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Sorption of Heavy Metals in Organic Horizons of Acid Forest Soils at Low Added Concentrations

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Abstract

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The individual adsorption/desorption of Cu, Pb, and Zn in six soil samples taken from organic horizons of acid forest soils is studied in batch experiments. These three metals were chosen because of the varying extent of their sorption to the soil organic matter. The initial concentration range for all metals is 0–200 mg/l. 0.01 mol/l $Ca(NO_3)_2$ was used as the background electrolyte. Soil samples were taken at random locations throughout a relatively small area and are characterized by small differences in mineralogical composition. Organic matter content and pH of soils are considered as the key factors causing differences in sorption/desorption behaviour of selected metals. In general, the sorption of all the three metals increased with a combination of higher pH value and increasing organic matter content. Anyway, the extent of the influence of these two characteristics on sorption behaviour of metals is different, for desorption significant differences were not determined. Copper sorption seems to reflect mainly the differences in organic matter content in addition to the differences in pH. The average amount of sorbed Pb was approximately 90%, Cu sorption averaged 60%, and that of Zn 30%. Desorption of Pb into 0.01 mol/l $Ca(NO_3)_2$ remained at approximately 4%, for Zn at 30%, and desorption of Cu reached up to 13% of the amount adsorbed. All the studied soils proved effective at immobilizing lead and copper, but zinc was relatively highly released from these soils, even when the sorbed amount was minimal. Different vegetational background of these samples (either beech or spruce forests) does not significantly influence the sorption extent of these metals as the lower pH of samples taken under spruce stands is probably compensated by higher organic matter content in these samples. The experimental data are fitted by the Freundlich equation and the parameters of this equation together with the adsorption and desorption efficiency are used for comparison of the behaviour of all the three metals among the six soils.

Keywords: acidic soils; adsorption; desorption; organic matter; risk elements

Besides the pH value, the soil organic matter plays a key role in the sorption of heavy metals, and its influence increases with its increasing content in soils. Sorption of heavy metals to organic matter in organic soils can exceed sorption to mineral soil constituents by several times (Lair *et al.* 2007). The key organic compounds influencing sorption of heavy metals are humic substances, namely humic acids (HAs) and fulvic acids (FAs), due to their high share in organic matter and their chelating and complexing characteristics. Humic substances are mixtures of different acids, they have high variability and their composition often differs according to the location or soil horizon in which they are present. At low soil pH, humic substances are bound mainly in the form of organo-mineral complexes, which present a surface with different sorption characteristics than each of these components individually (Barančíková & Makovníková 2003; Karpukhin & Bushuev 2007). Humic substances retain heavy metals mainly by pH-dependent formation of inner-sphere and/or outer-sphere complexes and cation exchange, but the form and extent of binding is different for each metal (Christl *et al.* 2001; Barančíková & Makovníková 2003; Gondar *et al.* 2006).

The three selected metals – Cu, Pb, and Zn – are characterized by a varying extent of their sorption onto the organic matter. Copper and lead show strong affinity for fulvic and humic acids and both metals form stable complexes with humic substances (Adriano 2001). Stronger tendency of these metals to form inner-sphere complexes with organic compounds is often attributed to the relatively higher values of electronegativity, smaller hydrated radius and/or lower pK_H values. Strong sorption can occur also because these two metals are borderline Lewis acids which favour the formation of a covalent bond with O-containing functional groups (-COOH, -OH) in organic compounds, which are characterized as hard Lewis bases (Alloway 1995). On the other side, the portion of Zn bound to humic substances is supposed to be relatively small compared to the other heavy metals. Zinc prefers sorption to the mineral fraction of soils and bonding is often expected as exchangeable (Gondar *et al.* 2006; Karpukhin & Bushuev 2007).

To study the sorption behaviour of metals in respect of varying quality and quantity of organic matter, we generated batch sorption experiments using organic topsoil samples. In order to compare the influence of two vegetational backgrounds on the retention of metals in soils, half of the samples were collected from spruce stands and half under beech stands.

Under the conditions of this experiment, we consider the influence of the mineral fraction on sorption/desorption of metals to be the same in all samples. The differences in mineralogical compositions among samples are negligible as the soil samples are taken at random locations throughout a relatively small area. The low pH of soils favours binding of metals to organic matter (Tipping 1981), and the high organic content in samples can minimize the effect of mutual interactions between the soil minerals and organic matter, which can, either chemically or physically, "block" sorption sites for metals (Lair *et al.* 2007). Especially when added amounts of metals are relatively small, and maximum adsorption is beyond the experimental range of their additions.

MATERIAL AND METHODS

Soil samples in the study. Six soil samples were collected from the top layer soil (H horizon) in the Jizerské hory Mts. located on the border between the Czech Republic and Poland. The soils are endangered by soil acidification, because this area was highly affected by emissions from power stations in the past century (Suchara & Sucharová 2002). The differences in the mineralogical composition of the selected soils are minimal. The soils have been detailedly described previously (Pavlů *et al.* 2007; Tejnecký *et al.* 2010, 2013). Half of the samples were taken under beech stands (b samples) and half under spruce stands (s samples). Soils, which were sampled under 170-year-old beech stands, were classified as Dystric Cambisols and the form of humus as moder. Soils, which were sampled under 90-year-old spruce stands, were classified as Entic Podzols and the form of humus was qualified as mor. Prior to storing in plastic bags for subsequent analysis, soil samples were air-dried, sieved through a 2-mm mesh, and homogenized.

Analytical methods. Selected properties of soils are listed in Tables 1 and 2. They were determined by commonly used methods: pH (KCl) potentiometrically in 1 mol/l KCl; effective cation exchange capacity (ECEC) is calculated as the sum of exchangeable Al which is extracted with 1 mol/l KCl and the content of Ca, Mg, Na, and K which is extracted with

Table 1. Selected properties of soils

Sample	pH (KCl)	S	N	C	C/N	OM (%)	A_{400}/A_{600}	Cu_{ar}	Pb_{ar}	Zn_{ar}
		(%)						(mg/kg)		
b1	3.37	0.09	0.86	15.16	17.61	32.45	5.89	37.15	222.50	32.05
b2	3.13	0.27	1.68	30.40	18.12	62.72	6.02	25.03	179.25	34.05
b3	3.46	0.08	1.19	18.92	15.88	41.40	6.86	25.95	166.00	35.90
s1	2.92	0.16	1.37	27.51	20.10	55.87	5.95	21.58	149.50	38.88
s2	2.95	0.15	1.18	23.85	20.22	49.09	5.68	30.50	268.75	35.05
s3	2.98	0.19	1.49	26.70	17.92	55.28	6.59	27.88	159.00	43.08

OM – organic matter; ar – aqua regia digestion

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Table 2. Characteristics of the soil sorption complex

Sample	H	Ca	Mg	K	Na	Al	ECEC (mmol/100g)	BS (%)
	exchangeable cations (mmol/100g)							
b1	4.01	0.07	0.20	0.31	0.13	10.69	15.41	4.44
b2	4.96	0.09	0.33	0.66	0.22	19.40	25.66	4.76
b3	4.27	0.05	0.20	0.39	0.14	15.68	20.74	3.61
s1	4.92	0.11	0.42	0.61	0.22	10.83	17.10	7.48
s2	4.82	0.19	0.34	0.49	0.24	14.59	20.67	5.87
s3	4.86	0.14	0.30	0.74	0.21	15.24	21.49	6.07

ECEC – effective cation exchange capacity; BS – base saturation

unbuffered 1.0 mol/l NH_4Cl (Skinner *et al.* 2001). The pseudototal concentrations of heavy metals were determined by aqua regia digestion (Cu_{ar}, Pb_{ar}, Zn_{ar}). The elements contents in the solution were determined by flame atomic absorption spectrophotometry (AAS) (Varian SpectrAA280 FS; Varian, Mulgrave, Australia) under standard conditions. Total concentrations of C, N, and S were measured using a Flash 2000 thermo elemental analyzer (Thermo Scientific, Cambridge, United Kingdom). Soil organic matter content was determined by the loss-on-ignition method (Nelson & Sommers 1996). The quality of humic substances was determined as A_{400}/A_{600} ratio of optical densities measured in 0.05 mol/l $Na_4P_2O_7$ soil extract at wavelengths 400 and 600 nm (Javorský 1987).

Monometal sorption experiments. Preliminary studies for determining appropriate sorption conditions, such as the equilibrium time and the soil:solution ratio, were carried out in accordance with OECD Guidelines for the Testing of Chemicals, Test No. 106 (2001). One gram of soil sample was equilibrated for 24 h at room temperature (20 ± 3°C) with 20 ml of Pb, Zn or Cu nitrate solutions in the concentration range of 0–200 mg/l using five different initial metal concentrations. 0.01 mol/l $Ca(NO_3)_2$ was used as the background electrolyte. According to literature (Schnitzer & Skinner 1967; Adriano 2001) calcium shows higher affinity for soil organic matter than Zn but lower than Cu and Pb. Because of the same charge and similar ionic radius of calcium, competition with heavy metals for exchange sites can be expected and the excess of calcium cations from background electrolyte forces heavy metals to the sites with higher affinity and reduces the nonspecific sorption of heavy metals (Violante *et al.* 2010).

$Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ are supplied by HiChem (maximum purity available). All solutions were prepared by mass with deviations of less than 0.5% from the desired concentrations. All initial solutions were undersaturated at the pH of the solution, which is in the range of 5.1–6.1. Precipitation under these acidic conditions is not expected, but cannot be totally excluded.

The equilibrated mixtures were centrifuged at 4000 rpm for 10 min, the aqueous phase was removed in the defined volume of 15–17 ml, filtered through Whatman 540 paper, pH was then measured and the metal concentrations determined. Desorption experiments followed immediately after the sorption. The supernatant removed from the tubes was replaced by an equal volume of metal-free 0.01 mol/l $Ca(NO_3)_2$. The new mixture was agitated for another 24 h, and again the pH values of the filtrates were determined and solutions were analyzed for target metals by AAS.

The adsorbed amount of each metal a (mg/kg) was calculated as the difference between the amount added initially and the amount remaining in solution after equilibration:

$$a = \frac{(c_i - c_{eq})V}{m}$$

where:

c_i – initial concentration of metal (mg/l)
c_{eq} – concentration measured in the filtrate (mg/l)
V – volume of solution added (ml)
m – mass of soil (g)

All the experiments, including controls and blanks, were performed in duplicate. All values were corrected for the value of the blank.

RESULTS AND DISCUSSION

Soil properties. All of the studied soils are strongly acidic with organically complexed aluminum as the

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main exchangeable cation. The pH values were in the range of 2.9–3.5; soil samples taken in the spruce forest were slightly more acidic. Base saturation was higher for s samples than for b samples. Total sulfur and nitrogen contents were very low in all samples. Carbon made up 47%, nitrogen 2–3%, and sulfur less than 0.5% of total organic matter. Organic carbon content in the samples was in the range of 15–30% and except for the b2 sample, the organic carbon content was lower for b samples than for s samples. Pavlů *et al.* (2007) attributed this result to the easier decomposition of leaves. The selected b samples showed higher variability in pH and in organic matter content than s samples. Sample b1 was characterized by the lowest content of organic matter and sample b2 by the highest. Sample b2 had also slightly lower pH than the other two b samples. The fact that the samples had been taken under two different vegetation covers did not result in significantly different A_{400}/A_{600} values. These values were similar for all samples and ranged from 5.68 (sample s2) to 6.86 (sample b3). This finding can be explained by unfavourable conditions under the stands. Higher A_{400}/A_{600} values indicate lower humus quality with dominating fulvic acids in the analyzed soils. Similar results, which characterized these soil samples, were determined also by Pavlů *et al.* (2007).

After the sorption and desorption shaking process, pH of the supernatants of all the three metals always decreased and was similar to that of soils, indicating displacement of H^+ and/or Al^{3+} from soil surfaces.

Individual sorption of metals. Differences among the sorption behaviour of selected metals by these samples are as expected. Copper and lead show a high sorption affinity to these samples, in contrast to zinc, whose sorption is several times lower. Even though the results from this experiment do not allow the determination of the amount of a particular metal associated with the particular fraction of soils, under the conditions of this experiment and due to the strong affinity of copper and lead to organic matter (Senesi *et al.* 1989; Adriano 2001), it can be expected that these two metals are highly associated with humic substances. In terms of adsorbate efficiency (percentage of metal adsorbed relative to the initial concentration of metal), the sorption of Cu in all samples was 48–89%, and almost all of the Pb added to soils was adsorbed. Zinc sorption was in the range of 22–41%. The sorbed amount in absolute values increases with the increasing initial concentration of each metal but decreases in all samples relative to this initial concentration. The decline in the adsorbate efficiency was approximately 22% for Cu, 8% for Zn, and 5% for Pb. The lowest sorption efficiency for all the three metals was determined in sample b1, the sample with the lowest organic matter content, but differences in these values for each metal among the rest of samples were minimal.

Sorption isotherms. The sorption isotherms of all the three metals are presented in Figure 1. The amount of metal adsorbed per gram soil (a) is represented as a function of equilibrium metal concentration in solution (c_{eq}). All sorption isotherms are satisfactorily described by the Freundlich equation, which

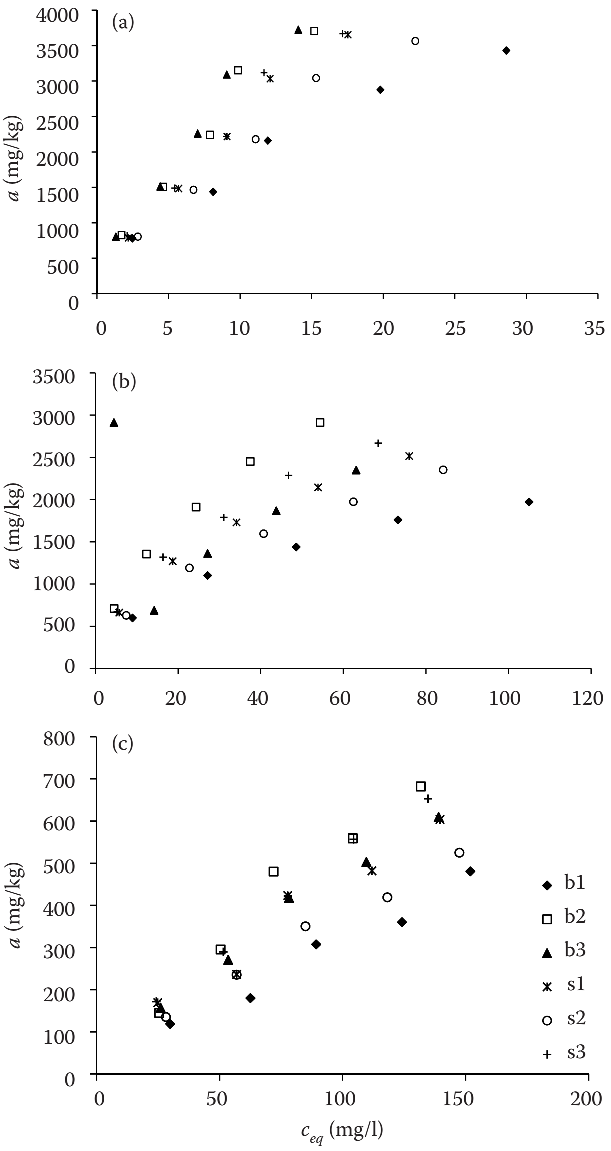

Figure 1. Sorption isotherms of (a) lead, (b) copper, and (c) zinc; a – adsorbed metal; c_{eq} – equilibrium metal concentration

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Table 3. The Freundlich parameters (K_f and $1/n$) for sorption of copper, lead, and zinc

Sample	Cu			Pb			Zn		
	K_f	$1/n$	$R^{2\,a}$	K_f	$1/n$	R^2	K_f	$1/n$	R^2
b1	236.38	0.46	0.99	438.28	0.62	0.99	4.26	0.93	0.97
b2	339.70	0.54	1.00	544.61	0.72	0.97	9.29	0.80	0.99
b3	354.44	0.50	1.00	597.74	0.70	0.97	11.18	0.76	0.99
s1	291.22	0.50	1.00	422.18	0.76	0.99	11.83	0.81	0.99
s2	222.25	0.53	1.00	385.20	0.73	0.98	12.11	0.81	1.00
s3	304.72	0.52	1.00	452.57	0.75	0.98	12.44	0.83	1.00

R^2 – coefficient of determination

generated two parameters K_f and $1/n$ (data reported in Table 3). This equation is often used for a low concentration of adsorbate and for the description of adsorption onto heterogeneous surfaces (Bradl 2004; Arias *et al.* 2006).

$$a = K_f c_{eq}^{\frac{1}{n}}$$

where:

a – quantity of sorbed metal (mg/kg)

c_{eq} – equilibrium concentration (mg/l)

n, K_f – empirical parameters

The Freundlich parameters are used for the interpretation of the experimental results and are calculated using a non-linear model based on the least sum of squared errors SSE (Bolster 2008). Even if these constants do not present meaningful physical quantities such as Langmuir parameters, they can show their relationship with soil properties (Adhikari & Singh 2003).

The $1/n$ value describing profiles of isotherms is indicative of metal affinity for the solute and determines the intensity of adsorption (Hooda & Alloway 1998). The sequence of $1/n$ values is Zn > Pb > Cu in all samples with minimal differences within each sorption. $1/n$ values are around 0.5 for copper, 0.6–0.8 for lead, and for zinc $1/n$ values were highest for all samples, in the range between 0.8–0.9. When interpreted, these $1/n$ values show that the amount of Cu adsorbed can be high, even if its concentration in solution is low. Conversely, low concentration of zinc in solution relates directly to its low adsorption.

The K_f coefficient relates to the extent of sorption and the sequence of this parameter is Pb > Cu > Zn for all samples. This is in accordance with other reports (Elliott *et al.* 1986; Sastre *et al.* 2007; Trakal *et al.* 2012). K_f for lead sorption ranges from 385.2 to 597.7, for copper from 222.3 to 354.4, and for zinc these values are several times lower, between 4.3 and 12.4. In the case of lead sorption by the studied samples, the availability of sorption sites does not seem to be the limiting factor, and its adsorption increased most steeply with the addition of metal. Higher sorption of this metal to mineral parts of soils and generally high affinity of lead for most functional groups in organic matter (Bradl 2004) can explain this finding. Comparing to lead, copper sorption is significantly lower in all samples. This result can be attributed to generally low affinity of copper to inorganic part of soils, as this metal is preferentially sorbed to organic fraction (Barančíková & Makovníková 2003; Gondar *et al.* 2006). The sorption of copper seemed to be more limited, despite a relatively higher number of functional groups in these organic samples and the ability of copper to displace other heavy metals from their sorption sites (Trakal *et al.* 2012). With this respect, copper preferential sorption to HAs rather than to FAs can be considered as the factor influencing copper sorption to humic substances, as for copper sorption the linkage of functional groups to aromatic structures is important (Schnitzer & Skinner 1967; Adriano 2001; Barančíková & Makovníková 2003). Sorption of Zn by the studied samples is several times lower when compared to Cu and Pb. The affinity of Zn for organic matter is generally low, but for fulvic acids it is described as being higher than that of copper as this metal is bound primarily to aliphatic structures, which are predominant in fulvic acids (Murray & Linder 1984). Despite low amounts of specific sites for zinc, a possible explanation of low sorption of zinc can be considered a competitive effect of other cations, which can block sorption sites for this metal. Aluminium, which is complexed in large amounts in these samples and is the main exchangeable cation, might than suppress sorption of zinc to exchangeable positions. Similarly,

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calcium from the background solution can compete for sorption sites with zinc. However, some studies showed the competition of calcium with zinc to be insignificant (Escrig & Morell 1997). The competitive effect of calcium could force zinc to the sites with higher affinity.

Differences in K_f parameters within the sorption of each metal are relatively small. In the case of zinc, these differences are also within experimental uncertainties. Nevertheless, the K_f values showed a common trend for sorption of all three metals and these values decreased with lower pH and decreasing C content. For lead and copper sorption, the lowest values of K_f were determined for sorption of these metals by sample s2, which is characterized by the lowest C content within s samples. The lowest value of K_f for zinc was observed for the sorption of this metal by sample b1, also the sample with the lowest C content but within b samples. These results suggest different extent of influence of pH on the sorption of selected metals, which will be discussed further.

Desorption. Desorption experiments allow an estimation of the type of binding of metals in soils. As can be seen from Figure 2, all these soils have good ability at retaining copper and lead. In contrast to lead and copper, it is evident that zinc was released in relatively higher amounts even if its adsorbed amount was minimal. Desorption of Zn into background electrolyte was the highest and ranged from 27 to 40%. Desorption of Pb was negligible (around 4%) and the average amount of Cu desorbed was in the range of 5–13%. Minimal desorption of copper and lead confirm mainly specific binding of these two metals. In contrast, desorption of zinc was comparably higher and can indicate that zinc is bound also by electrostatic interactions. In absolute values, the desorbed amounts of each particular metal differs, and their desorption increases with a higher initially adsorbed amount of metal. This can be attributed to the reduction of binding energy caused by a higher occupancy of binding sites (Arias *et al.* 2006). In relative values (percentage of metal desorbed relative to the initially adsorbed amount of metal), differences among samples are small. The most marked differences can be seen for the release of copper from sample b1 with the lowest organic C content, which showed more "favourable" behaviour of metal and a high amount of metals remained adsorbed, even if its concentration in solution is relatively low.

Effects of pH and organic matter on metals sorption. With respect to the pH value of soils and organic matter quality and quantity, it was difficult to evaluate their effect on sorption of metals, as differences in these characteristics were relatively small. Furthermore, in accordance with other reports (Gerriste & van Driel 1984; Hooda & Alloway 1998), it is apparent that metals responded to changes in these soil characteristics to varying extents. Despite different slopes and profiles of isotherms of the studied metals, their mutual distinguishing also differed, especially some of the zinc isotherms were almost identical.

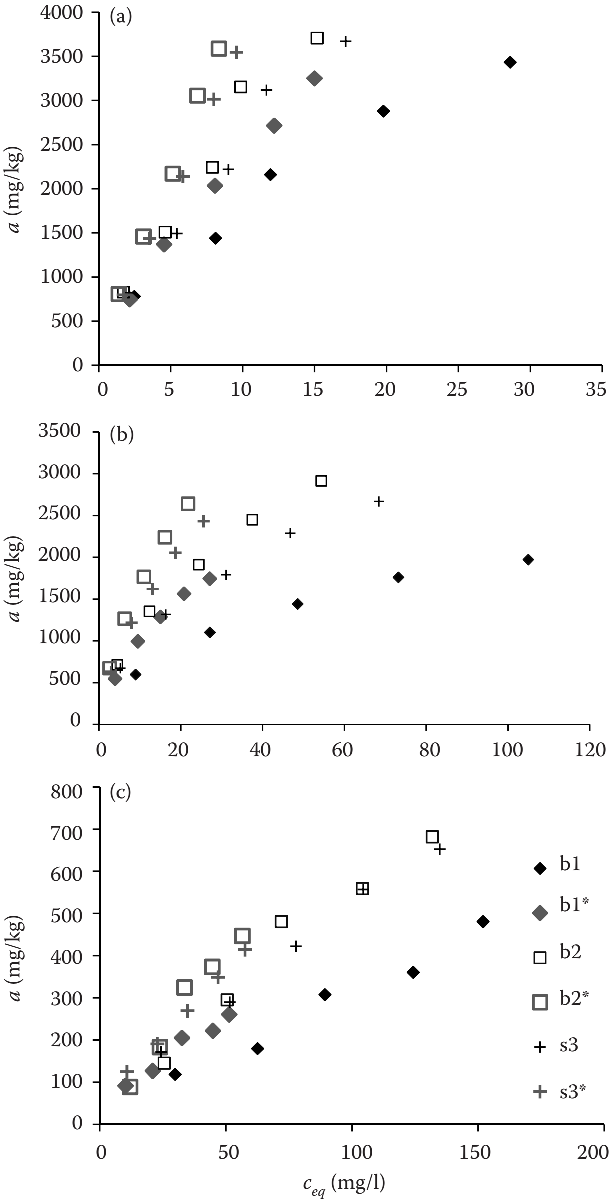

Figure 2. Sorption vs desorption of (a) lead, (b) copper, and (c) zinc from representative samples b1, b2, and s3; desorption is marked with asterisk; a – adsorbed metal; c_{eq} – equilibrium metal concentration

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Anyway, sorption of all the three metals seemed to follow general trends and increased with increasing pH and/or increasing organic matter content. All the three metals were sorbed to the lowest extent by sample b1, the sample with the lowest quantity of organic matter and the relatively higher sorption of all the three metals by sample b3 can be explained by its highest pH. Sorption of Cu seems to reflect mainly the differences in organic matter content in addition to the differences in pH. Sample b2, characterized by the highest organic matter content, adsorbs only copper in an apparently greater amount than the rest of the samples. To a similar extent as by sample b2 was lead adsorbed by sample b3 and zinc by sample s3. Lower pH of sample b2 may have been the cause of lower amount of lead adsorbed as compared to sample b3 and suggested strong influence of pH on sorption of lead. Also Freundlich K_f parameters indicate that lead sorption is highly controlled by pH. On the other side, zinc sorption seems to be more influenced by an increasing organic C content than by changes in pH.

Different vegetation cover does not result in significant differences in qualitative parameter A_{400}/A_{600} ratio between b and s samples. Anyway, it should be noted that A_{400}/A_{600} ratio does not provide sufficient information about the structural composition of each fraction of humic substances, which could be different at least because of differing vegetation background. In this respect, differences in structural composition of functional groups and/or in concentrations of elements such as nitrogen and/or sulfur in soils could still be considered. Despite carboxylic, phenolic, and alcoholic groups, which are believed to play a key role in metals binding by humic substances (Bäckström *et al.* 2003), sulfur and nitrogen groups in soils can form extremely strong binding positions for metals, and even if the amounts of these groups are low, they can be important for sorption at low added concentrations of metals (Abate & Masini 2002; Bäckström *et al.* 2003). Gregor *et al.* (1989) assumed a key role of nitrogen content in the affinity of humic substances towards copper. Difference in quality of organic matter is probably a reason for a greater sorption of Cu by sample s3, which was higher than sorption by sample s1 characterized by almost the same organic C content and pH as sample s3.

Metals can also respond to soil properties with regard to the concentration range in which they are studied (Christl *et al.* 2001). Different profiles of lead, copper, and zinc isotherms show that the extent of saturation of sorption sites for these metals is not uniform, and this can be another reason for their different response to changes in the above mentioned soil characteristics.

CONCLUSION

In sorption experiments, between 85–96% of added Pb was sorbed, Cu sorption was between 55–90%, and Zn sorption around 30%. The sorption isotherms are satisfactorily described by the Freundlich equation, with the highest K_f for lead, followed by Cu, and several times lower values were determined for Zn adsorption. The sequence of $1/n$ values is Zn > Pb > Cu in all samples. Desorption of initially adsorbed Zn into 0.01 mol/l $Ca(NO_3)_2$ ranged from about 10 to 50%, for Cu from 5 to 13%, and for Pb it fluctuated around 4%. There were no significant differences in desorption of metals between b and s samples and both groups of soils showed a high ability for immobilizing lead and copper. Zinc, on the other hand, was released by exchangeable reactions even when its adsorbed amount was low. The results from this experiment showed that all the three metals reflect general trends in sorption of metals by soils; increased sorption with higher pH and/or increasing organic matter content. The extent of the influence of these factors is metal-specific and the concentration range of metals in which their sorption is determined seems to be another important consideration for evaluating the extent of influence of these factors. Different vegetational background of these samples has no substantial influence on the extent of sorption of these metals as the lower pH of samples taken under spruce stands seems to be compensated by higher organic matter content in these samples. Even though the two studied vegetation covers did not significantly influence the qualitative parameter of humic substances – the A_{400}/A_{600} ratio – in these organic soils, the influence of organic matter quality cannot be excluded. This ratio does not provide information about the exact structural composition of samples. Copper sorption in particular seemed to reflect even small differences in organic matter composition.

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