

# Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn in acid soils

## I. Selectivity sequences

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### Abstract

The sorption and desorption of six heavy metals by and from the surface or immediately subsurface horizons of eleven acid soils of Galicia (N.W. Spain) were characterized by means of batch experiments in which the initial sorption solution contained identical mass concentrations of each metal. Concentration-dependent coefficients  $K_d$  were calculated for the distribution of the metals between the soil and solution phases, and the values obtained for initial sorption solution concentrations of  $100 \text{ mg L}^{-1}$  of each metal ( $K_{d100}$ ) were used, for each soil, to order the metals as regards their sorption and retention. Pb and Cu were sorbed and retained to a greater extent than Cd, Ni or Zn, which had low  $K_{d100}$  values. Pb was sorbed more than any other metal. Cr was generally sorbed only slightly more than Cd, Ni or Zn, but was strongly retained, with  $K_{d100}$  (retention) values greater than those of Pb and Cu in soils with very low CEC ( $<3 \text{ cmol}_{(+) } \text{ kg}^{-1}$ ). The sorption of Pb and Cu correlated with organic matter content, while the retention of these and the other metals considered appeared to depend on clay minerals, especially kaolinite, gibbsite, and vermiculite.

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### 1. Introduction

In recent years, increasing deposition of heavy metals on land (e.g. in fertilizers, pesticides, manure, sewage sludge or industrial emissions [1]) has given rise to considerable concern about its impact on the environment in general and human health in particular [2], particularly as regards groundwater contamination [3]. The sorption of deposited heavy metals by soil particles can minimize their passage into surface and subterranean waters, but at the same time creates the possibility that alteration of soil conditions may result in release of the accumulated load into the soil solution, thereby causing pollution of groundwater and/or contamination of plants [4]. Thus the fate of heavy metals, and the toxic risk they pose, depend crucially on their sorption–desorption equilibria and dynamics in the soils on which they are deposited, and on how these equilibria change in

response to changing environmental conditions [5,6]. Empirical investigation of these processes is essential, because although they depend on both the nature of the soil and the characteristics of the metal ions, it is the former that appear to have the greater influence [7,8]. Furthermore, since it is common for several different heavy metals to be present in polluted soils, it is desirable to investigate sorption–desorption behaviour in this complex situation. There have nevertheless been few studies of the sorption and desorption of multiple heavy metals from multi-component solutions by whole soil samples [7–9]. These processes can be characterized in part by the ratio  $K_d$  between the concentration of a given metal sorbed onto soil particles and the concentration left in solution at equilibrium [3,10]. However, because of the complexity of whole soil, and because of competition between different metals,  $K_d$  cannot be estimated as the slope of a linear isotherm (the procedure followed by Gao et al. [11]) because sorption and retention isotherms are usually only linear at quite low concentrations.

In this study we determined the competitive sorption and desorption of cadmium, chromium, copper, nickel, lead and zinc

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by samples of acid soils collected in Galicia (N.W. Spain). For each soil, and for both sorption and desorption, we ordered the metals by the  $K_d$  values obtained with a suitable total concentration of each metal; and we investigated the dependence of these selectivity sequences on soil properties.

## 2. Material and methods

### 2.1. Soils

The WRBSR [12] denominations of 11 acid soils in the Spanish province of Pontevedra were determined on the basis of the characteristics of their various horizons. Three are Humic Umbrisols (HU1, HU2, and HU3), and the others are a Distric Regosol (DR), an Umbric Acrisol (UA), a Eutric Regosol (ER), a Plagic Anthrosol (PA), a Thionic Fluvisol (TF), a Ferric Cambisol (FC), a Haplic Podsol (HP), and a Mollic Leptosol (ML). For heavy metal sorption and desorption experiments, samples were collected from the surface horizons of all these soils except the two Regosols. In these soils the immediately subsurface horizon was used because of the shallowness of the surface horizon (<2 cm). Surface horizons were preferred because it is these that are most affected in the first instance by heavy metal deposition. In each case, six samples were collected using an Eijkelkamp sampler model A, and were transported in polyethylene bags to the laboratory, where they were air dried, passed through a 2 mm mesh sieve, pooled, and homogenized in a vibratory solid sample homogenizer (a Fritsch Laborette 27). Three subsamples of the homogenized sample were used for soil analyses, and three for sorption/desorption experiments.

### 2.2. Soil analyses

For each soil, pH [13], the particle size distribution [14], organic carbon content [15], humified and non-humified organic matter contents [16,17], total and effective cation exchange capacities (CECs), and exchangeable cation content [18] of the chosen horizon were determined, oxides contents [19,20], and its <2  $\mu\text{m}$  fraction was analysed mineralogically [21].

### 2.3. Sorption/desorption experiments

#### 2.3.1. Sorption stage

In each experiment, cadmium, chromium, copper, nickel, lead and zinc were sorbed from a “sorption solution” that contained equal mass concentrations of each metal (between 5 and 400  $\text{mg L}^{-1}$  of each) and had been made up by addition of the metal nitrates to acetate buffer of pH 4.5 (0.02 M acetic acid, 0.02 M sodium acetate), a medium chosen to simulate acid spill conditions. In each experiment, 12 g of soil sample was suspended in 200 mL of sorption solution, and after equilibration by shaking for 24 h at 25 °C in a rotary shaker [7,8,22] this suspension was centrifuged at  $1800 \times g$  for 10 min. Metal concentrations in the supernatants were determined by ICP-OES, and the amount of each metal sorbed by the soil was calculated by difference.

Table 1  
Soil characteristics

Soil	HU1	HU2	HU3	DR	UA	ER	PA	TF	FC	HP	ML
OM ( $\text{g kg}^{-1}$ )	86.64 bc	30.63 fg	99.12 b	5.3 h	89.67 bc	19.65 gh	41.74 ef	13.3 h	14.49 h	125.37 a	76.38 c
NHOM ( $\text{g kg}^{-1}$ )	54.77 b	15.83 d	71 a	3.02 f	37.45 c	5.89 ef	29.59 c	3.17 f	13.44 de	59.43 b	50.15 b
HOM ( $\text{g kg}^{-1}$ )	31.87 c	14.8 d	28.12 c	2.28 e	52.22 b	13.76 d	12.15 d	10.13 d	1.05 e	65.94 a	26.23 c
pH ( $\text{H}_2\text{O}$ ) ( $\text{g kg}^{-1}$ )	4.7 g	4.9 f	5.1 d	5 e	4.6 h	4.51 l	6.3 c	6.6 a	6.4 b	4.4 j	4.9 f
pH (KCl) ( $\text{g kg}^{-1}$ )	4 i	3.9 j	4.4 f	4.2 g	3.7 k	4.8 d	5.5 b	6.6 a	5.2 c	3.4 l	4.1 h
Sand (%)	74.11 c	65.05 e	51.52 g	48.43 h	48.09 h	71.89 d	65.55 e	82.2 a	26.81 i	75.82 b	60.5 f
Silt (%)	2.87 i	20.09 c	33.66 a	29.63 b	25.68 d	1.82 i	5.24 g	8.29 f	34.31 a	10.75 e	6.97 f
Clay (%)	23.02 e	14.86 f	14.82 f	21.94 e	26.23 d	26.29 d	29.2 c	9.43 h	38.88 a	13.43 g	32.53 b
CIC(+) ( $\text{cmol}(+) \text{kg}^{-1}$ )	4.70	2.62	2.11	1.08	6.09	0.38	5.80	9.90	10.84	8.30	3.49
Fe oxide ( $\text{g kg}^{-1}$ )	12.38 cd	8.78d ef	12.17 cd	2.9 g	7.64 ef	10.77 cde	23.94 b	3.6 g	67.6 a	5.2 fg	9.27 cde
Al oxide ( $\text{g kg}^{-1}$ )	16.35 cd	11.6 def	16.08 cd	3.83 g	10.09 ef	14.22 cde	31.62 b	4.76 g	89.28 a	6.87 fg	12.24 cde
Mn oxide ( $\text{g kg}^{-1}$ )	0.27 b	0.04 ef	0.12 cd	0.0004 f	0.005 f	0.004 f	0.03 ef	0.03 ef	1.41 a	0.01 f	0.16 c
Quartz (% of total clay content)	+	+	++++	++	+	+++	++	+++	++	+++	+
Mica (% of total clay content)	++	tr	tr	++	+++	++	++	++	-	+	tr
Kaolinite (% of total clay content)	+++	+++	++	++++	+++	++	++++	+++	+++	++++	++++
Vermiculite (% of total clay content)	++	-	++	-	+++	-	tr	+	-	+	tr
Gibbsite (% of total clay content)	++	+++	++	+++	-	+++	-	tr	-	-	-
Hematite (% of total clay content)	-	-	-	-	-	+	+	-	++	-	-

Values of the same parameter followed by different letters differ significantly with  $p < 0.05$ . +, ++, +++, +++++: > 50%; ++, 30–10%; +, 10–3%; tr: < 3%; -: not detected.

### 2.3.2. Desorption stage

Desorption isotherms were constructed as per Madrid and Díaz-Barrientos [23]. The pellets obtained by centrifugation in the sorption stage were dried at 45 °C, weighed, and resuspended in 200 mL of the same buffer as above. These suspensions were equilibrated in a rotary shaker for 24 h at 25 °C, their pH was measured (all were of pH 4.5), and they were then centrifuged at  $1800 \times g$  for 10 min. Metal concentrations in the supernatants were determined by ICP-OES, and the quantities of metals retained by each soil were calculated by difference with respect to the amounts sorbed in the sorption stage.

Each sorption/desorption experiment was performed in triplicate.

Sorption and desorption data were fitted with Langmuir and Freundlich models [24]. In addition, for each stage of each experiment, the distribution of each metal  $i$  between soil and solution following equilibration was expressed in terms of the quotient

$$K_{d,i} = \frac{10^{-3}C_{i,\text{soil}}}{C_{i,\text{solu}}}$$

where  $C_{i,\text{soil}}$  is the concentration of metal  $i$  on the soil ( $\mu\text{mol g}^{-1}$ ) and  $C_{i,\text{solu}}$  is the concentration of metal  $i$  in solution ( $\mu\text{mol L}^{-1}$ ) [8,10,25,26]. For each soil, sorption and retention capacities for the six metals were compared using the quotient  $K_{d100}$  obtained

in experiments in which the initial concentration of each metal in the sorption solution was  $100 \text{ mg L}^{-1}$  [8].

### 2.4. Statistical analyses

The statistical significance of differences among means was determined by one-way analysis of variance (ANOVA) followed by least significant difference (LSD) tests. Freundlich and Langmuir isotherms were fitted to equilibrium data (where possible) by least squares fits to the linearized equations. The influence of soil characteristics on  $K_{d100}$  was investigated by linear correlation analysis. All statistical calculations were performed using SPSS 14.0 for Windows [27].

## 3. Results and discussion

### 3.1. Soil characteristics

There were significant differences among the 11 soils with respect to properties likely to influence the sorption and desorption of metals (Table 1). Soil pH ranged from 4.4 for HP to 6.6 for TF, total organic matter content from  $5.30 \text{ g kg}^{-1}$  for DR to  $125.37 \text{ g kg}^{-1}$  for HP, and HOM content from  $1.05 \text{ g kg}^{-1}$  for FC to  $65.94 \text{ g kg}^{-1}$  for HP.

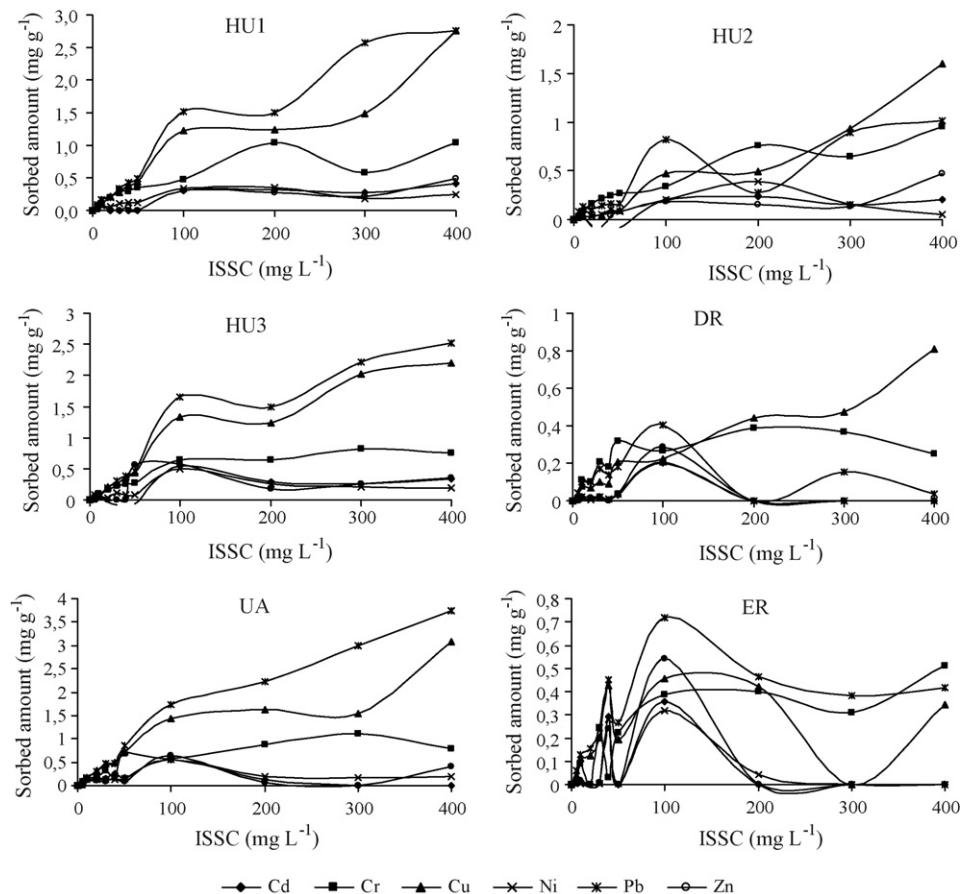


Fig. 1. Plots of the amount of each metal sorbed in the sorption stage of the experiments against its initial concentration in the sorption solution (ISSC), for HU1, HU2, HU3, DR, UA and ER soils.

The soil with lowest Fe oxide content was DR, with  $2.9 \text{ g kg}^{-1}$ . PA, with  $23.9 \text{ g kg}^{-1}$ , had almost twice as much as any other except FC, which had almost three times as much as PA,  $67.6 \text{ g kg}^{-1}$ . The Al oxide content of all soils was almost exactly 32% higher than their Fe oxide content. Mn oxide content was also highest in FC ( $1.41 \text{ g kg}^{-1}$ ), but was very low in all soils. Cation exchange capacities were also low, ranging from  $0.38 \text{ cmol kg}^{-1}$  for ER to no more than  $10.84 \text{ cmol kg}^{-1}$  for FC, the soil with the largest clay fraction (39%).

### 3.2. Sorption and desorption experiments

For each soil, Figs. 1 and 2 plots the amount of each metal sorbed in the sorption stage of the experiments against its initial concentration in the sorption solution, and Figs. 3 and 4 plots the quantity of each metal retained on the sorbent at the end of the desorption stage, likewise against its initial concentration in the sorption solution.

Adsorption can be described by four general types of isotherms (S, L, H, and C) using the classification of Sposito [28]. With an S-type isotherm the slope initially increases with adsorptive concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled. This type of isotherm indicates that at low concentrations the surface has a low affinity for the adsorptive, which increases at high concentrations [1]. The L-shaped (Langmuir) isotherm is characterized by a

decreasing by a decreasing slope as concentration increases since vacant adsorption sites decrease as the adsorbent becomes covered. Such adsorption behavior could be explained by the high affinity of the adsorbent for the adsorptive at low concentrations, which then decreases as concentration increases. The H type (high-affinity) isotherm is indicative of strong adsorbate–adsorptive interactions such as inner-sphere complexes. The C-type isotherms are indicative of a partitioning mechanism whereby adsorptive ions are distributed or partitioned between the interfacial phase and the bulk solution phase without any specific bonding between the adsorbent and the adsorbate [1].

The corresponding isotherms are described qualitatively in Table 2 using the classification of Sposito [28]. Most are irregular because of soil heterogeneity and between-metal competition for binding sites, especially in the case of desorption isotherms and the metals Cd, Ni and Zn. The sorption and desorption isotherm shapes of Pb, however, were identifiable for all soils except HU2, DR and ER: in most cases they were of H type for sorption and L type for desorption, or of L type for sorption and C type for desorption (the only exception was PA, which had L type isotherms for both sorption and desorption). The general lack of marked oscillation in the Pb isotherms suggests that, in keeping with the results of Fontes et al. [9] and Gomes et al. [7], the sorption of lead is little influenced by the presence of other metals, which is

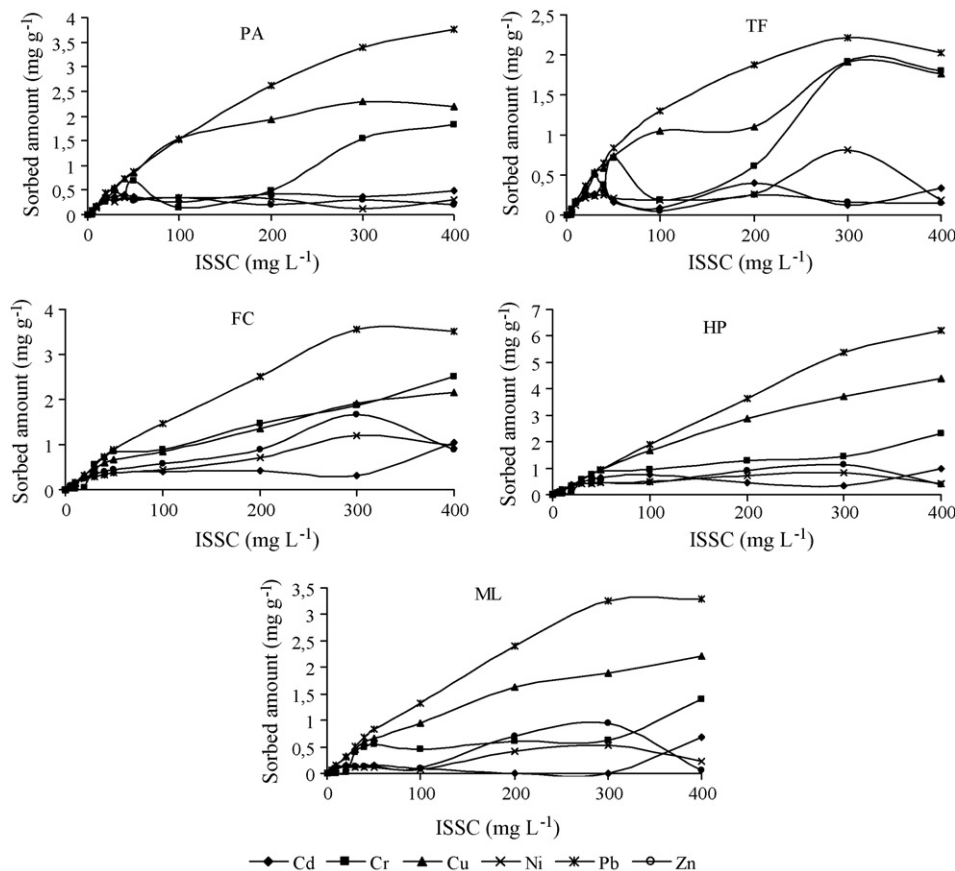


Fig. 2. Plots of the amount of each metal sorbed in the sorption stage of the experiments against its initial concentration in the sorption solution (ISSC), for PA, TF, FC, HP and ML soils.

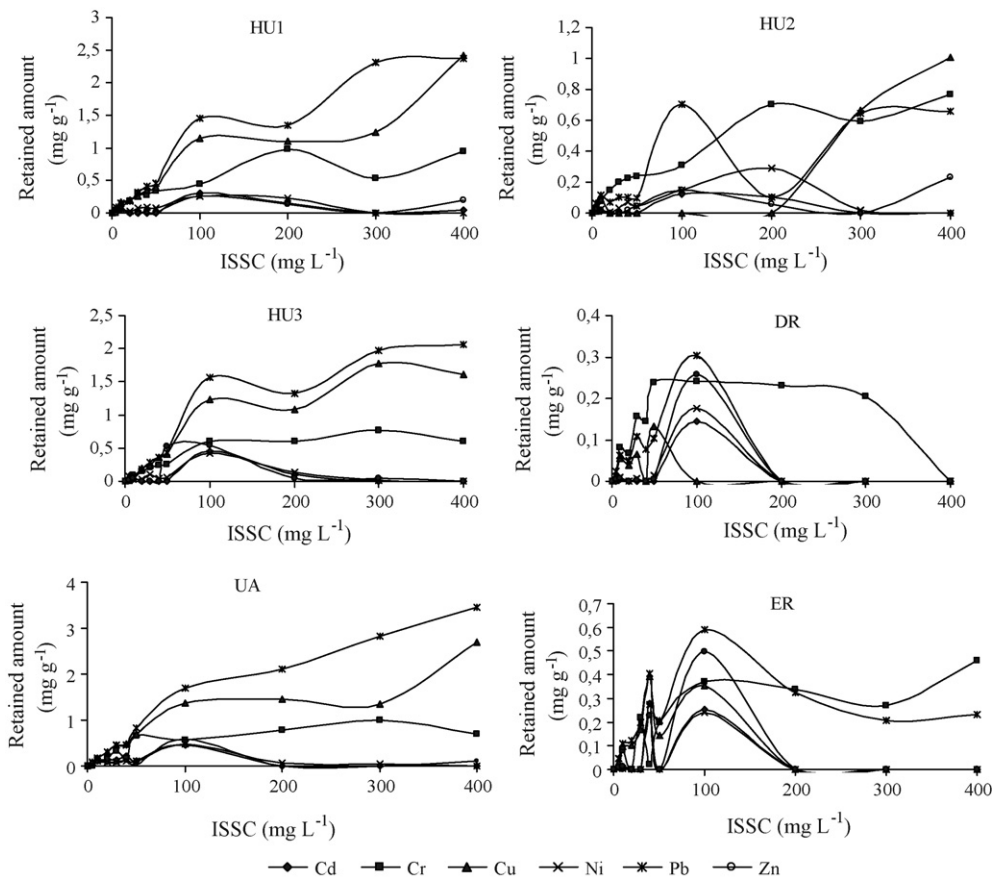


Fig. 3. Plots of the amount of each metal retained in the desorption stage of the experiments against its initial concentration in the sorption solution (ISSC), for HU1, HU2, HU3, DR, UA and ER soils.

attributable to its generally competing successfully for binding sites.

Table 3 shows the best adjustments for the Langmuir and Freundlich models of the obtained sorption and retention isotherms ( $R^2 > 0.7$ ).

For each metal, the number of soils for which sorption data could be fitted, and numbers for which these data were better fitted by each of the two isotherms, were as follows: for Pb, 10 (6 Langmuir isotherms, 4 Freundlich isotherms); for Ni, 9

(all Langmuir); for Cu, 8 (5 Langmuir, 3 Freundlich); for Cr, 5 (all Freundlich; Cr was the only metal for which the Freundlich isotherm fitted better than the Langmuir model more often than *vice versa*); for Zn, 5 (4 Langmuir, 1 Freundlich); and for Cd, 4 (3 Langmuir, 1 Freundlich). With respect to the desorption data, Table 3 shows that the total number of combinations of soil and metal for which either of the isotherms fitted well was fewer than for sorption. For Pb, the number of soils for which good fit was obtained was again 10 (7 for which better fit was obtained with

Table 2  
Curve types using the classification of Sposito [28] of sorption and desorption isotherms

Soil	Cd		Cr		Cu		Ni		Pb		Zn	
	Sorp	Des	Sorp	Des	Sorp	Des	Sorp	Des	Sorp	Des	Sorp	Des
HU1	-	-	L	L	-	-	L	-	H	L	-	-
HU2	-	-	L	-	S	-	-	-	-	-	S	-
HU3	-	-	L	-	L	-	-	-	H	L	-	-
DR	-	-	H	-	-	-	-	-	-	-	-	-
UA	-	-	L	L	L	L	-	-	H	L	-	-
ER	-	-	L	-	-	-	-	-	-	-	-	-
PA	H	-	S	S	H	L	H	-	L	L	H	-
TF	-	-	S	S	H	L	-	-	H	L	-	-
FC	-	-	-	-	H	L	L	-	L	C	-	-
HP	-	-	-	-	L	L	H	-	L	C	-	-
ML	-	-	-	-	H	L	-	-	L	C	-	-

Sorp, sorption isotherms; des, desorption isotherms; -, irregular curves.



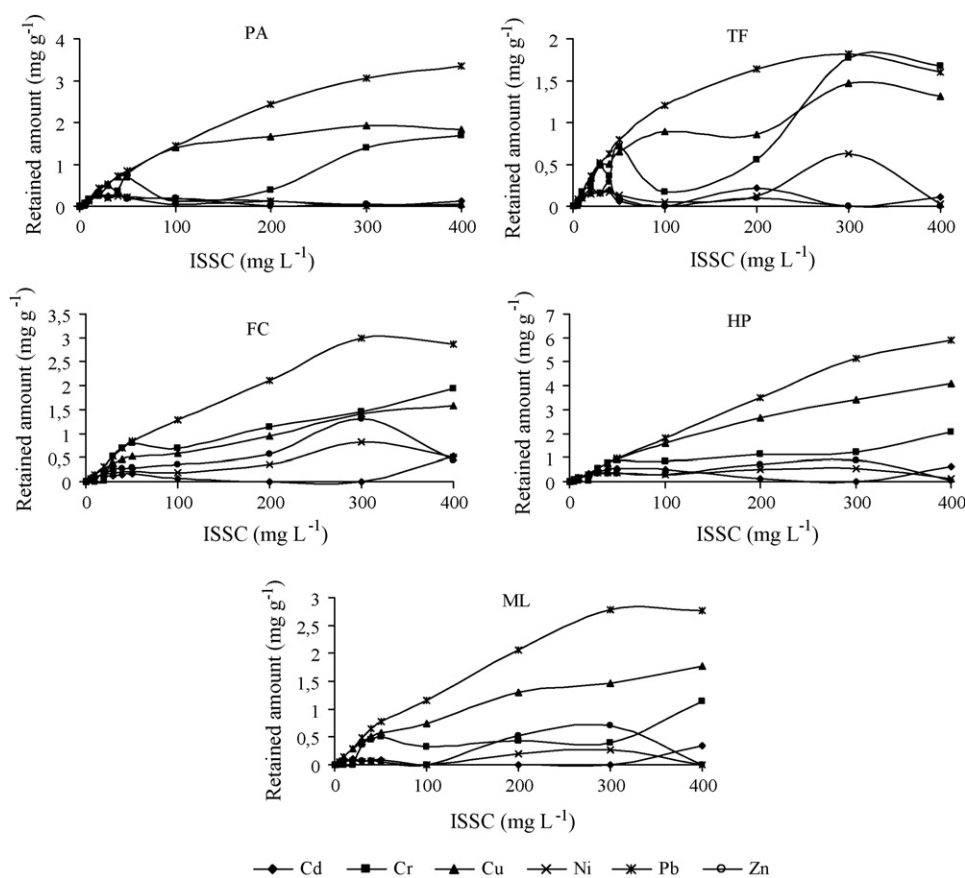


Fig. 4. Plots of the amount of each metal retained in the desorption stage of the experiments against its initial concentration in the sorption solution (ISSC), for PA, TF, FC, HP and ML soils.

the Freundlich isotherm, 3 with the Langmuir isotherm), for Cu it was again 8 (7 Langmuir, 1 Freundlich), and for Cr it rose to 6 (all Freundlich), but for Ni it fell to 6 (5 Langmuir, 1 Freundlich), and for Zn and Cd to 1 (Freundlich in both cases). Somewhat strikingly, the desorption data for Pb were generally better fitted by Freundlich equations, whereas the sorption data for this metal were generally better fitted by Langmuir equations.

The fact that data for only few soils were amenable to being fitted with Freundlich or Langmuir equations (and even then, not for all the metals) means that it is impossible to use the fitted parameters of these models for comparisons among soils. For these purposes we calculated the coefficients reflecting the distribution of metal between soil and solution at a fixed initial concentration in the sorption solution (ISSC) [8,10,25,26]. All comparisons in the remainder of this section are made on the basis of  $K_d$  values for an ISSC of  $100 \text{ mg L}^{-1}$  ( $K_{d100}$ ), a concentration chosen for compatibility with our earlier studies [8,22].

### 3.3. Selectivity sequences

Table 4 lists, for each soil, the selectivity sequences derived on the basis of  $K_{d100}$  values, which are also shown.

The salient features of the selectivity sequences for sorption are as follows. (1) All soils sorbed a greater proportion of total Pb than of any other metal. (2) The  $K_{d100}$  value of the second-

placed metal was more than twice that of the third-placed metal when and only when the second-placed metal was copper; the four soils for which copper was in lower than second place (HU2, DR, ER and FC) were precisely the four in which no vermiculite was detected, which suggests that vermiculite is essential for preferential sorption of copper. (3) In all soils except ML, the  $K_{d100}$  values of Cr, Cd, Ni and Zn differed by less than a factor of four from greatest to smallest (in almost all cases by less than a factor of three). (4) DR and ER, the two soils with lowest CEC, sorbed all metals relatively poorly, including lead; in both these soils, zinc had the second-highest  $K_{d100}$  value, and copper the lowest. (5) In HU2 and FC, sorption of Pb clearly dominated that of all the other metals. (6) The  $K_{d100}$  value of Cr was in second place in both HU2 and FC, and in third place in DR and five of the seven soils in which Cu was in second place.

The low  $K_{d100}$  values of Zn and Cd in comparison with Pb and Cu are in keeping with the greater absorption of the latter by three highly weathered Brazilian soils [9], and with the greater mobility of the former in a Brazilian Oxisol [29]. Also, the low  $K_{d100}$  values of Zn, Cd and Ni in comparison with Pb and Cu are in keeping with the results obtained with seven Brazilian soils by Gomes et al. [7], who related their results to a report that it was Ni, Zn and Cd rather than Pb, Cu and Cr that accumulated in plants grown on sludge-treated plots [30]. However, whereas in these latter studies Cr appears to have behaved like Pb and Cu, in the sorption phase of our experiments it behaved more

Table 3  
Freundlich and Langmuir correlations

Metal	Freundlich correlations				Langmuir correlations			
	Sorption isotherms		Desorption isotherms		Sorption isotherms		Desorption isotherms	
	Soil	$R^2$	Soil	$R^2$	Soil	$R^2$	Soil	$R^2$
Cd	FC	0.78			PA	0.96	FC	0.78
					TF	0.66		
					HP	0.71		
Cr	HU1	0.62					HU1	0.77
	HU2	0.71					HU2	0.79
	HU3	0.57					UA	0.66
	UA	0.51					FC	0.72
	PA	0.85					HP	0.53
						ML	0.72	
Cu	HU1	0.90	HU3	0.97	PA	0.99	HU1	0.92
	HU3	0.73	UA	0.73	TF	0.95		
	UA	0.92	PA	0.96	FC	0.98		
			TF	0.86	HP	0.99		
			FC	0.94	ML	1.00		
			HP	0.95				
			ML	0.97				
Ni			HU1	0.85	HU1	0.90	FC	0.87
			HU2	0.56	HU2	0.71		
			HU3	0.64	HU3	0.89		
			UA	0.66	UA	0.98		
			HP	0.58	PA	0.78		
					TF	0.79		
					FC	0.93		
Pb	HU1	0.96	ER	0.72	UA	0.96	HU1	0.95
	HU2	0.71	PA	0.98	ER	0.98	HU2	0.57
	HU3	0.72	TF	0.99	PA	0.99	HU3	0.91
	ML	0.99			TF	1.00	UA	0.97
					FC	0.98	FC	0.97
					HP	0.98	HP	0.88
						ML	0.97	
Zn	FC	0.95			PA	0.95	FC	0.87
					TF	0.82		
					HP	0.82		
					ML	0.65		

like Zn, Cd and Ni, which is more in accordance with the electronegativity ranking of these metals [6]: Cu (1.9) > Pb (1.8) = Ni (1.8) > Cd (1.7) > Cr (1.6) = Zn (1.6). The fact that the  $K_{d100}$  of Cr was nevertheless generally greater than those of Zn, Cd and Ni may be related to its having been applied in trivalent form (which is usually the form it actually adopts in soil [31]). That Pb was always sorbed more than Cu is not unusual [32–34], and may be related to its greater Misono softness parameter [28] and/or its greater first hydrolysis constant; the sorption, precipitation and chelation of Pb in soils are reviewed in Bradl [35].

In comparison with the  $K_{d100}$  sequences for sorption, those for retention of sorbed metal exhibit some significant differences. Pb, Cr and Cu, in this order or with Cr and Cu exchanged, occupy the first three places in all soils with CEC values greater than  $3 \text{ cmol}_{(+) } \text{ kg}^{-1}$  [36], but in those with lower CEC values the

first-placed metal is Cr and the second- and third-placed either Pb and Zn or Zn and Ni. Zn is retained proportionally more than Pb in the two soils with lowest CEC, ER and DR. In HU2, HU3 and ER, the preferential retention of Cr and relatively good retention of Zn may be partly due to the gibbsite content of these soils;  $\text{Cr}^{3+}$  is fixed primarily on gibbsite, vermiculite, smectite and hydrated micas [37], and Zn forms strong bonds with gibbsite [38–40]. HU3 also has relatively large quantities of Mn oxide, and DR is more than 10% kaolinite, which preferentially sorbs and retains Cr [41].

Further light may be thrown on the retention data by examining the ratio between the values of  $K_{d100}$  for the sorption and desorption stages (Table 5). This ratio tends to decrease in the order Cr > Zn > Ni > Cd > Cu > Pb, in which the first and last metals, Cr and Pb, have respectively the largest and smallest ionic potentials. The higher charge of Cr appears to make its

Table 4  
 $K_{d100}$  values and the corresponding selectivity sequences.

Soil	Sorption						Retention					
	<b>Pb</b> >	<b>Cu</b> >	Cr≥	Cd≥	Ni≥	Zn	Pb≥	Cr≥	Cu>	Zn>	Ni≥	Cd
HU1	69.2	25.0	5.9	4.0	3.8	3.4	493.2	414.3	285.8	143.0	69.4	64.5
HU2	<b>Pb</b> >	Cr≥	Cu≥	Cd≥	Ni≥	Zn	Cr>	Pb≥	Zn≥	Ni≥	Cd>	Cu
	13.7	3.8	3.1	2.3	2.1	2.1	271.0	121.8	95.2	51.8	35.3	0
HU3	<b>Pb</b> >	<b>Cu</b> >	Cr≥	Zn≥	Cd≥	Ni	Cr≥	Pb≥	Zn≥	Cu>	Ni≥	Cd
	61.6	28.5	7.6	7.0	6.9	5.3	597.9	478.4	409.1	316.6	148.5	110.8
DR	<b>Pb</b> ≥	<b>Zn</b> ≥	<b>Cr</b> ≥	<b>Cd</b> ≥	<b>Ni</b> ≥	Cu	Cr≥	Zn≥	Ni≥	Pb≥	Cd>	Cu
	4.2	3.0	2.6	2.1	1.9	0.1	179.6	154.6	103.6	56.4	49.5	0
UA	<b>Pb</b> >	<b>Cu</b> >	Zn≥	Cd≥	Cr≥	Ni	Pb≥	Cr>	Cu>	Zn≥	Ni≥	Cd
	110.8	39.9	8.1	7.7	7.1	6.5	907.2	837.5	374.5	183.8	121.8	89.9
ER	Pb≥	Zn≥	Cd≥	Cr≥	Ni≥	Cu	Cr>	Zn>	Pb≥	Ni≥	Cd≥	Cu
	9.4	6.2	4.1	4.1	3.2	2.7	535.7	234.7	90.7	59.9	48.1	32.2
PA	<b>Pb</b> >	<b>Cu</b> >	Zn≥	Ni≥	Cd≥	Cr	Pb>	Cu>	Cr>	Zn≥	Ni>	Cd
	147.2	64.8	4.0	3.8	3.4	1.5	452.8	198.7	57.4	25.1	21.4	4.2
TF	<b>Pb</b> >	<b>Cu</b> >	Cr≥	Ni≥	Cd≥	Zn	Pb≥	Cr≥	Cu>	Ni>	Cd=	Zn
	56.3	16.7	1.9	1.8	0.9	0.5	243.2	165.1	100.7	4.8	0	0
FC	<b>Pb</b> >	Cr≥	Cu≥	Zn≥	Ni≥	Cd	Pb≥	Cr>	Cu≥	Zn>	Ni>	Cd
	46.0	12.8	9.4	6.6	5.5	4.1	132.3	75.8	34.5	30.4	14.0	3.5
HP	<b>Pb</b> >	<b>Cu</b> >	Cr≥	Cd≥	Ni≥	Zn	Pb≥	Cu≥	Cr>	Cd≥	Zn≥	Ni
	217.1	81.5	14.3	9.9	5.9	4.9	629.7	378.4	207.0	43.7	38.1	34.9
ML	<b>Pb</b> >	<b>Cu</b> >	Cr>	Cd≥	Zn≥	Ni	Pb>	Cu≥	Cr>	Cd=	Zn=	Ni
	32.8	11.7	4.9	0.9	0.8	0.8	145.8	72.2	60.5	0	0	0

'>' and '≥' indicate differences greater than and less than a factor of 2, respectively; underscored groups differ by factors less than 3 and are marked successively starting at low  $K_{d100}$ ; in bold, metals higher in the sequence than the first '>' sign starting from the right.

Table 5  
 Values of  $K_{d100}$  (retention)/ $K_{d100}$  (sorption) (upper figures) and percentage retention (lower figures)

Soil	Cr	Zn	Ni	Cd	Cu	Pb
HU1	70	42	18.3	16.1	11.4	7.1
	95.5	84.8	75.0	98.5	92.0	94.4
HU2	71	45	24.7	15.3	0	8.9
	91.9	77.8	70.6	58.8	0	84.2
HU3	79	58	28	16.1	11	7.9
	95.9	94.3	85.7	81.6	92.8	94.9
DR	69	52	55	23.6	0	13.4
	89.6	88.1	84.8	70.6	0	72.2
UA	118	22.7	18.7	11.7	9.4	8.2
	97.2	89.5	85.7	81.3	94.7	97.5
ER	131	38	18.6	11.7	11.9	9.6
	97.1	91.1	73.1	70.0	61.0	81.8
PA	38	6.3	5.6	1.2	3.1	3.1
	71.4	53.1	49.1	17.4	89.8	94.3
TF	87	0	2.7	0	6.0	4.3
	88.2	0	16.7	0	82.9	91.5
FC	5.9	4.6	2.5	0.9	3.7	2.9
	78.8	59.3	41.3	14.7	62.6	87.0
HP	14.5	7.8	5.9	4.4	4.6	2.9
	89.7	61.8	59.5	64.1	94.0	96.6
ML	12.3	0	0	0	6.2	4.4
	71.4	0	0	0	75.4	86.9

binding more irreversible and so raise its place in the  $K_{d100}$  (retention) ranking, especially when CEC is especially low, while the large size of Pb cations has the reverse effect. That Pb nevertheless has the highest  $K_{d100}$  (retention) value in seven soils is probably due simply to the large amount of lead sorbed in the sorption stage of the experiments, to which HOM, vermiculite and Mn and Fe oxides will have contributed to varying degrees [41–46].

Interestingly, the  $K_{d100}$  (retention)/ $K_{d100}$  (sorption) values of metals in the soils at the bottom of Table 5 (PA, TF, FC, HP and ML) are almost without exception considerably smaller than those in the other soils (HU1–3, DR, UA and ER). Three of the former, TF, FC and HP, are the soils with the highest CEC values—attributable to high clay content and high oxides content in the case of FC, to high organic matter content in the case of HP, and perhaps to an effect of higher pH in the case of TF. Thus the higher CECs of these soils were associated largely with relatively reversible binding. The reversible binding of PA and ML may perhaps be linked to their both having kaolinite contents greater than 14%.

Of the four vermiculite-free soils in which Cu was not sorbed to a greater extent than any other metal except Pb (HU2, DR, ER and FC), two, HU2 and DR, failed to retain any Cu. HU2 has both low HOM content and low clay content (both 15%), while DR has somewhat greater clay content (22%) but very low HOM content (2.3%). The retention of Cu by FC can be attributed to its relatively high CEC, but ER has a very low CEC, in spite of its relatively high clay content (26%).



Table 6  
Pearson coefficients for linear correlation between  $K_{d100}$  and selected chemical and mineralogical soil characteristics, for each metal

	Cd	Cr	Cu	Ni	Pb	Zn
Sorbed						
Humified organic matter	0.589**	0.561**	0.684**	0.352*	0.689**	
Cation exchange capacity					0.400*	
Mica			0.419*			
Retained						
Humified organic matter			0.843**		0.779**	
Kaolinite	0.374*	0.563**	0.407*	0.390*	0.527**	
Vermiculite	0.354*	0.419*		0.350*	0.377*	

\* $P < 0.05$ ; \*\* $P < 0.01$ .

### 3.4. Correlations

Table 6 lists Pearson coefficients for statistically significant pairwise correlations between  $K_{d100}$  and soil characteristics. For most metals,  $K_{d100}$  (sorption) was significantly associated with soil HOM content, and Pb sorption was also influenced by CEC. In keeping with previous reports of the importance of chelation by organic matter for immobilization of lead [35,47], and with the strength of Cu bonds with humic substances (attributed to the relatively large ionic potential of Cu) [48], for these two metals HOM also correlated strongly with  $K_{d100}$  (retention), although in general it was kaolinite and vermiculite contents that correlated with this parameter. However, for Zn neither  $K_{d100}$  (sorption) nor  $K_{d100}$  (retention) showed significant correlation with any of the soil properties considered.

### 4. Conclusions

The sorption and desorption isotherms of most of the metal/soil combinations studied are irregular due to competition for binding sites and the heterogeneity of the soils, although sorption isotherms are in general rather more regular than desorption isotherms.

On the whole, Pb and Cu are sorbed and retained to a greater extent than Cd, Ni or Zn, which have low  $K_{d100}$  values indicative of ready replacement by the other metals. In all these soils, Pb is sorbed more than any other metal when all compete. Cr is in general sorbed only slightly more than Cd, Ni or Zn (and in some soils less), but is strongly retained, with  $K_{d100}$  (retention) values greater than those of Pb and Cu in soils with very low CEC ( $< 3 \text{ cmol}_{(+)} \text{ kg}^{-1}$ ).

Sorption of Pb and Cu correlates with organic matter content, while the retention of these and the other metals considered appears to depend on clay minerals, especially kaolinite, gibbsite, and vermiculite.

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