Effects of sewage sludge and barley straw treatment on the sorption and retention of Cu, Cd and Pb by coppermine Anthropic Regosols

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ABSTRACT

To evaluate the involvement of cation exchange in the competitive and separate sorption and retention of Cu^{2+}, Cd^{2+} and Pb^{2+} by soils developing from a copper mine spoil, and to determine the effects of sludge and barley straw treatment on the intensity and reversibility of sorption and retention, isotherms were constructed by means of batch sorption/desorption experiments in which displaced Ca^{2+}, Mg^{2+}, K^+ and Al^{3+} were also determined. Amendment with sludge and barley straw was associated with an increase in pH of about 4 units; approximately 75-, 1900- and 55-fold increases in CEC_e, organic matter content and Mn oxides content, respectively; and greatly increased capacity for the sorption and retention of Pb, Cu and Cd. Most heavy metal sorption came about through displacement of the predominant cation in the exchange complex (Al^{3+} in unamended soils, and Ca^{2+} in amended soils), but the greater total sorption from multi-metal solutions also involved the displacement of other exchangeable cations.

The parameter K_r clearly reflected the lower sorption and retention capacities of unamended minesoils ($K_r < 0.2$ for all three metals, as against $K_r \approx 0.54$ (Cd) or $K_r > 0.97$ (Pb and Cu) for amended minesoils); the competition for sorption sites in multi-metal solutions (for any given metal, the K_r for single-metal solutions was invariably greater than the corresponding K_r for multi-metal solutions); and the order of preference among metals for sorption and retention (Pb > Cd ≥ Cu for sorption on unamended soils, which had virtually no organic matter, an important Cu-binding component; Pb > Cu ≥ Cd otherwise). The values of the hysteresis index HI were likewise in agreement with previous results on the reversibility of the sorption of these metals, identifying Pb and Cd as the most and the least irreversibly sorbed metals, respectively.

The amendment combination investigated successfully increased the immobilization of Pb, Cu and Cd by this minesoil, but a change in the amendment dosage is necessary in order to achieve near-neutral pH and minimize the predominance of Ca^{2+} in the exchangeable cation complex.

1. Introduction

Unless nurtured appropriately, minesoils (the Anthropic Regosols developed over minespoil) are mechanically, physically, chemically and biologically deficient. They are shallow, texturally unbalanced, and unstructured; have low nutrient and organic matter contents; and the strong acidity caused by rapid, intense oxidation [1,2] results in the loss of large amounts of cations (Al^{3+}, Fe^{2+}, Mn^{2+}, etc.), which hinders biological development. In many minesoils, moreover, these mobilized cations include heavy metals such as Pb, Cd or Cu that can be toxic for vegetation [3] and can contaminate adjacent land and surface and underground waters.

For many years, some of these deficiencies have been tackled by the application of organic amendments. However, such amendments can themselves contain heavy metals, and thus worsen the condition of the treated minesoil in this respect. The evaluation of a minespoil treatment should therefore include investigation of its effects on the sorption and retention of heavy metals by the treated soil, which depend on factors that include oxides and organic matter contents, effective cation exchange capacity (CEC_e), and pH [4].

The term "sorption" is used to encompass adsorption, precipitation on soil particle surfaces, and fixation [5,6]. Furthermore, since the heavy metals pollution threat posed by minesoils generally concerns more than one metal, sorption and retention studies should take into account competition among metals for binding sites, which can lead to a metal being sorbed to a significantly lesser extent than in the absence of other metals [3,7,8].

The World Reference Base for Soil Resources [9] includes the new reference soil group Technosols. Technosols combine soils whose properties and pedogenesis are dominated by their technical origin and include, among others, soils derived from wastes

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originated from human activities [10,11]. Camps et al. [10] also reported that the liming materials confer high pH-buffering capacity, making the mixtures less susceptible to acidification, and thus, to heavy metal mobilization. Wastes can be effectively managed through the preparation of more or less complex mixtures, in which the proportions of each ingredient should be adjusted to provide an adequate environment for the formation of a new soil.

In the present work we investigated the effects of an amendment (Technosol) consisting of sewage sludge, barley straw and mussel shell (6:3:1) on the sorption and retention of Cu, Pb and Cd by soil developed over steep spoil heaps at an opencast mine in N.W. Spain from which chalcopyrite and pyrrotine had been extracted between 1973 and 1988 and road metal since then. The amendment had been applied as a 15 cm layer to a 760 ha area 2 years before samples were taken. In this study the chief pedological characteristics of samples of treated and untreated soil were determined; isotherms for the sorption of Cu, Pb and Cd from solutions containing one or all three, and for the corresponding desorption processes, were constructed by batch experiments.

The role of cation exchange was investigated by determining exchange between Cd, Cu and Pb, on the one hand, and Ca, Mg, K and Al on the other; standard isotherm models (Langmuir and Freundlich) were fitted; and sorption and retention capacities, and the irreversibility of sorption, were evaluated and interpreted using the parameters K_r [12] and HI [13], respectively.

2. Materials and methods

2.1. Soil samples

Samples of Anthropic Regosol [9] were taken from six sites on the spoil heaps of the former copper mine at Touro, A Coruña, Spain (42°52′34″N, 8°20′40″W). At three sites (AMS-1, AMS-2 and AMS-3) the spoil had been treated during the previous 2 years with a Technosol [10] of 15 cm of thickness formed with a mixture of sewage sludge, barley straw and partially crushed mussel shells at the proportions 6:3:1. At the other three sites (UMS-1, UMS-2 and UMS-3) treatment had not yet begun. In all cases the underlying spoil consisted mainly of amphibolites, chalcopyrite, limonite, garnets, and iron and copper sulfides.

At each site, five samples of the top 30 cm were taken using an Eijkelkamp sampler and were pooled in the field. The pooled samples were transported to the laboratory in polyethylene bags, air dried, passed through 2-mm-mesh sieves, and homogenized with a Fritsch Laborette 27 rotary sample divider. All analyses were performed on five subsamples of the pooled sample for each site (hereinafter referred to as a soil).

2.2. Soil analyses

Soil reaction was determined with a pH electrode in 2:1 water:soil mixtures [14].

Particle size distribution was determined following oxidation of organic matter with hydrogen peroxide, the larger fractions (down to 50 mm) being separated by sieving and the smaller material subjected to the international accepted procedure [15].

Organic carbon was quantified by the method of Walkey and Black [16]. Ca^{2+}, Mg^{2+}, K^+ and Na^+ were extracted with 0.2 M ammonium chloride buffered at the soil pH [17,18] and were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin Elmer Optima 4300 DV apparatus.

Native Cd, Cu and Pb were extracted by acid digestion in a polytetrafluoroethylene (PTFE) bomb heated in a microwave oven, using a 1:3:3 (v/v) mixture of concentrated nitric, hydrochloric and hydrofluoric acids [19], and were determined by ICP-OES. Exchangeable acidity was determined using a 1 M KCl replacing solution and titration to a phenolphthalein endpoint [20].

Oxides were determined by the method of Mehra and Jackson [21]: samples were shaken in a solution of sodium hydrogen carbonate and sodium citrate, and Fe, Al and Mn were determined in the extract by ICP-OES. Clay minerals were analysed by powder X-ray diffraction spectroscopy on a Siemens D-5000 diffractometer using a q–$2q$ (Bragg–Brentano) configuration, a Cu anode, 0.05° steps and a 10 s step time [22].

2.3. Sorption/desorption experiments

Data for isotherm construction were obtained in batch experiments by the method of Alberti et al. [23] and Gomes et al. [24], as modified by Harter and Naidu [25].

Soil samples (6 g) were added to 100 mL of "sorption solutions" containing 0.01 M $NaNO_3$ as background electrolyte and 0.01, 0.03, 0.05, 0.08, 0.10, 0.20, 0.30, 0.40, 0.50, 1.00, 2.00 or 3.00 mmol L^{-1} cadmium nitrate, copper nitrate and/or lead nitrate ("single-metal solutions" contained just one heavy metal at one of these concentrations; "multi-metal solutions" contained all three metals, each at the same one of these twelve concentrations).

The soil-and-solution mixtures were shaken in polyethylene centrifuge tubes for 24 h at 25 °C in a rotary shaker, and were then centrifuged at 5000 rpm. The pellet was set aside for the desorption phase of the experiment (see below), and the supernatant was filtered through Whatman 42 paper prior to ICP-OES analysis, which determined Cd, Cu and/or Pb and also, for evaluation of cation exchange, Ca, Mg, Na, K and Al.

To take exchange with the background electrolyte into account, the concentrations of the latter metals were corrected by subtraction of the values determined in an additional experiment in which the sorption solution contained only 0.01 M $NaNO_3$.

Data for desorption isotherms were obtained as per Madrid and Díaz-Barrientos [26]. The pellets obtained in the sorption phase of the experiments were dried at 45 °C, weighed, mixed with 100 mL of background electrolyte solution (0.01 M $NaNO_3$) in polyethylene centrifuge tubes, shaken for 24 h at 25 °C, and centrifuged at 5000 rpm, after which the supernatant was filtered through Whatman 42 paper and its Cd, Cu and/or Pb contents determined by ICP-OES.

The results of preliminary experiments showed that 24 h shaking was sufficient for equilibration of both sorption and desorption (results not shown). Further preliminary experiments established that drying metal-loaded pellets at 45 °C had a negligible effect on desorption (results not shown). In all the sorption/desorption experiments, soil-less controls were run and showed no interference; in particular, sorption of metals by filter paper was negligible. All sorption/desorption experiments were performed in triplicate.

2.4. Construction of isotherms and model fitting

Sorption isotherms were constructed by plotting the amount of metal sorbed during the 24 h equilibration period (in µmol per gram of dry soil) against the equilibrium concentration of metal in solution (in µmol L^{-1}); and desorption isotherms by plotting the amount of sorbed metal retained following desorption (in µmol per gram of dry soil) against the concentration of metal in solution following desorption (in µmol L^{-1}). The following models were then fitted, whenever possible, to the sorption or desorption isotherm data:

- a linearized Langmuir equation

$$\frac{C}{C_s} = \frac{1}{\beta_L K_L} + \frac{C}{\beta_L}$$

where C is the concentration of metal in solution at equilibrium (μmol L^{-1}), C_s is sorbed or retained metal per gram at equilibrium (μmol g^{-1}), β_L is the maximum sorption capacity (μmol g^{-1}) (corresponding to adsorption of a complete monolayer), and K_L is the Langmuir constant (L μmol^{-1}), which increases exponentially with the energy of sorption;
- the linearized Freundlich equation [27]

$$\log C_s = \log K_F + \frac{\log C}{n}$$

where the adimensional parameter n can be regarded as reflecting the energetic heterogeneity of the binding sites of the sorbent, and the Freundlich constant K_F which reflects sorption capacity.

2.5. Overall sorption and retention capacities, and hysteresis

The overall capacity of the soil from each site to sorb a given metal, or all three, was evaluated as the slope K_r [12] of the regression equation $C_{s,i} = K_r C_{p,i}$, where $C_{s,i}$ is sorbed metal i (μmol) per gram of soil at equilibrium, and $C_{p,i}$ is potentially sorbable metal i, i.e. the amount of metal i in the solution before contact with the soil, likewise per gram of soil.

K_r is adimensional and varies from 0 for totally non-sorbent soils to 1 for an ideal sorbent that completely eliminates metal i from solution [12]. To measure capacity for retention of sorbed metal in desorption experiments, K_r was calculated in the same way except that sorbed metal was replaced by metal retained at equilibrium; K_r is then 0 for a soil that completely releases all sorbed metal, and for a soil that releases no metal during the desorption phase of the experiment it adopts the value obtained using the corresponding sorption data.

The irreversibility of sorption was measured by an hysteresis index HI defined as the ratio between the K_r values for retention and sorption [13].

$$HI = \frac{K_{r,\text{retention}}}{K_{r,\text{sorption}}}$$

HI would be unity if sorption was totally irreversible, and zero if all sorbed metal were released.

2.6. Statistical analyses

The statistical significance of differences between the amounts of sorbed metal and released exchange complex cations was examined using Student's t-tests. The significance of other differences among means was estimated by analysis of variance (ANOVA), followed by least significant difference (LSD) tests. The occurrence of cation exchange was also investigated by means of pairwise Pearson correlation analyses between amounts of sorbed metal and released exchange complex cations. All statistical calculations were performed using SPSS for Windows, version 14.0.

3. Results and discussion

3.1. Soil characteristics

Untreated minesoils were of low pH (3.66–4.07), and had low organic matter ($\approx$0.02 g kg^{-1}) and exchangeable Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} contents, and low CEC$_e$ (2.03–2.15 cmol$_{(+)}$ kg^{-1}) (Table 1). Furthermore, the exchangeable cation profile was markedly unbalanced, there being about ten times more Ca^{2+} (0.45 cmol kg^{-1}) than any other cation except Al^{3+} (0.33 cmol kg^{-1}), although Al^{3+} accounted for a slightly greater proportion of CEC$_e$ than Ca^{2+} (about 50% as against 45%). Treated minesoils had much higher pH (8.02–8.39), organic matter content (25.00–52.52 g kg^{-1}), exchangeable Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} contents, and CEC$_e$ (156.61–157.12 cmol$_{(+)}$ kg^{-1}), but the imbalance among exchangeable cations was even more pronounced, Ca^{2+} now accounting for about 88% of CEC$_e$. A decrease in amendment dosage is necessary, in order to lower pH and minimize the predominance of Ca^{2+} in the exchangeable cation complex.

The amended soils also had higher Al and Mn oxides contents than the unamended soils (averages of 9.47 g kg^{-1} (Al) and 2.18 g kg^{-1} (Mn), respectively, as against 1.62 and 0.04 g kg^{-1}); lower Fe oxides contents (11.68 as against 34.75 g kg^{-1}); lower Cu contents (149 as against 244 mg kg^{-1}); and higher Pb contents (87 as against 17 mg kg^{-1}). However, the Cd contents of amended and unamended soils were similar, as were their textures. The clay fraction of both amended and unamended soils was dominated by kaolinite.

3.2. Sorption and cation exchange

The quantities of positive charge gained by the soil through sorption of Cd, Cu or Pb from single-metal solutions are shown in Fig. 1 together with the quantities of positive charge lost through concomitant displacement of exchangeable cations; the corresponding Pearson correlations are listed in Table 2. The sorption of all three metals by unamended soils was closely correlated with TCD (the total charge displacement due to displacement of Al^{3+}, K$^+$, Ca^{2+} and Mg^{2+}) and with Al^{3+} displacement, which generally accounted for almost all of TCD. In keeping with this (given the low CEC$_e$ values of these soils), all these sorption values were very low. The low CEC$_e$s and heavy metal sorption of unamended soils is attributable to their low clay and very low organic matter contents. The least sorbed metal was Cu, and since the charge afforded to the soil by Cu sorption was less than TCD, cation displacement might fully account for Cu sorption. By contrast, Cd and Pb must both have been sorbed by other mechanisms in addition to the displacement of exchangeable cations, which failed to match all sorbed Cd and Pb. For both these metals, sorption was correlated with the displacement of exchangeable cations other than Al^{3+}, namely Ca^{2+} for Cd and K$^+$ and Mg^{2+} for Pb, although only in the case of K$^+$ was the correlation at all close.

The quantities of heavy metals sorbed by the amended soils were 10–20 times greater than those sorbed by the unamended soils (Fig. 1), doubtless due to their very much greater organic matter contents, CEC$_e$, pH, and Mn oxide contents, which a number of authors have identified as the main determinants of heavy metal sorption and of the distribution of heavy metals between soil and soil solution [3,8,28–35]. As in the case of the unamended soils, the relationships between charge gained through sorption and lost through displacement of exchangeable cations suggest that displacement might account fully for Cu sorption but not for sorption of Cd or Pb.

As in the case of the unamended soils, the relationships between charge gained through sorption and lost through displacement of exchangeable cations suggest that displacement might account fully for Cu sorption but not for sorption of Cd or Pb. However, doubtless due to the predominance of Ca^{2+} in the exchange complex of these soils, the majority of TCD was now due to displacement of this cation, followed by Mg^{2+} and K$^+$, while hardly any Al^{3+} was displaced. In keeping with this, the displacements of Ca^{2+}, Mg^{2+} and K$^+$ were all quite closely correlated with heavy metal sorption, but the displacement of Al^{3+} was not. The displaced charge variable with which heavy metal sorption was best correlated was TCD, although the correlation was less close than for unamended soils (Table 2).

Table 1
Descriptive statistics of selected characteristics of the minesoils studied.

Characteristic		Unamended soils (UMS-n)				Amended soils (AMS-n)			
		Mean	SD	Max.	Min.	Mean	SD	Max.	Min.
	pH H$_2$O	3.90	0.22	4.07	3.66	8.18	0.19	8.39	8.02
	OM (g kg^{-1})	0.02	0.00	0.02	0.02	39.05	13.77	52.52	25.00
Oxide contents	Al Ox (g kg^{-1})	1.62	0.05	1.67	1.58	9.47	0.33	9.68	9.09
	Fe Ox (g kg^{-1})	34.75	0.46	35.20	34.28	11.68	0.32	9.09	11.31
	Mn Ox (g kg^{-1})	0.04	0.00	0.04	0.04	2.18	0.05	2.22	2.13
Exchangeable cations	CECe (cmol$_{(+)}$ kg^{-1})	2.09	0.06	2.15	2.03	156.71	0.10	157.12	156.61
	Na (cmol kg^{-1})	0.05	0.01	0.06	0.04	5.29	0.01	5.34	5.28
	K (cmol kg^{-1})	0.04	0.01	0.05	0.03	8.10	0.05	8.27	8.05
	Ca (cmol kg^{-1})	0.45	0.01	0.46	0.44	68.60	0.01	68.89	68.61
	Mg (cmol kg^{-1})	0.06	0.01	0.06	0.05	3.01	0.01	3.12	2.80
	Al (cmol kg^{-1})	0.33	0.01	0.34	0.32	0.03	0.01	0.05	0.02
Particle size distribution	Sand (%)	81.82	0.20	82.02	81.62	79.62	0.20	79.82	79.40
	Silt (%)	10.10	0.10	10.20	10.20	11.20	0.10	11.35	11.10
	Clay (%)	8.08	0.10	8.18	7.98	9.18	0.10	9.32	9.06
Heavy metal contents	Cd (mg kg^{-1})	1.51	0.00	1.62	1.50	1.45	0.13	1.58	1.32
	Cu (mg kg^{-1})	244.44	7.66	252.10	236.78	148.85	7.11	155.97	141.74
	Pb (mg kg^{-1})	17.07	0.75	236.78	16.32	87.20	1.84	89.05	85.36
	Abundance[a]								
Clay fraction	Vermiculite	–				X			
	Mica	X				tr			
	Kaolinite	XXXX				XXXX			
	Quartz	X				XX			
	Gibbsite	XX				X			

[a] tr, <3%; X, 3–10%; XX, 10–30%; XXX, 30–50%; XXXX, >50%.

Fig. 2 shows, for total heavy metal sorption from multi-metal solutions, data analogous to those shown in Fig. 1. As in the case of sorption from single-metal solutions, TCD was due mainly to displacement of Ca^{2+} in amended soils, and to displacement of Al^{3+} in unamended soils (in which both TCD and total sorption were again very low, as was to be expected in view of their low CEC$_e$s). In the latter, all exchangeable cation displacements except that of Ca^{2+} were significantly correlated with metal sorption, although in the case of Mg^{2+} the correlation was very poor; while in the former there was good correlation between metal sorption and the displacement of all cations except Al^{3+}, with Pearson correlation coefficients increasing in the order K$^+$ < Mg^{2+} < Ca^{2+} (Table 2). However, in neither soil type could displacement of exchangeable cations fully account for heavy metal sorption. The correlations between the sorption of each metal and the displacements of exchangeable cations were in all cases very similar to the corresponding correlations for total heavy metal sorption (Table 2).

3.3. Sorption and desorption isotherms

Figs. 3–6 show the sorption and desorption isotherms constructed for Cu, Cd and Pb in the various series of experiments, and Table 3 lists the corresponding Giles curve types [36] and the results of fitting Langmuir and Freundlich equations, when such fits were possible. The most regularly shaped isotherms were those of Pb, which regardless of the presence of other heavy metals were of type L for both sorption and retention on unamended soils and of type C for amended soils. No Giles curve type corresponded to Cd isotherms for desorption from unamended soils; in the other experimental contexts, Cd isotherms were of type H for both sorp-

Table 2
Pearson coefficients of correlation between sorption of Cd Cu, and Pb and displacement of exchangeable cations.

	Sorption from single-metal solutions					
	Cd	Cu	Pb	Cd	Cu	Pb
	Unamended soils (UMS-n)			Amended soils (AMS-n)		
Al	−0.961[**]	−0.974[**]	−0.973[**]	–	–	–
Ca	−0.539[**]	–	–	−0.846[**]	−0.870[**]	−0.867[**]
K	–	–	−0.857[**]	−0.757[**]	−0.813[**]	−0.793[**]
Mg	–	–	−0.405[*]	−0.866[**]	−0.872[**]	−0.872[**]
TCD	−0.920[**]	−0.963[**]	−0.973[**]	−0.873[**]	−0.883[**]	−0.899[**]

	Sorption from multi-metal solutions							
	Cd	Cu	Pb	Total	Cd	Cu	Pb	Total
	Unamended soils (UMS-n)				Amended soils (AMS-n)			
Al	−0.936[**]	−0.943[**]	−0.937[**]	−0.940[**]	–	–	–	–
Ca	–	–	–	–	−0.860[**]	−0.866[**]	−0.856[**]	−0.861[**]
K	−0.802[**]	−0.809[**]	−0.805[**]	−0.806[**]	−0.787[**]	−0.794[**]	−0.788[**]	−0.790[**]
Mg	−0.366[*]	−0.377[*]	−0.377[*]	−0.374[*]	−0.801[**]	−0.810[**]	−0.798[**]	−0.804[**]
TCD	−0.931[**]	−0.938[**]	−0.932[**]	−0.934[**]	−0.864[**]	−0.871[**]	−0.860[**]	−0.866[**]

[*] $p < 0.05$, statistical significance (two-tailed tests).
[**] $p < 0.01$, statistical significance (two-tailed tests).
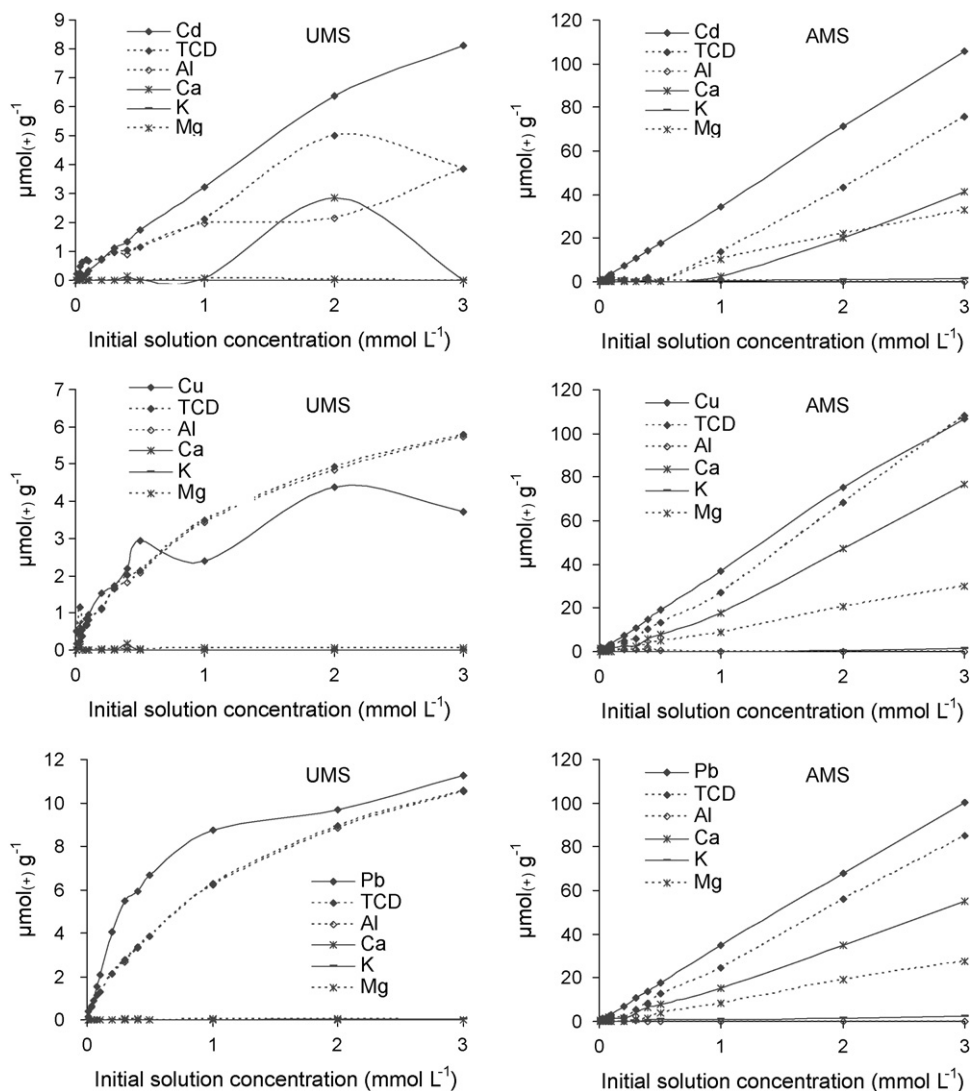
Fig. 1. Sorption of Cd, Cu and Pb from single-metal solutions as a function of initial solution concentration, together with the amounts of exchangeable cations that were displaced. TCD: Al + Ca + K + Mg.

tion and retention on amended soils in the presence of other heavy metals, and of type C otherwise. The only experimental contexts in which Giles curve types could be identified for Cu isotherms were sorption on amended soils (type C in both the presence and the absence of other heavy metals), and sorption (L) and retention (C) on unamended soils in single-metal solutions. Isotherms for total sorption or retention of heavy metals in multi-metal solutions were of type L except for sorption on amended soils, which had a type H curve.

As expected in view of the very low CEC_es of unamended soils, the isotherms suggest that they became near-saturated with heavy metal, and that accordingly, in multi-metal solutions, sorption and retention may have been significantly affected by competition between metals. In fact, as solution concentration increased, sorption from multi-metal solutions by unamended soils was increasingly dominated by Pb, probably due to the major sorbent components of these soils being kaolinite and Fe oxides, both of which have greater affinity for Pb [37–40] than for the other metals [33].

By contrast with the isotherms of unamended soils, those of amended soils, in keeping with their high CEC_es, show signs of deviation from linear sorption or retention behaviour only at the highest solution concentrations, and only those of Cd show depres-

sion attributable to competition in multi-metal solutions. In fact, although it is hard to see in Figs. 3–5, the absence of competition or saturation in amended soils at intermediate metal concentrations is suggested by the three metals being sorbed to practically equal extents under these conditions.

Only for two isotherms corresponding to desorption from unamended soils (Cd in the presence of other metals, and Cu in their absence) was it impossible to fit either the Langmuir or the Freundlich isotherm model. In all, 16 of the 28 experimental isotherms were fitted with Langmuir equations, and 24 with Freundlich equations, which were in fact fitted for all cases except for the retention of Cd or Cu on unamended soils. However, many of the fitted Freundlich equations have a physically quite implausible value of n, less than unity, that would mean an increase in affinity with sorption level. In all these cases of $n < 1$ except one, it was impossible to fit the Langmuir equation (which models saturation); and in the exceptional case, the Langmuir equation itself had a physically impossible negative sorption capacity parameter β_L. In fact, in all the cases in which it was impossible to fit a Langmuir equation, it was either also impossible to fit a Freundlich equation, or the value of n in the fitted Freundlich equation was either less than unity or only very slightly greater than unity (1.10 or 1.11).

Table 3
Giles curve types and mean results of fitting linearized Langmuir and Freundlich models to the sorption and retention isotherms.

Metal	Initial solution	S/R[a]	Soil type	Curve type	Langmuir[b]				Freundlich[c]			
					Equation	R^2	β_L	$K_L \times 1000$	Equation	R^2	n	K_F
Cd	Single-metal	S	UMS	C	nf				$y = 0.91x - 2.53$	0.96	1.10	0.003
			AMS	C	$y = 0.02x + 0.07$	0.99	50	285.71	$y = 0.67x + 0.86$	0.92	1.49	7.24
		R	UMS	–	$y = 1032x - 6975$	0.99	0.001	−147.98	nf			
			AMS	C	nf				$y = 0.9x + 1.1$	0.92	1.11	12.59
	Multi-metal	S	UMS	C	$y = 0.36x + 1104$	0.62	2.78	0.33	$y = 0.83x - 2.7$	0.99	1.20	0.002
			AMS	H	$y = 0.05x - 0.44$	0.99	20	−113.64	$y = 0.37x + 0.51$	0.69	2.70	3.24
		R	UMS	–	nf				nf			
			AMS	H	$y = 0.05x + 0.06$	0.97	20	833.33	$y = 0.68x + 0.79$	0.88	1.47	6.17
Cu	Single-metal	S	UMS	L	$y = 0.47x + 144.78$	0.96	2.13	3.25	$y = 0.56x - 1.49$	0.92	1.79	0.03
			AMS	C	$y = -0.61x + 2.1$	0.69	−1.64	−282.41	$y = 2.2x + 0.01$	0.80	0.45	1.02
		R	UMS	C	nf				nf			
			AMS	–	nf				$y = 2.28x + 0.17$	0.97	0.44	1.48
	Multi-metal	S	UMS	–	$y = 0.58x + 710.1$	0.60	1.72	0.82	$y = 0.56x - 1.86$	0.86	1.79	0.01
			AMS	C	nf				$y = 1.07x + 0.12$	0.67	0.93	1.32
		R	UMS	–	$y = 10053x - 55736$	0.89	0	−180.37	nf			
			AMS	–	nf				$y = 2.95x + 0.38$	0.71	0.34	2.40
Pb	Single-metal	S	UMS	L	$y = 0.18x + 22.16$	0.99	5.56	8.12	$y = 0.48x - 0.73$	0.97	2.08	0.19
			AMS	C	nf				$y = 1.58x + 1.9$	0.83	0.63	79.43
		R	UMS	L	$y = 0.22x + 1.8$	0.99	4.55	122.22	$y = 0.6x - 0.33$	0.95	1.67	0.47
			AMS	C	nf				$y = 2.25x + 1.61$	0.86	0.44	40.74
	Multi-metal	S	UMS	L	$y = 0.27x + 28.87$	0.90	3.70	9.35	$y = 0.44x - 0.76$	0.94	2.27	0.17
			AMS	C	nf				$y = 0.91x + 1.06$	0.62	1.10	11.48
		R	UMS	L	$y = 0.4x + 1.26$	0.82	2.50	317.46	$y = 0.51x - 0.33$	0.89	1.96	0.47
			AMS	C	nf				$y = 1.41x + 1.44$	0.65	0.71	27.54
Total	Multi-metal	S	UMS	L	$y = 0.13x + 196.3$	0.89	7.66	0.66	$y = 0.6x - 1.43$	0.93	1.66	0.04
			AMS	H	$y = 0.01x + 0.5$	0.99	123.46	15.49	$y = 0.59x + 0.54$	0.70	1.70	3.44
		R	UMS	L	$y = 0.36x + 10.3$	0.75	2.78	35.03	$y = 0.67x - 0.92$	0.77	1.50	0.12
			AMS	L	nf				$y = 1.43x + 0.49$	0.85	0.70	3.08

[a] S, sorption; R, retention.

[b] β_L in μmol g^{-1}, K_L in L μmol^{-1}.

[c] K_F in μmol$^{1-1/n}$ L$^{1/n}$ g^{-1}. nf: no fit.

Most of the cases in which it was impossible to fit a Langmuir equation, or in which the fitted equation contained a negative β_L, concerned sorption or retention on amended soils with experimental isotherms that consisted only of the initial pseudo-linear phase. Other cases concerned unamended soils with isotherms that are apparently dominated by the near-saturated phase. It may also be noted that in two of the four cases in which Langmuir equations with negative values of K_L were fitted it was impossible to fit a Freundlich equation; in another β_L was also negative; and in the fourth, for the sorption of Cd on amended soils from multi-metal solutions, the experimental isotherm clearly shows the suppression of sorption due to competition at high concentration. In no case was the negative K_L physically meaningful, because the experiments in which samples were equilibrated against background electrolyte solution showed no spontaneous desorption of native Pb, Cu or Cd.

When both Freundlich and Langmuir equations were fitted with meaningful parameters and one of them clearly fitted better than the other, the soil was generally unamended if it was the Freundlich equation that fitted best and amended if it was the Langmuir equation. Since binding site homogeneity is one of the assumptions made in the derivation of the Langmuir equation, the superiority of this equation for amended soils suggests that the population of binding sites that were occupied in amended soils was more homogeneous, energy-wise, than the population occupied in unamended soils. This would be in keeping with the almost linear experimental isotherms of amended soils (which suggest that almost all occupied sites were of similarly high energies) and the saturation of unamended soils (which implies a wide range of binding energies).

Within the limitations of their theoretical interpretation, the values of n in the fitted Freundlich equations are more or less consistent with the above interpretations of the experimental sorption isotherms. In particular, n indicates that the range of binding ener-
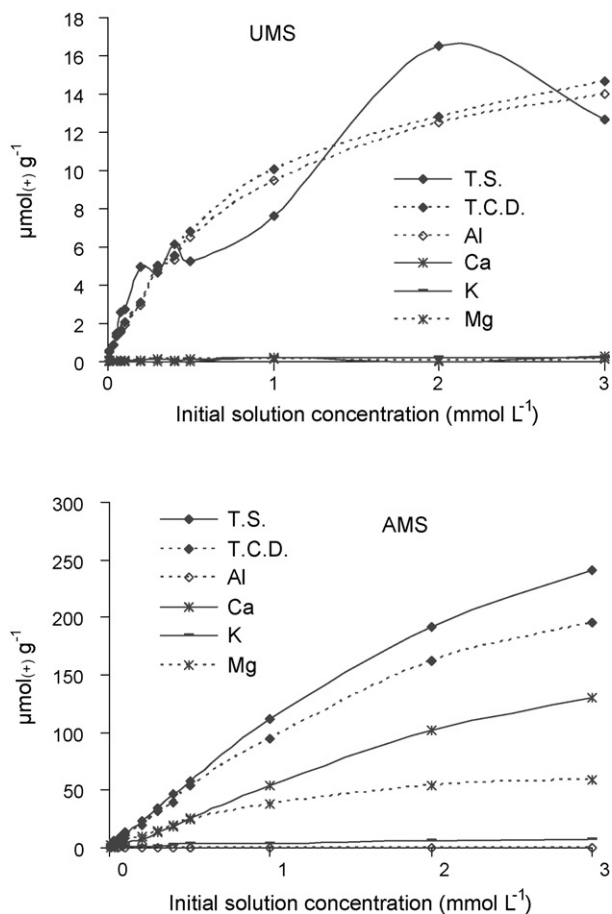
gies was (a) wider on unamended than amended soils except in the cases of Cd (which in unamended soils may have been restricted to low-energy sites) and total metal sorption (for which both types of soil had very similar n values, possibly as a result of averaging effects); (b) wider in multi-metal solutions than in single-metal solutions, especially in amended soils; and (c) widest for Pb on unamended soils but for Cd on amended soils. The interpretability of K_F as a measure of sorption capacity is supported by its being correlated with β_L, though only marginally if the fits for total metal sorption and retention are included ($r = 0.17$, $p = 0.052$; $r = 0.92$, $p < 0.0002$ if these fits are excluded). This correlation is in keeping with the rather narrow range of values of $1/n$ among the 13 isotherms for which both K_F and a positive β_L were calculated (11 of the 13 lie between 0.44 and 0.68). On this basis, K_F, like n, generally behaves in consonance with the discussion of the experimental sorption isotherms: the values for amended soils are all 2–3 orders of magnitude greater than the corresponding values for unamended soils; the values for sorption of individual metals from multi-metal solutions are with one exception smaller than the corresponding values for single-metal solutions; and the values for Pb are greater than those for Cu or Cd. To the extent allowed by the absence of fits for Cd and Cu on unamended soils, the same pattern is exhibited by the values of n and K_F for retention.

3.4. K_r values and reversibility

Because of the disparity among the physical assumptions underlying or justifying different theoretical models, some experimental isotherms are best fitted by one model and others by another. Some are well fitted by both models, but there is no model that adequately fits them all. Furthermore, the parameters of these models are ambiguous: that two experimental isotherms are well fitted by

Table 4
K_r and hysteresis index (HI) values for each combination of soil, metal, initial solution type and experimental phase (sorption or retention). R^2 values of the regressions affording K_r are shown in parentheses.

		UMS-1	UMS-2	UMS-3	AMS-1	AMS-2	AMS-3
Cd							
K_r	Single-metal sorption	0.1027 (0.9997)	0.0787 (0.9999)	0.0737 (0.9998)	0.9842 (0.7707)	0.9860 (0.8134)	0.9853 (0.7788)
	Competitive sorption	0.0352 (>0.9999)	0.0346 (>0.9999)	0.0326 (>0.9999)	0.5424 (0.7564)	0.526 (0.7321)	0.5539 (0.7777)
	Single-metal retention	0.0001 (0.9999)	0 (>0.9999)	0.0003 (0.9998)	0.9827 (0.7847)	0.9839 (0.8498)	0.9834 (0.8185)
	Competitive retention	0.0018 (>0.9999)	0 (>0.9999)	0 (>0.9999)	0.5355 (0.7579)	0.5201 (0.7337)	0.549 (0.7788)
HI	Single-metal	0.001	0	0.004	0.998	0.998	0.998
	Competitive	0.051	0	0	0.987	0.989	0.991
Cu							
K_r	Single-metal sorption	0.0545 (0.999)	0.0534 (0.9986)	0.0461 (0.9986)	0.9984 (>0.9999)	0.9985 (>0.9999)	0.9986 (>0.9999)
	Competitive sorption	0.029 (0.9999)	0.0318 (0.9999)	0.0284 (0.9999)	0.979 (0.9997)	0.9753 (0.9995)	0.9797 (0.9997)
	Single-metal retention	0.0115 (0.9993)	0.0184 (0.9988)	0.0122 (0.9989)	0.9977 (>0.9999)	0.9975 (>0.9999)	0.9973 (>0.9999)
	Competitive retention	0.0003 (>0.9999)	0.0015 (>0.9999)	0.0004 (0.9999)	0.9783 (0.9997)	0.9745 (0.9995)	0.9791 (0.9997)
HI	Single-metal	0.211	0.345	0.265	0.999	0.999	0.999
	Competitive	0.010	0.047	0.014	0.999	0.999	0.999
Pb							
K_r	Single-metal sorption	0.1432 (0.9877)	0.1592 (0.9905)	0.1521 (0.9889)	0.9998 (>0.9999)	0.9998 (>0.9999)	0.9998 (>0.9999)
	Competitive sorption	0.1248 (0.9888)	0.1456 (0.9914)	0.1044 (0.9868)	0.9956 (>0.9999)	0.9952 (>0.9999)	0.996 (>0.9999)
	Single-metal retention	0.1153 (0.9888)	0.1284 (0.9912)	0.1219 (0.9903)	0.9996 (>0.9999)	0.9996 (>0.9999)	0.9997 (>0.9999)
	Competitive retention	0.0949 (0.9897)	0.1144 (0.9925)	0.0753 (0.9882)	0.9953 (>0.9999)	0.9949 (>0.9999)	0.9958 (>0.9999)
HI	Single-metal	0.805	0.807	0.801	1	1	1
	Competitive	0.760	0.786	0.721	1	1	1
Total (Cd + Cu + Pb)							
K_r	Sorption	0.06 (0.9989)	0.0671 (0.9991)	0.0529 (0.9987)	0.8434 (0.9839)	0.8366 (0.9797)	0.8475 (0.9866)
	Retention	0.0294 (0.999)	0.0351 (0.9993)	0.023 (0.9989)	0.8408 (0.9836)	0.8373 (0.9794)	0.8456 (0.9864)
HI		0.49	0.5231	0.4348	0.9969	1	0.9978

a given model does not guarantee that the physical basis of the good fit is the same in both cases. For all these reasons, these parameters fail to allow reliable comparison of the overall capacities of different soils for sorption or retention of heavy metals under different conditions. It was to meet the need for such a measure that the parameter K_r described in Section 2.5 was defined [12].

Fig. 2. Total sorption TS of heavy metals (Cd + Cu + Pb) from multi-metal solutions as a function of the concentration of each metal in the initial solution, together with the amounts of exchangeable cations that were displaced. TCD: Al + Ca + K + Mg.
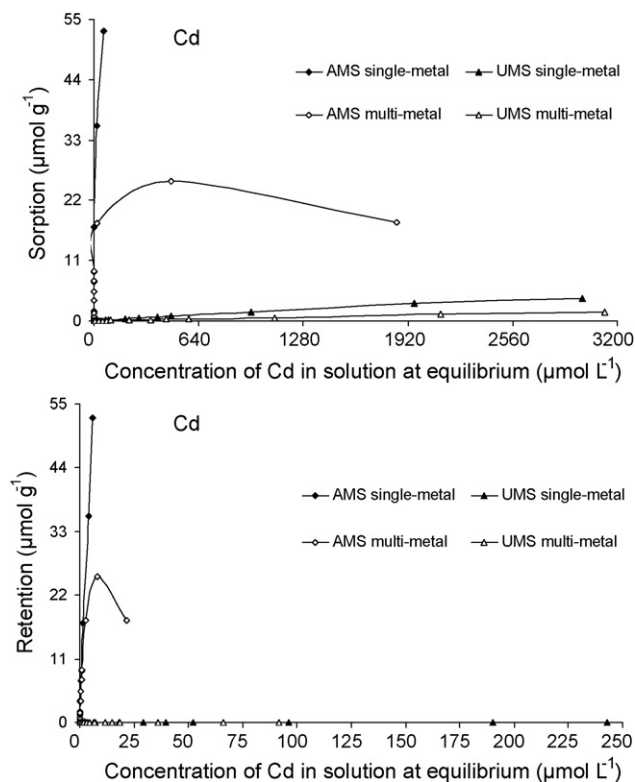
Fig. 3. Experimental isotherms for the sorption and retention of Cd on amended (AMS) and unamended (UMS) soils in single- and multi-metal solutions.
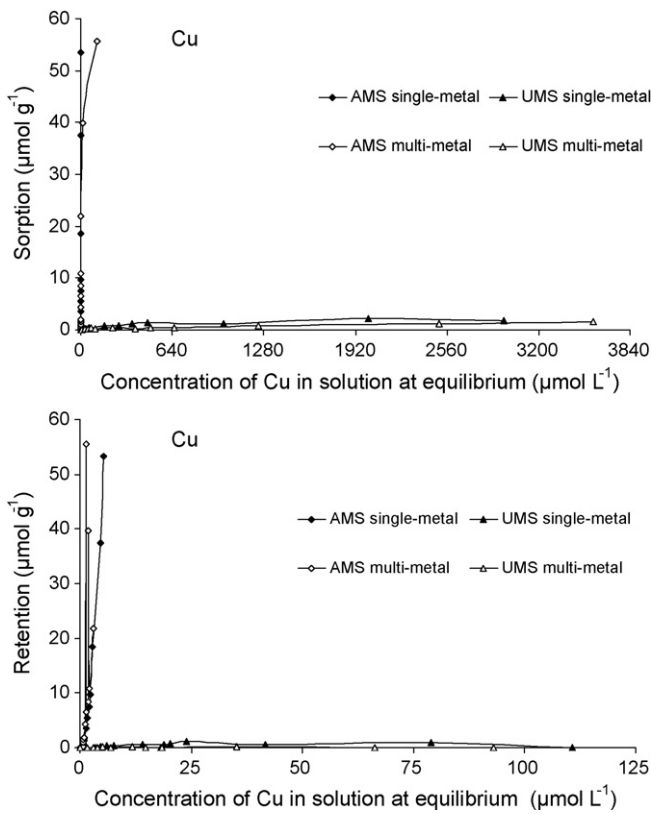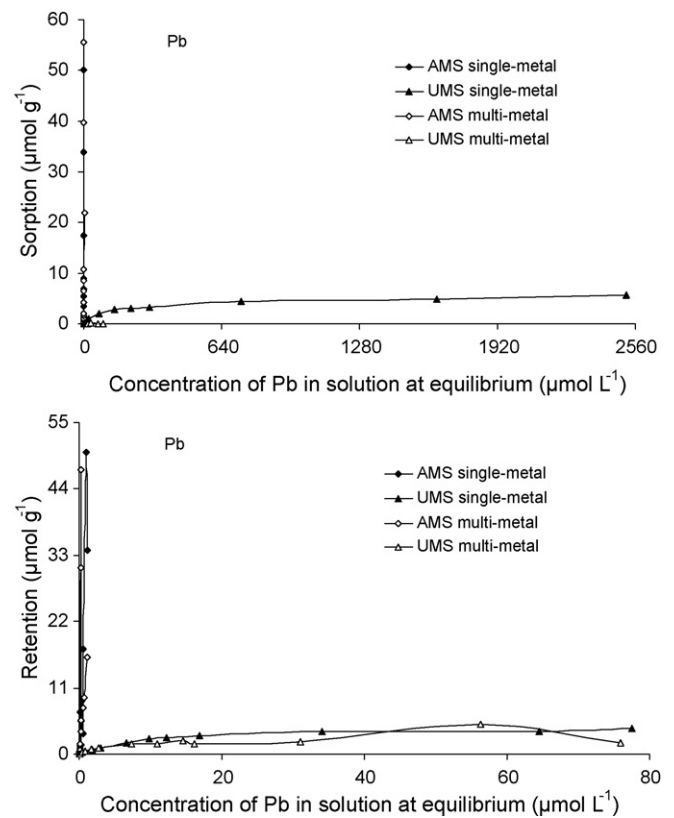
Fig. 4. Experimental isotherms for the sorption and retention of Cu on amended (AMS) and unamended (UMS) soils in single- and multi-metal solutions.

Fig. 5. Experimental isotherms for the sorption and retention of Pb on amended (AMS) and unamended (UMS) soils in single- and multi-metal solutions.

Table 4 lists the values of K_r obtained for the soils, metals and conditions considered in this study, together with the corresponding values of R^2 for the regression lines of which the K_r values are the slopes. The R^2 values are all greater than 0.73, and all except those for Cd and Cd + Cu + Pb in amended soils are greater than 0.98 (overall mean 0.9797), so K_r is a well-defined index of sorption or retention capacity. The K_r values clearly reflect the greater sorption and retention capacities of the amended soils in both single-metal and multi-metal solutions, and the greater sorption or retention of any single metal from single-metal rather than multi-metal solutions (the only exceptions in this respect concern the very small

K_rs for the practically negligible retention, by unamended soils, of Cd, which in amended soils exhibits the greatest difference in behaviour between single- and multi-metal solutions). For each experimental condition (solution type and experiment phase), the mean K_rs for each soil type also show that in general the capacity for sorption or retention of metals decreased in the order Pb > Cu ≥ Cd (Table 5). However, sorption on unamended soils exhibited the order Pb > Cd ≥ Cu. The poor sorption of copper by unamended soils may have been partly because of their lack of organic matter, which is especially important for Cu sorption; partly because of the prior

Table 5
Sorption and retention selectivity sequences and hysteresis sequences.

Selectivity sequences					
	Sorption from single-metal solutions	Sorption from multi-metal solutions	Comparison between sorption from single- and multi-metal solutions[a]		
			Cd	Cu	Pb
UMS soils	Pb > Cd > Cu	Pb > Cd = Cu	I > C	I > C	I = C
AMS soils	Pb > Cu > Cd	Pb > Cu > Cd	I > C	I > C	I > C
	Retention after sorption from single-metal solutions	Retention after sorption from multi-metal solutions	Comparison between retention after sorption from single- and multi-metal solutions		
			Cd	Cu	Pb
UMS soils	Pb > Cu > Cd	Pb > Cu = Cd	I = C	I > C	I = C
AMS soils	Pb > Cu > Cd	Pb > Cu > Cd	I > C	I > C	I > C

Hysteresis sequences		
	Single-metal solutions	Multi-metal solutions
UMS soils	Pb > Cu > Cd	Pb > Cu > Cd
AMS soils	Pb > Cu > Cd	Pb > Cu > Cd

[a] > or <: I or C are significantly different ($p < 0.05$).
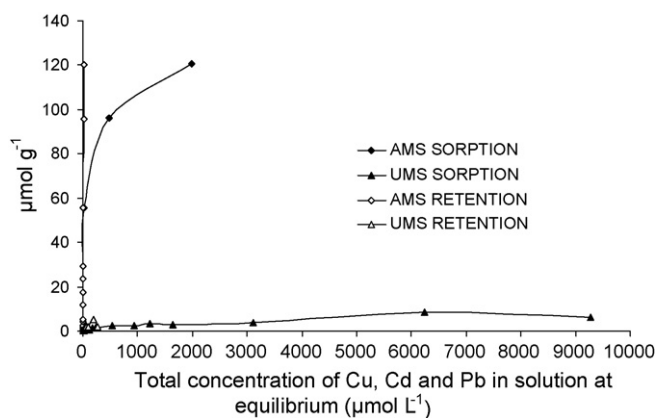
Fig. 6. Experimental isotherms for the total sorption and retention of heavy metals (Cu + Cd + Pb) on amended (AMS) and unamended (UMS) soils in multi-metal solutions.

occupancy of relatively Cu-specific binding sites by part of the high native Cu content of these soils; and, in the case of sorption from multi-metal solutions, partly due to competition from Pb, which as noted above is preferentially sorbed by the major sorbent components of these soils, kaolinite and Fe oxides.

Table 4 also lists values of the hysteresis index HI. According to this index, sorption on amended soils, with their high pH, $CEC_{e}s$ and organic matter and Mn oxide contents, was practically irreversible, though slightly less so for Cd than for the other metals. On unamended soils sorption was almost totally reversible for Cd and, in multi-metal solutions, for Cu; and to a large extent irreversible for Pb, which was nevertheless, like Cu, sorbed more reversibly in multi-metal solutions than in single-metal solutions. The greater irreversibility of Pb sorption on unamended soils, like its greater sorption, is attributable to the kaolinite and Fe oxides contents of these soils [37–40]. That the sorption of Cu by unamended soils was largely reversible is in keeping with the above-noted possibility of the prior occupancy of relatively Cu-specific binding sites by native Cu, since this may have forced added Cu to bind to sites for which it had less affinity; and since this effect will have been particularly acute when Cu competed with the other metals (especially Pb), it would also explain why Cu was sorbed more reversibly by unamended soils in the presence than in the absence of other metals.

4. Conclusions

(1) The amendments caused significant modification of the soil properties with most influence in the sorption and retention of Pb, Cu and Cd, being associated with a great increase in pH, CEC_e and organic matter content. These changes were undoubtedly largely responsible for the greatly increased metal-binding capacity of the amended soils.

(2) In both amended and unamended soils, most sorption of Pb, Cu and Cd came about through cation exchange. The cations displaced into single-metal solutions were mainly those that predominated in the exchange complex (Al^{3+} in unamended soils, and Ca^{2+} in amended soils), but the greater total sorption from multi-metal solutions also involved the displacement of other exchangeable cations.

(3) The parameter K_r clearly reflected:

(3.1) The lower sorption and retention capacities of unamended soils ($K_r < 0.2$ for all three metals, as against $K_r \approx 0.54$ (Cd) or $K_r > 0.97$ (Pb and Cu) for amended soils).

(3.2) The competition for sorption sites in multi-metal solutions (for any given metal, the K_r for single-metal solutions

was invariably greater than the corresponding K_r for multi-metal solutions).

(3.3) The order of preference among metals for sorption and retention (Pb > Cd $\geq$ Cu for sorption on unamended soils, Pb > Cu $\geq$ Cd otherwise; these preference orderings are in keeping with other analyses of the sorption of these metals).

(4) The values of the hysteresis index HI identified Pb and Cd as the most and the least irreversibly sorbed metals, respectively.

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