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Adsorption–Desorption Characteristics of Lead in Variable Charge Soils

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ABSTRACT

Adsorption–desorption processes of Pb at contaminated levels in two variable charge soils were investigated. The red soil (RAR) developed on the Arenaceous rock (clayey, mixed siliceous thermic typic Dystrochrept) adsorbed more Pb^{2+} than the red soil (REQ) derived from the Quaternary red earths (clayey, kaolinitic thermic plinthite Aquult). The maximum adsorption values (X_m) that were obtained from the simple Langmuir model were 52.6 mmol Pb^{2+} kg^{-1} soil and 29.9 mmol Pb^{2+} kg^{-1} soil, respectively, for the RAR and REQ. Adsorption of Pb^{2+} decreased soil pH by 1.10 unit for the RAR soil and 1.21 unit for the REQ soil at the highest loading. The adsorption equilibrium pH of RAR was higher than that of REQ at the same Pb^{2+} concentration. The distribution coefficient (K_d) of Pb in the soils decreased exponentially with increasing Pb^{2+} loading. Most of the adsorbed Pb^{2+} in the soils was not desorbed in the 0.01 mol L^{-1} $NaNO_3$ solution. After five successive extractions with $NaNO_3$, only 0–11% of the total adsorbed Pb^{2+} in the RAR soil was desorbed and the corresponding value of the REQ soil was 0–19%, indicating that the RAR soil had a greater affinity

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for Pb^{2+} than the REQ soil at the same Pb^{2+} loading. Different mechanisms might be involved in Pb^{2+} adsorption/desorption at different levels of Pb^{2+} loading and between the two soils.

Key Words: Adsorption; Desorption; Lead; pH; Variable charge soils.

INTRODUCTION

Lead contamination frequently occurs in the industrialized countries, most urban soils having total Pb levels above the geochemical "background levels" of 10–20 mg of Pb kg^{-1}.[1] Lead contamination of the environment arises from many industrial and agricultural sources, such as Pb contained in storage batteries, smelting and burning of coal, metal plating and finishing operations, fertilizers, pesticides, and from additives in pigments and gasoline.[2,3] The increasing consumption, production, and exploitation of the earth's raw materials, 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.[4]

Heavy metals including Pb pose great threats to soil quality and human health. They are used for a wide variety of industrial, urban, and agricultural production and can be toxic to humans.[4] Lead is classified as a carcinogen and is toxic to most living organisms at high exposures. Unlike many other trace metals there is no demonstrated biological need for Pb.[2] Lead 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. 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.[5]

Soil is an important sink for heavy metals due to its high metal retention capacities. Various solubility diagrams have been presented to explain the solubility of Pb and the interactions with various other mineral phases. Such diagrams, though a reasonable representation of pure synthetic systems, may be less applicable to soils. In soils, the presence of additional cations and anions, a heterogeneous adsorptive mineral phase, and an ill-defined organic matter component limit theoretical solubility diagrams to no more than a representation of potential trends. Reactive surfaces often control metal solubility in soils with low to moderate contamination, whereas with heavy loadings does mineral precipitation control metal solubility. In addition, dissolved organic matter can enhance metal solubility; organic matter in the solid phase contributes to metal adsorption and modifies reactive mineral surfaces.[6] At low pH in the environment, Pb exists primarily as the aqueous $Pb(H_2O)_6^{2+}$ ion, whereas at higher pH, it readily forms aqueous complexes with hydroxyl ions. Lead also forms ion pairs with chloride, sulfate, and carbonate.[2] Additionally, Pb is strongly adsorbed onto many mineral surfaces, especially oxides of iron and aluminum. Since only the dissolved form is readily bioavailable in the short term, the low solubility of Pb-bearing minerals such as carbonates, phosphates, and sulfides may control Pb bioavailability, depending upon soil conditions and the initial form of Pb contamination. The least soluble Pb minerals in aerobic soils are the lead phosphates. Consequently, in many situations, the soil solution concentration of phosphate may control the solubility and availability of Pb.[7] These solid-phase interactions contribute to the low levels of Pb commonly observed in aqueous environments.[2]

Variable charge soils (Oxisols, Ultisols, Andisols, and acid Alfisols) generally have low surface charge density with predominant pH-dependent charge. Surface charge in these systems also depends on the activities of potential-determining ions (H^+ and OH^-) and electrolyte concentrations.[8] 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), the variable charge soils may exhibit relatively low affinities for heavy metals.[9]

The persistence and mobility of Pb in the variable charge soils are dictated by the extent to which the metals are adsorbed onto the solid phases, which is a function of reactions affecting surface charge (i.e., pH and ionic strength).[10] Understanding mechanisms of metal adsorption in soils is important as these reactions control the strength of the metal–soil surface interactions. The stronger the interaction of Pb with soil surface, the less the likelihood of its contamination to the environment (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 co-precipitation of Pb with soil surfaces (i.e., covalent bond formation between contaminant metal and soil surface) cause the Pb to be strongly retained, in many cases irreversibly.[9] Additionally, Pb has a small hydrated radius ($Pb^{2+} = 0.401\,nm$); the great affinity of Pb for most functional groups in organic matter, which are hard Lewis bases-carboxylic and phenolic groups; as well as its high electronegativity (2.10) and pK_H (negative log of hydrolysis constant 7.78), make it a better candidate for electrostatic and inner-sphere surface complexation reactions.[9]

Understanding surface sequestering processes in soils should allow us to better evaluate the bioavailability and, hence, potential toxicity of trace metals to organisms, including human beings.[11] However, relatively little information is available on the characteristics of Pb adsorption–desorption in variable charge soils, which are widespread in China. The objectives of this research were to investigate the adsorption–desorption of Pb in two typical variable charge soils and to evaluate major factors and mechanisms involved in the surface reactions.

MATERIALS AND METHODS

Soils Samples

Two representative variable charge soils were used in this study: the RAR soil (clayey, mixed siliceous thermic typic Dystrochrept), derived from Arenaceous rock, and the REQ soil (clayey, kaolinitic thermic plinthite Aquult), developed on Quaternary red earths. Soil samples were collected at 0–20 cm from Longyou County (119°02′–120°20′E, 28°44′– 29°17′N), Zhejiang Province, Southeastern China.

Table 1. Basic properties of the tested soils.

Items		RAR soil	REQ soil
pH (H_2O) (1 mol L^{-1} KCl)		5.31/3.69	4.77/3.42
Organic matter (g kg^{-1})		12.9	25.8
Total Pb (mg kg^{-1})		46.07	29.61
Available Pb (mg kg^{-1}) (0.1 mol L^{-1} HCl, 1:5)		0.2232	0.445
CEC (cmol kg^{-1})		21.15	15.59
Exchangeable acidity (cmol kg^{-1})		1.097	2.9
Exchangeable H^+ (cmol kg^{-1})		0.856	0.789
Exchangeable Al (cmol kg^{-1})		0.24	2.11
Clay minerals		Kaolinite, Fe and Al oxides, chlorite, illite	Kaolinite, Fe, and Al oxides
Particle composition (%)	1–0.05 mm	56.97	9.86
	0.05–0.01 mm	27.68	23.77
	0.01–0.005 mm	4.07	13.92
	0.005–0.001 mm	8.88	24.62
	<0.001 mm	2.40	27.84

Composite samples of the soils were air-dried, ground, and passed through a 2 mm sieve prior to use. Some basic physicochemical properties of the soils are listed in Table 1. Based on X-ray diffraction analysis of powder samples, the dominant clay minerals in both soils were kaolinite, iron and aluminum oxides, and quartz. However, the RAR soil contained also small amounts of chlorite and illite (Table 1).

Soil pH was measured using a pH meter (Thermo Orion 250, Orion Research, Inc. Boston, MA, USA) at a soil to solution ratio of 1:2.5 in both deionized water and 1 mol L^{-1} KCl. Soil organic carbon was determined by the modified Tinsley method.[12] Total exchangeable acidity and exchangeable Al^{3+} and H^+ were determined by the 1 mol L^{-1} extraction–titration method.[13] Particle size distribution was measured by the hydrometer method.[14] The CEC and exchangeable bases were determined using 1 mol L^{-1} NH_4Cl (pH 7.0) following the procedure described by Bao.[13] Exchangeable Pb was extracted by 0.1 mol L^{-1} HCl at a soil to solution ratio of 1:5[13] and total Pb in the soil sample was determined by HF-$HClO_4$ digestion method.[15] The concentrations of Pb in the extract or digest were measured using atomic absorption spectrometry (AAS) in an acetylene-air flame (AA6800, Shimadzu, Kyoto, Japan). For the metals present in high concentrations the supernatant solution was diluted with deionized water and the concentrations were obtained directly from appropriate calibration curves prepared with the components of the extraction solution diluted by the same factor.

Adsorption of Pb^{2+} Ion

Portions of 2.0 g air-dried soil were placed into 100-mL polypropylene centrifuge tubes, and 50 mL of 0.01 mol L^{-1} $NaNO_3$ (pH 5.0) solution containing

0, 2.5, 5, 10, 25, 50, 100, 150, 200, 300, 400, 500 mg Pb L^{-1} [as $Pb(NO_3)_2$] were added to each tube. The suspensions were shaken at 200 rpm for 2 h at 25°C and then equilibrated in a dark incubator for an additional 22 h. No pH control was imposed. At the end of the designated time, the suspensions were centrifuged at $2000 \times g$ relative centrifugal force for 10 min and filtered. Ten milliliters of the filtrate were transferred into a 10-mL polypropylene centrifuge tube for measuring Pb^{2+} concentration using the AAS. Total amounts of adsorbed Pb^{2+} were calculated by the difference between the total applied Pb^{2+} and the solution Pb^{2+} in the equilibrium solution. The remaining solution was used for measuring pH.

Desorption of Adsorbed Pb^{2+} Ion

The tube with the soil residue separated from the supernatant solution by centrifugation was weighed to measure the residual Pb^{2+} in the solution. Fifty milliliters of 0.01 mol L^{-1} $NaNO_3$ (pH 5.0) were added to each tube containing the Pb-enriched soil residue. The suspensions were shaken at 200 rpm for 2 h at 25°C and equilibrated for an additional 22 h. The equilibrated suspensions were then centrifuged at $2000 \times g$ relative centrifugal force for 10 min and filtered. Ten milliliters of the filtrate were transferred into a 10-mL polypropylene centrifuge tube for measuring Pb^{2+} concentration. The remaining solution was used for measuring pH. In order to estimate the affinity of Pb^{2+} in soils, the desorption process was repeated five times (D1 to D5). The nonextractable fraction of the adsorbed Pb^{2+} was obtained by the difference between the total adsorbed Pb^{2+} and the total recovered Pb^{2+} by five successive extractions with the $NaNO_3$ solution (pH 5.0).[16]

The amounts of protons released during Pb^{2+} adsorption were quantified by titrating another 10 mL of the filtrate with standardized NaOH solution (0.004 mol NaOH L^{-1}, diluted from 0.02 mol NaOH L^{-1} freshly prepared and standardized before use).

All glassware and plastic-ware used in this study were previously soaked in 14% HNO_3 (v/v) and rinsed with deionized water. All reagents used were of analytical grade or better.

Statistical Analysis

All data were processed by Microsoft Excel, and the regression and other statistical analyses were conducted using the programs of Statistical Package SPSS 10.0.

RESULTS

Adsorption Isotherms of Lead

Adsorption isotherms of Pb were constructed to compare metal adsorption capacity between the two different soils. Lead adsorption was greater in the RAR than the REQ soil. Lead applied at 0–250 mg kg^{-1} was mostly adsorbed in both soils. Adsorption of Pb^{2+} increased steeply with Pb^{2+} concentration in the equilibrium solution at low concentrations (250–750 mg kg^{-1}) for both soils, then the increase diminished at the equilibrium Pb^{2+} concentrations >750 mg kg^{-1} (Fig. 1). The RAR soil adsorbed more Pb^{2+} than the REQ soil. At the highest level of added Pb^{2+} (12,500 mg kg^{-1}), the RAR soil adsorbed 80% of the applied Pb^{2+}, as compared with 43% for the REQ soil (Table 2), probably due to its higher CEC and pH (Table 1). Lead adsorption in both soils was well described by the Langmuir ($1/X = 1/X_m + 1/(X_m \times K) \times 1/C$) equation with a correlation coefficient (r^2) 0.98 for both soils. The

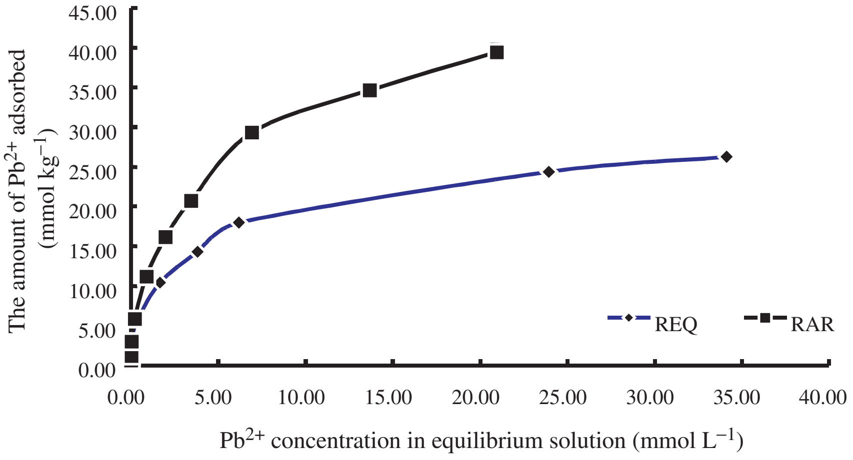

Figure 1. Isotherms of Pb^{2+} adsorption in the two variable charge soils. Data are means of three replications. *(View this art in color at www.dekker.com.)*

Table 2. The adsorption and desorption of Pb^{2+} in two variable charge soils.

Pb^{2+} added (mg kg^{-1})	RAR soil		REQ soil	
	Adsorption (%)	Desorption (%)	Adsorption (%)	Desorption (%)
0	100.00A	0.00H	100.00A	0.00G
62.5	100.00A	0.00H	100.00A	0.00G
125	100.00A	0.00H	100.00A	0.00G
250	100.00A	0.00H	100.00A	0.00G
625	98.99B	0.00H	97.87B	0.00G
1,250	96.58C	0.56G	93.71C	1.35F
2,500	92.66D	4.04F	86.23D	6.28E
3,750	89.15E	6.64E	78.92E	9.90D
5,000	85.79F	7.61D	74.39F	11.35C
7,500	80.90G	9.88C	53.44G	17.04B
10,000	71.70H	11.60A	50.42H	17.10B
12,500	79.70I	10.99B	43.49I	18.76A

Table 3. Adsorption maxima and binding energy related constant of the two soils from the Langmuir model.

Langmuir equation ($1/X = 1/X_m + 1/(X_m \times K) \times 1/C$)	X_m(mmol kg^{-1})	K(L mmol^{-1})	r^2
RAR soil	52.6	2.09	0.98
REQ soil	29.9	5.06	0.98

monolayer maximum adsorption (X_m) from the Langmuir equation is usually used for comparing potential adsorption capacity of different soils and soil components.[17] The X_m value was 52.6 mmol kg^{-1} for the RAR soil and 29.9 mmol kg^{-1} for the REQ soil. The physical meaning of K from Langmuir equation is not well defined. However, it is usually considered to relate the binding energy of Pb^{2+} adsorption. The greater the K value is, the more tightly the adsorbed Pb^{2+} is bonded. The REQ soil, though with a smaller adsorption capacity, had a greater K value than the RAR soil (Table 3). The product of X_m and K ($MBC = X_m \cdot K$) from the Langmuir equation reflects the maximum buffer capacity of the soil for Pb^{2+}. The value of MBC was 109.9 for the RAR and 151.3 for REQ soil, suggesting that the REQ soil had a greater buffering capacity for Pb^{2+} than the RAR soil.

H^+ Released by Pb^{2+} Adsorption

A proton release study was used to measure adsorption stoichiometry and to provide insight into the type of Pb surface complex that is formed on variable charge soils at various adsorption densities. There was a quadratic relationship between proton release and Pb^{2+} adsorption ($r^2 = 0.996$ and 0.991 for the RAR and REQ soil, respectively). The release of protons exponentially increased with increasing amount of Pb^{2+} adsorbed especially in the REQ soil (Fig. 2). The number of protons released per Pb^{2+} adsorbed increased with increasing initial Pb^{2+} concentrations and more protons per Pb^{2+} adsorbed were released in the REQ soil (Fig. 3). The moles of H^+ released per Pb^{2+} adsorbed ranged from 0.37 to 0.71 and 0.70 to 1.57, respectively for the RAR and REQ soil (Fig. 3), suggesting that bidentate surface complexes might present at higher Pb levels. More protons were released in the REQ than the RAR soil, which may be caused by more Pb^{2+} being specifically adsorbed onto positively charged sites in the former as compared with the latter.[16] These results indicate that both cation exchange and inner-sphere surface complexation reactions might have been involved in Pb^{2+} adsorption, and other exchangeable cations such as K^+, Ca^{2+}, and Mg^{2+} were probably replaced by Pb^{2+} earlier than H^+ and Al^{3+}.[16]

Effect of Pb Adsorption–Desorption on Soil pH

The pH of equilibrium solution significantly decreased with Pb^{2+} adsorption for both soils (Table 4). The pH of REQ soil decreased more than the RAR soil.

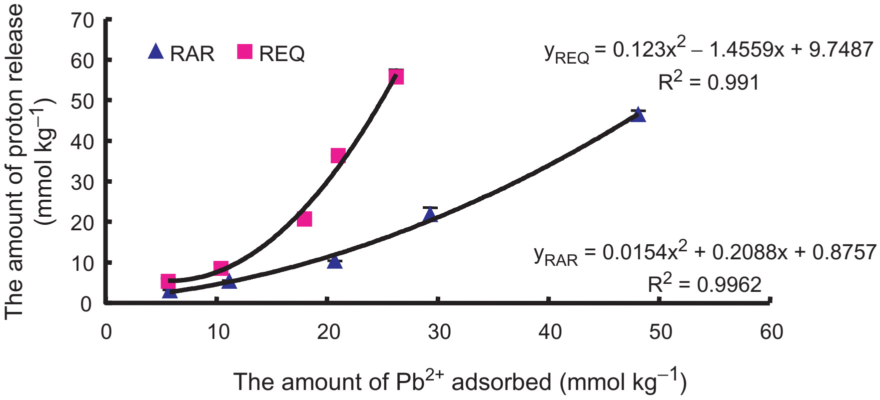

Figure 2. The amount of proton release in relation to Pb^{2+} adsorption in the two variable charge soils. Data are means of three replications. The amount of proton release for the control of the RAR and the REQ soil were 1.85 and 2.10 mmol kg^{-1}, respectively. *(View this art in color at www.dekker.com.)*

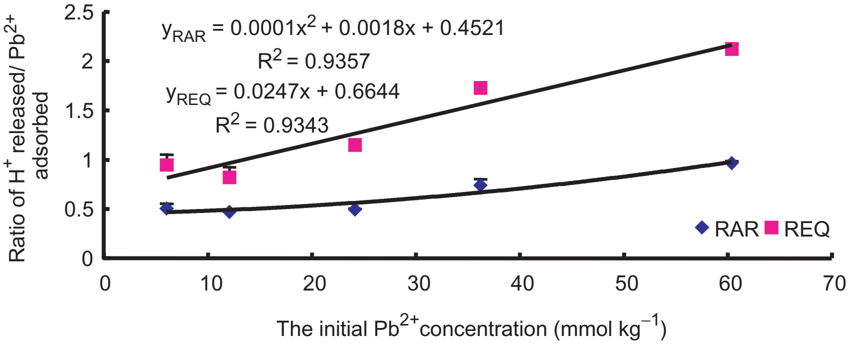

Figure 3. Effect of initial Pb^{2+} concentration on proton release per Pb^{2+} adsorbed in the two variable charge soils. Data are means of three replications. *(View this art in color at www.dekker.com.)*

The maximum pH drop was up to 1.10 unit for the RAR soil and 1.21 unit for the REQ soil. Obviously, H^+ and/or Al^{3+} were released during Pb^{2+} adsorption. Similar results were reported by Yu et al.[16] with Cu^{2+} adsorption. These results suggest that heavy metal contamination potentially causes soil acidification. The decrease in soil pH was quadratically correlated with the amounts of Pb^{2+} adsorbed for both the RAR and REQ soil ($r^2 = 0.97$, 0.98, for RAR and REQ, respectively) (Fig. 4).

Desorption of the adsorbed Pb^{2+} increased equilibrium solution pH, probably because of H^+ retention during Pb^{2+} desorption. Equilibrium solution pH generally increased with desorption and was lower when Pb^{2+} concentration in the equilibrium solution increased (Table 4). A greater decrease in equilibrium solution pH was

Table 4. Equilibrium solution pH in relation to Pb^{2+} adsorption–desorption.

pH	Pb concentration ($mg\,kg^{-1}$)	Ads	Des-1	Des-2	Des-3	Des-4	Des-5
RAR soil	0	5.75a A	6.01a A	6.21ab AB	6.13cd BC	6.23cde CD	6.43a A
	62.5	5.75a A	5.86ab AB	6.22ab AB	6.26bc B	6.43ab AB	6.17de CD
	125	5.64ab A	5.72bc BC	6.08bc ABC	6.50a A	6.51a A	6.33abc ABC
	250	5.48ab ABC	5.72bc BC	5.82d CD	6.30b AB	6.14de DE	6.15e CD
	625	5.56ab AB	5.63c BC	6.11bc AB	6.09de BCD	6.26cd CD	6.24cde BCD
	1,250	5.26d CD	5.57c CD	6.07bc ABC	5.97ef CDE	6.34bc BC	6.24cde BCD
	2,500	5.29cd CD	5.31d DE	6.31a A	5.76gf F	6.16de D	6.39ab AB
	3,750	5.16de DE	5.22de EF	6.21ab AB	5.77gh F	5.98f EFG	6.42ab A
	5,000	5.05e DEF	5.12def EF	6.16abc AB	5.90ef DEF	6.14de DEF	6.19de CD
	7,500	4.91g EFG	5.08ef EF	5.73d D	5.73h FG	5.96f G	6.16e CD
	10,000	4.78gh FG	5.06ef EF	6.01c BC	5.78gh F	6.19de CD	6.23ede BCD
	12,500	4.65h G	5.00f F	5.69d D	5.59i G	5.97f FG	6.29bcd ABCD
REQ soil	0	5.42a A	5.74a A	6.22a A	6.29a AB	6.58a A	6.47a A
	62.5	5.41a A	5.68ab AB	6.26a A	6.35a A	6.19de CDE	6.13g D
	125	5.38a A	5.68ab AB	6.09ab AB	6.39a A	6.43ab AB	6.29bcd BC
	250	5.37a A	5.58bc B	5.85c BC	6.16b BC	6.26cd BCD	6.27cde BCD
	625	5.12b B	5.55c B	5.88bc BC	6.06bc C	6.12de DEF	6.19defg CD
	1,250	4.93c C	5.31d C	5.8bc BCD	5.99c CD	6.4bc ABC	6.35bc AB
	2,500	4.83d C	5.06e D	6.24a A	5.80d E	6.08e DEFG	6.39ab AB
	3,750	4.65e D	4.91f D	6.07ab ABC	5.84d DE	5.88h H	6.36abc AB
	5,000	4.52f E	4.76g E	5.80c BCD	5.82d DE	5.9h FG	6.17efg CD
	7,500	4.36g F	4.71gh E	5.78c CD	5.62e F	6.03fgh F	6.17efg CD
	10,000	4.27h FG	4.64g E	5.53d DE	5.51e F	6.01fgh EFG	6.16fg CD
	12,500	4.21h G	4.64g E	5.31d E	5.51e F	5.94gh FG	6.26cdef BCD

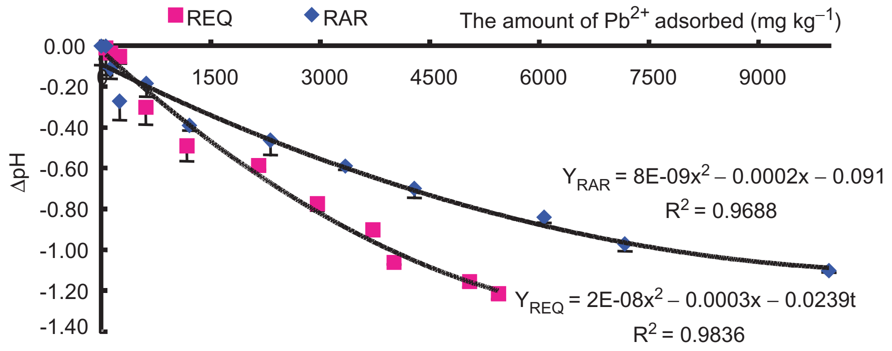

Figure 4. The pH changes in relation to Pb^{2+} adsorption in the two variable charge soils. The terms D1 to D5 represent the process of desorbed Pb^{2+} from each of the five successive extractions and the Ads represent the adsorption process. Data are means of three replications. The pH for the control of the RAR and the REQ soil were 5.75 and 5.42, respectively. *(View this art in color at www.dekker.com.)*

observed in the RAR soil than the REQ soil at low adsorbed Pb^{2+} ($<2500\,mg\,kg^{-1}$), but the reverse was true at higher Pb^{2+} concentrations, suggesting that different mechanisms are involved in the Pb^{2+} adsorption at different levels of Pb^{2+} loading and between the two soils. At high levels of adsorbed Pb^{2+}, pH seems to decrease less in both soils ($>5000\,mg\,kg^{-1}$), possibly because of approaching their maximum adsorption. After depletion of H^+, exchange of Pb^{2+} with cations such as Mg^{2+}, K^+, and precipitation at very high Pb levels may contribute to the less decrease in desorption equilibrium solution pH.

Distribution Coefficients of Pb^{2+}

The distribution coefficient is defined as the ratio of adsorbed Pb^{2+} to dissolved Pb^{2+}. That is the ratio of Pb^{2+} in solid phase to liquid phase. This parameter can reflect the affinity of Pb^{2+} to soil surface.[18] In this study, Pb^{2+} was almost completely adsorbed at low initial concentrations ($<250\,mg\,kg^{-1}$) and Pb^{2+} concentration in the equilibrium solution was below detection limits. As a result, the K_d values were not obtained for the low Pb^{2+} addition treatments. The K_d values was high at relatively low Pb^{2+} additions, decreased greatly with increasing initial Pb^{2+} concentrations from 250 to $5000\,mg\,kg^{-1}$ for both soils but slowly at higher Pb^{2+} concentrations ($>5000\,mg\,kg^{-1}$). This might be attributable to the high affinity of Pb^{2+} to some highly selective sites at low concentrations and low affinity for those less selective sites at high Pb^{2+} concentrations.[19] The RAR soil had a much higher K_d value than the REQ soil (Fig. 5). The difference may be attributed to the higher CEC and soil pH of the RAR soil, as compared with the REQ soil (Table 1).

The reaction of heavy metal adsorption on soils can be universally described as:

$$S(OH)_n + M^{2+} = (S-OM)^{(2-n)+} + nH^+ \tag{1}$$

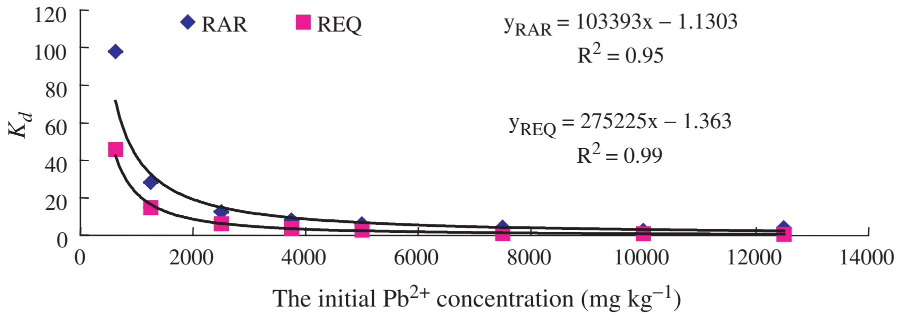

Figure 5. Effect of initial Pb^{2+} concentration on Pb^{2+} distribution coefficient (K_d) in the two variable charge soils. Data are means of three replications. *(View this art in color at www.dekker.com.)*

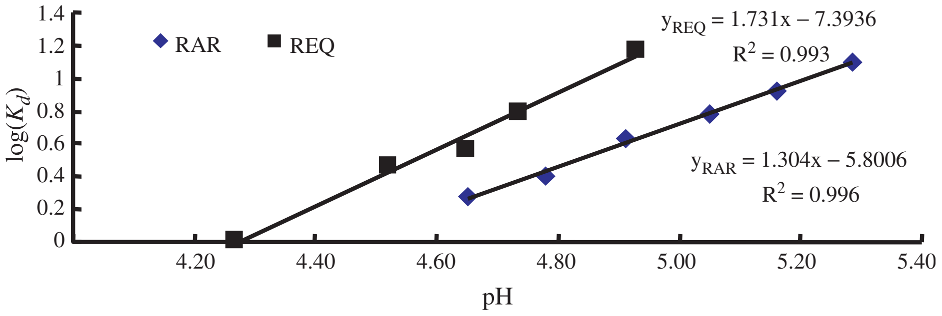

Figure 6. The relationship between K_d and pH of adsorption equilibrium. Data are means of three replications. *(View this art in color at www.dekker.com.)*

The linear form of Eq. (1) is expressed as

$$\text{Log}\ (K_d) = \log K' + n\text{pH} \tag{2}$$

where K_d is the distribution coefficient ; $K' = K \times a \times [\ \text{S(OH)}_n]$ is a constant; n is the average number of H^+ released by adsorbing one Pb^{2+}.

There was a linear relationship between the K_d value and solution pH of adsorption equilibrium for both soils ($r^2 = 0.996$ and 0.993 for the RAR and REQ soil, respectively) (Fig. 6). For variable charge soils, H^+ is released mainly through specific adsorption of Pb^{2+}, with a small contribution from nonspecific adsorption process. Therefore, the adsorption of Pb^{2+} on the variable charge soil surface involves mainly specific adsorption, with a small portion of nonspecific adsorption. These results suggest that even in the Fe and Al oxides-enriched soils, the adsorbed Pb still hold certain degree of bioavailability. In this study, a greater n value was observed with the REQ soil (1.731) than the RAR soil (1.304). This agreed with the previous finding that the adsorption equilibrium pH of the REQ soil was much lower than that of the RAR soil and it decreased more rapidly with the amount of Pb^{2+} adsorbed.

Desorption of Adsorbed Pb^{2+}

Desorption of the adsorbed Pb^{2+} was very small in the $0.01\,mol\,L^{-1}$ $NaNO_3$ (Table 2). No desorption occurred at the adsorbed Pb^{2+} up to $625\,mg\,kg^{-1}$. Desorption increased with increasing Pb^{2+} adsorption saturation for both soils, though with a lower rate. The RAR soil desorbed less Pb^{2+} than the REQ soil at the same Pb^{2+} concentrations. After five successive desorptions, the maximum amounts of Pb^{2+} desorbed accounted for only 11.6% of the adsorbed Pb^{2+} for the RAR soil and 18.7% for the REQ soil (Table 2). The RAR soil that had a greater adsorption capacity desorbed less Pb^{2+} than the REQ soil at the same amount of adsorbed Pb^{2+}.

The proportion of the adsorbed Pb^{2+} that was not desorbed by the $NaNO_3$ decreased with the increasing concentration of adsorbed Pb^{2+} (Figs. 7, 8). The portion of the Pb^{2+} adsorbed that was not desorbed by the five successive desorptions was likely related to high binding energy, and may not be available to plants.

There was a linear relationship between the amount of Pb^{2+} desorbed and the amount of adsorbed for the RAR soil but a quadratic relationship for the REQ soil ($R^2_{RAR} = 0.988$, $R^2_{REQ} = 0.996$), suggesting that the two soils may have different Pb^{2+} adsorption mechanisms. Both the RAR and REQ soil can retain a large amount of applied Pb^{2+}. This portion of residual Pb^{2+} after five successive desorptions measures the potential fixation of Pb^{2+} by the soils. This residual Pb^{2+} can be calculated by the regression equation of adsorption–desorption relationship

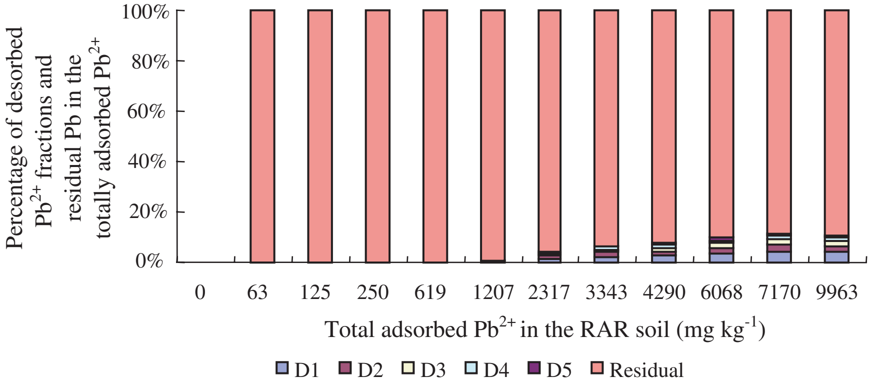

Figure 7. Fraction of five successive extractions and residual Pb^{2+} in the total adsorbed Pb^{2+} in the RAR soil. The terms D1 to D5 represent the fraction of desorbed Pb^{2+} from each of the five successive extractions and the residual Pb^{2+} represents the fraction of adsorbed Pb^{2+} that was not recovered by the five successive extraction with $0.01\,mol\,L^{-1}$ $NaNO_3$ (pH 5.0). Data are means of three replications. *(View this art in color at www.dekker.com.)*

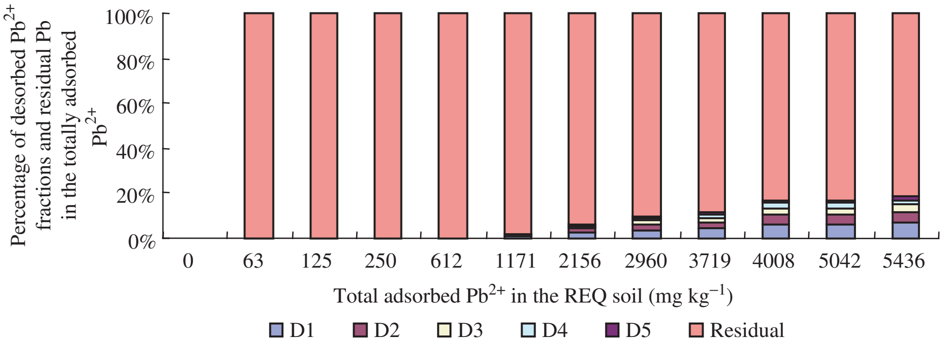

Figure 8. Fraction of five successive extractions and residual Pb^{2+} in the total adsorbed Pb^{2+} in the REQ soil. The terms D1 to D5 represent the fraction of desorbed Pb^{2+} from each of the five successive extractions and the residual Pb^{2+} represents the fraction of adsorbed Pb^{2+} that was not recovered by the five successive extraction with 0.01 mol L^{-1} $NaNO_3$ (pH 5.0). Data are means of three replications. *(View this art in color at www.dekker.com.)*

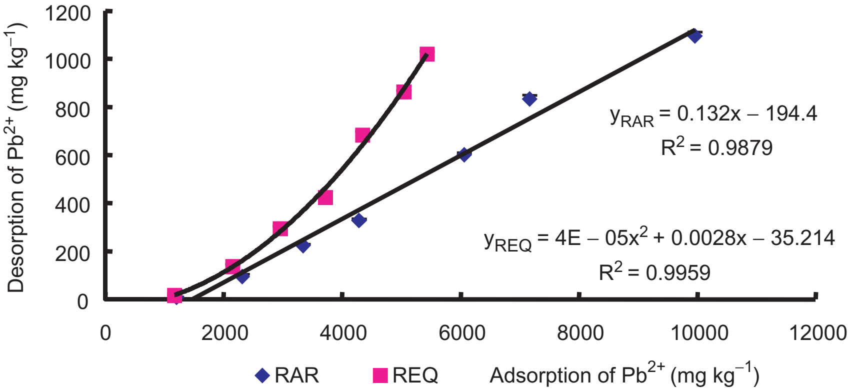

Figure 9. The relationship between Pb^{2+} adsorption and desorption. Data are means of three replications. *(View this art in color at www.dekker.com.)*

(Fig. 9). The amount of residual Pb^{2+} in the RAR soil was 1472.2 mg kg^{-1} and the corresponding value for the REQ soil was 973.9 mg kg^{-1}. These results agree with the previous finding that Pb^{2+} was more tightly adsorbed in the RAR than the REQ soil.

DISCUSSIONS

The difference in Pb^{2+} adsorption between the two variable charge soils may be attributed to the higher CEC and soil pH and small amounts of silicate clay minerals in the RAR soil, as compared with the REQ soil (Table 1). These results were in agreement with previous report of Chip Apple,[11] who suggested that metal adsorption was more dependent on clay type and CEC than amount of clay. Chip Apple[11] also indicated that soil pH plays a major role in the adsorption of heavy metals as it directly controls the solubility 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.[9,20–22] Increasing soil pH increases cationic heavy metal retention to soil surfaces via adsorption, inner-sphere surface complexation, and/or precipitation and multinuclear type reactions.[9,17] Several studies on metal adsorption by soils have demonstrated close relationships between metal adsorption and soil pH or CEC.[23] Soil pH has been found to be the predominant property that affects Cu, Zn, and Cd adsorption by soils.[24] Other studies have shown that CEC is the predominant property affecting adsorption of Pb,[25,26] Cd,[25] and Zn.[27] Other soil properties that are associated with metal adsorption (e.g., organic matter and clay content) can also influence metal adsorption through their CEC property.[25,26,28] Previous studies also showed that Zn and Pb adsorption by soil is closely related to CEC and pH.[29,30]

Different mechanisms might be involved in Pb^{2+} adsorption/desorption at different levels of Pb^{2+} loading and between the two soils. The RAR soil may have more adsorption sites and form much stronger surface complexes with Pb^{2+} than the REQ soil. Perhaps Pb^{2+} adsorption sites are different between the two soils. Lead adsorbed by the RAR soil may be mainly affected through cation exchange and diffusion into "dead-end" or micropores created by crystal defects and be less readily desorbed, but the formation inner-sphere complexes may be the predominant mechanism of Pb^{2+} adsorption in the REQ soil. Additionally, iron and aluminum oxides may contribute to the high affinity of Pb by the RAR soil.

There are still different opinions regarding Pb^{2+} adsorption mechanisms such as hydrolyzed/unhydrolyzed adsorption and monodentate/bidentate reactions. Barrow et al.[31] concluded that Pb^{2+} is adsorbed on goethite without hydrolyzing. Hayes and Leckie[32] were able to describe solutions using unhydrolyzed monodentate and bidentate Pb^{2+} surface species. Müller and Sigg[33] described Pb^{2+} adsorption on goethite as sorption of unhydrolyzed monodentate and bidentate Pb^{2+} surface species. Gunneriusson et al.[34] suggested that Pb^{2+} adsorbs on goethite as unhydrolyzed [$\equiv$FeO Pb^{2+}] complexes and hydrolyzed [$\equiv$FeOH Pb^{2+}] complexes. They also found that it is possible to adsorb more Pb^{2+} ions on goethite than the number of possible titratable surface sites should allow. Roe et al.[35] used XAFS spectroscopy to investigate Pb^{2+} adsorbed on goethite and suggested that Pb^{2+} adsorbs in an inner-sphere model at low sorption densities. At higher apparent sorption densities, they suggested that multinuclear Pb^{2+} adsorbent complexes occured, based on comparison to XAFS spectra of model compounds. Hohl and Stumm[36] concluded that Pb^{2+} uptake on γ-Al_2O_3 is consistent with inner-sphere, predominantly monodentate sorption of Pb^{2+} to oxygens on the mineral surface according to the reaction: $\equiv AlOH_{sfc} + Pb^{2+}\ (aq) = AlO_{sfc}\text{–}Pb^{+} + H^{+}$, where $\equiv AlOH_{sfc}$ is an amphoteric, structurally undefined surface functional group with zero net charge, and $AlO_{sfc}\text{–}Pb^{+}$ is a monodentate Pb^{2+} surface complex. These authors concluded that approximately 10% of the Pb^{2+} was bound to two surface functional groups (bidentate surface complexation). Davis and Leckie[37] concluded that adsorbed Pb^{2+} on γ-Al_2O_3 is inner-sphere and monodentate. In addition, they demonstrated that the proton release and Pb^{2+} uptake data are consistent with hydrolysis of Pb^{2+} during adsorption, as described by the following reaction: $\equiv AlOH_{sfc} + Pb^{2+}\ (aq) + H_2O = AlO_{sfc}\text{–}Pb(OH)^+ + 2H^+$. From the EXAFS results summarized that the surface complexes of Cr(VI) and As(V) change with surface coverage. At lower surface coverages, the monodentate complex is more prominent than at high coverages; with increasing coverage the spectra have an increasing contribution from the bidentate surface complexes. In addition, while the coordination numbers are somewhat qualitative, their values for both bidentate complex, increase with surface coverage. Therefore, it appears that the monodentate complex represents a significant portion of surface-complexed oxyanions at low surface coverage with diminishing proportions relative to the bidentate complexes at higher surface coverage.[38] Recent spectroscopic evidence has indicated that Pb^{2+} ions are adsorbed as mononuclear bidentate complexes to goethite at pH 6.[39,40]

Based on surface site heterogeneity as well as on spectroscopic evidence, one would expect monodentate complexes of Pb^{2+} to be more prevalent at low sorption densities, whereas at higher sorption densities bidentate complexes would dominate. Desorption of bidentate surface complexes is much more difficult than monodentate surface complexes. Accordingly, desorption rates would be expected to decrease as sorption densities increased.[2] However, our research suggested that desorption rates increased as sorption densities increased. Many questions remain to be answered about Pb^{2+} adsorption on variable charge soils. Further studies, especially molecular studies, are needed to identify the mechanism of Pb^{2+} adsorption/desorption in the variable charge soils.

Previous studies had shown that the number of H^+ released after one M^{n+} is adsorbed by the soil varied from 1 to 2. Hohl and Stumm studied Pb^{2+} sorption on γ-Al_2O_3 in 0.1 M $NaClO_4$ solutions and used a constant capacitance surface complexation model to describe the uptake curves. They observed that an average of 1.5 protons are released from the alumina surfaces for each Pb^{2+} adsorbed.[36] But Forbes et al.[41] found that approximately two H^+ are released from goethite surfaces for each Pb^{2+} adsorbed. They ascribed this behavior to one of two processes: Pb^{2+} adsorption in a bidentate mode to surface functional groups according to the reaction: $2[\equiv FeOH] + Pb^{2+} = [\equiv FeO]_2Pb^+ + 2H^+$; or hydrolysis of Pb^{2+} during adsorption, e.g., $[\equiv FeOH] + Pb^{2+} + 2H_2O = [\equiv Fe(OH)]Pb(OH)_2 + 2H^+$.[41] Normally, approximately one proton was released per Pb^{2+} ion specifically adsorbed onto the soil surface. The additional H^+ released may result from a change in the soil surface charge attributable to the specifically adsorbed Pb, hydrolysis of released Al^{3+}, the formation of mixed surface complexes, or a more complicated adsorption mechanism involved.[2] Rather, most surface complexation models, just as Eq. (2), generally assume that H^+ and metal ions bond to the same sites on oxide surfaces, and that all of these sites are titratable (i.e., their reactions with H^+ or OH^- ions can be measured) in the pH ranges commonly considered. This approach results in acidity constants that are averages over all types of proton-active sites on the surfaces. In addition, there are likely to be surface functional groups that actively complex metal ions, but not H^+ in the pH ranges commonly considered.[40] This attribute to the lessened H^+ released. These release stochiometries were ascribed to the formation of monodentate surface complexes, bidentate surface complexes, and the hydrolysis of Pb during adsorption.

It is possible that some surface functional groups bind metal ions, but not H^+ (or are not titratable) in the pH ranges commonly considered.[39] Also it is possible that some surface functional groups adsorb more Pb(II) ions than the number of possible titratable surface sites should allow.[40] As a result, it has often been necessary to construct surface complexation models assuming that only one or two sites on the surfaces are titratable, and metal ions are bound only to these sites.

A number of factors might contribute to the decreased adsorption equilibrium pH and the difference between the two soils. First of all, more H^+ is exchanged by the increased Pb^{2+} concentrations. Secondly, as Basta and Tabatabai[19,42] inferred in their article, at low heavy metal loadings, heavy metals might replace adsorbed Ca^{2+} and Mg^{2+} because they have less affinity to soil constituents than Al^{3+}. However, at higher heavy metal loadings, exchange reactions between heavy metals and Al^{3+} might happen, followed by hydrolysis of Al^{3+} that decreases solution pH, especially in soils that have significant amounts of exchangeable acidity and exchangeable Al^{3+}. Thirdly, the REQ soil had greater amounts of exchangeable Al and lower pH, as a result, the REQ soil had more hydroxylated surface and subsequently released more H^+ for the same amount of Pb^{2+} adsorbed than the RAR soil.

Even in contaminated soils, most of the Pb^{2+} present as insoluble forms, precipitated or bound to the soil surfaces. In our study, Pb^{2+} was almost completely adsorbed in both RAR and REQ soil at 0–250 $mg\,kg^{-1}$, the results indicate that the variable charge soil had a high fixation ability for Pb, and the bioavailability of Pb should be low in the variable charge soil. However, recent study indicates that although heavy metal such as Pb was tightly adsorbed in the soil with very limited mobility, its activation may be caused by increased input.[43]

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