Heavy metal distribution between fractions of humic substances in heavily polluted soils

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ABSTRACT

Soil organic matter is important in controlling heavy metal behaviour in soils. This study aims to determine the distribution of organically bound Cd, Pb, and Zn between humic and fulvic acids in 20 samples of heavily polluted Fluvisols. Traditional procedure of alkaline sodium hydroxide/pyrophosphate extraction of humic substances with consequent humic acids precipitation by acidification was used. All of the three metals were bound predominantly on fulvic acids (mean share was 98.4, 82.0, and 95.7% of total organically bound Cd, Pb, and Zn content, respectively). Mainly the level of pollution controlled the amount of metals bound on fulvic acids. On humic acids, a limited amount of specific sorption sites for the metals is expected. Lead content bound on humic acids was negatively correlated with soil pH. The results suggest relatively high potential mobility of organic fractions of heavy metals in soils under this study. The selectivity of alkaline extracting agent is briefly discussed.

Keywords: heavy metals; humic acids; fulvic acids; soil pollution; speciation

Soil organic matter is, together with soil pH, the most important parameter controlling heavy metal behaviour in soils. Heavy metals bound on insoluble humic substances are relatively immobile. On the other hand, binding on smaller organic molecules may increase metal mobility and bioavailability (e.g. Kabata-Pendias and Pendias 1992). Sorption sites on organic matter can be highly specific (Adriano 2001, Heredia et al. 2002). Angehrn-Bettinazzi et al. (1989) reported high ability of Pb to form complexes with insoluble humic substances, while Cd and Zn formed complexes with mobile organic substances of low molecular weight. Humic carboxylic -COOH and phenolic -OH groups are mainly involved in the formation of metal-humic complexes (Spark et al. 1997, Datta et al. 2001). Complexes of Pb and Cu with humic acids were found to be more stable than complexes of Cd and Zn (Waller and Pickering 1993, Pinheiro et al. 1994, Gao et al. 1999). Ladonin and Margolina (1997) attributed this effect to the forming of coordination complexes in the case of Pb and Cu, while Zn and Cd were characterized rather by ion exchange-type reaction. However, Basta et al. (1993) showed that both Cd and Pb complexation with organic matter was more important than their adsorption through cation exchange. The strength of metal-humic complexes is influenced by soil pH and ionic strength (Ladonin and Margolina 1997, Adriano 2001, Evangelou and Marsi 2001). Binding on humic acids may enhance metal sorption on mineral particles (Arias et al. 2002). Detailed knowledge of the interaction of heavy metals with humic substances in soils could be used in the development of remediation methods for polluted soils (Kolář and Ledvina 1998, Halim et al. 2003).

Most common chemical procedures for heavy metal speciation treat organic fraction in one extraction step neglecting a detailed distribution of metals between separate humic fractions (Tessier et al. 1979, Ure et al. 1993, and others). Increasing attention is paid to the interaction of heavy metals with humic and fulvic acids recently (e.g. Barančíková and Makovníková 2003). Assessment of this interaction and metal distribution between different fractions of humic substances is useful for a justified pollution risk assessment. Mathematical modelling is often exploited (e.g. Mountney and Williams 1992, Weng et al. 2002). Donisa et al. (2003) studied distribution of some heavy metals between fulvic and humic acid fractions in three soil profiles using traditional humus fractionation procedure. However, the authors admit that sodium pyrophosphate extraction may overestimate the amount of heavy metals really complexed with humic substances due to the effect of Na^+ on exchangeable cations and possible dissolution of some Fe oxides and the release of metals bound on them.

The aim of this paper is to assess the distribution of Cd, Pb, and Zn between humic (HA) and fulvic

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Supported by the Grant Agency of the Czech Republic, Grant No. 526/02/1516.

acids (FA) in heavily polluted soils and analyze the effect of soil properties on this distribution. Some problems of the traditional humus fractionation in relation to heavy metals are discussed.

MATERIAL AND METHODS

A set of 20 soil samples collected from the topsoil (0–15 cm) in the alluvium of the Litavka River in the district of Příbram was used. A principal soil unit in the alluvium was Fluvisol. The area is heavily polluted (Borůvka et al. 1996). In addition to naturally increased heavy metal contents due to the specific parent rock composition, there are two important sources of anthropogenic contamination: 1) atmospheric emissions of smelting plants working since the 19th century; 2) several river floods that delivered water contaminated by heavy metals from metallurgical plant setting pits there.

Soil samples were air-dried and passed through 2-mm sieves. Basic soil characteristics were determined by commonly used methods: pH_{H_2O} and pH_{KCl} potentiometrically, organic carbon content (C_{org}) oxidimetrically by a modified Tjurin method (Pospíšil 1964), clay content (particles < 0.001 mm) areometrically. Aqua regia digestion was used for the determination of pseudototal content of Cd, Pb, and Zn in soil (Cd_{AR}, Pb_{AR}, Zn_{AR}; ISO 1991). Metals were also extracted with 2M HNO_3 (Cd_{HNO_3}, Pb_{HNO_3}, Zn_{HNO_3}; Borůvka et al. 1996). Exchangeable (Cd_{exc}, Pb_{exc}, Zn_{exc}) and organically bound (Cd_{org}, Pb_{org}, Zn_{org}) metals were determined by a modified sequential extraction using 0.1M $Ca(NO_3)_2$ and 0.05M $Na_4P_2O_7$ (adjusted to pH 12 with NaOH), respectively; details were given in Borůvka et al. (1997). Determination of metal contents in extracts was performed by means of atomic absorption spectroscopy in air-acetylene flame.

Humus fractionation was done using a modified procedure according to Podlešáková et al. (1992). Soil humic substances were extracted with a solution containing 0.1M NaOH and 0.1M $Na_4P_2O_7$ (20 ml per 1 g of soil) with permanent shaking for 1 hour at laboratory temperature. Undissolved material was removed by centrifugation and filtration (supernatant I). 20 ml of the supernatant I were acidified with 5 ml of 1M H_2SO_4, centrifuged and filtered (supernatant II). The organic carbon content in both supernatants was determined oxidimetrically (Pospíšil 1964). Concentrations of Cd, Pb, and Zn in both supernatants were measured again by means of atomic absorption spectroscopy in air-acetylene flame. All measurements were done in three replicates. The amount of carbon in FA (C_{FA}) was based on carbon content in the supernatant II. The amount of carbon in HA (C_{HA}) was calculated as the difference between carbon content in the supernatants I and II. The differences of metal content between the two supernatants were used for the estimation of metals bound on HA (Cd_{HA}, Pb_{HA}, Zn_{HA}). However, metal content in both supernatants included not only metal forms bound on humic substances, but also a portion of exchangeable metals (Donisa et al. 2003). These forms would increase the estimate of the metals bound in FA; exchangeable metals are expected to stay in the solution during HA precipitation at low pH. Metals bound on FA (Cd_{FA}, Pb_{FA}, Zn_{FA}) were therefore calculated as the difference between organically bound metals determined in the two-step sequential extraction (where the exchangeable metals had been removed) and metals bound on HA.

All datasets were tested for normality; no transformation of data was necessary. Statistical analyses were performed using Statgraphics Plus v. 4.0 for Windows (Manugistics 1997).

RESULTS AND DISCUSSION

The set of samples under study included a range of soils from a strongly acid to slightly alkaline (Table 1). In average, humic substances accounted for approximately one fifth of the total organic

Table 1. Mean values, standard deviations, minimum and maximum values of basic soil properties and carbon of fulvic and humic acids (C_{FA} and C_{HA}, respectively)

Characteristic	Unit	Mean	*SD*	Minimum	Maximum
pH_{H_2O}		5.6	1.1	3.2	7.9
pH_{KCl}		5.1	1.1	2.7	7.7
C_{org}	mg/kg	22.3	7.6	10.4	40.0
C_{FA}	mg/kg	3.28	0.55	2.32	4.19
C_{HA}	mg/kg	1.21	0.44	0.59	2.69
Clay (< 0.001 mm)	%	6.0	2.6	2.7	10.9

Table 2. Mean values and standard deviations of the contents of separate fractions of heavy metals in soil (mg/kg)

Metal form	Parameter	Cd	Pb	Zn
Exchangeable	mean	6.71	19.4	300.1
	SD	6.24	44.7	296.3
Organically bound	mean	0.727	47.4	70.7
	SD	0.561	56.9	60.3
NaOH/$Na_4P_2O_7$ extract	mean	5.30	49.2	311.3
	SD	1.94	41.0	254.6
Fulvic acids	mean	0.656	40.9	66.1
	SD	0.510	48.7	57.1
Humic acids	mean	0.110	6.5	4.58
	SD	0.192	11.2	12.84
2M HNO_3 extract	mean	23.32	2271.9	2193.1
	SD	18.55	1380.5	1746.0
Aqua regia (15 samples)	mean	26.86	2440.3	3142.9
	SD	17.88	1545.2	2089.3

carbon. The share of HA was lower than the share of FA (mean ratio C_{HA}/C_{FA} was 0.34). Heavy metal contents showed relatively high variability (Table 2). No statistical difference was found between metal concentrations extracted by 2M HNO_3 and concentrations determined after aqua regia digestion in case of Cd and Pb. The results of these two procedures were comparable. The exchangeable form was more abundant than the organic one in the case of Cd and Zn. Lead was more abundant in the organic fraction. This confirms generally higher affinity of Pb to organic matter (Adriano 2001). Most organic forms of the metals represented the metals bound on FA. The highest share of HA fraction was found for Pb, though even here the FA fraction prevailed (Table 3). The distribution of the metals between FA and HA fractions generally corresponds to the results of Donisa et al. (2003). Molar ratio between metal and carbon in both fractions decreased in the order Zn > Pb > Cd; for all the three metals, molar ratio in the FA fraction was higher than the molar ratio in HA fraction. That means that the prevalence of FA fraction of metals over HA fraction is higher than it would correspond to the carbon ratio between the two humic fractions. Higher number of reactive groups on FA probably took effect.

The results of the extraction of humic substances require a short commentary. The amount of metals extracted by the solution of sodium hydroxide/pyrophosphate was higher than organic forms of metals determined by the sequential extraction (Table 2). As it was mentioned above, this extractant can release also exchangeable cations and possibly dissolve some of the Fe oxide fraction (Donisa et al. 2003). However, in our study, the extracted amount was lower than the sum of exchangeable and organically bound metals determined by the sequential extraction. The difference was relatively low and could be attributed to analytical error. Nevertheless, the difference was negatively correlated with soil pH ($r < -0.6$ for all the three metals)

Table 3. Mean share of metals bound on fulvic (FA) and humic acids (HA) on the total organically bound metal content (%), and mean molar ratio metal/carbon in the fractions (mmol/mol)

	Cd		Pb		Zn	
	FA	HA	FA	HA	FA	HA
Share (%)	98.4	1.6	82.0	18.0	95.7	4.3
Ratio (mmol/mol)	0.021	0.013	0.75	0.27	3.94	0.79

Table 4. Correlation between the content of heavy metals bound on FA and HA and the pseudototal metal content (determined after aqua regia digestion), total organic carbon (C_{org}), carbon of the corresponding humus fractions, and soil pH

	Cd		Pb		Zn	
	FA	HA	FA	HA	FA	HA
Aqua regia	0.873***	0.075	0.855***	0.024	0.928***	0.147
C_{org}	–0.049	0.120	–0.090	0.358	0.012	0.046
C_{FA} or C_{HA}	0.240	–0.172	0.216	0.550*	0.104	–0.115
pH_{H_2O}	0.118	0.005	–0.446	–0.720***	0.332	0.103
pH_{KCl}	0.173	–0.015	–0.360	–0.628**	0.367	0.144

*, **, *** significant at the probability level 0.05, 0.01, and 0.001, respectively

and in case of Cd and Pb it positively correlated with clay content (*r* = 0.59 and 0.79, respectively). Moreover, the difference between Pb extracted by the hydroxide/pyrophosphate solution and Pb_{org} was positively correlated with C_{org}. We can therefore hypothesize that the hydroxide/pyrophosphate extraction releases only the part of exchangeable metals bound on organic matter, while the exchangeable metals bound on mineral particles remain unaffected. However, further research is necessary to prove or reject this hypothesis.

The correlation analysis showed some specific features of metal binding on HA and FA (Table 4). The content of all the three metals in the FA fraction closely correlated with their pseudototal content determined after aqua regia digestion. Similar relationship was obtained also with metal content extracted by 2M HNO_3 (data not shown). No correlation of FA fraction of metals with basic soil properties and C_{FA} content was found. This indicates that the FA fraction of metals is controlled by the total metal content in soil, i.e. by the level of pollution. This seemingly unlimited capacity of FA for metal binding can be explained by the above-mentioned higher number of reactive groups. However, it also suggests that metal sorption on FA is not limited

Table 5. Factor analysis: factor weights of variables after varimax rotation of axes and estimated communalities

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Cd_{HNO_3}	0.946	0.149	–0.052	0.017	0.062	0.924
Cd_{FA}	0.904	–0.068	0.079	–0.110	0.260	0.907
Cd_{HA}	0.040	0.014	0.077	0.991	–0.007	0.989
Pb_{HNO_3}	0.895	–0.141	–0.164	0.027	–0.254	0.912
Pb_{FA}	0.322	–0.716	–0.030	0.079	–0.287	0.705
Pb_{HA}	–0.025	–0.828	0.369	–0.175	–0.153	0.876
Zn_{HNO_3}	0.943	0.265	0.080	0.065	0.067	0.975
Zn_{FA}	0.929	0.166	0.000	0.119	0.057	0.909
Zn_{HA}	0.141	0.079	–0.014	–0.003	0.930	0.891
C_{org}	–0.046	0.037	0.923	0.059	0.046	0.861
C_{FA}	0.172	–0.018	0.901	0.238	–0.077	0.904
C_{HA}	–0.174	–0.296	0.871	–0.238	0.024	0.934
pH_{H_2O}	0.230	0.935	–0.021	–0.002	–0.083	0.935
pH_{KCl}	0.293	0.886	0.014	–0.024	–0.068	0.877
Eigenvalue	4.592	3.097	2.609	1.168	1.134	
% of variation	32.80	22.12	18.64	8.34	8.10	

by specific sorption sites. On the contrary, metals in the HA fraction did not show any correlation with pseudototal content. This may indicate that there is a limited number of specific sorption sites. Nevertheless, Cd_{HA} and Zn_{HA} were in most cases very low, which may have increased relative error and makes an interpretation difficult. Lead in the HA fraction was positively correlated with C_{HA} and negatively correlated with soil pH values. This finding supports the statement by Brümmer et al. (1986) that metal binding on HA may decrease their concentration in soil solution. Also Adriano (2001) mentioned forming stable compounds of Pb with soil organic substances at low pH.

Factor analysis summarized the findings discussed previously (Table 5). Five factors were selected accounting for almost 90% of the total variability. The first factor, accounting for 32.8% of the total variability, reflected the level of soil pollution. It had significant weights for metal contents in 2M HNO_3 extract. High weights of this factor for Cd and Zn bound on FA show that this fraction is controlled by the level of pollution, weight for Pb_{FA} was lower, (0.322) which may indicate a slightly different mechanism of Pb binding on FA or a contribution of specific sorption sites for Pb even on FA. The second factor (22.1% of variation) shows the effect of soil pH. Low pH increases Pb sorption on both fractions of humic substances. The third factor (18.6%) is the factor of organic carbon content. From the metal contents, however, only Pb_{HA} showed relatively higher weight (0.369) at this factor. The fourth and fifth factors, each accounting only for about 8% of the total variability, are factors of Cd_{HA} and Zn_{HA}, respectively, showing no apparent effect of determined soil properties. The last three factors therefore suggest specific sorption of the three metals on HA; the specific sorption sites for each metal, however, seem different. Interrelationships among the variables are well apparent from the projection of factor weights (Figure 1).

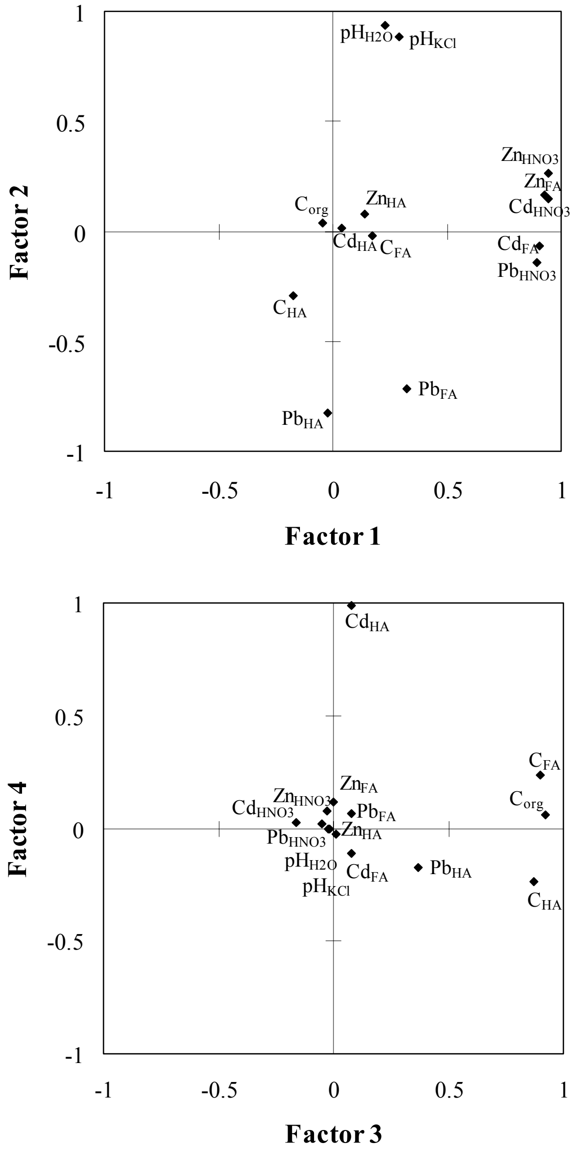

Figure 1. Factor analysis: projection of weights of the first four factors after varimax rotation of axes

We can conclude that all the three metals under the study were bound more on FA than on HA. Only Pb showed relatively higher affinity to HA compared to Cd and Zn. The amount of metals bound on FA was controlled mainly by the level of pollution. On humic acids, a limited number of specific sorption sites for each metal is suggested. The results could indicate relatively high potential mobility of the organic fraction of heavy metals in the polluted soil. Nevertheless, it must be taken into account that the two groups of humic substances are only operationally defined and they represent very heterogeneous mixtures of organic molecules. Further research is necessary in this field.

Acknowledgement

The authors are grateful to former visiting students Vicenta Máñez Martínez and Nuria Roca Pascual from Spain for their great help with laboratory work.

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Received on February 13, 2004

ABSTRAKT

Rozložení těžkých kovů mezi frakcemi huminových látek v kontaminované půdě

Půdní organická hmota je důležitým faktorem chování těžkých kovů v půdě. Tato studie měla za cíl stanovit rozložení organicky vázaného Cd, Pb a Zn mezi huminové kyseliny a fulvokyseliny ve 20 vzorcích silně kontaminované fluvizemě. Byl použit tradiční postup alkalické extrakce huminových látek směsí hydroxidu sodného a difosforečnanu tetrasodného s následným vysrážením huminových kyselin okyselením. Všechny tři kovy byly vázány převážně ve frakci fulvokyselin (průměrný podíl z celkového obsahu organicky vázaného kovu byl 98,4 % v případě Cd, 82,0 % v případě Pb a 95,7 % v případě Zn). Množství kovů vázaných na fulvokyseliny bylo ovlivněno především úrovní kontaminace. Na huminových kyselinách se předpokládá omezené množství specifických sorpčních míst pro jednotlivé kovy. Olovo vázané na huminové kyseliny bylo v negativní korelaci s pH půdy. Výsledky naznačují relativně vysokou potenciální mobilitu organicky vázaných těžkých kovů ve sledovaných půdách. Stručně je diskutována selektivita alkalického extrakčního činidla.

Klíčová slova: těžké kovy; huminové kyseliny; fulvokyseliny; kontaminace půdy; speciace

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