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Mercury Speciation in Sediments Affected by Dumped Mining Residues in the Drainage Area of the Idrija Mercury Mine, Slovenia

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Mercury (Hg) concentrations and Hg phases were investigated in contaminated sediments and flooded soils in the drainage area of the Idrija Hg mine, Slovenia. The main aim of this study was the analytical separation and quantification of cinnabar (HgS) and noncinnabar Hg compounds in sediments contaminated by mining residues. Separation of Hg phases was performed by means of a solidphase-Hg-thermo-desorption technique complemented by selective extraction of organically bound Hg. Speciation measurements indicate the occurrence of two major Ho forms: cinnabar the primary ore and an unspecified group of matrix-bound, noncinnabar Hg compounds. The results show that Hg concentrations and dispersion of the two Hg phases within the river system depend on the distribution of different sediment grain size fractions. Accumulation of cinnabar predominately occurs in coarse grained river sediments, where it constitutes on average more than 80% of total Hg (up to 1000 mg/kg) in present- and past day sediments. In contrast noncinnabar Ho was found to be enriched in areas where fine grained material was deposited reaching up to 40% of Hgtnt (1-60 mg/kg) in flooded soils and up to 55% (<1-18 mg/kg) in sediments of the Gulf of Trieste.

Introduction

The mercury mine of Idrija, Slovenia was in operation for more than 500 years until 1995 and left behind intense pollution of nearly all environmental compartments (1-6). Mercury emissions from the smelter, which reached up to 20 kg Hg daily (2), lead to high Hg concentrations in the atmosphere and to widespread pollution of soils by atmospheric Hg deposition (7). It was shown that atmospheric derived Hg in these soils is predominately bound to humic acids (8). The amount of red cinnabar, which was the primary ore (9), was found to be generally low or absent in soils, as there is no outcropping of cinnabar bearing units in this area. Besides the widespread contamination of soils, one of the most serious problems is the pollution of Idrijca and

Soca (called Isonzo in Italian) rivers and the Gulf of Trieste (GT) by dumped mining residues (Figure 1). At present mine tailings alongside the river Idrijca in the city of Idrija are the most important source of Hg contamination of river sediments (10). Previous studies (11) have shown that Hg phases in tailings mainly depend on the efficiency of the roasting technique, which increased from about 50% in the 15th to more than 90% in the 20th century (12). Due to this cinnabar is the predominant Hg species in tailings older than about 200 years, whereas mercury remaining in younger residues mostly exist as metallic Hg, either adsorbed to matrix components or organically bound Hg formed by humic acids percolating through the tailings from overlaying soils (11). During the operation of the mine, most of the mining residues were dumped directly into the river and were finally washed down the river during to the Gulf of Trieste. Gosar et al. (5) showed that Hg concentrations in the Idrijca river reach up to 1,300 mg/kg. Mercury concentrations in sediments and in water of the Gulf are as much as two or 3 orders of magnitude higher than in sediments of the central Adriatic Sea (13). In marine organisms Hg concentrations are even up to five times higher, than in the rest of the Mediterranean Sea (3). Mercury in eroded sediments and suspended matter enters the GT mainly as one of two fractions, either cinnabar or noncinnabar compounds, where the latter is assumed to consist mainly of organically bound Hg(II). In contrast to red cinnabar which is known to be stable and mostly insoluble, matrix-bound Hg, such as Hg associated with humic acids has the potential to be transformed to bioavailable Hg compounds such as methylmercury. The main aim of the present study was to distinguish between cinnabar and noncinnabar Hg compounds in past and present sediments of Idrijca, and Soca river and the GT and to describe mechanisms which determine the dispersion of these two Hg fractions within this hydrological system.

Materials and Methods

Bottom sediment samples of the rivers Idrijca and Soca were taken between the city of Idrija and the Isonzo river mouth (Figure 1). Overbank sediment profiles were taken by means of a stainless steel auger at the location IDB which is an alluvial plain about 38 km downstream from Idrija. Profiles of temporary flooded soils were taken from river terraces at the location TEM, 30 km downstream from Idrija. The difference in altitude between the lowest and the highest terrace is approximately 5 m. All cores were cut into 5 cm slices.

Bottom sediments from the Gulf of Trieste were collected using a light gravity core sampler. A 70 cm long sediment core was collected manually from sampling point AA1 at 21 m depth. Sampling locations are given in Figure 1. Distances of river sediments samples from the city of Idrija and of GT sediments from the Isonzo river mouth are given in Table 1

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. Synthetic red cinnabar (HgS), HgO and HgSO4 (Merck) was added (0.001M) to 30 g aliquots of quartz powder, respectively. Metacinnabar (black HgS) was precipitated from a HgCl₂ solution using Na-polysulfide. The precipitate was washed three times, freeze-dried and mixed with quartz powder as described above. A sample from river Bilina, Czech Republic was used as an in-lab reference sample for Hg contaminated

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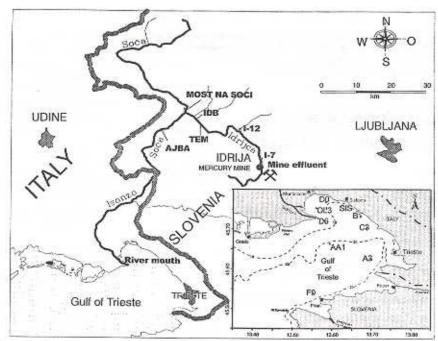


FIGURE 1. Map of the sampling area and position of sampling points in the drainage area of the rivers Idrijca and Soca and the Gulf of Trieste.

TABLE 1. Positions of Sampling Points and Hg Concentrations in Sediment Samples and Flooded Soils of Idrijca, Soca Rivers and the Gulf of Trieste and Distances of Sampling Points from the City of Idrija and Isonzo River Mouth

sample	Hg _{tot} (mg/kg)	Hg (mg/kg) extracted	loss (%)	position	distance (km)
mine effluent	987	n.d. ^d		46°00′.66 N/14°01′.74 E	0#
17	1329	n.d.d		46°01'.06 N/14°02'.04 E	1.5"
112	680	n.d. ^d		46°06'.05 N/13°57'.35 E	14.50
TEM	140-553	n.d. ^d		46°06'.09 N/13°49'.74 E	30°
IDB	15-207	n.d.d		46°08'.13 N/13°47'.11 E	38*
Most na Soci	22	n.d. ^d		n.d.a	42*
Ajba	40	n.d.d		46°01'.60 N/13°36'.15 E	534
Isonzo River mouth	30	n.d.d		n.d. ^a	90"
D6	18	19		45°43'.38 N/13°34'.22 E	1.15
OL3	3.9	2.01	49.7	45°44'.96 N/13°33'.42 E	3.08
D0	0.78	0.58	26	45°46'.15 N/13°36'.00 E	6.1b
SIS	5.68	4.7	17.3	45°45′.69 N/13°37′.62 E	7.00
AA1 (1-1.5 cm)	3.17	1.81	42.9	45°39'83N/13°35'.77 E	7.46
B1	4.84	3.05	37.1	45°44'10 N/13°39'.40 E	9.50
C3	3.98	2.97	25.4	45°42′.10 N/13°41′.10 E	11.96
A3	0.76	0.34	54.8	45°37′.40 N/13°41′.80 E	15.60
FO	0.126	0.09	28.6	45°32'.30 N/13°33'.00 E	20.46
Bilina	19	5	73.7	n.d. ^d	

^{*} Sampling points from the city of Idrija. 5 Sampling points from the Isonzo River mouth, 6 Mercury concentrations in sediments samples of the Gulf of Trieste and in an in-lab reference sample (Bilina), before (Hg_{fot}) and after HNO₃/H₂O₂-extraction, 4 n.d. = not determined.

sediment which is free of red cinnabar and where Hg is mostly organically bound. The sediments of Bilina river were contaminated by Hg containing effluents from a chlor-alkali plant. This sample was freeze-dried before analysis and tested to be free of metallic Hg (Hg(0) by Hg thermo-desorption analysis (Hg-TD).

Sample Preparation. For Hg-TD measurements all samples from the rivers and terraces, were air-dried and sieved to < 0.125 mm. Hg-TD analysis of sediment samples from the GT were carried out using freeze-dried bulk samples. For total-Hg analysis in different grain size fractions, river sediments were sieved to < 0.125 mm and to < 0.04 mm, and sediment samples from the GT to 0.12 mm and < 0.016 mm.

Total Mercury Analysis. Analysis of total Hg in all samples from the rivers and terraces were carried out by means of a cold vapor-atomic absorption (CV-AAS) Hg analyzer (Seefelder/HgA 254) after digestion of 3 g of the sample

material in aqua regia for 3 h at 160 °C. Values of total Hg in GT sediment samples were taken from a previous study (14).

Thermo-Desorption Analysis of Hg. 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 different temperatures. Mercury thermo-desorption curves were determined by means of an in-house apparatus, consisting of an electronically controlled heating unit 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 at continuous detection mode (1 s intervals). Interferences, mainly from pyrolysis products of organic matter, were compensated by means of continuous deuterium background correction. Measure-

ments were carried out at a heating rate of 0.5 °C/s and a N_2 -gas flow of 300 mL/min. Sample weight was 1 - ca. 200 mg dependent on the Hg content of the sample. Lowest level of detection under the given conditions is in the range of 40-50 ng if all Hg is released within a single peak (15). Results are depicted as Hg thermo desorption curves (TDC) which show the release of Hg(0) versus temperature. Quantification of Hg peaks was obtained by peak integration. Due to the partly overlapping of noncinnabar and cinnabar peaks, the amount of noncinnabar Hg was calculated by doubling the first half of this peak (150-250 °C). Cinnabar was then calculated as the difference between noncinnabar Hg and total Hg. This procedure is due to the observation that Hg desorbed from the matrix-bound Hg fraction is mostly normally distributed, in contrast to cinnabar which show an irregular release of Hg during decomposition.

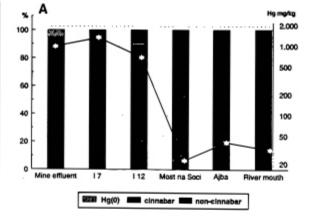
Determination of Organically Bound Mercury in GT Sediments. In sediment samples where separation of cinnabar and noncinnabar Hg could not be achieved by Hg-TD, analysis of Hg phases where supplemented by extraction of organically bound Hg. This fraction is known to be the most relevant matrix bound Hg fraction concerning potential transformation of Hg into bioavailable Hg forms. The used method was similar to that used by DiGulio and Ryan (16) to extract organic-sulfide bound Hg. Approximately 0.5 g of dried sample was placed in a polystyrene centrifuge tube and mixed with 2 mL of 0.02 M of HNO3. After 2 h of heating at 85 °C, 4 mL of 30% H2O2 was added. The samples were heated for an additional 2 h at 85 °C. The leached residues were washed twice with demineralized water and dried at 60 °C. The dried residue was weighed and digested in aqua regia and analyzed for the remaining Hg as described above.

Results and Discussion

Mercury Concentrations in River Sediments and Flooded Soils. The mercury concentration in sediment samples between the city of Idrija and the Isonzo river mouth decreases from more than 1,000 mg/kg near the mine effluent to about 30 mg/kg in samples taken at Isonzo river mouth (Figure 2A). The bottom sediment layer of the river was generally thin or even absent, which is mostly due to the high velocity of the riverine current, especially after heavy rains in autumn and spring. We assume that most mining residues, which were dumped into the river were washed to the Gulf within a relatively short period. Accumulation of sediment material was only found at fluvial plains and on river terraces which were flooded during high waters.

Mercury concentrations in the sediment core taken from the fluvial plain IDB 4 (Figure 4) range from 15 to 207 mg/kg (median = 145 mg/kg), whereas 14-30 mg in the deepest core sections are assumed to indicate times of low Hg production in the beginning of the mining activity. The distribution of Hg in this core shows a strong increase of Hg concentrations at 170 cm from less than 40 mg/kg to about 100 mg/kg. At about 110 cm Hg concentration increase again to a level of 150-200 mg/kg, which keeps more or less constant to the uppermost sediment layer. It is in doubt that this sequence shows sedimentation in chronological order due to erosion and re-deposition of sediments which is typically for fluvial plains. However, other cores taken from the same site show a similar course of Hg enrichment (17).

At the TEM site the distribution of mercury concentrations in the core of the lowest terrace (TEM 3) shows a different record than the IDB 4 core indicating that the conditions of sedimentation are of major importance. Here, Hg concentrations vary from 140 to 553 mg/kg (median = 227 mg/kg) showing 2.5 times higher Hg concentrations as found at the IDB site (Figure 4). This core shows highest Hg concentrations (553 mg/kg) in the deepest layer (112 cm). Hg concentration decrease to about 140 mg/kg at a depth of 50 cm and increase



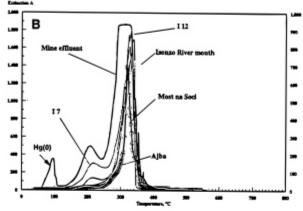


FIGURE 2. (A) Distribution of mercury phases and total Hg concentrations and (B) Hg—Thermo-desorption curves of sediment samples from Idrijca and Soca rivers taken at 6 different locations between the city of Idrija and Isonzo river mouth.

again to 447 mg/kg in the uppermost layer (Figure 4). The high Hg concentrations in the deepest core section indicate that this core does not show the complete record of Hg contamination going back to the times of the earliest mining activity. The decrease of Hg concentrations toward younger sediments is assumed to be due to lower amounts of Hg in the dumped mining residues as a result of improved efficiency of the roasting technique. However, both cores do not show a record which corresponds to the Hg production in Idrija, which shows a strong increase during the last 150 years (12). Moreover, it is reasonable that Hg concentrations in sediments are to a lesser extend dependend on production rates, but on smelting efficiency, ore grade and Hg phases occurring in the residues, which will be discussed below.

Mercury concentrations in the cores of the two upper terraces (TEM 2, TEM 1) show a pronounced gradual increase of Hg concentration to the upper soil layers. Compared to core TEM 3, Hg concentrations sharply decrease to 0.6–60 mg/kg (median = 7.1 mg/kg) in core TEM 2 and to 1.1–7.5 mg/kg (median = 3.1 mg/kg) in the core of the upper terrace (TEM 1). In contrast to sediments of IDB 4 and TEM 3, which contain also coarse grain fractions, mercury contamination of the flooded soils of the terraces TEM 2 and TEM 1 is assumed to be attributed to the deposition of mostly fine grained material. The minor deposition of coarser material, which typically shows higher Hg concentrations, explains the sharp decrease of Hg concentrations from the lowest (TEM 3) to the highest terrace (TEM 1) (Figure 4).

Mercury Concentrations in the Gulf of Trieste. Mercury concentrations in GT sediments were also found to be mainly determined by grain size fractionation when the plume of Isonzo river sediments dispersed in the Gulf of Trieste. Previous studies have shown that dispersion of Hg in the GT

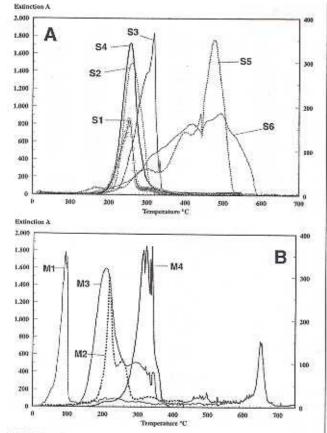


FIGURE 3. Thermo-desorption curves of standard Hg compounds: A: Hg in humic acids (S1), synthetic red cinnabar (S2), red cinnabar from Almadén (S3), metacinnabar (S4), HgO (S5) and HgSO₄ (S6), B: metallic Hg in carboniferous schists (M1), Hg in a forest soil sample collected at sample point TEM (M2), Hg in tailings younger than 100 years (M3), of cinnabar in dolomite (M4).

could be observed along four directions (13, 18, 19). Highest Hg concentrations were found within the Isonzo river mouth and in near shore sediments of the Italian sector, particularly alongside both sides of the river delta. Moreover, highest Hg concentrations (ca. 30 mg/kg) were found to be associated with nearshore coarse sediments, while Hg concentrations sharply decrease with distance from the river mouth to areas, where the smallest grain sizes settle down (Table 1). Here, more than 80% of all grain sizes were smaller than 0.016 mm and highest Hg concentrations were found in the fraction 0.016—0.002 mm. In a distance of more than 15 km from the river mouth Hg concentrations were reported to be generally below 1 mg/kg (19).

Covelli et al. (19) analyzed a sediment core (AA1) from the Gulf of Trieste taken 7.4 km distant from the river mouth. where mostly fine grained material was deposited. They found a steady increase of Hg concentrations from about 70 cm to 20 cm followed by a gradual decrease to the top layer (Figure 5C). They dated the beginning of the increase of Hg concentration to about 1800 with a maximum just before the beginning of the first World Word, based on a calculation which includes an estimated sedimentation rate, the enrichment factor and the amount of Hg produced in Idrija. These data indicate that before 1800 no Hg was deposited in this part of the Gulf despite that the mining activity in Idrija started as early as 1496. The authors concluded that the Hg record given in core AA1 reflects the historical record of Hg production in Idrija. However, Hg production data given by Mlakar (12) shows the period of the most intensive Hg production in the last decade of the 18th century, which is not recorded in the core AA1 (Figure 5c). The different cores

taken from Idrijca sediments and in the GT have shown that the Hg concentrations recorded in the cores depend to a large extent on the predominant grain size fraction deposited at the sampling sites. Moreover a closer look at data on Hg production rates, the ore grade, the amount of excavated ore and the efficency of the roasting process provided by Mlakar (12) indicates that those parameters could strongly influence the record of Hg concentrations in sediment cores, and do also show that high Hg concentrations in sediments do not necessarily hint to high Hg production and vice versa.

The data of Mlakar (1974) shows that between the 15th and 18th century the amount of excavated ore was below 10 × 103 metric tons, annually. Due to the high ore grade which reached up to 78%, the yield of Hg was high, reaching 50 to 100 metric tons anually until 1790 and a maximum production of about 700 metric tons anually in the last 10 years of the 18th century. In this period the efficiency of the roasting technique from its introduction in the 16th century to 1785 is reported to be only 50 to 65% (12). Due to the high ore grade and the low efficiency of the smelter, high amounts of cinnabar were released to the river, resulting in high Hg concentrations in sediments, despite that the volume of the extracted ore was comparatively small. It was found in earlier studies (11) and has been also assumed by other authors (20) that Hg concentrations in old mining residues are higher than in younger ones due to the low efficiency of the ore processing and high ore grades. One reason for the low efficiency is probably that the material at the time was not intensively crushed, so that the amount of fine grain material in the dumped mining residues was comparatively small. This could explain why no Hg enrichment was found in sediments older than 1800 at site AA1, where only fine grained material was deposited. Moreover, high ore grades and low roasting efficency explains the high Hg concentrations in deep sediment sections of core TEM 3. Between 1850 and 1970 mercury production reached another maximum, ranging between 300 and 500 metric tons, annually. As the ore grade decreased from several tens to less than 1% in the same period, the amount of excavated ore increased from less than 10 to 150×10^3 metric tons annually, in times of highest production (12). As the efficiency of the roasting process during this time increased to more than 90%, it becomes apparent that Hg concentrations, especially those of cinnabar, in the mining residues decreased, while the amount of mining residues strongly increased. This conditions will cause high amounts of sediment material with comparatively low Hg concentrations explaining e.g. the decrease of Hg concentrations in the upper part of core TEM 3. With the increasing amount of mining residues and the improved efficency of the roasting process, including intensive crushing of the ore, the amount of fine grained material in the mining residues is assumed to have strongly increased. The increasing amount of fine grained material in the mining residues could explain the increase of Hg concentrations in the upper sections of the cores TEM 2 and TEM 1 and also in core AA1. All three cores where taken from locations predominately fine grained material was deposited.

Mercury Phases in Sediments and Flooded Soils. The results of Hg thermo-desorption measurements show that all but one of the sediment and soil samples taken between Idrija and Isonzo river mouth show the same course of Hg release. All samples show double peak curves with one maximum between 150 °C and 250 °C and a second one between 250 and 350 °C (Figures 2B and 4). The second peak (250–350 °C) indicates the occurrence of red cinnabar, according to the curve of the cinnabar standard (Almadén) (Figure 3A). The thermal decomposition of red cinnabar typically shows several narrow, but high Hg peaks due to the breakdown of the cinnabar lattice, which cause a sudden release of high amounts of metallic Hg. Mercury release

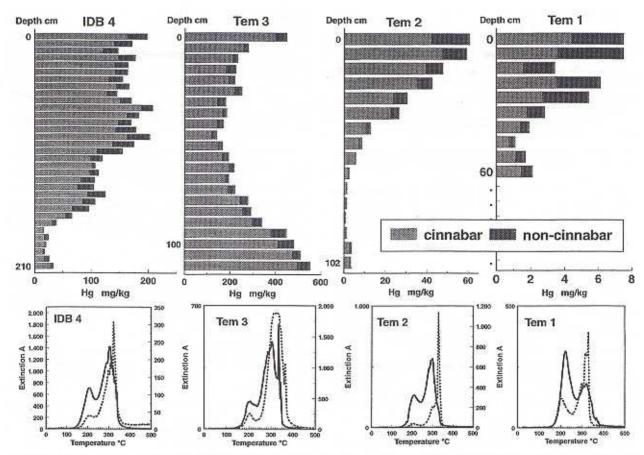


FIGURE 4. Calculated distribution of cinnabar and noncinnabar Hg compounds and Hg—Thermo-desorption curves of samples from core IDB 4 taken from an alluvial plain and in the cores TEM 1, TEM 2 and TEM 3 taken from river terraces. The two TDCs show the sample with the highest (full line) and the lowest amount (spotted line) of noncinnabar Hg.

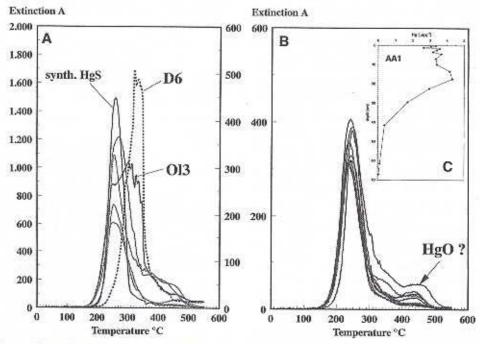


FIGURE 5. Hg-Thermo-desorption curves of samples taken from the Gulf of Trieste: A: bottom sediments, B: samples of core AA1 and C: the record of total Hg concentrations in the GT sediment core AA1 (19).

temperatures of red cinnabar varied slightly due to crystallinity and grain size. Microcristalline cinnabar, like that of the synthetic reference material (Merck), and also metacinnabar were found to show lower Hg release temperatures than fully cristalline cinnabar of the mining area. The first peak (150-250 °C) represents Hg release from noncinnabar Hg forms which are sorbed to organic, or mineral sediment, or soil components. Metallic mercury, typically released at temperatures below 100 °C (Figure 3B), was only detected in a sample taken near the mine effluent where it amounts to about 5% of total Hg (Figure 2B). The fate of the metallic Hg introduced with the mining residues is up to now unknown. We assume that it will be at least partly oxidized and bound to organic matter.

Figure 2b shows Hg-TDC of Hg in tailings, cinnabar bearing dolomite, Hg(0) bearing schists and forest soils polluted by atmospheric Hg deposition, which are the original materials contributing to the Hg load of the river sediments. Previous studies have shown that matrix bound Hg in tailings mostly exist as metallic Hg which is mainly adsorbed to mineral components. In forest soils atmospheric derived Hg was found to be predominately bound to the organic matter (11).

In Figures 3 and 4 the distribution of cinnabar and noncinnabar Hg compounds are depicted as cumulative bar charts giving the percentage of both fractions of total Hg as calculated by peak integration. Mean RSD was 13% for the detection of cinnabar and 6% for the detection of matrix bound Hg (n = 10).

Figure 3 shows Hg-TDC and the distribution of cinnabar and noncinnabar Hg compounds in the six selected bottom sediment samples taken between the city of Idrija and the Isonzo river mouth. The results show that cinnabar is the predominant Hg compound in all samples. Noncinnabar compounds in bottom sediment samples did not exceed 15% of total Hg. It seems that the amount of noncinnabar compounds decrease with distance from the mine, which is probably due to higher sedimentation of dumped mining residues closer to the mine (Figure 2B). Another reason might be, that after the junction of the rivers Idrijca and Soca in Most Na Soci, the contaminated material brought by Idrijca river is diluted by nonpolluted material brought by Soca river, which also explains the sharp decline in Hg concentrations. The most likely reason is that most fine grained material was already washed to the GT.

Distribution of Hg phases in IDB 4 core samples also show a clear predominance of cinnabar in all layers (Figure 4). Median percentage of noncinnabar Hg was 17% ranging from 5 to 30% of total Hg. These results indicate that distribution of Hg phases at this site does not vary to a large extend despite changes of Hg phases in the dumped mining residues. We assumed that this is due to a preferably deposition of coarse grained sediments bearing mostly cinnabar. The amount of fine grained sediments bearing noncinnabar compounds was generally low due to the high riverine current at this site.

In all sections of the profiles taken from the terraces, cinnabar was again the predominant Hg compound but the average amount of noncinnabar Hg clearly increased from 12% in core TEM 3 to 23% in TEM 2 and 40% in TEM 1 (Figure 4). Mean RSD here was 12% for the detection of cinnabar, and 5.3% for the detection of matrix bound Hg (n = 8). The relative increase of noncinnabar Hg compounds in the cores TEM 2 and TEM 1 is again a result of separation of grain sizes bearing different Hg fractions. The increasing percentage of noncinnabar compounds in the flooded soils on the higher terraces TEM 2 and TEM 1 is due to a preferably deposition of fine grained material on higher terraces during flood events. As discussed above, this assumption does also explain the sharp decrease of Hg concentrations from the lowest to the highest terrace. On the other hand Hg-TDC of forest soil samples collected about 20 m uphill from TEM 1 show about 98% of noncinnabar matrix bound Hg and only very small amounts of cinnabar (Figure 3B). In this area which is not flooded during high waters, all Hg in soils is derived from atmospheric Hg deposition attributed to the emissions of the smelter in Idrija. The small amounts of cinnabar in this sample might result from dust blown from the terraces. Regarding the total Hg content of 2.8 mg/kg in the forest soil sample it becomes clear that in the uppermost core section only 5.8% of noncinnabar of TEM 3, 15% of TEM 2 but up

to 90% of TEM 1 could be attributed to atmospheric Hg deposition. However, atmospheric deposition of Hg to grassland is usually lower than to forest soil, thus the part of atmospheric derived Hg in the TEM cores might be actually lower. We concluded that the relative increase of noncinnabar Hg compounds in core TEM 2 is mainly attributed to the deposition of noncinnabar Hg in fine grained sediment, whereas noncinnabar Hg compounds in soils of the uppermost terrace (TEM 1) are to a large extent supplied by atmospheric sources.

The records of cinnabar and noncinnabar compounds in the investigated sediment and soil cores do not show any variation which hint to changes of the composition of the dumped mining residues. From the high efficiency of the roasting technique, the low ore grade and the high amounts of excavated ore in the past 100 years, we expected to find higher amounts of noncinnabar Hg compounds in the sediments and flooded soils.

Mercury Phases in Sediments of the Gulf of Trieste. From all samples (n=33) taken from sediments of the Gulf of Trieste only two samples (D6 and OL3) show a cinnabar peak in the same temperature range ($230-350\,^{\circ}\text{C}$) which was found for the Hg release from river sediments (Figure 5A,B). Both samples were taken within or close to the river mouth where mostly coarse grained material has settled down (Figure 1). All other samples from the Gulf, consisting of mostly fine grained material (<0.590 mm), show the maximum of Hg release between 200 and 300 °C. An additional small peak between 400 and 500 °C was detected in most GT sediment samples, especially in those of core AA1 (Figure 5B). This peak has been also detected in tailing material and was assigned to the occurrence of Hg oxide (II) formed during the roasting process.

The temperature of maximum Hg release in GT sediment samples is generally lower than that of cinnabar in river sediments but higher than that of noncinnabar Hg in river sediments and soils (Figures 4 and 5). These samples show Hg release temperatures which are similar to those of synthetic red cinnabar (very fine grained) or metacinnabar (Figure 2a). This suggests that cinnabar in sediments of the Gulf shows lower Hg release temperatures as an effect of grain size. On the other hand it has to be considered that Hg(II) or Hg(0) sorbed to matrix components could be transformed to metacinnabar (black HgS) or to organomercury-sulfides under unoxic conditions. (21). It is most reasonable that actually both Hg compounds exist in these sediments.

Due to the wide overlapping of TDCs of metacinnabar, organo-mercury-sulfides and microcrystalline cinnabar those compounds could not be separated by Hg thermo-desorption analysis. To separate cinnabar from organically bound Hg, 10 selected sediment samples from the GT were treated with an oxidizing reagent, which is ought to extract the organicsulfide Hg phase. The amounts of extracted Hg listed in Table 1 show that there is a tendency of increasing amounts of Hg in the organic-sulfide phase with distance from the river mouth. Accordingly, no detectable losses were found in the sample D6 taken near the river mouth, where Hg-TDC indicate that all Hg occurs as cinnabar (Figure 5A). Highest losses were found for the sample A3 taken 15.6 km distant from the river mouth. However, the high percentage of extracted Hg from sample OL3 taken comparatively close to the shoreline indicate that settling of matrix bound noncinnabar Hg compounds does not only depend on distance from the river mouth but also on other parameters such as wind direction and currents. In the Bilinia sediment sample where almost all Hg is assumed to occur as organic-sulfide Hg, only 73% were extracted indicating that the extraction procedure used might be insufficient or that some of the Hg exists as metacinnabar. Therefore, the amount of Hg in the

organic-sulfide phase of the sediments might be actually higher than determined. The relative standard deviation of the extraction analysis was 17% on an average (n = 3).

These results also support previous studies (19, 22) which hint to the occurrence of increased amounts of noncinnabar, transformable Hg species in distant areas of the GT. Covelli et al. (19) showed that highest concentrations of methyl mercury occur in these external areas where the finer grained material of the Isonzo river plume has settled down. Moreover, benthic chamber experiments have shown that, far off the river mouth (AA1), 75% of total Hg is buried in the sediment, whereas 25% of total Hg, 23% in methylated form, is annually released from the sediment into the water column (23). This evidence is undoubtedly due to more mobile Hg species, whereas the extremely low solubility of cinnabar should not allow this form to be involved in fluxes at the water-sediment interface.

Our study has shown that still huge amounts of Hg are stored in areas where ancient sediments were deposited. Furthermore, it has been demonstrated that dispersion and accumulation of cinnabar and noncinnabar Hg compounds in sediments strongly depend on the distribution of respective grain size fractions with which those Hg phases are mainly associated. As a result line grained sediments may show comparatively low Hg concentrations but show the highest relative amounts of potentially transformable noncinnabar Hg. Despite that in nearly all samples most Hg exist as cinnabar, the amount of noncinnabar Hg compounds is nevertheless high amounting to 2.9 and 57.7 mg/kg in river sediments and still up to 1.9 mg/kg in GT sediments far off the river mouth.

Although dumping of mining residues has stopped now, soils of the drainage area of Idrijca river, highly contaminated by atmospheric Hg deposition, might become an important future source of mobile and transformable Hg compounds, finally deposited in the Gulf of Trieste. More research is needed here, as only little concern has been given to this subject up to now.

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Received for review December 1, 1999. Revised manuscript received May 22, 2000. Accepted May 23, 2000.

ES991334V