Central European Geology, Vol. 57/3, 265–285 (2014)
DOI: 10.1556/CEuGeol.57.2014.3.3

Distribution, geochemical fractionation and sorption of Cu and Pb in soils characteristic of Hungary

Péter Sipos[1]*, Tibor Németh[1], Chung Choi[2], Zoltán Szalai[3], Réka Balázs[1]

[1]Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary
[2]Department of Earth Sciences, University of Bristol, Bristol, United Kingdom
[3]Geographical Institute, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary

Knowledge of the distribution and sorption characteristics of trace metals in soils is essential because of their importance both from agricultural and environmental point of view. In this paper, an overview will be provided on the relationship between the behavior and sorption properties of Cu and Pb as well as major soil characteristics, based on the results obtained by several independent research projects carried out on this field at the Institute for Geological and Geochemical Research over the last 15 years. These projects were accomplished using methods with different approaches, e.g. studying metal characteristics by total metal content, selective chemical extractions and batch sorption experiments.

Our results show that both metals can be found in soils, primarily in the form of phases highly resistant to weathering. However, if they are mobilized, they are easily and strongly immobilized by soils rich in organic matter, with higher affinity for Cu than for Pb. In acid soils, on the other hand, the leaching of Cu is expected to be higher from such horizons when compared to Pb, especially when iron oxides, which immobilize Pb preferentially, are also present in these horizons. In mineral horizons the close association of Pb and iron oxides can be still expected, whereas Cu prefers to be bound both by clay minerals and iron oxides. In alkaline soils, however, precipitation of both metals as carbonates is a general feature. Our results obtained through different approaches presented in this paper were found to be effectively complementary to each other, providing a much deeper insight into soil-metal interaction than when they are used independently.

Key words: heavy metals, soil properties, sequential extraction, sorption experiment, mobilization, soil mineral phases

---

* Corresponding author; Budaörsi út 45, H-1112 Budapest, Hungary; E-mail: sipos@geochem.hu
Received: October 28, 2014; accepted: October 28, 2014

Introduction

Heavy metals are natural components of soils. Their main source is rock mineral weathering and their concentrations remain mostly below toxic levels in uncontaminated soils. The study of their distribution and sorption characteristics in soils is of primary importance, both from an agricultural as well as an environmental point of view, as some of them are essential trace elements (such as Cu) while others are among the most hazardous heavy metal contaminants (such as Pb), released mostly by anthropogenic activity into the environment. Human activities associated with agriculture, industry, vehicular traffic and mining resulted in the incorporation of increased amounts of such metals from both groups. They are believed to be easily accumulated in the topsoil, resulting in potential toxicity to living organisms (Alloway 1990). The evaluation of the behavior of these metals in the soil–water–plant system is of great interest because of its possible effects on the food chain.

Transformation of metal-containing minerals during pedogenesis affects the chemical speciation and bioavailability of metals. Soil chemical and physical properties like redox conditions and pH influence the rate of transformation of metals in soil, and, along with addition and depletion of salts, carbonates, clays, organic matter, determine absolute and relative changes in heavy metal contents through the soil profile. These multiple interaction processes result in complex patterns of element distribution in soil (Palumbo et al. 2000).

Total elemental contents provide little information on the mobility and bioavailability of the elements of interest. These properties of metals depend heavily on their physical and chemical forms. Sequential extraction, although operationally defined, can provide information about the association of heavy metals with geochemical phases in a soil; hence it helps to reveal the distribution of metals in fractions and to assess their mobility and toxicity. Generally, exchangeable and weak acid soluble forms are considered readily mobile and easily bioavailable, while the residual form is considered to be incorporated into the crystalline lattice of soil minerals and appears to be the most inactive. Other fractions, such as reducible or oxidizable ones, can be considered relatively active depending on the actual physicochemical properties of the soil (Lu et al. 2005).

The soil solution concentration, and hence the bioavailability or toxicity of these metals, are most likely controlled by sorption-desorption reactions on the surface of the soil colloidal materials. Batch equilibrium techniques are primarily used to study the retention of metals in soils. The sorption data can be described in this case by using isotherms. The analysis of these curves provides information about the retention capacity and the strength with which the sorbate is held on to the soil (Morera et al. 2001).

The aim of this paper is to show the distribution, geochemical fractionation and sorption properties of Cu and Pb in uncontaminated soils as a function of major soil properties. It provides a short summary of the results based on both published and unpublished data obtained by the studies of the Institute for Geological and Geochemical Research on this field over the last 15 years.

Materials and methods

In this paper the total Cu and Pb contents related to soil properties are presented for 48 samples from 15 soil profiles. Sampling was carried out in locations where heavy metal contamination potential from agricultural, industrial or traffic activities are expected to be minimal. Their major characteristics are shown in Table 1. Samples were taken from each genetic horizon of the soil profiles. To examine the effect of parent material on metal content and geochemical fractionation, eight out of the 15 profiles were forest soils (Luvisols and an Acrisol) developed on various geologic formations. The samples collected were air-dried in the laboratory, sieved through a 2-mm sieve and homogenized before the analyses. For the study of their total metal content and sequential extractions, samples were ground to fine powder (<10 mm) in an agate mortar. The studied samples represent a wide range of soil physical and chemical properties. Their pH values are between 4.00 and 8.87. Their total organic carbon and carbonate contents are up to 10.72% and 58.0%, respectively. They are characterized mostly by loam texture, with loam and clay content between 10.0 and 79.0%, as well as 1.0 and 35.0%, respectively, except for 5 samples representing sand, silt and silty clay textures.

For general characterization of the samples pH values were determined both from aqueous suspension and 1M KCl solution (using a 1:2.5 solid:solution ratio). Total organic carbon content was analyzed with a Tekmar–Dohrmann Apollo 9000N TOC instrument. The carbonate content of the samples was determined with the Scheibler calcimeter method. Particle-size distribution of the samples was analyzed using a Fritsch Analysette Microtech A22 laser diffraction instrument. The soil samples and clay fractions were characterized for mineralogical composition with a Philips PW1730 X-ray diffractometer (XRD). Total Fe, Cu and Pb contents were determined by ICP-MS (Perkin–Elmer Elan 9000) analyses after 4-acid digestion as follows: a 0.25 g split of each sample was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness. The residue was dissolved in HCl. The quality of the analyses was checked by the study of two standard reference materials (SRM). Analyzed and expected concentrations for the OREAS24P are 43 and 52 mg kg^{-1} for Cu, <5 and 2.9 mg kg^{-1} for Pb and 7.53 and 7.18% for Fe, respectively. Analyzed and expected concentrations for the OREAS45E are 780 and 753 mg kg^{-1} for Cu, 22 and 18.2 mg kg^{-1} for Pb and 24.88 and 24.12% for Fe, respectively.

The sequential extraction method after Li et al. (1995) was carried out on 31 selected samples (samples from profiles 1–6 for the Luvisols and samples from profiles 10–14 for the non-Luvisols) in triplicate. The extractions were carried out progressively on an initial weight of 1.0 g soil in five steps as follows: (1) exchangeable with 0.5 M $MgCl_2$; (2) weak acid soluble, extracted by 1M NaOAc at pH 5.0 with HOAc;

Table 1
The studied soil samples and their major characteristics

WRB soil type (location) parent material	Horizon	Depth (cm)	Texture	pH (H_2O)	pH (KCl)	TOC (%)	$CaCO_3$ (%)	Sand (%)	Silt (%)	Clay (%)	Cu (mg kg^{-1})	Pb (mg kg^{-1})
1. Luvisol (Zsitfapuszta)	A	0–15	silt loam	5.38	4.44	0.90	0.0	41.8	51.1	7.1	5.5	11.1
on alluvial sand	B	75–85	silt loam	5.27	4.38	0.21	0.0	22.3	64.5	13.2	13.2	8.3
	C	115–125	silt loam	5.34	4.29	0.12	0.0	17.0	70.4	12.6	17.4	10.7
2. Luvisol (Háromfa)	A	0–15	silt loam	4.34	4.16	1.56	0.0	20.2	72.1	7.7	7.9	12.1
on loess	B	65–75	silt loam	5.12	4.47	0.26	0.0	15.1	72.1	12.8	17.3	8.5
3. Luvisol (Kisbárkány)	A	0–5	silt loam	5.79	5.40	2.13	0.0	7.8	76.8	15.4	10.5	40.0
on siltstone	B	105–115	silt loam	4.76	3.66	0.30	0.0	5.9	71.8	22.3	14.4	27.2
	B	185–200	silt loam	5.20	3.71	0.24	0.0	6.4	72.4	21.2	13.0	27.4
	C	230–250	silt loam	5.55	3.96	0.21	0.0	6.0	70.8	23.1	15.9	32.4
4. Luvisol (Szentkút)	A	0–5	silt loam	4.98	4.17	2.69	0.0	7.1	75.0	18.0	14.6	40.9
on calcarenite	B	70–80	silt loam	5.38	4.26	0.77	0.0	5.3	73.0	21.7	16.1	31.5
	C	110–120	silt loam	7.88	7.02	0.98	28.7	18.9	66.8	14.3	11.4	18.7
5. Luvisol (Alsótold)	A	0–5	silt loam	5.94	4.80	1.96	0.0	4.7	77.2	18.0	28.0	37.4
on andesite	E	25–35	silt loam	6.15	5.24	1.75	0.0	5.1	79.0	15.9	21.7	34.0
	B	80–90	silt loam	6.08	4.67	0.47	0.0	2.5	73.6	23.9	28.3	31.7
	C	130–140	silt loam	6.35	4.92	0.39	0.0	3.2	72.6	24.2	31.8	31.4
6. Luvisol (Karancslapujtő)	A	0–5	silt loam	6.28	4.46	6.93	1.2	32.0	60.6	7.4	16.5	33.3
on calcareous siltstone	B	25–45	silt loam	6.09	5.26	0.42	0.8	24.4	60.6	15.0	16.6	29.9
	C	55–75	silt loam	8.26	7.60	0.47	27.0	32.6	53.3	14.1	12.8	17.4
7. Luvisol (Sopron I)	A	5–20	loam	4.40	3.40	2.33	0.0	49.0	28.0	23.0	27.0	30.0
on loess	A	20–60	loam	4.70	3.50	0.92	0.0	45.0	26.0	29.0	23.0	30.0
	B	60–100	loam	5.10	3.60	0.71	0.0	41.0	26.0	33.0	28.0	28.0
	B	100–140	loam	5.60	4.10	0.48	0.0	39.0	26.0	35.0	31.0	25.0
	C	140–160	sandy clay loam	7.60	7.20	0.32	6.2	51.0	28.0	21.0	18.0	24.0
8. Acrisol (Sopron II)	A	5–20	sandy loam	4.00	3.10	10.72	0.0	73.0	14.0	11.0	6.0	23.0
on leucophyillite	A	20–55	sandy loam	4.7	3.90	2.43	0.0	77.0	18.0	5.0	4.0	20.0
	B	55–90	sandy loam	4.70	4.10	0.55	0.0	77.0	18.0	5.0	4.0	12.0
	B	90–120	sandy loam	4.80	3.80	0.34	0.0	75.0	16.0	9.0	4.0	10.0
	C	120–200	sand	5.20	4.40	0.13	0.0	89.0	10.0	1.0	5.0	6.0

Table 1 (cont.)

WRB soil type (location) parent material	Horizon	Depth (cm)	Texture	pH (H_2O)	pH (KCl)	TOC (%)	$CaCO_3$ (%)	Sand (%)	Silt (%)	Clay (%)	Cu (mg kg^{-1})	Pb (mg kg^{-1})
9. Chernozem (Kláramajor)	A	0–10	silt loam	7.17	6.96	1.65	0.0	18.9	67.6	13.5	19.4	14.4
on loess	B	40–50	silt loam	7.12	6.94	1.20	0.0	34.3	54.7	11.0	16.1	12.3
	B	140–150	silt loam	7.51	6.80	0.76	0.0	29.9	55.5	14.6	12.5	7.5
	C	180–190	silt loam	8.14	7.76	0.18	19.4	36.6	50.7	12.7	7.3	4.4
10. Chernozem	A	0–10	silt loam	8.33	8.10	1.52	10.6	33.2	58.0	8.8	16.1	9.9
(Felsőboldogkáta) on loess	C	130–140	clay loam	8.70	8.34	0.53	28.3	25.5	46.0	28.5	8.5	4.9
11. Solonetz	A	0–10	silt loam	8.59	8.10	1.72	9.7	44.0	51.1	4.9	7.8	9.1
(Szentlőrinckáta I)	C	80–90	sandy loam	8.69	7.97	0.13	7.6	64.7	21.5	13.8	4.9	5.1
on sandy loess												
12. Solonetz	A	0–10	sandy loam	8.33	7.93	1.11	14.8	50.6	41.5	7.9	7.2	7.7
(Szentlőrinckáta II)												
13. Phaeozem (Tóalmás)	A	0–5	silt loam	8.03	7.85	0.24	13.5	30.7	61.1	8.1	14.0	16.7
on loess	AC	25–35	sandy loam	8.77	8.65	0.15	27.5	63.4	23.5	13.1	4.9	3.8
	C	140–150	sandy loam	8.87	8.61	0.04	26.6	58.7	26.1	15.2	6.0	4.2
14. Phaeozem	A	0–20	silt	8.25	7.71	2.01	58.0	2.4	87.9	9.7	9.0	17.0
(Ceglédbercel I)	A	20–50	silt loam	8.26	7.76	1.95	57.7	0.6	71.0	28.4	5.0	8.0
on alluvial sand	A	50–65	silt loam	8.33	7.82	1.76	54.5	0.4	70.3	29.3	10.0	19.0
	C	65–wt	silt clay loam	8.26	7.81	0.38	37.2	1.4	63.7	34.9	4.0	6.0
15. Phaeozem	A	0–50	silt loam	7.54	7.76	1.91	26.7	3.0	78.0	19.0	3.0	10.0
(Ceglédbercel II)	C	50–75	silt clay	8.19	7.9	0.41	22.3	0.0	52.0	48.0	2.0	<5
on alluvial sand	C	75–wt	silt clay	8.19	7.9	0.1	23.3	4.00	60.00	36.00	3.0	<5

wt = water table

(3) reducible, extracted by 0.04 M $NH_2 \cdot OH \cdot HCl$ in 25% (v/v) HOAc; (4) oxidizable, extracted by the mixture of 0.02 N H_2O_2, 30% HNO_3 and 3.2M NH_4OAc at pH 2.0; and (5) residual using the same 4-acid digestion as for the total metal analyses. The concentration of Fe, Cu and Pb were analyzed using the ICP-AES method (Jobin Yvon Ultima 2 sequential instrument) in the solutions. Recoveries of the studied metals were found to be between 94 and 125%.

Batch sorption experiments were carried out on 6 soil samples of two profiles (3A, 3B, 3C, 6A, 6B, 6C, where the number and letter indicate the number of the profile and the horizon, respectively) in duplicate. The samples were selected according to their contrasting characteristics: Profile 3 can be characterized by clay mineralogy dominated by montmorillonite and an A horizon with relatively low TOC content, whereas Profile 6 is of clay mineralogy with vermiculite; it has alkaline subsoil and topsoil with relatively high TOC. Metals were added to the solutions in the form of nitrate salts in the concentration range between 0.1 and 10 mM L^{-1}. The initial pH of the solutions were set to pH 5–6 to minimize the chance of precipitation of metal hydroxides still within the natural pH range of soils. The soils mixed with the solutions of different metal concentrations were shaken lengthwise for 48 hours at 25°C. Their concentrations in the equilibrium solutions were analyzed with the AAS method (Perkin–Elmer AAnalyst 300). The relative standard deviations for the studied metals were as follows: 1.71%, 13.8% and 9.41% for >1 mg L^{-1}, 1–0.1 mg L^{-1} and <0.1 mg L^{-1} Cu concentrations, respectively, and 1.82%, 13.1 and 19.9% for >1 mg L^{-1}, 1–0.1 mg L^{-1} and <0.1 mg L^{-1} Pb concentrations, respectively.

Results and discussion

Total Cu and Pb content and its relation to soil properties

Total Cu and Pb concentrations were very variable in the studied soils, although these variations (the coefficient of variation is 0.63 for Cu and 0.62 for Pb) are generally characteristic of natural soil metal concentrations. These values are in the range between 2.0 and 31.8 mg kg^{-1} for Cu and between 3.8 and 40.9 mg kg^{-1} for Pb, with median values of 12.6 and 16.9 mg kg^{-1}, respectively. Based on their geoaccumulation index calculated after Ji et al. (2008), the soil can be considered as not contaminated since their concentration values are mostly close to the geochemical background values, e.g. 19 mg kg^{-1} for Cu and 17 mg kg^{-1} for Pb (Ódor et al. 1997). These concentration values, even the maximum ones, are far below the threshold limit values of these elements for Hungary (75 mg kg^{-1} for Cu and 100 mg kg^{-1} for Pb) (KvVM-EüM-FVM decree No. 6/2009).

The studied soil types show significant differences in their Cu and Pb contents and distribution characteristics (Fig. 1). Luvisol samples generally show higher Cu and Pb concentrations than non-Luvisol ones, independently of their parent material. However, the distribution of the studied metals within the profiles shows significant differences. Total Cu concentration can be characterized by a slightly higher average

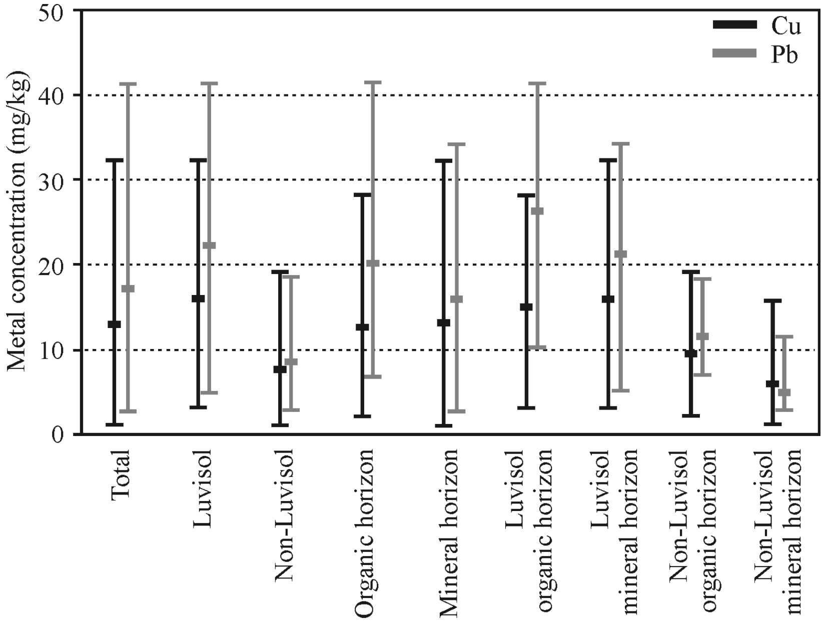

Fig. 1
Average Cu and Pb concentrations and their ranges in the studied samples (mg kg^{-1})

concentration value in the mineral horizons as compared to the organic ones in the Luvisol samples. This can be due to the fact that the major accumulation takes place in the mineral horizons of these soils, which can also be enhanced by inheritance from the soil parent material (Probst et al. 2003). On the other hand, in the non-Luvisol samples both total Cu and Pb show higher concentrations in the organic horizon than in the mineral ones and this is also true for Pb in the Luvisols. Non-Luvisol samples are expected to accumulate trace metals (such as Cu and Pb) together with soil organic matter in the topsoil (Brümmer et al. 1986). This enrichment of Cu and Pb in the organic horizons of the non-Luvisol samples can be related to their high affinity for soil organic matter. Additionally, these Luvisols can be characterized by significantly lower pH values (between 4.00 and 6.28 in aqueous suspension) in their topsoil than the non-Luvisols (between 7.17 and 8.59 in aqueous suspension), resulting in much higher chance for mobilization in the topsoil of Luvisols. This could be the reason for the slight accumulation of Cu in the mineral horizon of the Luvisols.

Linear correlations between the major soil properties and total Cu and Pb concentrations were carried out to assess which soil properties affect the distribution of the studied metals. The lead concentration of the studied soils is negatively correlated with soil pH_{KCl} ($r = -0.60$; $P < 0.05$), as was expected (Fig. 2a). This relationship is much weaker for Cu ($r = -0.43$; $P < 0.05$). This is in accordance with the observation that acidic Luvisols contain much higher amounts of Cu and Pb than the alkaline non-Luvisols. Total Cu content show close linear relationship with total Fe content of the soils (r = 0.67; P < 0.05) (Fig. 2b). This relationship is more pronounced for the Luvisol samples (r = 0.85; P < 0.05), but not characteristic for the non-Luvisol samples. This suggest that the formation of iron minerals in soils results in Cu accumulation (Sipos et al. 2011) and/or inherited Fe minerals are common host phases for this metal (Lång 2000). In the Luvisol samples, Cu also shows a strong linear relationship with the soil clay fraction (r = 0.81; P < 0.05) (Fig. 2c). The affinity of trace metals for soil fine fractions is related to their larger sorption surfaces (Hernandez et al. 2003). The close relationship between total Cu and soil Fe and clay content is in a good agreement with the fact that Cu was found to be enriched in the mineral horizon of the Luvisol samples where accumulation of pedogenic iron minerals and clay minerals can be expected. In the non-Luvisol samples, however, Pb showed close linear relationship with the total organic carbon content of the samples (r = 0.65; P < 0.05) (Fig. 2d). This supports the observation that Pb is generally enriched in the topsoil, which was found to be much more pronounced in the non-Luvisol than in the Luvisol samples.

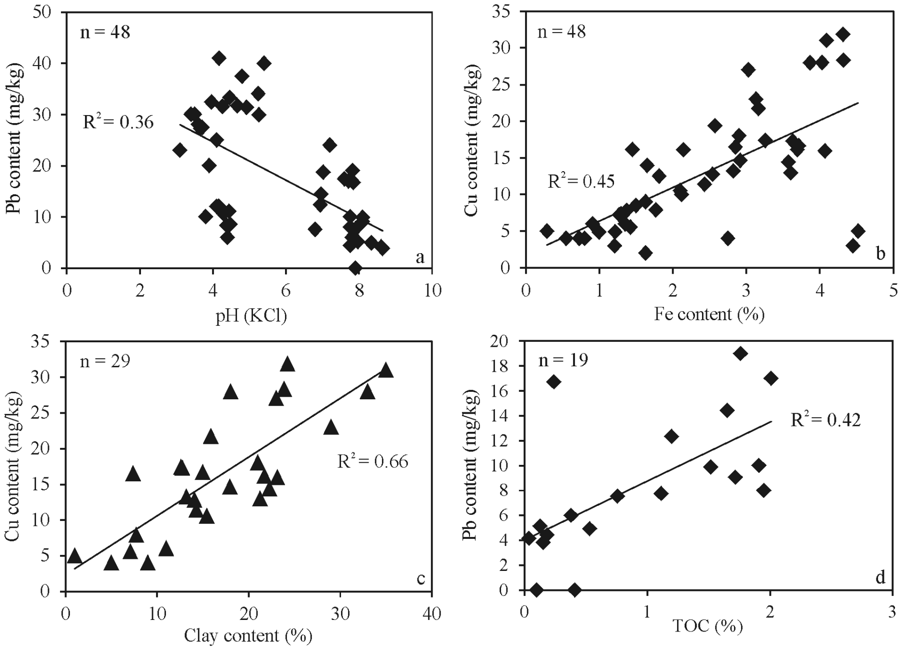

Fig. 2
Relationship between total metal content and some soil property for all (a and b), for Luvisol (c) and for non-Luvisol (d) samples

Fractionation of Cu and Pb and its relation to soil properties

The studied Luvisol samples contain not only higher metal amounts than non-Luvisol ones, but the fractionation of the studied elements also showed differences on that basis. Despite the variety of soil types and soil parent materials under analysis, the metals studied did not show large variations in their fractionation within the Luvisol and non-Luvisol groups (Fig. 3). Higher variance was found both for Cu and Pb in the easily soluble (exchangeable and acid extractable) fractions which are generally due to a few exceedingly high values not generally characteristic for the studied soil types. Due to the large similarity, average values of fraction ratios are presented below for each studied metal within the two groups established above.

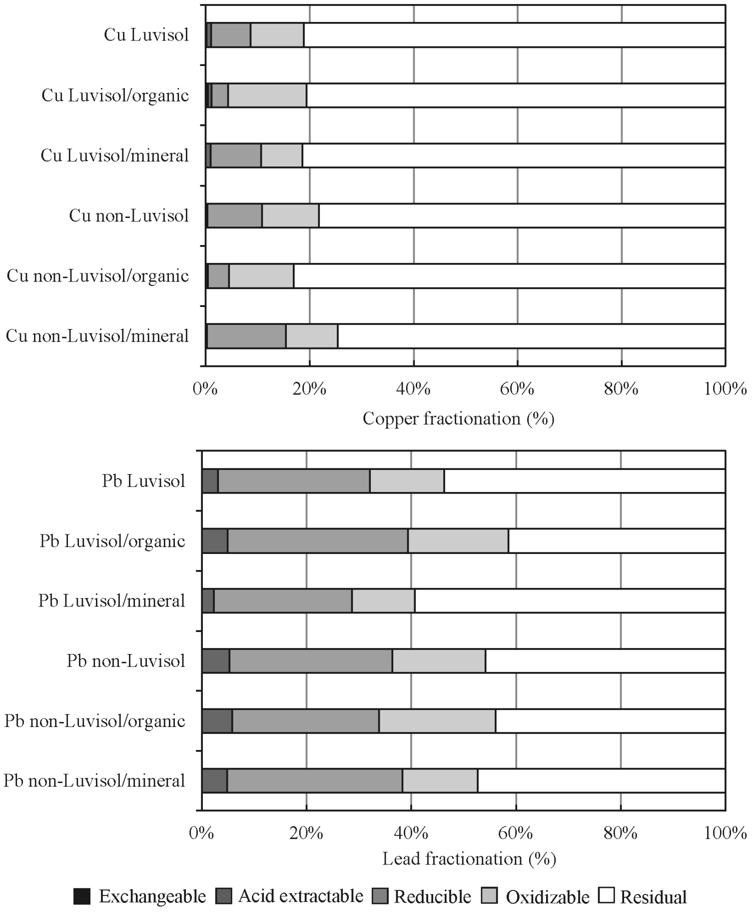

Fig. 3
Average ratios of the studied metals in the different fractions of the sequential chemical extractions used

The two studied metals show different fractionation patterns, both when compared to each other and between the two soil groups. The residual fraction is the most important one for both metals: on average 80.4 ± 9.1% and 49.8 ± 14.7% of total metal content can be bound to this fraction for Cu and Pb, respectively. The predominance of the residual fraction is generally found both in soils and sediments, even in contaminated ones (e.g. Usero et al. 1998; Bielicka-Giełdoń et al. 2013) and can be due to the presence of trace metals in phases resistant to weathering, such as silicates and (iron) oxides (Wilcke et al. 1998). This ratio, however, shows slight variance between the two soil groups for each metal. The average ratio and range of the residual fraction for Cu is quite similar for both Luvisols (81.6 ± 6.8%) and non-Luvisols (78.7 ± 12.0%). Additionally, the organic and mineral horizons of the Luvisols can be also characterized by similar residual Cu ratios (81.7 ± 9.8% and 81.5 ± 5.4%, respectively). However, it is much lower in the mineral (74.4 ± 14.1%) than in the organic (84.7 ± 4.6%) horizons for the non-Luvisol samples. The higher mobilization of Cu in mineral horizons of the non-Luvisol samples can be due to the presence of waterlogging periods in some profiles (Phaeozem and Solonetz, Profiles 11–13 in our case). In such soils the ratio of residual Cu is between 56.1 and 68.9% whereas it is between 71.7% and 89.1% in the Chernozems where waterlogging is not expected. Periodic reduction/oxidation during waterlogged conditions and aeration in soils results in dissolution and precipitation of soil iron oxides together with progressive scavenging of bivalent metals by specific sorption and occlusion due to precipitation of re-oxidized iron (Bingham et al. 1976). In contrast to copper, lead can be characterized by much lower ratios of residual Pb and by much higher variance between soil types and different horizons. This ratio is higher in the Luvisol (53.5 ± 16.6%) than in the non-Luvisol samples (44.0 ± 9.0%). It can also be explained by the effect of water-logged periods on weathering. In the case of the Luvisol samples there is a large difference between the organic (41.3 ± 10.6%) and mineral horizons (59.2 ± 16.0%) from this point of view. The much higher mobilization of lead in the topsoil can be related to the lower pH values in the organic horizons (5.05 ± 0.8 vs. 5.8 ± 1.0), as acidic conditions promote the mobilization of cationic metals in soils (Bradl 2004). In the case of the non-Luvisol samples, however, a more uniform picture can be drawn for this metal but the slight difference between the ratios of residual Pb for the organic (43.0 ± 8.5%) and mineral horizons (44.7 ± 10.0%) can also be observed.

The relationship between the metals' fractionation and soil properties were studied by linear correlation analyses (Tables 2 and 3). Both residual Cu and Pb show a close positive relationship with silt and total Fe content of the soils when all samples are under analysis. This latter relationship can be also found when the two soil groups are studied separately, although it is slightly weaker for Pb in the non-Luvisol samples. However, the increase in residual Cu and Pb is only related to that of the silt fraction in the non-Luvisol samples, whereas these metal fractions can rather be linked to the clay fraction in the Luvisol samples. These suggest that both residual Cu and Pb can be bound to iron-containing minerals in the studied soils, which is enriched in the silt and clay fractions for non-Luvisol and Luvisol samples, respectively. Magnetic susceptibility measurements of non-polluted soils by de Oliveira et al. (2000) showed that the amount of resistant iron minerals, such as magnetite (and hematite), which are also primarily responsible for the magnetic susceptibility of soils, could be considered as an important trace metal (such as Cu and Pb) sink in soils. The strong negative relationship between residual Cu and Pb and sand fraction is also characteristic of each sample group. This is in accordance with the enrichment of these metals in the fine soil fractions. Additionally, residual Pb also shows a negative relationship in the non-Luvisol samples with pH and carbonate content, as was expected from the similar feature of the total Pb content of these samples.

Table 2

Pearson correlation coefficients (at $P < 0.05$) for the relationships between copper concentrations in the different fractions of the sequential chemical extraction and selected soil properties

Soil property	Exchangeable	Acid extractable	Reducible	Oxidizable	Residual
			All		
pH (H_2O)	0.24	–0.33	–0.23	–0.21	–0.36
pH (KCl)	0.27	–0.45	–0.27	–0.26	–0.43
TOC	–0.03	–0.09	–0.41	**0.64**	0.14
$CaCO_3$	0.18	–0.32	–0.24	–0.31	–0.48
Sand	0.45	–0.55	–0.24	–0.18	**–0.74**
Silt	–0.36	0.41	0.18	0.28	0.69
Clay	–0.45	**0.61**	0.27	–0.18	0.43
Fe_{TOT}	–0.51	**0.71**	0.47	0.25	**0.78**
			Luvisol		
pH (H_2O)	–0.10	0.12	–0.12	0.06	0.20
pH (KCl)	–0.08	–0.11	–0.19	–0.11	0.02
TOC	–0.04	–0.20	–0.46	**0.70**	–0.03
$CaCO_3$	–0.08	–0.16	–0.25	–0.12	–0.18
Sand	0.56	–0.48	–0.27	0.19	**–0.62**
Silt	–0.56	0.20	0.21	–0.19	0.50
Clay	–0.40	**0.73**	0.27	–0.15	**0.60**
Fe_{TOT}	–0.51	**0.66**	0.53	0.06	**0.77**
			non-Luvisol		
pH (H_2O)	0.42	0.00	0.06	–0.56	**–0.82**
pH (KCl)	0.50	0.00	0.05	–0.40	**–0.71**
TOC	0.28	0.00	–0.54	0.39	**0.68**
$CaCO_3$	0.28	0.00	0.11	–0.50	**–0.66**
Sand	0.12	0.00	0.32	–0.47	**–0.84**
Silt	0.04	0.00	–0.35	**0.65**	**0.88**
Clay	–0.41	0.00	0.09	–0.46	–0.11
Fe_{TOT}	–0.43	0.00	–0.06	0.53	**0.87**

Note: Correlation coefficient values in bold correspond to $-0.60 \leq r \leq 0.60$

Table 3
Pearson correlation coefficients (at $P < 0.05$) for the relationships between lead concentrations in the different fractions of the sequential chemical extraction and selected soil properties

			All		
	Exchangeable	Acid extractable	Reducible	Oxidizable	Residual
pH (H_2O)		–0.20	–0.55	–0.44	–0.51
pH (KCl)		–0.26	–0.55	–0.43	**–0.61**
TOC		**0.64**	0.48	**0.61**	0.18
$CaCO_3$		–0.20	–0.46	–0.51	–0.42
Sand		0.09	–0.59	–0.54	**–0.76**
Silt		0.01	**0.63**	0.58	**0.66**
Clay		–0.30	0.13	0.11	**0.60**
Fe_{TOT}		0.02	0.44	0.43	**0.80**
			Luvisol		
pH (H_2O)		–0.23	–0.02	–0.02	0.15
pH (KCl)		–0.39	0.02	0.00	–0.06
TOC		**0.77**	0.52	0.59	0.07
$CaCO_3$		–0.22	–0.27	–0.26	–0.10
Sand		0.33	–0.24	–0.27	**–0.69**
Silt		–0.24	0.36	0.35	0.46
Clay		–0.36	–0.01	0.08	**0.81**
Fe_{TOT}		–0.14	–0.14	0.04	**0.63**
			non-Luvisol		
pH (H_2O)		0.27	–0.46	**–0.80**	**–0.61**
pH (KCl)		0.21	–0.29	**–0.68**	–0.53
TOC		–0.17	0.23	**0.74**	0.43
$CaCO_3$		–0.03	–0.27	**–0.71**	**–0.61**
Sand		0.22	–0.48	**–0.64**	–0.58
Silt		–0.06	**0.63**	**0.73**	**0.73**
Clay		–0.42	–0.41	–0.24	–0.40
Fe_{TOT}		–0.20	0.50	**0.89**	0.58

Note: Correlation coefficient values in bold correspond to $-0.50 \leq r \leq 0.50$. Exchangeable fractions cannot be evaluated because Pb concentrations were mostly below the detection limit of analytical method used.

Fractions (except the residual one) are often called comprehensively labile or mobile fractions (Kabala and Singh 2001). Among the labile fractions the reducible one shows the highest ratios for both metals, up to 30.5 and 53.1% for Cu and Pb, respectively. Its relative role is generally much higher for Pb than for Cu (Fig. 3). This fraction is primarily expected to dissolve soil iron oxides, and the high affinity of trace metal to these phases in soils is a well-known phenomenon (e.g. Cornu et al. 2005). Both metals show similar reducible ratios for both soil groups: 7.7 ± 6.8% and 10.5 ± 10.2% for Cu, and 28.9 ± 12.4% and 29.9 ± 9.6% for Pb in the Luvisols and non-Luvisols, respectively. Both Luvisols and hydromorphic non-Luvisols can be characterized by iron accumulation, mostly in their mineral horizons (Blume and

Schwertmann 1969). Large differences can be found when the organic and mineral horizons are compared. For Cu, generally three times higher reducible ratios were found in the mineral (9.7 ± 7.1% for Luvisols and 15.2 ± 11.5% for non-Luvisols) than in the organic horizons (3.2 ± 3.1% for Luvisols and 4.1 ± 0.6% for non-Luvisols). This phenomenon is explained by the fact that iron oxide formation primarily takes place in the mineral horizons of the studied soil types, e.g. in the accumulation horizon (B) of the Luvisols and in the waterlogged horizons (B, C) of the Phaeozems and Solonetz soils (Blume and Schwertmann 1969). These ratios are much more similar in the organic and mineral horizons for Pb in both soil groups (around 30% in each case), suggesting that iron migration within the soil profiles does not affect Pb distribution as much as that of Cu. The relationship between reducible Cu and soil properties was not found by the correlation analyses (Table 2); on the other hand, reducible Pb showed a close positive relationship with the silt fraction of the samples which was dominated by those from non-Luvisol profiles (Table 3). This is a similar feature to residual Pb, suggesting the joint presence of resistant and pedogenic lead-hosting phases (probably iron oxides) in the silt fraction of non-Luvisol samples. This feature is characteristic of water-logged soils, as was found by several studies (e.g. Sipos et al. 2011).

The oxidizable fraction has an almost similar ratio to that of the reducible one for Cu, except in the organic horizons where it is 3–5 times higher. In the case of Pb, however, its ratio is generally around half of the reducible fraction. Since the soil organic matter is primarily dissolved in the oxidizing step of the sequential extraction (Hall 1998), these ratios suggest that Cu has a similar affinity for soil organic matter and soil iron oxides in the mineral horizons. However, when the amount of soil organic matter is high (and that of iron oxides is low) enough, e.g. in the organic horizons, Cu tends to bind to organic matter rather than to iron oxides. On the other hand, although a slight increase in the oxidizable ratio of Pb can be observed in the organic horizons when compared to the mineral ones, the latter fractions are still dominant even in the organic horizons. This suggests that Pb is of lower affinity for soil organic matter than Cu in both soil groups. Metals' association with humic substances can be mostly justified on the basis of the hard-soft acid base concept by Pearson (1985). Although both Cu and Pb are borderline acids the previous one can be characterized as a harder acid than the latter one, resulting in higher affinity toward organic matter. On the other hand, both Cu and Pb were also found to be of high affinity to soil iron oxides. However, Cornu et al. (2005) found that metals forming stable hydroxide and carbonate complexes are preferentially bound to the (slightly) positively charged iron oxide surfaces. As Pb is much more able to form such complexes (hydroxide complexes in the acid Luvisol and carbonate ones in the alkaline non-Luvisol environments) than Cu, its higher affinity to iron oxides in the studied soils is expected. Although somewhat higher oxidizable ratios were found for both metals in the non-Luvisol (11.1 ± 5.2% for Cu and 17.0 ± 10.8% for Pb) than Luvisol samples (10.3 ± 7.1% for Cu and 14.2 ± 5.5% for Pb), a much more significant difference can be found when organic and mineral horizons are compared. We found that organic horizons can have a 1.5 to 2-times higher ratio of oxidizable Cu and Pb than the mineral horizons, independent of soil type, which can be related to the higher organic matter content of the topsoil.

As it can be expected, oxidizable Cu and Pb showed a close relationship with total organic content of the samples, primarily in the Luvisols and non-Luvisols, respectively (Tables 2 and 3). In this latter soil group both oxidizable metal fractions were also related to the silt fraction of the soils. Additionally, oxidizable Pb can be characterized by a positive relationship with total iron content and a negative one with sand, carbonate content and pH in the non-Luvisol samples. Such relationships cannot be explained by the geochemical or pedogenic characteristics of the studied metals or target phases. However, the joint enrichment of certain soil phases (such as resistant iron oxides and organic material) in some particle size fraction may occur without having any relationship between them.

The ratio of the weak acid soluble fractions is generally negligible for Cu (less than 1% of total Cu) and rarely exceeds 5% for lead. It is slightly higher in the organic horizons than in the mineral ones. These low ratios and high variances among the samples do not allow us to outline any clear relationships. This is also true for the exchangeable metal concentrations, which were, furthermore, often below the detection limit of the ICP-AES analyses. But when it is detectable in some samples its ratio never exceeds 0.5%. This is the general case for trace metals in soils since at natural soil metal concentrations mobile metal fractions are adsorbed at or precipitated as soil mineral phases fast (e.g. Aydinalp and Marinova 2003).

The acid-extractable Cu fraction showed a close positive relationship with clay and total Fe content of the samples but this is characteristic only of the Luvisols. On the other hand, acid-extractable Pb was related to the total organic carbon content in this soil group. These observations may suggest that Cu tends to adsorb on phases in the clay fraction (with iron content) and Pb rather on humic substances. This contradicts our findings on the behavior of these elements in the oxidizable and reducible fractions presented above. However, acid-extractable fractions only concern metal fractions which are easily mobilized from the surfaces of the soil constituents and do not allow us to distinguish between surfaces of different phases (Hall 1998). More specific analyses than simple extraction are necessary to estimate the real host phases of mobile trace metals in soils.

Sorption of Cu and Pb and its relation to soil properties

The results of the sorption experiments are presented in Table 4. The Langmuir and Freundlich isotherm equations were used to describe the sorption of the metals from the solution onto the studied soil samples. Both isotherms can be mostly used to fit the sorption data effectively for the studied samples. Sorption data is evaluated based on the Langmuir parameters Q_{max} and L as they provide useful information about the maximum sorption capacity of the adsorbent and about the affinity of the adsorbate for the surface, respectively, easing the comparison of the different samples. The relatively poor fit of the Langmuir isotherm for Cu sorption on the sample (6C) can be due

Table 4
Summary of the major parameters of the Langmuir and Freundlich isotherms received from the Cu and Pb sorption experiments

Sample	Cu						Pb					
	Langmuir			Freundlich			Langmuir			Freundlich		
	Qmax (mmol kg^{-1})	L	R^2	K_F (L mmol^{-1})	n	R^2	Qmax (mmol kg^{-1})	L	R^2	K_F (L mmol^{-1})	n	R^2
3A	126.6	2.03	0.98	74.7	0.262	0.99	196.1	1.70	0.95	102.9	0.270	0.99
3B	169.5	1.97	0.99	93.9	0.351	0.99	243.9	1.95	0.83	135.5	0.305	0.91
3C	204.1	1.48	0.98	102.2	0.362	1.00	212.8	5.22	1.00	138.1	0.270	0.98
6A	277.8	7.20	1.00	209.5	0.301	0.91	285.7	5.83	0.99	212.0	0.124	0.78
6B	172.4	1.57	0.98	90.0	0.319	1.00	222.2	3.75	0.99	138.3	0.163	0.95
6C	1111.1	45.00	0.57	3732.0	0.552	0.76	625.0	32.00	1.00	575.1	0.334	0.76

to the precipitation of Cu as carbonate in this sample, resulting in significantly different retention processes from those found in the other acidic-lightly acidic soil samples. Fontes et al. (2000) also found almost complete retention for Cu and Pb in limey soil samples. Their results indicated that the presence of carbonates in the soil created a new sorption site and also favored the precipitation of these metals. Mineralogical analyses of metal-treated soils by Sipos et al. (2008) showed that both Cu and Pb precipitated in alkaline soils as carbonates, but the sorption capacity of individual soil clay particles was also increased in such cases. Precipitation of cationic metals in soil occurs under alkaline conditions, relatively high metal concentrations, and low metal solubility, also in the case of the small number of specific adsorption sites (Brümmer 1986). In this sample the presence of carbonates led to an elevated pH level (soil pH = 8.26) which may have encouraged metal carbonate precipitation reactions. Young and MacDonald (1998) found that since Pb and Cu carbonates precipitate at lower pH than calcite, it is possible for these metals to precipitate in this form due to the dissolution of calcite. The equilibrium pH of the solution containing the highest metal concentrations was 6.87 and 5.92 for Cu and Pb, respectively. At this pH both Cu and Pb carbonates may form under natural soil conditions (Brookins 1988). As sorption isotherm parameters cannot be clearly evaluated for soils where precipitation occurs, only the carbonate-free samples will be compared separately below.

Among the carbonate-free samples, generally higher sorption capacity values were found for Pb than for Cu. Both metals can be characterized by high sorption affinities for soil components when compared to other transition metals, which is related to the differences in the metal-surface interaction (Berti and Jacobs 1996) and the effect of 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 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 and Zheng 2007).

The highest metal sorption was found for sample 6A with an almost similar sorption capacity for Cu (278 mmol kg^{-1}) and Pb (286 mmol kg^{-1}). This sample is characterized by the highest total organic carbon content (6.93%) among the studied ones. Based on the Langmuir parameter L related to the affinity of the adsorbent to the soil, both metals showed also the highest affinity for this sample. This suggests the important role of the soil organic matter in sorption of these metals. These results are in good agreement with those on the metal affinity sequence towards humic substances published by several authors (e.g. Sebastia et al. 2008). This trend follows the Irving–Williams series which describes the order of stability of organic-metal complexes. The order of this series arises in part from a decrease in ionic size and in part from ligand field effects (Huheey et al. 1993). This kind of behavior of metals during their sorption onto humic substances can also be justified on the basis of the Hard-Soft Acid Base concept (Pearson 1985). Additionally, direct extended X-ray absorption fine-structure spectroscopy observations by Manceau et al. (1996) on metal speciation in soils also showed that these metals form very stable chelate complexes, such as salicylate and catechol, resulting in much stronger binding when compared to mineral surfaces.

In the profile with montmorillonite, Cu sorption capacity decreases with the clay content from 204 to 127 mmol kg^{-1} despite the fact that its clay content decreases as total organic content increases. On the other hand, Pb showed the highest maximum sorption in the B horizon in this profile (244 mmol kg^{-1}), where clay minerals and pedogenic iron oxides are expected to accumulate. The B horizon of the soil containing vermiculite showed a similar sorption capacity (172 mmol kg^{-1}) to the B horizon of the soil containing montmorillonite (170 mmol kg^{-1}) for Cu, but the latter sorbed a bit higher amount of Pb (244 mmol kg^{-1}) than the former (222 mmol kg^{-1}). Although the clay content of sample 3B is higher (21 vs. 15%) its pedogenic iron content is lower than that of sample 6B (0.27% vs. 0.41%; data from Sipos et al. 2008). When the two types of soil clay mineralogy are compared, both metals can be characterized by higher affinity to the soil with montmorillonite than to that with vermiculite. According to Abollino et al. (2008), the affinity of these metals to vermiculite is high in a wide pH range (from 2.5 to 8) when compared to montmorillonite, where this range can be placed between the pH values of 6 and 8. As the equilibrium pH values are below this latter range for the studied acidic soil samples for both metals, the effect of pH is expected to be much higher for the samples with montmorillonite as the predominating clay mineral. This is in agreement with the observation of Abollino et al. (2003), who found that ion exchange is not the primary sorption process for the studied metals on montmorillonite and hence that they are more influenced by the pH. Due to the differences in the charge density of the studied metals Pb showed lower sorption capacity on montmorillonite. On the other hand, the effect of pH was found to be much less significant for metal sorption on vermiculite by Malandrino et al. (2006), so differences in their sorption could be related to their differences in the tendency to hydrolyze, which is higher for Pb than for Cu. However, the close association of soil iron oxides, primarily in the accumulation horizon of Luvisols, may significantly influence the metal sorption capacity of soils. This is supported by the transmission electron microscopy observation of Sipos et al. (2008) who found that the metal sorption capacity of individual clay particles in soils increases with their increasing Fe content. This can be due to the intimate association of these phases, probably in form of iron-oxide coatings on the surface of soil clay minerals. The joint presence of iron oxides and soil clay minerals may explain why we have observed higher lead than copper sorption on soils with montmorillonite, despite expecting the opposite to occur. The above-mentioned study by Sipos et al. (2008) also showed that Pb could be characterized by higher affinity to iron oxides than to clay minerals when compared to Cu, even when this latter metal was also present in the solution.

Summary and conclusions

In the studied soils with background metal concentrations, both Cu and Pb showed higher amounts in the acidic Luvisols than in alkaline non-Luvisols, although a higher rate of leaching can be expected in the former. Distribution of these elements within the profiles can be related to the major pedogenic processes characteristic of these soil types. Luvisols characterized by clay and iron oxide accumulation showed a slight Cu accumulation in their mineral horizons. On the other hand, alkaline non-Luvisols characterized by organic matter accumulation enrich both Cu and Pb in their organic horizons. This is also found for Pb in Luvisols, suggesting its accumulation in organic-rich horizons independent of soil type and characteristics.

Sequential extractions showed that Pb exhibited much higher mobility than Cu. The higher ratio of the residual fraction for Cu is in agreement with its enrichment in the mineral horizons in some soils. In this fraction both metals can be associated with resistant iron-containing phases, which are present in the clay and silt fractions of the Luvisols and non-Luvisols, respectively. The highest mobility was found in the mineral horizons of non-Luvisol samples for both Cu and Pb. This can be due to the occasional water-logging in some of these soils, resulting in more intense weathering and re-precipitation of iron and metal-containing phases, and also in their enrichment in the silt fraction. On the other hand, very similar residual ratios were found for Cu in soils where water-logging is absent, independent of soil types and properties suggesting its dominating presence in resistant phases. However, Pb showed much higher mobilization than Cu in the organic horizons of Luvisols as well, probably due to the acidic conditions and the presence of high amounts of organic material.

The fraction bound to pedogenic iron oxides is also significant for both metals but with much higher ratio for Pb than for Cu, independent of soil types as accumulation of such phases can be characteristic of both Luvisols and non-Luvisols with hydromorphism. This is supported by an increase of this ratio for Cu in the mineral horizons of both soil groups, whereas that of Pb does not, suggesting that iron migration within the soil profiles has much less effect on its distribution when compared to Cu.

As long as Pb showed higher amounts in the iron oxide-bound than in the organic matter-bound fraction, its reverse was found for Cu primarily in the organic horizons. The close relationship between organic matter-bound Pb and the iron content of the studied soils may suggest that the close association of Pb and Fe is primarily favored in the horizons rich in organic matter and/or that ternary complexes are preferentially formed there. However, this supposition requires expedient analyses to be proved correct.

Although high variance for the easily-soluble metal fractions was found for both metals in the studied soils, sorption analyses provided detailed information on the behavior of these metals in these fractions. In alkaline conditions, which are mostly characteristic of the non-Luvisols in our case, precipitation may be the primary immobilization process for both metals in form of carbonates, hydroxyl-carbonates and hydroxides. Generally, Pb showed higher sorption than Cu, which is in agreement with the observation that the former metal showed lower leaching from the topsoil of the acid Luvisol profiles than the latter. Both metals showed the highest affinity and sorption in the sample richest in organic matter, due to the fact that they are able to form stable chelate complexes. Samples characterized by clay mineral accumulation showed also high metal retention but the affinities of the studied metals for different kind of clay mineral species were highly dependent on pH. Moreover, it can be stated that joint accumulation of clay minerals and iron oxides significantly influence the sorption properties of samples with such characteristics, rendering the evaluation of results more difficult.

In conclusion, Cu and Pb reaching the topsoil in mobile form can be immobilized rapidly and strongly by soil organic matter with higher affinity for Cu than for Pb. At acidic conditions, slow leaching of both metals is expected, with higher efficiency for Cu as Pb is preferentially immobilized, especially in horizons where high amounts of both organic matter and iron oxides are present. Downward migration of Cu may result in its adsorption on clay surfaces and/or co-precipitation with iron oxides, whereas these latter phases are the preferred ones for the immobilization of Pb. At alkaline conditions, however, both metals are expected to be precipitated in form of carbonate and/or hydroxyl-carbonate.

Methods with different approaches used in this study to explore the effect of soil properties on Cu and Pb distribution and migration were found to be effectively complementary for each other. Data obtained from the sequential chemical extractions provide useful information to complete those obtained from the total metal contents, and, similarly, sorption data can be used to efficiently complete the results of sequential extraction data.

Acknowledgements

The authors are grateful for the financial support of the Hungarian Scientific Research Fund (OTKA K43445 and K105009). Péter Sipos also thanks for the support of the Bolyai János Research Scholarship of the Hungarian Academy of Sciences. Dr. Gábor Bozsó and Dr. Péter Csathó are also thanked for their relevant comments that helped to improve the manuscript.

References

Abollino, O., M. Aceto, M. Malandrino, C. Sarzanini, M. Mentasti 2003: Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. – Water Research, 37, pp. 1619–1627.

Abollino, O., A. Giacomino, M. Malandrino, E. Mentasti 2008: Interaction of metal ions with montmorillonite and vermiculite. – Applied Clay Science, 38, pp. 227–236.

Alloway, B.J. 1990: Heavy Metals in Soils. – Blackie and Sons, London.

Aydinalp, C., S. Marinova 2003: Distribution and forms of heavy metals in some agricultural soils. – Polish Journal of Environmental Studies, 5, pp. 629–633.

Berti, W.R., L.W. Jacobs 1996: Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. – Journal of Environmental Quality, 3, pp. 250–253.

Bielicka-Giełdoń, A., E. Ryłko, K. Żamojć 2013: Distribution, bioavailability and fractionation of metallic elements in allotment garden soils using the BCR sequential extraction procedure. – Polish Journal of Environmental Studies, 22, pp. 1013–1021.

Bingham, F.T., A.L. Page, R.J. Mahelr, T.J. Ganje 1976: Cadmium availability to rice in sludge amended soil under flood and non-flood cultures. – Soil Science Society of America Journal, 40, pp. 715–719.

Blume, H.P., U. Schwertmann 1969: Genetic evaluation of profile distribution of aluminum, iron and manganese oxides. – Soil Science Society of America Proceedings, 33, pp. 438–444.

Bradl, H.B. 2004: Adsorption of heavy metal ions on soils and soil constituents. – Journal of Colloid and Interface Science, 277, pp. 1–18.

Brookins, D.G. 1988: Eh-pH Diagrams for Geochemistry. – Springer-Verlag, New York.

Brümmer, G.W. 1986: Heavy metal species, mobility and availability in soils. – In: Bernhard, M., F.E. Brinckman, P.J. Sadler (Eds): Dahlem Workshop on the Importance of Chemical “Speciation” in Environmental Processes. – Springer-Verlag, Berlin, pp. 169–192.

Brümmer, G.W., J. Gerth, U. Herms 1986: Heavy metal species, mobility and availability in soils. – Zeitschrift für Pflanzenernährung und Bodenkunde, 149, pp. 382–398.

Cornu, S., V. Deschatrettes, S. Salvador-Blanes, B. Clozel, M. Hardy, S. Branchut, L. Le Forestier 2005: Trace element accumulation in Mn-Fe-oxide nodules of a planosolic horizon. – Geoderma, 125, pp. 11–24.

Elliot, H.A., M.R. Liberati, C.P Huang 1986: Competitive adsorption of heavy metals by soils. – Journal of Environmental Quality, 15, pp. 214–219.

Fontes, M.P.F., A.T. de Matos, L.M. da Costa, J.C.L. Neves 2000: Competitive adsorption of zinc, cadmium, copper, and lead in three highly weathered Brazilian soils. – Communications in Soil Science and Plant Analysis, 31, pp. 2923–2958.

Hall, G.E.M. 1998: Analytical perspective on trace element species of interest in exploration. – Journal of Geochemical Exploration, 61, pp. 1–19.

Hernandez, L., A. Probst, J.L. Probst, E. Ulrich 2003: Heavy metal distribution in some French forest soil: evidence for atmospheric contamination. – Science of the Total Environment, 312, pp. 195–219.

Huheey, J.E., E.A. Keiter, R.L. Keiter 1993: Inorganic Chemistry: Principles of Structure and Reactivity. – Harper Collins College Publishers, New York.

Ji, Y., Y. Feng, J. Wu, T. Zhu, Z. Bai, C. Duan 2008: Using geoaccumulation index to study source profiles of soil dust in China. – Journal of Environmental Science, 20, pp. 571–578.

Kabala, C., B.R. Singh 2001: Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. – Journal of Environmental Quality, 30, pp. 485–492.

KvVM-EüM-FVM decree No. 6/2009 on the threshold limit values for the protection of soil and water. – http://www.complex.hu/jr/gen/hjegy_doc.cgi?docid=A0900006.KVV

Lång, L.-O. 2000: Heavy mineral weathering under acidic soil conditions. – Applied Geochemistry, 15, pp. 415–423.

Li, X., B.J. Coles, M.H. Ramsey, I. Thornton 1995: Sequential extraction of soils for multielement analysis by ICP-AES. – Chemical Geology, 124, pp. 109–123.

Lu, A., S. Zhang, X. Shan 2005: Time effect on fractionation of heavy metals in soils. – Geoderma, 125, pp. 225–234.

Malandrino, M., O. Abollino, A. Giacomino, M. Aceto, E. Mentasti 2006: Adsorption of heavy metals on vermiculite: Influence of pH and organic ligands. – Journal of Colloid and Interface Science, 299, pp. 537–546.

Manceau, A., M.-C. Bosset, G. Sarret, J.-L. Hazemann, M. Mench, P. Cambier, R. Prost 1996: Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. – Environmental Science and Technology, 30, pp. 1540–1552.

McKenzie, R.M. 1980: The adsorption of lead and other heavy metals on oxides of manganese and iron. – Australian Journal of Soil Research, 18, pp. 61–73.

Morera, M.T., J.C. Echeverría, C. Mazkarián, J.J. Garrido 2001: Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. – Environmental Pollution, 113, pp. 135–144.

Ódor, L., I. Horváth, U. Fügedi 1997: Low-density geochemical mapping in Hungary. – Journal of Geochemical Exploration, 60, pp. 55–66.

Oliveira, T.S., M.P.F. Fontes, L.M. da Costa, A.H. Horn 2000: Relationship between magnetization and trace element contents in Brazilian soils from different parent materials. – Soil Science, 165, pp. 825–834.

Palumbo, B., M. Angelone, A. Bellanca, C. Dazzi, S. Hauser, R. Neri, J. Wilson 2000: Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. – Geoderma, 95, pp. 247–266.

Pearson, R.G. 1985: Absolute electronegativity and absolute hardness of Lewis acids and bases. – Journal of American Chemical Society, 107, pp. 6801–6806.

Probst, A., L. Hernandez, J.L. Probst, E. Ulrich 2003: Heavy metals in some French forest soils: Distribution, origin and controlling factors. – Journal of Physics IV France, 107, pp. 1107–1110.

Sebastia, J., F. van Oort, I. Lamy 2008: Buffer capacity and Cu affinity of soil particulate organic matter (POM) size fractions. – European Journal of Soil Science, 59, pp. 304–314.

Sipos, P., T. Németh, V. Kovács Kis, I. Mohai 2008: Sorption of copper, zinc and lead on soil mineral phases. – Chemosphere, 73, pp. 461–469.

Sipos, P., T. Németh, Z. May, Z. Szalai 2011: Accumulation of trace elements in Fe-rich nodules in a neutral-slightly alkaline floodplain soil. – Carpathian Journal of Earth and Environmental Sciences, 6(1), pp. 13–22.

Usero, J., M. Gamero, J. Morillo, I. Garcia 1998: Comparative study of three sequential extraction procedures for metals in marine sediments. – Environment International, 24, pp. 487–496.

Wilcke, W., S. Kretzschmar, M. Bundt, G. Saborío, W. Zech 1998: Aluminum and heavy metal partitioning in A horizons of soils in Costa Rica coffee plantations. – Soil Science, 163, pp. 463–471.

Young, R.N., E.M. MacDonald 1998: Influence of pH, metal concentration, and soil component removal on retentation of Pb and Cu by an illitic soil. – In: Jenne, E. (Ed.): Adsorption of Metals by Geomedia: Variables, Mechanisms, and Model Applications. – Academic Press, New York, pp. 229–254.

Zhang, M., S. Zheng 2007: Competitive adsorption of Cd, Cu, Hg and Pb by agricultural soils of the Changjiang and Zhujiang deltas of China. – Journal of Zhejiang University of Sciences A, 8, pp. 1808–1815.