Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry

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ABSTRACT

In order to determine the mobility of Pb, Zn and Cd in soils from the Příbram region (Czech Republic) heavily contaminated by metallurgy, two profiles of alluvial soils were closely studied. Total contents of heavy metals were determined after digestion with a mixture of HF and $HClO_4$. Heavy metal mobility was assessed using the mobility factor (MF) that represents the proportion of heavy metals present in the exchangeable and carbonate bound fraction based on the Tessier's sequential extraction procedure. The MF ranged from 2 to 46% for lead, 19 to 62% for zinc and 61 to 94% for cadmium. The profile distribution of zinc and cadmium showed a variable development with depth, which is caused by high amounts of these metals present in labile forms. The profile distribution of lead (the least mobile metal) is characterized by a gradual decrease with depth. The results indicate a higher contamination of the soil profile situated 2.5 km away from the smelter in comparison with the profile in its close vicinity. This fact confirms the existence of extreme fluvial contamination.

Keywords: soil; heavy metals; mobility; profile distribution

One of the anthropogenic activities that negatively influences the environment is metallurgical activity. Heavy metals that accumulate in soils in the vicinity of metal-processing factories can enter food chains and thus directly influence man's health. The risk of occurrence of these elements is mostly defined by their mobile fractions rather than their total concentration in soils (Němeček et al. 1998). The key to the determination of heavy metal mobility and thus the bioavailability is a precise definition of their distribution into separate soil fractions (Song et al. 1998, Li and Thornton 2001). The most common method used for the determination of trace element fractionation in soils and sediments is the method of sequential extraction. The number of successful applications of this method is rising because these extraction techniques provide information about heavy metal affinity to soil components and the strength of the bonds to the matrix (Narwal and Singh 1998). Sequential extractions provide information about mobile and stable fractions of heavy metals in soils and it is therefore possible to estimate the actual and potential mobility of the studied elements. Different types of sequential extractions were summarized in the work of Chao (1984).

There have been many variants of sequential extractions published, but most of them are based on the procedure suggested by Tessier et al. (1979). In many recent studies concerning determination of heavy metal speciation in contaminated soils and sediments (e.g. Durn et al. 1999, Rieuwerts et al. 1999, Song et al. 1999, Li and Thornton 2001) the original or a slightly modified procedure by Tessier et al. (1979), eventually the revised version suggested by Hall et al. (1996) has been used. The sequential extraction by Tessier allows separating heavy metals into the following fractions: (i) exchangeable, (ii) bound to carbonates, (iii) occluded in Fe and Mn oxides and hydroxides, (iv) forming organometallic complexes and sulfides, (v) strongly bound to silicates (Tessier et al. 1979). Heavy metal mobility is determined by the amount of the metal present in fractions (i) and (ii). Kabala and Singh (2001) highlight the fact that heavy metals in these fractions are mobile or easily mobilizable in natural soil conditions and therefore represent the highest environmental risk.

Soils in areas contaminated by metallurgical activities often contain high amounts of heavy metals. Many authors showed that soils in the vicinity of lead smelters contain more than 30 000 mg Pb/kg, 20 000 mg Zn/kg, and 90 mg Cd/kg (Gzyl 1995, Jung and Thornton 1996, Rieuwerts et al. 1999, Basta and Gradwohl 2000, Ettler et al. 2005).

The aim of this study was to determine the level of Pb, Zn and Cd contamination and mobility in selected alluvial soils in the Příbram region. Alluvial soils, compared to other soils, represent a specific soil group that can be contaminated not only by heavy particle deposition but also by contaminated water during floods (Borůvka et al. 1996).

MATERIAL AND METHODS

Description of the study area

The Příbram region, situated approx. 60 km SW of Prague (Czech Republic), has had a long history of Pb and Ag processing. The smelter itself is placed in the Litavka River valley, approximately 3 km NW of Příbram center. Anthropogenic contamination of alluvial soils in the valley of the river Litavka originates from two main sources. The first source are emission outputs from the metallurgical industry. The second and the more important one is represented by floods of contaminated water from metallurgical setting pits whose barriers have been damaged several times. The smelter has been operational since 1786. The Pb-Ag ore mined in the Příbram district had been processed here until 1972. Since then, ore processing has been replaced by secondary processing of Pb batteries.

Sampling sites

Two profiles of alluvial soils were sampled. They were localized 0.5 km (Profile 1) and 2.5 km (Profile 2) away from the smelter (distance between the profiles is 2.3 km) (Figure 1) in order to examine how the total contents of Pb, Zn and Cd change with increasing distance from the source of contamination. Soil samples were collected from dug pits down to the depth of 100 to 120 cm. Six and five horizons of studied soils were distinguished in the Profiles 1 and 2, respectively. The soils were classified as Gleyic Fluvisols (WRB 1998).

Sample preparation

All soil samples were air dried to constant weight, sieved through a stainless sieve (diameter 2 mm) and homogenized. An aliquot part of 30 g obtained by quartering was finely ground in a planetary agate mortar (Fritsch, Germany) and used for analytical procedures (total concentrations of Pb, Zn, Cd, total C and S). The fraction < 2 mm was used for sequential extractions in order to preserve in site soil composition.

Soil properties

Soil pH was measured using an inoLab Level 1 pH meter (Germany) in suspension soil/boiled distilled water (1:2 ratio). Soil stirring for 5 minutes preceded pH measurements. Total C and S concentrations were determined using a LECO CNS 2000 analyzer (MI, USA). For the cation exchange capacity, the soil was saturated by Na cations with 1M NaOAc. The adsorbed Na cations were subsequently released through the use of 1M NH$_4$OAc (Podlešáková et al. 1992). Sodium concentrations were determined using FAAS (Varian SpectrAA 200 HT, Australia).

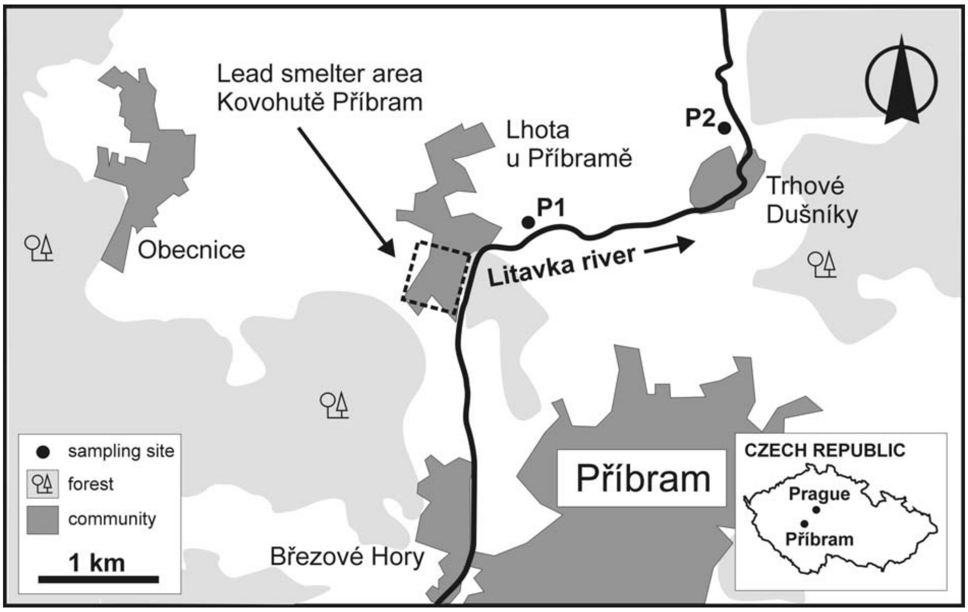

Figure 1. Location of the study area and soil profiles (P1 and P2)

Bulk concentrations

An amount of 0.2 g of dried sample was dissolved using a mixture of hot acids (10 ml of HF and 0.5 ml of $HClO_4$) and evaporated to dryness. This procedure was repeated with HF (5 ml) and $HClO_4$ (0.5 ml) in order to totally dissolve all the silicates present. The residue obtained was dissolved in 100 ml of 2% HCl. During the analytical procedure MilliQ+ deionized water and twice distilled acids HF, $HClO_4$, HCl (Merck, Germany) were used. Heavy metal concentrations in solutions were determined using a flame atomic absorption spectrometer (FAAS) Varian SpectrAA 200 HT (Australia) under standard analytical conditions.

Heavy metal mobility

In order to determine Pb, Zn and Cd mobility, the classical sequential extraction by Tessier et al. (1979) was used.

1 g of dried sample was placed into 100 ml PE centrifuge tubes. The extraction procedure was as follows:

(A) – exchangeable fraction. Samples were extracted with 8 ml of 1M $MgCl_2$ (pH = 7.0) and continually shaken for a period of 1 hour (at 20°C).

(B) – fraction bound to carbonates. The residue left after fraction A was extracted with 8 ml of 1M NaOAc (pH = 5.0) and continually shaken for a period of 5 hours (at 20°C).

(C) – fraction bound to Fe and Mn oxides and hydroxides. The residue left after fraction B was extracted with 20 ml of 0.04M $NH_2OH.HCl$ in 25% acetic acid (HOAc) and occasionally shaken for a period of 6 hours (at 96 ± 3°C).

(D) – fraction bound to sulfides and to organic matter. 3 ml of 0.02M HNO_3 and 5 ml of 30% H_2O_2 were added to the residue left after fraction C. A pH of 2.0 was achieved using HNO_3. This mixture was kept at 85 ± 2°C for a period of 5 hours and occasionally shaken. 5 ml of 30% H_2O_2 were added after 1.5 and 3 hours. 5 ml of 3.2M NH_4OAc in 20% HNO_3 were added into the cooled mixture.

(E) – residual fraction. 10 ml of HF and 2 ml of $HClO_4$ were added to the residue left after fraction D and the sample was evaporated. This procedure was repeated twice. The residue left was dissolved in 50 ml of 2% HCl.

All the leachates (except fraction E) were separated from the solid phase using centrifugation. Each residue was washed with 2 ml of deionized water before the following step in order to totally wash out the last reagent. The solution obtained was added to the leachate from the last step, acidified using 1 ml of concentrated HNO_3 dissolved in deionized water, transferred into a 50 ml flask, and Pb, Zn and Cd concentrations in all separate fractions were determined using FAAS (Varian SpectrAA 200 HT, Australia).

RESULTS AND DISCUSSION

Soil properties

Selected chemical properties of the studied soils are presented in Table 1. Soil pH reached lower value in the Profile 1 in comparison with the Profile 2. The highest total carbon content was detected in surface horizons (2.97% in Profile 1 and 2.94% in Profile 2) in both profiles. Cation exchange capacity varied from 11 to 29 cmol/kg.

Table 1. Location of the profiles and basic chemical properties of studied soils

Profile location	Distance to smelter	Horizons	Depth (cm)	pH (H_2O)	Total C (%)	Total S (mg/kg)	CEC (cmol/kg)
1	Lhota 0.5 km NE	Ahg	0–15	4.34	2.965	506.9	17.5
		Go	15–25	4.73	0.919	194.7	19.5
		Gro_1	25–35	4.79	0.914	102.7	18.0
		Mg	35–55	4.61	0.712	70.4	14.5
		Gro_2	55–85	4.94	0.191	26.0	16.5
		Gr	85+	4.96	0.147	15.8	11.0
2	Trhové Dušníky 2.5 km NE	Ah	0–15	6.03	2.944	367.5	29.5
		Go	15–25	5.53	0.660	97.6	14.5
		Gro	25–35	5.26	1.318	183.4	16.0
		Gor_1	35–50	5.18	1.038	139.5	15.0
		Gor_2	50+	5.50	0.577	67.4	16.5

Table 2. Mobility factors, sums of the fractions obtained by sequential extraction, and total contents of Pb, Zn and Cd

Profile location		Depth (cm)	*MF*			Sum of fractions			Total content		
			Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd
			(%)			(mg/kg)			(mg/kgú		
1	Lhota	0–15	26	23	61	4325	1984	23	4705	2014	26.0
		15–25	15	28	72	3074	3664	47	3150	3395	45.0
		25–35	46	43	94	1706	2164	49	1505	2084	24.5
		35–55	31	62	90	242	1561	21	55	1382	19.0
		55–85	26	39	85	78	468	5	15	501	3.0
		85+	34	36	81	81	357	4	20	333	3.0
2	Trhové Dušníky	0–15	21	19	71	4344	3660	33	4500	3687	31.0
		15–25	34	22	76	3416	2965	20	3640	3230	18.5
		25–35	31	25	81	2816	4970	42	3125	8728	67.5
		35–50	20	27	85	961	3997	42	875	3552	40.0
		50+	2	25	72	1252	2497	43	1185	2512	42.0

Total contents and mobility of Pb, Zn and Cd

Total Pb, Zn and Cd contents in separate horizons determined through HF and $HClO_4$ dissolution are summarized in Table 2 and Figure 2. Pb content ranged from 20 to 4705 mg/kg, Zn from 333 to 8728 mg/kg and Cd from 3.0 to 67.5 mg/kg. The determined contents considerably exceed Czech regulation limits (140 mg/kg for Pb, 200 mg/kg for Zn and 1 mg/kg for Cd) (Czech Regulation, 13/1994). The increased contents of heavy metals are most probably caused by floods of contaminated water (Borůvka et al. 1996) and, to a lesser extent, by industrial emission outputs originating from metallurgy (Rieuwerts et al. 1999, Ettler et al. 2005). Profile distributions of Zn and Cd are variable. This is caused by different soil development and the history of contamination. In the case of periodically flooded alluvial soils, the transfer of labile forms of heavy metals through the soil profile with the increase of their total contents in the depth could not be eliminated. This finding was published by Borůvka et al. (1996). It was confirmed that lead distribution shows a fluent decrease with depth (Figures 2a, b), which is in accordance with other studies (Borůvka et al. 1996, Ettler et al. 2005). Total Pb, Zn and Cd contents at Profile 2 were higher compared to Profile 1 (the only exception is the higher amount of Pb in the humic horizon). Profile 2 was also significantly more contaminated in deeper horizons than Profile 1. Cd content in this profile reached 42 mg/kg in the deepest horizon, while the content in the humic horizon was 31 mg/kg (Figure 2f). High contents of the studied elements are probably caused by a gradual migration of labile forms and their intensive accumulation in areas remoter from the smelter.

Determination of heavy metal mobility is based on the relative amount of the metal in the exchangeable fraction (A) containing the mobile forms and in the carbonate bound fraction (B) containing easily mobilizable phases. The mobility index of Pb, Zn and Cd was expressed as the mobility factor (MF) based on the following equation by Kabala and Singh (2001):

$$MF = [(A + B)/(A + B + C + D + E)] \times 100\ (\%)$$

The results are summarized in Table 2. Despite the relatively lower mobility of the carbonate bound fraction compared to the exchangeable fraction, the mobility factor represents overall potential mobility (Kabala and Singh 2001). The results confirmed the highest mobility of Cd in comparison to the other elements (Figures 2e, f), because of the highest values of MF; e.g. in the horizon Gro_1 (of Profile 1) the MF (Cd) reached 94%. The second most mobile metal was zinc (Figures 2c, d); in the horizon Mg of Profile 1 the MF (Zn) reached 62%. The increased contents of Cd and Zn in subsurface horizons of the studied profiles confirmed their high mobility. The lowest mobility of Pb presented in Figures 2a, b corresponds to the work of Němeček et al. (1998). The increased content of Pb in deeper horizons

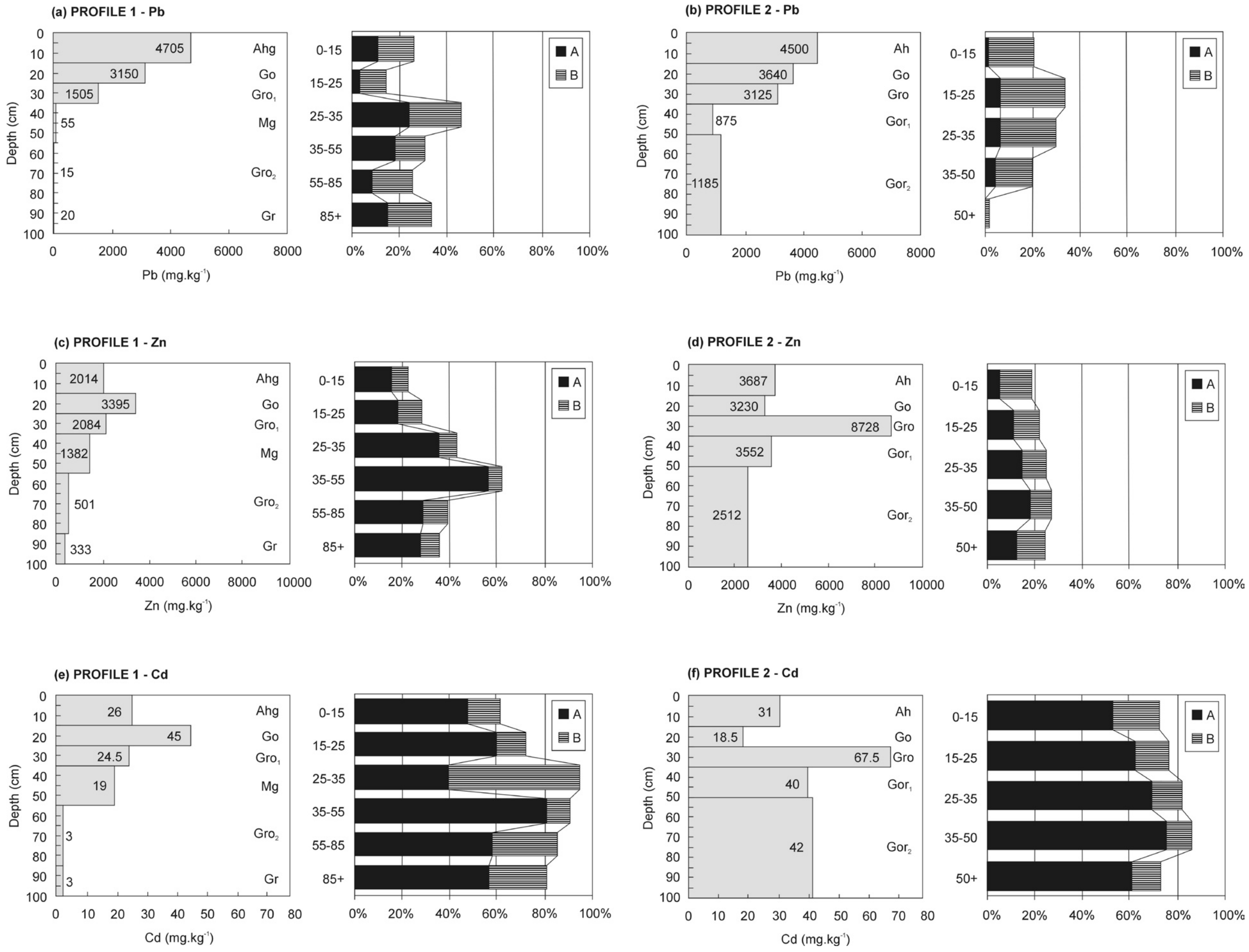

Figure 2. Lead, zinc and cadmium contents and distributions of exchangeable (A) and carbonate (B) fractions of sequential extraction by Tessier et al. (1979)

(especially at Profile 2) could be explained by historical contamination originating from long-term mining and smelting activities and partial transfer of Pb in soil profile. Moreover, low content of Pb mobile fractions was detected in the deepest horizon Gor$_2$ (Figure 2b).

The results presented above confirmed the heavy fluvial contamination of the studied alluvial soils by Pb, Zn and Cd and the presence of Cd and Zn in mobile exchangeable fraction. Therefore Cd and Zn represent the highest potential risk for the surrounding environment.

Acknowledgments

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ABSTRAKT

Mobilita olova, zinku a kadmia v aluviálních půdách silně kontaminovaných metalurgickou činností

S cílem ověřit mobilitu Pb, Zn a Cd byly podrobně studovány dva profily aluviálních půd Příbramska (Česká republika) silně kontaminovaných metalurgickou činností. Celkové koncentrace kovů byly stanoveny po rozkladu směsí kyselin HF a $HClO_4$. Mobilita těžkých kovů byla určena pomocí mobilitního faktoru (MF), který vyjadřuje poměrné zastoupení výměnné frakce a frakce vázané na karbonáty, stanovených Tessierovou sekvenční extrakcí. MF se pohyboval v rozmezí 2–46 % u Pb, 19–62 % u Zn a 61–94 % u Cd. Distribuce Zn a Cd v půdních profilech vykazovaly proměnlivý vývoj spolu s výrazným hloubkovým posunem, který byl způsoben právě vysokým zastoupením jejich labilních forem. Distribuce Pb jako nejméně mobilního kovu měla směrem do hloubky profilů plynule klesající charakter. Bylo zjištěno, že půdní profil vzdálený 2,5 km od hutního závodu je kontaminován mnohem více než profil v jeho těsné blízkosti. Tento fakt potvrzuje existenci extrémní fluviální zátěže.

Klíčová slova: půda; těžké kovy; mobilita; distribuce

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