

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} (retention) values, 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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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

by natural or anthropogenic changes in environmental conditions.

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

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

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

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

For each soil, sorption and retention capacities for the six metals, individually and jointly, were compared using the quotients K_{d100} and $K_{d\Sigma 100}$ 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. DTPA-extractable, CaCl_2 -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 3
Soil rankings by K_{d100} for sorption and retention, for each metal

Sorption											
Cd	HP> 9.88>	UA> 7.74>	HU3> 6.91>	ER> 4.14>	FC> 4.10>	HU1> 3.97>	PA> 3.39>	HU2> 2.32>	DR> 2.07>	TF> 0.9>	ML 0.89
Cr	HP> 14.34>	FC> 12.89>	HU3> 7.6>	UA> 7.14>	HU1> 5.93>	ML> 4.85>	ER> 4.06>	HU2> 3.79>	DR> 2.58>	TF> 1.92>	PA 1.53
Cu	HP> 81.51>	PA> 64.79>	UA> 39.86>	HU3> 28.48>	HU1> 25.03>	TF> 16.72>	ML> 11.74>	FC> 9.38>	HU2> 3.06>	ER> 2.74>	DR 0.07
Ni	UA> 6.49>	HP> 5.89>	FC> 5.45>	HU3> 5.26>	PA> 3.82>	HU1> 3.76>	ER> 3.17>	HU2> 2.11>	DR> 1.91>	TF> 1.85>	ML 0.79
Pb	HP> 217.12>	PA> 147.19>	UA> 110.75>	HU1> 69.16>	HU3> 61.65>	TF> 56.26>	FC> 45.98>	ML> 32.84>	HU2> 13.67>	ER> 9.44>	DR 4.22
Zn	UA> 8.08>	HU3> 6.98>	FC> 6.59>	ER> 6.23>	HP> 4.88>	PA> 4.04>	HU1> 3.4>	CR> 2.96>	HU2> 2.09>	ML> 0.81>	TF 0.51
Retention											
Cd	HU3> 110.82>	UA> 89.91>	HU1> 64.50>	DR> 49.50>	ER> 48.15>	HP> 43.69>	HU2> 35.33>	PA> 4.16>	FC> 3.49>	ML> 0.01>	TF 0.01
Cr	UA> 837.54>	HU3> 597.8>	ER> 535.75>	HU1> 414.33>	HU2> 270.99>	HP> 206.96>	DR> 179.64>	TF> 165.13>	FC> 75.85>	ML> 60.54>	PA 57.35
Cu	HP> 378.39>	UA> 374.48>	HU3> 316.56>	HU1> 285.79>	PA> 198.74>	TF> 100.67>	ML> 72.19>	FC> 34.50>	ER> 32.20>	DR> 0.02>	HU2 0.01
Ni	HU3> 148.47>	UA> 121.77>	DR> 103.58>	HU1> 69.38>	ER> 59.95>	HU2> 51.84>	HP> 34.89>	PA> 21.43>	FC> 14.02>	TF> 4.77>	ML 0.01
Pb	UA> 907.24>	HP> 629.69>	HU1> 493.22>	HU3> 487.38>	PA> 452.76>	TF> 243.21>	ML> 145.83>	FC> 132.35>	HU2> 121.83>	ER> 90.66>	DR 56.44
Zn	HU3> 409.09>	ER> 234.7>	UA> 183.8>	DR> 154.56>	HU1> 142.95>	HU2> 95.2>	HP> 38.12>	FC> 30.42>	PA> 25.09>	ML>= 0.01=	TF 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 $30 \mu\text{mol kg}^{-1}$

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

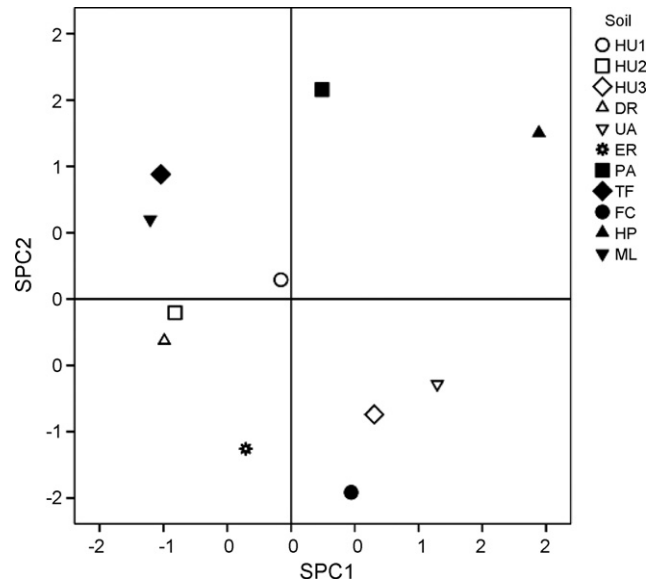


Fig. 1. The eleven soils plotted in the plane defined by SPC1 and SPC2, the first two components to emerge in a principal components analysis of K_{d100} (sorption) values.

and no better than fifth-best for any of the other metals (Table 3). The soils with poorest overall sorption capacities according to their $K_{d\Sigma 100}$ (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

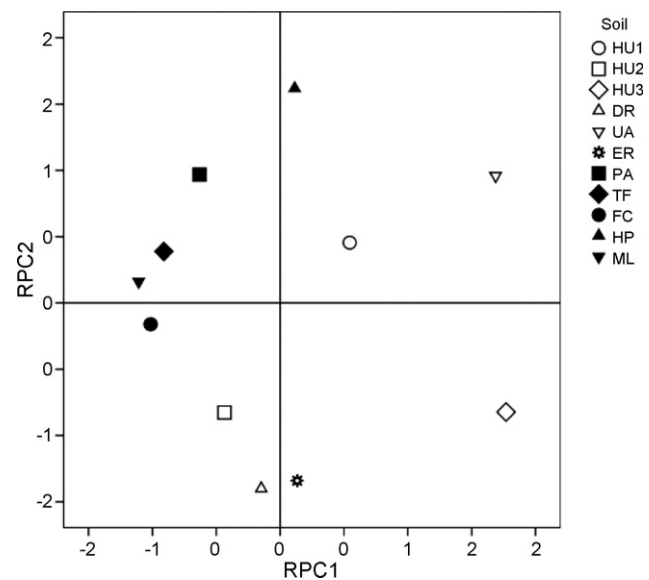


Fig. 2. The eleven soils plotted in the plane defined by RPC1 and RPC2, the first two components to emerge in a principal components analysis of K_{d100} (retention) values.

Table 5
Results of multiple linear regression of SPC1, SPC2 and RPC1, RPC2 on soil properties

Independent variables	Unstandardized coefficients		Standardized coefficients		<i>t</i>	Significance
	<i>B</i>	Standard error	Beta			
Dependent variable SPC1; R^2 0.913; significance $p < 0.001$						
(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 $p < 0.001$						
(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 $p < 0.001$						
(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 $p < 0.001$						
(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
Haematite	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 Component 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 serpentinic 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 $K_{d\Sigma 100}$ (sorption) is attested to by the close correlation between these two measures ($r = 0.905$, $p < 0.001$). Correlation between RPC1 and $K_{d\Sigma 100}$ (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 CEC and vermiculite content. The good correlation between SPC1 and $K_{d\Sigma 100}$ (sorption), and between RPC1 and $K_{d\Sigma 100}$ (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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