

# Influences of Ore Roasting Sites from the First Period of Mining on the Mercury Dispersion in the Surroundings of Idrija (Slovenia)

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## Introduction

The Idrija mercury mine has been the second largest mercury mine in the world. The total amount of mercury mined is estimated to be 153,000 tons, from which 45,500 tons was emitted into the environment. The production started in 1492; in the first decade the ore was roasted in piles. Afterwards it was roasted for 150 years in earthen vessels at various sites in the woods around Idrija.

Up to now 21 localities of ancient roasting sites have been established on the neighbouring hills and in more distant localities (GOSAR & ČAR, 2006). Roasting of ore in piles and in earthen vessels (Fig. 1) gave a very poor yield and resulted in considerable losses. Because of the high temperatures usually a third of earthen vessels cracked during burning and mercury escaped from the vessels. Large quantities of broken pottery (up to 2 m) can be found at the localities of old roasting sites.

The determined mercury contents in soils at old roasting sites are very high, and they surpass all hitherto described localities at Idrija and in its surroundings (GOSAR et al., 2006).

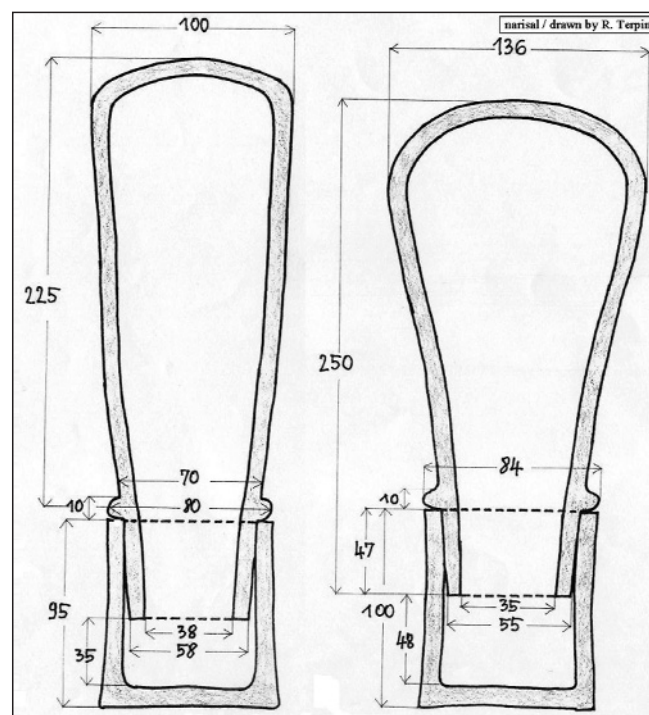


Fig. 1. Drawing of two types of earthen roasting vessels. Measures in millimeters (after ČAR & TERPIN, 2005).

## Materials and methods

Soil profile sampling was conducted at two localities of old roasting sites - Frbežene trate (soil profiles F1, F2 and F3; Fig. 2) and Pšenk (profile P1; Fig. 3; GOSAR & ČAR, 2006). Sampling of F1 and F2 was made by spade by deepening natural stream banks, while profiles F3 and P1 were dug to the depth 24 and 36 cm; deeper samples were taken with hand-drilling machine. The soil samples were air-dried and gently crushed in ceramic mortar; the fraction smaller than 2 mm was pulverized before chemical analysis. Hg was determined by means of cold vapor atomic absorption spectrometry CV-AAS after aqua regia digestion (mixture HCl, HNO<sub>3</sub> and water at 95°C). The reliability of analytical procedures was considered adequate for using the determined elemental contents in further statistical analysis.

## Pyrolysis of Hg

Determination of Hg phases by solid-phase-Hg-thermo-desorption is based on the specific thermal decomposition of Hg compounds from solids at different temperatures. An in-house apparatus, consisting of a furnace and a Hg detection unit was used. For Hg detection quartz cuvette is placed in the optical system of an atomic absorption spectrometer (Perkin Elmer AAS 3030) and Hg absorption is detected at 253.7 nm. Samples were

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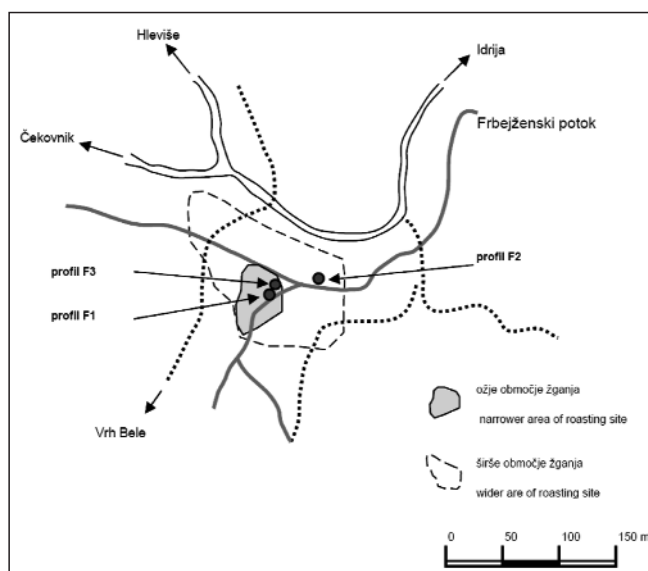


Fig. 2. Sketch-map of the Frbežene trate locality (after GOSAR & ČAR, 2006).

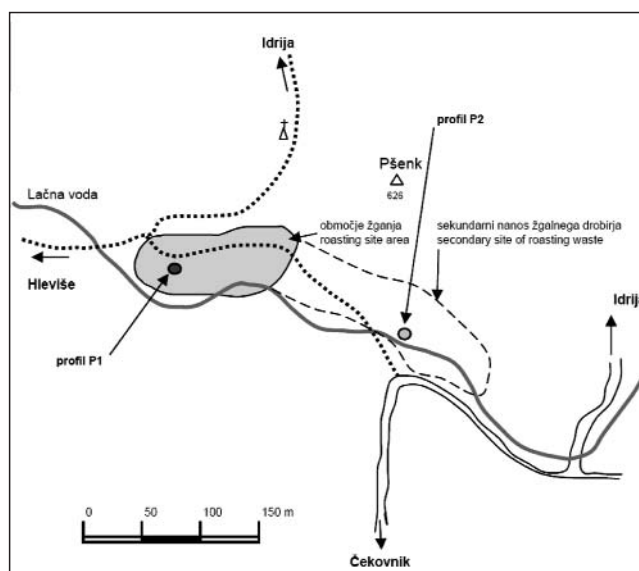


Fig. 3. Sketch-map of the Pšenk locality (after Gosar & Čar, 2006).

heated continuously at a rate  $0.5^{\circ}\text{C/s}$  in a  $\text{N}_2$ -gas flow of 300 ml/min. All released Hg compounds were transformed to  $\text{Hg}^0$  through thermal reduction by passing through a heated quartz glass tube ( $800^{\circ}\text{C}$ ), and detected by AAS in continuous detection mode with D2-background correction. The results are depicted as Hg thermo-desorption curves (MTDC), which show the release of  $\text{Hg}^0$  vs. temperature (Biester et al., 1999).

## Results

### Locality Frbežene trate

In all three profiles very high mercury contents (from 3,000 to 4,000 mg/kg) were found in the upper, with organic matter rich soil horizon (GOSAR & ČAR, 2006). In two profiles the contents rapidly decrease with depth, to about 10-times lower values already at 0.5 m depth. Below, the mercury contents decrease slowly, and reach a few mg/kg at the 1.3 m depth. In

the third profile the upper humic layer is followed downward by an additional humic layer containing very abundant pottery fragments. In this layer the maximum mercury contents were determined, 7.474 mg/kg (GOSAR & ČAR, 2006). The underlying loam contains between 1,000 and 2,000 mg/kg mercury (Fig. 4; GOSAR & ČAR, 2006).

### Locality Pšenk

Pšenk is one of the larger localities of roasting vessels fragments. The most abundant pottery remains are found in the upper western margin of the area. The considered profile P1 contains at top a 45 cm thick humic layer with 4,000 to 5,000 mg/kg mercury. Deeper the contents fall to around 100 mg/kg mercury (Fig. 5; GOSAR & ČAR, 2006). The calculations result in an estimated amount of 1.4 t mercury still present at the Pšenk locality, and in about 40 t of mercury on all roasting sites described up to present (Gosar & Čar, 2006).

## Results of the pyrolysis

The samples show double peak curves with one maximum between  $200^{\circ}\text{C}$  and  $250^{\circ}\text{C}$  and a second one between 250 and  $350^{\circ}\text{C}$ . The first peak indicates non-cinnabar compounds. Compared to the standard Hg compounds curves (BIESTER & MÜLLER, 1995), it is most reasonable that this peak represents Hg bound or sorbed to the matrix components. Those soil matrix components could be best described as organo-mineral agglomerates, which mean that they can include mineral components such as clay minerals or sesqui-oxides, but also organic components such as humic acids or biofilms sorbed to mineral surfaces. The second peak, which occurs in the higher temperature range, indicates the presence of cinnabar. Mercury in the investigated samples is in the form of cinnabar or bound to the matrix components (Figs. 6 and 7). The portion of cinnabar is the biggest in profile F2, while in profiles F3 and P1, cinnabar and non-cinnabar compounds are almost equally represented. The non-cinnabar fraction is assumed to be potentially bioavailable in contrast to cinnabar, which is known to be a very stable, mostly insoluble Hg compound under environmental conditions. The information of presence, abundance and distribution of the non-cinnabar Hg fraction is more important than the total metal fraction. Using this data it is possible to identify areas where mercury is present in a bioavailable form and can impact human health.

A detailed geochemical survey is being carried out to evaluate the extent of the pollution at historical roasting sites and to determine the changes in mercury speciation and transport through centuries.

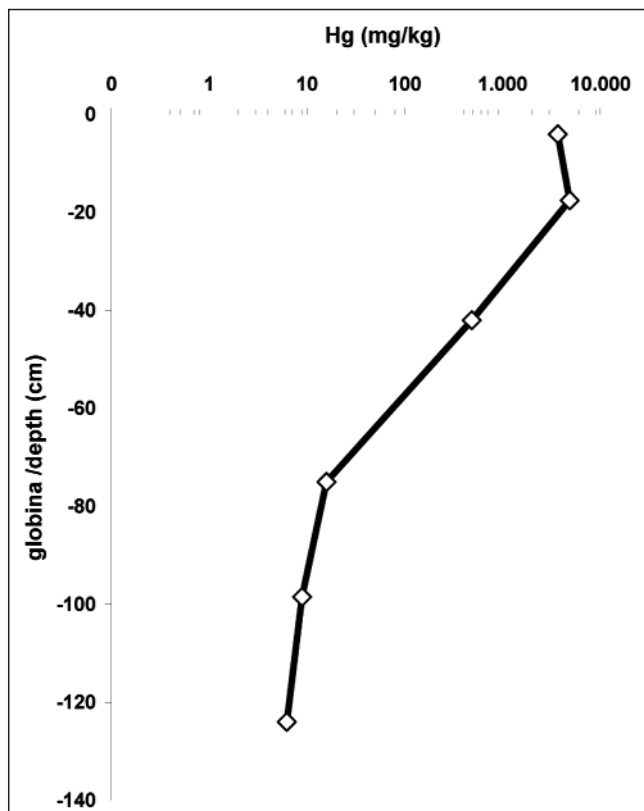


Fig. 4. Mercury contents in F3 profile at the Frbežene trate site (after GOSAR & ČAR, 2006).

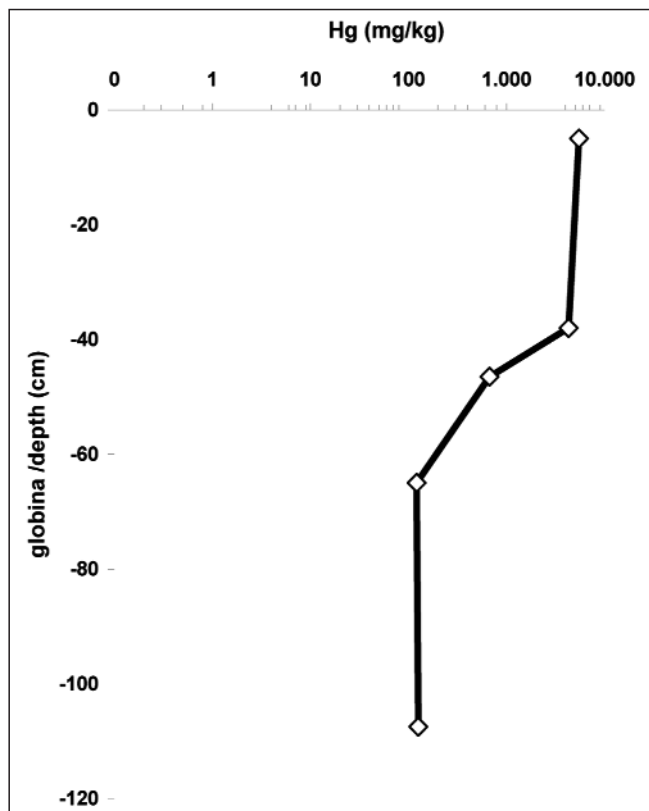


Fig. 5. Mercury contents in P1 profile at the Pšenk site (after GOSAR & ČAR, 2006).

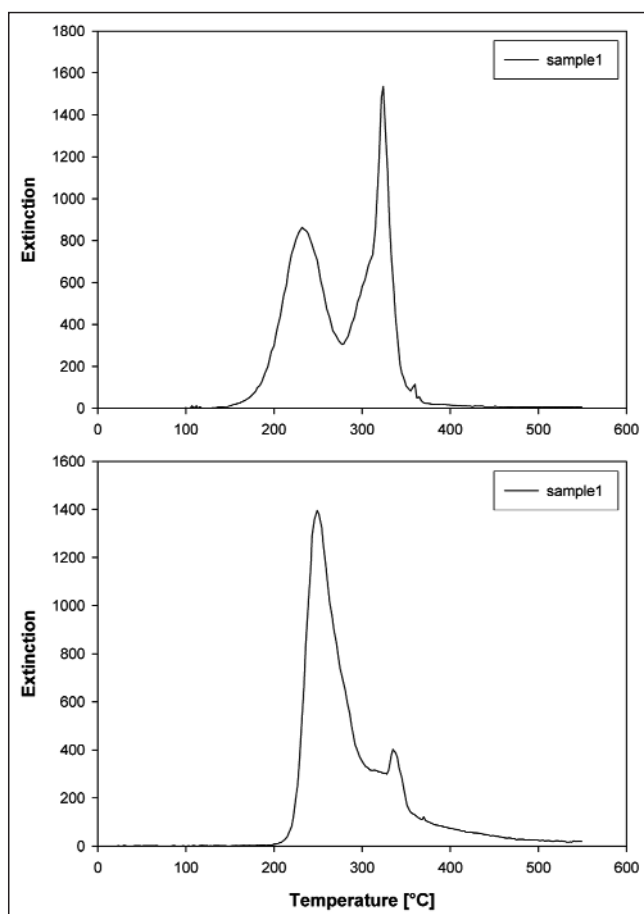


Fig. 6. Hg-thermo-desorption curves of F1 soil samples (0-10 and 40-50 cm)

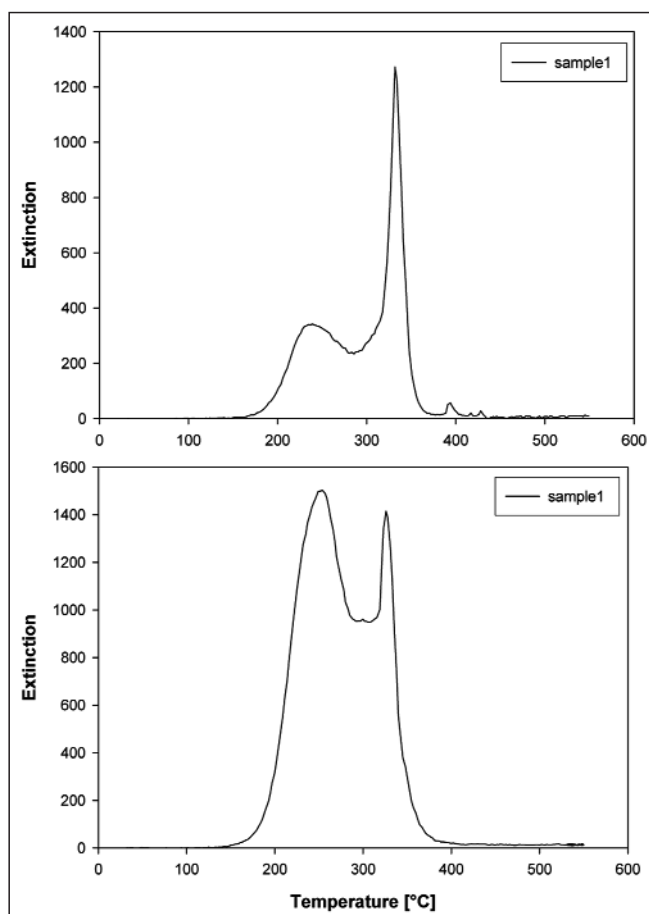


Fig. 7. Hg-thermo-desorption curves of P1 soil samples (0-10 and 40-50 cm)

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