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Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn in acid soils II. Soil ranking and influence of soil characteristics

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Abstract

In Part I of this paper we reported, for each of 11 acid soils, the rankings of six metals according to their sorption from solutions containing all six, and according to their retention under desorption conditions. Here, we analyse the same data from a different perspective: for each metal, we rank the soils by their capacities to sorb and retain it as reflected by soil/solution distribution coefficients K_{d100} measured using starting solutions containing 100 mg L⁻¹ of each metal. We also ranked the soils for overall heavy metal sorption and retention capacities using Kaplan's compound measure $K_{d\Sigma}$, and we investigated the influence of soil characteristics on K_{d100} and $K_{d\Sigma100}$ values. Overall capacity for sorption of heavy metals was positively related to HOM, kaolinite and Fe oxides contents, and negatively related to CEC and to vermiculite and haematite contents. Overall capacity for retention of heavy metals was positively related to HOM and kaolinite contents, and negatively related to CEC and vermiculite content. The good correlation between $K_{d\Sigma100}$ (sorption) and the first component extracted in a principal components analysis of K_{d100} (sorption) values, and between $K_{d\Sigma100}$ (retention) and the first component extracted in a principal components analysis of K_{d100} (sorption) values, and between $K_{d\Sigma100}$ (retention) and the first component extracted in a principal components analysis of K_{d100} (sorption) values, supports the adequacy of $K_{d\Sigma}$ as a measure of the overall capacity of a soil to sorb or retain heavy metals.

Keywords: Sorption; Desorption; Distribution coefficients; Heavy metals; Soil ranking; Soil

1. Introduction

Throughout the world there is growing concern that the heavy metal contents of soil are increasing as the result of industrial, mining, agricultural and domestic activities [1-3]. Although certain heavy metals, such as copper and zinc, are essential for plant growth as micronutrients, they are toxic at higher levels, as are metals such as lead, cadmium and mercury. Furthermore, the greater the toxic metals burden of the soil, the greater is the risk of non-localized pollution due to the metals leaching into groundwater; even though the soil can act as a buffer between the source of pollution and water bodies thanks to its remarkable ability to immobilize metal ions through various kinds of sorption mechanism (physical or chemical adsorption, surface precipitation, solid-state diffusion) [4–5], it may release sorbed metals if the corresponding equilibria are altered

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The soil components mainly responsible for binding metals - especially metal cations, the directly bioavailable form - are organic matter, clay minerals, and Fe and Mn oxides [5-6]. Depending on the relative proportions and compositions of these soil fractions, and on soil texture and total CEC (which itself depends mainly on soil organic matter and clay content), a soil will have more or less capacity to bind a particular heavy metal species, and will bind it more or less strongly. Soil organic matter can bind heavy metals both through ionic interactions and by complexation, especially in the case of lead, copper and zinc [7-10]. The CECs and sorption capacities of individual clay minerals depend on their specific surface areas and electrical charges: to mention only some of the most common minerals, CEC increases in the order kaolinite < mica < smectite < vermiculite [5,10,12,13]. Fe and Mn oxides are especially relevant for immobilization of lead and copper, although they also bind zinc, cobalt and chromium [5,11]. The oxidation state and hydrated ionic radius of the metal

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are also relevant to soil-metal bond strength, which increases with the valence of the metal species and decreases with increasing ionic radius.

The capacity of a soil for sorption and retention of a given metal species can be characterized in part by the ratio K_d between the concentration of metal sorbed onto soil particles from a solution of that species and the concentration left in solution at equilibrium [2,8]; for attainment of equilibrium it is generally considered sufficient to shake the soil with the solution for 24 h [14–16]. However, because of the complexity of whole soil and its chemistry [17–19], and because of competition between different metals, K_d cannot in general be estimated as the slope of a linear isotherm (the procedure followed by Gao et al. [15]), because sorption and retention isotherms are usually only linear at quite low concentrations; instead, K_d must be treated as a function of concentration. For overall evaluation of the capacity of a soil simultaneously to sorb and retain a set of several metals that compete for binding sites, $K_{d\Sigma}$ is defined in the same way as K_d , but using total metal concentration [8,9,18].

In this study we determined the competitive sorption and desorption of cadmium, chromium, copper, nickel, lead and zinc by samples of eleven acid soils collected in Galicia (N.W. Spain). The characteristics of these soils, and the K_d values determined in sorption and desorption experiments, were reported in Part I of this paper. In Part II we rank the soils by their K_d and $K_{d\Sigma}$ values, and analyse the influence of relevant soil properties on these values.

2. Material and methods

2.1. Soils and soil properties

The soils included in the study were three Humic Umbrisols (HU1, HU2, and HU3), 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). Samples were collected from the surface horizons of all these soils except the two Regosols, for which 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 episodes. In each case, the soil was characterized in terms of texture, pH, total organic matter content, humified organic matter (HOM) content, oxides contents (Fe, Mn and Al), clay mineral contents (quartz, mica, kaolinite, vermiculite, gibbsite, haematite), and CEC. Sorption/desorption experiments were performed in which (1) the soil sample was equilibrated for 24 h with a solution containing equal masses of cadmium, chromium, copper, nickel, lead and zinc (all as divalent cations except chromium, which was included as the trivalent cation); (2) the soil was separated from the solution by centrifugation; (3) the quantity of each metal sorbed onto the soil during equilibration was determined; and (4) desorption of the metals from the soil was determined after equilibration for 24 h with heavy-metal-free aqueous solvent. Details of soil sampling, analytical methods and experimental procedure are to be found in Part I of this paper.

In addition to the analyses mentioned above, endogenous Cd, Cr, Cu, Ni, Pb and Zn contents were determined by microwaving soil samples with 1:3:3 (v/v) nitric/hydrochloric/hydrofluoric acid in a Teflon bomb [20] followed by quantitation of the metals in the digestate by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin Elmer Optima 4300 DV apparatus. Endogenous available Cd, Cr, Cu, Ni, Pb and Zn contents were similarly determined by ICP-OES following extraction by the DTPA method [21].

2.2. Distribution coefficients K_d and $K_{d\Sigma}$

For each stage of each experiment (sorption and desorption), the distribution of each metal i between soil and solution following equilibration was expressed in terms of the quotient

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

where $C_{i,\text{soil}}$ is the concentration of metal *i* on the soil (µmol g⁻¹) and $C_{i,\text{solu}}$ is the concentration of metal *i* in solution (µmol L⁻¹) [8,14,22]. Joint distribution coefficients $K_{d\Sigma}$ were also calculated [8,9,18]:

$$K_{d\Sigma} = 10^{-3} \frac{(\sum_{i} C_{i,soil})}{(\sum_{i} C_{i,solu})}$$

For each soil, sorption and retention capacities for the six metals, individually and jointly, were compared using the quotients K_{d100} and $K_{d\Sigma100}$ obtained in experiments in which the initial concentration of each metal in the sorption solution was 100 mg L^{-1} [8].

2.3. Statistical analyses

The statistical significance of differences among means was estimated by analysis of variance (ANOVA) followed by least significant difference (LSD) tests. The possibility of grouping the soils studied on the basis of their K_{d100} values was investigated using principal components analysis (PCA). All statistical calculations were performed using SPSS 14.0 for Windows [23].

2.4. Results and discussion

Relevant soil characteristics other than endogenous heavy metal contents are reported in Table 1 of Part I. DTPAextractable, CaCl₂-extractable and total endogenous Cd, Cr, Ni, Zn, Cu and Pb contents are listed in Table 1 of the present paper. The extremely high Ni and Cr contents of FC and ML are due to their having developed over serpentinitic rock (the only soils studied to have done so), and may be expected to affect their sorption capacities, not only as regards Cr and Ni, but also in respect of other metals.

2.5. Soil rankings with respect to K_d and $K_{d\Sigma}$ values

In Part I, metals were ranked for each soil on the basis of K_{d100} values [21,8]. Table 2 lists the corresponding values of

Table 1
Native heavy metal contents of the soils studied

	Soil	HU1	HU2	HU3	DR	UA	ER	PA	TF	FC	HP	ML
Cd	Total heavy metal	1.96cd	3.43ab	4.36a	3.20bc	2.96bc	3.76ab	2.87c	3.22b	0.79e	3.97abc	1.97d
Cr	content (mg kg ^{-1})	70.47c	93.10c	73.90c	43.25c	15.83c	27.95c	62.76c	13.68c	2798.49a	77.61c	373.85b
Cu		28.04c	46.23b	31.41c	6.91e	4.79e	5.89e	27.95c	10.13de	84.20a	14.13d	27.47c
Ni		29.53c	40.54c	23.67c	8.79c	0.40c	1.94c	2.94c	0.25c	2525.62a	9.55c	163.22b
Pb		21.48b	45.79ab	27.96b	33.35ab	28.22ab	41.20ab	30.58b	41.76ab	23.11b	47.84a	16.69b
Zn		75.70b	106.90a	60.14b	20.01cd	17.37de	8.90e	24.59cd	36.32c	33.32cd	8.36e	25.49cd
Total		227.18	335.99	221.44	115.51	69.57	89.64	151.69	105.36	5465.53	161.46	608.69
Cd	DTPA-extractable	0.03b	0.00e	0.04a	0.00e	0.01de	0.00e	0.01d	0.01d	0.00e	0.02c	0.01d
Cr	contents (mg kg ^{-1})	0.03bc	0.03bc	0.02c	0.01c	0.23a	0.02c	0.02c	0.01c	0.01c	0.08bc	0.10b
Cu		0.86d	1.06c	1.23b	0.09f	0.59e	0.09f	4.49a	1.04e	4.48b	0.51e	0.49e
Ni		0.43d	0.15e	0.48d	0.01f	0.37d	0.03f	0.07f	0.23e	38.90a	1.37c	1.73b
Pb		2.09d	1.70e	0.79g	0.33hi	2.72b	0.43h	1.51f	2.39c	0.29i	4.01a	0.29i
Zn		0.64e	0.29f	0.23f	0.02g	0.62e	0.00g	1.49d	3.75b	0.17f	2.05c	0.21f
Total		4.08	3.23	2.79	0.46	4.54	0.57	7.59	7.43	43.85	8.04	2.83
Cd	CaCl ₂ -extractable	0.02ab	0.01cd	0.02a	0.00cd	0.00cd	0.00cd	0.01cd	0.00cd	0.00d	0.01bc	0.01cd
Cr	contents (mg kg ^{-1})	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.00b	0.013a	0.00b
Cu		0.01bc	0.03a	0.00bc	0.00c	0.01bc	0.00c	0.01bc	0.01b	0.00c	0.00bc	0.00bc
Ni		0.12cd	0.07cd	0.01d	0.00d	0.08cd	0.00d	0.00d	0.00d	9.89a	0.21c	0.65b
Pb		0.03b	0.08ab	0.07ab	0.11a	0.04bc	0.01c	0.05b	0.00c	0.02c	0.00c	0.03b
Zn		0.08c	0.16bc	0.01d	0.00d	0.25b	0.00d	0.00d	0.00d	0.00d	0.98a	0.04c
Total		0.26	0.35	0.11	0.11	0.38	0.01	0.07	0.01	9.91	1.213	0.73

In each row, values followed by different letters differ significantly (p < 0.05).

 $K_{d\Sigma}$. $K_{d\Sigma}$ was almost always greatest for HP, the only exceptions concerning sorption from solutions with 10 or 20 mg L⁻¹ of each metal (in both of which cases $K_{d\Sigma}$ was greatest for PA), and retention following sorption from solutions with 100 mg L⁻¹ of each metal, for which HU3 had the greatest $K_{d\Sigma}$ value. The

ranking of the soils by $K_{d\Sigma 100}$ (sorption) value was

$$\begin{array}{l} HP_{14.6} > > UA_{11.9} > HU_3 > FC_{8.8} > PA_{8.1} > HU_1 >> ER_{4.2} > TF_{4.2} > MI_{4.1} \\ > HU_2 > DR_{2.0} \end{array}$$

Table 2				
Joint sorption	and retention	distribution	coefficients ($K_{d\Sigma}$)

Concentration $(mg L^{-1})^a$	HU1 (L kg ⁻¹)	HU2	HU3	DR	UA	ER	РА	TF	FC	HP	ML
Sorption											
5	23.40	10.24	12.26	2.93	36.00	4.32	36.55	29.18	44.85	67.59	23.40
10	28.01	10.23	10.07	7.58	69.45	7.80	174.22	115.95	31.95	57.61	14.71
20	10.32	3.82	7.82	2.40	20.95	1.54	58.56	47.10	24.23	44.04	11.29
30	9.36	2.89	7.20	2.75	14.81	4.20	48.90	39.32	34.90	79.12	13.67
40	7.48	3.07	5.02	2.15	14.86	9.70	29.21	20.66	28.20	46.81	11.46
50	5.99	2.43	9.24	2.67	14.01	1.83	25.27	17.12	22.34	36.88	9.66
100	7.99	3.18	10.32	2.00	11.86	4.24	8.09	4.23	8.81	14.56	4.12
200	4.04	1.83	3.09	0.49	4.14	0.69	4.56	3.07	5.60	8.51	3.61
300	2.11	1.18	2.83	0.30	2.37	0.28	3.90	3.96	4.74	5.56	2.43
400	3.14	1.64	2.32	0.14	2.72	0.32	2.86	2.09	3.20	4.15	1.75
Retention											
5	93.13	31.96	95.93	6.80	124.75	44.75	139.98	98.10	54.06	242.57	61.28
10	171.43	73.15	140.49	33.32	169.78	86.92	213.70	129.26	51.06	280.12	65.26
20	119.62	40.10	180.85	14.81	162.23	31.57	221.82	137.40	50.47	240.55	71.58
30	167.77	50.10	233.65	28.37	247.55	77.59	135.06	120.94	76.65	311.65	115.79
40	124.99	47.46	157.81	26.12	192.96	256.36	141.20	115.39	74.19	290.11	113.82
50	122.52	45.60	224.25	26.49	206.30	45.66	118.84	112.52	70.39	253.93	97.00
100	191.80	66.47	288.27	75.99	256.25	97.56	73.84	46.92	36.57	123.39	40.15
200	105.31	52.83	88.26	6.48	90.25	24.75	50.49	50.56	38.38	119.67	50.36
300	51.21	27.37	77.47	5.25	78.96	14.84	63.04	65.45	49.90	118.82	45.13
400	69.78	25.10	32.95	0.01	69.67	20.68	60.44	52.12	42.09	110.92	45.83

where >> indicates a difference of more than $2 L kg^{-1}$; and the ranking by $K_{d\Sigma 100}$ (retention) value was

$$\begin{array}{l} HU3 > UA >> HU1 >> HP > ER > DR > PA > HU2 \\ > TF > ML > FC \\ 40 > TF > 37 \end{array}$$

where >> indicates a difference of more than $50 L kg^{-1}$.

The high $K_{d\Sigma100}$ (sorption) rankings of HP and UA are probably attributable to their having the highest humified organic matter contents (Part I, Table 1) [6]. The top-ranking soils for $K_{d\Sigma100}$ (retention), HU3, UA and HU1, have both high organic matter contents and considerable amounts of vermiculite, which has great capacity for fixation of heavy metals [11].

The low $K_{d\Sigma100}$ (sorption) rankings of HU2 and DR are attributable to a combination of low or lowish organic matter, clay and oxides contents, to low CEC, and to their neither of them containing any vermiculite (Part I, Table 1) [5]. The lowest $K_{d\Sigma100}$ (retention) rankings are those of ML and FC, the only soils developed over serpentinitic rock and those with the highest natural heavy metal contents (Table 1).

As indicated in Part I, there was a tendency for Cr, Cu and Pb to have higher K_{d100} values than Ni, Cd and Zn. For each of these metals, K_{d100} can be used to obtain soil rankings analogous to those shown above for $K_{d\Sigma100}$ (Table 2). For K_{d100} (sorption), the highest-ranked soil was in all cases one of the two top-ranking soils for $K_{d\Sigma100}$ (sorption): HP for Cr, Cu, Pb and Cd, and UA for Ni and Zn. Furthermore, HP was the second-ranked soil for Ni sorption, and UA the second- or third-ranked soil for sorption of Cu, Pb and Cd. Similarly, the K_{d100} (retention) rankings for the individual metals were generally headed by one of the top-ranking soils for $K_{d\Sigma100}$ (retention), HU3 (Cd, Ni and Zn) and UA (Cr and Pb). The exception was copper, which was best retained by HP, although UA and HU3 came in second and third place, respectively. In the following paragraphs, soil sorption and retention rankings are discussed for each metal in turn.

2.5.1. Cd

In keeping with the significant positive correlation between HOM and K_{d100} (sorption) for Cd that was reported in Table 4 of Part I of this work, the soils heading the K_{d100} (sorption) ranking for Cd, HP and UA, are those with the highest HOM contents. Complexes of humic acids with Cd²⁺, Cu²⁺ and Pb²⁺ have been reported to be the most stable complexes formed by heavy metal cations with components of soil organic matter [24]. Also, as noted above, HU3 and UA, the soils with the highest K_{d100} (retention) values for Cd (as well as for $K_{d\Sigma100}$), have both high organic matter contents and considerable quantities of vermiculite and kaolinite, both of which minerals correlated with Cd retention capacity (Part I, Table 4). Bonding to clay minerals has been reported to be the predominant process in the binding of Cd to soils, even though the coefficient of bonding energy is higher for organic matter than for clay [25]. Two soils, TF and ML, have K_{d100} (sorption) values < 1 L kg⁻¹ and K_{d100} (retention) values of only $0.01 \,\mathrm{L\,kg^{-1}}$. TF has the lowest clay content of any of the eleven soils, 9.4% (less than 10% of which is vermiculite); the second-lowest Fe oxides content, $3.6 \,\mathrm{g \, kg^{-1}}$; and the secondlowest organic matter content, 13.3 g kg^{-1} (although 76% of this organic matter is humified). ML, however, has the second-largest clay content, 32.5%, and a relatively large organic matter content, 76.4 g kg⁻¹.

2.5.2. Cr

The soils with the highest K_{d100} (sorption) values for chromium were HP and FC. FC has the highest CEC of the eleven soils, and HP the third-highest, probably because FC has the highest Mn oxides and clay contents (much of the clay being kaolinite, which is known to sorb Cr preferentially [26]) and HP has the highest organic matter and HOM contents. According to Bradl [5], Cr³⁺ is rapidly and specifically sorbed by Fe and Mn oxides and clay minerals, about 90% of added Cr³⁺ being taken up within 24 h. However, neither HP nor FC are among the five top-ranking soils for Cr retention. In the case of FC this is probably related to its extremely high native Cr content (Table 1) [27]: the release of labile native Cr into the desorption solution would "artificially" reduce K_{d100} (retention). The soils heading the Cr retention ranking are UA and HU3, both of which contain appreciable amounts of kaolinite and, in the case of UA, mica. Both kaolinite and mica have been reported to play an important role in the retention of Cr [26,28,29], and in this study K_{d100} for Cr retention correlated with the kaolinite (and vermiculite) content of the clay fractions (Part I, Table 4). The lowest-ranking soils for Cr sorption, PA and TF, have K_{d100} (sorption) values less than $2 L kg^{-1}$; PA is also the soil with the lowest K_{d100} (retention) value. In contrast to FC, PA has both low CEC and low Mn oxides content.

2.5.3. Cu

The five soils with the greatest K_{d100} (sorption) values, HP, PA, UA, HU3 and HU1, are also the five with the greatest K_{d100} (retention) values. For all five, K_{d100} (sorption) values for Cu are greater than for any other metal except Pb, and for HP and PA the same is true of K_{d100} (retention) values (Table 3). Cu has been reported to be sorbed in preference to other heavy metals by organic matter [30,31], which is attributed to its high charge/radius ratio enabling it to form stable complexes with humic substances [32,33], and by vermiculite [26]. The close correlation between Cu sorption and vermiculite content [34] is attributed to the high surface charge of the latter, 700–800 m² g⁻¹ [11], which results in the metal being sorbed in nondiffusible form. The relationship with organic matter is in keeping with the positive correlation between HOM content and K_{d100} for sorption and retention of copper observed in this study (Part I, Table 4); of the soils studied in this work, the four with greatest organic matter contents (HP, HU3, UA and HU1) are among the five top Cu-sorbers. UA also has the greatest vermiculite content of the soils studied. PA, however, has neither large amounts of organic matter nor more than trace amounts of vermiculite. The soils that sorb and retain least Cu, HU2, ER and DR, all have low organic matter content, low CEC, and no vermiculite.

2.5.4. Ni

Like Cd, Ni was best sorbed by UA and HP, the soils with the highest HOM contents; best retained by HU3 and UA; and

Table 3
Soil rankings by K_{d100} for sorption and retention, for each metal

	Sorption										
Cd	HP>	UA>	HU3>	ER>	FC>	HU1>	PA>	HU2>	DR>	TF>	ML
	9.88>	7.74>	6.91>	4.14>	4.10>	3.97>	3.39>	2.32>	2.07>	0.9>	0.89
Cr	HP>	FC>	HU3>	UA>	HU1>	ML>	ER>	HU2>	DR>	TF>	PA
	14.34>	12.89>	7.6>	7.14>	5.93>	4.85>	4.06>	3.79>	2.58>	1.92>	1.53
Cu	HP>	PA>	UA>	HU3>	HU1>	TF>	ML>	FC>	HU2>	ER>	DR
	81.51>	64.79>	39.86>	28.48>	25.03>	16.72>	11.74>	9.38>	3.06>	2.74>	0.07
Ni	UA>	HP>	FC>	HU3>	PA>	HU1>	ER>	HU2>	DR>	TF>	ML
	6.49>	5.89>	5.45>	5.26>	3.82>	3.76>	3.17>	2.11>	1.91>	1.85>	0.79
Pb	HP>	PA>	UA>	HU1>	HU3>	TF>	FC>	ML>	HU2>	ER>	DR
	217.12>	147.19>	110.75>	69.16>	61.65>	56.26>	45.98>	32.84>	13.67>	9.44>	4.22
Zn	UA>	HU3>	FC>	ER>	HP>	PA>	HU1>	CR>	HU2>	ML>	TF
	8.08>	6.98>	6.59>	6.23>	4.88>	4.04>	3.4>	2.96>	2.09>	0.81>	0.51
	Retention										
Cd	HU3>	UA>	HU1>	DR>	ER>	HP>	HU2>	PA>	FC>	ML>	TF
	110.82>	89.91>	64.50>	49.50>	48.15>	43.69>	35.33>	4.16>	3.49>	0.01>	0.01
Cr	UA>	HU3>	ER>	HU1>	HU2>	HP>	DR>	TF>	FC>	ML>	PA
	837.54>	597.8>	535.75>	414.33>	270.99>	206.96>	179.64>	165.13>	75.85>	60.54>	57.35
Cu	HP>	UA>	HU3>	HU1>	PA>	TF>	ML>	FC>	ER>	DR>	HU2
	378.39>	374.48>	316.56>	285.79>	198.74>	100.67>	72.19>	34.50>	32.20>	0.02>	0.01
Ni	HU3>	UA>	DR>	HU1>	ER>	HU2>	HP>	PA>	FC>	TF>	ML
	148.47>	121.77>	103.58>	69.38>	59.95>	51.84>	34.89>	21.43>	14.02>	4.77>	0.01
Pb	UA>	HP>	HU1>	HU3>	PA>	TF>	ML>	FC>	HU2>	ER>	DR
	907.24>	629.69>	493.22>	487.38>	452.76>	243.21>	145.83>	132.35>	121.83>	90.66>	56.44
Zn	HU3>	ER>	UA>	DR>	HU1>	HU2>	HP>	FC>	PA>	ML>=	TF
	409.09>	234.7>	183.8>	154.56>	142.95>	95.2>	38.12>	30.42>	25.09>	0.01=	0.01

sorbed and retained least by TF and ML. According to Bloomfield [34], the bonding of Ni to organic matter can be so strong as to mobilize the metal from carbonates and oxides, and reduce its sorption by clays. In this study, K_{d100} for Ni sorption correlated with HOM content, and K_{d100} for Ni retention with the kaolinite and vermiculite contents of the clay fraction (Part I, Table 4). The poor sorption and retention of Ni by ML is attributable to its having a high native Ni content, only 30 µmol kg⁻¹

Table 4

Results of principal components analyses of K_{d100} values for sorption and retention of heavy metals

Sorption principal component (SPC)	Initial eigenvalues				Loadings					
	Total	% of variance	Cumulative variance (%)	Cd	Cr	Cu	Ni	Pb	Zn	
Sorption										
SPC1	4.17	69.57	69.57	0.96	0.76	0.78	0.94	0.81	0.73	
SPC2	1.19	19.99	89.56	-0.09	-0.23	0.61	-0.26	0.58	-0.59	
SPC3	0.48	8.07	97.63							
SPC4	0.10	1.69	99.31							
SPC5	0.04	0.61	99.92							
SPC6	0.01	0.08	100							
Retention principal component (RPC)	Initial eigenvalues			Loadings						
	Total	% of variance	Cumulative variance (%)	Cd	Cr	Cu	Ni	Pb	Zn	
Retention										
RPC1	4.24	70.69	70.69	0.97	0.91	0.70	0.91	0.69	0.83	
RPC2	1.38	22.92	93.61	-0.17	-0.09	0.68	-0.33	0.71	-0.50	
RPC3	0.24	3.92	97.53							
RPC4	0.11	1.88	99.41							
RPC5	0.03	0.54	99.95							
RPC6	0.00	0.05	100							

of which is present in DTPA-extractable form (Table 1) [27].

2.5.5. Pb

Like copper, lead was best sorbed by HP and PA, best retained by HP and UA, and sorbed and retained least by ER, DR and HU2. Pb is sorbed and retained in preference to other metals by HOM, Fe oxides and Mn oxides [26]; HP and UA have the highest HOM contents of the eleven soils studied (UA also has one of the highest clay contents), while PA, though relatively poor in HOM, has the highest Fe oxides content. K_{d100} for Pb sorption correlated with HOM and CEC, and K_{d100} for Pb retention with HOM and with the kaolinite and vermiculite contents of the clay fraction (Part I, Table 4). DR, ER and HU2 all have low organic matter contents (DR the lowest of all eleven soils), low Mn oxides contents, and no vermiculite.

2.5.6. Zn

Zn was best sorbed by two soils with high organic matter contents and appreciable vermiculite contents, UA and HU3. The relatively strong binding of Zn by clays and organic matter was pointed out in Lindsay's review of the sorption and retention of this metal by soils [35], and we have previously reported that among the metals considered in this study, only copper is bound better than Zn by vermiculite [26]. Sorption and retention of Zn were least in two of the soils in which its binding is most clearly dominated by that of Pb, Cu and Cr, ML and TF (Part I, Table 4), and in the case of TF is in keeping with the low organic matter and clay contents of this soil.

2.6. Principal components analysis

To help identify patterns in their metal sorption and retention behaviour, the soils studied were considered as points in the six-dimensional spaces defined by their K_{d100} (sorption) and K_{d100} (retention) values, and these data were subjected to principal components analyses. In Figs. 1 and 2 the soils are plotted in the planes of the first two components to emerge from these analyses. In neither case is there a very pronounced tendency for the soils to cluster in distinct groups.

The first component identified in the analysis of the K_{d100} (sorption) data, SPC1 (Soil Principal Component 1), accounted for almost 70% of all variance, and together with the second component, SPC2 (Sorption Principal Component 2), it accounted for almost 90% (Table 4). Examination of the loading factors of the metals on these components suggests that SPC1 reflects overall sorption capacity, while SPC2 reflects the relative capacities of a soil for sorption of lead and copper on the one hand, and other metals, especially zinc, on the other. In keeping with its heading the $K_{d\Sigma 100}$ (sorption) ranking, HP appears furthest to the right in Fig. 1. Although it heads the sorption rankings for Cd and Cr (Table 3), and is second in the Ni ranking, it also heads the rankings for Pb and Cu, and the great difference between its K_{d100} values for these metals and the others (Pb, $217 L kg^{-1}$; Cu, $82 L kg^{-1}$; others, $5-14 L kg^{-1}$) places it in the top half of the figure; there it shares the top right quadrant with PA, which is the second-best sorber of Pb and Cu



Fig. 1. The eleven soils plotted in the plane defined by SPC1 and SPC2, the first two components to emerge in a principal components analysis of K_{d100} (sorption) values.

and no better than fifth-best for any of the other metals (Table 3). The soils with poorest overall sorption capacities according to their $K_{d\Sigma100}$ (sorption) rankings and SPC1 coordinates are TF, ML, HU2, and DR, and the soils with least preference for Pb and Cu are FC, ER, HU3 and UA, which head the Zn sorption ranking (Table 3). The fact that DR, which is lowest in the sorption rankings of both Pb and Cu (Table 3), has a higher SPC2 value than UA, which is third in these rankings, brings out the fact that SPC2 does not simply reflect Pb and Cu sorption, but the balance between sorption of these metals and sorption of the others, zinc especially, although as a measure of this balance SPC2 is skewed heavily towards sorption of Pb and Cu (Pb is



Fig. 2. The eleven soils plotted in the plane defined by RPC1 and RPC2, the first two components to emerge in a principal components analysis of K_{d100} (retention) values.

Table 5

Results of multiple	ole linear	regression	of SPC1.	SPC2 and RPC	C1, RPC2	on soil	properties
		<u> </u>					

Independent variables	Unstandardized coefficients	Standardized coeffic	cients	t	Significance	
	В	Standard error	Beta			
Dependent variable SPC1; R ²	² 0.913; significance <i>p</i> < 0.001					
(Constant)	-2.07	0.22		-9.36	< 0.001	
HOM.	0.07	0.01	1.39	12.67	< 0.001	
CIC ₍₊₎	-0.13	0.03	-0.46	-4.58	< 0.001	
Mica	0.33	0.12	0.21	2.71	0.012	
Kaolinite	0.11	0.02	1.09	4.96	< 0.001	
Vermiculite	-0.33	0.09	-0.64	-3.45	0.002	
Haematite	-0.05	0.01	-0.54	-3.84	0.001	
Fe oxides	0.06	0.01	1.04	10.05	< 0.001	
Dependent variable SPC2; R	2 0.977; significance <i>p</i> < 0.001					
(Constant)	-0.87	0.16		-5.59	< 0.001	
HOM	0.01	0.01	0.26	2.59	0.016	
CIC ₍₊₎	0.14	0.03	0.50	4.45	< 0.001	
Mica	1.14	0.15	0.71	7.71	< 0.001	
Kaolinite	-0.05	0.02	-0.52	-2.40	0.025	
Vermiculite	0.23	0.09	0.46	2.57	0.017	
Gibbsite	0.02	0.01	0.44	4.02	0.001	
Chlorite	-0.05	0.02	-0.41	-3.16	0.005	
Haematite	-0.02	0.01	-0.22	-2.20	0.038	
Mn oxides	1.35	0.58	0.56	2.31	0.031	
Fe oxides	-0.06	0.01	-1.09	-5.61	< 0.001	
Dependent variable RPC1; R	2 0.956; significance <i>p</i> < 0.001					
(Constant)	0.06	0.17		0.35	0.73	
HOM	0.05	0.00	0.92	13.54	< 0.001	
CIC ₍₊₎	-0.35	0.04	-1.25	-10.05	< 0.001	
Mica	0.59	0.13	0.37	4.76	< 0.001	
Kaolinite	0.17	0.02	1.68	8.44	< 0.001	
Vermiculite	-0.71	0.10	-1.40	-6.88	< 0.001	
Gibbsite	-0.02	0.01	-0.49	-3.89	0.001	
Chlorite	0.08	0.02	0.66	4.57	< 0.001	
Mn oxides	1.60	0.24	0.67	6.55	< 0.001	
Dependent variable RPC2; R	2 0.986; significance <i>p</i> < 0.001					
(Constant)	-2.14	0.09		-24.68	< 0.001	
HOM	0.03	0.00	0.52	11.24	< 0.001	
CIC(+)	0.20	0.01	0.72	15.82	< 0.001	
Mica	0.52	0.05	0.32	9.58	< 0.001	
Kaolinite	-0.05	0.01	-0.47	-4.30	< 0.001	
Vermiculite	0.27	0.05	0.54	5.37	< 0.001	
Gibbsite	0.02	0.00	0.32	4.39	< 0.001	
Chlorite	-0.05	0.01	-0.39	-4.29	< 0.001	
Heamatite	0.01	0.01	0.14	2.36	0.026	

HOM = humified organic matter; $CIC_{(+)}$ = cation exchange capacity.

preferentially sorbed by all the soils, followed in most cases – including HU3 and UA – by Cu; see Part I, Table 4).

Multiple linear regression of SPC1 and SPC2 on soil characteristics showed SPC1 to depend most on HOM, kaolinite and Fe oxides contents, and to be influenced by CEC and by vermiculite and haematite contents (Table 5). SPC2 was most strongly dependent, negatively, on Fe oxides content, and more weakly on clay minerals (positively on mica, vermiculite and gibbsite; negatively on kaolinite, chlorite and haematite) and on CEC, HOM and Mn oxides (positively in all three cases).

The first component identified in the analysis of the K_{d100} (retention) data, RPC1 (Retention Principal Component 1), accounted for just over 70% of all variance, and together with the second component, RPC2 (Retention Principal Compo-

nent 2), it accounted for over 93% (Table 4). Examination of the loading factors of the metals on these components suggests that RPC1 and RPC2 have exactly the same interpretations as SPC1 and SPC2, respectively, but for retention instead of sorption. In keeping with their places in the $K_{d\Sigma100}$ (retention) ranking, HU3 and UA are the soils appearing furthest to the right in Fig. 2, and ML, FC and TF the soils furthest to the left. The low RPC1 values of FC and ML may be due to their development over serpentinitic rock and their resulting high native Cr and Ni levels, which may interfere with their heavy metal retention capacity. The soil with the greatest RPC2 value is HP, followed at some distance by PA and UA; HP and UA top the soil rankings for retention of both Pb and Cu. In keeping with their places in the soil rankings for Pb, Cu and Zn (Table 3), the soils with least

preference for Pb and Cu, according to their RPC2 values, are DR and ER.

Multiple linear regression of RPC1 and RPC2 on soil characteristics showed the principal positive predictors of RPC1 to be kaolinite and HOM contents, and its principal negative predictors vermiculite content and CEC. The principal positive predictor of RPC2 was CEC, followed by HOM and vermiculite contents, and its principal negative predictor was kaolinite content.

Finally, the convergence of the concepts of overall sorption capacity embodied in SPC1 and $K_{d\Sigma100}$ (sorption) is attested to by the close correlation between these two measures (r=0.905, p<0.001). Correlation between RPC1 and $K_{d\Sigma100}$ (retention) is not so good (r=0.666), but is nonetheless significant (p<0.001).

3. Conclusions

In this study, the soils with the greatest overall capacity for heavy metal sorption were those with the highest organic matter contents. Those heading the heavy metal retention ranking had both high organic matter contents and clay fractions containing a significant proportion of vermiculite. Overall capacity for heavy metal sorption was positively related to HOM, kaolinite and Fe oxides contents, and negatively related to CEC and to vermiculite and haematite contents. Overall capacity for heavy metal retention was positively related to HOM and kaolinite contents, and negatively related to HOM and kaolinite contents, and negatively related to CEC and vermiculite content. The good correlation between SPC1 and $K_{d\Sigma100}$ (sorption), and between RPC1 and $K_{d\Sigma100}$ (retention), supports the adequacy of $K_{d\Sigma}$ as a measure of the overall capacity of a soil to sorb or retain heavy metals.

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