



Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a Fibric Histosol and its organo-mineral fraction

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ARTICLE INFO

Article history:

Received 13 November 2006
Received in revised form 13 June 2007
Accepted 12 February 2008
Available online 17 February 2008

Keywords:

Organic matter
Organo-mineral fraction
Sorption
Heavy metals
Langmuir isotherm

ABSTRACT

It has often been stated that the contribution of soil organic matter (OM) to the sorption of heavy metals can be evaluated using the surface horizon of a Histosol as typical of soil organic matter. However, components of Histosols other than organic matter, such as clay minerals and Fe or Mn oxides, can also sorb heavy metals. In this work we compared the heavy metal sorption and desorption behaviour of a Fibric Histosol H horizon with that of its organo-mineral fraction (OMF, defined as the fraction of wet particle size $<100\ \mu\text{m}$) in experiments in which Cd, Cr, Cu, Ni, Pb and Zn were sorbed simultaneously from solutions of various concentrations. The OMF sorbed the metals reversibly and apparently mainly at specific sites to each particular metal, in keeping with the good fit of Langmuir isotherms to the sorption data; greatest sorption capacity was for lead and copper. Whole H horizon appeared to include sites at which binding was less reversible and chromium competed with the other metals, especially copper. Organo-mineral fraction is suggested to evaluate the soil organic matter contribution to heavy metal fixation.

Published by Elsevier B.V.

1. Introduction

Heavy metals are introduced into soils by many vehicles, especially fertilizers, liming materials, and industrial and urban waste materials, including sewage sludge [1,2]. Their movement through a given soil, and the degree to which plants and other organisms are exposed to them, depend on their sorption and desorption by soil components, where “sorption” encompasses adsorption, surface precipitation and fixation [3–5]. Since several heavy metal cations can be present simultaneously, it is important that their sorption and desorption behaviour likewise be evaluated in each other’s presence (competitive sorption/desorption).

The soil property that most determines the sorption of heavy metals is organic matter (OM) content [6]; and in general, the binding of metal ions to organic matter often controls the concentration of free ion in the soil solution, which is the property of immediate relevance to the bioavailability and toxicity of the metal [7]. Soil OM consists of plant and animal products in various stages of decomposition (including living microorganisms) and the results of processes of chemical and biochemical organic syntheses that take place in the soil externally to living organisms.

Cu shows a strong affinity for soil organic matter so that the organic-fraction Cu is high compared to that for other metals even through the absolute amounts are low [8]. Copper complexation by organic matter in the form of humic and fulvic acids is an effective

mechanism of Cu retention in soils. It has been shown that Cu is most extensively complexed by humic materials [9] in comparison to other metals. The presence of soil organic matter also plays an important role in Pb adsorption. Soil organic matter may immobilize Pb via specific adsorption reactions, while mobilization of Pb can also be facilitated by its complexation with dissolved organic matter of fulvic acids [10,11]. The following preference series for divalent ions for humic acids and peat is indicated as follows: $\text{Cu} > \text{Pb} > \text{Fe} > \text{Ni} > \text{Co} = \text{Zn} > \text{Mn} = \text{Ca}$ [1]. Cr(III) is rapidly and specifically adsorbed by Fe and Mn oxides and clay minerals [6]

Of the various classifications of OM into subfractions, increasing importance has in recent years been given to the distinction between mineral-associated organic matter (MOM) and particulate OM (POM). POM consists mainly of fresh plant, microbial and animal debris, while MOM comprises humified and unhumified organic substances associated with mineral particles. POM and MOM are defined operationally in terms of physical separation procedures; as a result, MOM is unaltered in that it has not undergone the chemical modifications suffered by OM fractions defined by chemical extraction procedures, but is more heterogeneous than chemically defined fractions. In fact, operationally defined MOM comprises both organic matter and the mineral particles and other inorganic matter with which it is associated. In the remainder of this paper this combined OM-mineral association, as defined operationally by a wet-sieving method due to Andriulo et al. [12–14], will be referred to as the organo-mineral fraction (OMF).

Interactions with metals that have been attributed to humic substances, and hence to the OMF, include ion exchange, surface

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sorption, chelation, coagulation and peptization [15]. In particular, OMF compounds with S, O and/or N atoms capable of complexating metal cations play a major role in the retention of heavy metals by soils [16]. However, the OMF, as defined above, also contains other substances with capacity to sorb metal cations, notably clay minerals.

McLaren and Crawford [17] found OM as it exists in the soil to be more similar to peat than to material extracted by an extractant such as sodium citrate, and for this reason used samples of peat as OM in their work on the sorption of heavy metals by soil OM.

Andriulo et al. [12] and Galantini et al. [13] described a soil organic matter fractionation method by sieving (mechanical separation procedure). They used sieves of different mesh sizes to quantify the organic fractions. This methodology does not use conventional reagents like sodium citrate that can modify the organic matter composition and is adequate to obtain organo-mineral fraction. The methodology of Galantini consists of a particle size separation of the “free organic matter” from the “bound”, by sieving the soil sample through a 0.1 mm sieve.

The hypothesis of this work is that the use of surface horizons of Histosols is not suitable to deduce the influence of organic matter in heavy metals sorption. The surface horizon of Histosol presents, in addition to high organic matter contents, other components, in significant proportions, such as clays and Mn and Fe oxides. These soil components can interfere with the results of experiments that try to exclusively evaluate the role of the soil organic matter in heavy metal sorption.

In this work, organo-mineral fraction from the H horizon of the Fibric Histosol was isolated to make that the organic matter predominates front to other soil components with capacity of heavy metals sorption. Thus, the role of organic matter in heavy metal sorption will have less interference.

The main goal of this work is to evaluate the differences between the heavy metal sorption and retention capacities of an H horizon from a Fibric Histosol and of their organo-mineral fraction and to estimate the role of soil organic matter in heavy metal sorption.

2. Material and methods

Using an Eijkelkamp Model A sample ring kit, six samples were taken from the 30 cm deep surface horizon of a Fibric Histosol located in a seasonal wetland in Serra do Galleiro, Pontevedra, Spain (Chan Grande, 42°14'N 5°34'W, altitude 675 m). The samples were transported to the laboratory in polyethylene bags, air dried, passed through a 2 mm mesh sieve, and divided into six subsamples (three for analysing soil characteristics and three for sorption/desorption experiments) in a Fritsch Laborette 27 rotatory sample homogenizer/divider.

2.1. Soil analyses

Soil pH in water was determined with a pH meter using 2:1 (v:w) (water:soil) suspensions [18]. Particle size distribution was determined following oxidation of organic matter with hydrogen peroxide; the fraction >50 mm was further fractionated using sieves, and the <50 mm fraction by the international procedure [19]. Total organic carbon content was determined as per Walkey and Black [20]. The organo-mineral fraction was separated out by a wet-sieving procedure [12–14]: 50 g samples were suspended in 100 mL of water by shaking for 2 h in the presence of glass beads [21], and the fraction passing a 0.1 mm mesh sieve was defined as OMF. This slurry was dried at 30 °C in a forced draft oven, and after grinding in a mortar, its organic C content was determined as per Walkey and Black [20]. Fe, Al and Mn oxides were determined by extraction with a solution of sodium hydrosulphite and sodium citrate [22–23],

followed by determination of Fe, Al and Mn in the extract by inductively coupled plasma optical emission spectrometry (ICP-OES) in a PerkinElmer Optima 4300 DV apparatus. Total and effective cation exchange capacities (CECs) and exchangeable cation content were determined as per Hendershot and Duquette [24]. Mineralogical analysis of the clay fraction was performed by powder X-ray diffraction [25] in a SIEMENS D-5000 Bragg-Brentano (θ/θ) apparatus with a Cu anode, using 0.05° steps and 10 s/step [26].

2.2. Sorption/desorption experiments

2.2.1. Sorption stage

For both the whole H horizon and its OMF, sorption isotherms were constructed using “sorption solutions” that contained equal mass concentrations (between 5 and 400 mg L⁻¹) of Cd⁺², Cr⁺³, Cu⁺², Ni⁺², Pb⁺², and Zn⁺² as their nitrates in 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 sample was suspended in 200 mL of sorption solution, and after equilibration by shaking for 24 h at 25 °C in a rotary shaker [27,28] was centrifuged at 1800 × g for 10 min. Metal concentrations in the supernatants were determined by ICP-OES, and the amount of each metal sorbed by the sample was calculated by difference.

2.2.2. Desorption stage

Desorption isotherms were constructed as per Madrid and Díaz-Barrientos [29]. The pellets obtained by centrifugation in the sorption stage were dried at 45 °C, weighed, and resuspended in 200 mL of the same buffer as above, after which these suspensions were equilibrated in a rotary shaker for 24 h at 25 °C, their pH was measured (all were of pH 4.5), and they were then centrifuged at 1800 × g for 10 min. Metal concentrations in the supernatants were determined by ICP-OES, and the quantities of metals retained by each soil were calculated by difference with respect to the amounts sorbed in the sorption stage.

Each sorption/desorption experiment was performed in triplicate. From the data for each stage (sorption and desorption), isotherms were constructed for each metal by plotting its concentration in the aqueous phase following equilibration against the amount sorbed or retained by the sample.

The sorption and desorption isotherms were fitted with Langmuir and Freundlich models [30] by least squares, and for each sorption solution concentration c the distribution of each metal i between soil and solution following equilibration in each stage was expressed in terms of the quotient

$$K_{dc,i} = \frac{C_{i,soil}}{C_{i,solu}}$$

where $C_{i,soil}$ is the concentration of metal i on the soil ($\mu\text{mol g}^{-1}$) and $C_{i,solu}$ is the concentration of metal i in solution ($\mu\text{mol L}^{-1}$). The global heavy metal sorption and retention capacities of the whole H horizon and its OMF were compared using the quotient $K_{dc \Sigma sp}$ defined by Covelo et al. [31,32] after Kaplan et al. [33]:

$$K_{dc \Sigma sp} = \frac{\sum_i C_{i,soil}}{\sum_i C_{i,solu}}$$

3. Results and discussion

Table 1 lists the characteristics of the whole Fibric Histosol H horizon. Its total OM content was 156.4 g kg⁻¹, 40.7% of which (63.7 g kg⁻¹) belonged to the OMF. This horizon was of pH 5.4 and had a CEC of only 4.10 cmol(+) kg⁻¹, and its most abundant minerals were quartz, mica and kaolinite.

Table 1
Characteristics of the Fibric Histosol H horizon

Property	Whole H horizon
Total organic matter (g kg^{-1})	156.43
Particulate organic matter (g kg^{-1}) (POM)	92.75
Mineral-associated organic matter (g kg^{-1})	63.68
pH (H_2O)	5.4
pH (KCl)	4.4
Sand (%)	44.83
Silt (%)	17.42
Clay (%)	37.75
Quartz (% of clay)	33
Plagioclase (% of clay)	13
Mica (% of clay)	32
Kaolinite (% of clay)	17
Vermiculite (% of clay)	5
Cation exchange capacity ($\text{cmol}(+) \text{kg}^{-1}$)	4.10
Effective cation exchange capacity ($\text{cmol}(+) \text{kg}^{-1}$) ($\text{CEC}_{\text{e}(+)}$)	0.72
Mn oxides (g kg^{-1})	0.005
Fe oxides (g kg^{-1})	2.51
Al oxides (g kg^{-1})	3.32

Organo-mineral fraction from the H horizon of the Fibric Histosol was isolated [12,13] and their total organic matter content was 395 g kg^{-1} . The OMF was of pH 5.1 and had a CEC of $12.52 \text{ cmol}(+) \text{ kg}^{-1}$.

3.1. Sorption and desorption profiles

Fig. 1 plots the amounts of each metal sorbed by the H horizon and its OMF against their initial concentration in the sorption solution, and Fig. 2 shows analogous plots of the amounts retained at the end of the desorption stage of the experiments.

In the OMF the sorption and retention of copper and lead increased almost linearly with their initial concentration in the sorption solution, specially above sorption solution concentrations

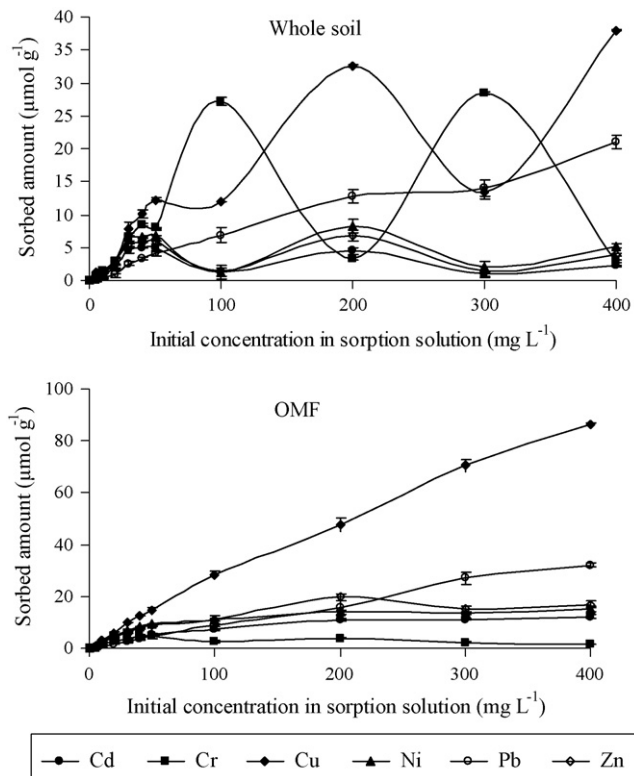


Fig. 1. Simultaneous sorption of six heavy metals by a Fibric Histosol H horizon (whole soil) and its organo-mineral fraction (OMF).

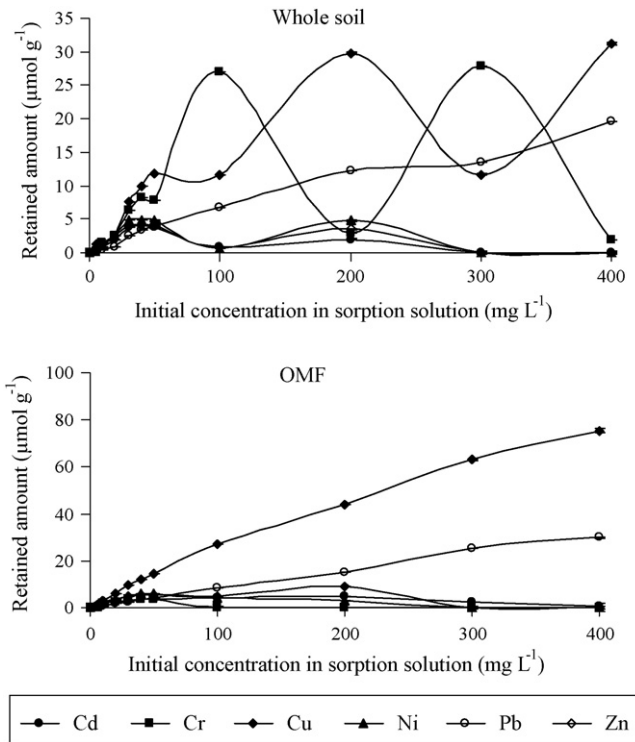


Fig. 2. Retention of sorbed heavy metals after equilibration with buffer (see Section 2). Top, whole H horizon; bottom, OMF.

of $100\text{--}200 \text{ mg L}^{-1}$, whereas this fact does not occur with the other metals. So that there are abundant Pb- and Cu-binding sites remained unoccupied even at the highest sorption solution concentration, while sorption of the other metals showed saturation. The fact that the fall in sorption of Ni, Cd, Zn and Cr was not greater suggests that each metal was largely sorbed at soil components like clays and oxides with higher affinity to sorb these metals than organic matter that sorb preferably Cu and Pb.

In the whole H horizon (Figs. 1 and 2) only the lead sorption and retention increased linearly with their initial concentration in the sorption solution whereas there are fluctuations in Cu and Cr sorption and retention. In fact, the observed fluctuations are compatible with the notion that in the whole H horizon copper and chromium are largely sorbed at binding sites that are specific to this pair of metals, and that they compete for these sites: for sorption from solutions with concentrations of 100 mg L^{-1} or more of each metal, the sum of sorbed copper and sorbed chromium, or of retained copper and retained chromium, is always close to $35 \mu\text{mol g}^{-1}$. This suggests that, in addition to the metal-specific sites of the OMF, the whole H horizon contains sites for which chromium competes with one or more other metals. This is especially so for copper. The fact that one of these two metals (Cu or Cr) is always sorbed or retained to a much greater extent than the other, without there being a systematic preference for one or the other, suggests that both metals autocatalyse their own sorption and/or actively inhibit that of the other. This fact does not occur in OMF sorption and retention data so that there are other soil components in whole horizon that influences these increases in Cr sorption. According to Bradl [6] Cr(III) is rapidly and specifically adsorbed by Fe and Mn oxides and clay minerals and this soil components do not predominate in OMF.

3.2. Model fitting

As a result of their irregularity, the data for sorption of the metals in the whole H horizon are fitted much less well by standard

Table 2
Best fitting sorption and desorption isotherms

Sorbent	Metal	Best fitting model	R ²	Equation	
Sorption isotherms					
Whole H horizon	Cd	Langmuir	0.73	$y = 0.68x - 43.76$	
	Cr	Langmuir	0.57	$y = 0.25x + 88.69$	
	Cu	Freundlich	0.77	$y = 0.37x + 0.16$	
	Ni	Langmuir	0.65	$y = 0.29x + 50.91$	
	Pb	Langmuir	0.92	$y = 0.06x + 2.21$	
OMF	Zn	Langmuir	0.65	$y = 0.44x - 10.72$	
	Cd	Langmuir	0.99	$y = 0.08x + 13.92$	
	Cr	Langmuir	0.89	$y = 0.51x - 63.62$	
	Cu	Langmuir	0.96	$y = 0.01x + 2.14$	
	Ni	Langmuir	0.99	$y = 0.07x + 16.92$	
Desorption isotherms	Pb	Langmuir	0.95	$y = 0.03x + 1.85$	
	Zn	Langmuir	0.99	$y = 0.06x + 17.7$	
	Desorption isotherms				
	Whole H horizon	Cd	^a		
		Cr	^a		
Cu		Freundlich	0.91	$y = 0.54x + 0.30$	
Ni		^a			
Pb		Langmuir	0.96	$y = 0.04x + 0.62$	
OMF	Zn	^a			
	Cd	Langmuir	0.67	$y = 1.04x - 54.99$	
	Cr	^a			
	Cu	Langmuir	0.97	$y = 0.01x + 1.19$	
	Ni	^a			
OMF	Pb	Freundlich	0.96	$y = 0.74x + 0.04$	
	Zn	^a			

Fits of Langmuir and Freundlich models were attempted.

^a Neither model fitted.

Langmuir or Freundlich sorption models than those for sorption in the OMF: for sorption in whole H horizon, the R² values of the best fitting models range from 0.57 to 0.92, but all except the value for Pb are less than 0.78, whereas for sorption in the OMF they range from 0.89 to 0.99 (Table 2). All the best fitting models are Langmuir models except that of Cu in the whole H horizon, which is a Freundlich model.

At high sorption solution concentration the retention of Cr, Ni, Zn and Cd falls to zero. Because of this, the only metals for which Freundlich or Langmuir models could be fitted to the retention data were Cu, Pb and, in the OMF, Cd (retention of which falls to zero more slowly than in the case of the other metals). The retention data for the most extensively sorbed metals Pb and Cu are well fitted by one or the other of these models, R² ranging from 0.91 to 0.97.

Some of the assumptions of the Langmuir model are that there is no interaction among sorbate molecules; that binding at one site does not affect binding at another; and that each binding site can bind just one sorbate molecule ("monolayer" sorption), the parameter β of the model reflecting the number of binding sites and hence the maximum amount of sorbate that can be sorbed [34]. Fig. 3 shows that for the OMF there was excellent correlation in this study between the theoretical sorption capacity β and the observed experimental maximum (R² = 0.997). This is in keeping with the good fit of the Langmuir models to the OMF sorption data, and thus supports the notion that in this soil fraction the binding sites are largely metal-specific. The correlation between β and observed maximum sorption was much poorer for the whole H horizon (R² = 0.570), in keeping with the poorer fit of the Langmuir models and the apparent existence, in the whole horizon, of binding sites at which the metals interfere with each other's sorption.

3.3. Distribution coefficients

Distribution coefficients (K_d) represent the affinity of the metallic cations in solution by the solid phase and they can be used to

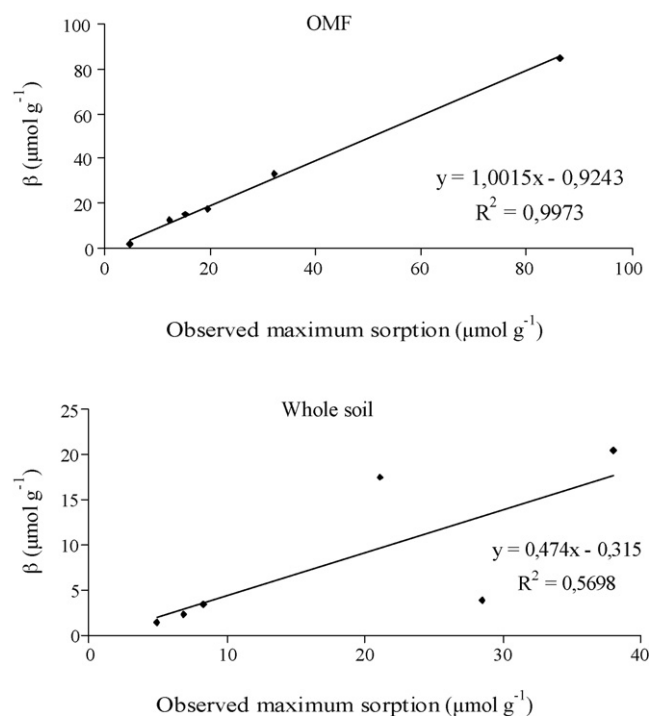


Fig. 3. Correlation between observed maximum sorption and the Langmuir equation parameter β , for the whole H horizon (top) and its OMF (bottom).

Table 3
 $K_{dc} \sum_{sp} (L kg^{-1})$ (see Section 2)

$c (mg L^{-1})^a$	Whole H horizon		OMF	
	Sorption	Retention	Sorption	Retention
5	32.07	101.03	35.88	72.47
10	290.62	358.42	66.35	147.57
20	188.60	278.79	46.68	108.36
30	48.38	168.46	40.88	113.41
40	33.53	162.59	32.31	99.93
50	23.62	139.40	26.90	88.59
100	9.01	511.18	13.41	50.94
200	5.77	105.71	7.96	39.47
300	3.03	160.05	5.99	30.45
400	2.93	57.11	5.22	26.99

^a Concentration of each metal in the initial sorption solution.

evaluate the sorption and retention of the metallic cations in soils [31]. High values of K_d indicate that the metal is retained by the solid phase through adsorption reactions, whereas low values indicate that an important proportion remains soluble.

As noted above, with the exceptions of lead and, in the OMF, copper, all the metals had nonlinear sorption and retention profiles. This ruled out characterization of their sorption or retention by the slope of the profile, as in Gao et al. [35]. Instead, we considered individual and joint distribution coefficients $K_{d_{100}}$ and $K_{d_{100} \sum_{sp}}$ calculated from the equilibrium concentrations of metal in soil and solution when the initial concentration of each metal in the sorption solution had been 100 mg L⁻¹ (the concentration at which sorption or retention of the non-dominant metals Cd, Cr, Ni and Zn began to level off or fall [28,31]).

$K_{d_{100} \sum_{sp}}$ allow us estimate the global heavy metal sorption and retention capacities [31–33]. For sorption, $K_{d_{100} \sum_{sp}}$ was greater for the OMF than for the whole H horizon (13.4 L kg⁻¹ as against 9.0 L kg⁻¹), while for desorption $K_{d_{100} \sum_{sp}}$ was greater for the whole H horizon (511.2 L kg⁻¹ as against 50.9 L kg⁻¹ for the OMF); see

Table 3. The discrepancy suggests that sorption by the OMF was more reversible than sorption by the whole horizon, and this idea is supported by examination of the ratios between $K_{d_{1,00}}$ for desorption and $K_{d_{1,00}}$ for sorption: in the whole H horizon these ratios range from 17.9 for Pb to 50 for Zn (all are greater than 34 except that of Pb), while in the OMF they range from 1.6 for Ni to 2.5 for Pb (Tables 5 and 4). The reversibility of sorption in the OMF once more supports the validity of the Langmuir model for sorption by this fraction.

3.3.1. Selectivity sequences

The $K_{d_{1,00}}$ values observed for sorption by the whole H horizon rank the metals in the order $\text{Cr} \approx \text{Pb} \gg \text{Cu} \gg \text{Cd} > \text{Zn} \approx \text{Ni}$, and the $K_{d_{1,00}}$ values for retention following the desorption stage in the order $\text{Cr} > \text{Pb} > \text{Cu} \gg \text{Cd} > \text{Zn} > \text{Ni}$, where \approx indicates a difference of less than a factor of 1.1 and \gg a difference of more than a factor of 4. Although the relationship between Cu sorption and Cr sorption commented on above limits the value of their inclusion in these rankings, it is clear from Table 5 that, together with Pb, at least one of these two metals was sorbed or retained to a much greater extent than Cd, Ni or Zn whenever the initial concentration in the sorption solution exceeded 20 mg L^{-1} . In the OMF, where sorption and desorption profiles were more regular, the analogous ranking are $\text{Pb} > \text{Cu} \gg \text{Cd} > \text{Zn} \approx \text{Ni} \gg \text{Cr}$ for sorption and $\text{Pb} > \text{Cu} \gg \text{Cd} > \text{Zn} > \text{Ni} \gg \text{Cr}$ for retention, in keeping with the known strong binding of Cu to humic substances [36] and with a report that the complexes formed by humic acid with Cu^{2+} , Pb^{2+} and Cd^{2+} are more stable than those formed with other divalent cations [37]. Assuming the validity of the interpretation of the sorption data in the previous subsections of this Discussion, the difference between the rankings of Cr in the whole H horizon and its rankings in the OMF must reflect the quantitative difference between Cr-specific reversible-binding sites in the OMF and Cr/Cu-specific, irreversible-binding sites in the fraction of larger particle size. The reversible Cr binding in the OMF is perhaps due as much to sites in clay minerals as to organic matter Cr is known to bind to kaolinite, mica and vermiculite [38], although the properties of these minerals will be altered by their association with organic matter in the OMF; while

Table 4
Distribution coefficients K_{dc} for sorption and desorption in the organo-mineral fraction

c (mg L ⁻¹) ^a	K_{dc} (L kg ⁻¹)					
	Cd	Cr	Cu	Ni	Pb	Zn
Sorption						
5	102.33	1.05	598.22	74.04	399.49	54.74
10	175.73	15.47	1065.05	89.29	1784.40	77.71
20	93.43	11.11	795.70	48.52	1081.93	44.79
30	48.71	10.29	796.61	39.35	930.81	38.18
40	45.39	7.76	697.40	28.02	790.49	27.96
50	33.15	6.33	534.04	22.05	664.61	22.29
100	14.37	1.35	189.15	8.46	232.96	9.21
200	6.69	0.76	63.49	3.77	107.04	6.94
300	4.24	0.31	44.80	2.28	82.86	2.78
400	3.49	0.17	34.85	1.91	56.63	2.31
Desorption						
5	61.25	0.14	954.59	60.03	693.75	38.44
10	135.29	165.46	749.54	88.94	1055.96	76.19
20	80.64	107.28	896.81	61.64	1129.79	51.82
30	73.42	103.49	1011.16	62.12	1226.55	56.52
40	69.76	88.51	940.51	49.83	1114.46	46.94
50	54.60	79.89	772.19	41.35	989.26	39.38
100	25.24	2.44	462.16	13.69	574.27	15.49
200	16.48	0.00	226.23	5.34	354.31	17.28
300	5.75	0.00	169.09	0.00	314.79	0.00
400	1.22	0.00	146.53	0.00	264.70	0.00

^a Concentration of each metal in the initial sorption solution.

Table 5

Distribution coefficients K_{dc} for sorption and desorption in the whole H horizon

c (mg L ⁻¹) ^a	K_{dc} (L kg ⁻¹)					
	Cd	Cr	Cu	Ni	Pb	Zn
Sorption						
5	80.76	0.85	2009.08	52.93	335.68	41.94
10	49897.17	123.41	127.84	724.19	3710.56	92467.24
20	111181.62	65.91	232.18	230.83	8243.73	304.69
30	65.27	29.63	303.44	34.91	1896.08	28.93
40	33.13	28.97	248.50	19.49	1138.01	16.73
50	21.49	15.94	181.13	14.01	557.77	12.27
100	1.37	71.04	14.67	0.78	69.79	0.82
200	3.34	0.94	25.39	2.88	55.18	2.62
300	0.44	7.40	3.62	0.42	19.79	0.29
400	0.92	0.44	10.12	0.85	29.34	0.75
Desorption						
5	76.30	0.26	2458.16	70.03	1281.71	55.65
10	579.99	1351.73	1027.84	246.25	1120.06	144.37
20	252.33	1897.09	1903.67	152.29	2319.66	131.06
30	110.76	1113.84	1337.45	78.70	2270.05	62.96
40	88.96	1306.85	938.37	66.69	1684.31	56.38
50	67.74	1026.27	735.15	54.28	1394.51	45.09
100	52.85	2566.85	715.20	26.99	1252.17	41.03
200	19.57	192.93	268.92	33.39	598.83	26.63
300	0.02	1131.19	182.75	0.01	577.73	0.01
400	0.01	49.41	114.90	0.02	316.27	0.01

^a Concentration of each metal in the initial sorption solution.

irreversible Cr binding in the non-OMF fraction may be due not only to POM but also to Fe and Mn oxides, which are also known to bind Cr^{+3} strongly [6].

4. Conclusions

Data sorption and retention in OMF and whole horizon indicate that there are other soil components in whole horizon that positively influences Cr sorption.

The good fit of the Langmuir models to the OMF sorption data supports the notion that in this soil fraction the binding sites are largely metal-specific. The poorer fit of the Langmuir models in the whole horizon indicates the apparent existence of binding sites at which the metals interfere with each other's sorption.

The difference between the rankings of Cr in the selectivity sequences of whole H horizon and its rankings in the OMF must reflect the quantitative difference between Cr-specific reversible-binding sites in the OMF and Cr/Cu-specific, irreversible-binding sites in the Fibric Histosol horizon.

Whole H horizon appeared to include sites at which binding was less reversible and Cr^{+3} competed with the other metals, Cu^{+2} especially therefore organo-mineral fraction is suitable to evaluate the soil organic matter contribution to heavy metal fixation.

Acknowledgements

This work was supported by the Spanish Ministry of Education and Science under project CGL2006-01016/BTE. In partnership with the University of Vigo, the Xunta de Galicia also supported the work through Parga Pondal contract awarded to E.F. Covelo.

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