ORIGINAL PAPER

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ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution

Received: 20 June 2003 / Revised: 2 August 2003 / Accepted: 14 August 2003 / Published online: 9 October 2003 © Springer-Verlag 2003

Abstract The Pb isotopic composition (206Pb/207Pb and ²⁰⁸Pb/²⁰⁶Pb) in smelter-impacted soils was measured using a quadrupole-based ICP-MS. Four forest/tilled soil profiles were sampled according to the distance from the lead smelter in Příbram (Czech Republic), prevailing wind direction, geological background and soil type. The results were compared with the Pb isotopic composition of bedrocks and waste materials from Pb metallurgy (smelting slags, air-pollution-control residues). The isotopic composition of soils confirms the predominant role of metallurgy on the general pollution in the area. The highly contaminated soils from the vicinity of the smelter contain up to 35,300 mg Pb kg⁻¹ and exhibit an isotopic composition close to that of car battery processing (²⁰⁶Pb/²⁰⁷Pb up to 1.177). A coupled concentration/isotopic study of soil profiles showed that the smelter-induced pollution had penetrated even to the mineral soil horizons, indicating an important vertical mobility of Pb contaminant within the soil profile. The calculated downward penetration rate of Pb in soils ranges from 0.3 to 0.36 cm year⁻¹.

Keywords Pb isotopes $\cdot {}^{206}Pb/{}^{207}Pb \cdot ICP-MS \cdot Soil \cdot Pollution \cdot Metallurgy \cdot Penetration rate$

Introduction

Lead is one of the most common anthropogenic contaminants in ecosystems. However, knowledge of Pb concentrations alone does not provide sufficient evidence of anthropogenic contamination, since a considerable amount of lead may also result from natural processes [1]. Recently, a number of studies showed the utility of stable Pb isotopes as tracers of pollution sources in peatbogs [2], sediments [3], soils [1, 4, 5, 6], snow samples and aerosols

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[7]. Lead ores display a characteristic isotopic composition (signature), which does not change during the physical or physicochemical processes associated with smelting, refining and manufacturing [7]. Thus, stable Pb isotopes represent a powerful tool for tracing the origin of contamination, such as coal or gasoline combustion and ore smelting [2].

The studies of Pb concentrations in soils contaminated by smelting activity represent the first step in evaluating the degree of pollution [8]. It has been found that in smelting areas, metallurgical activity is the principal source of soil pollution via atmospheric emissions [8]. Airborne Pb is accumulated in topsoil layers, but can be mobilised in deeper soil horizons [9, 10, 11].

The purpose of this article is to determine the Pb isotopic composition of individual horizons in four forest/ tilled soil profiles sampled in the vicinity of the lead smelter of Příbram, Czech Republic. The surface distribution of Pb in this area was studied by Rieuwerts et al. [8], who measured up to 58,500 mg Pb kg⁻¹ in superficial soil horizons. To date, no Pb isotopic data are available for such heavily polluted soil systems. This paper reports some new information on the application of Pb isotopes for tracing the pollution in soils extremely contaminated by Pb metallurgy. In order to clarify the origin, distribution and mobility of Pb in these soil profiles, additional Pb isotopic analyses were performed on other materials, such as (i) metallurgical slags previously studied by Ettler et al. [12], (ii) air-pollution-control (APC) residues from lead metallurgy resulting from historically different smelting technologies, (iii) bedrocks corresponding to each soil profile, (iv) galena (PbS) from the Příbram mining district and (v) fly-ash from gasoline combustion sampled in a tunnel in Prague, Czech Republic. This approach, together with the knowledge of historical evolution of smelting technologies in the area, is useful for the determination of the Pb penetration rate in soil profiles.

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Experimental

Sampling of soils and other materials

The studied soils originate from the vicinity of a secondary Pb smelter operating for more than 200 years, located 4 km NW from the centre of Příbram, Czech Republic. More information on smelter activity and metallurgical waste production is given elsewhere by Ettler et al. [12]. It is important to note that the smelting of polymetallic ores from the Příbram mining district was replaced in 1972 by smelting of old car batteries and other secondary Pb sources.

Four soil profiles were sampled as a function of the geological background, distance from the smelter and the prevailing direction of winds in the area. Profiles S1 (forest soil) and S2 (tilled soil) are located 1 km SE from the smelter stack in the prevailing wind direction (sampling site 1). The distance between profiles S1 and S2 was 20 m. These soil profiles were developed on the Proterozoic volcano-sedimentary complex (basalt veins in clastic sedimentary rocks), which belongs to the polymetallic ore formation of the Příbram mining district. The soils are classified as cambisols and are located in the area with the highest lead concentrations in topsoil layer [8]. Profiles S3 (forest soil) and S4 (tilled soil) are located 3 km NW from the smelter stack against the prevailing wind direction (sampling site 2). The distance between profiles S3 and S4 was 20 m. These soil profiles were developed on the Cambrian

geological units, composed of greywackes and conglomerates. The soils of these profiles are classified as gleyic cambisols.

Soils were sampled in a 1×1 -m-large pit according to the natural development of soil horizons. The soils were sampled down to the mineral horizon C. The surface horizon composed of fresh grass cover, and fresh litter (down to 4 cm maximum) was removed (Fig. 1). If a sampled horizon was thick, a splitting into two horizons according to depth was performed (profile S2, Fig. 1b). The debris of corresponding underlying bedrock was sampled under each soil profile (up to 5 kg of solid rock material). Soil samples were stored in plastic bags and immediately treated on returning to the laboratory.

Smelter-derived materials such as the lead–zinc metallurgical slags from historically different technologies previously studied by Ettler et al. [12] and the APC residues from flue gas treatment technology from 1986 were sampled thanks to the courtesy of the Technical Director of the Příbram smelter. A sample of galena from the Příbram mining district was obtained from the Mineralogical Collections of Charles University, Prague, Czech Republic. Fly-ash resulting from petrol combustion was sampled in September 2002 in the ventilation pipes of the Letná tunnel in Prague, Czech Republic.

Sample preparation and Pb concentration analysis

Soil samples were air-dried in the laboratory (to constant weight) and sieved through an acid-cleaned polyethylene 2-mm sieve and

Fig. 1a–d Depth evolution of Pb concentrations and ²⁰⁶Pb/ ²⁰⁷Pb isotopic ratios in smelterimpacted soils from Příbram, Czech Republic: **a** highly contaminated forest soil profile S1, **b** highly contaminated tilled soil profile S2, **c** less contaminated forest soil profile S3, **d** less contaminated tilled soil profile S4



homogenised. The aliquot part was finely ground in an agate mortar. A mass of 0.2 g of dry sample was dissolved in 10 mL of hot HF and 0.5 mL HClO₄ and evaporated to dryness. The procedure was repeated with 5 mL HF and 0.5 mL HClO₄ in order to totally remove silica from the sample. The residue was then dissolved in 2 mL nitric acid and diluted to 100 mL. All the acids used in the dissolution procedure were reagent grade (Merck, Germany) and double distilled. The MilliQ+ deionised water obtained from a Millipore system was used for all dilutions. Total Pb concentrations were determined by using a Varian SpectrAA 200 HT flame atomic absorption spectrophotometer under standard analytical conditions. Ten randomly selected samples were prepared in replicates. The RSD for Pb concentration measurements of second replicate were <3%. Other materials (slags, APC residues, tunnel fly-ash, bedrocks and galena) were finely ground in an agate mortar and subsequently dissolved by the same procedure as soil samples, with the exception of initial dissolved mass (0.05 g for slags, fly-ash and APC residues; 0.01 g for galena).

Pb separation

In order to minimise the matrix effect during the ICP-MS measurement of Pb isotopic ratios, a preliminary separation of Pb was performed by using a modified conventional separation technique [13, 14, 15]. Lead was separated in a clean air box by using 10-mL Eppendorf pipette tips filled with 5 mL of anion exchange resin AG1X8 (Bio-Rad). Before being placed in the tips, the exchange resin was cleaned in 6 N HCl for 7 days, and the tip apertures were filled with acid-washed glass fibres. From each dissolved sample an aliquot part containing 250 ng Pb was evaporated to dryness in a Teflon beaker (Savillex, USA). The residue was dissolved in 5 mL of 5 N HBr and left overnight on a hotplate. The next day the sample was evaporated to dryness and dissolved in 5 mL of 0.5 M HBr and loaded into the separation column. The sample in the column was washed twice with 5 mL of 0.5 N HBr and finally eluted with 2.5 mL of 6 N HCl into the Savillex Teflon beaker. The sample was evaporated to dryness and dissolved in 10 mL of 2% HNO₃. All the acids used in the lead purification procedure were double distilled. Procedural blank was lower than 10 ng Pb (4% as relative concentration). The final Pb concentration in purified sample was 25 ± 5 ng mL⁻¹ for all analysed samples.

ICP-MS measurements of Pb isotopes

A VG Elemental PlasmaQuad 3 quadrupole-based ICP-MS was used for the isotopic measurements of lead. Detailed analytical conditions are given in Table 1. Calibration against the NIST SRM 981 (a common lead isotopic standard) was performed after every

 Table 1
 Operating conditions used for ICP-MS measurements

 of lead isotopes (VG Elemental PQ3)

Parameter	Value		
RF power (W)	1,350		
Gas flows (L min ⁻¹) (Ar 5.0)	Cooling 13.5, auxiliary 1.3, carrier 0.78		
Acquisition time	10×50 s		
Nebuliser	Meinhard-type, conical, microconcentric		
Acquisition mode	Peak jump		
Points per peak	3		
Dwell time (ms)	10.24		
Quad settle time (ms)	10		
Replicates	10		
Detector mode	Pulse		

sample in order to correct mass bias and dead time effects. During the analytical procedure, the following isotopes were measured: ²⁰⁰Hg, ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²⁰⁹Bi. The standard Hg correction was used for the ²⁰⁴Pb isotope. Subsequently, only ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios are discussed, as they show the most significant differences between contaminated and natural background materials and are mostly interpreted in environmental studies [16]. The standard error for ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb measurements was <0.3% RSD and <0.4% RSD (1*σ*), respectively. The accuracy of the measurements was controlled by AGV-2 (andesite; ²⁰⁶Pb/²⁰⁷Pb=1.2085±0.0006, ²⁰⁸Pb/²⁰⁶Pb=2.0415±0.0013) and BCR-2 (basalt; ²⁰⁶Pb/²⁰⁷Pb=1.2007±0.0007, ²⁰⁸Pb/²⁰⁶Pb=2.0635±0.0016) reference materials certified by the US Geological Survey (1998).

Results and discussion

Pb concentration profiles

Sampling site 1 (highly contaminated soils S1 and S2)

Extremely high Pb concentrations were found in the subsurface horizons of the forest soil located in the prevailing wind direction (profile S1, up to $35,300 \text{ mg Pb kg}^{-1}$, Fig. 1a). The highest concentrations were in surface and subsurface forest soil horizons (A₀ and A₁) and significantly decreased with depth. The highly contaminated tilled soil profile S2 (Fig. 1b) showed relatively stable Pb concentrations in surface and subsurface horizons A and B. This is likely caused by annual ploughing and subsequent mixing of surface soil horizons [10]. The bulk Pb concentrations in tilled soil were two orders of magnitude lower than in forest soil. This phenomenon is likely related to (i) possible stronger bonding of Pb to organic matter in forest soils or to (ii) annual decrease due to Pb uptake by plants cultivated on the tilled soils. The Pb concentration in bedrock corresponding to the same geological unit and sampled below the soil profiles S1 and S2 was relatively high $(96.7 \text{ mg kg}^{-1}).$

Sampling site 2 (less contaminated soils S3 and S4)

Lead concentrations in profiles S3 and S4 from the less contaminated area were significantly lower than in profiles S1 and S2 (Fig. 1). This result is strictly related to the distance of the area from the smelter stack (3 km against the prevailing wind direction), and to relatively low background Pb concentrations $(2.50 \text{ mg kg}^{-1} \text{ in bedrock})$ (Fig. 1). Again, there was a significant difference in Pb concentration trends in forest and tilled soils. Forest soil in this less contaminated area (profile S3) had the highest Pb concentrations in subsurface A₁ horizon, attaining 1,126 mg Pb kg⁻¹ (Fig. 1c). In contrast, the highest Pb concentration in tilled topsoil (profile S4) was 210 mg Pb kg⁻¹ (Fig. 1d). The Pb concentrations in less contaminated tilled soils were also significantly lower than in forest soils, due to possible Pb uptake by plant cultivation. In both profiles, the Pb concentration dropped significantly with depth (Fig. 1).

Material	²⁰⁶ Pb/ ²⁰⁷ Pb			²⁰⁸ Pb/ ²⁰⁶ Pb		
	Value	1σ	RSD (%)	Value	1σ	RSD (%)
Slag from lead metallurgy (ore processing)	1.165	0.004	0.3	2.104	0.005	0.2
Slag from lead metallurgy (secondary battery processing)	1.169	0.004	0.3	2.100	0.007	0.3
APC residue from metallurgy (ore processing)	1.167	0.003	0.2	2.098	0.004	0.2
APC residue from metallurgy (battery processing)	1.177	0.003	0.2	2.081	0.004	0.2
Galena from the Příbram mining district	1.164	0.002	0.2	2.099	0.006	0.3
Fly-ash from petrol combustion (tunnel of Letná, Prague, CZ)	1.135	0.001	0.1	2.129	0.002	0.1

Fig. 2 Three-isotope plot (²⁰⁶Pb/²⁰⁷Pb versus ²⁰⁸Pb/²⁰⁶Pb) showing the distribution of isotopic compositions of smeltercontaminated soils from Příbram and other materials. underlying bedrocks and data reported in literature (EU and US aerosols are from the compilation of Hamelin et al. [18]; European petrol from Monna et al. [17]; American petrol and natural Pb from Teutsch et al. [6]; petrol-contaminated soils from Israel from Erel et al. [10]; Ag-Pb mining at Příbram from Novák et al. [2])



Isotopic composition in soil profiles

The Pb isotopic composition involving the most significant isotope ratio ²⁰⁶Pb/²⁰⁷Pb revealed a different behaviour between forest/tilled soils at each sampling site (Fig. 1). The bedrock of the two different sampling sites showed a distinct difference in 206Pb/207Pb composition (Fig. 1); the bedrock of soil profiles S1 and S2 had an isotopic composition close to that of galena or waste products of ore metallurgy (²⁰⁶Pb/²⁰⁷Pb=1.166, Fig. 1a, b, Table 2). In contrast, the isotopic composition of the bedrock of soil profiles S3 and S4 was significantly more radiogenic (²⁰⁶Pb/²⁰⁷Pb= 1.220, Fig. 1c, d) and corresponded rather to the natural Pb isotopic signature observed by Teutsch et al. [6] (Fig. 2).

The highly contaminated forest soil profile S1 exhibited a ²⁰⁶Pb/²⁰⁷Pb curve with a maximum in the subsurface horizon attaining the value of 1.174 (Fig. 1a). The increase in the 206Pb/207Pb isotopic ratio may be related to car battery smelting, taking into account the fact that APC residue from car battery processing technology operating around 1986 showed the isotopic value of 1.177 (Table 2; Zdeněk Kunický, personal communication). The surface horizon showed the isotopic signature corresponding rather to recent car battery processing (²⁰⁶Pb/²⁰⁷Pb≈1.17). It is evident that the recent car battery smelting technology is characterised by a slightly lower ²⁰⁶Pb/²⁰⁷Pb value than the APC residue from 1986, as evidenced by the isotopic signature of slag from recent car battery processing (1.169, Table 2). In horizon C of the forest profile S1, a significant drop in the ²⁰⁶Pb/²⁰⁷Pb isotopic ratio was observed down to the value of 1.166 (Fig. 1a). This value was close to that of slag from ore smelting (1.165) or galena from the Příbram district (1.164) (Table 2). This phenomenon indicates an extensive pollution of mineral horizon C due to long-term smelting of ores in the district. Even in mineral horizon C, the Pb concentration level was ten times higher than that of the geochemical background.

The Pb isotopic composition in tilled soil profile S2 had more stable behaviour (Fig. 1b). The effect of ploughing in the top 20 cm of the profile is illustrated by the relatively constant 206Pb/207Pb values and it is in a good agreement with Pb concentration data (Fig. 1b). The ²⁰⁶Pb/²⁰⁷Pb values varied slightly from 1.169 to 1.171 and decreased to the ²⁰⁶Pb/²⁰⁷Pb value of 1.166 in the bedrock (Fig. 1b).

Significantly different ²⁰⁶Pb/²⁰⁷Pb isotopic evolutions were characteristic for the less contaminated soil profiles S3 and S4. The topsoil from the forest soil profile S3 showed the ²⁰⁶Pb/²⁰⁷Pb value of 1.172, probably significantly influenced by car battery smelting (²⁰⁶Pb/²⁰⁷Pb of APC residue is 1.177). In deeper horizons, a distinct decrease in the isotopic ratio down to the value of 1.167 corresponds to a higher contribution of Pb originating from oresmelting processes (Fig. 1c). With increasing depth (below 14 cm), an evolution to higher ²⁰⁶Pb/²⁰⁷Pb values corresponding to uncontaminated geological background was observed (²⁰⁶Pb/²⁰⁷Pb isotopic ration of bedrock was 1.220, Fig. 1c).

A similar trend was observed in the less contaminated tilled soil profile S4 (Fig. 1d). A significant increase in the ²⁰⁶Pb/²⁰⁷Pb isotopic ratio with depth may be consistent with a lower contribution of the anthropogenic component (Fig. 1d). Tilled soil showed a relatively homogeneous isotopic composition in surface horizons with an isotopic signature close to that of car battery smelting (Fig. 1d). Nevertheless, it is impossible to determine more precisely the influence of different components in this profile due to the annual homogenisation of surface horizons by ploughing.

Three-isotope plot

²⁰⁶Pb/²⁰⁷Pb versus ²⁰⁸Pb/²⁰⁶Pb plots were used for the direct determination of sources of pollution for a large number of natural and anthropogenic materials [2]. Automotive (petrol combustion) pollution sources strictly depend on the utilisation of ores for Pb-additives and differ in the USA and Europe (Fig. 2). The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb values of smelter-impacted soils and other reference materials were included in the three-isotope plot in order to determine the possible influence of other pollution sources (Fig. 2). The isotopic composition of smelter-contaminated soils formed a distinct population in the centre of the plot close to the isotopic composition of galena from the Příbram mining district. The bedrock sampled under the soil profiles S1 and S2 was also within this population. In contrast, the composition of bedrock sampled under the profiles S3 and S4 corresponded rather to the crustal Pb composition given by Teutsch et al. [6]. Similarly, the isotopic signature of fly-ash from petrol combustion sampled in the Letná tunnel from Prague was in agreement with the isotopic composition of petrol used in Europe [17]. The APC residue from Pb battery smelting exhibited a more radiogenic composition and was separated from the principal population of soil isotopic composition (Fig. 2, Table 2). The general visualisation of isotopic composition in the three-isotope plot clearly showed the predominant role of metallurgy in the studied Pb polluted soils.

Sources of Pb pollution

Simple binary mixing models are used for the estimation of Pb origin. These models are based on the calculation of contributions from various anthropogenic/natural sources [13]. However, these models work satisfactorily only if the isotopic signatures of the two end-members (e.g. contaminant and natural background) are significantly different. In the case of the studied soils, we noted only a minor difference between heavily and less contaminated horizons (Figs. 1 and 2). Furthermore, it is evident that Pb metallurgy had a predominant role in Pb contamination even in mineral horizons (Fig. 2). Nevertheless, the binary mixing model proposed by Monna et al. [13] was used to evaluate the percentage contribution of car battery versus ore processing to the general Pb contamination:

$$X_{\rm A} = \frac{\left(\frac{206\,{\rm Pb}}{207\,{\rm Pb}}\right)_{\rm sample} - \left(\frac{206\,{\rm Pb}}{207\,{\rm Pb}}\right)_{\rm B}}{\left(\frac{206\,{\rm Pb}}{207\,{\rm Pb}}\right)_{\rm A} - \left(\frac{206\,{\rm Pb}}{207\,{\rm Pb}}\right)_{\rm B}} \times 100\%$$
(1)

where X_A is the percentage fraction of end-member A and $({}^{206}\text{Pb}/{}^{207}\text{Pb})_{\text{sample}}$, $({}^{206}\text{Pb}/{}^{207}\text{Pb})_A$ and $({}^{206}\text{Pb}/{}^{207}\text{Pb})_B$ are isotopic ratios in the sample, end-member A and end-member B, respectively. Such a calculation can be performed only for the forest soils, conserving the natural development of individual horizons. The choice of end-members is crucial and can induce several significant discrepancies during the calculation as detailed below:

- 1. It is difficult to trace a detailed historical evolution of signatures from the smelting activity. It is probable that in the last decade, the isotopic signature of car battery processing products dropped from 1.177 (APC residue from 1986) to 1.169 (slag from recent car battery processing) (Table 2, Fig. 1). This is probably the reason why the isotopic composition of the very superficial horizons is rather close to the value of 1.17 (Fig. 1).
- 2. The mixing calculation can be performed by using the APC residues, historically emitted by the smelter chimney stack and corresponding to two different technologies. The APC residue from car battery processing represented the end-member A (206Pb/207Pb=1.177) and the APC residue from ore processing corresponded to the end-member B. However, if we select these two distinct end-members, the surface horizon of profile S1 exhibiting the isotopic value of 1.17 will yield only 36% of car battery processing contribution. This is certainly an erroneous value, considering that car battery processing technology worked since 1972. In this case, it is evident that surface horizons were fully contaminated by emissions from car battery smelting, which dropped slightly in ²⁰⁶Pb/²⁰⁷Pb isotopic composition in during the last decade (Figure 1, see also point 1). For this reason, the binary mixing calculation was applied only on the subsurface horizons (Fig. 3).
- The isotopic composition of the 14- to 20-cm-deep horizon in the forest profile S3 (²⁰⁶Pb/²⁰⁷Pb=1.173) will definitely be the result of mixing between the Pb

Fig. 3 Fraction of Pb attributed to different contamination sources in forest soil profiles S1 and S3. Calculation was performed by using the binary mixing model of Monna et al. [13] using different end-members: *APC residue from car battery processing (206Pb/207Pb= 1.177) and APC from ore processing (²⁰⁶Pb/²⁰⁷Pb=1.167); #APC residue from ore processing and "natural" signature



from ore processing and natural Pb derived from bedrock, despite the similarity with the isotopic composition of the surface horizon contaminated by Pb derived from car battery processing. For this reason, the proposed end-members must be modified as shown in Fig. 3, taking into account the isotopic signature of APC residue from ore processing (²⁰⁶Pb/²⁰⁷Pb=1.167) and bedrock $(^{206}\text{Pb}/^{207}\text{Pb}=1.220).$

The estimation of percentage fraction of Pb derived from car battery processing is useful for the determination of Pb penetration rate within the soil profile. The binary mixing model showed that in profiles S1 and S3, Pb derived from car battery processing penetrated down to the depth of 9 cm and 11 cm, respectively (Fig. 3). The velocity of vertical Pb migration in soils was obtained by dividing the depth of the horizon by the exposition time, corresponding to 30 years of car battery processing in the smelter (from 1972 to the date of sampling in 2002). This calculation yielded penetration rates of Pb of 0.3 and 0.36 cm year⁻¹ for profile S1 and S3, respectively. These values corresponded well to the value of 0.29 cm year⁻¹ given by Miller and Friedland [9] for hardwood forest soils and to the value of 0.5 cm year⁻¹ observed in Mediterranean soils by Erel et al. [10]. In heavily contaminated soils Puchelt et al. [11] estimated that the Pb mobility may reach approximately 0.8 cm year⁻¹. Miller and Friedland [9] quoted that in mineral horizons, the penetration rate could be even more rapid, ranging from 0.82 to $1.97 \text{ cm year}^{-1}$ [9]. As a result, a further strong penetration of Pb may be assumed within the mineral horizon C.

Conclusions

The measurement of Pb isotopes (²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/ ²⁰⁶Pb ratios) by quadrupole-based ICP-MS proved to be a powerful tool for tracing the pollution in soils heavily polluted by metallurgy. The isotopic compositions of soils from

the Příbram district were compared with isotopic signatures of reference materials from lead smelting (galena, slags, APC residues) and petrol combustion (fly-ash from the tunnel). The coupled concentration/isotope approach confirmed the predominant role of Pb smelting on the general contamination of soils in the area. A binary mixing model [13] was used for tracing the degree of smelterinduced pollution with depth. The Pb contamination penetrated downwards to the mineral horizon C. The migration velocity of Pb down the soil profile ranges from 0.3 to 0.36 cm year⁻¹ corresponding to hardwood forest soils.

Acknowledgements This study was financed by the research project FRVŠ 2271/2002 and by Charles University (J13/98: 113100005). The authors thank Zdeněk Kunický, Technical Director of the Příbram Smelter (Kovohutě Příbram) for facilitating sampling of soils and waste materials from lead metallurgy. Marek Chvátal (Charles University) is acknowledged for the sample of galena from the Příbram district and Dr Ondřej Šebek for help with FAAS analyses. Dr Martin Novák (Czech Geological Survey) is thanked for a fruitful discussion. The reviews of two anonymous referees helped to improve the first version of the manuscript.

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