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Mercury deposition/accumulation rates in the vicinity of a lead smelter as recorded by a peat deposit

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ABSTRACT

Mercury (Hg) concentration profiles and historical accumulation rates were determined in three ^{210}Pb-dated cores from a peat deposit in the vicinity of a lead (Pb) smelter at Příbram, Czech Republic. The Hg concentrations in peat samples ranged from 66 to 701 $\mu g\,kg^{-1}$. Cumulative Hg inventories from each core (for the past ~150 yr) varied by a factor of 1.4 (13.6–18.5 $mg\,Hg\,m^{-2}$), indicating variations of net Hg accumulation rate within the peat deposit. Historical changes in vegetation cover (leading to variable interception by trees) are probably responsible for this variation in space and time. The uncorrected Hg accumulation rates peaked between the 1960s and 1980s (up to 226 $\mu g\,m^{-2}\,yr^{-1}$). Recent findings show that Hg records from peat tend to overestimate historical levels of Hg deposition. Therefore we used the mass loss compensation factor (MLCF) to normalize Hg accumulation rates. These corrected Hg accumulation rates were significantly lower (maximum 129 $\mu g\,m^{-2}\,yr^{-1}$) and better corresponded to changes in historical smelter emissions, which were highest in the 1960s. The agreement between the corrected Hg accumulation rates in the uppermost peat sections (2–38 $\mu g\,m^{-2}\,yr^{-1}$) and biomonitoring of atmospheric deposition by mosses in several recent years (4.7–34.4 $\mu g\,m^{-2}\,yr^{-1}$) shows the usefulness of MLCF application on Hg accumulation in peat archives. However, the MLCF correction was unsuitable for Pb. The recent Pb deposition rates obtained by an independent biomonitoring study using mosses (0.5–127 $mg\,m^{-2}\,yr^{-1}$) were better correlated with net Pb accumulation rates recorded in peat (7–145 $mg\,m^{-2}\,yr^{-1}$) than with corrected rates obtained by the MLCF approach (1–28 $mg\,m^{-2}\,yr^{-1}$).

1. Introduction

Mercury (Hg) is one of the most studied inorganic contaminants due to its pathogenic effects on biota, including humans. The ore mining and processing are important point sources of Hg for the atmosphere. Numerous studies have focused on Hg distribution and speciation in environmental samples in the vicinity of Hg-mining areas, but relatively few have investigated Hg distribution in the environments contaminated by base metal smelters, where Hg is only a minor contaminant (Rieuwerts and Farago, 1996; Henderson et al., 1998; Rieuwerts et al., 1999; Ettler et al., 2007). Although ombrotrophic peat is generally used as the most reliable archive of historical atmospheric deposition of contaminants (Roos-Barraclough et al., 2006; Shotyk et al., 2003; Bindler, 2003; Givelet et al., 2003), minerotrophic peat has also been used for this purpose (Monna et al., 2004; Baron

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et al., 2005). Peat records of historical metal deposition in the vicinity of the smelters are still rare in the literature (Sonke et al., 2003; Rausch et al., 2005; Mihaljevič et al., 2006; Klaminder et al., 2008).

Recently, the use of peat archives to reconstruct the effect of anthropogenic Hg emissions on Hg deposition/accumulation is widely discussed (Bindler, 2003, 2006; Biester et al., 2002, 2003, 2007; Roos-Barraclough et al., 2002, 2006; Bindler, 2006). Biester et al. (2007) suggested that numerous processes of Hg retention, migration and loss in peat are still poorly understood. Many recent papers discuss different reasons for possible overestimation of calculated Hg accumulation rates in peat. One is mass loss from highly decomposed peat layers, compared to younger, less decomposed peat layers (Biester et al., 2002, 2003). A method of correction of Hg accumulation rates using the mass loss compensation factor (MLCF) was proposed by Biester et al. (2003). The second reason for the overestimation of Hg accumulation rates is related to inaccurate dating of peat. Biester et al. (2007) showed that smearing of ^{210}Pb in the uppermost peat (acrotelm) could lead to underestimation of peat ages and subsequently to overestimation of metal accumulation rates in peat. Because of within-bog variability, some studies suggest analysis of multiple cores to determine the variation in historical accumulation of contaminants in the peat (Bindler et al., 2004; Bindler, 2006; Rothwell et al., 2007).

This paper describes the Hg concentration profiles and accumulation rates in the vicinity of a lead (Pb) smelter at Příbram (Czech Republic), which has been in operation for over 200 yr, using three ^{210}Pb-dated peat profiles. The accumulation rates of Hg are compared with those of Pb—another organically bound contaminant. The correction of Hg and Pb accumulation rates for peat decomposition is discussed in relationship to known production of the local mines and smelter and with recent deposition biomonitoring using mosses. These data are the first contribution to the knowledge of the historical and recent Hg deposition/accumulation in the Czech Republic.

2. Materials and methods

2.1. Sampling

Three cores were retrieved in November 2003 at a peat deposit at the Brdy Hills, approximately 10 km W of the Pb smelter and 12 km WNW of the main polymetallic mining area in Příbram (Fig. 1), Czech Republic. The distance between the individual cores was ~700–1000 m (details given in Mihaljevič et al., 2006). The vegetation was dominated by *Sphagnum* mosses and *Carex* species and the peat deposit was surrounded by Norway spruce (*Picea abies*). The cores were taken using a PVC cylinder (10 cm in diameter) with a sharpened bottom edge. Insertion of cylinder was facilitated by cutting the peat with a sharp stainless-steel knife and special care was taken to minimize compaction. Each core was frozen and sawn into 2 cm sections. The individual sections were weighed prior to and after drying to calculate the peat density. Drying was performed at laboratory temperature and each section was homogenized in an agate mortar prior to further processing.

2.2. Dating of peat samples

The peat cores were dated using ^{210}Pb α spectrometry after acid digestion of peat samples (Vile et al., 1995). The detailed information on chemical preparation of peat samples is given in Mihaljevič et al. (2006). The α activity was measured by a Canberra series 10 Plus multichannel analyzer, a Canberra PIPS 450 mm^2 semiconductor detector, and an Ortec 142A preamplifier (counting time between 7 and 26 h according to the activity of individual samples). The age of individual peat samples was

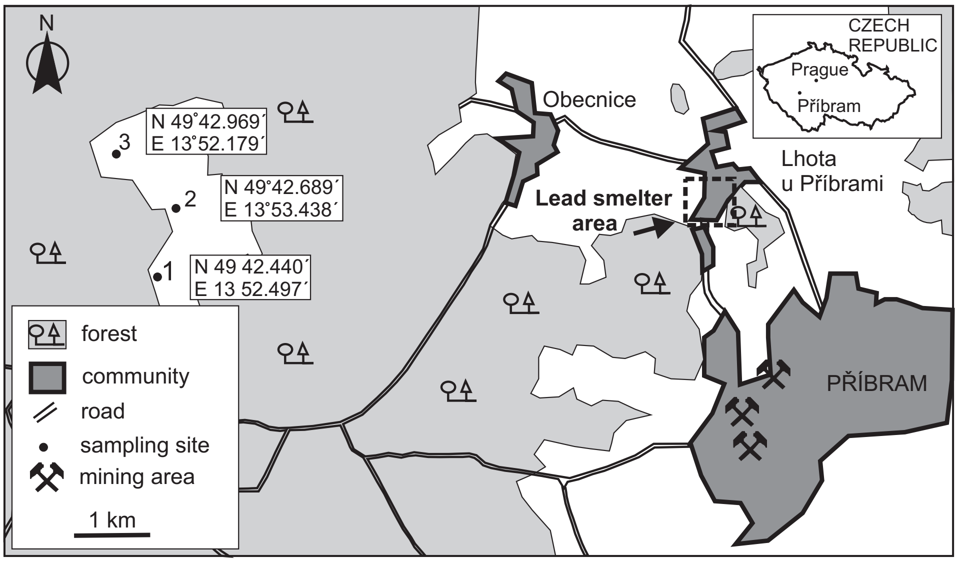

Fig. 1. Location of sampled peat deposit, smelter and mining areas in the Příbram district.

calculated according to the "constant rate of supply" (CRS) model developed by Appleby and Oldfield (1978). The deviations in the individual determinations include both standard deviation (SD) of the 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.

2.3. Analysis of Hg and other components

Analysis of total Hg in individual samples was performed by cold-vapor atomic absorption spectrometry (CV-AAS) using a LECO Altec AMA 254 Hg analyzer under standard analytical conditions recommended by the manufacturer for solid samples (10 s drying time, 300 s decomposition time). The Hg determinations of each peat sample were performed in triplicate, yielding smallRSD of $<4\%$. Quality control of Hg measurements was ensured by the analysis of QCM1 standard reference material (SRM) "River sediment 1" (manufacturer Analytika Praha Ltd., Czech Republic). Repeated measurements yielded $1560 \pm 20\,\mu g\,Hg\,kg^{-1}$ ($n = 3$), corresponding well to the certified value of $1550 \pm 140\,\mu g\,Hg\,kg^{-1}$.

Total organic carbon (C) and total nitrogen (N) were determined using a Thermo Sison 1108 Elemental Analyzer (Thermo, USA) under standard analytical conditions. The quality of C and N measurement was checked by repetitive analysis of a acetanilide standard, with an error $<2\%$.

Peat samples were mineralized by dry ashing in a Linn (Germany) programmable furnace (sample: 0.5 g, maximum temperature: 450 °C, step temperature increase: $1\,°C\,min^{-1}$). The ash was subsequently dissolved in mineral acids (HF, $HClO_4$, HNO_3) and transferred to 100 ml HDPE bottles (Azlon, UK). The stock solution was diluted to obtain 2% solution (v/v) HNO_3 and analyzed for Fe by FAAS (Varian 280 FS, Australia) and for Pb by ICP-MS (VG Elemental Plasma Quad 3, UK) under standard analytical conditions. Peat samples were analyzed for the content of Pb (as an additional contaminant for the comparison purposes) and Fe, being recognized as indicator of Fe-oxide presence responsible for Hg enrichments in minerogenic fens (Franzen et al., 2004). The quality control of the dissolution and analytical procedures was verified by standard reference materials (NIST 1575, Pine needles and NIST 1515, Apple leaves). The differences between measured and certified values did not exceed 5% RSD.

2.4. Calculation of annual Hg accumulation rates

The Hg accumulation rates (AR_{Hg}) were calculated according to the methodology proposed by Givelet et al. (2003): e.g.,

$$AR_{Hg} = 10 \times [Hg] \times BD \times PAR \tag{1}$$

where AR_{Hg} is the net accumulation rate of Hg ($\mu g\,m^{-2}\,yr^{-1}$), [Hg] is the Hg concentration (in $\mu g\,kg^{-1}$), BD is the bulk density of the peat ($g\,cm^{-3}$) and PAR is the net peat accumulation rate ($cm\,yr^{-1}$). PAR was calculated using ages of individual peat layers.

Humification may have a significant effect on Hg accumulation in peat (Biester et al., 2003, 2007). Consequently, the MLCF was calculated for individual peat horizons to correct the net Hg accumulation rates. The MLCF is useful for normalization of peat accumulation rates to the same degree of humification by referring the C accumulation rates of individual peat segments to reference sections of highly humified peat at the bottom of cores. The calculation of MLCF was performed according to Biester et al. (2003)

$$MLCF = (AR_{Cref}/AR_{Ci}) \tag{2}$$

where AR_{Cref} is the carbon accumulation in the reference section ($g\,m^{-2}\,yr^{-1}$) and AR_{Ci} is the carbon accumulation in the studied peat section i ($g\,m^{-2}\,yr^{-1}$). The net Hg accumulation rates calculated by Eq. (1) were multiplied by the MLCF value for each section to obtain the corrected values of Hg accumulation in peat.

3. Results and discussion

3.1. Dating of peat cores

The ^{210}Pb activities and ages of individual peat layers are reported in Table 1. For all three cores total ^{210}Pb activities varied in the range 0.017–0.578 $Bq\,g^{-1}$ and showed a general decreasing trend with the depth. The local maxima in depths of 5–8 cm may result from the downward leaching and accumulation of ^{210}Pb in the acrotelm (uppermost peat), which was suggested at numerous peat deposits (see Biester et al., 2007 and references therein). This phenomenon may be responsible for possible errors in dating of the uppermost peat layers whose ages are then underestimated (Biester et al., 2007) leading to overestimation of the accumulation rate.

Calculation of supported ^{210}Pb activity was based on means of peat segments in the bottom parts of individual cores (Table 1). In some deeper segments the calculated unsupported ^{210}Pb activities were slightly negative (i.e., supported ^{210}Pb activity used as a reference value was higher than total ^{210}Pb activity in a given horizon); this probably indicates that supported ^{210}Pb activity varied in time (Appleby, 2008). To overcome this problem the gamma spectrometric indirect measurements of supported ^{210}Pb activity in each peat segment would be useful (Sonke et al., 2003; Roos-Barraclough et al. 2006). For calculation of cumulative inventories of unsupported ^{210}Pb activities, the negative values were set to zero.

3.2. Concentration profiles of Hg and other elements

The profiles for Hg, Pb, Fe and C concentration, peat density, ash content, and values of $Hg \times N/C$ and C/N are reported in Fig. 2. Lower C concentration (Fig. 2f) and higher ash content (Fig. 2h) compared with ombrotrophic peat indicate that the peat profiles are minerogenic below 12–14 cm (Fig. 3e). The minerogenic character of the studied peat profiles is also confirmed by significantly

Table 1
Depth profiles of total and unsupported ^{210}Pb activities (Bq g^{-1}) and ages of the individual peat sections

Section (cm)	Core 1			Core 2			Core 3		
	Total ^{210}Pb (Bq g^{-1})	Unsupported ^{210}Pb (Bq g^{-1})[a]	Date (year, SD)	Total ^{210}Pb (Bq g^{-1})	Unsupported ^{210}Pb (Bq g^{-1})[a]	Date (year, SD)	Total ^{210}Pb (Bq g^{-1})	Unsupported ^{210}Pb (Bq g^{-1})[a]	Date (year, SD)
0–2	0.362	0.343	2003±0	0.412	0.378	2003±0	0.445	0.424	2003±0
2–4	0.358	0.339	2001±1	0.367	0.334	2001±1	0.359	0.337	2000±2
4–6	0.422	0.404	1999±1	0.425	0.392	1999±1	0.578	0.556	1996±3
6–8	0.531	0.512	1996±2	0.428	0.395	1995±2	0.247	0.225	1984±3
8–10	0.389	0.371	1991±3	0.356	0.323	1992±2	0.205	0.184	1979±3
10–12	0.317	0.299	1987±3	0.273	0.240	1987±3	0.128	0.107	1973±4
12–14	0.289	0.270	1981±4	0.303	0.269	1983±3	0.146	0.125	1965±5
14–16	0.263	0.245	1973±5	0.220	0.187	1976±6	0.116	0.094	1952±5
16–18	0.202	0.183	1964±6	0.176	0.143	1959±10	0.090	0.069	1943±8
18–20	0.175	0.156	1952±8	0.079	0.046	1933±13	0.116	0.095	1933±8
20–22	0.096	0.077	*1935±11*[b]	0.042	0.009	1906±15	0.026	0.004	1914±13
22–24	0.062	0.043	*1921±14*	0.032	−0.001[c]	1894±17	0.021	0.000	*1903±13*[b]
24–26	0.036	0.017	*1909±19*	0.028	−0.006[c]	*1866±24*[b]	0.019	−0.002[c]	*1888±17*
26–28	0.052	0.033	*1890±19*	0.037	0.004	*1838±25*	0.074	0.052	*1872±14*
28–30	0.023	0.005	*1872±24*	0.034	0.0003	*1807±33*	0.023	0.001	*1855±20*
30–32	0.017	−0.002[c]	*1852±29*	0.036	0.003	*1774±37*	0.023	0.001	*1837±21*
32–34	0.022	0.003	*1830±35*	0.044	0.010	*1738±34*			
34–36	0.017	−0.001[c]	*1807±40*	0.041	0.008	*1699±46*			
36–38				0.040	0.007	*1658±54*			

[a] Calculated from total ^{210}Pb activities by subtracting supported ^{210}Pb activity (core 1: 0.0186 Bq g^{-1} as mean of sections 30–36 cm; core 2: 0.0334 Bq g^{-1} as mean of sections 22–32 cm; core 3: 0.0216 Bq g^{-1} as mean of sections 24–26 cm and 28–32 cm).
[b] Dates in *italics* estimated by extrapolation.
[c] Negative unsupported ^{210}Pb activities were considered as 0 when cumulative unsupported ^{210}Pb activity was calculated.

higher bulk peat density in the bottom of studied peat cores (often >0.2 g cm^{-3} below a depth of 20 cm) (Fig. 2d).

The C/N ratios can be used as an indicator of the peat humification degree; peat sections with higher C/N ratio indicate lower peat humification (Malmer and Holm, 1984; Biester et al., 2003). For cores 1 and 2 the C/N ratios are generally lower in the deeper parts of the cores, indicating higher degree of humification in these sections (Fig. 2g). Correction of Hg concentrations to N/C ratios (N is more variable than C, Biester et al., 2003) shows trends similar to the uncorrected Hg concentration profiles (Fig. 2e).

The Hg concentration ranges from 66 to 701 μg kg^{-1}. The concentrations in the individual peat horizons are enriched in Hg with respect to local bedrock (Cambrian graywackes, conglomerates and arkoses), which contains 31±11 μg Hg kg^{-1} (Fig. 2a). All profiles have a subsurface maximum, but there are differences in Hg concentration among the three cores (Fig. 2a). Core 1 has a large concentration peak between 8 and 30 cm (up to 433 μg Hg kg^{-1}). A sharp peak in Hg concentration occurs in core 2 from 16 to 18 cm (701 μg Hg kg^{-1}) with another maximum from 24 to 26 cm (400 μg Hg kg^{-1}). Core 3 has one concentration maximum from 12 to 14 cm (404 μg Hg kg^{-1}) (Fig. 2a).

The Pb and Hg concentration profiles are similar in trend (Fig. 3b) and are positively correlated ($R^2 = 0.62$). In contrast, significantly different concentration patterns occur for Fe (Fig. 2c). Enrichment in subsurface peat layer occurs for cores 1 and 3 related probably to the fluctuation of water table or downward migration in the root zone (Franzen et al., 2004). Core 2 has a maximum Fe concentration in section from 17 to 25 cm. This section of the core also exhibits lower C concentrations (higher ash content) and is enriched in other lithogenic elements such as Zr and Ti suggesting input of lithogenic material (data not shown, see Mihaljevič et al., 2006). However, the Fe concentrations in the peat cores are far lower than those in minerogenic peats at other sites (e.g., up to about 25% in peat from Magellanic Moorlands, Chile) where Fe is proposed to have and effect on mobility of Hg (Franzen et al., 2004).

3.3. Hg inventories

The Hg concentration profiles and cumulative Hg inventories plotted against the cumulative peat mass are shown in Fig. 3. Changes of Hg concentrations above the cumulative peat mass value of ~4 g cm^{-2} are relatively consistent for all three cores (Fig. 3a). Cumulative Hg inventories for all three cores versus cumulative peat mass are almost identical in the upper part of each profile, but differ significantly below the cumulative peat mass of ~4 g cm^{-2} (Fig. 4b). The selected "equivalent point" in peat with cumulative peat mass of 5.66±0.09 g cm^{-2} (depth 28–30 cm) corresponds to an inventory of Hg deposited during past ~150 yr (dates for individual profiles are: 1872±24, 1807±33 and 1855±20). Cumulative Hg inventories representing the past ~150 yr are 14.8, 18.5 and 13.6 mg Hg m^{-2} for peat cores 1, 2 and 3, respectively. Mercury inventories from three cores within the same peat deposit therefore vary by factor of 1.4. Similarly, cumulative Hg inventories were plotted against

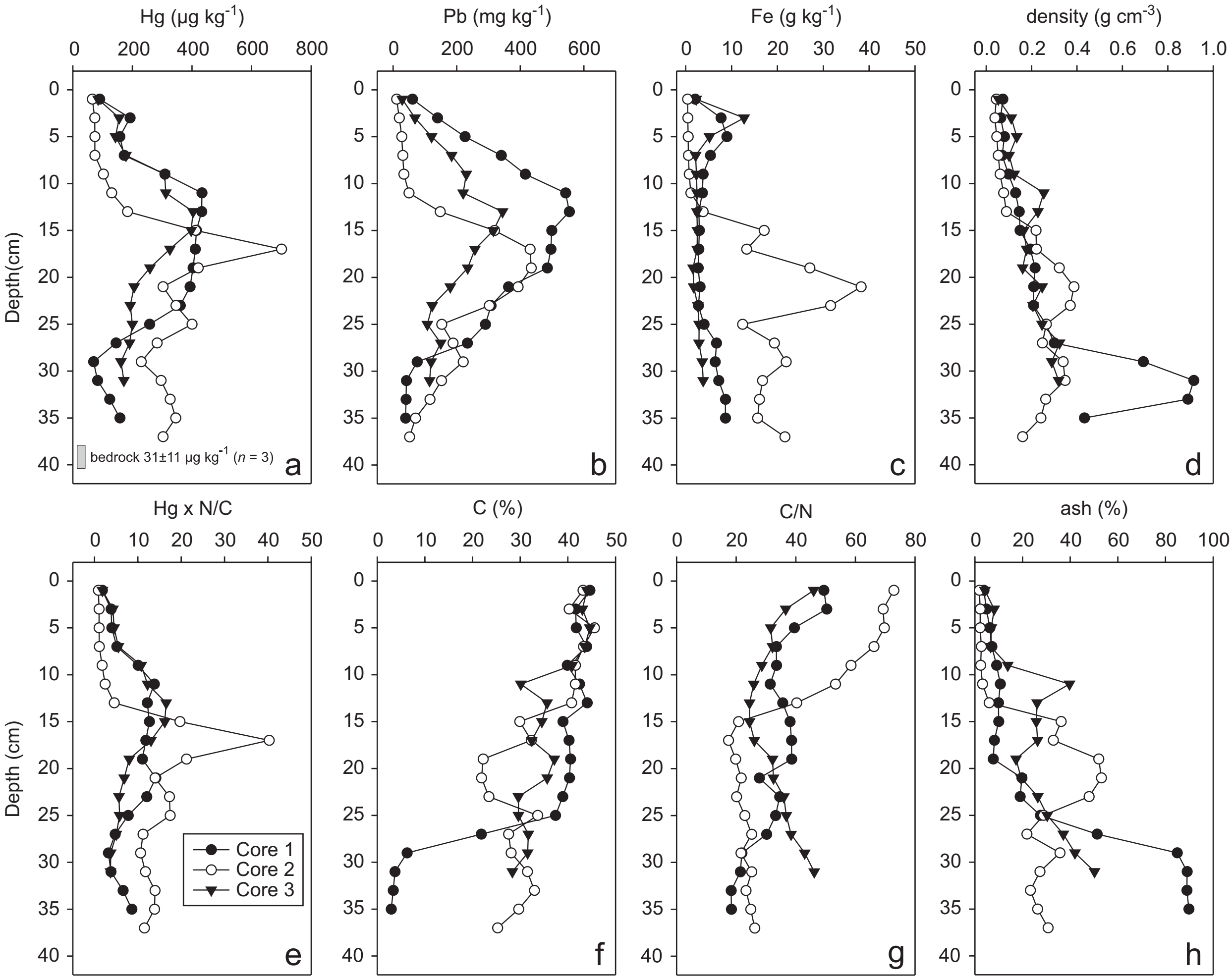

Fig. 2. Concentration profiles of Hg, Pb, Fe, C and Hg × N/C and C/N, density and ash content in peat cores.

cumulative unsupported ^{210}Pb inventories and 95% of cumulative ^{210}Pb inventory was used as an "equivalent point" (Malmer and Holm, 1984) (Fig. 3c). The cumulative unsupported ^{210}Pb inventory was calculated according to Sonke et al. (2003)

$$A_{\text{inventory}} = \sum (^{210}\text{Pb})_i \times d_i \times \rho_i \quad (3)$$

where $(^{210}\text{Pb})_i$ is the unsupported ^{210}Pb activity (Bq g^{-1}) in peat section i, d_i is the thickness of section i (cm), and ρ_i is the bulk density of section i (g cm^{-3}). Here again the Hg inventories vary between 8.5 and 11.6 mg Hg m^{-2}, i.e. by the same factor of 1.4 (Fig. 3c). Such within-peat variations occur in the literature; they are explained as caused by differences or changes in vegetation (tree canopies or microtopography in open bogs), which can locally increase the atmospheric deposition of Hg (Norton et al., 1997; Bindler et al., 2004; Bindler, 2006; Coggins et al., 2006). Similarly high inventories of Hg were also observed in the mor layer close to a smelter (Rönnskär, northern Sweden), with values up to 7.5 mg Hg m^{-2}, indicating a nearby point pollution source (Klaminder et al., 2008). Mercury inventories from other European peat sites are significantly lower, indicating probably more distant sources of contamination: 2.04–3.67 mg Hg m^{-2} (last 76–113 yr) in Ireland (Coggins et al., 2006), 0.85–3.4 mg Hg m^{-2} (last 110 yr) in Sweden (Bindler et al., 2004), 0.21–1.11 mg Hg m^{-2} (last 100 yr) in Norway (Steinnes and Sjøbakk, 2005).

3.4. Uncorrected and corrected Hg accumulation rates

Due to the relatively shallow and young peat (see for example low C contents in the bottom of peat core 1), it was not possible to evaluate pre-industrial (background) Hg fluxes. It is probable that long-term ore mining and processing in the Příbram district undoubtedly elevated the historical bulk Hg accumulations recorded in three peat profiles in comparison with other peat deposits in remote areas (e.g., Bindler, 2003, Biester et al., 2003). This influence can be implied from the fact that even the deepest horizons of peat cores (with high ash content) yield significantly higher Hg concentrations compared to

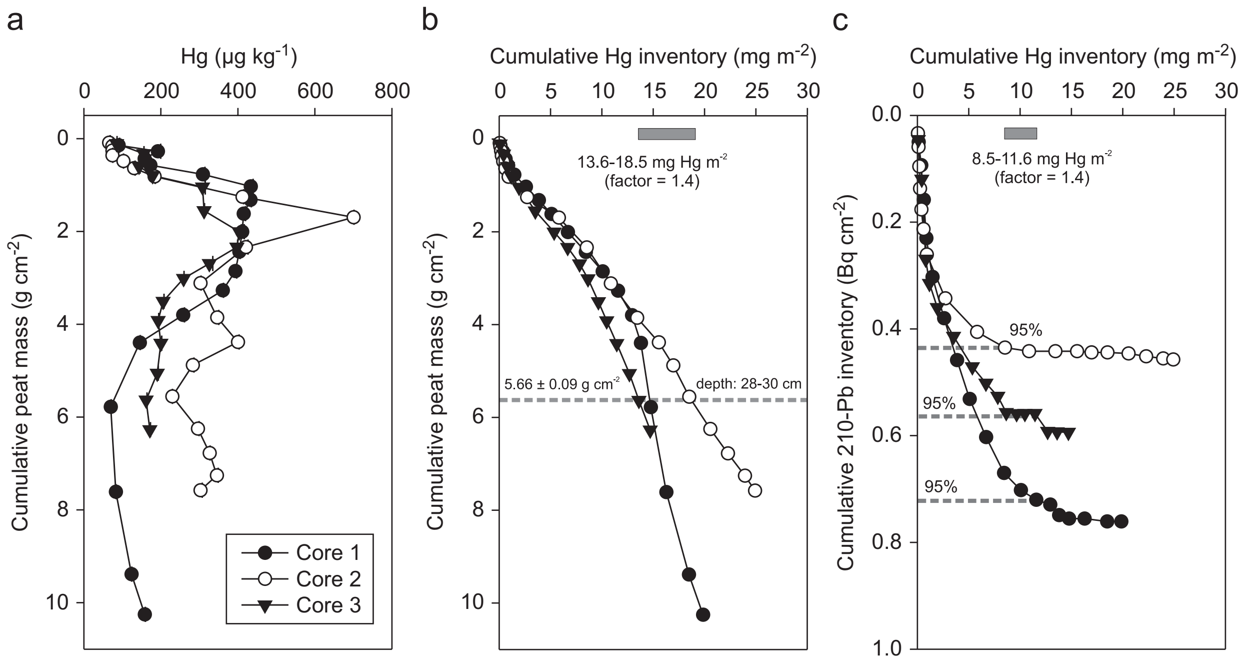

Fig. 3. Mercury concentration profiles and cumulative Hg inventories plotted against the cumulative peat mass and cumulative ^{210}Pb inventories.

the local bedrock (~30 μg Hg kg^{-1}). It is however important to stress that deeper parts of studied profiles are minerogenic and relatively high Hg contents (first hundreds of μg kg^{-1}) were also observed in minerogenic peats even at remote sites (e.g., Franzen et al., 2004).

All three peat cores show similar trends in uncorrected Hg accumulation with the highest peaks in the subsurface peat sections corresponding to ages between the 1960s and 1980s (Fig. 4). Core 1 is characteristic with the local maximum of net Hg accumulation in the depth 32–34 cm (dated to 1830 ± 35) corresponding probably to a lithogenic enrichment (98 μg Hg m^{-2} yr^{-1}), and a steep increase up to 225 μg Hg m^{-2} yr^{-1} at a depth of 10–12 cm (dated to 1987 ± 3). Enrichment also occurs in the uppermost peat section of this core (131 μg Hg m^{-2} yr^{-1}). Core 2 exhibits a local maximum between 1880 and 1920 (depth 20–26 cm), which might correspond to a peak in the polymetallic ore mining in the Příbram district (Fig. 4). The maximum net Hg accumulations in the range of 144–150 μg Hg m^{-2} yr^{-1} were observed in this core in section dated to 1959 ± 10 to 1976 ± 6 (depth 14–18 cm). The uppermost horizon of core 2 had a net Hg accumulation rate of 58 μg Hg m^{-2} yr^{-1}. For core 3, a local maximum in net Hg accumulation rate occurred between 1860 and 1880, followed by a steep increase after 1940, attaining the value of 226 μg Hg m^{-2} yr^{-1} at a depth 10–12 cm dated to 1973 ± 4. As for the other cores, the surface peat sections have a high Hg accumulation rate (61–98 μg Hg m^{-2} yr^{-1}) (Fig. 4). Even higher peaks of Hg accumulation rates were found in peat cores and O-horizons of forest soils in the vicinity of a smelter in northern Sweden. There, Hg accumulation rates reached 360 μg m^{-2} yr^{-1} (Klaminder et al., 2008). This peak corresponded in time to the highest smelter production in the early 1970s. A significant increase of Hg accumulation rates in the uppermost peat layers observed in our cores may be an artifact resulting from underestimation of ages by ^{210}Pb chronology and subsequent overestimation of Hg fluxes (Bindler, 2006; Biester et al., 2007).

Numerous researchers have recently suggested that the net Hg accumulation rates might be unrealistically high (Biester et al., 2002, 2003, 2007; Bindler, 2006). Due to concerns about peat mass decomposition and its effect on quantitative records of Hg in peat (Biester et al., 2003; Bindler, 2006) we applied MLCF. Although the selection of reference sections seems to be somewhat arbitrary, the C/N ratio of reference samples is probably the most important parameter describing the degree of humification. Malmer and Nils (1984) found that surface peat layers with low degree of humification generally exhibit the C/N ratios > 35, whereas highly humified peat exhibits the C/N ratios between 20 and 35. Thus, for the calculation of MLCF, the reference sections from the catotelm (high-humified peat) corresponding to a depth 28–30 cm were selected. In core 1, the section with C/N ratio 21.9 was dated to 1872 ± 24 and was selected because deeper sections exhibited significantly lower C contents, probably due to high contribution of lithogenic material. In cores 2 and 3, the selected reference sections were dated to 1807 ± 33 and 1855 ± 20 and have C/N ratios 21.6 and 43, respectively. The C/N ratios in core 3 showed a C-shape pattern (Fig. 2g) indicating probably changes of humification in peat profile (a similar phenomenon was observed by Biester et al., 2003). As deeper sections in this core exhibited even higher C/N ratios, the section at a depth 28–30 cm with the C/N ratio of 43 was selected as reference. An example of calculation of uncorrected and

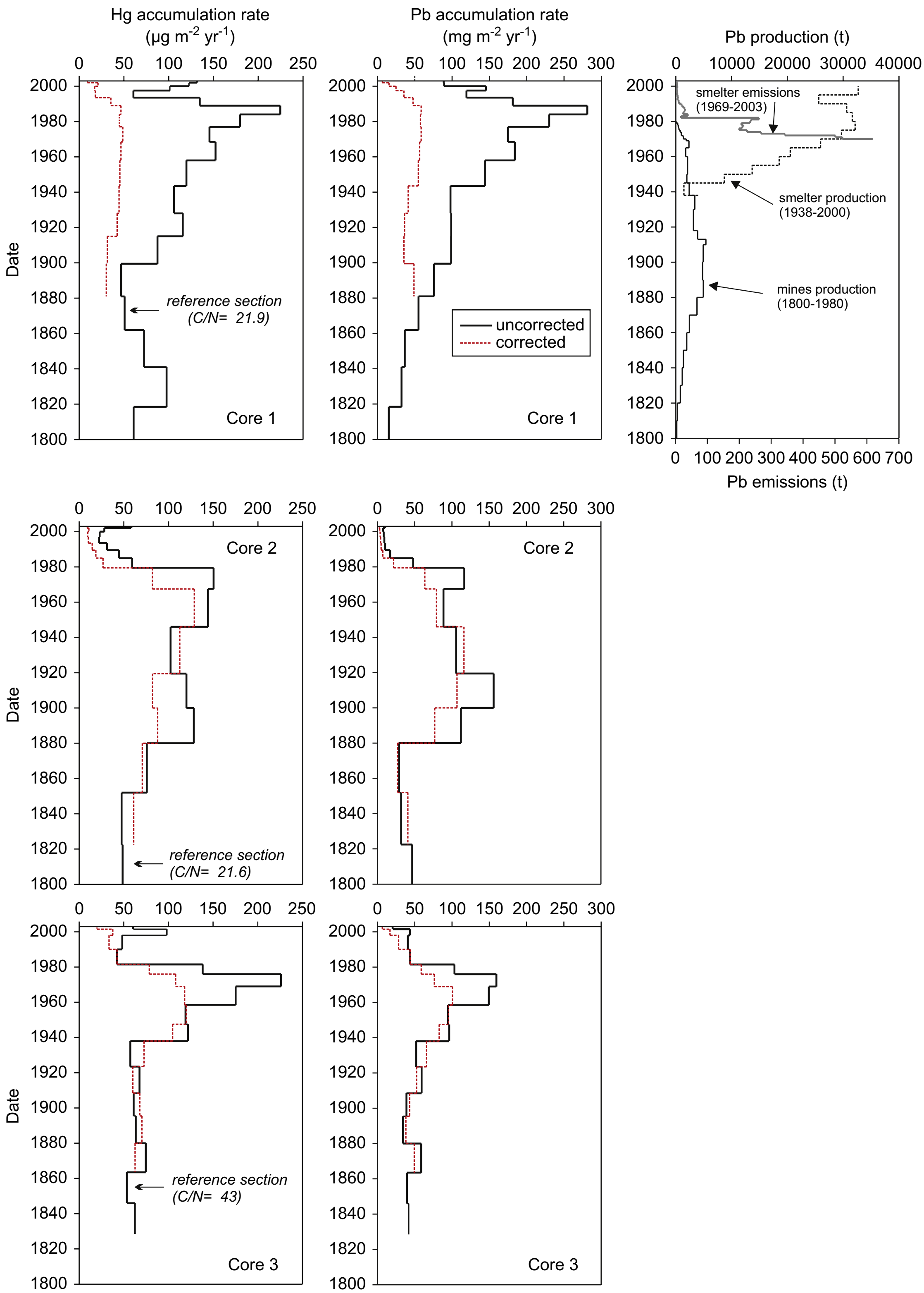

Fig. 4. Uncorrected and corrected Hg accumulation trends ($\mu g\,m^{-2}\,yr^{-1}$), Pb accumulation trends ($mg\,m^{-2}\,yr^{-1}$) and Pb production and emissions at Příbram. Correction of accumulation rates on basis of Biester et al. (2003).

Table 2
Example of calculation of uncorrected and corrected Hg and Pb accumulation trends in peat core 2

Section (cm)	^{210}Pb date (yr ± SD)	Interpolated date[a] (yr)	C accumulation rate ($g\,m^{-2}\,yr^{-1}$)	MLCF[b]	Hg accumulation rate		Pb accumulation rate	
					Uncorrected ($\mu g\,m^{-2}\,yr^{-1}$)	Corrected ($\mu g\,m^{-2}\,yr^{-1}$)	Uncorrected ($mg\,m^{-2}\,yr^{-1}$)	Corrected ($mg\,m^{-2}\,yr^{-1}$)
0–2	2003 ± 0	2002	383	0.16	58.2	9.0	9.8	1.5
2–4	2001 ± 1	2000	154	0.39	28.2	10.9	7.5	2.9
4–6	1999 ± 1	1997	141	0.42	23.0	9.7	8.4	3.5
6–8	1995 ± 2	1993.5	130	0.46	22.3	10.2	9.1	4.2
8–10	1992 ± 2	1989.5	126	0.47	31.2	14.7	10.2	4.8
10–12	1987 ± 3	1985	142	0.42	44.5	18.7	17.0	7.1
12–14	1983 ± 3	1979.5	131	0.45	59.2	26.8	47.8	21.6
14–16	1976 ± 6	1967.5	109	0.54	150	81.9	117	63.5
16–18	1959 ± 10	1946	66	0.89	144	129	88.6	79.2
18–20	1933 ± 13	1919.5	54	1.10	102	113	106	116
20–22	1906 ± 15	1900	87	0.68	120	82.2	156	107
22–24	1894 ± 17	1880	87	0.69	128	87.9	112	76.7
24–26	1866 ± 24	1852	64	0.93	75.8	70.6	29.0	27.0
26–28	1838 ± 25	1822.5	46	1.29	47.5	61.0	31.6	40.7
28–30	1807 ± 33	1790.5	59	Reference	48.6		46.6	

[a] Date of the bottom of each peat section (calculated according to Vile et al., 1995).
[b] MLCF– mass loss compensation factor (calculated as a ratio of C accumulation in a reference section and that in a given section, according to Biester et al., 2003).

corrected Hg (and Pb) accumulation rates using the MLCF approach is reported in Table 2.

The corrected Hg accumulation rates were obtained for a period at least 130 yr. The corrected Hg accumulation rates in core 1 significantly decreased in comparison with the uncorrected values (by a mean factor of 4.3). A slight increase of Hg accumulation rate was observed after 1920 with a peak between 1973 and 1987 (maximum value of 48 $\mu g\,Hg\,m^{-2}\,yr^{-1}$) (Fig. 4). Cores 2 and 3 show a very consistent record of Hg accumulation with highest values in late 1950s and 1960s (core 2: 128 $\mu g\,Hg\,m^{-2}\,yr^{-1}$; core 3: 118 $\mu g\,Hg\,m^{-2}\,yr^{-1}$). Significantly lower, corrected Hg accumulation rates in the case of core 1 (compared to cores 2 and 3) can be related to higher C accumulation rates (mean values are 197, 123 and 152 $g\,m^{-2}\,yr^{-1}$ for cores 1, 2 and 3, respectively, in segments where the correction was applied). This is also manifested by significantly higher cumulative peat mass for this core (Fig. 3). The within-deposit variability in C accumulation is a common phenomenon, observed at numerous sites (e.g., Ohlson and Økland, 1998). This can be related to the sampling position of core 1 within the peat deposit (Fig. 1); it is located close to the forested area and higher C accumulation rates might be related to higher input of the organic material from the tree canopies.

3.5. Comparison with Pb accumulation, smelter production and biomonitoring

The MLCF correction has the same effect on Pb accumulation rates (Fig. 4). This approach is questionable for Pb, because some recent studies showed that Pb concentrations in peat are less related to degree of peat decomposition than Hg concentrations. For example, the data from Dumme Mosse in Sweden show that Hg is strongly correlated with C/N ($R^2 = 0.67$) (C/N ratio is used as a proxy of decomposition, where lower ratios indicate higher degree of peat decomposition). In contrast, Pb exhibited no relationship to the C/N ratio (Bindler, 2006). The same comparison for our cores show low correlation with C/N for both elements, but slightly better for Hg (Hg: $R^2 = 0.32$; Pb: $R^2 = 0.21$). It could be that C is lost from peat as methane, CO_2, or dissolved organic carbon and some elements strongly bound to organic material (such as Hg, which can be volatilized) are related to this loss (Bindler, 2006).

Although smelter-derived Hg emission rates are unknown, the maxima of corrected Hg accumulation rates better correlate with the evolution of Pb emissions than uncorrected Hg accumulation rates do. The Pb emissions from the smelter were reported since 1969 only, when they reached 624 $t\,Pb\,yr^{-1}$. The Pb emissions sharply declined after 1969, with one maximum in 1982 (259 $t\,Pb\,yr^{-1}$), and reached 0.99 $t\,Pb\,yr^{-1}$ in 2003 (Mihaljevič et al., 2006; www.kovopb.cz). The significant decrease of Pb emissions from the smelter was related to the improvement of flue-gas cleaning technologies, which may have affected Hg similarly.

Direct measurements of Hg deposition fluxes are unavailable. We compared our results with recent deposition studies using mosses. The Příbram district has the highest Hg concentration in forest floor humus for the Czech Republic (Suchara and Sucharová, 2002). Biomonitoring studies (Sucharová and Suchara, 2004), using the moss species *Pleurozium schreberi*, estimated that the Hg deposition rates in the Příbram area ranged from 4.7 to 34.4 $\mu g\,m^{-2}\,yr^{-1}$ in 1999. Such values fit well within the net corrected (for C accumulation rates) accumulation rates of Hg obtained from the studied peat profiles (2–38 $\mu g\,Hg\,m^{-2}\,yr^{-1}$ between 1996 and 2003; Fig. 4). The same biomonitoring study showed that Pb deposition rates in the area (0.5–127 $mg\,m^{-2}\,yr^{-1}$ in 1999) fit better with our uncorrected accumulation rates obtained from peat cores (7–145 $mg\,m^{-2}\,yr^{-1}$ between 1996 and 2003) than with the MLCF-corrected values (1–28 $mg\,m^{-2}\,yr^{-1}$).

Regardless of possible overestimation of accumulation rates in the uppermost sections due to ^{210}Pb smearing, and thus underestimation of peat ages (Biester et al., 2007), it seems that the MLCF approach for correction of metal accumulation rates in peat may be applicable in some cases. It appears applicable for Hg but probably not for Pb. The application of this approach originally developed for ombrotrophic peat bogs should be tested further on other minerogenic sites. Further investigation of biogeochemical processes of Hg cycling (accumulation, retention, and release) in peat is necessary to interpret satisfactorily the historical Hg deposition rates in this type of archive.

4. Conclusion

Three ^{210}Pb-dated cores from a peat deposit 10 km from the Pb smelter at Příbram (Czech Republic) were studied to determine historical Hg accumulation rates in an area affected by historical ore mining and smelting. The Hg concentrations in peat ranged from 66 to 701 $\mu g\,kg^{-1}$. Using the Hg accumulation rates corrected to mass loss (Biester et al., 2003), the peat cores provided a record of Hg deposition/accumulation better corresponding to the historical evolution of mining/smelting activities than the uncorrected Hg accumulation trends. These corrected Hg accumulation rates also correspond better to deposition rates derived from moss biomonitoring. Cumulative Hg inventories back to ~1850 from individual cores varied by 40%, probably because of variability in Hg deposition and accumulation related to the effects of vegetation on interception of Hg from the atmosphere and differences in C accumulation rates. This study emphasizes the necessity of multiple sampling at peat deposit and dating more than one peat core to reconstruct correctly the contaminant deposition/accumulation in the vicinity of smelting sites.

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References

Appleby, P.G., Oldfield, F., 1978. The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to sediment. Catena 5, 1–8.

Appleby, P.G., 2008. Three decades of dating recent sediments by fallout radionuclides: a review. The Holocene 18, 83–93.

Baron, S., Lavoie, M., Ploquin, A., Carignan, J., Pulido, M., De Beaulieu, J.L., 2005. Record of metal workshops in peat deposits: history and environmental impact on the Mont Lozère Massif, France. Environmental Science and Technology 39, 5131–5140.

Biester, H., Kilian, R., Franzen, C., Woda, C., Mangini, A., Schöler, H.F., 2002. Elevated mercury accumulation in a peat bog of the Magellanic Moorlands, Chile (53°S)—an anthropogenic signal from the Southern Hemisphere. Earth and Plantery Science Letters 201, 609–620.

Biester, H., Martinez-Cortizas, A., Birkenstock, S., Kilian, R., 2003. Effect of peat decomposition and mass loss on historic mercury records in peat bogs from Patagonia. Environmental Science and Technology 37, 32–39.

Biester, H., Bindler, R., Martinez-Cortizas, A., Engstrom, D.R., 2007. Modeling the past atmospheric deposition of mercury using natural archives. Environmental Science and Technology 41, 4851–4860.

Bindler, R., 2003. Estimating the natural background atmospheric deposition rate of mercury utilizing ombrotrophic bogs in southern Sweden. Environmental Science and Technology 37, 40–46.

Bindler, R., Klarqvist, M., Klaminder, J., Förster, J., 2004. Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat record? The example of Store Mosse, Sweden. Global Biogeochemical Cycles 18, GB3020.

Bindler, R., 2006. Mired in the past–looking to the future: geochemistry of peat and analysis of past environmental changes. Global and Planetary Change 53, 209–221.

Coggins, A.M., Jennings, S.G., Ebinghaus, R., 2006. Accumulation rates of the heavy metals lead, mercury and cadmium in ombrotrophic peatlands in the west Ireland. Atmospheric Environment 40, 260–278.

Ettler, V., Rohovec, J., Navrátil, T., Mihaljevič, M., 2007. Mercury distribution in soil profiles polluted by lead smelting. Bulletin of Environmental Contamination and Toxicology 78, 12–16.

Franzen, C., Kilian, R., Biester, H., 2004. Natural mercury enrichment in a minerogenic fen—evaluation of sources and processes. Journal of Environmental Monitoring 6, 466–472.

Givelet, N., Roos-Barraclough, F., Shotyk, W., 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulations in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years). Journal of Environmental Monitoring 5, 935–949.

Henderson, P.J., McMartin, I., Hall, G.E., Percival, J.B., Walker, D.A., 1998. The chemical and physical characteristics of heavy metals in humus and till in the vicinity of the base metal smelter at Flin Flon, Manitoba, Canada. Environmental Geology 34, 39–58.

Klaminder, J., Bindler, R., Rydberg, J., Renberg, I., 2008. Is there a chronological record of atmospheric mercury and lead deposition preserved in the mor layer (O-horizon) of boreal forest soils? Geochimica et Cosmochimica Acta 72, 703–712.

Malmer, N., Holm, E., 1984. Variation in the C/N-quotient of peat in relation to decomposition rate and age determination with ^{210}Pb. Oikos 43, 171–182.

Mihaljevič, M., Zuna, M., Ettler, V., šebek, O., Strnad, L., Goliáš, V., 2006. Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic). Science of the Total Environment 372, 334–344.

Monna, F., Galop, D., Carozza, L., Tual, M., Beyrie, A., Marembert, F., Château, C., Dominik, J., Grousset, F.E., 2004. Environmental impact of early Basque mining and smelting recorded in a high ash minerogenic peat deposit. Science of the Total Environment 327, 197–214.

Norton, S.A., Evans, G.C., Kahl, J.S., 1997. Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to nearby Sargent Mt Pond, Maine, USA. Water, Air, and Soil Pollution 100, 271–286.

Ohlson, M., Økland, R.H., 1998. Spatial variation in rates of carbon and nitrogen accumulation in a boreal bog. Ecology 79, 2745–2758.

Rausch, N., Ukomaanaho, L., Nieminen, T.M., Krachler, M., Shotyk, W., 2005. Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in acidic, ombrotrophic bog impacted by a smelter, Harjavalta, Finland and comparison with reference sites. Environmental Science and Technology 39, 8207–8213.

Rieuwerts, J.S., Farago, M.E., 1996. Mercury concentrations in a historic lead mining and smelting town in the Czech Republic: a pilot study. Science of the Total Environment 188, 167–171.

Rieuwerts, J.S., Farago, M.E., Cikrt, M., Bencko, V., 1999. Heavy metal concentrations in and around households near a secondary lead smelter. Environmental Monitoring and Assessment 58, 317–335.

Roos-Barraclough, F., Martinez-Cortizas, A., García-Rodeja, E., Shotyk, W., 2002. A 14 500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. Earth and Planetary Science Letters 202, 435–451.

Roos-Barraclough, F., Givelet, N., Shotyk, W., Norton, SA., 2006. A ten-thousand year record of mercury accumulation in peat from Caribou Bog, Maine, USA. USA Environmental Science and Technology 40, 3188–3194.

Rothwell, J.J., Ewans, M.G., Lindsay, J.B., Allott, T.E.H., 2007. Scale-dependent spatial variability in peatland lead pollution in the southern Pennines, UK. Environmental Pollution 145, 111–120.

Shotyk, W., Goodsite, M.E., Roos-Barraclough, F., Frei, R., Heinemeier, J., Asmund, G., Lohse, C., Hansen, T.S., 2003. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the ^{14}C "bomb pulse curve". Geochimica et Cosmochimica Acta 67, 3991–4011.

Sonke, J.E., Burnett, W.C., Hoogewerff, J.A., van der Laan, S.R., Vagronsveld, J., Corbett, D.R., 2003. Reconstructing 20th century lead pollution and sediment focusing in a peat land pool (Kempen, Belgium), via ^{210}Pb dating. Journal of Paleolimnology 29, 95–107.

Steinnes, E., Sjøbakk, T.H., 2005. Order-of-magnitude increase of Hg in Norwegian peat profiles since the outset of industrial activity in Europe. Environmental Pollution 137, 365–370.

Suchara, I., Sucharová, J., 2002. Distribution of sulphur and heavy metals in forest floor humus of the Czech Republic. Water, Air, and Soil Pollution 136, 289–316.

Sucharová, J., Suchara, I., 2004. Distribution of 36 element deposition rates in a historic mining and smelting area as determined through fine-scale biomonitoring techniques, Part I: relative and absolute current atmospheric deposition levels detected by moss analyses. Water, Air, and Soil Pollution 153, 205–228.

Vile, M.A., Novák, M.J.V., Břízová, E., Wieder, R.K., Schell, W.R., 1995. Historical rates of atmospheric Pb deposition using ^{210}Pb dated peat cores: corroboration, computation, and interpretation. Water, Air, and Soil Pollution 79, 89–106.