

SORPTION OF COPPER AND LEAD ON SOILS AND SOIL CLAY FRACTIONS WITH DIFFERENT CLAY MINERALOGY

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Abstract: There are numerous results on the characteristics of metal sorption by total soil samples or soil clay fractions separately. However, not many have focused on the comparison of these characteristics of total soil and clay fraction samples from the same soil. In this study Cu and Pb batch sorption experiments were carried out on samples from the genetic horizons of two Luvisol profiles characterized by vermiculite and montmorillonite as dominant clay minerals, respectively. Freundlich K_F and n parameters for Cu and Pb sorption on the total soil samples unanimously show the primary role of the soil organic matter, as well as the preference of vermiculite over montmorillonite in the retention of both metals. These results were effectively completed by those from the experiments performed on soil clay fractions. It was shown that the generally higher affinity of Pb than Cu to the studied soils is primarily due its very strong affinity to the soil organic components. Additionally, in the studied acidic-slightly acidic Luvisol samples sorption of Pb on clay surfaces seems to be much more inhibited when compared to Cu. Consequently, combined study of sorption properties of total soil samples and soil clay fractions helps us in better understanding the sorption process of potentially toxic metals in soils.

Key words: potentially toxic metals, vermiculite, montmorillonite, Freundlich curve, Luvisol

1. INTRODUCTION

Potentially toxic metals are natural components of soils. In the last few decades, however, their concentration and mobility significantly increased primarily in industrial and urban areas due to anthropogenic activities, such as mining (Andráš et al., 2008), smelting (Damian et al., 2008a), traffic (Secu et al., 2008) etc. Increase in metal mobility results in the elevated entering of these elements to the food chain (Lăcătușu & Lăcătușu, 2008) and consequently they pose a serious health risk to human (Gazdag & Sipter, 2008).

As sorption is a major process for accumulation of potentially toxic metals in soils, its study is of utmost importance for the understanding of how metals are transferred from a liquid mobile phase to the surface of a solid phase (Bradl, 2004). Sorption of potentially toxic metals by soil depends on factors such as the nature of mineral and organic constituents, the nature of the metal, the composition of the soil solution as well as the pH and Eh (McLaughlin et al., 2000). While these latter two factors may

show significant daily variation (Szalai, 2008) the mineral components can be regarded as relatively stable characteristics of soils (Turpault et al., 2008).

Metals in soils are not homogeneously distributed over the various particle size fractions, suggesting that particle size exercises a determining influence on the partitioning of chemical elements. The distribution characteristics of potentially toxic metals with soil particle size are primarily the function of mineral composition and amount of sorption sites in each size fraction. The increasing metal concentrations with decreasing particle size were found both in contaminated and uncontaminated soils (Song et al., 1999; Acosta et al., 2009), and it indicated that the behavior of metals was governed by the sorption processes in this size range (Qian et al., 1996). The accumulation of metals in the clay fraction can be attributed to the enrichment of soil components with high surface area, such as clay minerals, organic matter and Fe-Mn-oxides (Förstner, 1980; Tiller, 1985; etc.).

Batch equilibrium techniques are widely used to study the retention of metals in soils and the sorp-

tion data are described by using curves. The analysis of curves may provide information about the retention capacity and the sorption strength by which the sorbate is held onto the soil (Green-Pedersen et al., 1997). Determination of sorption capacity of soils should play a very important role in all discussions related to soil contaminant loadings, buffering capacities and critical loads for potentially toxic metals (Fontes & Gomes, 2003).

1973) and are among the most frequent soil clay minerals in Hungary (Németh & Sipos, 2006), while Luvisols are one of the most frequent soil type in this country covering about 10% of its area (Stefanovits, 1970).

2. MATERIALS AND METHODS

2.1. Characterization of the studied profiles and samples

The samples were collected from the genetic horizons of a Calcic (P9) and a Haplic Luvisol (P13) profile, both with silt loam textures. The profile P9 was developed on an Oligocene pelagic siltstone which can be characterized by significant mica (up to 30%) and calcite (up to 20%) content. This rock was contacted by a Miocene andesite laccolite resulting in the partly transformation of mica to chlorite. The profile P13 formed on a Miocene pelagic siltstone with significant mica (up to 30%) content but with no carbonate. The sampling sites are almost free of anthropogenic contamination and they are far from the main roads and industrial activities (Fig. 1). The samples were air dried and passed through a 2 mm sieve before the analyses.

Some physico-chemical properties of the studied soil profiles are shown in table 1. The pH of the profile P9 is slightly acidic (between pH 6.09 and 6.28) except in its horizon C_k, where it is slightly alkaline (pH = 8.26) due to the presence of pedogenic and inherited calcite. Contrarily, the profile P13 can be characterized by an acidic pH in each of its horizons (between pH 4.76 and 5.79). The TOC content in the horizon A of the profile P9 (6.93%) is much higher than that of profile P13 (2.13%). The CEC values of the studied samples are significantly higher in the profile P13 (between 25 and 38 cmol/kg) than in profile P9 (between 12 and 24 cmol/kg) due to the higher clay content of the former when compared to the latter one (between 15 and 22% for P13 and between 7 and 15% for P9). The CEC values are only similar in their uppermost horizons, where the high TOC content of the sample from the profile P9 compensates the effect of the higher clay content of the sample from the profile P13 on CEC. Both profiles can be characterized by clay illuviation in their B_t horizons (up to 15 and 22% of clay content in the profiles P9 and P13, respectively). The dominant clay minerals are vermiculite in the A and B_t horizons of the profile P9 and chlorite in the C_k horizon of this profile, while it is montmorillonite in the profile P13. Additionally, illite occurs also in all of the studied samples (up to 10-40% of total clay minerals) with its highest amounts in the uppermost horizons.

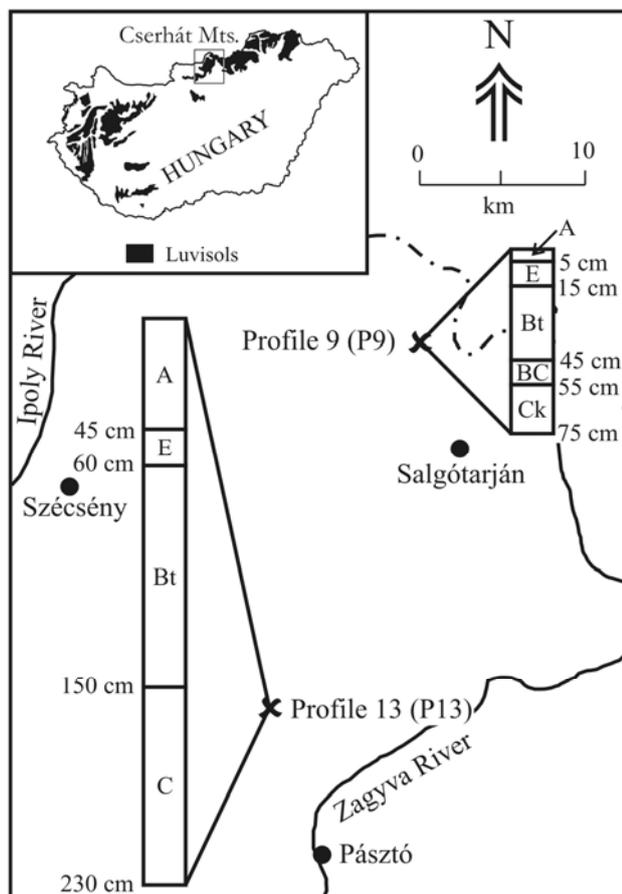


Figure 1. Sketch map showing the location and the scheme of the sampled profiles, as well as the spread of Luvisols in Hungary.

There are several studies on the characteristics of metal sorption by total soil samples or soil clay fractions separately. However, not many have focused on the comparison of these characteristics of total soil and clay fraction samples from the same soil. In this case, the aim of the study was to compare sorption characteristics of copper and lead on total soil samples and soil clay fractions (< 2 μ m) from the different genetic horizons (A, B and C) of two Luvisol profiles containing vermiculite and montmorillonite as dominant clay minerals, respectively. Clay minerals may play an important role in sorption of toxic elements on soils (Andráš et al., 2009). Vermiculite and montmorillonite can be characterized by the highest sorption capacity for metals among clay minerals (Weaver & Pollard,

Table 1. Some physico-chemical properties of the studied soil samples.
Ver = vermiculite, Ill = illite, Chl = chlorite, Mm = montmorillonite

Sample	Texture	Sampling depth (cm)	pH (H ₂ O)	pH (KCl)	TOC (%)	CEC (cmol/kg)	CaCO ₃ (%)	Silt (%)	Clay (%)	Clay type
P9A	Silt loam	0-5	6.28	4.46	6.93	24.2	0.00	61	7	Ver, Ill
P9B _t	Silt loam	25-45	6.09	5.26	0.42	22.8	0.80	61	15	Ver, Ill
P9C _k	Silt loam	55-75	8.26	7.60	0.47	12.4	27.00	53	14	Chl, Ill
P13A	Silt loam	0-5	5.79	5.40	2.13	25.1	0.00	77	15	Mm, Ill
P13B _t	Silt loam	105-115	4.76	3.66	0.30	38.7	0.00	72	22	Mm
P13C	Silt loam	185-200	5.20	3.71	0.24	31.7	0.00	72	21	Mm, Ill

More detailed characterization of the profiles can be found in the papers by Sipos (2004) and Németh & Sipos (2006).

2.2. Analytical techniques

Soil pH (both in H₂O and KCl) was measured by a Radelkis OP 211 analyzer. Total organic carbon content of the samples was analyzed by Tekmar Dohrmann Apollo 9000N N-DIR spectrometer. Soil cation exchange capacities were determined by the sodium acetate method (USEPA, 1986). The CaCO₃ content of the samples was studied using the calcimeter Bernard method. Particle size distributions of the samples were determined by Fritsch Analysette Microtech A22 laser diffraction analyzer.

The soil samples and clay fractions were characterized for mineralogical composition using a Philips PW 1710 X-ray diffractometer (XRD). Mineral composition of the bulk soil was determined on random-powdered samples by semi-quantitative phase analysis after the method by Bárdossy et al. (1980). Clay minerals were identified from the clay fractions of bulk samples by XRD diagrams obtained from parallel-oriented specimens. Separation of the clay fractions (< 2µm) were performed by sedimentation in aqueous suspension. The following diagnostic treatments were carried out for all of the samples: ethylene glycol solvation at 60°C overnight, Mg saturation followed by glycerol solvation at 95°C overnight, K saturation, heating on 350 and 550°C for 2 hours.

Metal concentrations in the solutions of the sorption experiments were analyzed by a Perkin Elmer AAnalyst 300 atomic absorption spectrometer (AAS). The relative standard deviations for the studied metals were 1.6% for Pb and 2.8% for Cu in the duplicate samples.

2.3. Sorption experiments and data evaluation

Batch sorption experiments were carried out in polypropylene centrifuge tubes of 50 ml by mix-

ing 200 mg sample with 20 ml solution containing various concentrations of the studied metals, which were added to the solutions in form of nitrates (Cu(NO₃)₂·2.5H₂O and Pb(NO₃)₂). The highest added metal concentrations in solutions were 10 mmol/L and the following dilution rates of these solutions with distilled water were used: 0.5, 0.25, 0.1, 0.05 and 0.025. The maximum metal concentrations correspond about to 2000 mg/L for Pb and 600 mg/L for Cu, which seem to be very high regarding the natural metal content of a soil, but they may occur in case of heavy metal pollution. For example, such a high solution concentration of metals can be found in acid mine drainage systems (España et al., 2005). The samples mixed with the solutions of different metal concentrations were shaken lengthwise for 48 hours at 25°C. Then they were separated by centrifugation at 3000 rpm for 20 minutes.

The amount of metals sorbed by the studied soil samples were calculated using the equation:

$$Q = \frac{(C_i - C) \cdot V}{W}$$

where Q is the adsorbed metal amount per unit weight of solid (mmol/kg), C is the equilibrium metal concentration in the solution (mmol/L), C_i is the initial metal concentration in the solution (mmol/L), V is the volume of the solution (mL) and W is the weight of the air-dried soil (g). The sorption of the metals from the solution onto the studied soil samples can be described by the Freundlich curve equation with a very good fit (generally R² > 0.9; see Tables 2. and 3.). It is based on the following relation:

$$Q = K_F \cdot C^{1/n}$$

where K_F and n are constants related to sorption capacity and affinity, respectively (Limousin et al., 2007). The classification of the sorption curves were done after the suggestions of Hinz (2001).

3. RESULTS

The results of the sorption experiments are summarized in the tables 2 and 3 for Cu and Pb, respectively. They show that extremely high Freundlich sorption capacity (K_F) values can be found for Cu (but partly also for Pb) in the sample containing high amount of calcite and also in its clay fraction (samples P9C_k and P9C_k CF). These high K_F values can be due to the alkaline conditions resulted by the presence of 27% CaCO₃ in the sample which may enhance the rate of metal precipitation on the one hand and also that of metal sorption on the other. According to Fontes et al. (2000), liming of soils results in creation of new sorption sites for metals and also metal precipitation due to the presence of carbonates. As significantly different retention processes can be expected for the studied metals in this sample, their discussion will be omitted below. Owing to this fact, all other studied samples which are characterized by acidic-slightly acidic conditions can be more effectively compared.

Table 2. Results of the Cu sorption experiments. CF = clay fraction, K_F , $1/n$ = Freundlich constants, R^2 = fit of the Freundlich curve

Sample	Curve type	K_F (mmol/kg)	$1/n$	R^2
P9 A	H1	210	0.30	0.91
P9 A CF	H1	293	0.25	0.96
P9B _t	L1	90	0.32	0.99
P9B _t CF	L1	158	0.25	0.99
P9C _k	L1	3733	0.55	0.76
P9C _k CF	L1	4229	0.65	0.88
P13A	L1	75	0.26	0.99
P13A CF	L1	223	0.38	0.85
P13 B _t	L1	94	0.35	0.99
P13B _t CF	L1	139	0.43	0.99
P13C	L1	102	0.36	0.99
P13C CF	L1	146	0.45	0.99

The detailed explanation of the different processes for the same metals and samples as in this study can be found in an earlier paper by Sipos (2009). The fact, however, that only the calcareous sample exhibits higher sorption capacity for Cu than for Pb, is in alignment with the observation by Sipos et al. (2008) on the same samples. According to their analytical electron microscopy analyses, Cu shows much higher sorption on surfaces of the mineral phases when compared to carbonate free samples, while Pb rather precipitates as carbonate in this sample.

Table 3. Results of the Pb sorption experiments. CF = clay fraction, K_F , $1/n$ = Freundlich constants, R^2 = fit of the Freundlich curve

Sample	Curve type	K_F (mmol/kg)	$1/n$	R^2
P9 A	H1	205	0.16	0.92
P9 A CF	H1	361	0.20	0.79
P9B _t	H1	139	0.21	0.93
P9B _t CF	H1	182	0.19	0.99
P9C _k	H1	536	0.16	0.96
P9C _k CF	H1	350	0.10	0.99
P13A	L1	103	0.27	0.99
P13A CF	L1	155	0.25	0.94
P13 B _t	L1	135	0.30	0.91
P13B _t CF	L1	136	0.33	0.99
P13C	L1	138	0.27	0.98
P13C CF	L1	144	0.32	0.99

3.1. Copper sorption

The Cu sorption curves for the studied samples can be classified mostly as L1-type curves except in the case of the sample with the highest TOC content (P9A) where H1-type curve was found both for the total soil sample and for its clay fraction (Fig. 2). The L curve suggests a progressive saturation of the solid, while H curve is a particular case of the L curve, where the initial slope is very high showing almost complete retention at low initial metal concentrations. Subtype 1 suggests that the theoretical monolayer has not been completed in each case (Limousin et al., 2007). Both types of curve shape suggest the high affinity of Cu to the studied samples. However, the retention of Cu is almost complete at low initial metal concentrations (up to 1.25 mmol/L) in the sample P9A and its clay fraction, while some proportion of copper remains in solution also at its low initial concentrations for all samples poor in organic matter.

The highest sorption capacity (Freundlich K_F values) for Cu was found in the sample P9A, which is about twice as much as in the other studied samples as shown by the K_F values (Table 2). All other studied samples can be characterized by quite similar K_F values for Cu. Among these samples, the higher the clay content the higher the K_F values for Cu. However, when the samples with similar clay content but different clay mineralogy are compared (e.g. samples P9B_t and P13A), slightly higher K_F value can be found for the sample containing vermiculite (P9B_t) in spite of the fact that this sample is less rich in organic matter.

Higher K_F values were found for the clay fractions when compared to total soil samples in each

case (Table 2). This phenomenon was expected as soil components having high surface area enrich in the clay fraction of soils. The highest difference was found for the sample P13A, where three times higher sorption capacity was found for Cu in the clay fraction than in the total soil sample (Fig. 4). When samples poor in TOC are compared, those containing montmorillonite show lower increase in K_F values in their clay fractions than total soil samples (around 1.5), while that one characterized by vermiculite show slightly higher values (1.75) (Fig. 3).

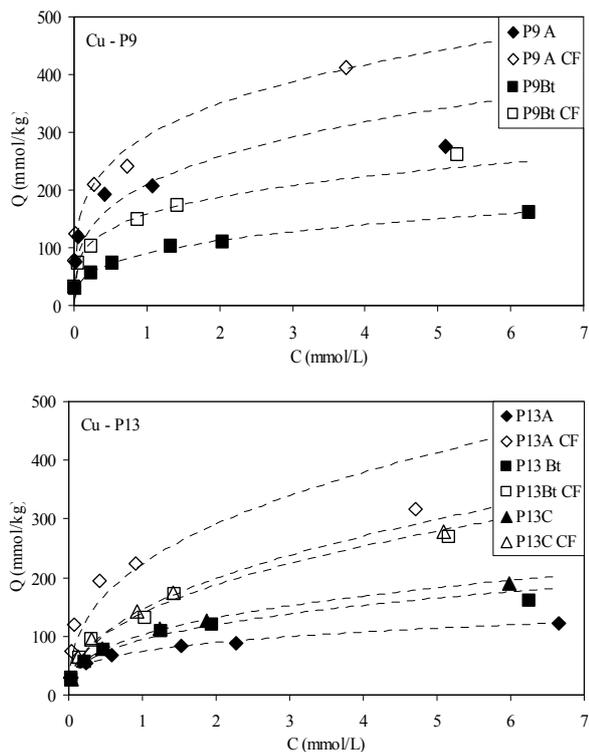


Figure 2. Copper sorption curves of the studied soil and soil clay fraction (CF) samples. Q = sorbed copper amount (mmol/kg), C = equilibrium copper concentration (mmol/L).

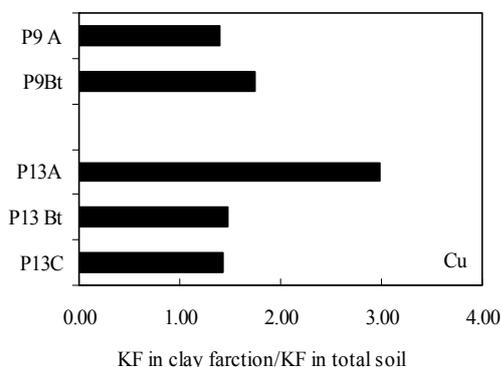


Figure 3. Ratio of Freundlich affinity (K_F) values in the clay fraction and total soil samples for copper.

Freundlich n values related to sorption affinity show both similarity and dissimilarity when the two

studied profiles are compared. In accordance with curve shapes, the highest affinity (e.g. lowest $1/n$ values) can be found in the uppermost samples which are rich in TOC. Contrarily, the difference lies in this that higher Cu affinity was found for clay fractions than in total soil samples in the soils containing vermiculite, while its reverse is true for the soil containing montmorillonite.

3.2. Lead sorption

The shapes of Pb sorption curves distinguish between the two studied profiles much more than for Cu as H1-type curve is characteristic of the samples from the profile P9 and L1-type for those from the profile P13 (Figure 4). First of all, this suggests the highest affinity of Pb to the samples from the profile P9 than for those from the profile P13 primarily at low initial Pb concentrations, which is shown by the almost complete retention of Pb even up to 2.5 mmol/L initial metal concentration.

Generally, the K_F sorption capacity values for Pb were found to be higher than that of Cu in the studied samples. Similarly to Cu, significantly higher K_F values for Pb were found in the sample with highest TOC content (P9A) and the samples from the deeper horizons can be also characterized by similar values. The uppermost sample from the profile P13 exhibits the lowest sorption capacity for Pb (Table 3). However, the higher sorption capacity values for Pb found in the total soil samples could not be found in the case of soil clay fractions as quite similar values were found for Pb as for Cu (Table 2 and 3). Additionally, significantly different sorption behavior of lead from that of Cu was found when sorption capacities of clay fractions and total soil samples are related. The clay fractions of the uppermost horizons of the two studied profiles show significantly higher Pb sorption capacity than the total soil samples: 1.8 and 1.5 times higher K_F values for the profile P9 and P13, respectively. In these cases only the K_F ratios of Pb differ from that of Cu (Fig. 3 and 5). As compared to Cu, the clay fraction and total soil sample characterized by vermiculite show much smaller difference in their sorption capacities for Pb showing that the enrichment in vermiculite exert much higher effect for Cu than for Pb. Interestingly, no differences between the sorption capacities of clay fractions and total soil samples were found in the mineral horizons from the profile containing montmorillonite.

The sorption affinity values (Freundlich n) for Pb also show similarity to Cu, e.g. higher Pb affinity was found for clay fractions than in total soil samples in the soils containing vermiculite, while its

reverse is true for the soil samples containing montmorillonite (Table 3). Highest Pb affinities were also found in the organic matter rich samples. However, total soil sample showed the higher Pb affinity in the uppermost horizon of the profile P9, while the reverse was true for the A horizon of the other studied profile (P13) when total soil samples and clay fractions are compared.

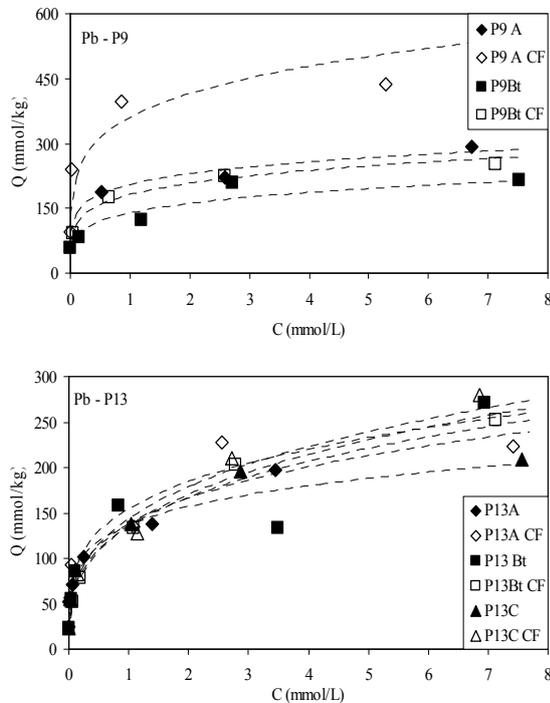


Figure 4. Lead sorption curves of the studied soil and soil clay fraction (CF) samples. Q = sorbed lead amount (mmol/kg), C = equilibrium lead concentration (mmol/L).

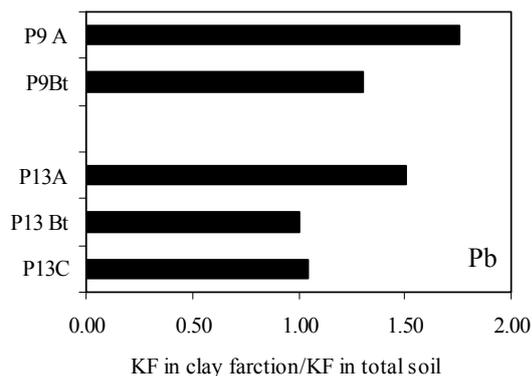


Figure 5. Ratio of Freundlich affinity (K_F) values in the clay fraction and total soil samples for lead.

4. DISCUSSION

Both the high K_F and n values for Cu in the samples rich in organic matter suggest the preliminary role of soil organic matter in sorption of this metal. The high affinity of Cu to soil organic matter was also

found by other studies (e.g. Sebastia et al., 2008; Damian et al., 2008b), and it can be justified both on the basis of stability of metal-organic complexes (the Irving-Williams series) (Huheey et al., 1993) and the Hard-Soft Acid Base concept (Pearson, 1985). Additionally, the results on the clay fractions also show that the soil organic matter enrich more significantly in the clay fraction in the profile P13 than in the profile P9. This may suggest that the former one can be characterized by more degraded organic matter in its uppermost horizon which is also shown by the ratios of K_F values in the clay fractions and total soil samples. The quality of soil organic matter significantly affects the sorption properties of metals on soils (Vaca-Paulín et al., 2006). However, further studies on soil organic matter are needed to draw more exact conclusions about the relation of organic matter and metal sorption in these soils.

When samples with different clay mineralogy are compared the preference of Cu sorption on the soil containing vermiculite over the one with montmorillonite was found. According to Abollino et al. (2008), the affinity of metals to vermiculite is high in a wide pH range between 2.5 and 8 when compared to montmorillonite, where this pH range can be found at pH values between 6 and 8. As the studied samples can be characterized by acidic-slightly acidic pH, which is characteristic of Luvisols (Stefanovits, 1971), the Cu shows higher sorption on vermiculite than on montmorillonite. Additionally, the mineralogical characteristics of swelling clay minerals (e.g. hydroxy-interlayering, association with oxides etc.) may also significantly influence their metal sorption properties (Németh et al., 2005; Németh et al., 2010).

Generally higher sorption capacity values for Pb were found in the total soil samples when compared to Cu. Both Pb and Cu can be characterized by high sorption affinity to soil components among potentially toxic metals which may be due to the differences in the metal-surface interaction (Berti & Jacobs, 1996) and the effect of the pH on the behavior of different metals in the sorption process (McKenzie, 1980). The higher sorption of Pb than that of Cu on soils was found by many other studies and can be explained by the differences in pK values for the first hydrolysis products of these metal ions (Elliot et al., 1986; Zhang & Zheng, 2007). According to the K_F values for total soil samples, Pb also showed the highest affinity to the samples rich in organic matter, followed by the ones characterized by vermiculite and at least by that containing montmorillonite. Due to this parallelism to Cu, similar conclusions can be drawn for Pb at the first look about the role of soil components and the differences in soil organic matter quality of the studied samples. According to the

XAFS study of Strawn & Sparks (2000), Pb sorption could be only found on the soil organic matter before organic matter removal from different soil types. This metal preferentially forms very stable chelate complexes, such as salicylate and cathecol resulting in much stronger binding when compared to mineral surfaces (Manceau et al., 1996).

Contrarily, results on clay fractions suggest the different sorption behavior of Pb when compared to Cu. It was found that the enrichment in the clay mineral content of the studied samples exerts much higher effect for Cu than for Pb both in the case of the samples with vermiculite and montmorillonite. In other words, further enrichment in montmorillonite of the P13B and P13C samples do not result in the increase of Pb sorption. To sum up, Pb seems to show much lower affinity both to vermiculite and montmorillonite when compared to Cu. Abollino et al. (2003) found that the ion exchange is not a primary sorption process both for Cu and Pb on montmorillonite, and hence they are more influenced by the pH. Due to the relatively low charge density of Pb, this metal showed the lowest sorption capacity for montmorillonite among seven studied metals including also Cu. Similar affinity characteristics for the sorption of these metals on vermiculite was found by Malandrino et al. (2006).

5. CONCLUSIONS

When sorption parameters of Cu and Pb for the total soil samples are under evaluation, the followings can be concluded for both metals: (1) the primary role of organic matter, (2) the preference of vermiculite over montmorillonite in the acidic-slightly acidic conditions of Luvisols, and (3) the different behavior of the uppermost samples from the two studied profiles probably due to the differences in their organic matter quality. Contrarily, significantly different sorption behavior of Pb from that of Cu was found when sorption capacities of clay fractions and total soil samples are related. The enrichment in the clay mineral content of the samples exerts much higher effect for Cu than for Pb for both soil clay mineralogy studied. Consequently, combined study of sorption properties of total soil samples and soil clay fractions helps us in better understanding the sorption process of potentially toxic metals in soils.

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