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Competitive sorption and desorption of heavy metals by individual soil components

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Abstract

Knowledge of sorption and desorption of heavy metals by individual soil components should be useful for modelling the behaviour of soils of arbitrary composition when contaminated by heavy metals, and for designing amendments increasing the fixation of heavy metals by soils polluted by these species. In this study the competitive sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by humified organic matter, Fe and Mn oxides, kaolinite, vermiculite and mica were investigated. Due to the homogeneity of the sorbents, between-metal competition for binding sites led to their preferences for one or another metal being much more manifest than in the case of whole soils. On the basis of k_{d100} values (distribution coefficients calculated in sorption–desorption experiments in which the initial sorption solution contained 100 mg L^{-1} of each metal), kaolinite and mica preferentially sorbed and retained chromium; vermiculite, copper and zinc; HOM, Fe oxide and Mn oxide, lead (HOM and Mn oxide also sorbed and retained considerable amounts of copper). Mica only retained sorbed chromium, Fe oxide sorbed cadmium and lead, and kaolinite did not retain sorbed copper. The sorbents retaining the greatest proportions of sorbed metals were vermiculite and Mn oxide, but the ratios of k_{d100} values for retention and sorption suggest that cations were least reversibly bound by Mn oxide, and most reversibly by vermiculite.
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Keywords: Sorption; Desorption; Heavy metals; Clay; Organic matter; Oxides; Distribution coefficient; Selectivity sequence

1. Introduction

Numerous land treatments or other practices, including the application of fertilizer or sewage sludge, the disposal of effluent on land, and industrial activity, can lead to soils acquiring heavy metal contents substantially in excess of natural levels, with the consequent risk of uptake by plants, pollution of surface or underground waters, and propagation through the food chain [1]. The risk of leaching or uptake by plants depends on the concentration of pollutant in the soil solution, which in turn depends on the sorption–desorption equilibria that govern the partition of pollutant between soil solution and soil solids, soil colloids especially [2,3]. The toxic potential of heavy metals in soil thus depends on soil composition, particularly the amount and type of clay minerals [4–6], organic matter [7,8] and iron and manganese oxides [9–11]. For example, in previous work we found that organic matter, Fe and Mn oxides, and clay and mica contents largely determine competitive sorption and desorption of heavy metals by certain soils in Galicia (N.W. Spain) [12–14]. Determination of the sorption and desorption behaviour of these soil components in isolation is a necessary first step towards the construction of models allowing prediction of the behaviour of soils of arbitrary composition. In the work described here we accordingly studied the simultaneous sorption and desorption of six heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) by kaolinite, vermiculite and mica (common clay minerals in N.W. Spain), by synthetic Fe and Mn oxides, and by humified organic matter (HOM) from a Fibric Histosol H horizon.

2. Materials and methods

2.1. Sorbent materials

2.1.1. Oxides

Fe and Mn oxides were prepared as per McLaren and Crawford [15]. Briefly, iron oxide (96% Fe_2O_3) was obtained by adding sodium hydroxide to ferric chloride solution, and manganese oxide (97% MnO_2) by slowly adding hydrogen peroxide

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to potassium permanganate solution; in each case, the resulting precipitate was washed thoroughly with de-ionized water, dried at 55 °C, and ground in a vibratory ball mill.

2.1.2. Clay minerals

Kaolinite and mica were supplied by Caolines de Vimianzo (Spain), and vermiculite by Süd-Chemie-Spain. Their mineralogical analysis was done by X-ray diffraction in a SIEMENS D-5000 diffractometer with crystalline powder. To measure the samples, a q-2q configuration (Bragg-Brentano system) was used with a Cu anode and 0.05 passes with a time of 10 s per pass [16]. The commercial kaolinite was 90% kaolinite and 10% mica, the commercial mica 97% mica and 3% quartz, and the commercial vermiculite (Sepiolite) > 91% vermiculite, < 3% quartz, < 3% mica and < 3% calcite.

2.1.3. Humified organic matter (HOM)

HOM was obtained from the H horizon of a Fibric Histosol by the method of Andriulo et al. [17] and Galantini et al. [18], which avoids the use of aggressive reagents that modify the properties of the extract. A 50 g sample of the H horizon was air-dried, suspended in 100 mL of water, and shaken for 2 h in the presence of 5 mm glass beads (to disrupt soil aggregates [19]). The fraction passing a 0.1 mm sieve (HOM) was then dried in a forced air oven at 30 °C, ground in a mortar, and characterized ($pH_{H_2O} = 5.1$, $pH_{KCl} = 4.5$, $CEC_{(+)} = 12.52\ cmol_{(+)}\ kg^{-1}$, organic matter content $389\ g\ kg^{-1}$ as determined by the method of Walkey and Black [20]). In previous work we found that HOM so defined accounted for practically all adsorption of heavy metals by the H horizon of origin [21].

2.2. Competitive sorption/desorption experiments

2.2.1. 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 $400\ mg\ L^{-1}$ 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 sorbent material was suspended in 200 mL of sorption solution, and after equilibration by shaking for 24 h at 25 °C in a rotary shaker [12,22,23] was centrifuged at $1800 \times g$ for 10 min. Metal concentrations in the supernatants were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Perkin-Elmer Optima 4300 DV apparatus, and the amount of each metal sorbed by the sorbent was calculated by difference.

2.2.2. Desorption stage

Desorption was evaluated as per Madrid and Díaz-Barrientos [24]. The pellets obtained by centrifugation in the sorption stage were dried at 45 °C, weighed, and resuspended in 200 mL of acetate buffer, after which these suspensions were equilibrated in a rotary shaker for 24 h at 25 °C and 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 material were calculated by difference with respect to the amounts sorbed in the sorption experiments.

Each sorption/desorption experiment was performed in triplicate. In each stage of each experiment, following equilibration, pH measurement confirmed that the pH of the medium was still 4.5.

2.3. Isotherm fitting

Sorption and desorption data were fitted with Langmuir and Freundlich models [25] by least squares. For each stage of each experiment, the distribution of each metal *i* between sorbent and solution following equilibration was expressed in terms of the distribution coefficient:

$$k_{d,i} = 10^{-3}\,\frac{C_{i,\mathrm{sorb}}}{C_{i,\mathrm{solu}}}$$

where $C_{i,\mathrm{sorb}}$ is the concentration of metal *i* on the sorbent ($\mu mol\ g^{-1}$) and $C_{i,\mathrm{solu}}$ is the concentration of metal *i* in solution ($\mu mol\ L^{-1}$). Following Kaplan et al. [26], joint distribution coefficients $k_{d\sum sp}$ were also calculated for each sorbent material [13]:

$$k_{d\sum sp} = 10^{-3}\,\frac{\sum_i C_{i,\mathrm{sorb}}}{\sum_i C_{i,\mathrm{solu}}}$$

The sorption and retention capacities of the sorbent materials were compared using the distribution coefficients k_{d100} and $k_{d\sum sp100}$ obtained in experiments in which the initial concentration of each metal in the sorption solution was $100\ mg\ L^{-1}$ [13].

2.4. Statistical analysis

Where possible, linearized Freundlich and Langmuir isotherms were fitted to equilibrium data by least squares [25]. The k_{d100} data for retention of metals by the sorbent samples were subjected to principal components analysis. All statistical calculations were performed using SPSS 14.0 for Windows [27].

3. Results and discussion

3.1. Sorption and desorption data

For each sorbent material, Fig. 1 plots the amount of each metal sorbed in the sorption stage of the experiments against its initial concentration in the sorption solution (ISSC), and Fig. 2 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. In general, sorption profiles were similar to retention profiles. For most sorbents, if not all, increasing ISSC, which increased the competition among cations for binding sites, clearly resulted in the metals for which the sorbent had least affinity being totally or proportionally excluded by the preferentially sorbed metal or metals. This effect is more marked for these relatively homogeneous sorbents than for whole soils.

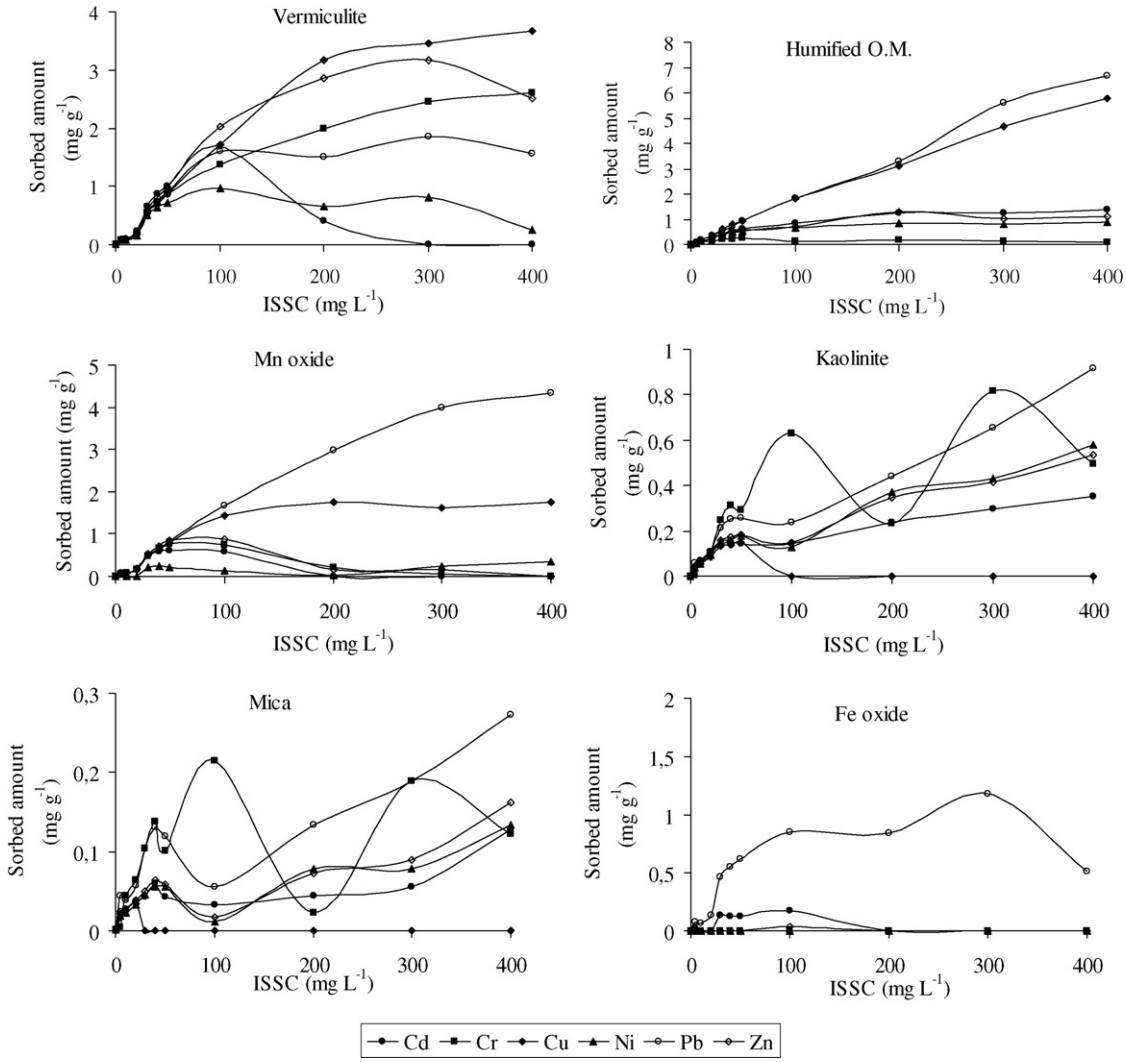

Fig. 1. Plots of the amount of each metal sorbed in the sorption stage of the experiments against its initial concentration in the sorption solution (ISSC), for each sorbent.

Fe oxides only sorbed or retained lead (up to about 5 μmol g^{-1}) and, from solutions with concentrations not exceeding 100 mg L^{-1}, cadmium. By contrast, Mn oxides sorbed and retained up to about 15 μmol g^{-1} of chromium and zinc (with sorption/retention peaks corresponding to ISSCs of 50–100 mg L^{-1}) as well as up to 20–25 μmol g^{-1} of lead (maximum starting from 400 mg L^{-1} solutions) and copper (from 100 to 400 mg L^{-1} solutions). Sorption/retention of cadmium and nickel on Mn oxides did not exceed about 5 μmol g^{-1}, but like that of chromium and zinc peaked at ISSCs of 50–100 mg L^{-1}.

Kaolinite sorbed or retained up to about 15 μmol g^{-1} of chromium but virtually no copper (especially with ISSCs greater than 50 mg L^{-1}). Sorption of nickel, zinc, lead and cadmium lay in between these extremes, increasing more or less linearly with ISSC following a minor local maximum at 50 mg L^{-1}; nickel behaved very like zinc, and lead very like cadmium. Retention at the end of the desorption stage followed much the same pattern except that cadmium was hardly retained at all when ISSC was greater than 100 mg L^{-1}, at which concentration nickel, zinc, lead and cadmium were all retained to very similar extents.

Sorption onto mica showed a pattern very similar to sorption onto kaolinite, although it was about four times less intense and sorption of copper ceased at an ISSC of 20 mg L^{-1}. However, the only metal retained on mica when the when ISSC was greater than 50 mg L^{-1} was chromium (which moreover was not retained when ISSC was 200 or 400 mg L^{-1}).

Vermiculite sorbed up to 45–55 μmol g^{-1} of copper, chromium and zinc, up to about 15 μmol g^{-1} of cadmium and nickel, and less than 10 μmol g^{-1} of lead. Copper sorption rose with ISSC, levelling out at around ISSC = 200 mg L^{-1}; chromium sorption was still rising at 400 mg L^{-1}; zinc sorption peaked at 300 mg L^{-1}. Cadmium sorption fell after a peak at an ISSC of 100 mg L^{-1}; nickel sorption reached a plateau at ISSC = 100 mg L^{-1} and fell off after ISSC = 300 mg L^{-1}; while lead sorption rose initially but levelled off at ISSC = 100 mg L^{-1}. Retention by vermiculite exhibited a quite similar pattern, except that the highly sorbed metals underwent appreciable desorption (about 5 μmol g^{-1} for zinc and copper, and over 10 μmol g^{-1} for chromium), retention of both cadmium and nickel fell off after a peak at ISSC = 100 mg L^{-1},

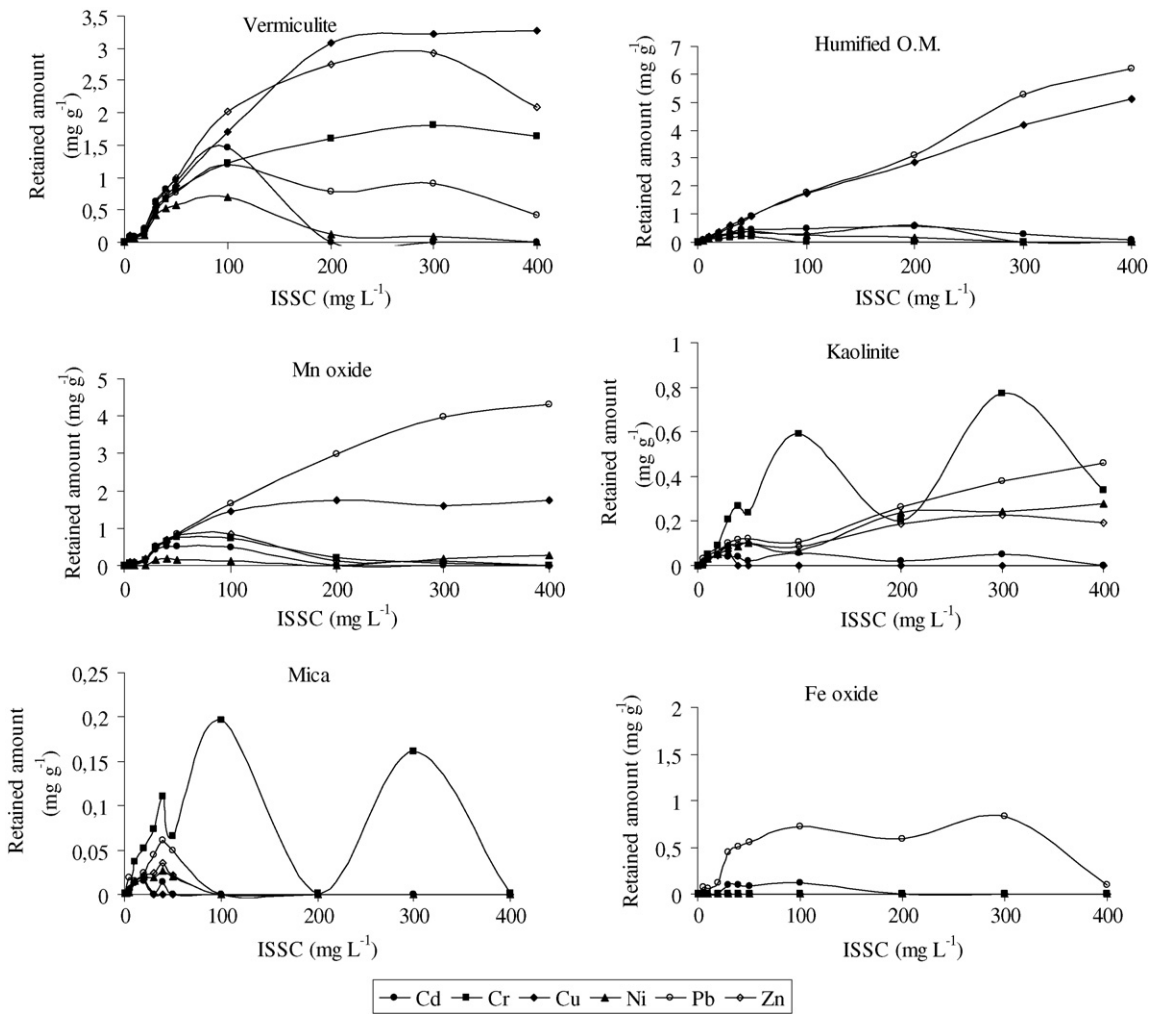

Fig. 2. Plots of the amount of each metal retained in the desorption stage of the experiments against its initial concentration in the sorption solution (ISSC), for each sorbent.

and lead retention had already levelled off by about ISSC = 30 mg L^{-1}.

On HOM, both sorption and retention of copper rose almost linearly with ISSC to the highest values for any metal on any sorbent, about 90 μmol g^{-1} for sorption and 80 μmol g^{-1} for retention. The sorption profiles of lead, nickel and cadmium were likewise almost linear, lead sorption rising to about 30 μmol g^{-1} and sorbed nickel and cadmium to 1015 μmol g^{-1}; but whereas hardly any lead was subsequently desorbed, nickel, cadmium and the other metals (except copper) underwent almost complete desorption when ISSC was greater than 200 mg L^{-1}. Zinc sorption and retention peaked at about 15 and 10 μmol g^{-1}, respectively, at an ISSC of 200 mg L^{-1}. Chromium sorption never rose above about 5 μmol g^{-1}, and both sorption and retention of this metal peaked at ISSC = 50 mg L^{-1}.

3.2. Fitted isotherms

Table 1 lists the binding affinity and binding capacity parameters of the Langmuir and Freundlich equations fitted to the sorption and retention data in those cases where a fit with $R^2 > 0.75$ was possible (18 metal/sorbent combinations for sorption and 7 for retention). The fact that only 25 of the 72 potential isotherms could be fitted is attributable to the competitive effects noted in the first paragraph of Section 3.1, since both the Langmuir and the Freundlich models assume the presence of just a single sorbate [28].

Almost all the sets of data fittable by Freundlich isotherms were for sorption or retention on kaolinite. In the case of sorption, the only metals that did not comply with this model on kaolinite were copper (which was not sorbed at all at ISSCs greater than 50 mg L^{-1}) and chromium (which exhibited a curiously fluctuating sorption profile on both kaolinite and mica). The Freundlich model also provided an acceptable description of the sorption of lead on Fe and Mn oxides, the retention of lead on kaolinite and HOM, and the retention of nickel on kaolinite.

Almost all the sets of data fittable by Langmuir isotherms were for sorption or retention on vermiculite and HOM. Langmuir isotherms fitted the sorption data of all the metals on HOM, and of all except cadmium on vermiculite (Table 1).

Quantitatively, the Langmuir equation fitted more sets of sorption data than the Freundlich equation, and the fit was on average better. These differences were less pronounced for the retention data.

Table 1
Parameters of Freundlich and Langmuir isotherms fitted to equilibrium data for the sorption and desorption stages of the experiments

Metal	Material	R^2	Freundlich	
			n	k_F ($L^{1/n}$ $\mu mol^{(1-1/n)}$ g^{-1})
Sorption				
Cd	Kaolinite	0.8409	2.922	0.178
Ni	Kaolinite	0.89	2.334	0.182
Pb	Kaolinite	0.952	2.366	0.142
	Fe oxide	0.7733	2.874	0.425
	Mn oxide	0.7538	2.290	1.773
Zn	Kaolinite	0.8955	2.542	0.221
Metal	Material	R^2	Langmuir	
			β ($\mu mol\ g^{-1}$)	$k_L \times 1000$ ($L\ \mu mol^{-1}$)
Sorption				
Cd	HOM	0.9943	12.422	5.782
Cr	Vermiculite	0.9878	50.505	5.291
	HOM	0.8927	1.979	−7.941
Cu	Vermiculite	0.9999	51.546	244.332
	HOM	0.9595	84.746	5.510
	Mn oxide	0.9953	19.268	−30.998
Ni	Vermiculite	0.7856	5.476	−3.522
	HOM	0.9957	15.106	3.912
Pb	Vermiculite	0.992	7.899	2659.664
	HOM	0.9447	33.445	16.202
Zn	Vermiculite	0.9886	40.323	−98.140
	HOM	0.9875	17.361	3.254
Metal	Material	R^2	Freundlich	
			n	k_F ($L^{1/n}$ $\mu mol^{(1-1/n)}$ g^{-1})
Desorption				
Ni	Kaolinite	0.8868	0.887	0.015
Pb	Kaolinite	0.9808	0.843	0.012
	HOM	0.9602	1.361	1.095
Metal	Material	R^2	Langmuir	
			β ($\mu mol\ g^{-1}$)	$k_L \times 1000$ ($L\ \mu mol^{-1}$)
Desorption				
Cu	Vermiculite	0.9975	47.170	159.279
	HOM	0.9667	83.333	10.122
Pb	Vermiculite	0.8103	2.836	−338.388
Zn	Vermiculite	0.9419	36.496	95.139

3.3. Distribution coefficients and selectivity sequences

The fact that data for only half the sorbents 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 sorbents or, for half the sorbents, among metals. For these purposes we calculated the coefficients reflecting the distribution of metal between sorbent and solution at a fixed ISSC [29–32]. All comparisons in the remainder of this section are made on the basis of k_d values for an ISSC of 100 mg L^{-1} (k_{d100}; see Table 2), a concentration chosen for compatibility with our earlier studies [13].

Fe oxide preferentially sorbed and retained lead (followed by cadmium and, in the case of sorption, zinc; no other metals were sorbed), but because of its very limited total sorption capacity only sorbed more lead than kaolinite and mica, and only retained more lead than kaolinite, mica and vermiculite. That Fe oxide sorbs more lead than kaolinite has also been reported by Abd-El Fattah and Wada [33] (who likewise found it to sorb more lead than humus).

Mn oxide preferentially sorbed and retained lead, followed by copper, and exhibited least preference for nickel and cadmium. It was the material that sorbed most lead, and that retained most lead, copper, chromium and nickel. These findings are in keeping with a report of high affinity of soil Mn oxides for lead, copper and nickel [34], which was attributed to higher-valence manganese.

The metal sorbed preferentially by kaolinite and mica was chromium, followed a long way behind by lead. Chromium was

Table 2
Distribution coefficients k_{d100} (L kg^{-1}) calculated from equilibrium data for the sorption and desorption stages of the experiments, and the selectivity sequences they imply

Metal	Kaolinite		Mica		Vermiculite		HOM		Fe oxide		Mn oxide	
	Sorption	Retention	Sorption	Retention	Sorption	Retention	Sorption	Retention	Sorption	Retention	Sorption	Retention
Cd	1.39	12.99	0.31	nd	89.5	143.38	14.37	25.24	1.74	33.18	7.59	114.86
Cr	9.74	306.48	2.46	264.14	55.75	164.38	1.35	2.44	nd	nd	13.27	1762.9
Cu	nd	nd	nd	nd	3457.28	3258.42	189.15	462.16	nd	nd	147.24	4539.11
Ni	1.35	22.75	0.11	nd	19.14	51.58	8.46	13.69	nd	nd	1.51	61.41
Pb	2.68	18.38	0.56	nd	117.91	61.56	232.96	574.27	15.44	98.12	1176.6	12203.03
Zn	1.43	30.81	0.15	nd	2212.06	2951.43	9.21	15.49	0.33	nd	14.29	528.67

	Sorption	Retention
Selectivity sequences		
Kaolinite	Cr > Pb > Zn > Cd > Ni > Cu	Cr > Zn > Ni > Pb > Cd > Cu
Mica	Cr > Pb > Cd > Zn > Ni > Cu	Cr > Cd = Cu = Ni = Pb = Zn
Vermiculite	Cu > Zn > Pb > Cd > Cr > Ni	Cu > Zn > Cr > Cd > Pb > Ni
HOM	Pb > Cu > Cd > Zn > Ni > Cr	Pb > Cu > Cd > Zn > Ni > Cr
Fe oxide	Pb > Cd > Zn > Cu = Ni = Cr	Pb > Cd > Cu = Ni = Cr = Zn
Mn oxide	Pb > Cu > Zn > Cr > Cd > Ni	Pb > Cu > Cr > Zn > Cd > Ni

The entry "nd" indicates that no sorption or retention was detected.

also the metal that was preferentially retained by these sorbents (mica retained no other); in the case of kaolinite, this finding was in agreement with those of Wei et al. [35] and Chantawong et al. [36]. Copper was neither sorbed nor retained on either kaolinite or mica.

Vermiculite preferentially sorbed and retained copper, followed by zinc, sorption and retention of these metals being more than an order of magnitude greater than for any other metal. This preference for copper is in keeping with Harter's finding that the sorption of copper by Ap and B2 horizons of several northeastern United States soils was highly correlated with their vermiculite content [37]. However, for all metals except lead, k_{d100} for sorption on vermiculite was at least twice k_{d100} for sorption on any other substrate (in the case of zinc, 154 times). By contrast, vermiculite was relatively inefficient in retaining sorbed metals: only for cadmium and zinc did it have the highest k_{d100} value, and for copper and lead k_{d100} was smaller for retention than for sorption, whereas k_{d100} was greater for retention than for sorption for all other metal/sorbent combinations for which k_{d100} for sorption exceeded 1000 L kg^{-1}. The relatively poor retention of copper is somewhat surprising in view of its having been reported that part of the copper sorbed by vermiculite (and other silicate clays) is bound in non-diffusing form.

Finally, HOM, like Mn oxide, preferentially sorbed and retained lead and copper, the k_{d100} values of all other metals being at least an order of magnitude smaller. Both the sorption and retention selectivity sequences of HOM are in keeping with the finding of Takamatsu and Yoshida [38] that divalent cations of lead, copper and cadmium formed the most stable complexes with humic acid, and the stability of complexes of lead with soil organic matter has also been stressed by Bradl [39] and Pinheiro et al. [40]. Stevenson pointed to the relatively high charge-to-radius ratio of copper as responsible for its strong bonds with humic substances [41].

The aggregate distribution coefficients $k_{d\sum sp100}$ for sorption, in decreasing order, were as follows: 77.85 for vermiculite, 14.71 for Mn oxide, 13.41 for HOM, 2.59 for mica, 0.74 for Fe oxide, and 0.62 for kaolinite. For retention, $k_{d\sum sp100}$ was 605.07 for Mn oxide, 194.18 for vermiculite, 57.38 for mica, 50.94 for HOM, 22.08 for kaolinite, and 12.3 for Fe oxide. These aggregate data suggest that whereas vermiculite and Mn oxide play a major role in the sorption and retention of heavy metal cations, the contributions of kaolinite and Fe oxide to these processes are relatively insignificant, although the importance of these contributions in any given soil will of course depend on the relative proportions of these components (with regard to mica, it should also be borne in mind that this sorbent only retained chromium to a measurable extent and sorbed very little of anything else).

Interestingly, the sorbents that showed the widest between-metal variation in k_{d100} values (vermiculite, Mn oxide and HOM), showed relatively little variation between metals as regards sorption–desorption hysteresis, as reflected by the k_{d100} (retention)/k_{d100} (sorption) ratio, although the variation in this parameter did tend to increase with value. Thus k_{d100} (retention)/k_{d100} (sorption) ranged from 0.5 to 2.7 for vermiculite, from 1.6 to only 2.5 for HOM, from 7 to 31 for kaolinite, and from 15 to 133 for Mn oxide (for mica and Fe oxide there are too few data for evaluation). The same order is shown by the $k_{d\sum sp100}$ (retention)/$k_{d\sum sp100}$ (sorption) ratio: 2.5 for vermiculite, 3.8 for HOM, 36 for kaolinite, and 41 for Mn oxide. By this measure, the most retentive sorbent was thus generally Mn oxide, and the least retentive vermiculite and HOM. In other words, although vermiculite tended to sorb more metal than Mn oxide, sorption by vermiculite and HOM was relatively reversible, whereas sorption by Mn oxide was not. This would explain why it was possible to fit Langmuir isotherms to the data for almost all vermiculite/metal and HOM/metal combinations.

Table 3
Results from Principal Component Analysis (PCA)

	Loading on components	
	PC1	PC2
Principal component analysis (PCA)		
Desortion k_{d100}		
Cd	0.912	−0.354
Cr	0.735	0.662
Cu	0.991	0.054
Ni	0.906	−0.250
Pb	0.735	0.672
Zn	0.645	−0.750

3.4. Principal components analysis

To help identify patterns in the metal retention behaviour of the sorbents, the sorbent samples were considered as points in the six-dimensional space defined by their k_{d100} (retention) values for each metal, and these data were subjected to principal components analysis. The first two components, PC1 and PC2, respectively, accounted for 69% and 27% of the total variance. The loadings of the metals on these components (Table 3) suggest that whereas PC1 indicates a general capacity to retain simultaneously sorbed metals, PC2 indicates discrimination between chromium and lead on the one hand, and zinc (and to a lesser extent cadmium and nickel) on the other. Accordingly, in the PC1–PC2 plane, Mn oxide occupies the upper right quadrant, vermiculite the lower right quadrant, and the other sorbents left-hand locations near the PC1 axis (Fig. 3).

4. Conclusions

Due to the homogeneity of the sorbents used in this study, between-metal competition for binding sites led to their preferences for one or another metal being much more manifest than in the case of whole soils.

With few exceptions, the binding of metals to these sorbents in the presence of competitors failed to comply with Langmuir or Freundlich models. Most of the exceptions concern vermiculite and HOM, which appear to bind more reversibly than the other sorbents considered.

On the basis of k_{d100} values for sorption, kaolinite and mica preferentially sorbed chromium; vermiculite, copper and zinc; HOM, Fe oxide and Mn oxide, lead (HOM and Mn oxide also sorbed considerable amounts of copper).

Mica only retained sorbed chromium, Fe oxide sorbed cadmium and lead, and kaolinite did not retain sorbed copper. The sorbents retaining the greatest proportions of sorbed metals were vermiculite and Mn oxide, but the ratios of k_{d100} values for retention and sorption suggest that metals were least reversibly bound by Mn oxide, and most reversibly by vermiculite.

These results should be taken into account when designing treatments to increase the heavy metal fixation capacity of soils polluted by heavy metals.

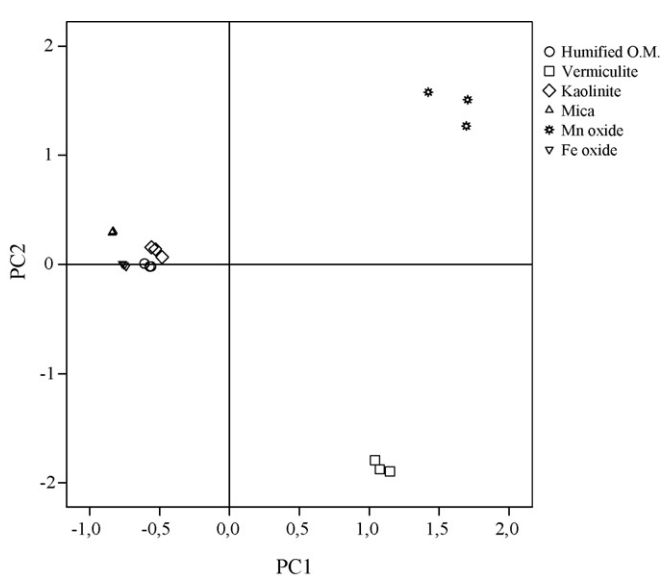

Fig. 3. Loadings of metals on the first two components extracted by principal components analysis of the k_{d100} (desorption) data for all sorbent samples and plotted in the plane.

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