Competitive adsorption of Cd, Cu, Hg and Pb by agricultural soils of the Changjiang and Zhujiang deltas in China[*]

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Abstract: Soils can often be contaminated simultaneously by more than one heavy metal. The sorption-desorption behavior of a metal in a soil will be affected by the presence of other metals. Therefore, selective retention and competitive adsorption of the soils to heavy metals can affect their availability and movement through the soils. In this study, the simultaneous competitive adsorption of four heavy metals (Cd, Cu, Hg, and Pb) on ten agricultural soils collected from the Changjiang and Zhujiang deltas, China was assessed. The results showed that the competition affected the behavior of heavy metal cations in such a way that the soils adsorbed less Cd and Hg, and more Pb and Cu with increasing total metal concentrations, regardless of the molar concentration applied. As the applied concentrations increased, Pb and Cu adsorption increased, while Cd and Hg adsorption decreased. The adsorption sequence most found was Pb>Cu>Hg>Cd. The maximum adsorption capacity for the heavy metal cations was calculated, and affected markedly by soil properties. The results suggest that Hg and Cd have higher mobility associated to the lower adsorption and that Pb and Cu present the opposite behavior. Significant correlations were found between the maximum adsorption capacity of the metals and pH value and exchangeable acid, suggesting that soil pH and exchangeable acid were key factors controlling the solubility and mobility of the metals in the agricultural soils.

Key words: Competitive adsorption, Adsorption sequence, Heavy metals, Agricultural soils
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INTRODUCTION

Soils can often be contaminated simultaneously by several heavy metals (Calabrese *et al*., 1997; Kock and Rotard, 2001; Xiong *et al*., 2005), and there is a competitive adsorption on soil colloids among the metals present in the system. In this situation, selective retention and competitive adsorption of the metals by the soils become of major importance in determining their availability to plants and their movement through the soils. The risks of environmental toxicity posed by the metals are a function of their mobility and availability. The movement of

heavy metals in soil profiles has received considerable attention, since even a slow transport through soils and subsoil materials may result in an increased content of heavy metals in the groundwater (Alloway, 1995; Li and Shuman, 1997; McBride *et al*., 1997). However, up to date, the fate and transport of metals, particularly adsorption-desorption, and physical conditions involved in the soil process are not fully understood. Lack of this information makes it difficult to predict the mobility of metals in agricultural soils. It is required to understand the processes of soil-heavy metal interactions, in particular, their mobility and retention, since these are essential factors that control groundwater contamination.

The availability and mobility of heavy metals in the soils can be assessed using adsorption-desorption experiments. Studies on adsorption of heavy metals, either individually or in a competitive situation, are

important in determining the capacity of soils to respond to the introduction of these pollutants into soil systems (Moreno *et al.*, 2006; Reddy and Dunn, 1986; Srivastava *et al.*, 2005). Several studies have found that soil properties correlated with adsorption and mobility of heavy metals are pH, organic matter (OM), cation exchange capacity (CEC), specific surface area, free iron oxides, clay minerals, exchangeable Ca. However, the role of soil properties in controlling metal mobility could vary with soils and heavy metals, with most metals being most mobile in acidic, coarse-textured soils (Amacher *et al.*, 1986; Fontes *et al.*, 2000; Gray and McLrren, 2006; Harter, 1983; Jopony and Young, 1994; King, 1988; Mesquita and Carranca, 2005; Slavek and Pickering, 1988). The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution.

Adsorption of heavy metals has been modelled on various minerals and soils in single-element systems. However, little work has been done to model the adsorption of heavy metals onto soils in multi-element systems (de Matos *et al.*, 1999; Lee *et al.*, 1996; Srivastava *et al.*, 2005; Vega *et al.*, 2006; Zhang *et al.*, 2006). Therefore, the main objectives of the study were to evaluate the retention and mobility sequences of four heavy metals applied together to the agricultural soils by means of adsorption-desorption, and to investigate the relationship between soil properties and adsorption of heavy metals by the soils.

MATERIALS AND METHODS

Soil samples

Ten surface soil samples with a wide range of properties were collected at 0~15 cm depth from different areas of the Changjiang and Zhujiang deltas, China. The soil samples were air-dried at 25 °C and ground to pass through a 2-mm sieve. Sub-samples from each soil were further ground to pass through a 0.15-mm sieve for chemical analysis.

Measurement of soil properties

Soil pH was measured in water at a soil:water ratio of 1:1 using a pH meter. OM was determined by wet digestion (ACCC, 1983). Particle composition of the soil samples was determined using the mi-

cro-pipette method (Miller and Miller, 1987). Free Fe was extracted with citrate-bicarbonate-dithionote. CEC and exchangeable acid were estimated using standard methods (Institute of Soil Science, Chinese Academy of Sciences, 1978).

Sorption experiment

Sorption of Cd, Cu, Hg, and Pb was performed in two replicates, by equilibrating 1 g air-dried soil with 25 ml 0.01 mol/L $CaCl_2$ solution containing concentrations of 2, 8, 20, 40, and 60 mg/L of all four heavy metals in the same concentration. The metal cations were applied in forms of $CdCl_2$, $CuCl_2$, $HgCl_2$, and $Pb(NO_3)_2$ diluted in 0.01 mol/L $CaCl_2$ solution. The soil suspensions were shaken continuously for 8 h at 25 °C (equilibrium time was determined by a preliminary experiment). At the end of the designated period, the suspensions were centrifuged at 6500×g relative centrifuge force for 30 min and the supernatant was passed through Whatman #42 filter paper. The Cd, Cu, Hg, and Pb concentrations in the filtrates were determined using atomic absorption spectrometry. The difference between the initial amount of metal in solution and the amount remaining in solution after the reaction period was assumed to be adsorbed by the soil.

RESULTS

Competitive adsorption of four heavy metals

Basic properties of the ten agricultural soils are listed in Table 1. pH value, OM, exchangeable acid, CEC, free Fe_2O_3 and clay content varied greatly among the soils, and ranged from 4.75 to 7.82 for pH, 19.90 to 51.18 g/kg for OM, 0.00 to 1.06 cmol/kg for exchangeable acid, 6.34 to 15.58 cmol/kg for CEC, 10.04 to 28.41 g/kg for free Fe_2O_3, and 6.2% to 34.4% for clay content, respectively.

Fig.1 presents the relationships between the equilibrium concentration (EC) of Cd, Cu, Hg, and Pb, and amount of adsorbed metal cations after the adsorption experiment. All soils had similar trend in competitive adsorption with differences only in relative amounts. For the lower concentrations applied, the amount of EC was low for every metal cation, showing that almost all of the metals were adsorbed by the soils. As the applied concentrations increased,

Pb and Cu maintained their strong affinity with the soil surfaces while the Cd and Hg were displaced from the soil surfaces. The result showed clearly that competition for adsorption sites affected the heavy metal cation behavior in such a way that the soils adsorbed less Cd and Hg and more Pb and Cu, with increasing concentrations.

Considering the non molar equality for heavy metal applied concentrations, the sorption affinity between the metal cations and the soil surfaces can be calculated as the amount of each metal present in the adsorption complex, i.e., the share of a given metal in the total amount adsorbed by the soil expressed as percent. Fig.2 presents these values of four metals in

Table 1 Basic properties of the tested soils

| Soil classification	Location	pH (H_2O)	OM (g/kg)	Exchangeable acid (cmol/kg)	CEC (cmol/kg)	Free Fe_2O_3 (g/kg)	Clay (%)
Stagnic Anthrosols (SAT1)	Jiangsu	7.82	43.22	0.00	15.58	14.19	34.0
Stagnic Anthrosols (SAT2)	Zhejiang	5.60	34.98	0.32	13.45	21.97	34.4
Stagnic Anthrosols (SAT3)	Zhejiang	5.12	51.18	1.06	12.47	20.31	20.5
Stagnic Anthrosols (SAT4)	Zhejiang	5.42	19.92	0.24	14.59	10.04	6.2
Stagnic Anthrosols (SAT5)	Guangdong	5.69	28.14	0.10	6.34	22.43	17.6
Stagnic Anthrosols (SAT6)	Guangdong	6.04	19.90	0.09	8.74	28.41	17.2
Stagnic Anthrosols (SAT7)	Zhejiang	6.20	28.74	0.04	13.99	22.93	28.2
Udic Ferrisols (UFRI1)	Guangdong	4.75	33.33	0.86	6.82	28.86	37.2
Udic Ferrisols (UFRI2)	Zhejiang	4.75	10.01	3.83	6.13	29.13	26.0
Udic Ferralisols (UFRA)	Guangdong	5.40	6.66	0.75	4.06	34.18	71.0
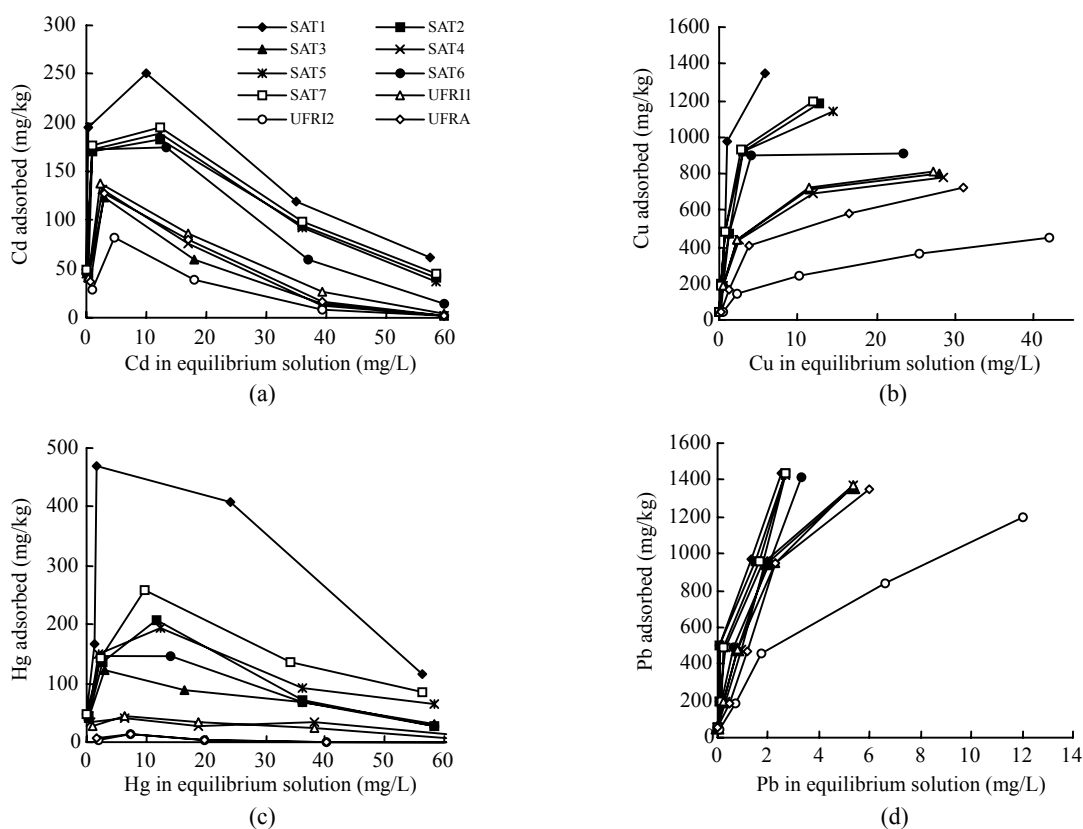
Fig.1 Relationship between equilibrium concentration and amount of adsorbed metal cation for each soil at co-existence of Cd (a), Cu (b), Hg (c), and Pb (d)

the adsorption complex for each soil. At the lowest applied concentration, the heavy metals were adsorbed proportional to their relative molar concentration. Cu, with the highest molar concentration, occupied >45% of the adsorption complex, whereas Hg, with the lowest molar concentration, had the smallest portion (<15%). As the concentration increased, competition started to occur and the proportion of Pb and Cu increased compared with Cd and Hg. Fig.2 shows that competition is relatively weaker in soils (SAT1, SAT2, SAT7) with higher capacity to adsorb cations, and changes in the percentage of each metal cation adsorbed in the soils are not significant at the applied concentration of <20 mg/L. The weaker competition may be due to the more available sites for almost all the metal cations in the adsorption complex. On the other hand, competition among the metals is very strong in soils with lower capacity to hold metal cations (UFRI2, UFRA, SAT4), where more Cd and Hg are dislocated from the adsorption complex and substituted by Pb and Cu, even when low concen-

tration of metals was added. In the field situation, this could impose a much higher risk of Cd and Hg contamination of aquifers, groundwater, etc., through leaching of the metals in the soil profile and also a much higher risk of making them available for uptake by plants.

Selectivity sequences

As applied concentration of the metals increased, the amount of each of Cu and Pb adsorbed increased and that of each of Cd and Hg decreased (Fig.2). In order to estimate the differences in the adsorption strength among heavy metals and soils, the difference between the adsorption in the first level (2 mg/L) and the last level (60 mg/L) of applied concentration was calculated in percentage. In Table 2 it is possible to visualize the relative strength of each heavy metal in the overall competition. Positive value represented the increase in adsorption capacity of the metals as applied concentration of the metals increased, while negative value indicated the decrease in adsorption
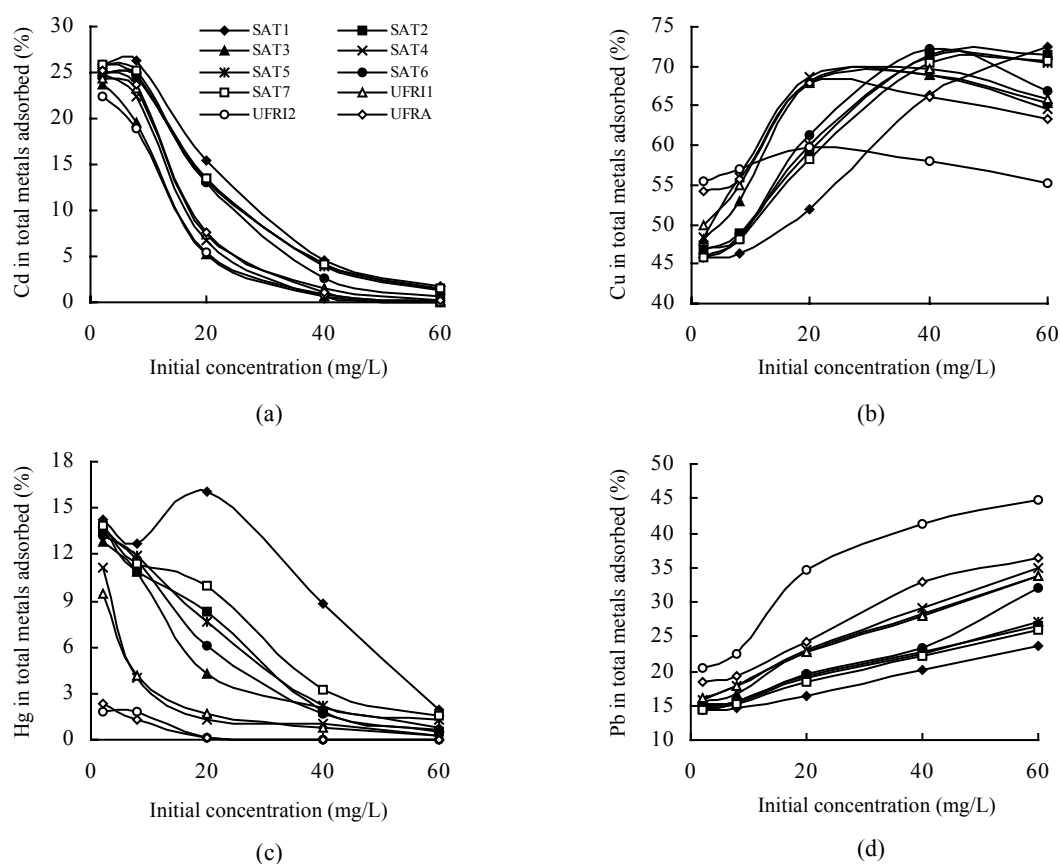

Fig.2 Percentage of each metal cation adsorbed in the soils for each applied concentration
(a) Cd; (b) Cu, (c) Hg; (d) Pb

capacity of the metals as applied concentration of the metals increased. For most soils, Pb showed the greatest increase in adsorption, whereas Cd showed the greatest decrease.

Table 2 Proportion of increase or decrease in the adsorption of heavy metals between the first level and the last level of applied concentration for the different soils

Soils	Metal cations (%)[*]			
	Pb	Cu	Cd	Hg
SAT1	65.76	58.19	−92.81	−86.17
SAT2	79.79	52.36	−94.39	−96.32
SAT3	120.35	35.77	−99.78	−93.97
SAT4	122.62	33.79	−99.79	−97.14
SAT5	84.90	50.01	−94.98	−90.65
SAT6	111.34	45.78	−97.83	−95.40
SAT7	80.22	54.67	−94.03	−88.57
UFRI1	108.72	31.59	−99.37	−97.83
UFRI2	118.26	−0.46	−99.65	−100.00
UFRA	99.04	17.02	−99.56	−100.00

[*] $y=(1-a/b)\times100\%$, where y is the proportion of increase or decrease in the adsorption of heavy metals (%), a is the adsorption at the last level of applied concentration, b is the adsorption at the first level of applied concentration
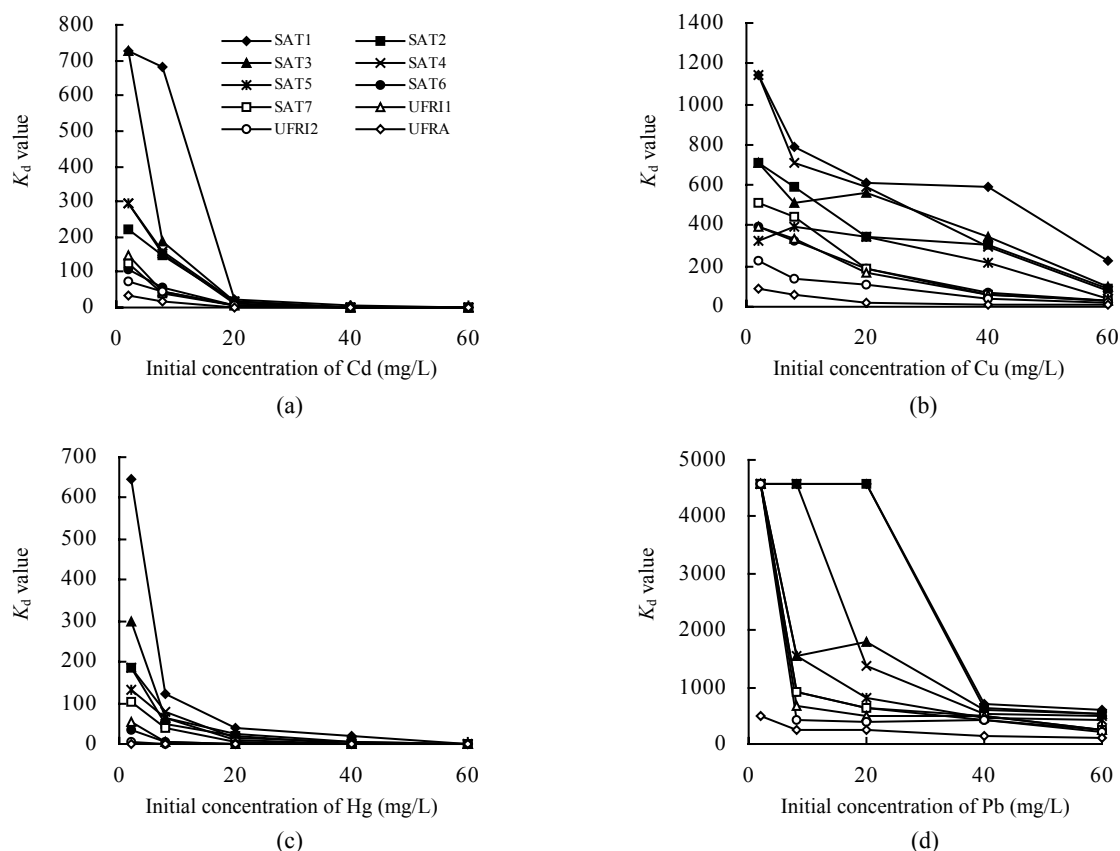
Distribution coefficient (K_d), a ratio of concentration of sorbed metal to concentration of the metal in solution, is also a useful parameter to study selectivity sequences. It is the distribution coefficient for partition of the ion between soil and soil solution (Anderson and Christensen, 1988; Gao *et al.*, 1997). Fig.3 shows that K_d values for all four metals decreased significantly with increasing the initial concentrations of the metals. However, the decrease in K_d values for Cd and Hg were much greater than those for Pb and Cu. K_d values for Cd and Hg were close to zero at applied initial concentration of 60 mg/L. Based on these results, a competitive adsorption order could, therefore, be derived (Table 3). The general selectivity sequence found was Pb>Cu>Hg>Cd.

Adsorption capacity of the soils to heavy metals

The total adsorbed amount of heavy metals increased with increasing applied concentration of the metals (Fig.4). Langmuir isotherms were constructed using the sum of equilibrium concentration and the

Fig.3 Distribution coefficient (K_d) of four metals as a function of applied initial concentrations of the metals
(a) Cd; (b) Cu; (c) Hg; (d) Pb

Table 3 The selectivity sequence of the metals adsorption for the different soils

Soils	Selectivity sequences	Soils	Selectivity sequences
SAT1	Pb>Cu>Hg>Cd	SAT6	Pb>Cu>Hg>Cd
SAT2	Pb>Cu>Cd>Hg	SAT7	Pb>Cu>Hg>Cd
SAT3	Pb>Cu>Hg>Cd	UFRI1	Pb>Cu>Hg>Cd
SAT4	Pb>Cu>Hg>Cd	UFRI2	Pb>Cu>Cd>Hg
SAT5	Pb>Cu>Hg>Cd	UFRA	Pb>Cu>Cd>Hg
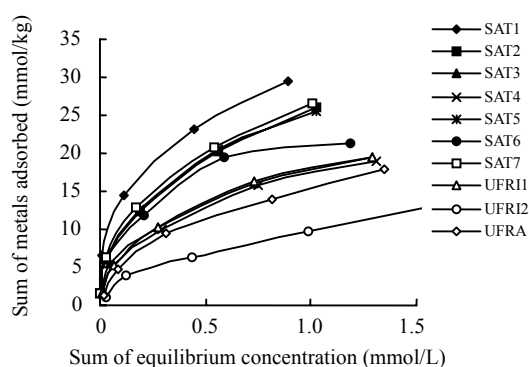
Fig.4 Relationships between total adsorbed metal cations and sum of equilibrium concentration

Table 4 Langmuir equations ($C/Q=C/Q_m+K/Q_m$) with determination coefficient (r^2) and maximum adsorption capacity (Q_m) for all soils

Soils	Langmuir equation	Q_m (mmol/kg)	r^2
SAT1	$Y=0.033X+0.0024$	30.46	0.981
SAT2	$Y=0.036X+0.0051$	28.16	0.966
SAT3	$Y=0.047X+0.0081$	21.16	0.974
SAT4	$Y=0.047X+0.0098$	21.11	0.975
SAT5	$Y=0.037X+0.0044$	27.19	0.971
SAT6	$Y=0.043X+0.0048$	23.17	0.990
SAT7	$Y=0.035X+0.0042$	28.25	0.970
UFRI1	$Y=0.045X+0.0099$	22.14	0.980
UFRI2	$Y=0.065X+0.0280$	15.37	0.944
UFRA	$Y=0.047X+0.0150$	21.09	0.978

X and Y represent $1/Q_m$ and C/Q of Langmuir equations ($C/Q=C/Q_m+K/Q_m$), respectively

sum of adsorbed metal cations for each applied concentration. The Q_m, maximum adsorption capacity, which is the estimate of the maximum amount of heavy metals that the soil surfaces can hold, was calculated from the Langmuir equation. The results showed that the Q_m ranging from 15.37 to 30.46 mmol/kg varied greatly (Table 4), suggesting that the soils could have different buffering capacities for these pollutants. The sequence of adsorption capacity was: SAT1>SAT7>SAT2>SAT5>SAT6>UFRI1> SAT3>SAT4>SUFRA>UFRI2. SAT1 had the highest maximum adsorption values and could probably receive and hold higher heavy metal loadings. On the other hand, UFRI2 and UFRA, due to their low values of maximum adsorption and low buffering capacities, will more easily reach their critical load and be more vulnerable to heavy metal inputs.

Soil maximum adsorption capacity should be considered an essential characteristic when discussing "critical loads and buffering capacities" for heavy metals. Particularly for strongly contaminated soils, the capacity of the soil to adsorb and retain heavy metals is the most important aspect to be considered when critical loads and buffering capacities are discussed.

The evaluation of the influence of soil properties on the total metal-adsorption capacity of the soil was examined by correlation analysis (Table 5). The maximum adsorption capacity (Q_m) was influenced mainly by pH value and exchangeable acid, as shown by the highly significant simple correlation coefficients between these variables. The results indicate that pH is a key factor controlling the solubility of metal in the soils. Yong and Phadungchewit (1993) reported that a change in soil solution pH can result in a corresponding change of the dominant retention mechanisms of heavy metals in soils. At high soil solution pH, precipitation prevails. As pH decreases, precipitation becomes less important, and cation exchange becomes dominant. The pH effects were also thought to relate to the exchange of H^+ with heavy metals and the effect of pH on dissolution-precipitation and oxidation of Fe and Mn oxides (King, 1988). As soil pH increased there was an increase in the metal adsorption and there was also an increase of the metal precipitation. This shows that the mobility of all the heavy metals decreased with the pH increase. The phenomenon can be related to both the increasing of the specific and non-specific adsorption and to the precipitation reaction. It seems that the soils with higher pH values adsorbed more metals compared with most of the low pH soils, suggesting that the increase in the hydrolyzed forms of cations and CEC of the soils with the increase in pH was as important as the nature of the adsorbent materials.

Table 5 Correlation coefficients between Q_m for each metal and soil property

Property	Correlation coefficients (r^2)
pH	0.767**
Organic C	0.522
Exchangeable acid	−0.784**
CEC	0.534
Free Fe_2O_3	−0.392
Clay	0.005

** $P<0.01$

CONCLUSION

The competitive adsorption experiment showed that the most frequent heavy metal selectivity sequence was Pb>Cu>Hg>Cd. Cadmium has the highest mobility associated to the lowest adsorption and Pb and Cu present the opposite behavior. At low levels of the applied metal concentration, the heavy metals occupied a percentage proportional to their relative molar concentration in solution. At higher levels, the occupation increased for the strongest competitors, namely Pb and Cu, and decreased for the weakest competitors, Cd and Hg. The soil properties showed significant correlation to the capacity of soils to adsorb heavy metals. Maximum adsorption capacities for heavy metals, based on Langmuir isotherms, were mainly related with pH and exchangeable acid. The results indicated that pH was a major factor controlling the retention and movement of the metals in the soils. Therefore, keeping high soil pH was an effective measure to reducing risk of metal leaching from the soil.

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