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Mercury Distribution in Soil Profiles Polluted by Lead Smelting

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The smelting industry is one of the most important sources of anthropogenic contamination of the environment today. In the vicinity of nonferrous metal smelters, high concentrations of toxic compounds (especially metals and metalloids) have been detected in soils and vegetation (e.g., Ettler et al., 2005a; Suchara and Sucharová, 2002; Svoboda et al., 2000). In these instances, smelter emissions are assumed to be the dominant source of soil contamination (Ettler et al., 2005a,b). In the vicinity of a Pb smelter, Ettler et al. (2004) found that metals such as Pb strongly migrate downwards in soils and accumulate in mineral soil horizons.

The form of metal in smelter emissions varies significantly. The smelter emissions in traditional Hg-mining areas are mainly composed of elemental Hg^0, coming from the vapor produced and emitted by roasting furnaces (Fernández-Martínez et al., 2006). In contrast, the emissions from Pb smelters are mainly composed of Pb-sulfates and Pb-chlorides, and no specific Hg-bearing phases were detected in fly ash by the mineralogical methods (Ettler et al., 2005b). Nevertheless, soil Hg concentrations can be high enough to be considered a severe contaminant even in areas polluted by Pb smelting (Rieuwerts and Farago, 1996). Interestingly, little attention has been given to Hg concentrations in soils and vegetation in the vicinity of primary and secondary Pb smelters. This article describes the differences in total Hg concentrations between undisturbed forest and tilled soil profiles affected by a Pb smelter at Příbram, Czech Republic. Mercury sources and the vertical migration of mercury through soils are discussed.

Materials and Methods

The mining and smelting district of Příbram, Czech Republic, is known for its Pb-Ag-Zn polymetallic mineral deposits, which were mined and processed from the Middle Ages until the 1970s. Since 1974, the Pb smelter in the district operates as a secondary smelter that processes Pb scrap, mainly car batteries (more information on smelter operations is recorded in Ettler et al., 2001, 2005b). Topsoils in the area are highly contaminated by Pb (up to 58,500 mg/kg), Zn (up to 21,900 mg/kg), Cu (up to 2444 mg/kg), and Cd (up to 96 mg/kg), as reported elsewhere (e.g., Rieuwerts et al., 1999).

The pilot study of Rieuwerts and Farago (1996) in the Příbram district pointed out the Hg contamination of topsoils. Later, elevated Hg contents in coniferous forest floor humus of the Příbram district were reported by Suchara and Sucharová (2002). The distribution of Hg in smelter- and mining-affected areas of Příbram was not yet investigated.

In this study, eight soil profiles were investigated at four sampling sites that were various distances from the smelter stack (1 km and 2 km downwind and 1 km and 4 km upwind). At each sampling site, one forest soil profile (coniferous stand) and one tilled soil profile (farmed area) were sampled. The detailed description and GPS positions of each soil sampling site are reported elsewhere (Ettler et al., 2005a). Soils were classified as Typic or Aquic Dystrudepts in the soil order Inceptisols. Soils were sampled to represent each of the major morphological horizons

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Table 1 Hg concentrations and physicochemical properties in smelter-affected forest and cultivated soils, bedrock, and fly ash from Pb metallurgy

Parameter	Units	Forest soil (n = 15)		Cultivated soils (n = 15)		Bedrock (n = 4)	Fly ash
		Range	Mean	Range	Mean	Range	Mean
Hg	μg/kg	97–6485	1490	73–605	289	33–222	1312
pH	Standard Units	3.39–4.03	3.58	4.15–5.62	4.74		
TOC	%	1.7–48.6	30.5	0.3–5.0	2.1		
TIC	%	< 0.05–0.08	0.06	< 0.05–0.09	0.07		
S_{tot}	%	< 0.02–0.38	0.19	< 0.02–0.05	0.03		
CEC	$cmol_c/kg$	6.46–42.16	24.06	3.47–10.66	6.38		
Fe_o	g/kg	1.47–8.82	3.48	0.56–3.62	2.16		
Mn_o	g/kg	0.03–2.18	0.46	0.19–1.36	0.77		
Al_o	g/kg	0.76–5.34	2.00	0.09–1.45	0.87		

TOC, total organic carbon; TIC, total inorganic carbon; CEC, cation exchange capacity; Fe_o, Mn_o, Al_o = oxalate-extractable Fe, Mn, and Al

from the excavated soil pits. The top surface horizon, composed of fresh litter and fresh grass cover, was removed. The pieces of underlying bedrock were sampled at the bottom of each soil pit. Soils were air-dried and sieved through a 2-mm polyethylene sieve. The sieved soils were used for the determination of physicochemical properties. Soil and bedrock samples, and fly ash from the Příbram secondary Pb smelter, were finely ground in agate mortar prior to the determination of total Hg content.

Soil pH was determined using a 1:2 (v/v) ratio of soil and deionized water suspension. The concentrations of total inorganic and organic carbon (TIC, TOC) and total sulfur (S_{tot}) were determined using a Eltra Metalyt CS1000S elemental analyzer. Cation exchange capacity (CEC) was determined as the sum of basic cations (i.e., Ca, Mg, K, and Na) and Al extracted with 0.1 M $BaCl_2$ solution and extractable acidity. Basic cations and Al were determined by flame atomic absorption spectrometry (FAAS; Varian SpectrAA 200 HT). Soil acidity was measured by back titration with 0.05 M NaOH (ICP Forest Manual, 2003). Oxalate-extractable Fe, Al, and Mn (corresponding to amorphous Fe, Al, and Mn oxides) were determined in 0.2 M ammonium oxalate/oxalic acid solution at pH 3. The contents of Fe, Al, and Mn in extracts were determined by FAAS.

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. The determinations were performed in triplicate (relative standard deviation [RSD] was < 3%). Quality control of Hg measurements was assured by the analysis of standard reference material ‘‘river stream sediment 1,’’ produced by Analytika Co (Praha, Czech Republic). Triplicate measurements yielded 1578 ± 42 μg/kg, corresponding well with the certified values 1550 ± 70 μg/kg.

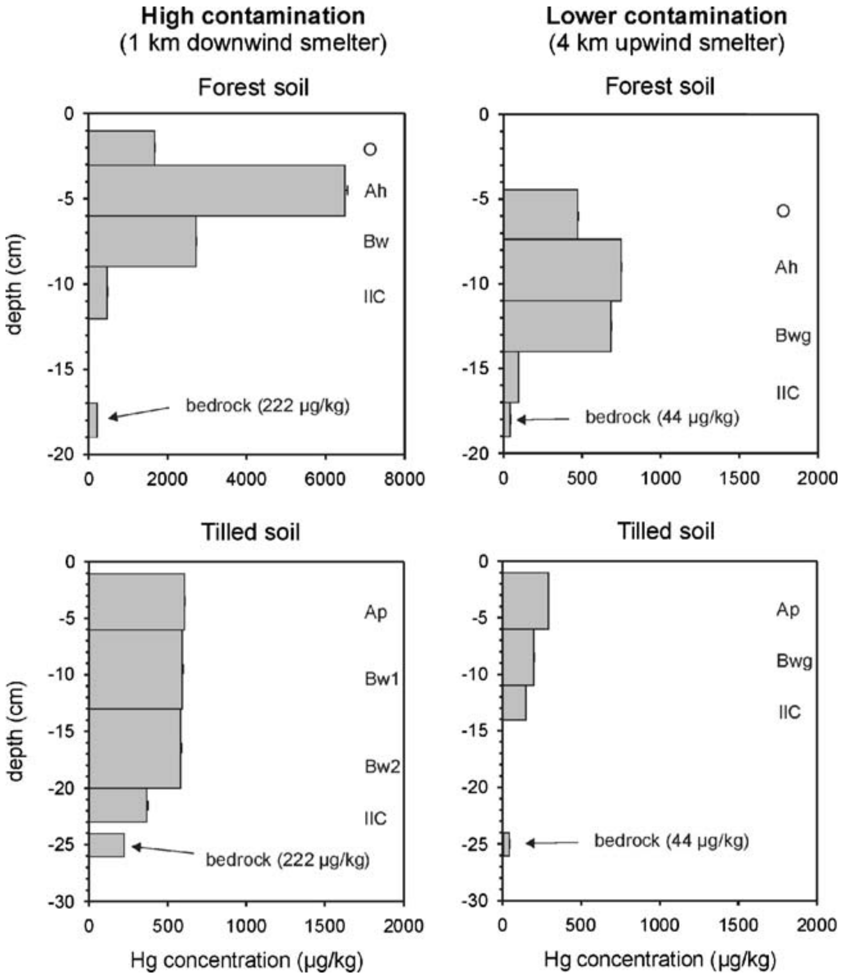
The statistical data treatment was performed using the NCSS software (Hintze, 2001). Each of the 30 samples was considered to be a vector with 11 variables (sample pH, CEC, base saturation, acidity, TOC, TIC, total S, oxalate-extractable Fe, Mn and Al, bulk Hg concentration). As a result, a data matrix with dimensions of 30 × 11 was used to calculate Pearson correlation coefficients. Values lower than detection limits (DL) were removed from the dataset (this was done only for some TIC and S_{tot} values).

Results and Discussion

Selected physicochemical properties of all studied soils are shown in Table 1. Forest soils are more acidic (mean pH 3.58) and are significantly more organic (mean TOC 30.5 %) than cultivated soils. Similarly, total S is generally higher in forest soils. This phenomenon can be related to a higher supply of S (derived from smelter emissions) because of a higher interception of tree canopy in forested area. Note that Ettler et al. (2005a) found the presence of anglesite ($PbSO_4$) by X-ray diffraction analysis in these smelter-affected forest soils, also contributing to the higher S content. Higher oxalate-extractable Fe and Al were observed for forest soils (Table 1). Significantly higher values of CEC detected in forest soils were related to the higher exchangeable pool of basic cations bound to the surfaces of organic matter and amorphous Fe and Al oxides.

Although the actual efficiency of the emissions control in the smelter is > 99% (Ettler et al., 2005b), it is presumed that historical emissions from the smelter stack were significantly higher and are responsible for the high degree of soil contamination. In 1960s, the particulate emissions were approximately 500 times higher than today (Vurm, 2001). In addition, historical fly ashes derived from ore processing were probably richer in Hg than those derived

Fig. 1 The vertical Hg distribution in forest and cultivated soil profiles



from car battery processing. Although specific Hg-bearing minerals are not common in the Příbram polymetallic mining district, trace Hg contents were detected in galena (PbS) and sphalerite (ZnS) that were historically mined and processed at Příbram (Bambas, 1990).

Physicochemical parameters of forest O and Ah horizons were similar, with the exception of bulk Hg contents. The O horizons exhibit lower Hg concentrations than Ah horizons (Fig. 1). This phenomenon can be related either to (i) vertical migration of Hg or to (ii) lower contamination of currently deposited litter that forms O horizons. Mercury concentrations were much higher in forest soils ranging up to 6485 µg/kg, whereas the maximum Hg concentrations in cultivated soils were ten times lower, that is, 605 µg/kg (Table 1). Figure 1 shows the vertical Hg distribution in the most and the least contaminated forest and cultivated soil profiles (located downwind and upwind of the smelter, respectively).

A comparison of total Hg concentrations in individual soil horizons and in the underlying bedrock can be used to determinate the degree of contamination. All soil horizons are enriched in Hg with respect to the bedrock concentrations (2 to 70 times for forest soils and 2 to 9 times for cultivated soils). These increased concentrations could be attributable to either (i) higher inputs from above caused by deposition and downward migrations, and/or (ii) magnification of concentrations caused by natural weathering processes in soils. The highest Hg contents were observed in subsurface horizons Ah of forest soils (Fig. 1). In contrast, an effect of ploughing and mixing, documented by uniform Hg concentrations in surface horizons, was observed in all cultivated soil profiles (Fig. 1).

Mean Hg concentrations were generally one order of magnitude lower in cultivated soils than in forest soils from the same locality (Table 1). This observation likely reflects the higher efficiency that tree canopies have as compared with herbaceous vegetation in scavenging particulates from the atmosphere, which results in greater throughfall, stemflow, and litterfall deposition (Rea at al., 2002). Recently, Sheehan et al. (2006) observed that Hg deposition in litterfall is much greater than in precipitation. Because of this deposition, litter in forested areas at Příbram district has corresponded to significantly increased Hg concentrations (see also Ettler et al., 2005a; Rieuwerts and Farago,

Table 2 Pearson correlation coefficients between total Hg concentration and physicochemical parameters for all studied soils (n = 30)

	Hg
pH	–0.558 *
TOC (total organic carbon)	0.439 *
TIC (total inorganic carbon)	–0.239
S_{tot} (total sulfur)	0.743**
CEC (cation exchange capacity)	0.149
BS (base saturation)	–0.123
Acidity	0.707**
Fe_o (oxalate-extractable Fe)	0.947**
Al_o (oxalate-extractable Al)	0.245
Mn_o (oxalate-extractable Mn)	–0.694**

* statistically significant at $p < 0.1$

** statistically significant at $p < 0.001$

1996). In addition, it is possible that Hg uptake and removal in harvested crops can result in significantly lower Hg concentrations in cultivated soil from agricultural areas. The Hg concentration profiles (Fig. 1) show evidence of a high vertical mobility. If magnification of Hg concentration because of weathering would be negligible, the vertical Hg mobility could be estimated by combining the known time of the Příbram smelter operation (continuously for 220 years) and the depth of Hg enrichment in undisturbed forest soil horizons with respect to bedrock (see also Ettler et al., 2004, for Pb vertical mobility calculations). Then, the calculated vertical Hg mobility would correspond to 0.03–0.07 cm per year.

The correlation coefficients between total Hg concentrations and physicochemical properties of soils are shown in Table 2. Although correlation coefficients do not demonstrate causality, they can be useful indicators of possible Hg binding mechanisms between physicochemical parameters and Hg distribution in soil.

Negative correlations with pH ($p < 0.1$) and positive correlation with acidity ($p < 0.001$) are consistent with the higher Hg contamination in more acidic forest soils. But such relationships could indicate coincident trends; the acidity is not directly influencing the retention of Hg in soil, because pH was negatively correlated with TOC content ($p < 0.001$). Significant correlations with TOC ($p < 0.1$) and oxalate-extractable Fe ($p < 0.001$) show that organic matter (Yin et al., 1996) and amorphous Fe oxides (Kinniburgh et al., 1978) are the most important sinks for Hg binding. The significant correlation between Hg and loss-on-ignition (LOI), observed by Rieuwerts and Farago (1996) on the topsoils from the same site, reflected a strong affinity of Hg for organic matter. Similarly, a significant positive correlation was found by Tack et al. (2005) between organic carbon and baseline Hg concentrations in Flemish soils, showing that TOC could be a good predictor of Hg concentrations.

It is important to note that Hg concentrations in the forest floor humus (Suchara and Sucharová, 2002) frequently exceed the limit 800 µg Hg/kg defined by Czech legislation (Czech Regulation 13/1994). Our study shows that organic, Ah and Bw horizons of forest soil profiles can be assumed to be polluted. However, this maximum permissible threshold was not exceeded in any of the horizons of cultivated soils in this study. According to the deposition loads calculated by Suchara and Sucharová (2002) for the Czech Republic, the forest soil profiles in the vicinity of the Příbram Pb smelter can be ranged within the soils affected by the very high levels of landscape loads (> 1250 µg Hg/kg).

Although few studies have focused on Hg contamination in the vicinity of primary/secondary Pb smelters, the present study shows evidence of soil Hg contamination that appears to be greatest in forest soils downwind of the smelter. Furthermore, there is some evidence of the vertical mobility of Hg, indicating that the individual soil horizons are enriched with respect to the uncontaminated, underlying bedrock. Further research is needed to determine the direct Hg speciation in the fly ash from the Pb smelter operations. Furthermore, the studies on Hg chemical fractionation and bioavailability in the present soils, using sequential extraction analyses (e.g., Bloom et al., 2003), are in progress in our laboratories.

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