

# The influence of humic acid quality on the sorption and mobility of heavy metals

G. Barančíková<sup>1</sup>, J. Makovníková<sup>2</sup>

<sup>1</sup>*Soil Science and Conservation Research Institute, Prešov, Slovakia*

<sup>2</sup>*Soil Science and Conservation Research Institute, Banská Bystrica, Slovakia*

## ABSTRACT

Mobile and potentially mobile forms of heavy metals are probably one of the most important toxic hazards in the environment. Besides pH, which is a factor influencing the mobility/availability of heavy metals to the greatest extent, the content and mainly the quality of soil organic matter play a very important role in the evaluation of heavy metal behaviour in the environment. The fraction of metals bound to organic compounds is exclusively associated with humic substances and particularly with humic acids (HA). A relationship between the parameters reflecting the actual structure of humic acids and mobile or potentially mobile fractions of heavy metals was studied in 12 soil localities representing different soil types. It can be stated on the basis of the acquired data that heavy metals tend to form complexes with soil organic matter that are different for each metal. The results suggest that copper is bound mainly in an unavailable form (significant correlations of fraction IV with HA parameters) and cadmium prefers exchangeable forms (significant correlations of fraction I with HA parameters) and is more available. It can be assumed on the basis Spearman's correlations that mobile fractions of cadmium are predominantly bound to the aliphatic part of humic substances, and copper prefers strong bonds to humic acids with a high degree of humification.

**Keywords:** humic acid parameters; cadmium; copper; sequential analysis

The understanding of heavy metal (HM) behaviour in a soil system is one of the most important tasks in environmental sciences. The sorption of heavy metals by soil constituents is determined by selective sequential extraction of heavy metals from soil samples. A lot of authors (Mestek and Volka 1993, Borůvka et al. 1997, Schalscha et al. 1999, etc.) dealt with evaluation of the influence of selected soil parameters on the mobile and potentially available content of heavy metals. It is well known that the variation in soil properties such as pH, organic matter content and its quality, texture, quantity and quality of sorption sites may significantly influence the distribution as well as availability to plants. The main factors affecting the mobility of heavy metals in soil are: pH, content and quality of soil organic matter, content and quality of clay fraction, iron and manganese oxides. In our previous paper (Makovníková 2000) we tried to estimate relations between selected soil properties and available fractions of heavy metals. Besides soil pH, which is a key parameter, the content and mainly the quality of soil organic matter can influence the availability of heavy metals in soil. Humic substances represent a significant proportion of total organic carbon in the global carbon cycle. The predominant fraction of humic substances is humic acids (HA) that are very active in interacting with inorganic contaminants (Senesi 1993). Excellent sorption properties of humic acids that depend on their chemical structure were reported by many authors (Mestek and Volka 1993, Zhang et al. 1997, Barančíková et al. 1997a, Santos et al. 2002, etc.). In our previous paper (Makovní-

ková 2000) a significant relationship between mobile/potential available heavy metal fractions and one of the coarse qualitative parameters of HA –  $Q_6^4$  (the ratio of optical densities measured in humic acid solution at 465 and 665 nm) was found. In the present paper we decided to study relationships not only between basic quantitative ( $C_{org}$ ) and qualitative ( $Q_6^4$ ,  $C_{HA}/C_{FA}$ ) parameters of soil organic matter but also between some parameters reflecting the real humic acid structure and mobile/potentially mobile heavy metal fractions.

## MATERIAL AND METHODS

Bonds of heavy metals in soil were evaluated and HA were isolated in 12 localities representing the most important agricultural soil types. Soil samples were collected from the topsoil (depth 0–0.1 m). The soils were classified according to the World Reference Base (1998). Soil types and basic characteristics of soil localities are shown in Tables 1 and 2. Soil basic properties represent a wide range of soil parameters. By selective sequential extraction procedure (Zeien and Brümmer 1989) seven fractions of heavy metals were determined: fraction I – mobile, fraction II – exchangeable, fraction III – occluded in manganese oxides, fraction IV – associated with organic matter – release of metals in this group assumes that the binding mechanisms for metals in association with organic matter include complexation, adsorption and chelation, fraction V – occluded in iron oxides, frac-

Table 1. Soil types of studied localities

Locality	Soil types
Macov	Carbonate Chernitsa on carbonate neogenic sediments
Voderady	Carbonate Chernozem on loess
Topoľníky	Typical Fluvisol on carbonate meadow sediments
Nacina Ves	Gleyic Fluvisol on non-carbonate meadow sediments
Liesek	Luvisol Pseudogley on loess loams
Stakčín	Typical Pseudogley on loess loams
Donovaly	Typical Pseudogley on loess loams
Sihla	Dystric acid Cambisol on granulites
Raková	Arenic Cambisol on flysch
Malanta	Gleyic Luvisol on loess loams
Moravský Ján	Arenic Regosol on non-carbonated wind-blown sands
Sitno	Typical Andosol on andesites

tion VI – bound with well crystallized Fe oxides, fraction VII – structurally bound elements in silicate or residual forms. Cd content was analysed by electrochemical AAS-Varian Spectra A 300/400 Zeeman, Cu content by flame AAS-Varian Spectra A 300/400 in flame  $C_2H_2$  – air. Organic carbon content ( $C_{org}$ ) was determined by wet combustion (Nikitin 1972). Humus fractionation was determined by Kononovova and Beľčikova method (1961) in which the amount of humic acid carbon –  $C_{HA}$  and fulvic acid carbon –  $C_{FA}$  and the ratio of optical densities measured in humic acid solution at 465 nm and 665 nm ( $Q_6^4$ ) were determined. Humic acids (HA) were isolated according to the IHSS method (Swift 1996). Elemental analysis of HA was determined by using C, H, N Perkin-Elmer CHN 2400 analyser. Oxygen was calculated from the difference. The carboxyl groups of HA were determined according to Schnitzer and Gupta (1965). Optical density values of

1% solutions of HA at 600 nm ( $E_{600}^{1\%}$ ) were obtained using a Specol 11 spectrometry.  $^{13}C$  Nuclear Magnetic Resonance (NMR) spectra of HA were obtained using a Varian VXR-300 NMR spectrometer at an observation frequency of 75.4 MHz for  $^{13}C$ . Subdivision of the spectrum was made by the commonly used scheme of Malcolm (1990). Aromatic carbon ( $C_{ar}$  %) is represented in the  $\delta$  106–157 ppm spectral region. Aliphatic carbon ( $C_{aliph}$  %) is represented in the  $\delta$  15–106 ppm spectral region. The degree of aromaticity of HA ( $\alpha$ ) was calculated by the procedure of Hatcher et al. (1981). Statistical results were evaluated in STATGRAPHIC 5.0. Spearman's correlation coefficients, which are less sensitive to deviations of groups from normality (nonparametric correlation coefficients), were applied to evaluate Cd/Cu bioavailability.

## RESULTS AND DISCUSSION

### Heavy metal fractions in soil samples

Total content of heavy metals in the studied soil localities represents a wide range of single metals Cd (0.14–0.58 mg/kg) and Cu (6.74–27.68 mg/kg). The total content of 5 localities exceeded the background value in Slovak soils (0.29 mg/kg) in the case of Cd and 1 locality in the case of Cu (23 mg/kg). The percentages of total concentrations in various fractions depend, among others, on soil type, soil reaction, content of soil organic matter, complexation by organic ligands and competition with other cations. As you can see from Figure 1, cadmium is predominantly situated in first three fractions that represent mobile or potentially available fractions. As it can be seen in Figure 2, cadmium is the most mobile in acidic soils (Sihla locality – 63.4% in fraction I), whereas in alkaline soils cadmium is rather immobile (Voderady locality – 1.62% in fraction I). The highest percentage of total Cu content was found mainly in fraction IV (HM associated with organic matter, Figures 1 and 3). As it can be

Table 2. Basic characteristics of soil localities

Locality	pH/KCl	$C_{org}$ (%)	$Q_6^4$	$C_{HA}/C_{FA}$	$N_t$ (mg/kg)	Clay (%)	Cd total (mg/kg)	Cu total (mg/kg)
Macov	7.48	1.68	3.84	1.00	1875	49.54	0.35	17.17
Voderady	7.55	1.28	4.20	0.99	1733	39.91	0.26	17.09
Topoľníky	7.35	1.02	4.10	0.49	1610	39.43	0.19	17.57
Nacina Ves	5.04	1.63	4.70	0.74	2310	65.95	0.32	27.68
Liesek	4.57	1.14	5.30	0.57	1278	39.00	0.28	9.74
Stakčín	6.32	1.13	5.80	0.56	1435	42.11	0.38	20.12
Donovaly	6.80	5.63	6.23	0.38	6230	34.86	0.46	23.00
Sihla	4.20	3.58	6.39	0.46	2350	28.09	0.15	7.25
Raková	4.34	1.40	5.62	0.28	1820	39.18	0.58	18.80
Malanta	5.15	1.28	4.10	1.17	1413	39.69	0.22	18.52
Moravský Ján	3.53	0.82	4.20	0.71	615	6.14	0.14	6.74
Sitno	4.51	7.27	4.45	0.68	7825	22.78	0.30	22.37

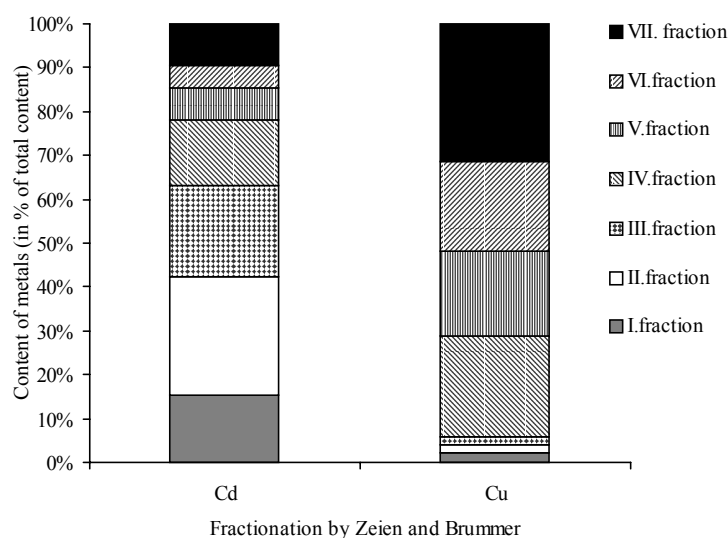


Figure 1. Distribution of Cd and Cu in the whole set of soils (% of total content)

seen from Figure 3, the highest amount of Cu associated with organic matter was found on very strong humic Andosol (Sitno locality).

From the aspect of heavy metal availability, the most important is mobile fraction (fraction I) and fractions representing potentially available amounts of heavy metals: exchangeable (fraction II), occluded in manganese oxides (fraction III) and organically bound (fraction IV). These fractions are the most interesting from the aspect of heavy metal behaviour in soil and represent potential toxic haz-

ards. Mobile and potentially available amounts of heavy metals in our samples decrease in the order: Cd (77.67%) > Cu (28.68%).

#### Characteristic of soil organic matter in soil samples

The content and quality of soil organic matter in the studied localities are very different. On the basis of  $C_{HA}/C_{FA}$  and  $Q_6$  values (Table 2), Chernitsa, Chernozem and Luvi-

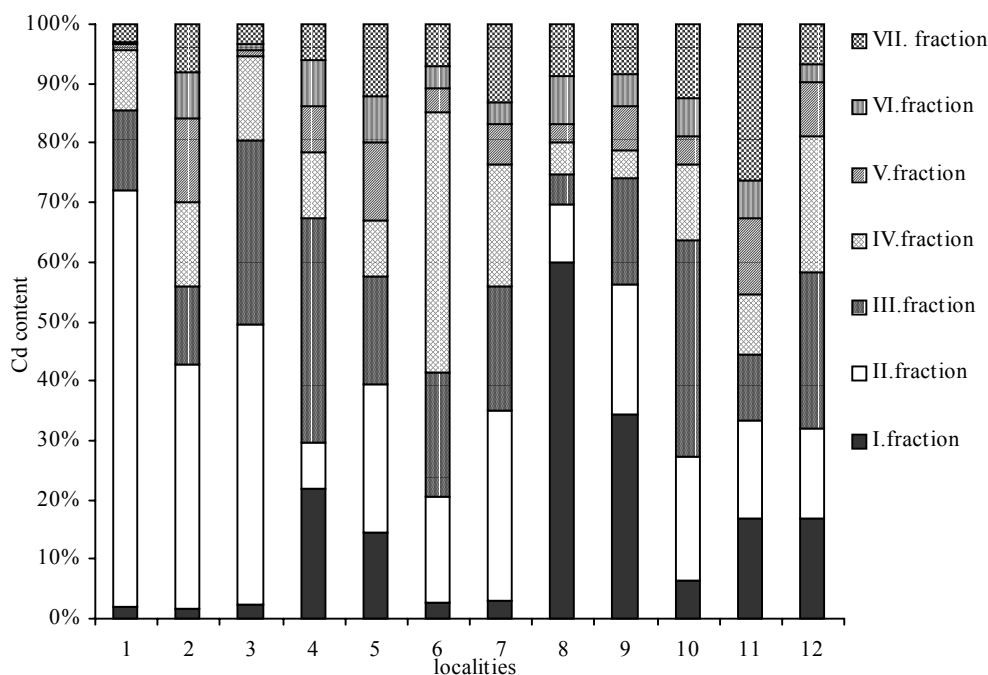


Figure 2. Distribution of Cd in individual localities (1 – Macov, 2 – Voderady, 3 – Topoľníky, 4 – Nacina Ves, 5 – Liesek, 6 – Stakčín, 7 – Donovaly, 8 – Sihla, 9 – Raková, 10 – Malanta, 11 – Moravský Ján, 12 – Sitno)

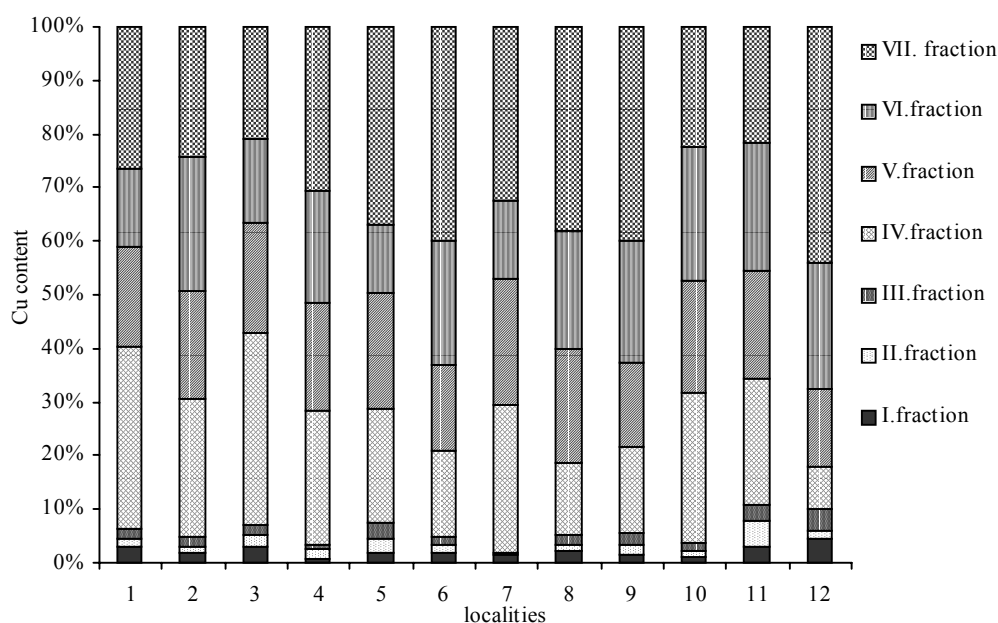


Figure 3. Distribution of Cu in individual localities (1 – Macov, 2 – Voderady, 3 – Topoľníky, 4 – Nacina Ves, 5 – Liesek, 6 – Stakčín, 7 – Donovaly, 8 – Sihla, 9 – Raková, 10 – Malanta, 11 – Moravský Ján, 12 – Sitno)

sol represent more stable and mature soil humus contrary to Pseudogley and Cambisols. Different quality of soil organic matter is also confirmed by the values of basic parameters of chemical composition of humic acids (Tables 3 and 4).

The basic chemical parameter for humic acid is elemental analysis. As you can see from Table 4, the highest content of C and the lowest content of H and also the lowest H/C ratio characteristic of the aromatic structure in HA from Chernozem, Chernitsa and Andosol were found and are typical of these soil types (Barančíková et al. 1997b, Barančíková 2002). Metal binding also increased with higher proportions of nonprotonated aro-

matic carbon (Preston 1996). Lower C and higher H content and the higher H/C ratio in Gleysols and Cambisols were determined (Table 3).

A spectral method in the visible spectral region is a great contribution to the knowledge of chemical structure of HA. UV-VIS spectroscopy provides evidence of carboxylic complexing sites in HA involved in charge transfer complexes with metal ions. Optical parameter  $E^{1\%}_6$  should express the humification degree of HA (Kumada 1981). The  $E^{1\%}_6$  data in Table 3 indicate that the humification degree decreases significantly in this order: Chernozem > Andosol > Chernitsa > Regosol > Fluvisol > Luvisol > Gleysol > Cambisol.

Table 3. Content and quality of soil organic matter and elemental composition, optical parameter and carboxyl groups of humic acids

Locality	C <sub>org</sub> (%)	C <sub>HA</sub> /C <sub>FA</sub>	$Q^4_6$	C <sub>atom.</sub> (%)	H <sub>atom.</sub> (%)	O <sub>atom.</sub> (%)	O/H	H/C	$E^{1\%}_6$	COOH*
Macov	1.68	1.00	3.84	43.70	34.50	18.00	0.523	0.789	25.00	4.10
Voderady	1.28	0.99	4.20	47.60	31.63	17.92	0.567	0.665	32.44	4.30
Topoľníky	1.02	0.49	4.10	41.82	37.93	16.51	0.435	0.910	21.80	3.87
Nacina Ves	1.63	0.74	4.70	39.11	41.19	16.77	0.407	1.053	8.96	2.56
Liesek	1.14	0.57	5.30	41.58	40.09	15.59	0.389	0.964	13.66	2.78
Stakčín	1.13	0.56	5.80	39.67	42.30	15.24	0.360	1.066	7.00	2.41
Donovaly	5.63	0.38	6.23	39.40	40.34	16.55	0.410	1.020	14.00	3.11
Sihla	3.58	0.46	6.39	39.70	41.01	16.00	0.390	1.030	11.00	2.71
Raková	1.40	0.28	5.62	38.80	41.49	16.10	0.388	1.070	9.00	2.45
Malanta	1.28	1.17	4.10	43.41	36.16	17.18	0.475	0.833	13.76	2.38
Moravský Ján	0.82	0.71	4.20	42.60	37.25	16.69	0.448	0.874	22.00	3.62
Sitno	7.27	0.68	4.45	43.40	34.39	19.12	0.556	0.793	27.50	4.28

\*meq/1 g HA

Table 4. Relative intensities (% of total area) for the selected  $^{13}\text{C}$  NMR signals of humic acids

HA	%		Total area		$\text{C}_{\text{aliph}}$ (%)	$\text{C}_{\text{ar}}$ (%)	$\alpha$ (%)
ppp range	15–43	43–87	106–143	157–184	15–106	106–157	
Macov	19.24	17.04	32.61	17.92	41.23	38.05	48.00
Voderady	14.18	13.52	43.43	16.97	30.04	41.75	62.85
Topoľníky	24.80	18.03	30.18	16.16	46.52	34.10	42.92
Nacina Ves	20.04	24.02	29.79	13.72	49.08	33.09	42.55
Liesek	23.93	21.85	28.46	13.99	50.50	34.05	40.48
Stakčín	21.25	24.32	28.85	13.84	50.68	33.48	41.12
Donovaly	23.68	25.55	22.74	17.48	53.57	27.08	33.57
Sihla	24.51	22.92	25.07	16.75	52.54	29.98	36.33
Raková	25.35	23.91	24.07	13.38	53.83	30.70	36.19
Malanta	14.49	21.74	34.15	14.84	41.09	33.28	50.09
Moravský Ján	21.08	19.13	32.07	16.25	41.77	38.60	48.03
Sitno	10.62	18.22	34.22	19.80	34.54	41.25	52.07

The major ligand sites for a metal ion in HA are oxygen-containing functional groups. Carboxyl groups are believed to play a prominent role in the bonds of metal ions by soil HA (Senesi 1993, Barančíková et al. 1997a, Coccozza and Miano 2002). The content of COOH groups is suggested to represent a valuable index of humification, thus implying that HA from Chernozem has the highest degree of humification confirmed also by the elemental composition and value of optical parameter (Table 3).

$^{13}\text{C}$  NMR represents one of the most important spectroscopic methods of HA chemical structure identification.  $^{13}\text{C}$  NMR contributed to authentic knowledge of HA structure by quantitative analysis of individual carbon types and it can provide evidence for metal – HA bonds. As you can see from Table 4, HA from different soil types are different mainly in aliphatic and aromatic carbon and then in the degree of aromaticity ( $\alpha$ ). In agreement with elemental analysis, content of carboxyl groups and optical parameter, the highest aromaticity in Chernozem and Andosol HA was found contrary to Gleyosol and Cambisol HA (Table 4).

### Interactions between heavy metals and humic acids

Heavy metals tend to form complexes with organic matter (humic and fulvic acids) in the soil that are different for each metal (Stevenson 1982). Significant positive correlations between organic matter and all forms of Cu/Zn suggest that these metals have strong affinity to organic matter (Zhang et al. 1997). Organic matter plays an important role not only in forming complexes but also in retaining heavy metals in an exchangeable form. These two properties affect each heavy metal differently. For example, Cu is bound and rendered unavailable, chiefly through the formation of complexes, while Cd is retained in an exchangeable form and is more readily available (Zalidis et al. 1999). In our previous paper (Makovníková

2000) besides pH, significant Spearman's correlations were found between mobile/potentially available heavy metal fractions and coarse qualitative parameter reflecting the HA structure –  $Q^4_6$ . Because the parameters of elemental analysis, content of carboxyl groups and mainly  $^{13}\text{C}$  NMR parameters actually reflect the HA composition, we try to find relations not only between basic quantitative and qualitative parameters of soil organic matter but also between parameters of HA and mobile/potentially available heavy metal fractions. In this paper Spearman's correlation coefficient of Cd/Cu and parameters of HA structure are presented.

As you can see from Table 5, significant correlations between the mobile (fraction I) fraction of cadmium and HA parameters confirmed the bond of this fraction to the aliphatic part of organic matter (negative correlation of carbon and positive correlation of hydrogen, and mainly positive correlation of unsubstituted aliphatic carbon and carbon singly bound to O and N heteroatoms and negative correlation of aromatic carbon and then positive correlation of  $\text{C}_{\text{aliph}}$  and negative correlations of  $\text{C}_{\text{ar}}$  and  $\alpha$ ). This finding is in agreement with Preston (1996), who reported that the peak at 51 to 54 ppm assigned to CH carbons was correlated positively with conditional formation constants for Cd. It can be assumed that cadmium could be bound predominantly to aliphatic structures which are predominant in water-soluble humic substances.

As you can see from literature data (Zhang et al. 1997, Schalscha et al. 1999, Santos et al. 2002), copper is bound predominantly to organic matter. Our data suggest that fraction IV copper is bound predominantly to organic matter with a high degree of humification. This declaration should be confirmed by negative correlation of H/C ratio and aliphatic carbon and positive correlation of carbon content and degree of aromaticity. According to Preston (1996), metal binding increased with higher proportions of nonprotonated aromatic carbons. As you can see from Table 5, Cu should participate in complex-

Table 5. Spearman's coefficients of Cd and Cu fractions (% of total contents) and selected soil properties and HA parameters

Soil/HA parameters	Cd				Cu			
	I	II	III	IV	I	II	III	IV
pH/CaCl <sub>2</sub>	<b>-0.9</b>	<b>0.775</b>	<b>0.727</b>	<b>0.560</b>	0.461	0.138	-0.133	<b>0.71</b>
Corg	0.196	0.223	-0.100	-0.19	-0.375	<b>-0.749</b>	-0.48	<b>0.587</b>
Q <sub>6</sub> <sup>4</sup>	<b>0.539</b>	-0.476	-0.151	-0.05	-0.314	0.336	-0.144	<b>-0.817</b>
C <sub>HA</sub> /C <sub>FA</sub>	-0.418	0.0592	0.1	0.155	-0.055	0.000	-0.141	<b>0.546</b>
C	<b>-0.636</b>	0.451	-0.336	0.155	0.489	0.028	0.191	<b>0.600</b>
H	<b>0.582</b>	<b>-0.538</b>	0.282	-0.08	-0.356	0.009	-0.160	<b>-0.700</b>
H/C	<b>0.636</b>	<b>-0.515</b>	0.264	-0.173	-0.37	0.028	-0.105	<b>-0.718</b>
O/H	<b>-0.564</b>	0.451	-0.155	0.200	0.279	-0.165	0.068	<b>0.773</b>
E <sub>6</sub> <sup>1%</sup>	0.082	-0.164	-0.264	0.12	-0.233	-0.193	0.073	-0.120
COOH	-0.464	0.488	<b>-0.555</b>	0.06	<b>0.630</b>	0.220	0.296	0.390
Unsubstituted C <sub>aliph</sub> (15–43 ppm)	0.482	-0.32	-0.064	-0.39	0.178	0.275	0.406	-0.460
C <sub>aliph</sub> bond to O, N (43–87 ppm)	0.500	-0.5103	0.364	0.12	<b>-0.621</b>	-0.285	-0.447	<b>-0.560</b>
C <sub>ar</sub> C-C, C-H bond (106–143 ppm)	<b>-0.564</b>	0.228	0.182	0.230	0.270	0.110	0.018	<b>0.630</b>
COOH (157–184 ppm)	-0.436	0.419	-0.455	0.17	0.384	-0.440	-0.182	0.490
C <sub>aliph</sub> (15–106 ppm)	<b>0.582</b>	-0.264	0.000	-0.246	-0.242	-0.083	-0.009	<b>-0.691</b>
C <sub>ar</sub> (106–157 ppm)	<b>-0.609</b>	0.383	-0.264	0.146	<b>0.580</b>	<b>0.532</b>	0.383	0.455
α	-0.509	0.155	0.009	0.246	0.270	0.156	0.064	<b>0.591</b>

Spearman's coefficient in bold – statistically significant

ation with carboxyl groups (correlation with carboxyl carbon). The evidence of the prominent role played by COOH groups was also reported by Senesi (1993), Mestek and Volka (1993) and Coccozza and Miano (2002). Predominant bonds of Cu to HA can be confirmed by positive correlations with the basic qualitative parameter of soil organic matter – C<sub>HA</sub>/C<sub>FA</sub> (Table 3). Strong bonds of Cu to HA were also reported by Pospíšilová et al. (2001).

The behaviour of heavy metals in soil principally depends on soil properties. Besides pH, the quality of organic matter plays a very important role in mobility, availability and complexity of heavy metals. One of the most important fractions of soil organic matter is humic acids that also participate in interactions with heavy metals.

It can be confirmed on the basis of our results that heavy metals tend to form complexes with organic matter in soil that are different for each metal. Our results suggest that copper is bound mainly in the unavailable form (significant correlations of fraction IV with HA parameters) and cadmium prefers the exchangeable form (significant correlation of fraction I with HA parameters) and is more available. It can also be concluded on the basis of the acquired data that the mobile fraction of cadmium is predominantly bound to the aliphatic part of organic matter, and copper prefers strong bonds to humic acids with a high degree of humification.

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## ABSTRAKT

### Vliv kvality huminových kyselin na sorpci a mobilitu těžkých kovů v půdě

Mobilní a potenciálně mobilní formy těžkých kovů představují jedno z nejdůležitějších toxických rizik v životním prostředí. Při hodnocení vlivu těžkých kovů na životní prostředí hrají kromě půdní reakce, která nejvíc ovlivňuje mobilitu a přístupnost těžkých kovů, důležitou úlohu také obsah a hlavně kvalita půdní organické hmoty. Frakce kovů vázané na organickou hmotu jsou asociovány s humusovými látkami a hlavně s huminovými kyselinami (HK). Na 12 půdních lokalitách, které představují rozdílné půdní typy, byl sledován vzájemný vztah mezi parametry odrážejícími skutečnou strukturu huminových kyselin a mobilními, resp. potenciálně mobilními frakcemi těžkých kovů. Na základě získaných údajů můžeme konstatovat, že těžké kovy mají tendenci vytvářet rozdílné komplexy s organickou hmotou v půdě. Výsledky poukazují na fakt, že měď je vázána hlavně v nedostupných formách (signifikantní korelace IV. frakce s parametry HK) a kadmium preferuje vyměnitelné formy (signifikantní korelace I. frakce s parametry HK) a je dostupnější. Na základě Spearmanových korelací můžeme také předpokládat, že mobilní frakce kadmia jsou vázány především na alifatickou část humusových látek, zatímco měď preferuje vazby na huminové kyseliny s vysokým stupněm humifikace.

**Klíčová slova:** parametry huminových kyselin; kadmium; měď; sekvenční analýza

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*Corresponding author:*

RNDr. Gabriela Barančíková, CSc., Výskumný ústav pôdoznalectva a ochrany pôdy, Reimanova 1, 080 01 Prešov, Slovensko  
tel.: + 421 517 731 054, fax: + 421 517 723 184, e-mail: bar@vupop.sk

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