Bull Environ Contam Toxicol (2008) 80:237–241
DOI 10.1007/s00128-007-9352-y

Distribution and Speciation of Mercury in Mine Waste Dumps

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Received: 14 May 2007 / Accepted: 26 December 2007 / Published online: 18 January 2008
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Abstract Mine waste dumps of historic mercury mines represent environmental threat. In the central Czech Republic, Hg ores were mined at two sites for more than 150 years. Mine wastes collected from dumps near Hg mines were elevated in total Hg (up to 120 µg g^{-1}). Thermal-desorption method revealed that most of Hg (>80%) in studied waste material was present as cinnabar (HgS), that is relatively stable in soils and resistant to formation of highly toxic methyl–Hg. Nevertheless minor part (<14%) of total Hg was identified as mineral surface bound Hg, which might undergo methylation and thus represents potential long-term environmental risk.

Keywords Mercury · Mine waste · Mercury speciation · Thermo-desorption analysis

Mercury is a ubiquitous pollutant, which enters the environment from both natural and anthropogenic sources. Among anthropogenic sources, Hg mining and smelting represent important sources of Hg pollution (Ebinghaus et al. 1998). The ecosystems surrounding Hg mining sites are usually highly contaminated (Biester et al. 1999; Loredo et al. 2005). Historical mining activities leave behind a legacy of contaminated mine dumps, which may serve as a permanent source of Hg for the environment. Therefore, the precise knowledge of Hg content and its forms in the waste material is essential to (1) evaluate the environmental risks and (2) assess the potentials for future Hg migration.

In the central Czech Republic (CR), Hg ores were mined at two sites at Jedová Hora (Poison Mountain) and Svatá (Saint). These mines produced considerably less Hg ore compared to well-known mines in Europe, such as Almaden (Spain) and Idrija (Slovenia). The mining wastes at these sites were piled at mine dumps without any precautions to avoid its spreading and, former mine dumps of different age and composition still remain at original locations. According to previous studies (e.g., Loredo et al. 2005) chemical and physical dispersion of Hg to the environment surrounding the mine dumps might occur in future and may cause local contamination problems.

The region of central CR was evaluated as the most Hg contaminated area according to the litter horizon studied in the entire country (Suchara and Sucharová 2002). Reported Hg concentrations in the litter horizons of the coniferous forest sites ranged from 0.9 to 1.25 µg g^{-1} in central CR. Another study in central CR reported Hg concentrations up to 6.5 µg g^{-1} in soils directly affected by Pb smelting (Ettler et al. 2007). Available data on Hg concentrations in Czech soils are rather scarce, but up to date, no information is available concerning Hg in Czech mine wastes.

The aim of this study was to provide initial insight into mercury sources in mine wastes of two abandoned mercury mines in central Czech Republic.

Materials and Methods

Mine waste samples were taken at dumps of two historical Hg mines, Jedová Hora and Svatá. The sampling sites are

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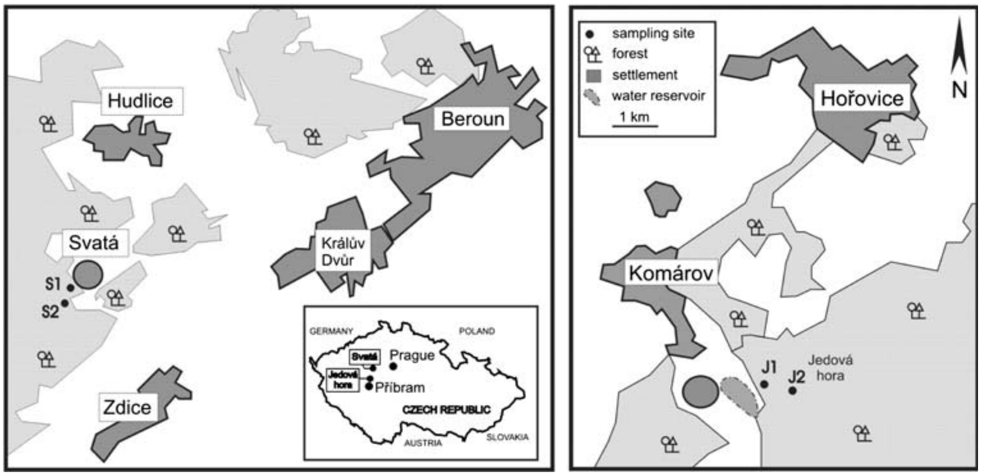


Fig. 1 Locations of studied mine waste dumps in the Czech Republic and detailed positions of each sampling site (S1, S2, J1, J2)

approximately 50 km SW of Prague, the capital of CR (Fig. 1). Mercury ore at both sites was cinnabar (HgS) that was produced as a byproduct of Ordovician iron ore mining. At Svatá, Hg mining was conducted from the second half of the 16th century till 1760. At Jedová Hora, Hg mining started in the 18th century and continued till 1870 (Sattran et al. 1978). The annual production of cinnabar at Svatá ranged from 100 to 500 kg. In total, the production during the mine operation (about 90 years) was estimated to be 10–20 tons of HgS (Velebil 2004). Amount of HgS mined at Jedová Hora was reportedly much greater than at Svatá (Sattran et al. 1978), but there is no exact information available on the total production. Velebil (2003) estimated the total production of 7.8 tons of HgS in the period from 1778 to 1779.

Mine waste material was sampled on two mine dumps at Svatá (S1 and S2) and on two dumps at Jedová Hora (J1 and J2) (Fig. 1). Areas of dumps at both sites with developed soils are recently covered with mixed forests (mostly European beech and Norway spruce). Mine waste material was sampled from the top 10 cm, and at the bottom of 1 m deep pits at each sampling site. All samples were freeze-dried, sieved (2 mm) and homogenized.

Concentration of total Hg was determined by a cold vapor-atomic absorption (CV-AAS) Hg analyzer AMA-254 (Altec Co., Czech Republic). Quality control was ensured using the commercially available standard reference material “river stream sediment 1” (Analytika Co.). Triplicate measurements of this material yielded $1.58 \pm 0.04\ \mu g\ g^{-1}$, corresponding well with the certified values $1.55 \pm 0.07\ \mu g\ g^{-1}$.

Mercury speciation analysis was carried out using a thermo-desorption (TD) method, which has been successfully applied to specify Hg-binding forms in solid material (e.g., Windmöller et al. 1996; Biester et al. 1999). The analysis was performed using a custom-made device that combines a programmable oven (Clasic, Czech Republic) placed into the Ar path of an ICP-OES (thermo-elemental Iris Intrepid II). The samples (150–200 mg, depending on the total Hg concentration) were heated in the oven with a temperature gradient $40°C\ min^{-1}$ up to 800°C in the presence of an Ar stream. The volatilized Hg was detected at 184.9 nm in a continuous detection mode. The results of TD analysis are presented as Hg thermo-desorption curves (TDC) representing the release of Hg versus temperature. Peak areas of TDC from natural samples were evaluated using peak fitting module of OriginPro software (ver. 7.03).

Thermo-desorption properties of standard Hg compounds (such as Hg^0, HgO, $HgCl_2$, and HgS) were evaluated in order to obtain optimal experimental setup. Effect of sorbent matrices on Hg release was calibrated with Hg(II) adsorbed onto standard materials such as clay minerals, Fe-oxyhydroxides and humic acid. In particular we used kaolinite and montmorillonite (Sigma Aldrich) and Fe-oxyhydroxides, goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), that commonly occur in soils, prepared according to Cornell and Schwertmann (1996). Hg(II) adsorption to the mineral samples was performed as follows: 1 g of the solid material was suspended in a 5 mL solution of $40–800\ \mu g\ Hg\ mL^{-1}$ (prepared from a stock solution of $1{,}000\ \mu g\ Hg\ mL^{-1}$ of $HgCl_2$). The suspension pH was not adjusted. The suspension was vigorously shaken at room temperature for 1 h, then left intact for 24 h. After supernatant removal by centrifugation, the obtained solid material was rinsed with distilled water and dried at 60°C. Adsorption of Hg(II) to humic acid (Sigma Aldrich) was prepared according to Arias et al. (2004).

Mine waste pH was determined using a 1:2 (v/v) ratio of waste material and deionized water suspension. Oxidizable carbon (C_{ox}) was determined by the sulfochromic oxidation method (ISO 14235 (1998)). Total sulfur (S_{tot}) was determined as $BaSO_4$ by gravimetric method. The X-ray diffraction analyses (XRD) were carried out using a PANalytical X’Pert Pro diffractometer with Cu Kα radiation at

40 kV and 30 mA, and step scanning at 0.05°/300 s in the range 3–80° 2θ.

Results and Discussion

Selected physicochemical properties of mine waste samples are given in Table 1. The mine wastes from Jedová Hora were in the neutral to basic range, but the samples from Svatá were acidic (Table 1). Higher waste pH at Jedová Hora was probably caused by the presence of siderite ($FeCO_3$) and other carbonates in the mine waste material. Top layers of mine dumps were generally rich with organic matter at both sites (C_{ox} up to 15.72%). Higher S_{tot} concentrations (Table 1) in selected samples were probably related to the presence of ore minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and baryte ($BaSO_4$) in mine dumps (Velebil 2003).

The XRD analysis revealed that the sampled waste material from Jedová Hora consisted mainly of goethite, hematite (α-Fe_2O_3), siderite and kaolinite. In waste material from Svatá, Fe-oxyhydroxides (goethite, hematite), clay minerals (kaolinite, illite) and quartz were identified. Presence of clay minerals and Fe-oxyhydroxides suggested relatively favorable conditions for Hg adsorption to the mineral surfaces.

Mercury concentrations in the mine waste samples were highly variable (Table 1). Mercury concentrations in mine waste at Svatá were relatively low (0.7–1.2 $\mu g\ g^{-1}$), and at both sampling sites (S1 and S2) Hg concentrations did not exceed the limit defined by Czech legislation for soils (0.8 $\mu g\ g^{-1}$, Czech Regulation 13/1994 (1994)). The highest Hg concentrations were found at Jedová Hora in the samples from the bottom of 1 m deep pits (up to 120 $\mu g\ g^{-1}$). Such high concentrations may be attributed to vertical migration of Hg from the upper layer of the dump.

In general, mine waste materials are reported to be very heterogeneous as they may contain Hg in the form of HgS, metallic Hg^0 or as Hg(II) bound to mineral or organic components (Biester et al. 1999). Prepared standard samples were analyzed at first to identify thermo-desorption properties of different Hg forms and binding environments. TDC obtained from the analysis of standard Hg compounds were similar to these obtained by other authors (e.g., Biester and Scholz 1997; Feng et al. 2004).

In Fig. 2a, the first peak for the standard metallic Hg-bearing sand represents Hg^0 and the second peak represents Hg(II) formed by oxidation of Hg^0 (Windmöller et al. 1996). TDC obtained from the standard samples indicate that the Hg release temperature from clay minerals range from 336 to 347°C (Fig. 2b). TDC of the Fe-oxyhydroxides included two peaks (Fig. 2b), with the first peak (300–330°C) being more intensive than the second peak (450–520°C). The two peaks perhaps represent the weakly- and strongly-bound Hg, respectively. Peak areas of the double peak TDC depended on the total Hg concentration used for saturation of Fe-oxyhydroxides (50–800 $\mu g\ mL^{-1}$, data not shown). Similar to other studies (e.g., Biester et al. 1999), Hg bound to humic acid (HA) was released at higher temperatures than weakly-bound Hg to mineral components (Fig. 2b).

The TD analysis of Jedová Hora samples showed two major peaks in the temperature range from 25 to 800°C (Fig. 3a, b). We propose that the first peak at 320 (J1) and 336°C (J2) corresponds to the release of weakly-bound Hg, either from clay minerals or Fe-oxyhydroxides (Fig. 2b). The second peak at 438°C (J1) and 450°C (J2) suggests the presence of HgS, due to the correspondence of this peak with that of the HgS standard (Fig. 2a).

The samples taken at the top of mine dumps and those taken at the bottom of the 1 m pits showed similar TDC patterns. Higher peak intensities of bottom samples J1 and J2 in comparison to top sample at the same locations (Fig. 3a, b) correspond to differences of total Hg concentrations in these samples (Table 1). TDC for samples from Svatá showed similar pattern with two major peaks (Fig. 3c, d). The major fraction of Hg in mine waste was released at 456°C, with only a minor fraction released at 340°C. The TDC for the S2 samples (Fig. 3d) correspond to significantly lower Hg concentrations (Table 1).

Table 1 Hg concentrations and physicochemical properties of mine waste

	Hg ($\mu g\ g^{-1}$)	pH_{H20}	C_{ox} (%)	S_{tot} ($mg\ kg^{-1}$)	CEC ($cmol\ kg^{-1}$)
Svatá					
S1	1.2 ± 0.03	5.11	3.74	80	30.3
S2 top (10 cm)	0.8 ± 0.04	4.88	15.72	1,380	62.6
S2 bottom (1 m)	0.7 ± 0.02	5.51	3.53	<50	33.9
Jedová Hora					
J1 top (10 cm)	50 ± 4.1	6.67	12.06	1,740	22.7
J1 bottom (1 m)	120 ± 14.7	7.73	2.07	1,040	51.9
J2 top (10 cm)	86 ± 14.7	6.76	7.55	1,140	43.6
J2 bottom (1 m)	101 ± 8.9	8.09	2.36	730	24.4

Fig. 2 TDC of Hg for (**a**) known Hg compounds and metallic Hg-bearing sand, and (**b**) clay minerals, Fe-oxyhydroxides and humic acid (HA) saturated by $HgCl_2$

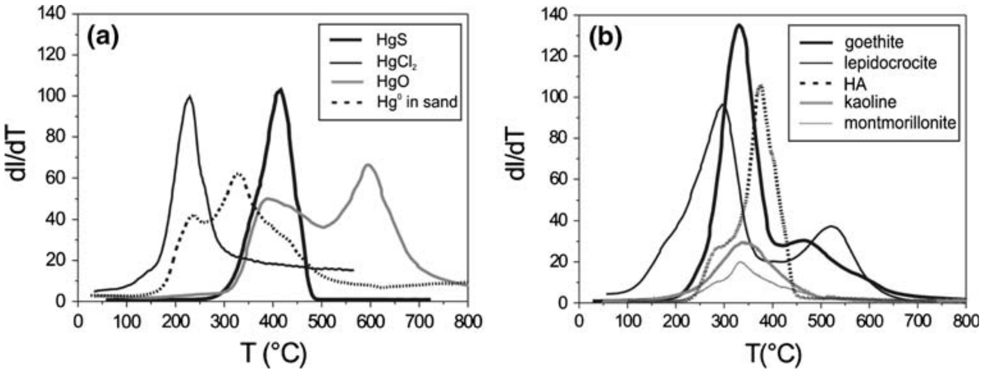
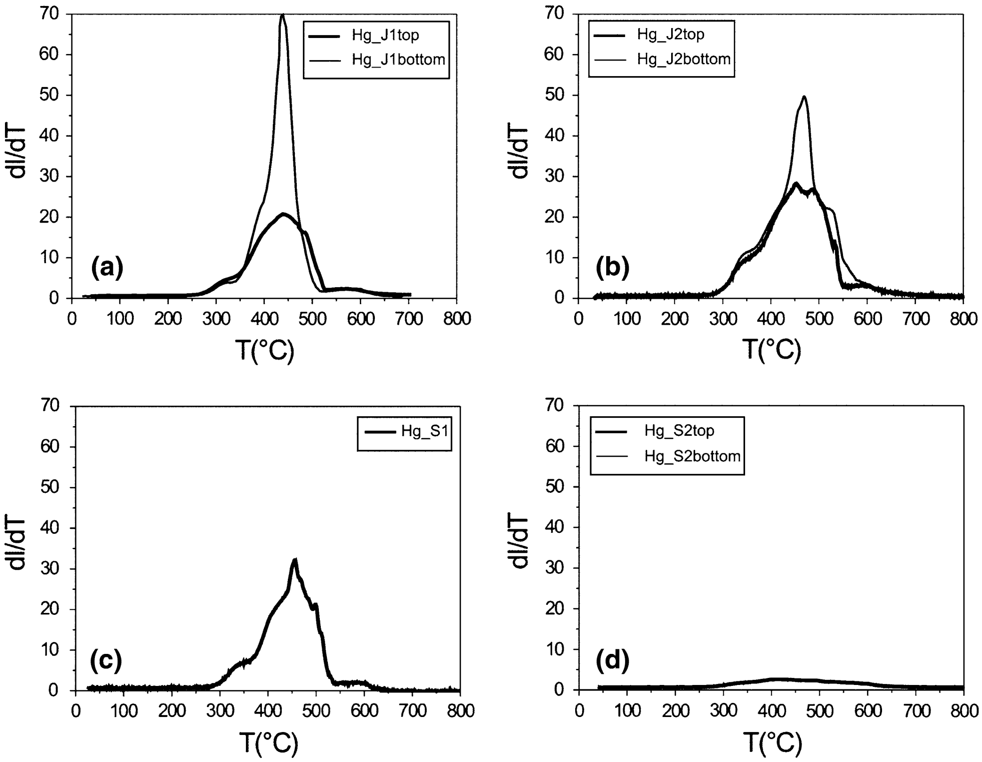


Fig. 3 TDC of Hg in mine waste samples from Jedová Hora (**a** and **b**) and Svatá (**c** and **d**)



Peak area analysis suggests that in most samples studied here, 80%–90% of total Hg is present as HgS, and only 12%–14% of total Hg is weekly adsorbed to the mineral components. Cinnabar is a solid with limited solubility and a slow oxidation kinetics (Ravichandran et al. 1998). HgS dissolution has been reported in the presence of high sulfide concentrations and at $pH > 6$ (Wang and Driscoll 1995). We propose that Hg detected as adsorbed to mineral surface of clays or Fe-oxyhydroxides in this study originated most probably from leaching or weathering of HgS. Comparing the standards elemental Hg was not detected by TD analysis in any of the samples.

Samples containing mostly HgS, which is relatively stable in the subsurface environment of the mine waste dumps, are not subject to any significant methylation that results in the formation of highly toxic methyl–Hg (Gray et al. 2003). However, Hg associated with mineral surfaces may undergo methylation processes, and thus, may represent a potential long-term environmental risk.

Acknowledgments The study was supported by grant No. B300130615, Grant Agency of the Czech Academy of Sciences (ASCR). Long-term financial support for the project was provided by the Institute of Geology of ASCR, project No. AV0Z30130516. We thank to V. Ettler for helpful comments and A. Amirbahman for help with final version of the article.

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