DIVISION S-2—SOIL CHEMISTRY

Selectivities of Potassium-Calcium and Potassium-Lead Exchange in Two Tropical Soils

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ABSTRACT

Measurement of cation selectivity in soils provides important information about the affinity and binding strength of a particular cation on soil surfaces. Gaines-Thomas (K_{GT}) selectivity coefficients were determined for a variety of K/Ca and K/Pb ratios on an Oxisol and Ultisol soil from Puerto Rico. The calculated K_{GT} values indicated a preference for K^+ over Ca^{2+} or Pb^{2+}. The selectivity for Pb^{2+} was significantly greater than that for Ca^{2+} due to Pb^{2+}'s larger hydrated charge density relative to that of Ca^{2+}. The patterns of selectivity were independent of metal type. The selectivity of the Oxisol for Ca^{2+} or Pb^{2+} exhibited no trend and changed little with changes in divalent metal surface coverage. The Ultisol displayed a decrease in selectivity for Ca^{2+} and Pb^{2+} with increasing surface coverage of these ions. This was attributed to the presence of smectite in the Ultisol, which was able to partially collapse when K^+ saturated. Some of the Pb sorption in the soils was due to chemisorption. The Oxisol chemisorbed ≈ 3000 mg Pb kg^{-1} while that value for the Ultisol was ≈ 1900 mg kg^{-1}. The differences were due to the greater quantities of Fe/Al oxides and organic matter in the Oxisol relative to the Ultisol. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) spectroscopy detected discrete Pb-C phase in both soils. The C was from organic matter. Under experimental conditions, any Pb-carbonate phase would not have been stable. It was possible Pb was associated with organic sulfhydral groups. The selectivity exhibited by soil systems for various nutrient and heavy metals is important in elucidating how available these metals will be for plant/animal uptake as well as their mobility and stability in the soil environment.

L EAD IS AN IMPORTANT HEAVY METAL that may threaten soil quality and human health at elevated levels (Adriano, 1986; Kabata-Pendias and Pendias, 1992). It is one of the most widespread elemental contaminants worldwide (Nriagu, 1998) and has been shown to cause anemia, kidney disease, brain damage, impaired function of the peripheral nervous system, high blood pressure, reproductive abnormalities, developmental defects, abnormal Vitamin D metabolism, and in some situations death (Hrudey et al., 1995; USEPA, 1992). The average concentration of Pb in the earth's crust is 13 mg kg^{-1} (Brown et al., 1999). Release of this metal into soils via a variety of industrial, urban, and agricultural applications has lead to very high soil Pb concentrations of up to several thousand milligrams per kilogram (Adriano, 1986; Davies, 1992; Forstner, 1995; Ma and Rao, 1997).

In many cases, much of the Pb in uncontaminated and contaminated soils is not present in readily available fractions (RAF; we have operationally defined RAF-Pb to equal the water-soluble and salt exchangeable fractions of Pb found in soils). In several studies looking at the sequential extraction of Pb (and other heavy metals) from contaminated soils, researchers have shown the amount of RAF-Pb relative to the total soil Pb is generally ≤ 1 to 10% (Boruvka et al., 1997; Kabala and Singh, 2001; Ma and Rao, 1997). This corresponded to RAF-Pb ranging from ≈ 0.4 to 4000 mg kg^{-1} (3.9×10^{-4} to 3.9 cmol$_c$ kg^{-1}) using the high RAF value of 10%. Thus, depending on a soil's cation-exchange capacity (CEC) and the types of cations on the cation-exchange sites, Pb potentially has the ability to occupy part or a majority of these sites.

The degree to which a cation adsorbs to an exchanger depends largely on its selectivity relative to other cations in the soil solution (McBride, 1994). A cation with high selectivity for a particular soil surface (exchanger) will be preferentially adsorbed relative to one with lower selectivity. Many studies, considering sorption of heavy metals (i.e., Pb, Cu, Zn, Cd, and Ni) added to soils and pure minerals (i.e., goethite, alumina, kaolinite, and zeolite), have inferred higher Pb selectivity relative to other heavy metals based on differences in total amount of metals sorbed or desorbed (Ahmed et al., 1998; Gao et al., 1997; Pardo, 2000; Yong and Phadungchewit, 1993). These studies did not focus on the exchangeable Pb fraction. Ahmed et al. (1998) examined competition for zeolite exchange sites between Pb^{2+} and K^+, however, no known studies have determined Pb selectivity nor selectivity coefficients relative to the important cations commonly found on soil cation-exchange sites (i.e., Ca, Mg, K, and Na). These cations may compete strongly with Pb for adsorption.

Understanding how Pb competes for exchange sites in soils, at varying concentrations and saturations on the exchanger relative to a typical cation (i.e., Ca or K), would provide useful information about Pb selectivity and, thus, mobility and diffusion in soils. In the soils used in this study, Ca^{2+} plus K^+ occupied 23 and 31% of Oxisol and Ultisol cation exchange sites, as deter-

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Abbreviations: AAS, atomic adsorption spectroscopy; CEC, cation exchange capacity; EDX, energy dispersive X-ray; I, ionic strength; K_{sp}, solubility product constant; K_{GT}, Gaines-Thomas selectivity coefficient; PDI, potential determining ions; pK_H, negative log of the hydrolysis constant; RAF-Pb, readily available fraction of lead; SEM, scanning electron microscopy; TGA, thermal gravimetric analysis; XRD, X-ray diffraction; $\Delta G_{EX}°$, standard Gibbs free energy of exchange; ΔH_{hyd}, hydration energy; % R, percent recovery.

mined by extraction with neutral 1 M $NH_4C_2H_3O_2$, respectively. Though these ions represented under one-third of native-soil cation exchange sites, it was our intention to compare the exchange selectivity of divalent/monovalent systems. Thus, we excluded Al from the present study.

The objective of this research was to study and compare exchange reactions involving K^+/Ca^{2+} and K^+/Pb^{2+} using calculated selectivity coefficients in two highly weathered tropical soils. Lead and Ca were chosen as Pb is an important cationic contaminant in soils worldwide (Nriagu, 1998) and is known to undergo both specific and non-specific adsorption reactions in soil. Calcium, on the other hand, does not specifically adsorb to soil surfaces and is commonly found in high relative concentrations on soil cation exchange sites. Potassium was selected as it is a common monovalent cation found in most soils and generally does not specifically adsorb to non-vermiculitic soils. (McBride, 1994; Sparks, 1995).

MATERIALS AND METHODS

Soil Samples

The surface horizons (0–15 cm) of two highly weathered Puerto Rican soils, an Oxisol and Ultisol, were sieved to an aggregate size of between 0.25 and 0.5 mm, by passing the soil particles through a 0.5-mm round-hole sieve with the aid of a rubber stopper, before being used in this study. This particle-size range was chosen as these soils were composed of strong, microaggregates of predominantly clay-sized particles (>55%; Table 1). Furthermore, soil particles <0.25 mm did not allow solution to flow through our columns in the selectivity experiments explained below. These tropical soils were selected for study because relative to temperate region soils, little is known about the selectivities of K/Ca and K/Pb exchange in these systems. The important mineralogical and chemical properties of these soils are presented in Table 1.

Mineralogy of the soil clay fractions (<2 μm) was determined via X-ray diffraction (XRD) analysis using CuKα radiation. Magnesium- and K-saturated samples were scanned at $2°$ 2θ min^{-1} on ceramic tiles at 25°C. The K-saturated tiles were further scanned following heat treatments of 110, 300, and 550°C (Whitting and Allardice, 1986). Thermal gravimetric analysis (TGA, 25–1000°C) was used to confirm and supplement the XRD data enabling quantification of soil clay mineralogy (<2 μm). Particle size was determined by the pipette method (Gee and Bauder, 1986) following removal of Fe oxides by dithionite-citrate-bicarbonate (Mehra and Jackson, 1960). Organic C content was found by $K_2Cr_2O_7$ digestion (Nelson and Sommers, 1996) and pH measurements were made in H_2O (soil/solution ratio 1:2) using a pH meter equipped with combination gel-filled glass electrode. Specific surface areas were obtained via six-point BET-N_2 adsorption (Quantachrome Corporation, 1996). The CEC was determined by adding the 1 M KCl extractable acidity to cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) exchanged by neutral 1 M $NH_4C_2H_3O_2$ (pH 7) as described in Thomas (1982). Concentration of Fe + Al was determined via USEPA Method 3051 (USEPA, 1995). In Standard Reference Material 2709 (San Joaquin Soil), Fe had a percentage recovery (%R) of 88% while Al had %R of 39%. These results are similar to those presented by Chen and Ma (1998). All metals were determined by flame atomic absorption spectrophotometry (AAS) or inductively coupled argon plasma atomic emission spectroscopy and analyses were performed on duplicate samples (1 assay for XRD and TGA).

Determination of Exchangeable Cations

Duplicate columns, for each soil type, holding between 3 to 5 g of soil were constructed (and weighed) to allow for unsaturated flow. Solutions containing differing amounts of KNO_3 and/or $Ca(NO_3)_2$ or KNO_3 and/or $Pb(NO_3)_2$ were passed through the soil using a combination of gravity and a suction of 20 cm of water applied to the bottom of the column. The solution compositions were as follows: 15 mM KNO_3, 14.25 mM KNO_3 + 0.25 mM $M(NO_3)_2$, 13.5 mM KNO_3 + 0.5 mM $M(NO_3)_2$, 12 mM KNO_3 + 1 mM $M(NO_3)_2$, 9 mM KNO_3 + 2 mM $M(NO_3)_2$, 6 mM KNO_3 + 3 mM $M(NO_3)_2$, 3 mM KNO_3 + 4 mM $M(NO_3)_2$, and 5 mM $M(NO_3)_2$ where M^{2+} = Ca^{2+} or Pb^{2+}. The ionic strength (I) and pH of each solution were held constant at 15 mM and 4.7, respectively. The pH of the solutions was adjusted with 10 mM HNO_3. The adjustment of solution pH resulted in changes of $I \leq 0.2\%$. It was necessary that both the pH and I of each of the solutions were matched. Changes in soil solution pH and I lead to changes in the surface charge of variably charged soil colloids, thus, metal adsorption in these systems changes (Uehara and Gillman, 1981; van Olphen, 1977).

Soil columns were flushed with 20 mL of 0.5 M KNO_3 (≈20 pore volumes assuming 5 g of soil and a gravimetric water content of 0.2). All flushes were in 10-mL aliquots unless stated otherwise. This was followed by passing 40 mL of 15 mM KNO_3 through the columns to ensure soils were K-saturated before the start of any adsorption experiments. The latter flushing solution was used to ensure soil solutions had an I = 15 mM. The K/Ca and K/Pb solutions were then added to the soils until the concentrations in the column effluents were C/C_o (effluent/eluent) = 1 and 0.95 for K/Ca and K/Pb, respectively (usually ≥100 pore volumes).

After solution equilibration, the columns containing wet soils were weighed to correct for any occluded K, Ca, and Pb remaining in the soil pores. The adsorbed metals were then extracted with five washes of 5-mL aliquots of 0.5 M $Mg(ClO_4)_2$. The effluent was collected and refrigerated. Before analysis of K^+, Ca^{2+}, and Pb^{2+}, on the flame AAS, samples were diluted to alleviate matrix interferences. Furthermore,

Table 1. Pertinent soil physicochemical properties.

Sample	Organic matter	PZNC†	pH	CEC‡	Sum H + Al	Fe + Al§	Clay mineralogy¶	Texture#	Specific surface area
	%			— cmol$_c$ kg^{-1} —			— % —		m² g^{-1}
Oxisol	4.1	3.7	4.9	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	11.0	7.1	8.6	k(45) > q(23) > s(17) > go(15)	12-29-59	37.8

† Point of zero net charge.
‡ Cation-exchange capacity.
§ Fe + Al was determined via USEPA Method 3051 (USEPA, 1995) and is operationally defined as those amounts of Fe + Al corresponding to Fe/Al oxides.
¶ k = kaolinite, go = goethite, gi = gibbsite, s = smectite, q = quartz. Values in parenthesis represent the percentage of each mineral in the <2-μm soil fraction.
# sand–silt–clay.

the method of standard addition (Willard et al., 1988) indicated the $Mg(ClO_4)_2$ matrix did not significantly interfere with K^+, Ca^{2+}, or Pb^{2+} recoveries during AAS analysis. Preliminary experiments indicated this amount of $Mg(ClO_4)_2$ satisfactorily desorbed all exchangeable K, Ca, and Pb. Duplicate values of metal concentration at each concentration step were averaged and standard deviations calculated.

The soils undergoing Ca additions were re-equilibrated with KNO_3 and the cycle of solution addition at a different K^+/Ca^{2+} ratio, as described above, was repeated. Since Pb^{2+} specifically adsorbs to many soil colloids, each of the soils to which different concentrations of Pb were added were removed from the columns, dried, and digested in concentrated HNO_3 according to USEPA Method 3051 (USEPA, 1996). This was done to ascertain levels of non-exchangeable Pb in the samples. Furthermore, subsamples (2 at each Pb step) of these soils were viewed under a SEM-EDX spectroscopy. This was done to determine discrete Pb phases/associations within the soils.

Determination of Equilibrium Selectivity Coefficients

Binary heterovalent exchange reactions between bivalent and monovalent counter ions $(A^{2+} \rightarrow B^+)$ in the tropical Oxisol and Ultisol soils were studied according to the generic reaction,

$$A^{2+} + 2BX \leftrightarrow AX_2 + 2B^+ \qquad [1]$$
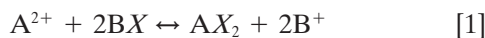
$$K_{EX} = (a_{AX_2} \times a_B^2)/(a_{BX}^2 \times a_A) \qquad [2]$$

where X represents 1 mol of negative charge per unit mass of soil, A^{2+} is either Ca^{2+} or Pb^{2+}, B^+ equals the amount of monovalent cations $(K^+ + H^+)$ reacting in the system, K_{EX} is the equilibrium constant for the exchange reaction, and 'a' represents the activity of the cations on the exchanger or in solution. Hydrogen was grouped with K^+ as our data and other research have shown the exchange selectivity for the proton on pure clays, resins, and soils is near that for K^+ and Na^+ (Coulter, 1969; Foscolos and Barshad, 1969; Rhue and Mansell, 1988).

The Gaines-Thomas approach, which assumes the activity of adsorbed cations equals their equivalent fractions on the exchanger $(E; mmol_c\ kg^{-1})$, was used to calculate binary selectivity coefficients (K_{GT}) for combinations of Ca^{2+}, Pb^{2+}, and K^+ ion species.

$$K_{GT} = (E_{AX_2} \times a_B^2)/(E_{BX}^2 \times a_A) \qquad [3]$$

Activities (a) in Eq. [3] were calculated as products of single-ion activity coefficients, as estimated with the extended Debye-Hückel equation, and single-ion molar concentrations in the equilibrium solutions (McBride, 1994).

A thermodynamic nonpreference isotherm for heterovalent exchange between bivalent and monovalent counter ions (Eq. [1]) was calculated with the equation (Sposito et al., 1983)

$$E_j = 1 - \left[1 + \frac{2}{rTN}\left(\frac{1}{E_i^2} - \frac{1}{E_i}\right)\right]^{-1/2} \qquad [4]$$

where E_j is the equivalent fraction of adsorbed divalent cation $(Ca^{2+}$ or $Pb^{2+})$, E_i is the equivalent fraction of monovalent cation in the equilibrium solution, r is γ_A/γ_B where γ_A and γ_B are single-ion activity coefficients of cations A^{2+} and B^+, and TN is equal to the total cation concentration in $mol_c\ L^{-1}$.

The thermodynamic nonpreference isotherm is delimited by having (i) the standard Gibbs free energy of the exchange reaction (ΔG_{EX}°) equal zero (i.e., system at equilibrium) and (ii) the exchanger phase activity coefficients are unity (ideal mixture). Therefore, according to chemical thermodynamics,

cation exchange does not exhibit selectivity if $K_{EX} = 1$ and the exchanger phase exhibits properties of an ideal solid solution (Sposito et al., 1983).

RESULTS AND DISCUSSION

Cation-Exchange Capacity Differences under Ca^{2+}, Pb^{2+}, and K^+ Saturation

The measured CECs of the Oxisol and Ultisol soils varied as a function of the saturating cation added—Ca^{2+}, Pb^{2+}, and K^+. This was determined by extraction of these cations from soils saturated with 5 mM $Ca(NO_3)_2$, 5 mM $Pb(NO_3)_2$, or 15 mM KNO_3, respectively (Table 2). The Ca^{2+}–saturated soils had the highest CECs followed by those that were Pb^{2+}–saturated. The K^+–saturated soils gave the lowest values of CEC. The CEC determined via the method expressed in Table 1 (sum of basic cations via 1 M $NH_4C_2H_3O_2$ + H^+ and Al^+ extracted with 1.0 M KCl) yielded CEC values between those found for Pb^{2+}– and K^+–saturated soils. Deist and Talibudeen (1967), Maes and Cremers (1977), and Rhue and Mansell (1988) have all shown higher measured CECs with divalent cations compared with monovalent ones even when the saturating cations were present at different values of I. Furthermore, the soil in the Rhue and Mansell (1988) study was an Ultisol composed of components similar to the soils used in our study. Their soil had 2.6% organic C as well as kaolinite, hydroxy-interlayered vermiculite, gibbsite, and quartz as the dominant minerals in the clay fraction.

The differences in CEC between the divalent and monovalent systems were due, at least in part, to mutual competition of K^+ and H^+ for cation-exchange sites. At pH 4.7, the equilibrium pH of all solutions used in this study, previous research on the Oxisol and Ultisol indicated that Al^{3+} and Fe^{3+} were not solubilized and, thus, did not participate in cation exchange (Appel et al., 2002; Rhue et al., 2002). Under experimental conditions, the Oxisol and Ultisol soils had net negative charges (point of zero net charge [PZNC] values of 3.7 and 2.3, respectively; Table 1). Thus, the main soil components capable of cation exchange in the Oxisol were organic matter and kaolinite and in the Ultisol were organic matter, kaolinite, and smectite. Other mineral components (gibbsite and goethite) were positively charged at this pH and I.

Organic matter derives its surface charge from the adsorption/desorption of potential determining ions (PDI, H^+, and OH^-) while kaolinite obtains its surface charge from both adsorption and desorption of PDI and

Table 2. Cation-exchange capacity (CEC)† of the Oxisol and Ultisol as a function of the saturating cation.‡

Soil	Ca^{2+}	Pb^{2+}	K^+	$H_{Pb}^\ddagger$	$H_K^\ddagger$
			cmol$_c$ kg^{-1}		
Oxisol	6.0 (±0.2)	4.3 (±0.1)	2.8 (±0.4)	1.7 (±0.7)	3.2 (±0.5)
Ultisol	13.0 (±0.7)	11.2 (±0.2)	9.8 (±0.6)	1.8 (±0.2)	3.2 (±0.9)

† Numbers in parenthesis are standard deviations of the means.
‡ CEC of Pb^{2+} + $H_{Pb}^\ddagger$ = CEC in Ca^{2+}; CEC of K^+ + $H_K^\ddagger$ = CEC in Ca^{2+}. $H_{Pb}^\ddagger$ is the amount of exchangeable H^+ found by subtracting the CEC in Pb^{2+} from the CEC in Ca^{2+} while $H_K^\ddagger$ is the amount of exchangeable H^+ found by subtracting the CEC in K^+ from the CEC in Ca^{2+}.

through isomorphous substitution during crystallization indicating these soil components have high affinities for H^+ (Barrow, 1987; van Olphen, 1977). This suggests that differences in CECs between the Ca^{2+}–saturated system and the Pb^{2+}– or K^+–saturated systems were due to competition for organic matter and kaolinite, and most likely smectite in the case of the Ultisol (Altin et al., 1999), negatively charged exchange sites between H^+ and Pb^{2+} or H^+ and K^+, respectively. The amount of H^+ saturation on the soil cation-exchange sites was determined by difference (Table 2).

Table 2 shows H^+ occupied 29 and 53% of the exchange sites when the Oxisol was saturated with Pb^{2+} and K^+, respectively. The corresponding values of H^+ for the Ultisol were 13 (Pb^{2+} saturation) and 24% (K^+ saturation) of this soil's cation-exchange sites. The Oxisol has a much larger quantity of kaolinite and organic matter than the Ultisol (Table 1), which gives the Oxisol a much higher affinity for H^+ relative to the Ultisol (Barrow, 1987; van Olphen, 1977).

There are some noteworthy differences in CEC measured in the divalent cation systems, Ca^{2+} vs. Pb^{2+}, between these soils. The Oxisol and Ultisol had (1.7 and 1.8 $cmol_c\ kg^{-1}$, respectively) greater CEC when Ca^{2+}–saturated as compared with Pb^{2+}–saturated conditions (Table 2). Results from a speciation study of the same soils showed the dominant Pb solution species, from Pb-saturated soils, were Pb^{2+} and $PbNO_3^+$ while the main solution specie from Ca-saturated soils was Ca^{2+}. The $PbNO_3^+$ decreased the CEC relative to the CEC measured in Ca due to an increased ability of H^+ to compete for cation exchange sites with $PbNO_3^+$ (Appel et al., 2002).

Determination of Calcium and Lead Selectivity

The preference of a given ion for an exchanger is given by a selectivity coefficient (Helfferich, 1962). Values of the experimentally determined selectivity coefficients (K_{GT}) for $Ca^{2+} \rightarrow K^+ + H^+$ and $Pb^{2+} \rightarrow K^+ + H^+$ exchange reactions on the Oxisol and Ultisol soils are displayed in Fig. 1. All compositions of $K^+ + H^+$, Ca^{2+}, or Pb^{2+} on the exchanger yielded Ca^{2+} and Pb^{2+} selectivity coefficients <1 for the two soils studied. This meant that $K^+ + H^+$ had a larger selectivity for soil cation-exchange sites. Plotting equivalent fractions of adsorbed divalent cations vs. their equivalent fractions in solution along with the nonpreference isotherm (Eq. [4]), highlights this point (Fig. 2). It is evident from this figure that all soil-metal curves were below the nonpreference isotherm. This provides further evidence for the higher relative $K^+ + H^+$ selectivity in the Oxisol and Ultisol.

Many investigators have shown higher selectivity for K^+ over Ca^{2+} in kaolinite and kaolinitic soils, which was an abundant mineralogical component of our soils (Oxisol and Ultisol have 49 and 45% kaolinite in their clay fractions, respectively), at most K/Ca ratios on the exchanger (Levy et al., 1988; Levy and Hillel, 1968; Udo, 1978). This is at least partly due to the fact that most clays behave as weak field exchangers. This means that the charge density of soil clays is generally not great
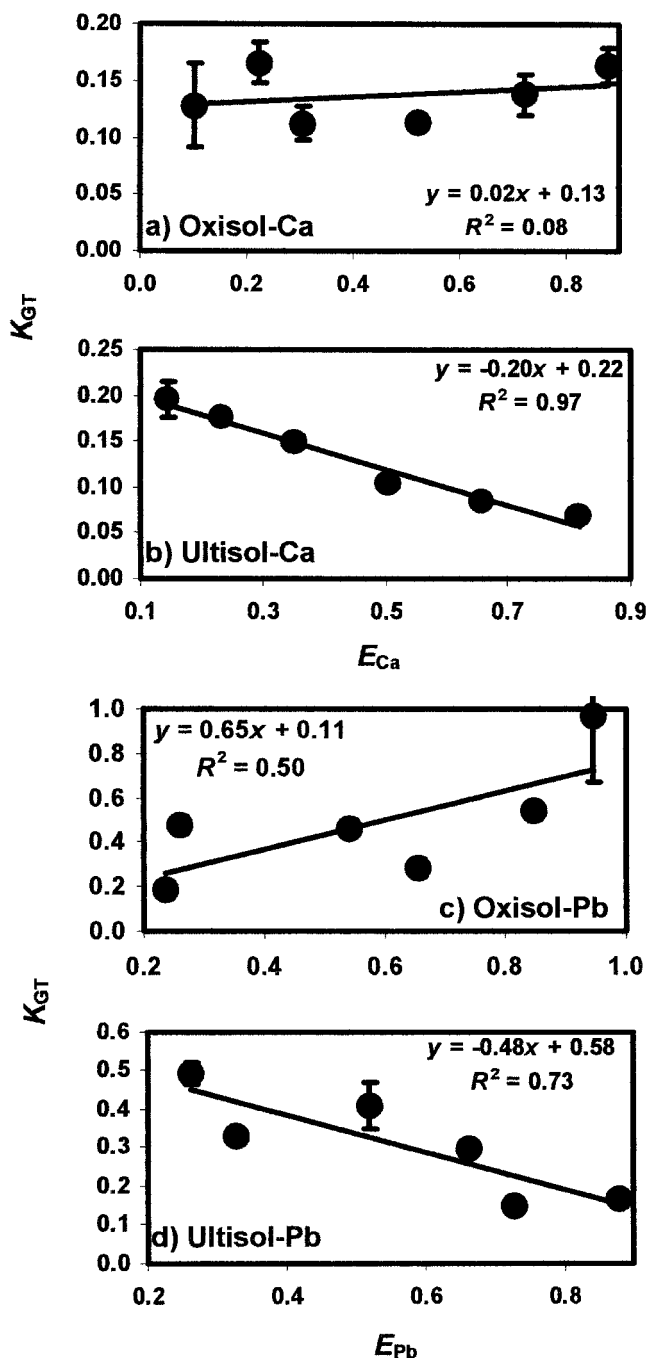

Fig. 1. Gaines-Thomas selectivity coefficients (K_{GT}) vs. equivalent fractions of Ca^{2+} on the exchanger (E_{Ca}) in the (a) Oxisol and (b) Ultisol or Pb^{2+} on the exchanger (E_{Pb}) in the (c) Oxisol and (d) Ultisol.

enough to remove water of hydration from adsorbing cations. Therefore, selectivity may be related to the hydrated charge density and hydration energy (ΔH_{hyd}; $kJ\ mol^{-1}$) of a particular adsorbing cation (Juo and Barber, 1969; Rhue et al., 2002).

The order of increasing charge density ($mol_c\ m^{-2}$) for several important colloidal soil materials commonly found in soils is goethite (pH = 9; 0.43×10^{-6}) $<$ smectite (1.27×10^{-6}) $<$ vermiculite (3.13×10^{-6}) $<$ kaolinite (6.40×10^{-6}) $<$ organic matter (7.74×10^{-6})

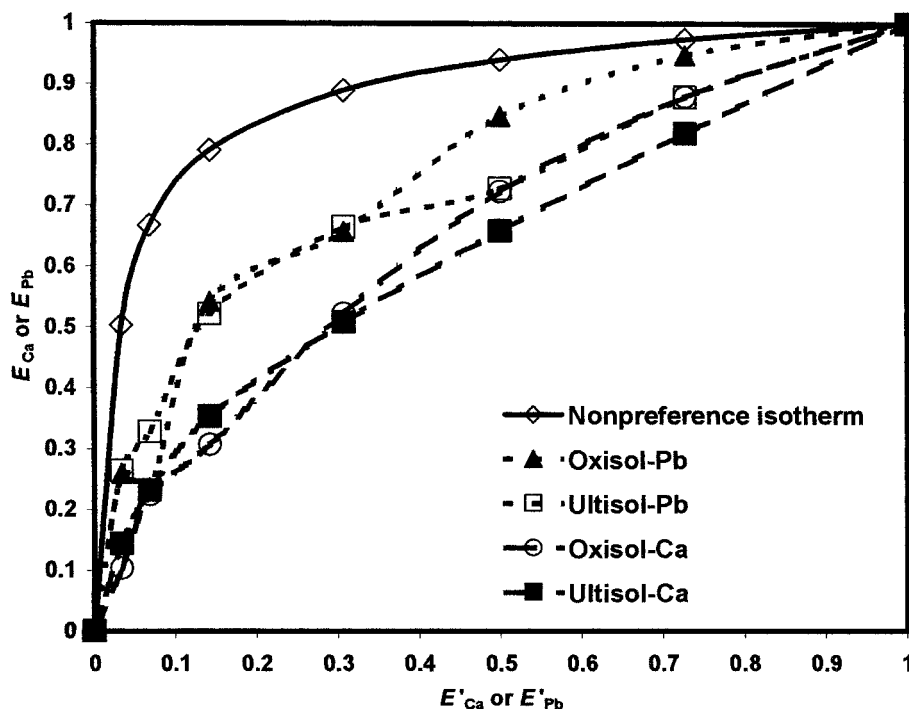**Fig. 2. Exchange isotherms for Pb²⁺ or Ca²⁺ replacing K⁺ on exchange sites as well as heterovalent exchange nonpreference isotherm on the Oxisol and Ultisol soils. E_{Ca} and E_{Pb} = equivalent fractions of either Ca²⁺ or Pb²⁺ on the exchanger and E'_{Ca} and E'_{Pb} = equivalent fractions of either Ca²⁺ or Pb²⁺ in the equilibrium solution.**

(McBride, 1994; Thompson et al., 1989). The order of increasing hydrated charge density (cation valence/hydrated radius, Å) and ΔH_{hyd} (kJ mol⁻¹) of the important cations in our study is K⁺ (0.30) < Ca²⁺ (0.49) < Pb²⁺ (0.50) and K⁺ (−321) < Pb²⁺ (−1480) < Ca²⁺ (−1592), respectively (Nightingale, 1959; Wulfsberg, 2000). Due to kaolinite's relatively high charge density, allowing it to dehydrate or partially dehydrate weakly hydrated cations (i.e., K⁺), as well as its abundance in the chemically active fraction of our soils, it was not surprising the Oxisol and Ultisol had a preference for K⁺ over Ca²⁺ or Pb²⁺ at all ratios of K⁺ in our study. Furthermore, selectivity coefficients for Pb²⁺ were significantly larger than those for Ca²⁺ ($p \leq 0.01$) in both the Oxisol and Ultisol soils. This was attributed to slightly larger hydrated charge density and lower ΔH_{hyd} for Pb²⁺ relative to Ca²⁺, thus, enabling Pb²⁺ to out-compete Ca²⁺ for exchange sites (McBride, 1994).

Generally, the selectivity of a preferred ion on the exchanger increases with decreasing saturation of that ion (Gast, 1972). Using a least squares fitting approach in Fig. 1, it is evident that this holds true for the Ultisol soil but not for the Oxisol. The negative slopes of the Ultisol-Ca and -Pb lines (Fig. 1b, d) indicate that as the amount of K⁺ (preferred ion) on the exchanger decreases, its selectivity increases (going from left to right on the figures). Contrarily, the Oxisol-Ca and -Pb lines remain relatively constant or slightly increase with increasing divalent metal saturation (i.e., K_{GT} for K⁺ stays the same/decreases with decreasing K⁺ saturation).

The data suggests that, in the Ultisol, there were exchange sites possessing different binding energies for K⁺ (Gast, 1972). At low amounts of K⁺ on the exchanger, this cation was predominantly retained by higher energy sites. With increasing K⁺ saturation on the exchanger, these higher energy sites became saturated and K⁺ then went to lower affinity sites. The Ultisol soil had ≈17% smectite in the clay fraction. This mineral has been shown to collapse around K⁺ ions while partially dehydrating this ion (Page et al., 1963, 1967) and it most likely comprised the high-energy K⁺ binding sites in this soil. In a thermodynamic study looking at Ca/K exchange in two soils, Sparks and Jardine (1981) found the binding energy of K⁺ was larger in the soil having more interlayer surface charge compared with the one having less 2:1 phyllosilicate minerals.

The Oxisol-Ca and -Pb lines display no definite trend in selectivity as indicated by the low R^2 values (Fig. 1a, c). The selectivities for these metals may be considered unchanging with changes in cation composition on the exchanger. This soil did not possess any interlayer exchange sites as did the Ultisol. It was composed of minerals having only external exchange sites (Table 1). Therefore, the data suggest that these external binding sites all exhibit similar affinity and binding energy for K⁺ (Appel et al., 2002; Gast, 1972). Consistent with the above, Appel et al. (2002) observed no changes in the enthalpy of either Ca²⁺ or Pb²⁺ adsorption with increased surface coverage of these ions on this soil.

Nonexchangeable Lead

Lead readily undergoes chemisorption reactions in soils, organic matter, and pure minerals under a variety of reaction conditions (Bargar et al., 1998; Pardo, 2000;

Strawn, 1998; Xia et al., 1997a). Lead also readily participates in cation-exchange reactions with soil surfaces (Yong and Phadungchewit, 1993). Thus, it is necessary to partition total Pb sorption between electrostatic ion exchange reactions and those involving formation of Pb-soil surface bonds.

The ability of Pb to take part in chemisorption reactions has been attributed to the relatively high affinity of Pb for many organic matter functional groups, which may range from hard Lewis bases like carboxylic and phenolic groups to soft Lewis bases such as sulfhydral groups (Pb^{2+} is a borderline Lewis acid); Pb's electronegativity (2.10), enabling it to pull electron density away from soil surface functional groups during bond formation; and its relatively low pK_H (negative log of hydrolysis constant, 7.78) allowing it to form chemical bonds with soil surfaces in hydrolyzed form (Bruemmer et al., 1986; McBride, 1994).

The Oxisol soil irreversibly (not exchangeable with K^+) sorbed significantly more ($p \leq 0.05$) Pb than the Ultisol (2975 ± 694 and 1848 ± 472 mg Pb kg^{-1} of Oxisol or Ultisol soil, respectively). The Oxisol had a greater abundance of both organic matter (4.1 and 1.9% for the Oxisol and Ultisol, respectively) and Fe/Al oxides (28.7 and 8.6% for the Oxisol and Ultisol, respectively) compared with the Ultisol (Table 2). These soil components probably accounted for the greater chemisorption of Pb in the Oxisol. Both materials have been shown to be important in the irreversible sorption of heavy metals and especially Pb (Bargar et al., 1997a, b; Gao et al., 1997; Sauve et al., 1998, 2000).

The SEM-EDX was used to identify specific phases of Pb on the soil surfaces. Both soils showed discrete Pb-C phases (Fig. 3). The C was from organic matter. Under experimental conditions, any Pb-carbonate solid phase would not have been stable (Gustafsson, 2002). The elemental dot maps show where Pb and C are present together. In these areas, the other elements (i.e., Al, Fe, O, and Si) are absent. It seems unlikely O was not part of the Pb-C phase as Xia et al. (1997a, b) have shown C-O functional groups are important in Pb chemisorption to organic matter.

However, Pb may have been associated with sulfhydral groups from organic matter maintaining the possibility O was not present in the area of Pb soil surface complexation. Lead forms stronger bonds with S relative to OH soil surface functional groups. Since S^{2-} and OH^- may be considered analogs for pertinent Pb soil surface binding sites, the K_{sp} values for PbS (9.04×10^{-29}) and $Pb(OH)_2$ (1.42×10^{-20}) demonstrate the high relative strength of the Pb-S soil surface bond (Lide, 1990; McBride, 1994). It is difficult to unequivocally determine if Pb was associated with S in our soils as the absorption edges for these elements overlap (Pb, $M\alpha$ = 2.346 keV and S, $K\alpha$ = 2.308 keV). Elucidation of the importance of S in Pb chemisorption requires further research.

The instrument Pb detection limit was ≈3000 mg kg^{-1} (W. Acree; personal communication, 2001), thus, it is possible not all discrete Pb phases were detected. However, solid phase precipitation was ruled out as a retention mechanism under the conditions of our study due
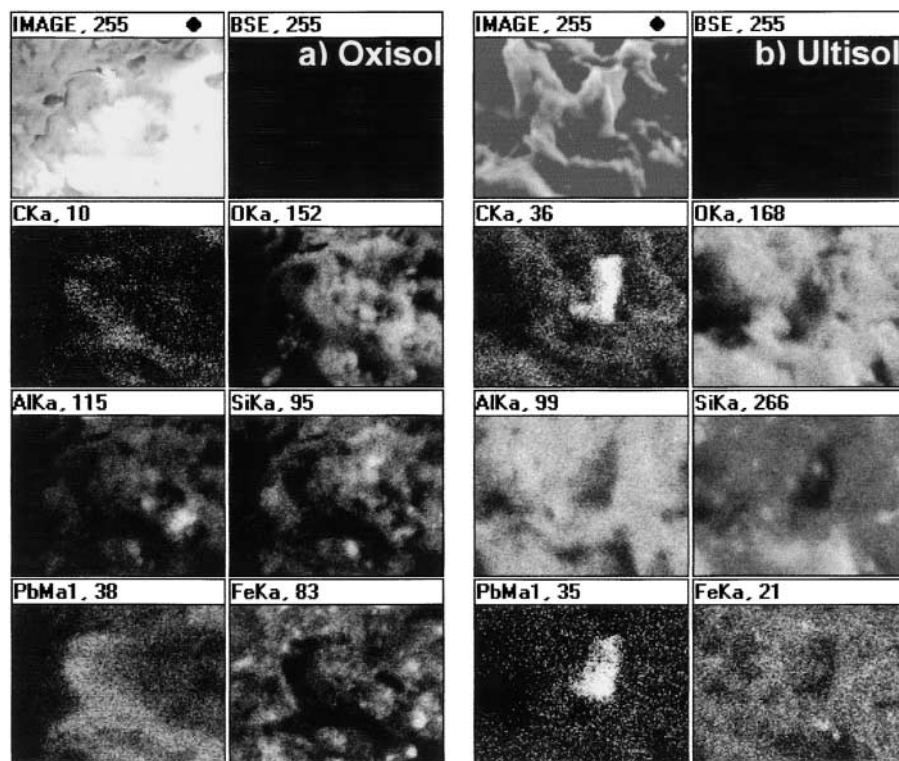

Fig. 3. SEM-EDX elemental dot maps of (a) Oxisol and (b) Ultisol soil samples. Light areas of the dot maps indicate elevated concentrations of a particular element. The first letter/s in the upper right-hand corner of each box represent/s the particular element of concern, Ka = K-α excitation energy; Ma1 = M-α 1 excitation energy, and the numbers correspond to the relative elemental intensities in counts per second.

to the low reaction pH 4.7 and relatively low Pb concentrations. Visual MINTEQ software (Gustafsson, 2002) confirmed soil solutions were undersaturated with respect to $Pb(OH)_2$ and $PbCO_3$ ($PCO_2 = 10^{-4.5}$ MPa). Thus, inner-sphere complexation reactions were the most likely nonexchangeable retention mechanisms involving Pb and Oxisol and Ultisol surfaces.

CONCLUSIONS

Data collected from sorption isotherm studies enabled a better understanding of K/Ca and K/Pb interactions in two highly weathered tropical soils from Puerto Rico (Oxisol and Ultisol). Gaines-Thomas selectivity coefficients were calculated for a range of K/Ca and K/Pb ratios on soil exchange sites. The soils exhibited a preference for K^+ over Ca^{2+} or Pb^{2+} at all ratios of K^+ on the exchanger. Kaolinite, which was abundant in the Oxisol and Ultisol, has high selectivity for K^+ due to its relatively high charge density and the low hydration energy for K^+. This explained our soils' high affinity for K^+.

Soil composition played a larger role than metal type in the patterns of selectivity for the cations studied. Selectivity for Ca^{2+} and Pb^{2+} changed little/stayed the same in the Oxisol and decreased in the Ultisol with increasing concentrations of Ca^{2+} or Pb^{2+} on the exchanger. The Oxisol was composed entirely of colloids having external surface exchange sites while the Ultisol possessed some smectitic material (17%). The interlayers of 2:1 layer silicates have been shown to have high affinity for K^+. This is probably why the selectivity for Ca^{2+} and Pb^{2+} decreased with increasing divalent metal saturation in the Ultisol.

Lead was irreversibly sorbed at all concentration steps in both soils. The Oxisol had $\approx$3000 mg nonexchangeable Pb kg^{-1} while that value in the Ultisol was significantly less at $\approx$1900 mg kg^{-1}. The Oxisol had more organic matter and Fe/Al oxides than the Ultisol, which probably accounted for the greater irreversible Pb sorption in the Oxisol. The SEM-EDX was used to identify discrete Pb phases on the soil surfaces to elucidate the nature of Pb binding to our soils. The data suggested chemisorption was the dominant mechanism of irreversible Pb sorption. There were discrete Pb-C phases detected in both soils where the C was from organic matter. Soil solutions were undersaturated with respect to solid phase $Pb(OH)_2$ and $Pb(CO_3)_2$ formation ruling out precipitation as a retention mechanism for Pb.

The data collected in the sorption isotherm study enabled improved understanding of surface sorption reactions involving Ca^{2+}, K^+, and Pb^{2+} and tropical soil surfaces. Depending on heavy metal soil contamination levels as well as soil properties, Pb^{2+} and other heavy metals may occupy a fraction to a significant portion of soil cation-exchange sites. Therefore, understanding how the selectivity of a particular heavy metal changes with its surface coverage is important in elucidating how available this metal will be for plant/animal uptake as well as its mobility and stability in the soil environment.

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