and are often found together at sites contaminated with heavy metals. Therefore, it is important for environmental scientists and engineers to understand the chemistry of Pb and Cd interactions in soils to understand their bioavailability.

Heterogeneous soil systems are composed of both organic and inorganic constituents with differing affinities for heavy metals. In addition, heavy metals themselves exhibit varying affinities for soil surfaces. For example, Pb and Cu are strongly sorbed to soil surfaces while Cd and Zn generally have lower affinities for sorption sites. Variability in heavy metal affinity for soil sorption sites has been attributed to a given metal's hydrolysis constant (pK_H), electronegativity, Lewis acidity, charge density and solubility (K_{SP}) of precipitates including hydroxide and carbonate (McBride, 1994; Pardo, 2000; Sparks, 2003).

A contaminated site may receive doses of these metals at varying times. For example, soils at battery recycling centers may receive high quantities of Pb from car batteries at one time and then later receive inputs of Cd from household batteries. Understanding how particular metals may interact and compete for soil sorption sites, when entering a soil system at different times, is of considerable interest to those involved in environmental remediation. Also, ascertaining the mechanisms of reactions between heavy metals and soil surfaces is helpful because it sheds light on the strength and stability of metal surface binding in soil.

Useful information as to how metal cations are sorbed to soil surfaces may be obtained by determining the relative distribution

of the sorbed metal retained at exchange sites and in non-exchangeable soil fractions (e.g. non-specifically sorbed vs. specifically sorbed; Tiller et al., 1984). Sorption/desorption studies generally employ the use of a neutral salt solution (for example, $Ca(NO_3)_2$, $CaCl_2$, or $NaNO_3$) to desorb previously sorbed metals from soils or mineral components. In most cases, studies considering the sorption/desorption of Cd and Pb have indicated Pb was much less desorbable than Cd (Pardo, 2000; Adhikari and Singh, 2003). However, Ainsworth et al. (1994) found Cd desorption to be less than that of Pb at pH 3 on aged hydrous iron oxide. It was suggested this was most likely due to the incorporation of Cd but not Pb into the oxide mineral structure.

Sequential extraction procedures have also been employed to assess the relative affinities of both Pb and Cd to different soil fractions (exchangeable, carbonate bound, Fe and/or Mn oxide bound, residual; Tessier et al., 1979). In several studies, more Cd was found in the exchangeable fraction compared to Pb for soils where heavy metals were added directly (Kaasalainen and Yli-Halla, 2003; Lu et al., 2005), or applied via fly ash (Lim et al., 1997) or biosolids amendments (Sloan et al., 1997).

Previous studies have yielded valuable information regarding the interactions of Pb and Cd with soil and mineral surfaces. However, further information concerning the interactions of the metals with each other and specificity of sorption sites for a given metal species can be obtained by employing a modified approach to the traditional sorption/desorption and/or sequential extraction procedures. In addition, considerable research has focused on the interactions of heavy metals when added together to temperate region soils and/or soil components. In contrast, relatively few studies have dealt with competitive sorption reactions involving heavy metals and tropical soils, and no known research has looked into reactions of Cd and Pb in soils when these two metals are added sequentially.

Therefore, the objectives of this research were to investigate how adding Pb and Cd, sequentially or concurrently, to three tropical soils affects their (i) retention, (ii) modes of sorption, and (iii) competition for sorption sites.

2. Materials and methods

2.1. Materials

A portion or majority of the A-horizons (0−15 cm) of three tropical soils from Puerto Rico were used in this study. A Mollisol (fine loamy, mixed,

isohyperthermic Cumulic Haplustoll) was sampled from the Lajas Valley area near the southwest coast, an Oxisol (clayey, oxidic, isohyperthermic Typic Acrorthox) was taken from the east coast near Mayaguez, and an Ultisol (clayey, mixed, isohyperthermic Typic Tropohumults) was obtained near Corozal in the central mountainous area (Beinroth, 1982). The three soils will be referred to as the Mollisol, Oxisol, and Ultisol soils. All soils were air-dried and passed through a 0.5 mm sieve. Table 1 presents selected physicochemical properties of the soils used in this study, which were determined using standard procedures (Appel and Ma, 2002; Appel et al., 2003).

2.2. Sequential addition of metals

To determine the extent to which these metals compete for sorption sites and their mechanisms of sorption in a soil, metals were added to a soil sequentially or concurrently. Specifically, five treatments were used, i.e. Pb, Cd, Pb + Ca, Cd + Ca, and Pb + Cd (Table 2). Lead and Cd were used in the experiment as they are toxic heavy metals commonly found together at heavy metal contaminated sites. Since Ca is typically the most abundant exchangeable cation in soils, the extent of Ca sorption, in the presence of either Pb or Cd, was used to assess how the heavy metals compete with a common, naturally occurring soil cation. The five treatments represented five different orders of metal addition. Table 2 summarizes the order of metal addition with corresponding metal concentrations for each treatment.

Both the amounts of metal sorbed (S) and exchanged (E) were determined in this experiment. Take Treatment 1 for example; Pb was added to the soils first, followed by Cd. Specifically, 30 mL of 1.2 mM $Pb(NO_3)_2$ in $NaNO_3$ background electrolyte ($I = 0.01$ M) was added to ~ 1.00 g soil in a pre-weighed 50 mL centrifuge tube. The suspension was then equilibrated on a reciprocating shaker for 24 h at 25 ± 3 °C. Preliminary kinetic studies indicated a 24 h reaction period was sufficient to achieve apparent equilibrium under these conditions. The sample then was centrifuged and the supernatant collected and refrigerated at 4 °C for subsequent analysis of the amount of Pb sorbed (S1Pb), which was determined by difference using flame atomic absorption spectrophotometry (FAAS). The sorbed Pb (S1Pb) was displaced by 5 washings with 20 mL aliquots of 0.1 M $NaNO_3$, shaking for 1 h between washes. Extracts were combined and stored at 4 °C prior to analysis of exchangeable Pb (E1Pb), with concentration being corrected for occluded/pore water E1Pb. The amount of sorbed Pb that was not exchanged by the $NaNO_3$ washes was operationally defined as being specifically sorbed or sorbed to high affinity sites (Yong and Phadungchewit, 1993). The I of the soil solutions was readjusted to 0.01 M via two 30 mL washes with 0.01 M $NaNO_3$, shaking for 1 h during each rinse.

The supernatants were then discarded and 30 mL of 1.2 mM $Cd(NO_3)_2$ in $NaNO_3$ background electrolyte ($I = 0.01$ M) was added to the soils and the suspensions were shaken for 24 h at 25 ± 3 °C. The samples were centrifuged and the supernatants collected and refrigerated (4 °C) for subsequent analysis of the amounts of sorbed Cd (S2Cd), which was found by difference, as well as any Cd-replaceable Pb (R1Pb). The soil was again washed 5 times with 0.1 M $NaNO_3$, shaking for 1 h during each wash, to remove sorbed Cd (S2Cd). The extracts were combined and stored in a refrigerator (4 °C) prior to analysis of exchangeable Cd (E2Cd) using FAAS (E2Cd concentration also being corrected for occluded/pore water E2Cd). As before, sorbed Cd (S2Cd) remaining

Table 1
Selected physicochemical properties of the three soils used in this study

Sample	Organic matter (%)	PZNC[a]	Soil pH	Eq. pH[b]	CEC (cmol$_c$ kg^{-1})[a]	Sum H + Al (cmol$_c$ kg^{-1})	Total Fe + Al (%)	Clay mineralogy[c]	Texture[a]	Specific surface area (m^2 g^{-1})
Oxisol	4.1	3.7	4.9	4.0	3.1	1.7	28.7	k(49) > go(38) > q(7) > gi(6)	10−34−56	41.9
Ultisol	1.9	2.3	4.7	4.6	11.0	7.1	8.60	k(45) > q(23) > s(17) > go(15)	12−29−59	37.8
Mollisol	1.2[d]	−	6.9	5.0	20.9	−	6.90	k(48) > s(32) > m(na) > q(na)	39−39−22	17.3

[a] PZNC, point of zero net charge; CEC, cation exchange capacity; texture, % sand−% silt−% clay.

[b] Average equilibrium soil-solution pH after soil (~ 1 g) had been treated with 30 mL of Pb, Cd, Pb + Ca, Cd + Ca, or Pb + Cd solution.

[c] k, kaolinite; gi, gibbsite; go, goethite; s, smectite; m, mica; q, quartz. Values in parentheses represent the percentage of each mineral in the <2 μm soil fraction (na, not available).

[d] This soil does not meet classification requirements for a Mollic epipedon in terms of organic matter content according to Soil Conservation Service (1994); however, the soil is still classified as a Mollisol by the authors based on location from where the sample was taken.

Table 2
Sequential and concurrent additions of Pb, Cd, and Ca to three tropical soils

Treatment	1st metal/s added	mmol 1st metal added L^{-1}	2nd metal added	mmol 2nd metal added L^{-1}
1	Pb	1.2	Cd	1.2
2	Cd	1.2	Pb	1.2
3	Pb + Ca	1.2 of each	Cd	1.2
4	Cd + Ca	1.2 of each	Pb	1.2
5	Pb + Cd	1.2 of each	None	None

on the soil surfaces was operationally defined as specifically sorbed or sorbed to high affinity sites (Tiller et al., 1984). The concentration of sorbed Pb remaining on the soil after the initial extraction with 0.1 M NaNO$_3$, but removed by the second extraction with 0.1 M NaNO$_3$ was referred to as replaceable Pb (R2Pb). An initial metal concentration of 1.2 mM was used as prior experiments demonstrated this concentration allowed expression of the maximum metal sorption capacity of the Oxisol and Ultisol soils.

2.3. Pretreatment of soil samples

Prior to initiation of this experiment, a rigorous soil pre-treatment was necessary to insure the differences in Pb and Cd sorption were truly due to differences in metal affinity for sorption sites. Preliminary data had showed a systematic increase in sorption of the second metal added to the soils. This was postulated to result from physical breakdown of the soil structure, due to shaking, resulting in increased metal exposure to sorption sites. The hypothesis was confirmed when Cd was initially added, exchanged with a neutral salt, and then added again to the soils. The second addition of Cd resulted in more sorption of this metal than its initial addition. In order to offset this effect, all soils underwent cation exchange reactions where 0.1 M KNO$_3$ and 0.1 M NaNO$_3$ were added in alternating fashion until a constant Na-saturated and K-saturated CEC was obtained.

2.4. Statistical methods and quality control

Each treatment was replicated five times. Significant differences between treatments based on least squares means ($p \leq 0.01$) were calculated using SAS (SAS Institute, 1996) by comparing the amounts of metal sorbed, exchanged, or replaced for different treatments and soils.

Lead, Cd, and Ca were analyzed by FAAS, which was calibrated with at least three standards prepared in the same matrices as the samples. Correlation coefficients (r^2) for the standard lines were ≥ 0.99. Every 10 samples run on the FAAS were followed by blank analysis as well as a continuing calibration verification (CCV) to check the accuracy of the standard line. Blank analysis was used to check for matrix interferences, which were not present. If percent recoveries of the CCVs were not within $\pm 5\%$ of their known values, a new calibration line was generated and the necessary samples were re-analyzed.

3. Results and discussion

3.1. Sequential metal addition

The sequence of metal addition had little influence on the extent to which Pb was retained by the Oxisol, Ultisol, or Mollisol soil (Fig. 1). The differences of sorbed Pb (S1Pb vs. S2Pb) and exchanged Pb (E1Pb vs. E2Pb), when Pb was added to the soils before Cd as compared to when it was introduced to the soils after Cd, were insignificant. For example, the amounts of Pb sorbed or exchanged in the Oxisol soil were 19.8 (S1Pb) and 18.6 (S2Pb) mmol kg^{-1}, and 9.9 (E1Pb) and 9.2 (E2Pb) mmol kg^{-1}, respectively (Fig. 1a). However, different from the Oxisol and Ultisol soils (up to 43–50% of
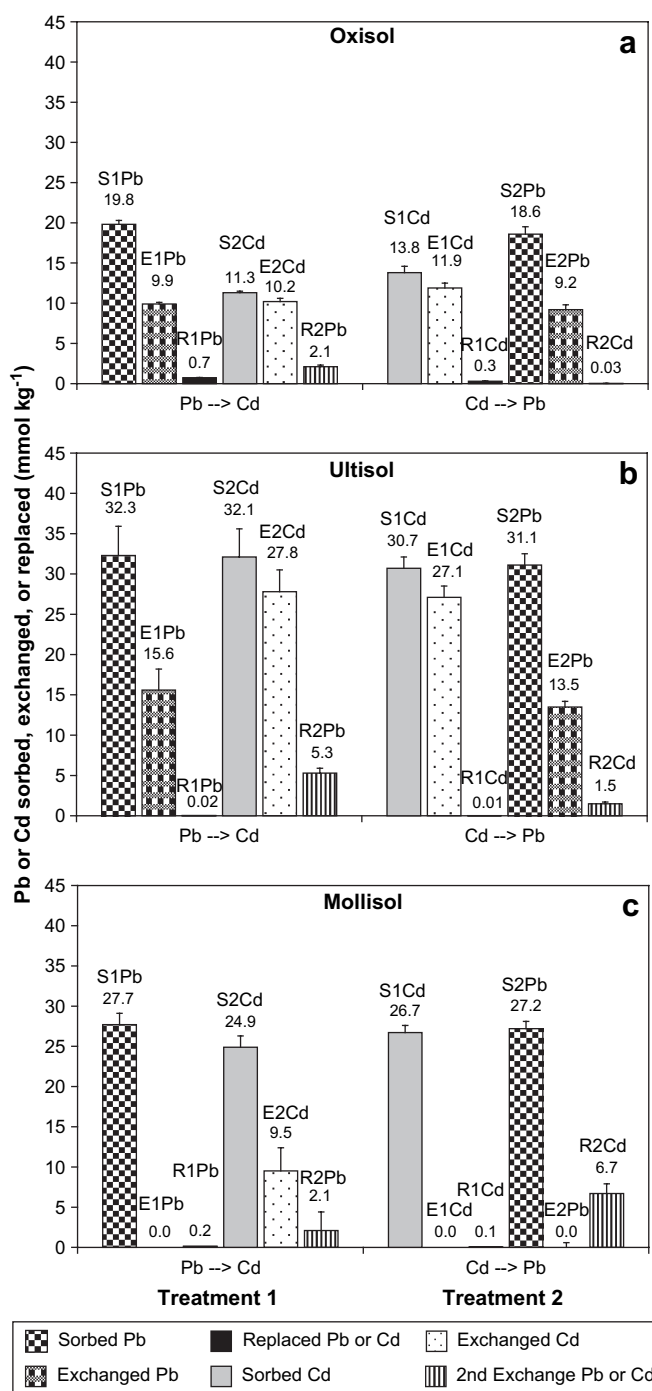

Fig. 1. Monometal sequential addition of Pb $\rightarrow$ Cd (Treatment 1) or Cd $\rightarrow$ Pb (Treatment 2) to the (a) Oxisol, (b) Ultisol, and (c) Mollisol soils. S, E, and R represent the amount of sorbed, exchanged, or replaced metal, respectively. The numbers following the letter designations indicate the order of metal addition to the soils. These designations are applicable for each of the soils in this figure.

sorbed Pb was exchangeable in these two soils), the Mollisol soil had no exchangeable Pb (no detectable E1Pb and E2Pb) regardless of when it entered the soil (Fig. 1c).

The trend for Cd was different. There was no difference between the sorbed Cd (S1Cd and S2Cd) in the Ultisol and Mollisol soils (Fig. 1b,c), and between the exchangeable Cd (E1Cd and E2Cd) in the Oxisol and Ultisol soils (Fig. 1a,b). The Oxisol

soil, however, showed a significant ($p = 0.01$) decrease in the amounts of sorbed Cd (S1Cd = 13.8 vs. S2Cd = 11.3 mmol kg^{-1}; Fig. 1a) when Cd was introduced to the soil after Pb as opposed to when it entered the soil prior to Pb. Also, the Mollisol soil had no appreciable exchangeable Cd when it was introduced before Pb, though 38% (9.5 out of 24.9 mmol kg^{-1}; Fig. 1c) of the sorbed Cd was exchangeable when it was added to the Mollisol soil after Pb. Therefore, if Pb is introduced to these soils prior to Cd, it has the ability to inhibit Cd sorption onto both exchange and high affinity sorption sites but not vice-versa.

After a metal had been exchanged by Na, little (R1Pb ≤ 0.7 mmol kg^{-1}) Pb was replaced by Cd and even less Cd (R1Cd ≤ 0.3 mmol kg^{-1}) was replaced by Pb in all soils in Treatments 1–4 (Figs. 1 and 2). Thus, neither of the metals effectively replaced the other from high affinity sorption sites. However, all soils in Treatments 1–4 (especially the Mollisol in Treatments 2 and 4) exchanged additional amounts of the first metal added to the soils after going through the entire sorption/desorption scheme (R2). For example, the Oxisol soil (Fig. 1a, Treatment 1) originally sorbed 19.8 mmol Pb kg^{-1} (S1Pb), of which 50% was exchangeable (E1Pb = 9.9 mmol kg^{-1}) and nearly 7% of the remaining Pb was later replaced by Cd (R1Pb = 0.7 mmol kg^{-1}). This soil sorbed 11.3 mmol Cd kg^{-1} (S2Cd), 90% of which was exchanged by Na (E2Cd = 10.2 mmol kg^{-1}). This second Na extraction then replaced 21% of the remaining sorbed Pb (R2Pb = 2.1 mmol kg^{-1}), which had been previously unexchangeable by Na and unreplaceable by Cd.

The explanation does not appear to be a question of reaction kinetics, as most ion exchange processes occur on millisecond time scales once an ion has reached the vicinity of an exchange site (Sparks, 2003). Furthermore, the amounts of replaceable metal (R1) were very low, $\leq 7\%$ of the remaining sorbed metal after exchange, and in most cases much less than what was previously exchanged by Na. This suggested virtually a complete replacement of the exchangeable fraction (E1) by 0.1 M Na after five washings.

The possibility exists that the system remained in a state of disequilibrium. Under this hypothesis, metal initially present as an irreversibly sorbed phase (i.e., non-exchangeable and non-replaceable) had a tendency to shift from high affinity sites to sites of lower affinity once the lower affinity sites had been purged. This could be done to maintain an equilibrium amount of metal on the high and low affinity sorption sites as the first exchangeable fraction was decanted/removed prior to addition of the subsequent metal.

In the study performed by Strawn (1998), Pb was shown to be completely desorbed within several days in montmorillonite and Al$_2$O$_3$ systems. In this study, however, the desorbed phase was continually removed from the reaction vessel. Gunneriusson (1994) and Gunneriusson et al. (1994) reported complete reversibility of sorbed Pb and Cd on goethite. In the above studies, inner-sphere complexes were inferred in the original sorbed phases using either extended X-ray absorption fine structure spectroscopy (EXAFS) or the constant capacitance model. However, Strawn and Sparks (2000) found only 32–76% of the sorbed Pb were desorbed from the soil after 6 h.
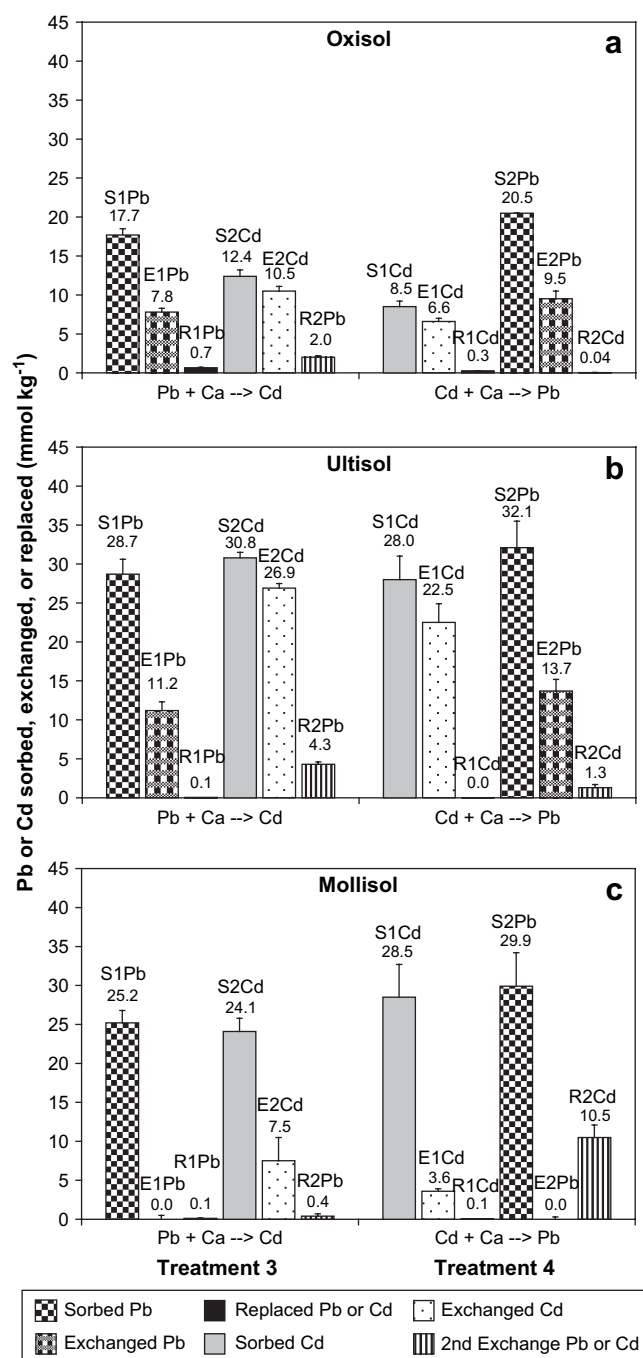

Fig. 2. Bimetal additions of Pb + Ca → Cd (Treatment 3) and Cd + Ca → Pb (Treatment 4) to the (a) Oxisol, (b) Ultisol, and (c) Mollisol soils. S, E, and R represent the amount of sorbed, exchanged, or replaced metal, respectively. The numbers following the letter designations indicate the order of metal addition to the soils. These designations are applicable for each of the soils in this figure.

3.2. Mechanisms of metal sorption

The Oxisol, Ultisol, and Mollisol soils had CECs of 3.1, 11.0, and 20.9 cmol$_c$ kg^{-1}, respectively (Table 1). These CEC values equate to possible retention maximums of Cd^{2+} or Pb^{2+} at cation exchange sites of ≈ 16 (Oxisol), 55 (Ultisol), and 105 (Mollisol) mmol kg^{-1} (based on charge balance) in these soils. It was expected the amounts of Pb or Cd sorbed

by the soils would have been proportional to their CECs, however, this was not the case for either Pb or Cd (Fig. 1). The amounts of Pb sorbed (S1Pb) by the Oxisol, Ultisol and Mollisol soils were 19.8, 32.3 and 27.7 mmol kg^{-1}, respectively in Treatment 1, and the corresponding numbers for Cd (S1Cd) were 13.8, 30.7, and 26.7 mmol kg^{-1} in Treatment 2 (Fig. 1). The fact that greater CEC did not result in greater metal sorption by the three soils suggests that both exchangeable and high affinity sites contributed to metal sorption (Fig. 1). The amounts of Pb or Cd added to the soils, on a charge basis (30 mL of 1.2 mM Pb^{2+} or Cd^{2+} added to 1 g soil ≈ 7.2 cmol$_c$ kg^{-1}) only exceeded the CEC of the Oxisol soil.

Information regarding the modes of metal sorption in the three soils (especially the Ultisol and Mollisol soils) can be obtained by looking at the exchangeable Pb or Cd fractions. For a given soil, we noticed the sorbed and exchanged amounts of Pb or Cd were approximately equal (e.g. S1 = S2 and E1 = E2; $p > 0.01$) between Treatments 1 and 2 except for Oxisol-S1Cd vs. S2Cd and Mollisol-E1Cd vs. E2Cd (Fig. 1). In the Oxisol and Ultisol soils, less than half of the initially sorbed Pb was exchangeable whereas $\geq 78\%$ of the initially sorbed Cd was exchangeable (Figs. 1 and 2). For the Mollisol soil, none of the Pb and up to 38% of the Cd was exchangeable.

Tiller et al. (1984) used a similar method to partition sorbed Cd, Ni, and Zn between high affinity/specific sorption sites and lower affinity/exchange sites. They described the sorbed metal fraction that was retained by soils after washes with 0.01 M Ca(NO$_3$)$_2$ as being specifically sorbed or sorbed to high affinity sorption sites. Thus, exchangeable metals were sorbed only to lower affinity sites.

As ascertained by X-ray absorption spectroscopy such as EXAFS and XANES (X-ray absorption near edge structure spectroscopy), the mechanism for inner-sphere complexation of a metal to a soil surface (e.g., goethite, gibbsite, and organic matter) usually involves formation of covalent bonds between the metal and an oxygen originating from a soil surface. The oxygen may be either from an organic (Xia et al., 1997a,b) or inorganic (Scheidegger et al., 1998; Strawn, 1998) surface functional group. For layer silicates, however, irreversible or non-exchangeable metal sorption may be via several mechanisms. On such materials, reaction may occur at clay edge sites (McBride, 1989; Pardo, 2000; Strawn and Sparks, 1999), as occlusion into cavities/deformities on planar surfaces (Nakhone, 1997), and as fixation in interlayer positions of 2:1 phyllosilicates. This last mechanism is a possibility when the selectivity exhibited by the interlayer for a metal ion—Ca, Cd, and Pb in this study—is much larger than the selectivity of the interlayer for the extracting ion (Na in this study) (Sposito et al., 1983).

However, XRD (X-ray diffraction) confirmed Na$^+$ was able to replace Pb^{2+} and, thus, presumably Cd^{2+} as well, from the interlayer of smectite in the Mollisol and Ultisol (data not shown). Ceramic tiles covered with the <2 μm fractions of these soils were saturated with Na$^+$, which was scanned moist using XRD, then saturated with Pb^{2+}, which was again scanned moist using XRD, and finally saturated with Na$^+$ a second time and again scanned moist using XRD. The d-spacing of the smectite peaks was measured after each saturation. The Na$^+$-saturations produced similar d-spacings (14.64 Å for the Mollisol and 14.55 Å for the Ultisol), while those for Pb^{2+} were ≈ 15.03 Å (Mollisol) and 14.24 Å (Ultisol). Since the Na$^+$-saturated smectite d-spacings were similar before and after Pb^{2+}-saturation for the two soils, the interlayer of smectite did not appear responsible for the irreversible sorption of Pb^{2+} (or presumably Cd^{2+}).

The Mollisol soil, which had the highest CEC among the three soils (Table 1), had a much lower exchangeable Cd fraction than the other soils. This soil sorbed much greater amounts of Pb and Cd than the Oxisol and Ultisol soils when these metals were added together (Fig. 3a). In Treatments 1−4 (Figs. 1 and 2), this soil exchanged from 0 to 38% of the originally sorbed Cd and yet none of the Pb. This was likely due to the fact that the added Cd and Pb in these treatments probably did not saturate all the available high affinity sorption sites. Thus, even after repeated extractions with Na, all the added Pb and most of the added Cd were retained by this soil (Serrano et al., 2005).

3.3. Pb and Cd affinity for soil surfaces

Figs. 1−3a demonstrated the preference of these soils for Pb relative to Cd regardless of the order in which Pb was added. The differences between sorbed Pb and sorbed Cd for a given soil were significant ($p < 0.01$; except for those in the Ultisol of Treatments 1 and 2, and those in the Mollisol of Treatment 2). These differences in soil affinity for Pb and Cd have been observed by others for tropical soils and/or pure oxidic mineral systems (Kinneburgh et al., 1976; Puls et al., 1991) as well as for soils low in Fe/Al oxides (Lu et al., 2005; Pardo, 2000). This is usually attributed to differences in metal characteristics and resultant affinity for sorption sites (Appel and Ma, 2002; McBride, 1994).

For example, the hydrated radius of Pb^{2+} is smaller than that of Cd^{2+} (Pb^{2+} = 0.401 nm; Cd^{2+} = 0.426 nm; Nightingale, 1959), favoring coulombic interactions of Pb with exchange sites. Furthermore, Pb has a greater affinity for most functional groups in organic matter including carboxylic and phenolic groups, which are hard Lewis bases. This is mainly attributed to the differences in chemical properties between the two metals. Lead is a harder Lewis acid (Pb^{2+} is a borderline Lewis acid while Cd^{2+} is a soft Lewis acid), has a higher electronegativity (2.33 and 1.69 for Pb and Cd, respectively); and has lower pK_H (negative log of hydrolysis constant; 7.71 and 10.1 for Pb and Cd, respectively) than Cd. Each of these factors makes Pb a better candidate for inner-sphere surface sorption/complexation reactions compared to Cd (Wulfsberg, 2000; McBride, 1994).

Lead (Pb^{2+}) also has 2 valence electrons in its 6s atomic orbital (and empty p orbitals of only slightly higher energy), which can form, depending on the Pb−O symmetry, molecular orbitals with O 2p atomic orbitals originating from an oxide surface. This orbital overlap stabilizes the Pb−O complex.
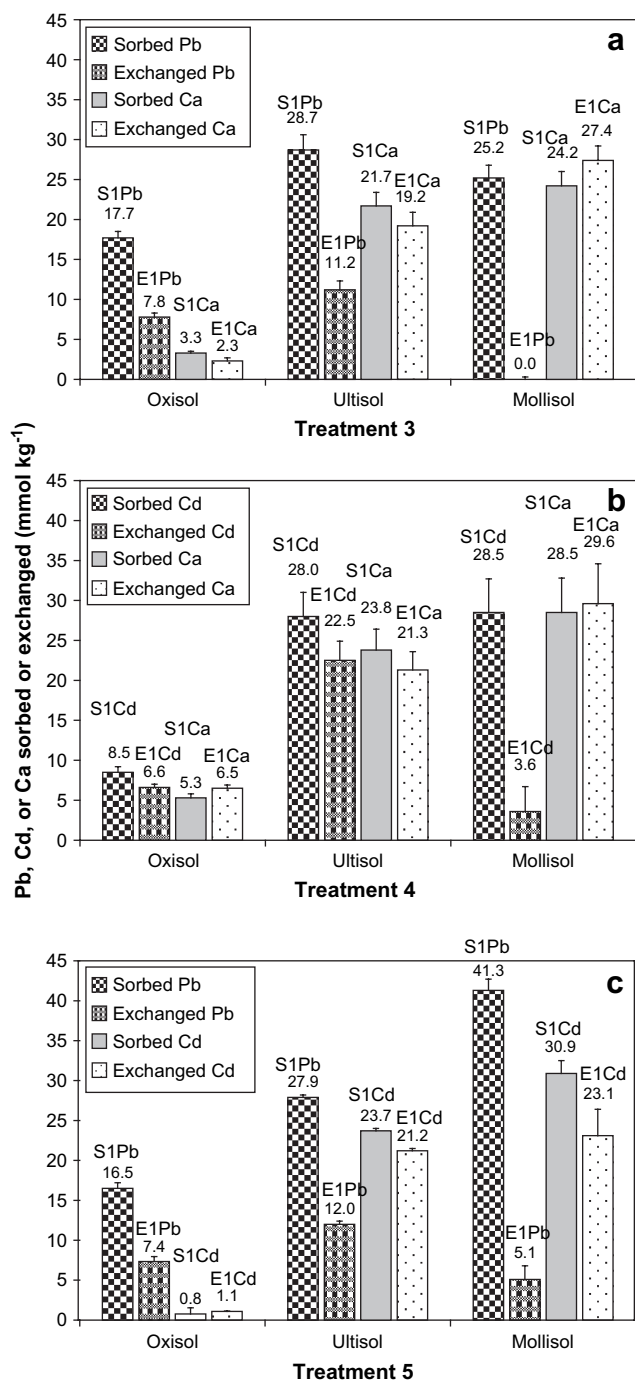
Fig. 3. Competitive interactions between Pb, Cd, and Ca when (a) Pb + Ca (Treatment 3), (b) Cd + Ca (Treatment 4), and (c) Pb + Cd (Treatment 5) were added concurrently to the Oxisol, Ultisol, or Mollisol soils. S and E represent the amount of sorbed or exchanged metal, respectively. The number "1" following the letter designations indicates these metals were added concurrently to the soils. These designations are applicable for each of the soils in this figure.

On the other hand, Cd^{2+} has a filled 4d valence atomic orbital, which participates minimally in electron sharing with O 2p atomic orbitals from oxide surfaces. This disfavors formation of Cd—oxide covalent bonds, and is consistent with the data presented in Figs. 1 and 2 as well as with the above discussion on inner-sphere surface complexation reactions.

3.4. Non-exchangeable Pb:Cd ratios

The Oxisol and Ultisol, composed predominantly of 1:1 phyllosilicates and Fe/Al oxides, primarily sorbed Cd at exchange sites. The Mollisol clay, composed almost entirely of phyllosilicates, probably sorbed most Cd on organic matter and in the interlayer position of 2:1 minerals instead. The sorption of Cd by these three soils had little effect on the amount of non-exchangeable (sorbed minus exchanged) Pb, with the non-exchangeable Pb remaining relatively constant throughout all sequences for these soils (ranging from 9.1 to 11 mmol kg^{-1} for the Oxisol soil, from 15.9 to 18.4 mmol kg^{-1} for the Ultisol soil, and from 25.2 to 29.2 mmol kg^{-1} for the Mollisol soil).

In Treatments 1–4 (Figs. 1 and 2; Pb and Cd added singly or concurrently with Ca), the ratios of non-exchangeable Pb:Cd (NERs) were slightly higher when Pb was added first to the soils (Treatments 1 and 3) as compared to when Cd was added first to the soils (Treatments 2 and 4; Table 3). Since the amount of non-exchangeable Pb did not change to a great extent throughout these treatments, the ability of this metal to inhibit the retention of Cd at high affinity sites, thus, was demonstrated. This was because the Pb:Cd NERs were consistently higher when Pb was added to the soils first as opposed to when Cd assumed this position. Furthermore, in Treatment 5 (Fig. 3a; Pb and Cd added concurrently) this effect was manifest to an even larger extent.

In Treatments 1–4, the Mollisol retained nearly equal amounts of non-exchangeable Pb and Cd. The Oxisol and Ultisol, on the other hand, had higher Pb:Cd NERs because these soils demonstrated a marked preference for Pb, relative to Cd, at high affinity sites.

3.5. Sites of Cd and Pb retention

Some researchers have suggested that high affinity Pb and Cd sorption sites in soils and sediments may be different (Hansen and Maya, 1997; Pardo, 2000). However, our data suggest that Pb and Cd probably compete for many of the same high affinity sites (Serrano et al., 2005). This was important for the Oxisol and especially for the Mollisol soils. Cadmium sorption at high affinity sites was lower when it was introduced to the soils after Pb compared to the opposite sequence (Figs. 1 and 2). Also, Cd was more exchangeable when Pb and Cd were added to the soils concurrently for the Oxisol, Ultisol, and Mollisol soils, with all (100+%), 90%,

Table 3
Pb:Cd NERs[a] (non-exchangeable ratios) for the Oxisol, Ultisol, and Mollisol soils according to treatment

Treatment/s	Oxisol	Ultisol	Mollisol
1 and 3	6.4	4.1	1.7
2 and 4	5.4	4.0	1.1
5	9.1	6.4	4.6

[a] NERs were calculated by taking (sorbed Pb − exchanged Pb)/(sorbed Cd − exchanged Cd) for an indicated treatment number.

and 75% of the Cd remaining being exchangeable, respectively (Fig. 3a). These data may be compared with values of 87, 87, and 23% exchangeable Cd for the Oxisol, Ultisol, and Mollisol, respectively when Cd was added to each soil by itself (Figs. 1 and 2).

It is also interesting to note that the trend of Pb:Cd NERs of the soils (Oxisol > Ultisol > Mollisol) paralleled the proportions of variable charged surfaces (oxidic minerals, 1:1 phyllosilicates, and organic matter), and were opposite CEC trends (Table 1). Therefore, on a relative basis, compared to Cd, Pb appeared to have a very high specificity for variable charged surfaces compared to constant surface charge materials (Brummer et al., 1983; Forbes et al., 1976; Jenne, 1968; McKenzie, 1980).

In Figs. 1 and 2, except for exchangeable Cd in the Mollisol, it was apparent that the amounts of exchangeable Pb and Cd changed little (E1 vs. E2, $p > 0.01$) in all soils regardless of when these metals were introduced. Therefore, the irreversible sorption of these metals appeared to occur at sites different from the colloid exchange sites, which has been suggested in another study performed on these soils (Appel et al., 2002). This was especially important for exchangeable Cd. In most cases $\leq 50\%$ sorbed Pb was exchangeable. This left a large quantity of Pb sorbed to high affinity sites but did not change the quantity of exchangeable Cd.

3.6. Pb, Cd, and Ca interactions

Calcium and Cd had similar influence on Pb sorption by the Oxisol and Ultisol soils. The amounts of sorbed and exchanged Pb in the presence of equal amounts of Cd (Fig. 3a) and Ca (Fig. 3b) were not significantly different ($p \geq 0.2$). Furthermore, compared to single addition of Pb (Fig. 1a and b), except for the Mollisol soil in Treatment 5, Ca and Cd decreased the amounts of sorbed Pb in all three soils while having little effect on the non-exchangeable Pb fraction (Figs. 1–3). Therefore, these metals had only a minor competitive effect on Pb adsorption and did not appear to compete with this metal for high affinity sorption sites. The similarities between Cd and Ca were not surprising because $Cd^{2+\leftarrow}$ and Ca^{2+} both have similar hydrated radii (4.26 and 4.12 Å, respectively; Nightingale, 1959) and low or endothermic electron affinities relative to Pb (Ca, Cd, and Pb electron affinities being 29, <0.00, and -35 kJ mol^{-1}, respectively), which minimizes electron sharing or covalent bond formation with soil surfaces (Wulfsberg, 2000). Thus, coulombic-type interactions are favored with other charged species or surfaces for $Ca^{2+\leftarrow}$ and Cd^{2+}.

Echeverria et al. (1998) and Yong and Phadungchewit (1993) reported on the competitive sorption of various heavy metals in mineral and soil systems. They reported decreased sorption of Cd, Cu, Pb, and Zn when these metals were added together compared to when they were added alone to soils. The former authors reported greater binding strength/retention of Pb compared to Cd in soils. In a study investigating the extractability of mineral soil-sorbed Cu, Cd, Pb, and Zn with 1 M CaCl$_2$, Sastre et al. (2006) reported that much of the

sorbed Cd was exchangeable (>51%) while the exchangeable Pb fraction was only 2.6−48% of the sorbed amount. Hansen and Maya (1997) also reported $\geq 90\%$ of added Pb sorbed to suspended sediments in the presence of CaCl$_2$ ($I = 0.05$ M), while $\leq 70\%$ of the added Cd was sorbed under the same conditions.

The amounts of Pb and Cd sorbed by the Mollisol soil, when these metals were added concurrently (Fig. 3a), was greatly and significantly ($p < 0.01$) larger than when Pb or Cd was added singly (Fig. 1c) or with Ca (Fig. 2c). The amounts of sorbed Pb increased from 27.7 to 41.3 mmol kg^{-1} whereas the amounts of sorbed Cd increased from 26.7 to 30.9 mmol kg^{-1}. However, the amount of Pb + Cd sorbed to high affinity sites in this soil in Treatment 5 (≈ 44 mmol kg^{-1}; Fig. 3a), was similar to the amount of Pb + Cd sorbed to high affinity sites in Treatments 1 and 3 (42−43 mmol kg^{-1}; Figs. 1c and 2c). Interestingly, the total amount of Pb + Cd sorbed to high affinity sites in Treatments 1, 3, and 5 was less than the total amount Pb + Cd sorbed to high affinity sites in Treatments 2 and 4 (≈ 54 mmol kg^{-1}; Figs. 1c and 2c). This seems to reaffirm that Pb out-competes Cd for high affinity sorption sites in this soil. In Treatments 1, 3, and 5, Pb was added to the soil prior to or with Cd. In Treatments 2 and 4, Cd was introduced before Pb. This suggests that Pb and Cd compete for the same high affinity sorption sites in this soil. Salim et al. (1996) observed similar behavior when extracting Cd, Ni, and Pb from clay-rich sediments spiked with >1000 mg metal kg^{-1}, using 1 M MgCl$_2$. Only small amounts of Pb were extracted while most of the Cd was found in the exchangeable fraction.

It was difficult to ascertain Ca's effect on Pb and Cd sorption for the Ultisol and Mollisol soils, as the amounts of sorbed Pb + Ca (Fig. 3b) or Cd + Ca (Fig. 3c) never exceeded the soil CEC values of 11.0 and 20.9 cmol$_c$ kg^{-1}, respectively. However, for the Ultisol soil, we noticed that most ($\geq 80\%$) of the sorbed Cd and Ca were exchangeable (Fig. 3b and c) while only 39% of the added Pb was exchangeable. For the Mollisol, >100% of the sorbed Ca was exchangeable suggesting release of some residual Ca upon extraction with Na. However, 100% of Pb was and $\approx 87\%$ of Cd was retained with the same extraction. Therefore, under the conditions of our experiment, Pb and Cd behaved similarly and were sorbed to high affinity sites (e.g. organic matter and 2:1 layer silicate interlayers) in this soil, while Ca behaved as an exchangeable cation instead.

For the Oxisol soil, Ca significantly reduced the amount of Cd sorbed compared to single Cd addition (Figs. 3c vs. 1a, respectively). As with the other two soils, nearly all sorbed Ca was exchanged with Na and sorbed Cd + Ca represented 86% of the Oxisol's CEC. Competitive sorption was observed between Cd and Ca as the number of sorption sites was more limited in this soil. Differences between soil colloid affinity for Pb compared to Ca were also detected (Hansen and Maya, 1997).

Benjamin and Leckie (1981a,b) and Serrano et al. (2005) observed similar behavior in their studies looking at the competitive adsorption of Cd and Pb. They concluded that if two or more metals compete for the same binding sites, adsorption of

a more strongly bound metal (e.g., Pb in this study) forces the more weakly sorbed metal to be retained at weaker sites (i.e., exchange sites). This is consistent with our data.

4. Conclusions

Studies employing traditional approaches to sorption/desorption as well as sequential extraction techniques have provided valuable information regarding heavy metal interactions with soil surfaces and partitioning of these species among various soil fractions. However, further important information was obtained in this study using a sequential sorption/desorption approach. The sequential sorption procedure enabled determination of how Pb and Cd interact when introduced to soils at different times, along with the specificity of soil sorption sites for one metal over another. The procedure also provided evidence concerning sorption mechanisms.

Apparently due to Pb's chemical characteristics (relatively high electronegativity, low pK_H, small hydrated radius, and electronic structure), this metal was sorbed in preference to Cd or Ca regardless of the order in which it entered soil systems. Cadmium, on the other hand, was sorbed and/or retained at high affinity sites to a greater extent when it was added to the soil prior to Pb. Thus, at a contaminated site receiving Pb and Cd inputs at different times, Cd may be more mobile when introduced to soils after Pb compared to the opposite scenario. Experimental approaches like the one used in this research should be applied to other heavy metal systems in order to assess the widespread applicability of the technique as well as to better understand soil-metal contaminant interactions.

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