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# Binding of mercury in soils and attic dust in the Idrija mercury mine area (Slovenia)

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**Abstract**

Total Hg concentrations and Hg speciation were determined in soils and attic dust in a 160 km$^2$ area around Idrija mercury mine. Attic dust as well as a sample of soil was collected at 100 locations. Mercury phases were separated into cinnabar and non-cinnabar compounds via a thermo-desorption technique. The amount of the non-cinnabar fraction is important since it is potentially bioavailable and results are needed for further risk assessment studies.

The concentrations of Hg in attic dust are many times higher than in surrounding soils and the attic dust/soil ratio changes with distance. The highest concentration ratios were identified at the greatest distance from the source of pollution and the lowest close to the source of pollution.

This confirms the impact of air emissions on the wider area around Idrija. Furthermore the spatial mercury distribution in the attic dust shows that the influence of atmospheric emissions caused by the Idrija smelter resulted in impacts on the environment on a regional scale. The portions of non-cinnabar compounds increase with distance from the mercury source in both sampling media. Non-cinnabar fractions were found to be enriched in distant areas where fine grained material was deposited. There were two different transport mechanisms of dust particles and gaseous Hg(0) during the mercury production period. Obviously coarse grained particles, with mostly cinnabar-bound Hg settled in the immediate vicinity of the smokestack of the smelter, whereas the fine grained fraction could be dispersed further ahead. This is represented by the percentage of cinnabar-bound Hg in attic dust and soil decreasing with distance from the smelter. Gaseous Hg(0) is probably bound to fine and ultrafine aerosols with longer residence time against deposition. The consequence is that fine grained material with $Hg^{2+}$ and $Hg^0$ prevails in remote localities and is bound in soils and dust with matrix and organic matter as non-cinnabar mercury compounds.

The distributions of mercury species in attic dust and soils along the Idrijca River show that in the region from Idrija to Spodnja Idrija the portions of cinnabar and non-cinnabar are about equal, while in the upper and in the lower Idrijca valley non-cinnabar bound mercury prevails.

The applicability of attic dust for tracing the mercury halo in the Idrija area was successfully shown.


*Keywords:* Mercury speciation; Thermo-desorption technique; Attic dust; Soil; Environmental risk; Mercury mining; Idrija mercury mine; Slovenia

## 1. Introduction

500 years of mining and processing ore in one of the largest mercury deposits in the world – the Idrija – left

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behind serious pollution problems in different environmental compartments. During the operating period of the mine, 107,500 t of Hg were produced. Taking into account the losses during mining and inefficient smelting, the total amount of mercury mined is estimated to be at least 153,000 t (Mlakar, 1974; Miklavčič, 1999; Dizdarevič, 2001). It has been estimated that 45,500 t of mercury were emitted into the environment during the operating period of the mine, which ceased production in 1994 (Dizdarevič, 2001). The mine is currently in the final stage of its gradual shut down due to the lack of reserves, low ore grade, low Hg prices and environmental reasons.

Intensive mercury mining in Idrija left a legacy of highly polluted environment. The mercury dispersion halo has been formed in a wide circle around Idrija. Its origin is partly geogenic, but mostly technogenic. This paper discusses its extension and characteristics, which were established on the basis of the total Hg concentrations and Hg speciation analysis in soil and attic dust. The main aim of this study was to define mercury binding in soil and attic dust in wider Idrija surroundings using a mercury-thermo-desorption technique, and to establish spatial distribution of total mercury and mercury species. The amount of non-cinnabar fraction is important for further risk assessment studies as it is potentially bioavailable.

## 2. History of investigations of mercury environmental impact in Idrija

Between 1969–1974, when mercury production in Idrija was at its peak, the first intensive studies of mercury in the environment began. High mercury contents in soil, rainfall and plants were established by Byrne and Kosta (1970). The results published by Kosta et al. (1974) provided a broad range of data on the degree of mercury pollution in the environs of Idrija and its distribution and chemical binding in various living organisms. During full mine and smelter production, about 20 kg of mercury were emitted daily into the atmosphere from the smelter chimney alone as vapour or absorbed on smoke particles (Kosta et al., 1974; Kosta et al., 1978).

Gnamuš (1992) pioneered the use of biologic indicators in monitoring and assessing the mercury impact on terrestrial ecosystems. Total mercury concentrations in higher plants from the Idrija area were found to contain above 1 mg/kg dry weight as an average from two sampling campaigns. At a somewhat more distant locality (Srednja Kanomlja) Hg levels were about 100 times lower. In continuation of the study the abundance of mercury in soil close to smeltery (mean 1256 mg/kg, $n=14$) and in plants growing thereon (mean 42 mg/kg) were determined (Gnamuš et al., 2000; Gnamuš, 2002). In the wider surroundings of Idrija, the average Hg concentrations in soil amount to 288 mg/kg ($n=96$) and in plants up to 14 mg/kg ($n=48$).

The spatial distribution of mercury in soil on an 8× 14 km area with Idrija at the center was studied by Hess (1993) in a regular 1 km grid (127 sample sites). Concentrations above 10 mg Hg/kg were detected in soils in valleys and at foot of slopes, and lower values in higher parts and at margins of the sampled area. In 10 selected samples the contents of the most dangerous form of mercury, methylated mercury, were also determined. The selected samples contained<0.003 to 0.2 mg of methyl Hg/kg.

Palinkaš et al. (1995) reported results of Hg pollution in the vicinity of the Idrija mercury mine. Soils were sampled at 52 locations distributed in an irregular grid. The maximum value (87.6 mg/kg) was determined in the mining area. The mean mercury concentration in the soils was 15 mg/kg. The distribution of mercury along four vertical profiles suggests a predominant influence of fallout on the accumulation of Hg.

The first study of Hg phases in Idrija area using mercury-thermo-desorption technique was performed on tailings (Biester et al., 1999). The results indicate that the type of mercury binding is primarily dependent upon the efficiency of roasting technique and prevailing mercury species in roasted ore. In older tailings the predominant Hg species is cinnabar (HgS) due to incomplete roasting, whereas in tailings of the 20th century the amount of cinnabar in the material was lower due to (1) higher efficiency of the roasting process and (2) the increasing use of ores bearing native Hg. In younger tailings metallic Hg sorbed to mineral matrix components is the predominant Hg binding form. Despite the lower total Hg concentrations found in younger tailings, the long-term risk potential of its mobile matrix-bound $Hg^0$ is higher than in that of older tailings bearing mostly immobile cinnabar (Biester et al., 1999).

Because most of the roasted ore tailings were dumped into the Idrijca riverbed, the contents of mercury in the sediments of Idrijca and Soča-Isonzo Rivers (Gosar, 1992; Gosar, 1997; Gosar et al., 1997; Biester et al., 2000; Horvat et al., 2000, 2003), as well as in marine sediments at the mouth of the Soča-Isonzo River and in the Golf of Trieste (Kosta et al., 1978; Covelli et al., 1999; Horvat et al., 1999; Širca et al., 1999a,b; Biester et al., 2000; Covelli et al., 2001), are significantly above background. Studies of mercury speciation in sediments and soils from floodplains (Biester et al., 2000) indicate the occurrence of two major Hg forms; cinnabar and an unspecified group of matrix-bound Hg compounds, which were assumed to be potentially bioavailable. The results show that Hg concentrations and dispersion of the two Hg forms in

sediments strongly depend on grain size. Accumulation of cinnabar predominantly occurs in coarse grained river sediments, where it constitutes, on average, more than 80% of total Hg in present- and past day sediments. In contrast, non-cinnabar Hg was found to be enriched in areas where fine grained material was deposited reaching up to 40% in flooded soils and up to 55% of total Hg in sediments of the Gulf of Trieste.

Kocman et al. (2004) separated Hg phases in contaminated soil in the Idrija Hg-mine region by a selective sequential extraction procedure complemented by volatilization of elemental mercury. Fractionation measurements indicated cinnabar as the predominant Hg fraction, followed by $Hg^0$. Accumulation of cinnabar predominantly occurred in coarse grained flood plain sediments, where on average it constituted more than 80% of total Hg. In contrast, non-cinnabar fractions were found to be enriched in areas where fine grained material was deposited, reaching up to 60% of total Hg (Kocman et al., 2004).

There is a very good agreement with estimated percentages of the cinnabar fraction in different soils of the area. The main difference is that Biester et al. (1999, 2000) did not find any elemental mercury and Kocman et al. (2004) did. This could be an effect of the sample preparation procedure.

## 3. Materials and methods

### 3.1. Material – attic dust

The term dust usually comprises street dust and household dust (Culbard et al., 1988; Fergusson and Kim, 1991; Fergusson, 1992; Rasmussen et al., 2001). However, other types of dust have also been studied in the past. A particular type of household dust, attic dust, has been used in the present work. Attic dust is defined as dust that accumulates on wooden carpentry of attics, the spaces in which the influence of inhabitants is minimized. Attic dust is derived predominantly from external sources through aerosol deposition and as a result of soil dusting. There is a little influence from household activities (Šajn, 1999, 2003). Its mineralogy includes phyllosilicates (montmorillonite and illite), and calcite and dolomite in areas of outcropping carbonate rocks (Šajn, 1999). The deposition of attic dust seems to be continuous through time in undisturbed attics. Its chemistry, therefore, reflects the average historical levels of the atmospheric pollution.

In previous geochemical studies (Šajn, 1999, 2002, 2003, 2005), the properties of attic dust in Slovenia (regional-scale) were established. Attic dust was also successfully applied in tracing a plutonium halo, a result of atomic bomb experiments, in Nevada (Cizdziel et al., 1998, 1999).

Close to each sampling location an old house with intact attic carpentry was chosen. Most of the selected houses were at least 100 years old. To avoid collecting particles of tiles, wood and other construction materials, the attic dust samples were brushed from parts of wooden constructions that were not in immediate contact with roof tiles or floors.

### 3.2. Sampling

Soils and attic dust samples were taken during summer months of the years 2000 and 2001. In the most polluted areas, such as Idrija and Spodnja Idrija, an average of four samples per $km^2$ were taken, whereas in more distant areas sampling densities were approximately 1 sample per $km^2$ (Fig. 1). At a chosen location a sample of attic dust was taken from the nearest suitable house, as well as a sample of soil in its immediate vicinity. We considered this sufficient for encompassing the most affected areas in Idrija and estimating the mercury contents in them.

Soils were sampled from the surface to a depth of 15 cm. In the Idrija town itself, we sampled urban soil, such as soil from gardens and on grass verges. In the surroundings of Idrija, we took samples from grasslands. One soil sample represents the composite material sampled from a middle sampling point and four points 10 m N, E, S and W. The mass of such a composite was about 1 kg. There were 100 soil samples collected in an area of 160 $km^2$.

The research area was divided into three parts (Fig. 1, Table 1). The first part (Area 1) (8.8 $km^2$), also the most polluted one, includes the towns of Idrija, Spodnja Idrija and the Idrijca River valley between them. In this area, 32 samples of soil and attic dust were taken. The second, intermediately polluted area (51 $km^2$), includes the area in the vicinity of the towns of Idrija and Spodnja Idrija (31 samples). The third area (108.7 $km^2$) includes a wider area around both towns. It was covered by a thin grid of 37 sampling points.

### 3.3. Sample preparation

The soil and attic dust samples were air-dried. The size fraction of attic dust smaller than 0.125 mm was prepared for chemical analyses by sieving (Šajn, 1999). Soil samples were gently crushed in a ceramic mortar and passed through a sieve with 2 mm openings. The fraction smaller than 2 mm was pulverised before chemical analyses (Darnley et al., 1995; Salminen et al., 1998). After *aqua-regia* digestion (1 h, 95 °C) mercury

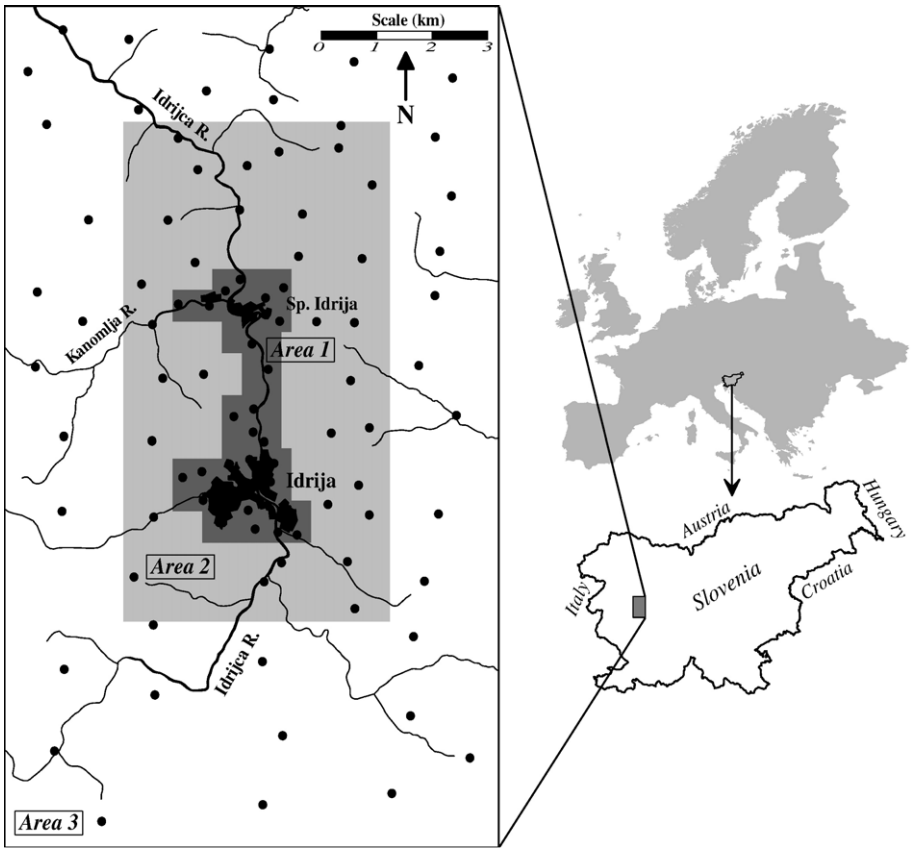


Fig. 1. Map of researched areas with sampling locations.

was determined using Cold Vapor Atomic Absorption Spectrometry (CVAAS).

Quality was assured by shipping samples to the laboratory in a random succession to distribute any errors due to laboratory performance. Objectivity was assured through the use of neutral laboratory numbers. Accuracy was estimated by blind determinations of geological standards SJS-1, GXR-6 and SO-1. Reliability of determinations was assessed as very satisfactory. The means of Hg concentration in the standards differ by less than 15% of the recommended values.

### 3.4. Analyses of Hg speciation

Determination of Hg phases by solid-phase-Hg-thermo-desorption is based on the specific thermal desorption or decomposition of Hg compounds from solids at specific temperatures. Mercury thermo-desorption curves were

Table 1
Contents of Hg (mg/kg) and HgS (%) in attic dust and soil regarding area of sampling

| Area (km$^2$) | | $n$ | Attic dust | | | Soil (0–15 cm) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Me | LQ–UQ | Min–Max | Me | LQ–UQ | Min–Max | CR |
| Hg | 1 (8.8) | 32 | 129 | 48–219 | 20–1055 | 47 | 24–98 | 3.3–973 | 2.8 |
| Hg | 2 (51.3) | 31 | 17 | 8.7–38 | 1.8–387 | 3.2 | 1.1–6.5 | 0.40–75 | 5.4 |
| Hg | 3 (108.7) | 37 | 6.1 | 3.7–21 | 0.58–191 | 1.0 | 0.52–1.9 | 0.30–13 | 6.1 |
| HgS | 1 (8.8) | 32 | 43 | 29–50 | 10–92 | 49 | 36–73 | 11–98 | 0.88 |
| HgS | 2 (51.3) | 31 | 15 | 7–22 | 0.50–50 | 30 | 13–36 | 0.50–92 | 0.50 |
| HgS | 3 (108.7) | 37 | 7 | 1–14 | 0.50–97 | 21 | 8–33 | 0.50–85 | 0.33 |

$n$ – no. of samples; Me – median; LQ – lower quartile; UQ – upper quartile; Min – minimum; Max – maximum; CR – concentration ratio (attic dust/soil).

determined by means of using an in-house apparatus, consisting of a furnace and a Hg detection unit. For Hg detection a quartz cuvette, where the thermally released Hg is purged through, is placed in the optical system of an atomic absorption spectrometer (Perkin Elmer AAS 3030) and Hg absorption is detected at 253.7 nm in continuous detection mode (1 s intervals). Interferences, mainly from pyrolysis products of organic matter, were compensated by means of continuous deuterium background correction. Measurements were carried out at a heating rate of 0.5 °C/s and using a $N_2$-gas flow of 300 ml/min. Sample weight was 1–200 mg, depending on the Hg content of a sample. The lowest level of detection in given conditions is in the range of 40–50 ng if all Hg is released within a single peak (Biester and Scholz, 1997). The results are depicted as Hg thermo-desorption curves (MTDC), which show the release of Hg(0) vs. temperature. Depending on the total Hg content in the samples, 20–250 mg of material or approximately 2 mg of quartz-diluted standard Hg compounds were used for MTD measurements. Standard materials for Hg-thermo-desorption characteristics of defined Hg compounds were obtained by mixing synthetic or natural Hg compounds with quartz powder. Cinnabar from the Almadén Hg mine, Spain, was used as a standard for fully crystallized natural red cinnabar. MTDCs of standard materials are illustrated in Fig. 2.

A quantitative measure of the amount of an Hg fraction released as a function of temperature was obtained by peak integration. Due to the partial overlapping of non-cinnabar and cinnabar peaks, the amount of non-cinnabar Hg was calculated by doubling the first half of this peak (200–250 °C) as Hg released from this Hg fraction is normally distributed. The content of cinnabar was then calculated as the difference between non-cinnabar Hg and total Hg. Hg speciation was focused on the distinction of cinnabar from non-cinnabar, which are potentially bioavailable Hg compounds.

## 4. Results and discussion

### 4.1. Total mercury

The results of statistical analyses revealed the highest medians (129 mg/kg for attic dust, 47 mg/kg for soil) in Area 1 (Fig. 3, Table 1), which includes the towns of Idrija and Spodnja Idrija, and the Idrijca River valley between them. Medians in the intermediate Area 2 were 17 mg/kg for attic dust and 3.2 mg/kg for soil. Medians in the most distant Area 3 were 6.1 mg/kg for attic dust and 1.0 mg/kg for soil (Fig. 3, Table 1).

The mercury concentrations in soil exceed the critical allowed value for mercury in soil (10 mg/kg; Uradni list, 1996) on 19 $km^2$ of the study area. The highest values occur in the Idrijca River valley near the pollution source, i.e. the smokestack, while lower values prevail at higher elevations and tend to decrease with the distance from Idrija (Table 2, Fig. 4). Spatial distributions of mercury contents in soil and attic dust are in good agreement (Figs. 3 and 4), and they depend very much upon the morphology of the terrain. The Spearman correlation coefficient ($R$) between contents in the two sampling media concerning the whole set of samples is 0.76 (significant at $p<0.05$; Table 2, Fig. 5). There is also a strong relationship between the contents of Hg in both

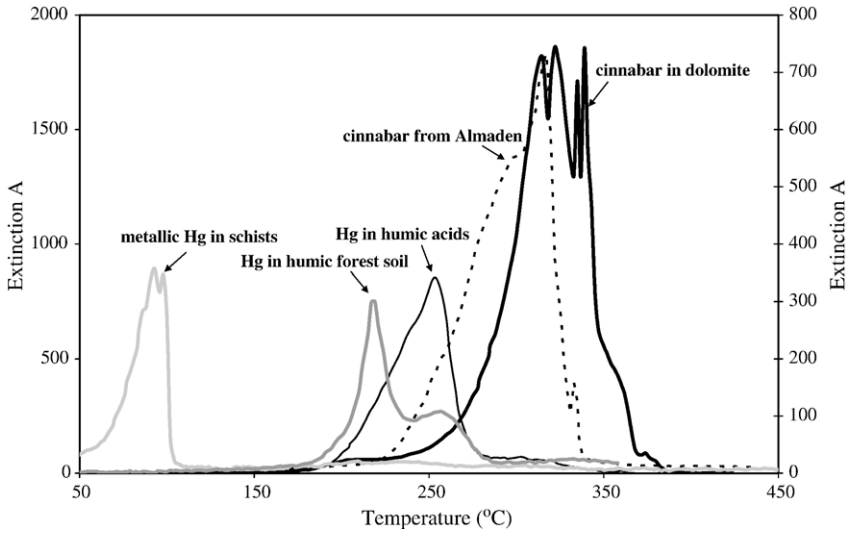


Fig. 2. Hg-thermo-desorption curves of standard materials.

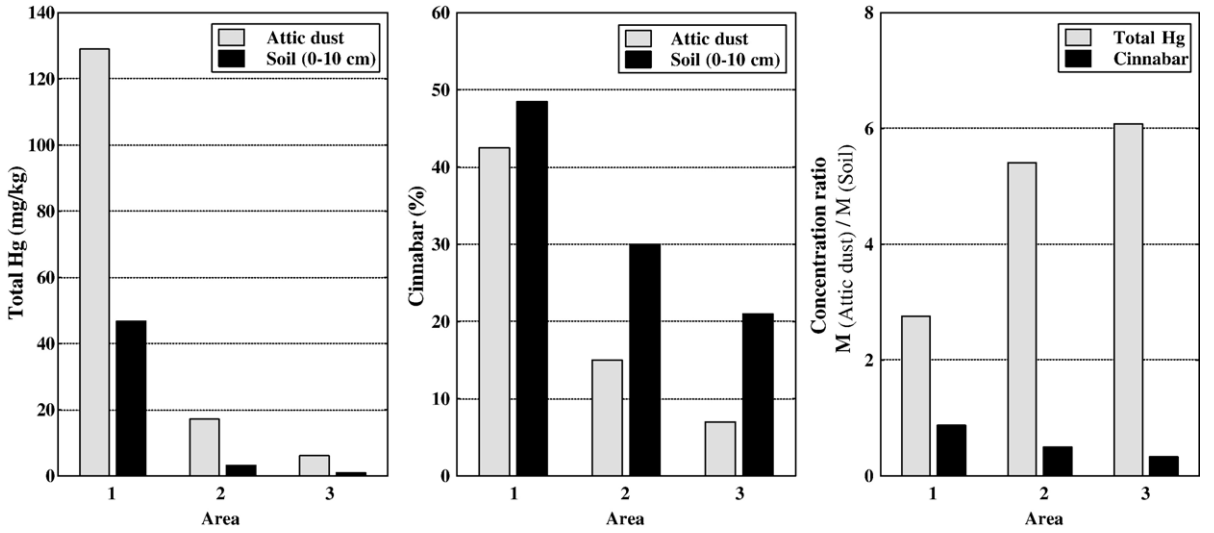


Fig. 3. Column plot of median values of Hg $_{(T)}$ (left), HgS (center) and concentration ratios of Hg $_{(T)}$ and HgS (right) vs. investigated area.

sampling media, and between height above sea level (−0.72 for attic dust,−0.81 for soil; Table 2) and the distance from the smokestack of the smelter, which was the main anthropogenic source of mercury (−0.56 for attic dust,−0.65 for soil; Table 2).

Mercury concentrations in attic dust and in soils along the Idrijca River (Figs. 6 and 7) show similar patterns. The distribution of mercury that was transported by air along the Idrijca River valley depends mostly on the distance from the source of pollution, shape of the valley and local winds blowing along the valley. The highest concentrations in soil and attic dust were found near the source of pollution, i.e. the smokestack of the smelter and they decrease exponentially down the valley.

The contents of Hg in attic dust are many times higher than in soils (Table 1), but the concentration ratio (attic dust vs. soils) changes with distance. The highest concentration ratios were identified in Area 3, which is in the greatest distance from the source of pollution. The median Hg contents in attic dust exceed the one in soils by more than 6 times (Table 1, Figs. 3 and 8). The lowest concentration ratio was found in Area 1, the closest to the source of pollution, where the median Hg contents in attic dust exceed the median in soils by less than 3 times (Table 1, Figs. 3 and 8). Therefore, attic enrichment factor increases with the distance from the pollution source.

The only exception to this rule are the localities where atmospheric emission is not the only source of mercury. In the locations where soil parent material is the main source of mercury, the situation could be reversed. That is evident in unsmelted ore wastes, primary ore smelting residues, ore residue dumps, outcropping of mineralised rocks and in locations of old ignition facilities, or in places where the smelting residues were used for road construction or other building purposes. These are located mainly in the town of Idrija or close by.

### 4.2. Speciation of Hg

The results of Hg thermo-desorption measurements show that soil and attic dust follow similar processes of Hg release. The samples show double peak curves with one maximum between 200 °C and 250 °C and a second one between 250 and 350 °C. Mercury thermo-desorption curves of some representative samples selected from various sampling sites are given in Fig. 9. The first peak (200–250 °C) indicates non-cinnabar Hg compounds.

Table 2
Matrix of correlation coefficients, $n=100$ (Spearman rank order $R$ coefficients used; all correlations are significant at $p<0.05$)

| | $Z$ | D | $Hg_{(A)}$ | $Hg_{(S)}$ | $HgS_{(A)}$ | $HgS_{(S)}$ |
|---|---|---|---|---|---|---|
| $Z$ | 1.00 | | | | | |
| $D$ | 0.42 | 1.00 | | | | |
| $Hg_{(A)}$ | −0.72 | −0.56 | 1.00 | | | |
| $Hg_{(S)}$ | −0.81 | −0.65 | 0.76 | 1.00 | | |
| $HgS_{(A)}$ | −0.36 | −0.68 | 0.49 | 0.60 | 1.00 | |
| $HgS_{(S)}$ | −0.52 | −0.48 | 0.53 | 0.64 | 0.39 | 1.00 |

$Z$ – altitude above sea level (m).
$D$ – absolute distance from smelter chimney (m).
$Hg_{(A)}$ – Total mercury content in attic dust (mg/kg).
$Hg_{(S)}$ – Total mercury content in soil (mg/kg).
$HgS_{(A)}$ – Percentage of mercury bound to cinnabar in attic dust.
$HgS_{(S)}$ – Percentage of mercury bound to cinnabar in soil.

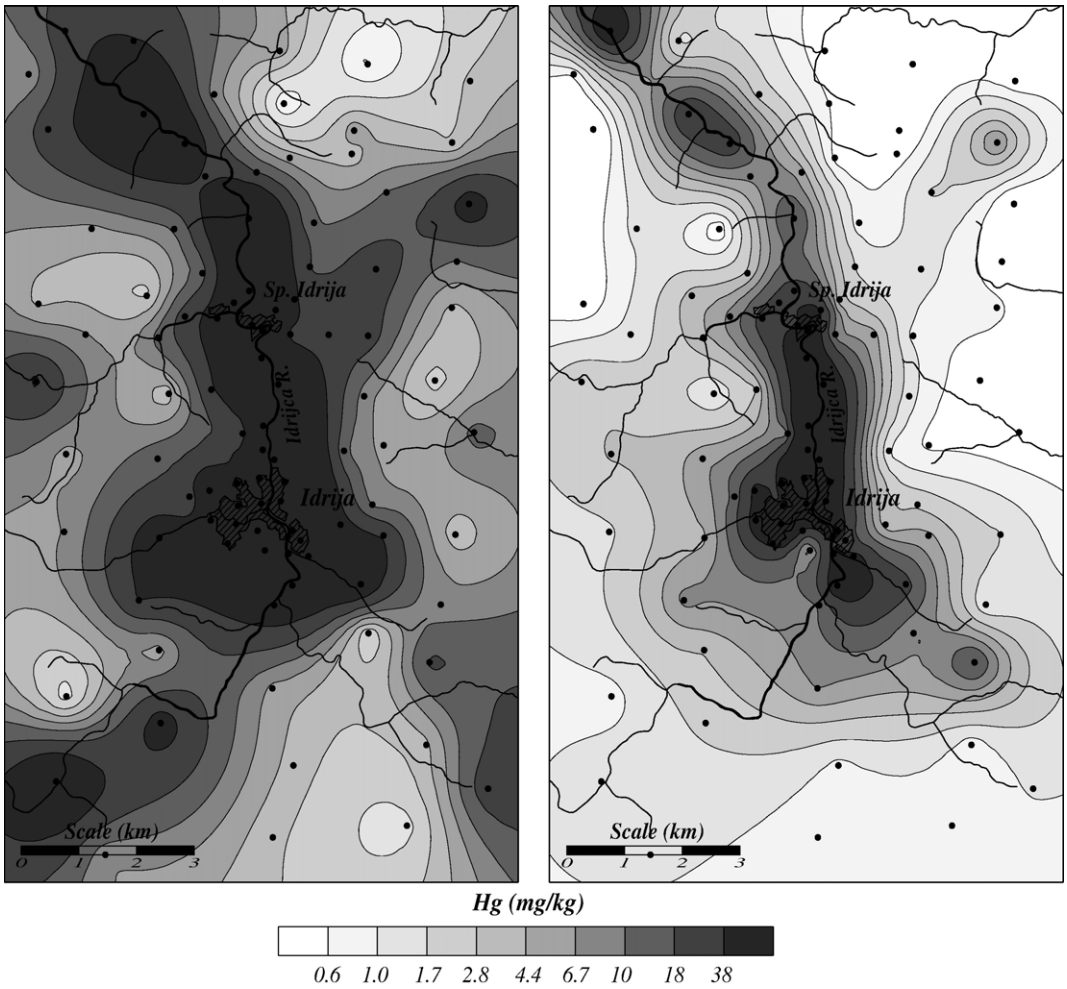


Fig. 4. Spatial distribution of mercury in attic dust (left) and in soil (right) with sampling locations.

Compared to the curves of the tailing material (Biester et al., 1999) or that of humic acid bound Hg of a forest soil sample (Biester et al., 2000) it is most reasonable that this peak represents Hg which is bound or sorbed to matrix components. Those soil matrix components could be best described as organo-mineral agglomerates, which means 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. Metallic mercury, typically released at temperatures below 100 °C, was not detected. The non-cinnabar Hg 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 in environmental media is more important than the total metal content. Using these data it is possible to identify areas where mercury is present in a bioavailable form and can impact on human health.

Typical Hg thermo-desorption curves presented in Fig. 9 show soil and attic dust samples where mercury is predominantly present in non-cinnabar compounds in both sampling media (location I-527) and equally in cinnabar compounds and in non-cinnabar compounds in attic dust and predominantly in non-cinnabar compounds in soil (location I-503). In location I-520, which is situated very close to the smelter chimney, the cinnabar prevails in attic dust mainly as a result of the settling of cinnabar dust particles from production area and smoke gases. Location I-518 is situated on the old smelter waste dump and very close to the chimney. Mercury in both samples is bound predominantly in cinnabar.

The portion of cinnabar in soil is generally bigger than that in attic dust. In the total research area, the weighted

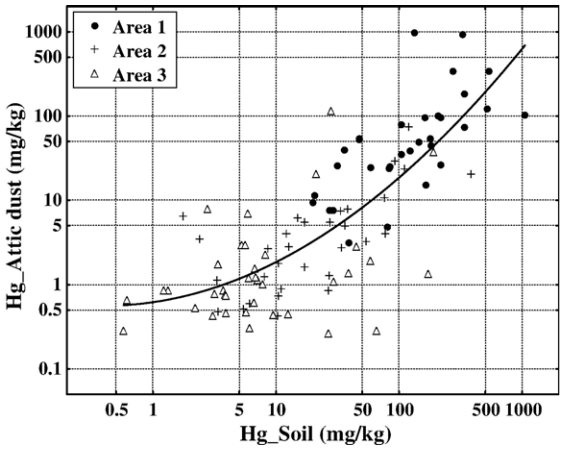


Fig. 5. Scater diagram Hg $_{(T)}$ in attic dust vs. Hg $_{(T)}$ in soil.

average of total cinnabar-bound Hg in attic dust is 6.7%, while in soils it is 18%. The highest medians (43% for attic dust, 49% for soils) were identified in Area 1 (Fig. 3, Table 1), which included the towns of Idrija, Spodnja Idrija and the Idrijca River valley running between them. In the intermediate Area 2 (Fig. 3, Table 1), the medians are 15% for attic dust and 30% for soils. In the most distant Area 3 (Fig. 3, Table 1), the medians of the contents of cinnabar (HgS) are 7% for attic dust and 21% for soils. The portions of non-cinnabar compounds increase with distance from the mercury source in both environmental samples.

The sources of mercury in soils and attic dust can be the bedrock and/or anthropogenic atmospheric emissions. Atmospheric emissions were the major factor of spreading mercury into the environment. Hg gases and dust particles (including small particles of cinnabar) have spread far into the Idrija environs. Mercury is therefore present in soils and attic dust far from Idrija at localities far from the outcrops of ore-rich rocks. In Area 1 there are mutual mercury impacts on the environment from the atmosphere and the soil parent material. The mercury-rich parent material in the Area 1 is the bedrock of Pront-area, where ore-bearing rocks containing native mercury and cinnabar crop out (Čar, 1998; location I-503 on Fig. 9). Additionally, mercury is present in smelter wastes dumped on the banks of the Idrijca River. The type of mercury binding in smelter waste depends mostly on the efficiency of the roasting technique and prevailing types of mercury in roasted ore (Biester et al., 1999). In tailings from the 19th century, situated at the left side of the river, most of the mercury occurs as cinnabar. Location site I-518 (Fig. 9) was most probably influenced from this waste as well as from very strong atmospheric influences as it is situated only 545 m away from the

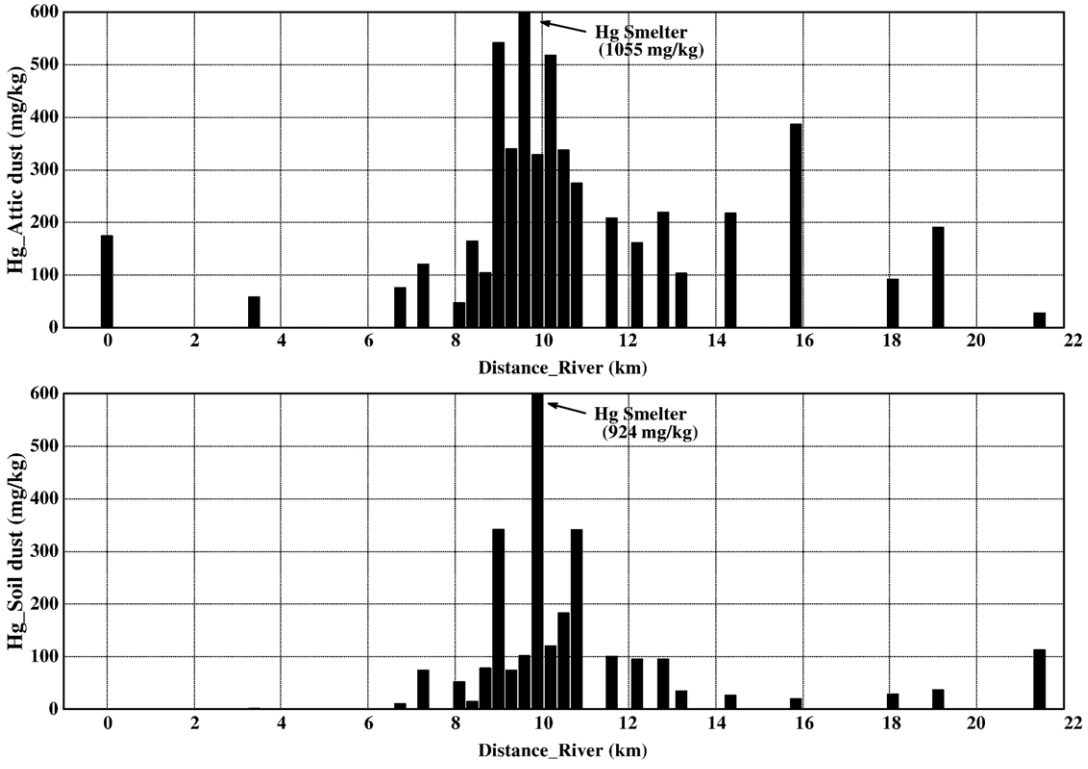


Fig. 6. Column plot of Hg $_{(T)}$ in attic dust (above) and soil (below) vs. distance along the Idrijca River valley.

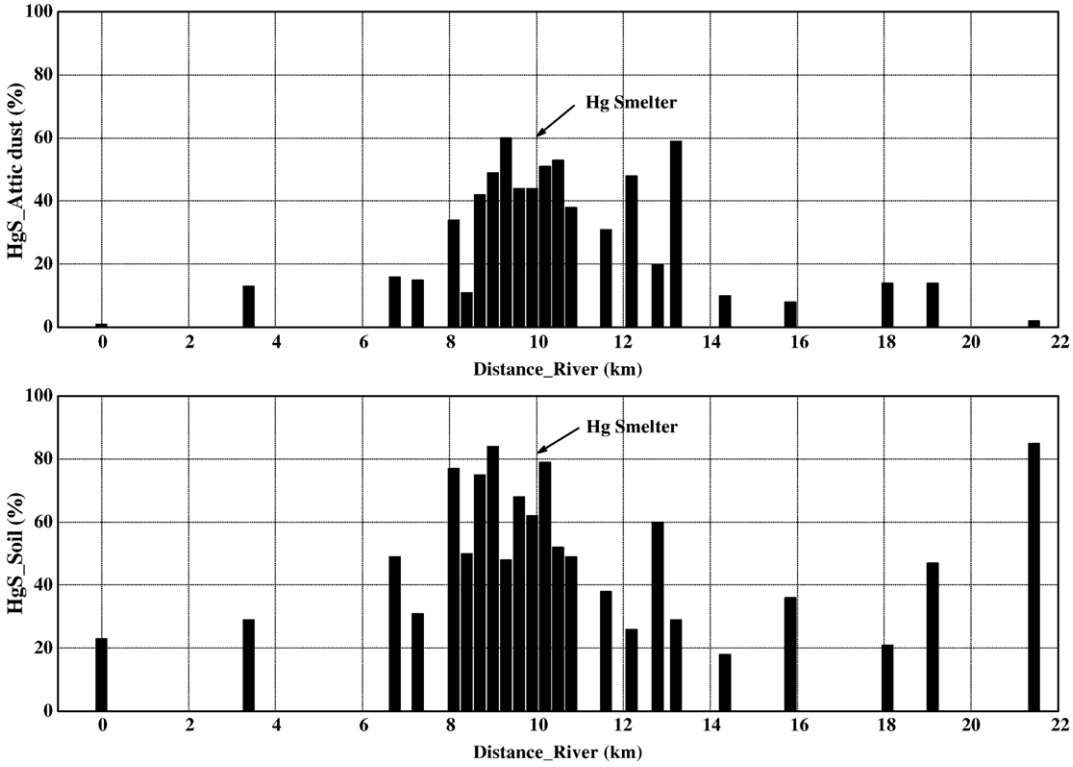


Fig. 7. Column plot of HgS in attic dust (above) and soil (below) vs. distance along the Idrijca River valley.

smelter chimney. Mercury is predominantly bound as cinnabar in soil and attic dust from this location. In tailings of the 20th century, situated at the opposite side of the river, non-cinnabar bound mercury prevails (Biester et al., 1999). In places where there is cinnabar in the soil parent material, cinnabar-bound mercury prevails in soils and attic dust. Most of the mercury in other localities are bound to soil matrix components. Previous studies have shown that Hg in those soils is preferentially bound to functional groups of organic matter such as humic acids (Biester and Scholz, 1997; Biester et al., 2000).

The correlation coefficient ($R$) between the portions of cinnabar in attic dust and in soils is 0.39 (Table 2), which is relatively low but still statistically significant (at $p<0.05$). Relatively good functional connection existed between total contents of mercury and cinnabar bound mercury (Fig. 10). Correlation coefficient ($R$) between the contents of Hg and portion of cinnabar is 0.49 for attic dust

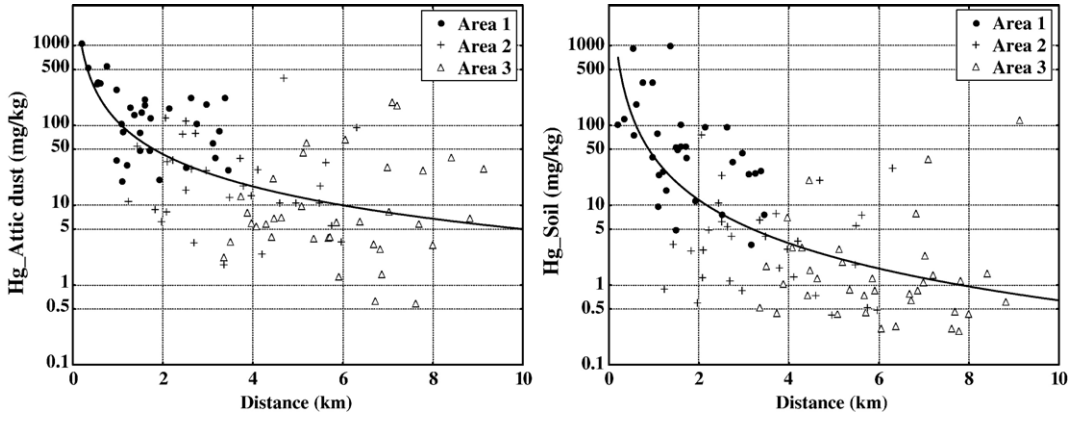


Fig. 8. Scatter diagram Hg $_{(T)}$ in attic dust (left) and soil (right) vs. distance.

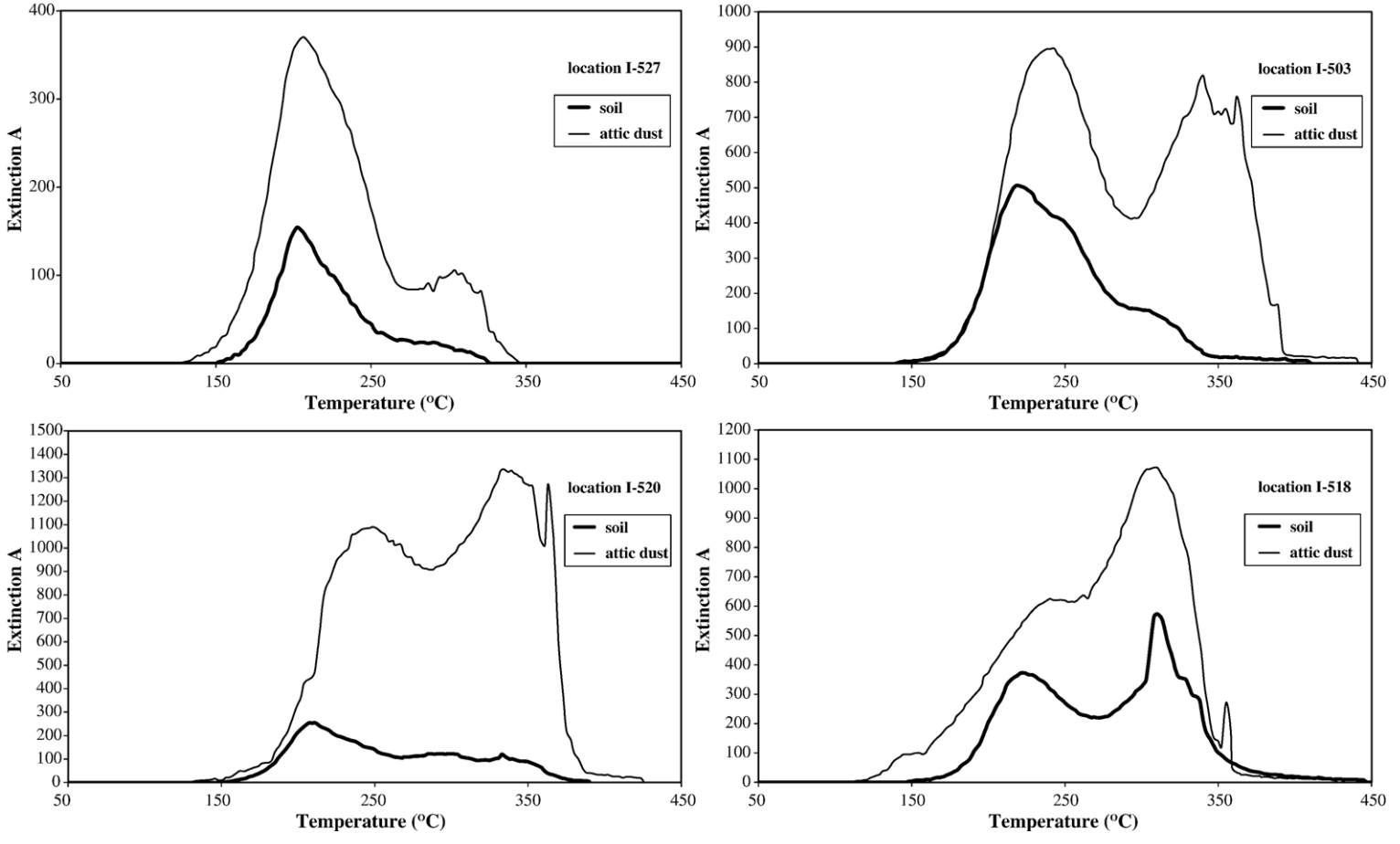


Fig. 9. Typical Hg-thermo-desorption curves show soil and attic dust samples where mercury is predominantly present in non-cinnabar compounds in both sampling media (location I-527) and equally in cinnabar compounds and in non-cinnabar compounds in attic dust and predominantly in non-cinnabar compounds in soil (location I-503). In location I-520 cinnabar prevails in attic dust and non-cinnabar in soil. Mercury prevailingly bound in cinnabar in soil and attic dust in location I-518.

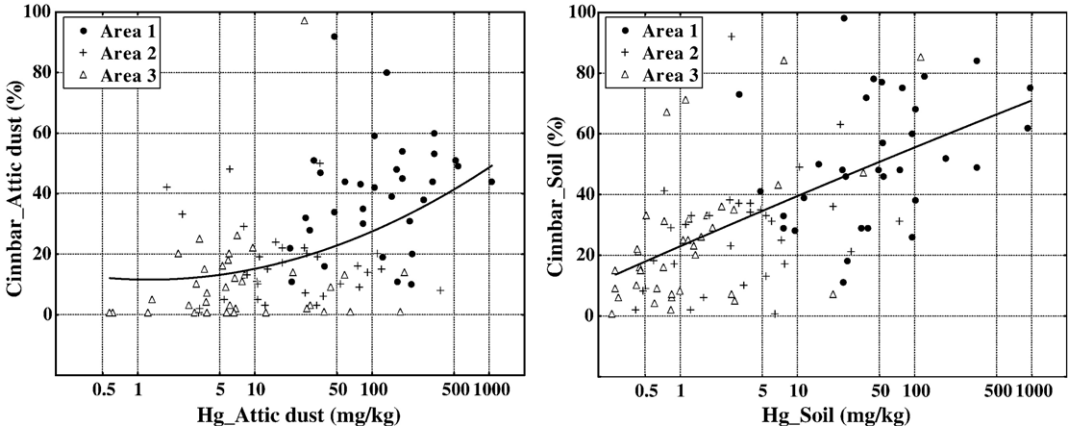


Fig. 10. Scatter diagram HgS vs. Hg $_{(T)}$ in attic dust (left) and HgS vs. Hg $_{(T)}$ in soil (right).

and 0.53 for soils (Table 2). Relatively high values of correlation coefficients were calculated between the portions of cinnabar (HgS) in both sampling media and between height above sea level and distance from the smokestack of the smelter (Table 2). The portion of cinnabar (HgS) in attic dust, however, is in much stronger negative correlation with the distance from the smokestack of the smelter ($R=-0.68$) than the portion of cinnabar in soil ($R=-0.48$), while the later correlates better with the height above sea level ($R=-0.52$).

We can explain our results with two different transport mechanisms; (1) dust particles and (2) gaseous Hg (0) during the mercury production period. Atmospheric deposition of dust particles was controlled by the Stokes law, which describes how fast spherical bodies fall through viscous liquids or air, assuming laminar flow. Gravitational settling of dust particles was very high in the vicinity of the smelter. Obviously, coarse grained particles with mostly cinnabar bound Hg settled down in the immediate vicinity of the smokestack of the smelter. The process mentioned above explains why the percentage of cinnabar bound Hg in attic dust and soil decreases with the distance from the smelter. Gaseous Hg(0) is probably bound to fine and ultrafine aerosols with longer residence time against deposition. As a consequence, fine grained material with $Hg^{2+}$ and Hg(0) prevails in remote localities and is bound to soils and dust with matrix and organic matter.

Non-cinnabar fractions were found to be enriched in distant areas (Area 3, 93% in attic dust and 79% in soil), where fine grained material was deposited. Despite the lower total mercury concentrations in soil and attic dust from Area 3, the long-term risk potential of mobile non-cinnabar fractions in this material is significant. In contrast to cinnabar, which is known to be stable and mostly insoluble, matrix-bound Hg, such as Hg associated with humic acid, has the potential to be transformed to bioavailable Hg compounds, such as methylmercury.

The results show that the median of proportions of cinnabar in attic dust is about 90% of those in soils (Table 1, Fig. 3). The highest concentration ratios (attic dust vs. soils) between the portions of cinnabar bound mercury were identified in Area 1, which is closest to the pollution source. The lowest ratio between the portions of cinnabar-bound mercury was found in Area 3, which are the most distant sampling points from the smelter. This can be explained with the two described mechanisms of mercury transportation during the time of Hg production in Idrija.

The distributions of cinnabar and non-cinnabar bound mercury in attic dust and soils along the Idrijca River (Figs. 6 and 7) show about equal portions between them in the region from Idrija to Spodnja Idrija, while in the upper and in the lower Idrijca valley the non-cinnabar bound mercury prevails. The portion of non-cinnabar bound mercury in attic dust strongly increases with the distance from the source of pollution.

## 5. Conclusions

The concentration ratio between total Hg in attic dust and soil and the percentage of non-cinnabar bound Hg in both sampling media increase with the distance from the pollution source. Spatial mercury distribution in attic dust also shows that the influence of atmospheric emissions caused by the Idrija smelter resulted in impacts on the environment on a regional scale.

The most important, potentially bioavailable mercury fraction, the non-cinnabar Hg, is more abundant in attic dust than in soil. The portion of non-cinnabar bound mercury is relatively enriched (compared to cinnabar) in remote areas in soils and attic dust, and it is well correlated

with the distance from the pollution source. Potential health risk could occur in Area 1, that is in the cities of Idrija and Spodnja Idrija, where the total content of Hg is very high. In this area the estimated median for soil is 47 mg/kg and for attic dust 129 mg/kg. Moreover, the content of non-cinnabar Hg is also very high, with half of Hg in this area bound in the non-cinnabar form in soils and attic dust.

It has been established that attic dust is a very useful environmental matrix for geochemical mapping of environmental pollution. The comparison of total mercury contents and portions of non-cinnabar bound mercury in attic dust and soil at the same location was very useful for distinguishing between geogenic and anthropogenic sources. The advantage of attic dust vs. soil sampling is evident especially in the case of less clear anthropogenic anomalous patterns.

The attic dust fixed on wooden roof carpentry was proven to be a useful sampling medium, especially for recording the processes in the atmosphere during the time of smelter activities. The disadvantage of the attic dust is that it is available only in the preserved intact attics of the historically settled areas.

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