Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic)

M. Mihaljevič a,⁎, M. Zuna a, V. Ettler a, O. Šebek b, L. Strnad b, V. Goliáš a

a Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic
b Laboratories of Geological Institutes, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

Received 12 May 2006; received in revised form 15 September 2006; accepted 18 September 2006
Available online 1 November 2006

Abstract

The content and the isotopic composition of lead (Pb) were studied in a peat deposit on the ridge of the Brdy Hills, in the vicinity of the Příbram metallurgical works, in the Czech Republic. Quadrupole ICP MS was employed to determine the elemental composition and \(^{206}\text{Pb}/^{207}\text{Pb} \) and \(^{208}\text{Pb}/^{206}\text{Pb} \) isotope ratios. The individual layers were dated using \(\alpha \) spectrometric measurement of the \(^{210}\text{Pb} \) activity. The historical time period covered by the studied cores reached back to the 18th century. The Pb concentration in the studied profiles varied from 10 to 550 mg kg\(^{-1} \). The \(^{206}\text{Pb}/^{207}\text{Pb} \) ratio varied in the range from 1.154 to 1.194 in the individual parts of the profile. The metallurgy of the Pb ores (\(^{206}\text{Pb}/^{207}\text{Pb} \sim 1.16 \)), lithogenic Pb (\(^{206}\text{Pb}/^{207}\text{Pb} \sim 1.2 \)), metallurgical processing of automobile batteries (\(^{206}\text{Pb}/^{207}\text{Pb} \sim 1.17 \)) and the combustion of coal (\(^{206}\text{Pb}/^{207}\text{Pb} \sim 1.17 – 1.19 \)) yield isotopic signatures that determine the isotope compositions of the individual profiles. Deposition rates between 15 mg m\(^{-2} \) year\(^{-1} \) at the beginning of the 19th century and 320 mg m\(^{-2} \) year\(^{-1} \) in the 1980s were determined in the dated profiles. The increased deposition rates determined on the dated profiles correspond to the increasing production of Pb ores in the Příbram mining area at the turn of the 19th and 20th centuries. The maximum for metallurgical production corresponds to the highest deposition rates recorded in 1960s and 1970s. The current deposition rate of 5–89 mg m\(^{-2} \) year\(^{-1} \) Pb is related to erosion of contaminated soils and waste dumps.

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Keywords: Pb pollution; Pb isotopes; Metallurgy; Peat profile; Deposition; Příbram

1. Introduction

Lead (Pb) isotopes constitute an instrument for obtaining information on the pollution of the contemporary and historical environment. Especially the \(^{206}\text{Pb}/^{207}\text{Pb} \) ratio has been found useful for this purpose. These ratios have been studied in soils (Ettler et al., 2004), stream sediments (Renberg et al., 2002), peat profiles (Farmer et al., 2005) and also, e.g., in foodstuffs (Mihaljevič et al., 2006). Comparison of isotope ratios enables estimation of the fingerprint of the most common lithogenic, vehicular and industrial Pb in the particular matrix. The contribution of the selected isotope ratios (sources) to the resultant fingerprint of Pb in the given environment can be calculated on the basis of a simple binary model (e.g. Farmer et al., 1996).

The first mining and smelting activities in the Příbram district probably date back to the Celtic civilization (4th–1st century BC). The history of the mining and processing of Ag and Pb ores in this area has been
documented since Middle Ages (Bambas, 1990; Vurm, 2001). Although the extent of these activities was not comparable with the huge mining and smelting between 17th century and the present, we assume that the background concentrations of metals and metalloids in the surrounding geosphere have increased since that time.

Elevated Pb contents have been found in forest and agricultural soils (Rieuwerts and Farago, 1996; Ettler et al., 2005a), in mosses (Sucharová and Suchara, 2004; Suchara and Sucharová, 2004) and in stream sediments (Ettler et al., 2006) in the vicinity of the Příbram metallurgical works. Lead migration in the soil profile and the \(^{206}\text{Pb}/^{207}\text{Pb}\) isotope ratios of soils and Pb compounds contaminating soil profiles are well known (Ettler et al., 2004). On the basis of the isotopic composition of Pb derived from ore and car battery processing and natural Pb, Ettler et al. (2004) calculated the contributions of these isotopic sources in the surrounding forest soils.

The peat profile represents a suitable archive of historical pollution (e.g. Kemper et al., 1997; Shotyk et al., 1998, in Czech Republic e.g. Ettler and Mihaljević, 1999; Novák et al., 2003). Recording of the isotope composition of Pb in the peat archive provides a good document of the course of historical ore mining and ore metallurgy (e.g. Monna et al., 2004; Baron et al., 2005). The mobility of Pb in a peat profile is not clear. While some works do not exclude the mobility of Pb (Urban et al., 1990), others consider that Pb compounds are immobile in a peat profile (Shotyk et al., 1997) or have very low mobility (Vile et al., 1999). Research on historical pollution has been performed, not only on upland bogs, but also on minerotrophic fens (Monna et al., 2004).

This work was carried out in the Brdy Hills, which are located 8 km west of the Příbram metallurgical works. The intent of this paper is (i) to compare the deposition rate of Pb recorded in the dated profile of a nearby peat bog with its anthropogenic emissions from the Příbram smelter; (ii) to determine the effect of the main sources on the Pb distribution in the peat profile on the basis of the isotopic Pb composition and factors of its enrichment and (iii) to simultaneously confirm its immobility during diagenesis of the studied peat deposit.

2. Methods

2.1. Site descriptions and sampling

Seven peat cores were taken in unforested parts of the top ridge of the Brdy Hills (865 m above sea level, average precipitation 710 mm year\(^{-1}\)), 9 km WSW of Příbram (Fig. 1). All the cores were taken on November 23, 2003. The vegetation was dominated by Sphagnum mosses and Carex species. The studied peatland is occasionally fed by streams from the surrounding small catchment area and has minerogenic character. The unforested part of the bog was surrounded by a spruce (Picea abies/L./Karst) forest. Cambrian psamitic and pelitic sediments are located in the basement of the peat deposit. The cores were taken using a PVC sampling tube (10 cm, length of 60 cm) in unforested areas of the peat deposit. The sampler had a saw-toothed, sharpened lower edge to reduce peat compacting when taking the individual cores. The collected cores were transferred to the laboratory in the sampling tubes, frozen and, after removal from the tube, each core was divided into 2-cm
sections, dried at laboratory temperature and homogenized in an agate mortar. The individual sections were weighed prior to and after drying to calculate the peat density.

2.2. Peat processing

The peat was mineralized in a Linn (Germany) programmable furnace by the dry ashing of 0.5 g of sample with a temperature increase of 1 °C min⁻¹ to a maximum temperature of 450 °C. The total mineralization time was 10 h. The ash content was determined gravimetrically. Mineralization of the peat by dry ashing with subsequent dissolution of the ash in acids does not affect the Pb yield for determination of its concentration and isotopic composition (e.g. Kylander et al., 2004; Norton et al., 1997). The sample was subsequently dampened with deionized water (DIW, MilliQ+, Millipore, USA) and dissolved in 5 ml of concentrated HF and 0.5 ml of concentrated HClO₄. The mixture of acids was evaporated to near dryness and this step was repeated once. The residue was dissolved in 2 ml of concentrated HNO₃, transferred to a 100 ml volumetric flask, filled to the mark with DIW and transferred to a 100 ml HDPE bottle (Azlon, UK). The stock solution was diluted to 2% (v/v) HNO₃ for determination of Pb and Ti and to 5% (v/v) HCl for determination of Zr.

Analytical-grade acids (Merck, Germany) and DIW were used to prepare the solutions and, in the case of HNO₃ and HCl, these were also distilled under the boiling point in a quartz apparatus. The Pb, Ti and Zr contents were determined by ICP MS (VG Elemental PQ3, UK) under the conditions given in Table 1. The quality of the analytical data and the procedure were verified using NIST 1575 (Pine needles) and NIST 1515 (Apple leaves) standard reference materials. The differences in the measured and certified values did not exceed 5% relative standard deviation (RSD).

2.3. Determination of the Pb isotopic composition

The isotopic composition of Pb was determined by ICP MS (VG Elemental PQ 3, UK). Because of the high Pb concentrations and low contents of the mineral components, it was not necessary to separate Pb as described, e.g. for soil samples (Ettler et al., 2004). The Pb isotopic composition was determined in solutions diluted to a concentration of ≤ 20 μg l⁻¹ Pb. The measured isotopes and measuring conditions are listed in Table 1. Correction for the mass bias was performed using NIST SRM 981 (Common lead) between measurements of the individual samples. The standard errors for measurement of the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios were <0.3% RSD and <0.4% RSD, respectively. The accuracy of the measurements were tested on reference materials BCR 2 (basalt; ²⁰⁶Pb/²⁰⁷Pb= 1.2007±0.0007, ²⁰⁸Pb/²⁰⁶Pb=2.0635±0.0016) and AGV 2 (andesite; ²⁰⁶Pb/²⁰⁷Pb=1.2085±0.0006, ²⁰⁸Pb/²⁰⁶Pb=2.0415±0.0013) certified by the US Geological Survey (1998).

2.4. Dating of peat cores

Three of the seven collected cores were dated. The layers of the peat cores were dated using ²¹⁰Pb α spectrometric separation of Po on an Ag disk (e.g. Vile et al., 1999). 1 ml of ²⁰⁹Po (NIST 4326) tracer diluted to an activity of 0.337 Bq ml⁻¹ was added to 3 g of homogenized dried sample in a 250 ml beaker and the mixture was then leached with 10 ml of concentrated HCl and 10 ml of concentrated HNO₃, 2 ml H₂O₂ and 50 ml DI water and was heated for 12 h on a heating plate at 60 °C. The samples were slowly evaporated to dryness and then 5 ml of concentrated HCl and 50 ml DI water were added. The samples were brought to boil with careful mixing and carefully boiled for approx. 5 min. The mixture was then filtered (Whatman 42) and the filter funnel with the mixture was washed several times with 2% (v/v) HCl. Then 5 ml H₂O₂ were added to the filtrate and this was evaporated to an almost dry salt. Then 2 ml of concentrated HCl was added to the beaker
and the sample was evaporated to dryness. This step was repeated twice to ensure complete removal of nitrates. The residue was moistened with 2 ml of concentrated HCl and then dissolved in 150 ml of 0.3 M HCl. The beakers were covered with watch glasses and the solutions were heated to 60 °C, 0.5 g of ascorbic acid was added for complexation of any Fe present and the solutions were stirred for 1 h. Silver disks (diameter 2 cm) were immersed in the solutions and Po was adsorbed on their unprotected side for 12 h at a temperature of 60 °C. The α activity of 209Po and 210Po was determined using an apparatus consisting of a Canberra series 10 Plus multichannel analyzer, a Canberra PIPS 450 mm2 semiconductor detector and an Ortec 142A preamplifier. The measuring time for the individual samples was selected so that the total RSD did not exceed 10%. The counting time of the individual samples varied between 7 and 26 h according to their activity. The age of the individual layers was calculated under the assumption of a “constant rate of supply” (CRS) (Appleby and Oldfield, 1978) and deviations in the individual determinations include both the SD of the actual measurement and errors incurred through application of the CRS model to the individual data. The relative standard deviations (RSD) of the individual data were calculated according to the propagation error law.

2.5. Calculation of the anthropogenic contribution and Pb deposition rate

Of the total amount of Pb in the peat material, the amount of lithogenic origin was calculated according to Eq. (1) and subsequently employed for calculation of the anthropogenic amount of Pb (Eq. (2)).

\[
[Pb]_{\text{lit}} = [M]_{\text{sa}} \cdot \frac{[\text{Pb}]}{[M]}_{\text{crust}}
\]

where \([Pb]_{\text{lit}}\) is the concentration of Pb of lithogenic origin in the sample (mg kg\(^{-1}\)), \([M]_{\text{sa}}\) is the concentration of the reference element (Ti, Zr) in the sample (mg kg\(^{-1}\)) and \(([Pb]/[M])_{\text{crust}}\) is the average composition of the Earth’s crust (Wedepohl, 1995)

\[
[Pb]_{\text{ant}} = [Pb]_{\text{tot}} - [Pb]_{\text{lit}}
\]

The Pb enrichment factors (EF Pb (Ti), EF Pb (Zr)) were calculated according to Eq. (3).

\[
\text{EF Pb}(Zr) = \frac{(Pb/Zr)_{\text{sample}}}{(Pb/Zr)_{\text{crust}}}
\]

where \((Pb/Zr)_{\text{crust}}\) is the average composition of the Earth’s crust (Wedepohl, 1995). An analogous equation was used for calculation of the Ti-normalized Pb enrichment factors (EF Pb (Ti)).

The deposition rate was calculated by interpolation of the age and of the Pb content (Vile et al., 1995) according to Eq. (4).

\[
Pb_{\text{dep}} = \frac{(m \ast [Pb]/S)/t_a}{1000}
\]

where \(Pb_{\text{dep}}\) is the rate of deposition of Pb on the peat surface (mg m\(^{-2}\) year\(^{-1}\)), \(m\) is the mass of the particular layer in (g), \([Pb]\) is the concentration of Pb in the sample (mg kg\(^{-1}\)), \(S\) is the surface area of the core (m\(^2\)) and \(t_a\) is the period of accumulating of the particular layer (years).

3. Results

3.1. Peat dating

The sampled cores reached to a depth of approx. 40 cm. The changes in the 210Po activities and the ages of...
Fig. 3. Profiles of the Pb concentration, the $^{206}\text{Pb} / ^{207}\text{Pb}$ ratio and the ash content in the individual peat cores.
Fig. 4. Profiles of the lithogenic and anthropogenic Pb contents as calculated on the basis of the Ti and Zr concentrations.
the individual layers of the dated profiles are depicted in Fig. 2. The variation in the $^{210}$Pb activity was similar for all three cores and varied in the range 19–578 Bq kg$^{-1}$. On the surface of the cores, the $^{210}$Pb activity varied in the range 362–445 Bq kg$^{-1}$ and then culminated in the compact peat layer at a depth of 4–8 cm (Fig. 2b). All the $^{210}$Pb profiles exhibit a subsurface maximum corresponding to transformation of Sphagnum tissue with lower ability to absorb Pb into the humus layer. The $^{210}$Pb activities decreased approximately exponentially to depth. An activity decrease of between 19 (profile 3A) and 36 (profile 1) Bq kg$^{-1}$ was observed at a depth of 24–26 cm. After these minima, an increase in the $^{210}$Pb activity in the range 37–74 Bq kg$^{-1}$ (profiles 2C and 3A, respectively) was again found at greater depths of 26–28 cm. Because of this deviation, the equilibrium $^{210}$Pb activity was not calculated as the average of several last nondecreasing values, but rather as the average values of the lowest activities at the base of the profile.

3.2. Pb concentration and isotopic data

Fig. 3 depicts the variation in the Pb content, the $^{206}$Pb/$^{207}$Pb isotopic ratio and the ash content in the dated peat profiles. The Pb content in the peat material varies in the range 10–550 mg kg$^{-1}$. The absolute values have a similar trend in the individual profiles. There was a substantial enrichment in Pb at a depth above 30 cm, maxima were found at a depth of 12–20 cm (340–554 mg kg$^{-1}$) and the content then decreased towards the surface. Profile 1 has a Pb variation with one sharp peak, while profiles 2C and 3A exhibit a clear local minimum in the Pb concentration at a depth of 24–26 cm (153 mg kg$^{-1}$, 107 mg kg$^{-1}$ respectively—Fig. 3).

The Pb isotopic ratios vary in the range of values 1.154–1.194 ($^{206}$Pb/$^{207}$Pb) and 2.069–2.115 ($^{208}$Pb/$^{206}$Pb). At the base of the profiles, at sites with low Pb concentrations, the $^{206}$Pb/$^{207}$Pb ratio $\approx 1.194 \pm 0.003$ (profile 1), and this ratio decreases towards the surface in dependence on the increase in the Pb concentration (Fig. 3). The maximum values of the Pb concentrations (554 mg kg$^{-1}$) in profile 1 correspond to the $^{206}$Pb/$^{207}$Pb ratio $\approx 1.165 \pm 0.003$. The decrease in the $^{206}$Pb/$^{207}$Pb ratio is slow for some of the cores (e.g. profile 3A) but is rapid in others (profile 1). As the Pb concentration decreases towards the surface layer, there is a slight increase in the $^{206}$Pb/$^{207}$Pb ratio to a value of 1.168±0.003 (61 mg kg$^{-1}$ Pb, profile 1). The other profiles generally have a similar trend, with some differences especially in the Pb isotopic composition at the base of the profile.

Fig. 4 depicts the variation in the Pb, Ti and Zr contents and the subsequently calculated factors for enrichment in EF Pb (Zr) and EF Pb (Ti), and the anthropogenic and lithogenic Pb contents according to Eqs. (2) and (3) in the dated profiles 1 (Fig. 4a) and 2C (Fig. 4b). The studied profiles differ in the trends in the Ti and Zr contents. The discrete peaks of the Ti and Zr contents are present for core 2C (18–22 cm), while the Zr and Ti contents of the other cores (1, 3A) increase with depth. The Ti and Zr values coincide with the ash contents in the profiles. The maximum Pb concentration corresponds to the maximum concentration of anthropogenic Pb. Peat profile 1 exhibits a significant increase.
in Pb for both types of standardization compared to the Earth’s crust in the period around 1952±8. For this period, anthropogenic Pb attains a value of 484 mg kg$^{-1}$. The maximum value of the anthropogenic concentration (540 mg kg$^{-1}$ Pb) corresponds to approximately 1987±3.

A difference is apparent between the variations in Pb and Pb$_{\text{ant}}$ between profiles 1 and 2C. Profile 1 exhibits one peak in the Pb content, with an increase in Pb$_{\text{ant}}$ starting at a depth of 30 cm. Profile 2C has a local minimum in Pb and Pb$_{\text{ant}}$ at a depth of 24–26 cm, dividing the Pb peak into the stages prior to and after 1866.

4. Discussion

4.1. Dating the profiles

In the profiles, the $^{210}$Pb activities decrease exponentially with depth; at a level of 24–26 cm in all the profiles, a decrease in the activity compared to the overall trend is apparent and, on the other hand, an increase was observed in the 26–28 cm layer. According to the calculation, the 24–26 cm layer corresponds to the years 1909±19 (profile 1), 1866±24 (profile 2C) and 1888±17 (profile 3A). In the period from 1825 to 1925 (Czech Hydrometeorological Institute data), temperature minima were observed in two subsequent 50-year stages in the entire Central Bohemian region. Variability could occur in the accumulation of humolite during these prolonged cold periods. Simultaneously, the prolonged freezing of the soil profile could lead to fluctuations in $^{222}$Rn emissions that, following deposition, would be reflected in the profile of the $^{210}$Pb activity.

4.2. Sources of Pb and trends in the $^{206}$Pb/$^{207}$Pb ratio in time

The extraction of polymetallic ore deposits and especially metallurgical works at Příbram caused observable pollution of the surroundings by heavy metals, especially Pb. The Pb concentrations in the soil attained values of 37,300 mg kg$^{-1}$ in the immediate vicinity of the metallurgical works (Rieuwerts and Farago, 1996). Ettler et al. (2005a) give similar concentrations in the soil around the Příbram metallurgical works and explained the elevated concentrations in forest soils (up to 35,300 mg kg$^{-1}$) by interception by the tree canopy, with subsequent re-deposition in soil by precipitation or through contaminated litter deposition. Suchara and Sucharová (2004) found Pb contents in the range 184–81,041 mg kg$^{-1}$ in forest humus in the vicinity of Příbram.

Although they are not located down-wind of the smelter in the main NW–SE wind direction (Fig. 1), the studied peat deposit was affected by Pb mining and metallurgy, similar to the surrounding soils. Although they are located in the close vicinity, the individual peat cores have different maximum Pb concentrations and there are also slight differences in the shapes of their Pb concentration profiles. It is probable that this could be caused by the action of the tree canopy located over this peat bog in the past.

The sources of Pb in the vicinity of Příbram with their typical isotope fingerprints (values from Ettler et al., 2004, 2006) include: rocks of the Cambian basement ($^{206}$Pb/$^{207}$Pb ≈ 1.201–1.22), galena mined from the Příbram ore-mining area ($^{206}$Pb/$^{207}$Pb ≈ 1.164), historical and recent products of Pb metallurgy ($^{206}$Pb/$^{207}$Pb ≈ 1.64).

Fig. 6. Deposition rates of Pb in the dated peat profiles.
Pb ≈ 1.164–1.165), air pollution control (APC) residues from ore processing (206Pb/207Pb ≈ 1.167) and APC residues from battery processing (206Pb/207Pb ≈ 1.177). Substantial sources of anthropogenic Pb pollution in Europe include the combustion of coal (206Pb/207Pb ≈ 1.17–1.19; Novák et al., 2003) and automobile fuel Pb (206Pb/207Pb ≈ 1.067–1.135; Monna et al., 1997; Ettler et al., 2004). Lithogenic components (206Pb/207Pb ≈ 1.2) and also historical metallurgy contributed to the Pb content in the peat at the base of the individual profiles (Fig. 3). From the 17th to the middle of the 19th century, the 206Pb/207Pb isotope ratios varied in the range 1.172 ± 0.004 to 1.194 ± 0.003. The processing of Pb ores between the 1870s and 1890s led to a decrease in the isotopic composition to a value ranging from 1.170 ± 0.005 to 1.167 ± 0.006. There was a slight increase in the 206Pb/207Pb ratio at the turn of the 19th to 20th century to a value of 1.174 ± 0.003 (Fig. 3). A local maximum in the Ti and Zr normalized contents (Fig. 4) was found in this part of the profile ratio, indicating the potential impact of coal combustion on the Pb fingerprint in this period (1906 ± 15). However, it is not possible to exclude the same source as at the bottom of the profile, i.e. a combination of lithogenic Pb (dust fall-out) and Pb of metallurgical origin. In the 1820–1830 period, the isotope fingerprints varied in a relatively narrow interval between values of 1.163 ± 0.003 (profile 1) and values of 1.166 ± 0.004 (profile 3A). At the end of the 1980s and beginning of the 1990s, there was a slight decrease in the 206Pb/207Pb ratio to values of 1.159–1.164. The values of the 206Pb/207Pb ratio increase slightly at the surface of the profiles (206Pb/207Pb ≈ 1.168 ± 0.003), which could be connected with the effect of simultaneous processing of automobile batteries, which can exhibit various, but generally higher isotopic signatures than the Pb ores from Příbram (data from Ettler et al., 2004). The Pb isotopic ratios in a major part of the profile lie in the interval of values 206Pb/207Pb ≈ 1.15–1.17 formed by a combination of processing of ore and of secondary Pb raw materials and lithogenic Pb and, possibly at the turn of the 19th and 20th centuries, ores and coal. Because of the small differences in the compositions of the individual signatures and several potential significant sources, the conventional mixing equations (e.g. Monna et al., 1997; Ettler et al., 2004) cannot be employed in this case to calculate the relative contributions.

4.3. Ore mining, metallurgical production and course of Pb deposition

The first written record of metallurgical activities at Příbram dates back to 1311; however, mining of Ag–Pb ores in this area became more extensive in the middle of the 16th century (Vurm, 2001). The two metals were obtained simultaneously by roasting sulphide ores with subsequent smelting in the Příbram smelter. Fig. 5 depicts the progress of historical production of Pb in the Příbram district, the amount of Pb produced in the smelter (1938–2000) and the Pb emissions in the second half of the 20th century. While the amount of Pb ores mined culminated at the turn of the 19th and 20th centuries, the greatest amounts of Pb were produced in the 1980s when, because of the reduction in mining at Příbram, domestic and imported ores, concentrates and secondary Pb raw materials, including automobile batteries, were processed. There was a slow increase in ore mining and processing from the end of the 18th and throughout the 19th century. A sharp increase in Pb production occurred especially at the end of the 19th century and was dependent on the introduction of steam engines into mining and metallurgy in the 1840s. Pb production in the 19th century peaked in 1885 (Vurm, 2001, Pb production was 5981 t year⁻¹). The amount of Pb produced decreased to 4113 t Pb and 2470 t Pb in 1913 and 1923, respectively. Pb production increased slightly to 3316 t Pb in 1933, followed by a decrease during World War II (Vurm, 2001). Overall Pb production culminated in the 1980s (Fig. 5). Pb emissions from Příbram metallurgical technology began to be measured quantitatively at the end of the 1960s and exhibited values corresponding to 624 t Pb year⁻¹ in 1969 and then decreased as a consequence of installation of dust-removal equipment (filters). Breakdown of the dust-filtering units led to peak emissions in 1982, when the smelter was covered by toxic dust. The dust-removal technology has undergone constant improvement since 1982 and overall emissions gradually decreased to a value of 1.2 t Pb year⁻¹ in 1999.

The shapes of the deposition curves of the individual profiles differ slightly, but reflect the overall Pb production in the Příbram area (Fig. 6). At the beginning of the 19th century, Pb deposition varied in the range 15–41 mg m⁻² year⁻¹. The Pb deposition recorded in the peat profiles gradually increased from this time and the first maximum appeared at the turn of the 19th to 20th century (118 mg m⁻² year⁻¹ and 135 mg m⁻² year⁻¹, profiles 1 and 2C, respectively). The atmospheric flux of Pb culminated in the 1970s (320 mg m⁻² year⁻¹ and 250 mg m⁻² year⁻¹, profiles 1 and 2C, respectively). A deposition maximum was recorded in profile 3A in the 1960s (220 mg m⁻² year⁻¹). The increase in Pb production in the 1960s to 1970s is apparent and high emissions from metallurgy were also recorded (Fig. 5). A maximum in the Pb deposition in the 1980s can still be seen in profile 1.
Although emissions from the Příbram metallurgical works decreased significantly at the beginning of the 1980s (with the exception of a single breakdown in 1982), an explanation for the maximal deposition rates in this period can also be found in qualitative changes in the emission composition. The Příbram metallurgical works began to process secondary Pb scrap, especially automobile batteries, instead of Pb ores, from the 1970s. Sobanska et al. (1999) state that the 1–10 μm (39.5%) and 10–50 μm (30.5%) grain-size fractions predominate in emissions from primary Pb metallurgy (ore processing) and that, from a mineralogical standpoint, these emissions consist particularly of low-solubility Pb sulphides and sulphates. A recent work of Ettrler et al. (2005b) indicated that fly ash and APC residues from secondary lead metallurgy consist mainly of highly soluble Pb chlorides (lauronite, PbOH)Cl, potassium lead chloride, KCl-2PbCl2, caracolite, Na2Pb3 (SO4)3Cl and cotunnite, PbCl2), formed because of the presence of PVC boxes and grids from automobile batteries in the blast furnace charge. In addition, a smaller grain fraction predominates in this fly ash, with 94% of particles smaller than 2 μm (Ettrler et al., 2005b). Metallurgical processing of automobile batteries thus yielded fly ash particles that are not only more reactive, but are also capable of more distant transport in the atmosphere than coarse particles, which fall out more effectively from the atmosphere through gravitation in the vicinity of their sources (Hinds, 1982). Since the 1980s, there has been a rapid decrease in the atmospheric flux of Pb in connection with modern emission control technologies in the Příbram smelter. In 2003, Pb deposition varied considerably in the range 5–89 mg m−2 year−1. Sucharova and Suchara (2004) state Pb deposition rates of a similar order of magnitude (0.5–127 mg m−2 year−1) with greater distribution for the same area, based on measurements of the composition of the moss Pleurozium schreberi. A Pb flux of 0.49 mg m−2 year−1 in 2001 in the Central Bohemian area, which was not affected by Pb metallurgy, was measured by Navrátíl et al. (2004). Although the metallurgical works have employed more modern and environmentally sound technology since 1998, in cooperation with the Varta company, and Pb is no longer used as an anti-knock additive for petrol, elevated Pb deposition fluxes continue to be prevalent in the area because of wind erosion of the material of historical mining and smelting dumps and contaminated soils.

5. Conclusions

The content of Pb and the 206Pb/207Pb isotopic composition of peat in the vicinity of the Příbram mining/smelting district (Czech Republic) understandingably reflect the historical development of mining activities and processing of Pb ores and secondary raw materials in the Příbram smelter. Maximum Pb deposition rates have been identified for the 1960s and 1970s, when the amount of Pb emitted from Příbram metallurgy culminated. Elevated deposition rates were also identified at the turn of the 19th and 20th centuries at the time of maximum production in the Příbram area. The connection between the deposition rates and the historical production confirm the immobility of Pb captured in the peat profile. The slight variability of the Pb deposition within the studied peat bog could be connected with the position of the profile in relation to trees that could have been located here in the past.

Acknowledgement

The authors are grateful to Marie Fayadová for assistance with the laboratory work, Dana Pýchová (Czech Hydrometeorological Institute) for provision of climatic data and Ing. Martin Březovský for permission to enter the studied locality. The reviews of two anonymous reviewers helped considerably in improving the original manuscript. This work was carried out with financial assistance from GAUK Project No. 271/2006/B GEO. Madeleine Štulíková is thanked for correction of the English in the paper.

References

Ettrler V, Mihaljević M, Šebek O, Molek M, Grygar T, Zeman J. Geochemical and Pb isotopic evidence for sources and dispersal of
metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic. Environ Pollut 2006;142:409–17.


Norton SA, Evans GC, Kahl JS. Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic big heath bog and to nearby Sargents Mt. Pond, Maine, USA. Water Air Soil Pollut 1997;100:271–86.