

## Mercury distribution and speciation in soils affected by historic mercury mining in the Czech Republic

M. HOJDOVÁ <sup>(1,2)</sup>, T. NAVRÁTIL <sup>(1)</sup> and J. ROHOVEC <sup>(1)</sup>

<sup>(1)</sup> Institute of Geology, Academy of Sciences of the Czech Republic, Rozvojová 269, 165 00 Praha 6, Czech Republic  
(e-mail: hojdova@gli.cas.cz)

<sup>(2)</sup> Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6,  
128 43 Prague 2, Czech Republic

**Abstract** Historic Hg mines represent an environmental threat due to high contamination of waste material with Hg. The ecosystems surrounding Hg mining sites and regions are usually significantly contaminated. In the central Czech Republic, Hg ores were mined at Jedová hora ("Giftberg") since the 18<sup>th</sup> century till the end of the 19<sup>th</sup> century. Mine wastes dumped near the Hg mine contained elevated concentrations of total Hg (up to 120 µg.g<sup>-1</sup>).

Vertical Hg distribution and chemical forms of Hg in soil profiles were studied to assess the extent of contamination in the mining area. It is obvious that historic mining works are responsible for dispersion of Hg on soils in the area. The highest Hg contents were observed in subsurface soil horizons (up to 10 µg.g<sup>-1</sup>) and in mineral horizons of soil profile located downhill the mining works (up to 9 µg.g<sup>-1</sup>). In comparison with the waste material, where more than 80% of Hg occurred as HgS, the soils contained predominantly Hg adsorbed to mineral components (up to 79%) and only a minor part occurred as HgS.

**Key words:** *mercury, mercury mining, contaminated soils, thermo-desorption analysis*

### Introduction

Areas of historic Hg mining are of environmental concern because of toxic Hg compounds present in discarded waste material and high contamination of the surrounding ecosystems (Biester et al. 1999; Gray et al. 2003). In the central Czech Republic (CR), Hg ores were mined at Jedová hora ("Poison Mountain"). In comparison with the world's famous mines the production of Hg was of a local importance. Wastes generated during the mining activity were dumped near the Hg mine and contained elevated concentrations of total Hg (up to 120 µg.g<sup>-1</sup>). Most of Hg was presented as cinnabar (HgS) that is relatively resistant to weathering in soils. Minor part of Hg was identified as matrix-bound, thus it has the potential to be transformed into bioavailable Hg compounds (such as methyl-Hg) and could become long-term environmental risk. This study focus on potential environmental impact of the old mining works and describes a preliminary assessment of the extent of contamination. This includes evaluation of vertical distribution of Hg in soil profiles and identification of various Hg compounds in individual soil horizons.

### Materials and Methods

Studied area of historic Hg mining (Jedová hora) is located approximately 50 km SW of Prague, the capital of the Czech Republic. Mercury ore was cinnabar (HgS) and it was gained as a byproduct of Ordovician iron ores mining. The mine was in operation since the 18<sup>th</sup> century till 1870 (Sattran et al. 1978). Velebil (2003) estimated the production of 7.8 tons of HgS in the period from 1778 to 1779, but there is no exact information available on the total production.

Mine wastes are generally located on steep hillsides and the soils were classified as Haplic or Dystric Cambisols. The area is recently covered with mixed forests (mostly European beech and Norway spruce).

Three soil profiles (P1, P2, P3) near the Hg mine were sampled as a function of various hillsides. Soil samples were taken from individual morphological horizons from the excavated soil pits. 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). The determinations were performed in triplicate (relative standard deviation (RSD) was < 15%).

Mercury speciation analysis was carried out using a thermo-desorption (TD) method, which has been successfully applied to specify Hg-binding forms in solid materials (e.g. Windmüller et al. 1996; Biester et al. 1999). The analyses were performed using a custom made device, combining a programmable oven (Clasic, Czech Republic) placed into Ar path of 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  $40^{\circ}\text{C}\cdot\text{min}^{-1}$  up to  $600^{\circ}\text{C}$  in a dynamic Ar atmosphere. The escaping Hg species from the sample were detected at 184.9 nm in 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 TDCs from natural samples were evaluated using Peak Fitting Module of OriginPro software (ver. 7.03).

Thermo-desorption properties of standard Hg compounds ( $\text{Hg}_0$ ,  $\text{HgO}$ ,  $\text{HgCl}_2$  and  $\text{HgS}$ ) were evaluated in order to obtain optimal experimental setup. Effect of matrices on Hg release was calibrated with  $\text{Hg}^{2+}$  adsorbed onto standard materials such as clay minerals, Fe-oxyhydroxides and humic acid. In particular we used kaoline and montmorillonite (Sigma Aldrich) and Fe oxides commonly occurring in soils, goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ), prepared according to Cornell and Schwertmann (1996). Adsorption of  $\text{Hg}^{2+}$  to humic acid (Sigma Aldrich) was prepared according to Arias et al. (2004).

## Results and Discussion

Studied soils were mostly acidic with pH values ranging from 3.2 to 5.8. Surface horizons of forest soils were rich in organic C (up to 47.9 wt.%) and similarly showed higher  $S_{\text{tot}}$  concentrations (up to  $1700\text{ mg}\cdot\text{kg}^{-1}$ ).

Figure 1 shows the vertical Hg distribution. Almost all samples contained elevated total Hg concentration compared to average concentrations in non-contaminated soils ( $0.01\text{-}0.5\text{ }\mu\text{g}\cdot\text{g}^{-1}$ ; Alloway 1995). Generally, the highest Hg contents were observed in subsurface soil horizons Ah (Figure 1). This could be related to surface dispersion of Hg from the mine dumps and Hg coupling to organic matter. The lowest Hg concentrations were found in the profile P1 located on the hill above the mining works (Figure 1a) and it did not exceed the limit defined by Czech legislation for soils ( $0.8\text{ }\mu\text{g}\cdot\text{g}^{-1}$ ; Czech Regulation 13/1994). Samples of P2 and P3 did not show decrease in Hg content with depth which would be expected in weathered soil profiles (Navarro et al. 2006). Content of Hg was very variable with the highest Hg content in mineral horizon C in P3 (Figure 1c).

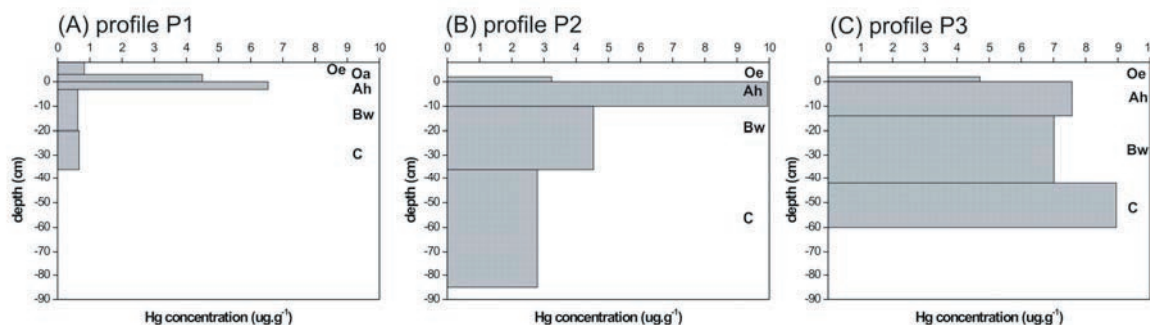
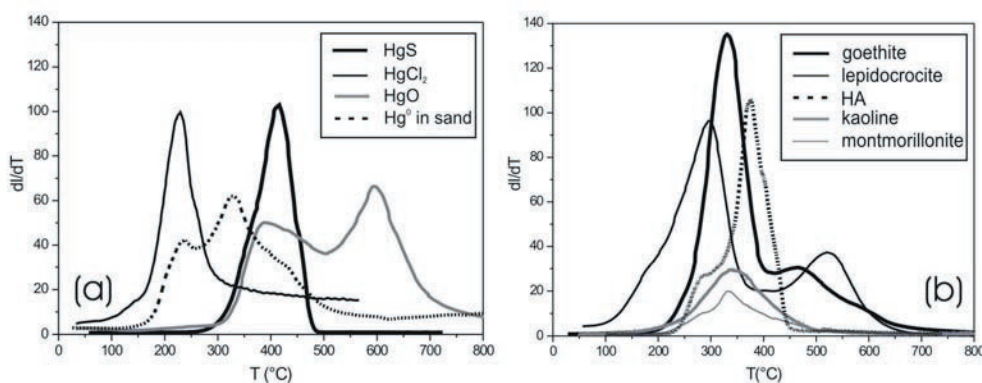


Figure 1. Vertical Hg distribution in soil profiles.

Chemical forms of Hg in soils affected by mining activities were identified by thermo-desorption analysis. Prepared standard samples were analyzed at first to identify thermo-desorption (TD) properties of individual Hg forms and Hg bindings, which were expected to be present in soils.

Releasing temperatures of Hg from analyzed standard Hg compounds were similar to these obtained by other authors (e.g. Biester and Scholz 1997; Feng et al. 2004).

Thermo-desorption curves obtained from standard comparative samples indicate that the release temperatures of Hg from clay minerals ranged from 336 to 347°C (Figure 2b). Thermo-desorption curves of the Fe-oxyhydroxides included two peaks (Figure 2b). The first peak in the range from 300 to 330°C was more intensive than the second one between 450 and 520°C. With respect to lower releasing temperature, the first peak represented Hg weekly bound onto surfaces of Fe-oxyhydroxides, while higher releasing temperature reflected stronger Hg bond (perhaps inside the crystalline structure of Fe-oxyhydroxides.) Similar to other studies (e.g. Biester et al. 1999) Hg bound to humic acid (HA) was released at higher temperatures than Hg weakly bound to mineral components (Figure 2b).

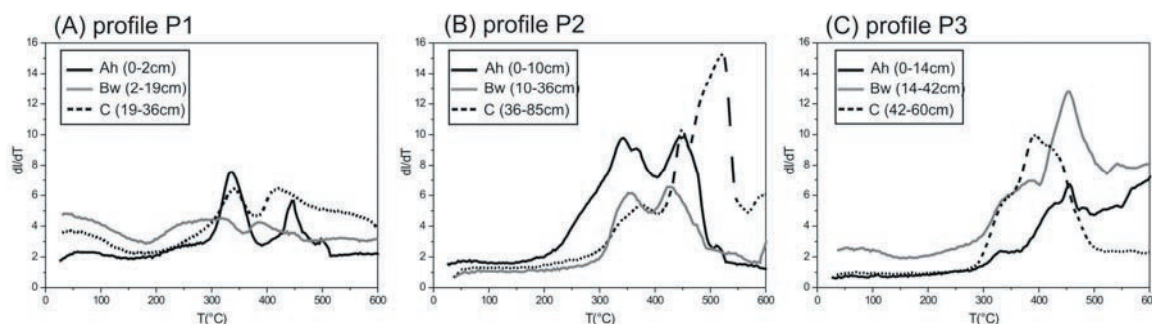


**Figure 2.** TDC of Hg for (a) simple Hg compounds and metallic Hg bearing sand, (b) clay minerals, Fe- oxyhydroxides and humic acid (HA) saturated by HgCl<sub>2</sub>.

In the next step, TD analysis was carried out on samples of contaminated soils from individual horizons of 3 soil profiles. Samples from profile P1 directly unaffected by mining showed TD curves with 3 major peaks in the temperature range from 25 to 600 °C (Figure 3a). The first maximum at 300-310°C corresponded to Hg released from mineral surfaces of either clay minerals or Fe-oxyhydroxides (Figure 2b). The second peak at 400-450°C indicated presence of HgS (see TDC of HgS standard for comparison, Figure 2a). The third peak at 500-540°C was assigned to Hg strongly bound perhaps into the crystalline structure of Fe-oxyhydroxides.

Hg-TDC of the samples from P2 displayed similar pattern to soils from P1 defined by 3 different peaks: 354-366°C, 430-450°C and 510-530°C. TDC of soil from horizon Ah showed only 2 peaks at 346°C and 445°C indicated the absence of Hg bound probably into crystalline structure of Fe oxides.

In profile P3 Hg was released from soil at 2 different temperature ranges 327-372°C and 384-450°C (Figure 3c). This suggested the presence of Hg weekly bound to mineral surfaces (Figure 2b) and that in the form of HgS (422 °C peak, Figure 2a).



**Figure 3.** Hg-TDC of soil samples from individual soil horizons.

In comparison with the waste material, where more than 80% of Hg occurred as HgS (Hojdová et al. 2007), the soils in the area contained more Hg bound to mineral components. In soils of P1 60-70% of Hg was identified as bound to mineral components (on the mineral surfaces or in the crystalline structure) and only 30-40% existed as HgS.

In individual horizons of P2 the occurrence of Hg forms was very variable. In mineral horizons (Bw, C) 20-44% occurred as HgS and up to 79% of Hg was bound to mineral components. In subsurface soil horizon Ah 39% of Hg occurred as HgS and 61% as weakly bound to mineral surfaces.

Contrary to P1 and P2, in the most contaminated soil profile P3 Hg occurred predominantly as HgS (60-80%) and 20-38% of Hg was weakly adsorbed to mineral components.

## Conclusions

Vertical Hg distribution and chemical forms of Hg in soil profiles were studied to assess the extent of contamination in historic Hg mining area. It is obvious that historic mining works are responsible for dispersion of Hg on soils in the area. The highest Hg contents were observed in subsurface soil horizons and in mineral horizons of soil profile located downhill the mining works. In comparison with the waste material the soils contained predominantly Hg adsorbed to soil mineral components and only minor part occurred as HgS. Solubility of HgS is very low, but Hg sorbed to mineral components was shown to be more mobile (Biester et al. 1999) and could represent long-term environmental risk.

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