Concentration, pH, and Surface Charge Effects on Cadmium and Lead Sorption in Three Tropical Soils

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ABSTRACT

Reactions of heavy metals with soil are important in determining metal fates in the environment. Sorption characteristics of two heavy metals, Cd and Pb, in three tropical soils (Mollisol, Oxisol, and Ultisol) from Puerto Rico were assessed at varying metal concentrations (0 to 1.2 mM) and pH values (approximately 2 to 7). All soils sorbed more Pb than Cd. Sorption maxima were obtained for each metal for the Oxisol and Ultisol soils, but not the Mollisol. Sorption appeared to depend more on soil mineralogy than organic matter content. Sorption isotherms were linear within the sorption envelope with similar slopes for each soil–metal curve, when plotting metal sorption as a function of pH. Cadmium and Pb isotherms yielded average slopes of approximately 36 ± 1 and 28 ± 1 units (percent increase in metal sorption per 1-unit increase in pH), respectively. Metal sorption depended more on metal type than soil composition. Cadmium sorption displayed a greater pH dependence than Pb. Cadmium sorption was less than or equal to the amount of negative surface charge except at pH values greater than the point of zero net charge (PZNC). This suggests that Cd was probably sorbed via electrostatic surface reactions and/or possible inner-sphere complexation at pH > 3.7. However, the amount of Pb sorbed by the Oxisol was greater than the amount of negative surface charge, suggesting that Pb participates in inner-sphere surface reactions. Lead was sorbed more strongly than Cd in our soils and poses less of a threat to underlying ground water systems due to its lower mobility and availability.

T$_{\text{HE INCREASING CONSUMPTION}}$, production, and exploitation of the earth's raw materials (fossil fuels and minerals), coupled with the exponential growth of the world's population over the past 200 years, have resulted in environmental buildup of waste products, of which heavy metals are of particular concern (Adriano, 1986; Purves, 1977). Soils are an important sink for these metals due to soils' high metal retention capacities.

Important heavy metals posing threats to soil quality and human health include Cd and Pb. They are used for a wide variety of industrial, urban, and agricultural applications and can be toxic to humans (Adriano, 1986; Angelone and Bini, 1992; Forstner, 1995; Kabata-Pendias and Pendias, 1992). People exposed to low levels of Cd over time may incur kidney damage as well as lung, bone, cardiovascular system, liver, and reproductive system damage (Hrudey et al., 1995; USEPA, 1992). In children, Pb has been known to cause decreases in IQ scores, retardation of physical growth, hearing problems, impaired learning, as well as decreased attention and classroom performance. In individuals of all ages, Pb may 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).

Many studies have evaluated heavy metal concentrations, mobilities, and partitioning in temperate soils (Barbarick et al., 1998; Chang et al., 1984; Gong and Donahoe, 1997; Jang et al., 1998; Johnson and Petras, 1998; Jordan and LeChevalier, 1975) as well as pure mineral specimens and synthetic analogs (i.e., kaolinite, gibbsite, goethite; Balistrieri and Murray, 1982; Bibak, 1994; Dalang et al., 1984; Eick et al., 1999; Forbes et al., 1976; Haas and Horowitz, 1986; Jenne, 1968; Puls et al., 1991; Rose and Bianchi-Mosquera, 1993); however, relatively few experiments have been conducted on tropical soils (Hanafi and Maria, 1998; Hanafi and Sjiola, 1998; Hue and Ranjith, 1993; Naidu et al., 1997; Wilcke et al., 1998). This has resulted in a large disparity between what is known about heavy metal contamination in temperate region soils compared with their tropical counterparts.

The properties of many tropical soils differ significantly from properties of soils in temperate regions. Whereas temperate region soils are composed of clays with mostly permanent negative surface charge, highly weathered tropical soils (Oxisols, Ultisols, Andisols, and acid Alfisols) generally have low surface charge density and consist, predominantly, of materials with variable charge or pH-dependent charge (McBride, 1994). Surface charge in these systems depends on activities of potential-determining ions (H^+ and OH^-) and electrolyte concentrations (Barrow, 1987; van Olphen, 1977). Depending on soil pH, these surfaces can be negatively or positively charged or exhibit a point where the net total charge on the particle is zero (PZC).

Due to their low negative surface charge densities at common pH values (4–5), highly weathered tropical soils may exhibit relatively low affinities for heavy metals (McBride, 1994). The persistence and mobility of Cd and Pb in these soils are dictated by the extent to which the metals sorb to solid phases, which is a function of reactions affecting surface charge (i.e., pH and ionic strength; Naidu et al., 1997).

Increasing ionic strength (I) and the pH to greater than the PZC in tropical soil systems increases negative surface charge (Marcano-Martinez and McBride, 1989; van Olphen, 1977; van Raij and Peech, 1972). Many researchers have shown increased Cd and/or Pb sorption in tropical soils and/or in pure oxidic mineral systems (i.e., goethite) with increasing pH (Bruemmer et al.,

Abbreviations: BET, Brunauer–Emmett–Teller; CEC, cation exchange capacity; I, ionic strength; pH$_{50}$, pH of 50% sorption; PZC, point of zero charge; PZNC, point of zero net charge.

1988; Davis and Leckie, 1978; Dzombak and Morel, 1986; Kinneburgh et al., 1976; Naidu et al., 1994; Puls et al., 1991; Rose and Bianchi-Mosquera, 1993; Tiller et al., 1984) due mainly to increased negative surface charge.

However, little research has been done directly comparing surface charge with heavy metal sorption in variable-charge systems. Naidu et al. (1994) looked at the effects of this parameter on the sorption of Cd in some highly weathered soils while Haas and Horowitz (1986) did a similar experiment on kaolinite. Knowledge of surface charge as it changed with pH enabled these researchers to determine the PZC. This information allowed them to propose probable mechanisms of Cd sorption (i.e., molecular-level information) from their macroscopic data.

Understanding mechanisms of metal sorption in soils is important as these reactions dictate the strength of the metal–soil surface interaction. The stronger the interaction of Cd and/or Pb with the soil surface, the less the likelihood of environmental contamination (plant and ground water). On a relative basis, exchange reactions (i.e., reversible electrostatic or outer-sphere reactions) render the metals most labile, whereas inner-sphere complex formation and coprecipitation with soil surfaces (i.e., bond formation between contaminant metal and soil surface) cause the Cd and Pb to be retained strongly and in many cases nearly irreversibly (McBride, 1994).

The literature is replete with research considering the sorption of heavy metals in temperate-region soils as a function of pH, I, initial metal concentration, and effect of background electrolyte. However, relatively little has been published on the effects of these variables on Cd or Pb sorption in highly weathered tropical soils. With this in mind, the objectives of this research were to investigate how varying initial metal concentrations and soil solution pH and I affect surface charge as well as the sorption of Cd and Pb in tropical soils (Oxisol, Ultisol, and Mollisol).

MATERIALS AND METHODS

Soil Samples

The surface horizons (0–15 cm) of three tropical soils from Puerto Rico were sampled between 1996 and 1998, air-dried, and ground to a particle size of 0.5 mm prior to being used in this study. A Mollisol (fine loamy, mixed, isohyperthermic Cumulic Haplustoll) obtained from the Lajas Valley area near the southwest coast, an Oxisol (clayey, oxidic, isohyperthermic

Typic Acrorthox) sampled near Mayaguez on the west coast, and an Ultisol (clayey, mixed, isohyperthermic Typic Tropohumult) taken from the central mountainous area near Corozal were used. The soils were selected based upon their varying physicochemical properties. The important mineralogical and chemical properties of these soils are presented in Table 1.

Mineralogy of the soil clay fractions (<0.2 μm) was determined via X-ray diffraction (XRD) analysis using CuKα radiation. Magnesium- and K-saturated samples were scanned at $2°2\theta$ min^{-1} on ceramic tiles at 25°C. The K-saturated tiles were further scanned following heat treatments of 110, 300, and 550°C (Whittig and Allardice, 1986). Thermal gravimetric analysis (25 to 1000°C) was used to confirm and supplement the XRD data. Particle size was determined by the pipette method (Gee and Bauder, 1986) following removal of iron 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 to solution ratio = 1:2) using a pH meter equipped with combination gel-filled glass electrode. Specific surface areas were obtained via six-point Brunauer–Emmett–Teller (BET)–N_2 adsorption (Quantachrome Corporation, 1996). The cation exchange capacity (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). Total Fe and Al was determined by microwave digestion of soil samples according to USEPA Method 3051 (USEPA, 1995). All metals were determined by either inductively coupled plasma–atomic emission spectrometry (ICP–AES) or flame atomic absorption spectroscopy (AAS) and analyses were performed on duplicate samples (one assay for X-ray diffraction [XRD] and thermal gravimetric analysis [TGA]).

Determination of Cadmium and Lead Sorption

All experiments were performed under ambient laboratory conditions with no environmental gas control. Samples were not filtered before metal analysis on the flame AAS as prior experiments demonstrated no significant differences in metal concentrations between unfiltered samples and samples filtered through 0.45-μm Millipore (Bedford, MA) filters. Furthermore, there were three replicates for each treatment.

Sorption Isotherms as a Function of Initial Cadmium and Lead Concentration

Sorption isotherms for Cd and Pb were determined in three soils to ascertain the effects of soil and metal on soil–metal sorption capacity. A method similar to that of Naidu et al. (1994) was used to construct Cd and Pb sorption isotherms. Soil (approximately 1 g) was equilibrated with 30 mL of aqueous solution for 24 h at 25 ± 3°C on a reciprocating shaker in 50-mL polyethylene centrifuge tubes. Preliminary kinetic studies indicated that a 24-h reaction period was sufficient to

Table 1. Pertinent soil physicochemical properties.

Sample	Organic matter	PZNC†	pH	CEC‡	Sum H + Al	Total Fe + Al	Clay mineralogy§	Texture¶	Specific surface area
	%			—— cmol$_c$ kg^{-1} ——		—— % ——			m^2 g^{-1}
Oxisol	4.05	3.7	4.92	3.1	1.7	28.7	k > gi > go > q	10/34/56	41.9
Ultisol	1.86	2.3	4.74	11.0	7.1	8.6	k > is ≈ go > q	12/29/59	37.8
Mollisol	1.16#	–	6.86	20.9	–	6.9	is/v > m > k > q	39/39/22	17.3

† Point of zero net charge.
‡ Cation exchange capacity.
§ k, kaolinite; gi, gibbsite; go, goethite; is, interlayered smectite; is/v, interlayered smectite + interlayered vermiculite; m, mica; q, quartz.
¶ Sand/silt/clay.
# Does not meet classification requirements for quantity of organic matter necessary for a Mollic epipedon (Soil Conservation Service, 1994); however, soil classified as Mollisol based on location from which sample was taken.

achieve equilibrium conditions when using a reciprocating shaker. Aqueous solutions were prepared in $NaNO_3$ to have a final I of 0.01 M after addition of $Cd(NO_3)_2$ or $Pb(NO_3)_2$. The above ionic strength was chosen as preliminary experiments showed no significant differences between Cd and Pb sorption in solutions having I of 0.005 and 0.01 M. The former I value is representative of tropical soils (Gillman and Bell, 1978), whereas the later is typical of nonsaline temperate soils (McBride, 1994). Cadmium and Pb concentrations ranged from 0 to 1.2 mM as prior analysis demonstrated this concentration range allowed expression of the maximum metal sorption capacity of the Oxisol and Ultisol soils. After equilibration, the samples were centrifuged and the supernatant refrigerated (4°C) for later analysis of Cd and Pb on a flame AAS. The amount of Cd or Pb sorbed was calculated from the difference between the amount that was added and the portion remaining in solution after equilibration (soil blanks to which only 0.01 M $NaNO_3$ was added did not have a significant amount of either Cd or Pb).

Sorption of Cadmium and Lead as a Function of pH

Sorption of Cd and Pb was determined at varying pH values to elucidate pH effects on surface charge and metal sorption in representative tropical soils. Soil solutions containing approximately 1 g soil and 29 mL of 0.007 M $NaNO_3$ were prepared in 50-mL polyethylene centrifuge tubes. Suspension pH values of approximately 2 to 7 were attained by adjustment with either HNO_3 or NaOH. The solutions were shaken for 24 h at 25 ± 3°C, after which the pH was measured and readjusted if necessary. This was performed until the suspension pH values were stable at the desired levels. One milliliter of Cd or Pb, as nitrate salts, was then added at a metal concentration of 36 mM so the final metal concentration and I in the suspensions were 1.2 mM and 0.01 M, respectively. After metal addition, the solutions were shaken for 24 h at 25 ± 3°C. Suspension pH was measured and the samples were centrifuged. The supernatant was collected and analyzed for Cd, Pb, Al, and Fe on the flame AAS. Aluminum and Fe were measured to check for the dissolution of oxide minerals. It was found that at the lowest pH values (approximately 2.5), <2% of the total Al and <0.1% of the total Fe was dissolved from the soil samples indicating little oxide dissolution. Adjustment of pH affected I by a maximum of 20% and sample volume by no more than 3%.

Blank solutions containing only 1.2 mM $Cd(NO_3)_2$ or $Pb(NO_3)_2$ in 0.01 M $NaNO_3$ were titrated with NaOH to check for formation of solid phases. The addition of base yielded no precipitate in the presence of Cd in the pH range of this study; however, at pH ≥ 5.9 a solid phase was detected in the Pb-containing solution [supersaturated with $Pb(OH)_2$; Gustafsson, 2000].

Surface Charge

To elucidate possible Cd and Pb sorption mechanisms in the Oxisol and Ultisol, negative surface charge was estimated by measuring Na^+ retention as a function of pH (in the absence of Cd^{2+} or Pb^{2+}; $I = 0.01$ M) and compared with the amount (equivalents, $mmol_c$ kg^{-1}) of sorbed Cd and Pb. The negative surface charge of kaolinite (Kga-2) was also estimated as it was the dominant mineral component in these two soils. The Mollisol was not included as it was composed predominantly of permanent charge material (Table 1) and has little pH-dependent charge.

A modified method of Marcano-Martinez and McBride (1989) and Schofield (1949) was used. Air-dried samples of 2 g (<0.5 mm) were placed in preweighed 30-mL polyethylene centrifuge tubes to which 20 mL of 1 M NaCl was added. The samples were shaken for 1 h and centrifuged, with the supernatant being discarded. Amounts of 20 mL of 0.5 M NaCl were then added to the tubes, with sample pH being adjusted with HCl or NaOH to span the expected points of zero net charge (PZNC). This was followed by 12 h of shaking, centrifugation, and supernatant removal. The 0.5 M NaCl wash and pH adjustments were performed two more times, with shaking times of 1 h. The rigorous washing procedure was carried out to ensure exchange sites were saturated with Na^+ and Cl^-. Five washes were then performed with 20 mL of 0.01 M NaCl, with pH readjustment (no pH readjustment on last wash) and shaking for 1 h between washes.

After the final NaCl wash, supernatant pH (equilibrium pH) was measured. The supernatants were discarded and samples weighed to compensate for any entrained NaCl solution. Adsorbed Na^+ and Cl^- were then displaced by five washings with 20-mL aliquots of 0.5 M NH_4NO_3. Extracts were combined and filtered through 0.45-μm Millipore nylon filters and stored in a refrigerator prior to analysis. Concentrations of Na^+ (determined by inductively coupled argon plasma [ICAP]–AES) and Cl^- (found colorimetrically; Domask and Kobe, 1952) displaced were corrected for occluded NaCl in the soil volume and used as measures of negative and positive charges, respectively, to determine the soil PZNC values and the amount of negative surface charge as it varied with pH.

Statistics

The SAS program (SAS Institute, 1996) was used to calculate the means and least significant differences ($p < 0.01$) between the amounts of Cd or Pb sorbed for various treatments in different soils.

RESULTS AND DISCUSSION

Sorption Isotherms as a Function of Initial Cadmium and Lead Concentration

Sorption isotherms of Cd and Pb were constructed to compare metal sorption capacity between different soils and metals (Fig. 1). Lead sorption was greater than Cd sorption in the Oxisol and Ultisol samples at an initial metal concentration of >0.1 mM ($p < 0.01$). The Mollisol sample sorbed roughly equal amounts of Cd and Pb up to an initial metal concentration of 0.4 mM ($p \geq 0.8$). This type of sorption behavior is typical of Mollisols and other temperate-region soils (Hooda and Alloway, 1994, 1998) due in part to their mineralogy (yielding a higher CEC), higher pH, and generally greater amount of sorption sites compared with highly weathered tropical soils (McBride, 1994; Table 1).

The preference exhibited by these soils for Pb over Cd (Fig. 1) has been observed by others (Gao et al., 1997; Pardo, 2000; Phillips, 1999) and may be attributed to Pb's smaller hydrated radius (Pb^{2+} = 0.401 nm, Cd^{2+} = 0.426 nm; Nightingale, 1959); the greater affinity of Pb for most functional groups in organic matter, which are hard Lewis bases—carboxylic and phenolic groups (Pb^{2+} is a borderline hard Lewis acid while Cd^{2+} is a soft Lewis acid); as well as its higher electronegativity (2.10 and 1.69 for Pb and Cd, respectively) and pK_H (negative log of hydrolysis constant; 7.78 and 11.70 for Pb and Cd, respectively), making it a better candidate

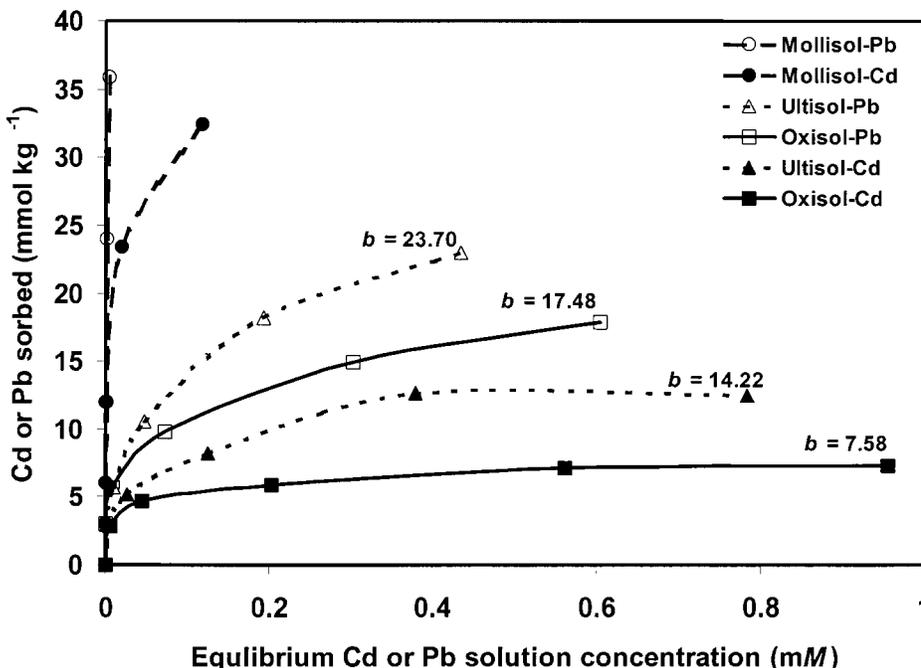**Fig. 1. Cadmium and Pb sorption isotherms ($I = 0.01$ M NaNO$_3$). b is the sorption maximum as determined by the linear form of the Langmuir equation in units of mmol kg^{-1}. Ultisol and Oxisol, $R^2_{Pb\&Cd} = 0.99$.**

than Cd for electrostatic and inner-sphere surface complexation reactions (Huheey, 1983; McBride, 1994).

At the maximum initial metal concentration (1.2 mM), the Oxisol and Ultisol soils exhibited sorption maxima (L-type sorption), as determined by the linearized form of the Langmuir equation (Eq. [1]), for both metals while the Mollisol (H-type sorption) did not. However, in the latter soil, the sorption isotherm for Cd began to bend at the two highest initial metal concentrations (0.8 and 1.2 mM), suggesting an approach toward a sorption maximum. This was not evident when Pb was added at the same concentrations:

$$C/(x/m) = 1/(kb) + C/b \qquad [1]$$

The equilibrium solution metal concentration (mM) is given by C, x/m is the amount of metal sorbed in mmol kg^{-1} of soil, b is the sorption maximum (mmol kg^{-1}), and k is a constant relating to the binding energy of Cd or Pb to the soil.

Metal sorption followed the general trend of Mollisol > Ultisol > Oxisol and Pb > Cd (significantly different at $p < 0.01$ at metal concentrations of 0.8 and 1.2 mM). The trends reflected the differences in soil clay mineralogy and CEC but were contrary to the clay quantity and BET surface area values for these three soils (Table 1). The Mollisol contained the highest amount of permanent charge minerals (highest CEC) but the lowest clay content and BET surface area among the three soils. The Oxisol (high clay content and highest relative surface area) consisted exclusively of variable-charge materials (1:1 phyllosilicates, Fe and Al oxides, and organic matter) and had the lowest CEC of the three soils. Therefore, in our soils, metal sorption was more dependent on clay type than amount of clay and BET (external) surface area was not a good predictor of the soils'

ability to sorb metals. Also, the data suggest that if organic matter was the critical factor in metal sorption in these soils, the Oxisol would have sorbed the greatest amount of metals as it contained the most organic matter of the three soils. As this was not the case, the inorganic colloidal fraction appeared to be the dominant sorbent for the two metals, which is consistent with results obtained by Hanafi and Sjiaola (1998) for Cd and Zn sorption in tropical soils from Malaysia.

Sorption of Cadmium and Lead as a Function of pH

Soil pH plays a major role in the sorption of heavy metals as it directly controls the solubilities of metal hydroxides, as well as metal carbonates and phosphates. Soil pH also affects metal hydrolysis, ion-pair formation, organic matter solubility, as well as surface charge of iron and aluminum oxides, organic matter, and clay edges (Bruemmer et al., 1986; McBride, 1994; Sauve et al., 1988a,b). Increasing soil pH increases cationic heavy metal retention to soil surfaces via adsorption, inner-sphere surface complexation, and/or precipitation and multinuclear type reactions (McBride, 1994; Sparks, 1995). This phenomena has been demonstrated by many researchers in a variety of temperate region soils and soil mineral analogs in both batch and column studies (Altin et al., 1999; Basta et al., 1993; Kinneburgh et al., 1976; Rose and Binachi-Mosquera, 1993; Yong and Phadungchewit, 1993).

Soil sorption of Cd and Pb in our experiment followed the expected trend of increased metal sorption with increased soil pH (Fig. 2). The pH$_{50}$ values (pH at 50% metal sorption; Kinneburgh et al., 1976) followed a similar trend as those found for the isotherm study: Molli-
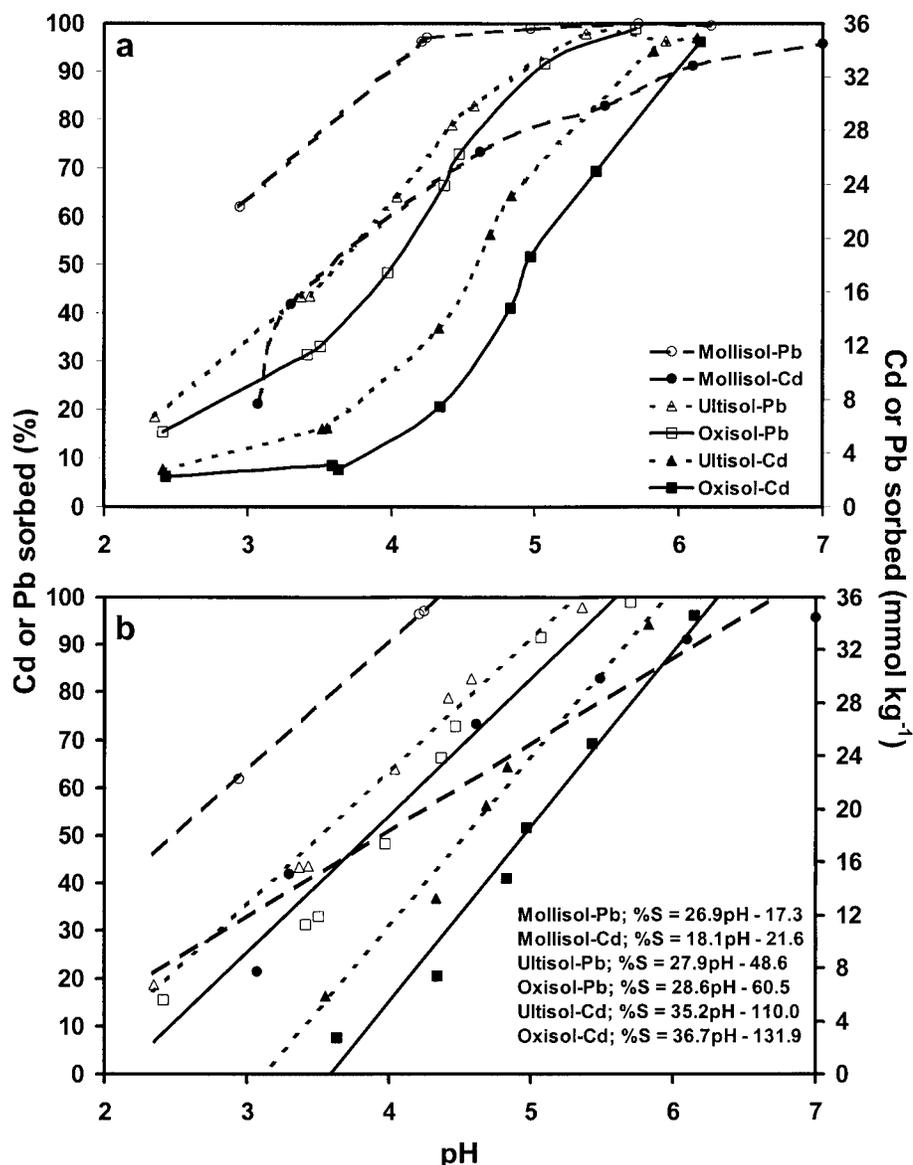
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Fig. 2. (a) Cadmium and Pb sorption as a function of pH ($I = 0.01\ M$ NaNO$_3$). (b) Sorption envelopes of Cd and Pb using a linear model ($R^2 > 0.91$). Points where the $\Delta\%$ sorbed was $\leq 8\%$ when ΔpH was approximately 1 were omitted ($I = 0.01\ M$ NaNO$_3$; %S = percent sorbed).

sol–Pb (2.45, linear interpolation) $<<$ Mollisol–Cd (3.55) $<$ Ultisol–Pb (3.62) $<$ Oxisol–Pb (4.00) $<$ Ultisol–Cd (4.60) $<$ Oxisol–Cd (4.92). The only significant differences ($p < 0.01$) in pH$_{50}$ values (within a soil order) were those found for Mollisol–Pb and Mollisol–Cd. Within a soil type, Pb had lower pH$_{50}$ values than Cd, which is similar to results published by Kinneburgh et al. (1976) for Fe and Al oxides.

Data in Fig. 2a identified regions along the pH continuum where sorption behavior was most affected by pH (sorption envelope), and other areas where sorption increased less (ΔpH of approximately 1 resulted in a $\Delta\%$ sorbed of $\leq 8\%$). Furthermore, in the sorption envelope the slopes of the sorption curves appeared to be similar. Therefore, in the low sorption areas (as defined above), the data points were removed and straight lines were fit to the remaining data yielding lines with $R^2 \geq$ 0.91 (Fig. 2b).

Slopes of the lines (excluding Mollisol–Cd data) suggest that metal sorption depended more on metal type than on soil composition (Fig. 2b). The slopes of the Pb sorption curves were similar and within ± 1 unit of each other, whereas those of Cd had slightly more variability. A unit increase in pH resulted in approximately 28 and 36% (average of Oxisol and Ultisol values, respectively) increase in Pb and Cd sorption, respectively. Therefore, Cd sorption occurred over a narrower pH range than Pb regardless of soil composition. This behavior can be attributed to a greater tendency of Pb to undergo both inner- and outer-sphere surface reactions than Cd over a wide pH range. An anomaly to the above generalization was the Mollisol–Cd line, which exhibited the lowest slope of all soil–metal lines (approximately one-half that of the Oxisol–Cd and Ultisol–Cd lines). This was indicative of sorption phenomena occurring over a larger pH range compared with the other soils (Fig. 2).
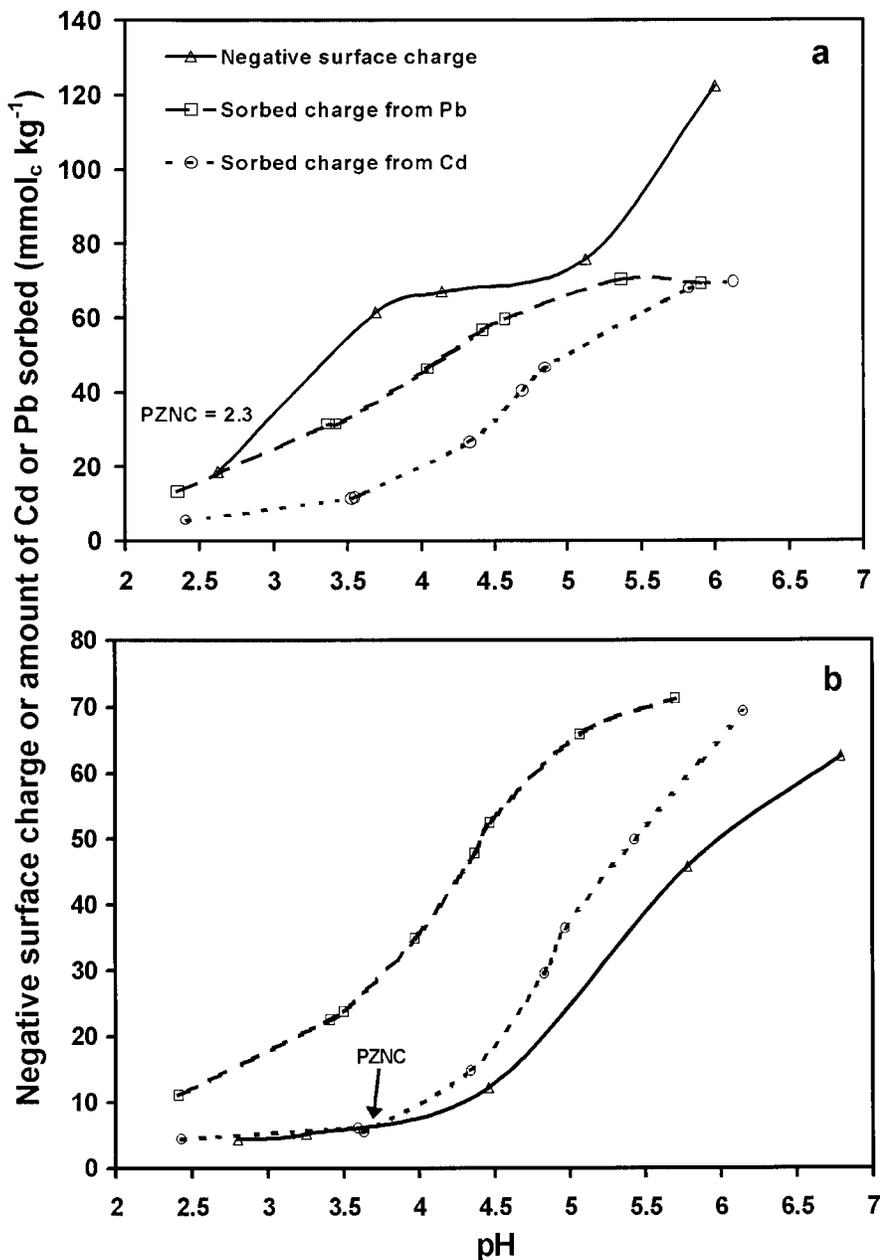
Fig. 3. Relationship between the amount of sorbed Cd or Pb and the amount of negative surface charge for the (*a*) Ultisol and (*b*) Oxisol as a function of pH (*I* = 0.01 *M* NaNO$_3$ or NaCl). Complete sorption of added Cd or Pb corresponds to 72 mmol$_c$ kg^{-1}.

Cadmium(II) is a closed-shell cation (valence orbital is full—d^{10}) that favors coulombic-type reactions (Huheey, 1983) at soil surfaces as opposed to inner-sphere surface reactions (electron sharing). Thus, Cd sorption should increase more than Pb sorption with increases in soil CEC. Hanafi and Sjiaola (1998) observed that CEC was highly positively correlated (*r* = 0.89) to the sorption of Cd^{2+} and Zn^{2+} (d^{10} cations) in acid tropical soils. Naidu et al. (1998) found Cd sorption to depend strongly on surface charge density in tropical soils while Zachara et al. (1992) found that sorption of Cd on the edges of layer silicates and on Fe and Al oxides was controlled by the CEC (at pH < 6.5).

Surface charge on the Mollisol predominantly originated from minerals with constant surface charge (Table

1), and its negative surface charge density should not have increased much over the pH range of this experiment (approximately 2 to 7) compared with the Oxisol and Ultisol. Thus, the Mollisol–Cd curve had a relatively flat slope (approximately 18 units) compared with the sorption curves of the other soils (Fig. 2b). Yong and Phadungchewit (1993) reported similar sorption behavior for Cd on montmorillonite; metal sorption occurred over a wider pH range on montmorillonite than on kaolinite or illite. They also observed lower pH$_{50}$ values for Pb than Cd in clayey soils (ΔpH$_{50}$ of approximately 2 units). In contrast to the Mollisol, the Oxisol and Ultisol soils in our study were predominantly composed of minerals with variable charge (Table 1). These two latter soils displayed great increases in negative surface
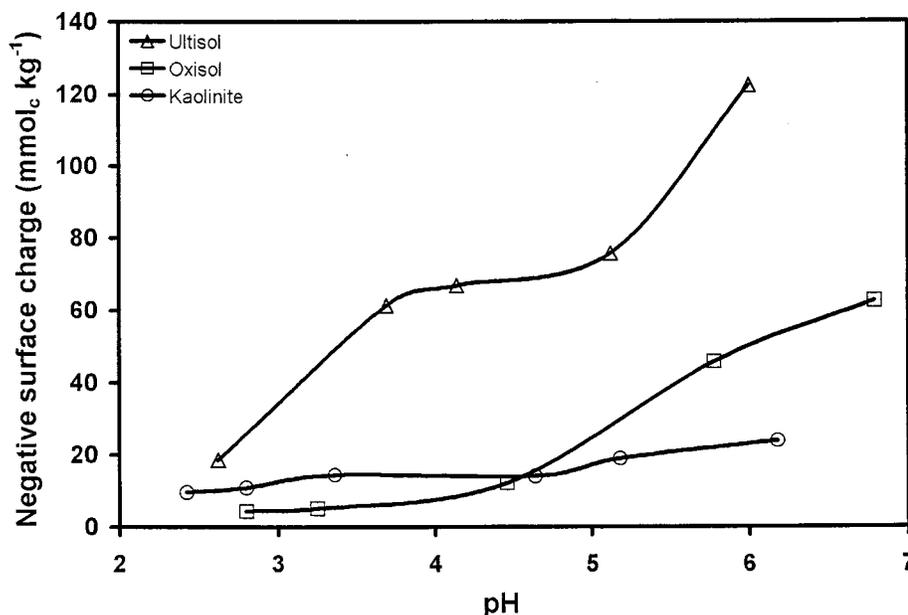
Fig. 4. **Relationship between the net negative surface and pH ($I = 0.01$ M NaCl).**

charge with increasing pH (Fig. 3). It follows that the sorption curves of these soils had steeper slopes of Cd sorption as a function of pH (approximately 36 units) than in the Mollisol soil. Naidu et al. (1994) also reported steep sorption isotherms for Cd in two Oxisols with increasing pH.

Surface Charge and Cadmium and Lead Sorption

Comparing the amount of negative surface charge to the amount of sorbed Cd^{2+} or Pb^{2+} (mmol$_c$ kg^{-1}), as a function of pH, yielded information regarding the nature of the reactions occurring on the surfaces of the Oxisol and Ultisol soils. The PZNC values of the Ultisol and Oxisol were approximately 2.3 and 3.7, respectively. At pH values below the PZNC, the soil surfaces had net positive charge and would, therefore, be prone to electrostatically repel cations. The Oxisol retained metals below its PZNC, whereas sorption curves are above zero (≥ 5 mmol$_c$ kg^{-1}) at pH < 2.5 (Fig. 2a) for the Ultisol. As cation retention would not be favored when the soil surfaces contained net positive charge, this sorption behavior could be indicative of inner-sphere surface complexation or adsorption to sites possessing some negative charge (e.g., permanent charge sites such as vermiculite, smectite, and/or organic matter).

Figure 3 further elucidates the nature of the metal surface interactions by presenting the relationship between pH and the amount of sorbed Cd^{2+} or Pb^{2+} (expressed in equivalents, mmol$_c$ kg^{-1}) and the negative surface charge determined from adsorption of Na$^+$. In most cases, the Ultisol had more negative surface charge at a given pH than the amount of either Cd^{2+} or Pb^{2+} sorbed. An exception may possibly be found for the sorption of Pb at pH ≤ 2.6, where the surface charge and Pb sorption curves intersect (Fig. 3a), but the data are inconclusive. Yong and Phadungchewit (1993) observed Pb sorption at pH < 2 in several clayey soils that

retained much less Cu, Zn, and Cd at about the same pH values. We suggest that the sorption reactions were mainly nonspecific (electrostatic) at low pH, with some evidence of specific inner-sphere surface complexation of Pb at pH ≤ 2.6. However, oxide solubility and the 0.01 background I become highly dependent on pH at these low values (<2.5); thus, ascertaining modes of metal sorption with any certainty becomes difficult.

The amount of Pb sorbed by the Oxisol, at any pH, was well above the amount of negative surface charge (>10 mmol$_c$ kg^{-1}), while the amount of Cd sorbed closely mirrored the quantity of negative surface charge up to the PZNC (Fig. 3b). The data suggest both inner- and outer-sphere reactions of Pb with the soil surface, whereas Cd probably sorbs to exchange sites. However, above a pH of approximately 3.7, the amount of Cd sorbed exceeded the CEC, which may suggest inner-sphere surface complexation.

Soil solutions were undersaturated with respect to solid formation of Cd(OH)$_2$ and Pb(OH)$_2$ as well as CdCO$_3$ and PbCO$_3$ (PCO$_2$ = $10^{-4.5}$ MPa). Furthermore, when matrix blanks [solutions containing NaNO$_3$ + Cd(NO$_3$)$_2$ or Pb(NO$_3$)$_2$] were titrated with base, no solid phase was formed in the presence of Cd in the pH range of the experiment. However, there was evidence for Pb(OH)$_2$ (s) only at pH ≥ 5.9. Figure 3 shows that the highest pH values in experiments involving Pb were 5.9 and 5.7 for the Ultisol and Oxisol, respectively. Thus, solid-phase precipitation can generally be ruled out as a retention mechanism here.

Regarding the negative surface charge curve for the Ultisol (Fig. 3a), we noticed that the negative surface charge appeared to be buffered between pH values of approximately 3.7 to 4.7 (relatively flat slope) while the Oxisol (Fig. 3b) did not exhibit such behavior. Upon comparing the negative surface charge curves for these soils and kaolinite as a function of pH, we noticed similarities only in the shapes of the Ultisol and kaolinite

curves (Fig. 4). This was surprising in that both soils were dominated by kaolinite in the clay mineral fractions (approximately 45 and 49%, respectively, for the Ultisol and Oxisol soils). However, the Oxisol contained more than twice as much organic matter as the Ultisol (Table 1), which most likely overshadowed kaolinite's buffering capacity as was witnessed by the latter soil in the pH range 3.7 to 4.7.

CONCLUSIONS

Experiments conducted on the sorption of Cd and Pb in tropical soils from Puerto Rico indicated greater affinity of Pb for soil sorption sites than Cd. The sorption maxima (estimated from the linearized Langmuir equation) were greater (approximately 10 mmol kg^{-1}) for Pb than for Cd in the Oxisol and Ultisol. The Mollisol failed to demonstrate a sorption maximum for either metal as the treatment concentrations in our experiment (0 to 1.2 mM metal) were not high enough to show this behavior. This soil exhibited a preference for Pb over Cd. Metal sorption as a function of pH yielded similar results, where pH$_{50}$ values increased in the order: Mollisol–Pb < Mollisol–Cd < Ultisol–Pb < Oxisol–Pb < Ultisol–Cd < Oxisol–Cd. These trends are in agreement with soil CEC variation and inversely related to soil organic matter contents, clay contents, and BET surface areas. Soil mineralogy (i.e., clay type; presence of 2:1 permanent charge clay minerals) was more important for Cd and Pb sorption than the quantity of organic matter and the external surface area in these soils.

Within the sorption envelopes (ΔpH of approximately 1 resulted in a Δ% sorbed of >8%), Cd sorption curves had similar slopes across all soils (excluding Mollisol–Cd) as did the Pb sorption curves for each of the soils. Straight lines were fit to the data yielding $R^2 \geq 0.91$ and slopes of 28 ± 1 and 36 ± 1% increase in Pb or Cd sorption per 1-unit increase in pH, respectively. We conclude that metal type is more important than soil composition for the sorption of either Cd or Pb in our soils. Furthermore, pH had a larger effect on Cd sorption than on Pb sorption.

Plots of negative surface charge and sorbed Cd or Pb (Oxisol and Ultisol only) vs. soil pH were used to suggest possible sorption mechanisms (outer- vs. inner-sphere). Both soils probably sorbed Cd electrostatically in the low pH ranges (<4) and possibly through inner- and outer-sphere reactions above pH 4. At pH > 4, the negative surface charge closely mirrored or was greater than the amount of sorbed Cd in these soils. The amount of Pb sorbed, on the other hand, was much larger (≥10 mmol$_c$ kg^{-1}) than the amount of negative surface charge throughout the pH range (2.5 to 6.5) for the Oxisol, suggesting both inner- and outer-sphere reactions. Evidence for inner-sphere reactions of Pb and the Ultisol surface sorption sites, especially at pH > 2.6, was inconclusive. Therefore, Pb demonstrated a higher affinity for tropical soil sorption sites relative to Cd. The former metal also confirmed its ability to take part in inner-sphere surface reactions (especially at pH < PZNC),

rendering it much less bioavailable and mobile in the soil environment, compared with Cd.

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