The impact of mercury mining on the Gulf of Trieste

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Abstract

The Idrija mine, Slovenia has severely enhanced the mobilisation of Hg by mining activities, and Hg-laden material remains in the region. The tailings and contaminated soils are continuously eroded and serve as a continuous source for the river, the flood plains and the Gulf of Trieste. The paper presents data of the recent study which aims to assess the extent of contamination of Gulf of Trieste after the closure of the Hg mine. Mercury and methylmercury were measured in various environmental compartments (estuarine and marine waters, sediments, and organisms) during 1995-97 period. Data obtained show that even 10 years after closure of the Hg mine, Hg concentrations in river sediments and water are still very high and did not show the expected decrease of Hg in the Gulf of Trieste. A provisional annual mercury mass balance was established for the Gulf of Trieste showing that the major source of inorganic mercury is still the River Soča while the major source of methylmercury is the bottom sediment of the Gulf.

1 Introduction

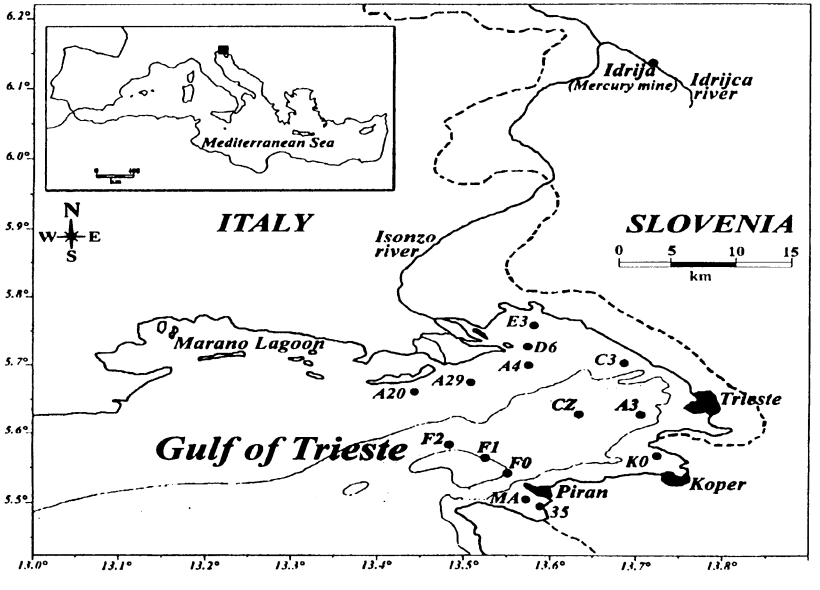
The biogeochemistry of mercury (Hg) has received considerable attention recently because of the toxicity of methylmercury (CH_3Hg^+, abbreviated as MMHg), the accumulation of Hg in biota, and its biomagnification in aquatic food chains. Hg attacks the central nervous system, and concerns about Hg are based on its effects both ecosystems and human health. The principal pathway for human exposure is the consumption of contaminated fish. Numerous recent studies have concluded that the majority, if not all, of the Hg that is bioaccumualted through the food chain is as MMHg [1,2]. Therefore, knowledge of the concentration, transport, and dynamics of MMHg in aquatic ecosystems is needed to predict the potential impact on humans, as well as on aquatic life. Recently, the U.S. Environmental Protection Agency (EPA) set a new guideline for methylmercury in the diet: 0.1 microgram of mercury per kilogram of body weight per day (0.1 μg/kg/day). This is 4.7 times as strict as the World Health Organization's (WHO's) standard of 0.47 μg/kg/day. An average concentration of Hg in fresh and marine fish is about 0.2 mg/kg. In practical terms this means that and average person weighing 60 kg can only consume about 30 g of fish per day [3]. Recent study on mercury levels in humans has shown that inhabitants near the Lagoon of Grado and Marano in the Northern Adriatic, consuming a diet rich in local seafood are exposed to a higher risk of exceeding the recommended weekly intake [4]. In the Gulf of Trieste mercury concentrations frequently exceed 0.5 mg/kg [5], which in practical terms means that local population should limit its consumption of fish to only one meal per week.

2 Study area

The Idrija mercury mine is situated 50 km west of Ljubljana, Slovenia, and it is the site of the second largest Hg mine in the world which was in operation continually for 500 years until about 10 years ago. Over five million metric tonnes of Hg ore was mined, and much of the residues were spread around the town and its vicinity. It has been estimated that 73% of the Hg mined was recovered with the remainder dissipated into the environment. The Idrija mine has severely enhanced the mobilisation of Hg by mining activities, and Hg-laden material remains in the region. Most importantly, the smelting processing of Hg ore over the centuries and the venting of the mine shafts which release native Hg (Hg^0), caused extremely elevated levels in airborne Hg. Concentrations of Hg in air

exceed 2.5 μg/m^3 during active mining periods, and even today, airborne Hg levels near the abandoned smelter and around the mine shafts are very high at over 300 ng/m^3. Hg levels in sediments and flood plain deposits in the area are very elevated as well. Soils in the Idrija valley are also naturally rich in Hg. Hence, although the ultimate source of Hg in the Idrija region is from base deposits, the majority of material that resides in surficial materials, including deep sediments and along the banks of the river are derived primarily from Hg re-mobilized by mining activities, mostly by smelting [6-9]. Some recent studies have shown that the area even today, continues to supply high quantities of Hg into the river systems of the Idrijca and Soča and reaches the Gulf of Trieste some hundred km downstream where river system empties into the NE Adriatic Sea [10-12]. Recent estimates of Hg balance in the Gulf have shown that the annual input through river Soča discharges is about one ton and a half [11].

Figure 1. Location of Idrija, the rivers Idrijca and Soča (the Soča becomes the Isonzo in Italy), and sampling points in the Gulf of Trieste.



Furthermore, it is well known that the Northern Adriatic is a subject to serious pollution problems, accompanied with eutrofication, anoxic conditions at the bottom, and winter and summer temperature stratification [13, 14]. All these favour transformation of inorganic mercury to more toxic MMHg, which is responsible for the elevated Hg values in marine organisms which frequently exceed the value of 0.5

mg/kg, which is set as the maximum permissible level according to WHO and Slovenian legislation. Moreover, due to deteriorated water quality in the Gulf of Trieste, Hg tends to accumulate in some marine food from mariculture areas, which represents a social and economic problem to the local population [5].

3 Sampling and chemical analysis

Sampling in the marine environment (Figure 1) was performed on three occasions during 1995/96:

- June 1995: high river discharge and biological productivity
- September 1995: low river discharge, stratified conditions in the Gulf, and occasional anoxic conditions at the bottom
- March 1996: low biological productivity period.

Fresh water samples in the river Soča from the bridge near Monfalcone, Italy were sampled twice in November 1997, before and after heavy raining period.

Water samples were collected at the surface (0.5 m depth) and on the bottom (1m above the sediment) by a scuba diver in one litter acid-cleaned Teflon or Pyrex bottles. Samples were stored at 4°C until further processing in the laboratory. Water samples were filtered (0.45 um Nucleopore filters) in order to determine dissolved and particulate bound total Hg and MMHg. Sediment samples were collected using metal free corers (l =30 cm, ϕ = 5 cm) and sectioned at 2 cm intervals. Wet samples were analysed. Results are expressed on a dry weight basis.

Zooplankton was samples using 220 um nets, stored in pre-cleaned Teflon containers and freeze dried. Fish was caught in June 1996 by a local fisherman. Fish muscles were taken for analysis.

Reactive Hg in water samples was determined immediately after sampling using $SnCl_2$ reduction of easy available Hg^{2+} in non-acidified water samples. Total Hg in water samples was analysed by CV AFS or CV AAS after BrCl/UV oxidation [15, 16]. Total Hg in sediment and biological samples was determined by CV AAS after acid digestion[15]. MMHg in water, sediments and suspended matter was determined by solvent extraction, aqueous phase ethylation, gas chromatographic separation, pyrolysis and CV AFD detection [17,18]. MMHg in some of the biological samples was determined by a simplified procedure using HCl leaching, ion-exchange separation, UV oxidation and determination by CV AAS [19]. All analytical methods were regularly validated and performed under good quality control system.

4 Results and discussion

Levels of total, dissolved, and reactive Hg are shown in Table 1. In the vicinity of the estuarine plume, dissolved Hg concentrations were relatively low showing significantly higher concentration in the surface layer than in the bottom. The difference in the central part of the Gulf was relatively small. In contrast, MMHg concentrations were about 10 times higher in the bottom layer (up to 60pg/l) than at the surface (below 5 pg/l) indicating the importance of sediment as the secondary source of this toxic Hg compound. The proportion of reactive Hg was variable ranging from 3-22% of total hg in surface waters close to the river mouth to a max. of 60% in bottom waters. No significant differences were observed in dissolved and reactive Hg during the two sampling periods. The same applies to total Hg in surface waters. However, a significant increase of total Hg in bottom waters has been observed for the September sampling period. The distribution coefficient (K_d) of total Hg between solid and dissolved phase (l/kg) in the estuarine plume was 10^7, while in the coastal waters it varied from 10^5 to 10^6, showing strong association with particulate matter. K_d for MMHg in river water was around 10^4, indicating that MMHg is less strongly associated with particulates than inorganic Hg.

Table 1. Mercury in water samples of the Gulf of Trieste. Results are given in ng/l.

Sampling	Dissolved Hg		Total Hg		Reactive Hg	
Station/period	Surface	Bottom	Surface	Bottom	Surface	Bottom
D6 June-95	4.90	1.31	12.6	4.51	1.20	1.40
Sept-95	4.73	0.89	11.5	12.7	5.1	0.98
A4 June-95	3.47	1.08	10.1	2.40	3.92	0.96
Sept-95	3.74	1.08	11.8	9.73	3.92	0.96
A29 June-95	1.53	1.28	4.10	3.45	1.02	0.75
Sept-95	-	-	-	-	-	-
A20 June-95	2.31	1.34	9.42	2.73	2.00	0.84
Sept-95	2.65	1.28	7.99	4.93	3.72	0.86
CZ June-95	0.97	1.18	1.25	1.31	0.97	1.18
Sept-95	0.52	0.83	1.32	2.37	0.78	0.66
F2 June-95	0.95	1.23	2.47	1.66	0.40	0.64
Sept-95	0.54	0.18	1.71	0.77	0.28	0.33
F0 June-95	0.68	1.09	1.93	2.38	0.64	0.85
Sept-95	0.18	0.78	0.51	1.35	0.29	0.47

Results for total Hg in surface sediments and short cores (0-10 cm) (Figure 2) show that Hg is homogeneously distributed throughout the cores and does not show the expected decrease of Hg in the Gulf of Trieste in recent years. The ratio of MMHg to total Hg in sediments

increases with the distance from the river mouth and it is in positive correlation with the percentage of clayey fraction (Figure 3). Benthic fluxes for total and MMHg were also measured in the central part of the gulf and it was estimated that about 74% of total is buried in sediment, while 26% of total Hg, of which 25% is in the methylated form, is annually recycled and released from the water-sediment interface [20].

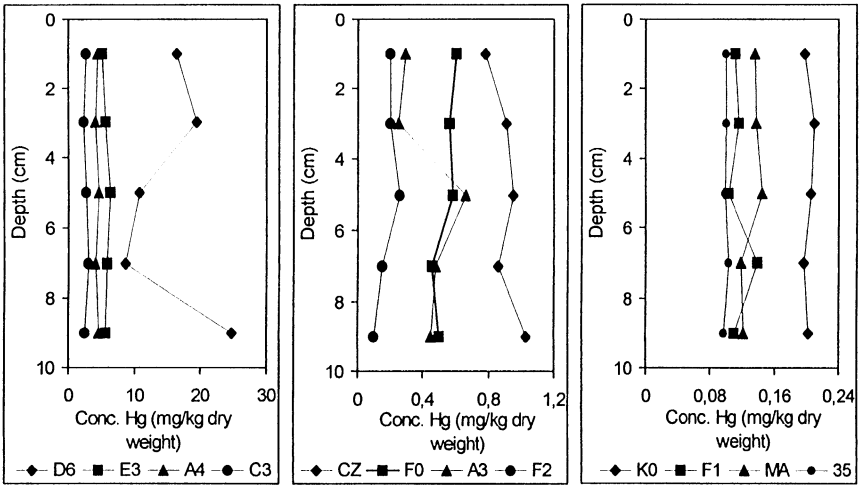


Figure 2. Vertical distribution of total Hg in sediments (1995)

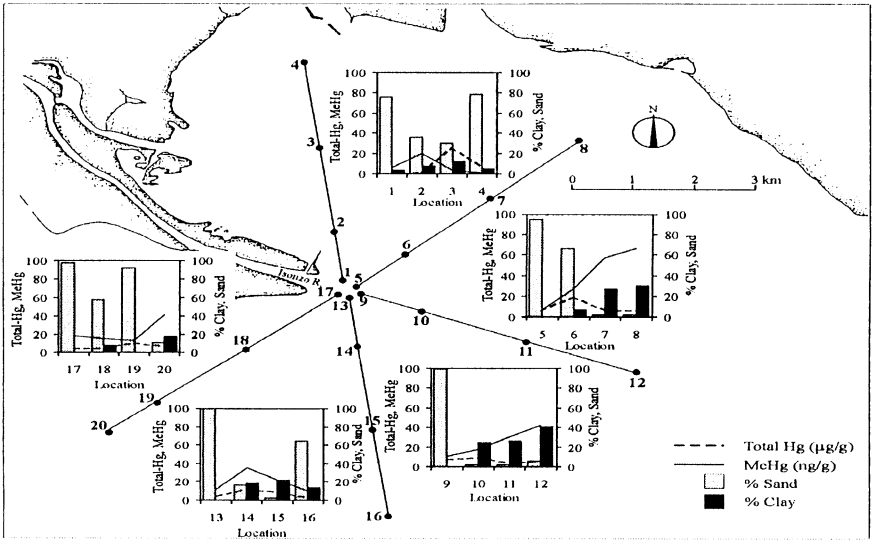


Figure 3. Total and MMHg in sediments near the River Soča mouth

The relationship between the size (age) and Hg and MMHg content in fish muscle was studied in two non-migratory fish species, that were caught in the same area (Stations F1 and F0) at the same time (June 1996). Total Hg was measured in fish muscle and the data are presented in Figure 4. The Grey mullet (*Mugil cephalus*) is herbivorous fish and contains lower concentrations of total Hg than Common pandora (*Pagellus erythrinus*) which is a benthic carnivorous fish. The Hg levels are comparable to data obtained for the wider Adriatic[21]. Interestingly, no significant correlation between Hg and MMHg levels and weight (age) was observed. In the case of Common pandora this may be due to the fact that 34 (out of 36) fish were only 2 years old and so had not yet developed the predicted relationship. The Grey mullet shows a better relationship between age and Hg concentrations probably due to better representativenes of the age of the fish. It is interesting to note that the % of MMHg in fish muscle was in most cases much lower than 100%. This is in contrasts with most of the studies which show that with age the % of MMHg should increase. Further investigations are in progress that will explain this unusual behavior of Hg speciation in studied fish species.

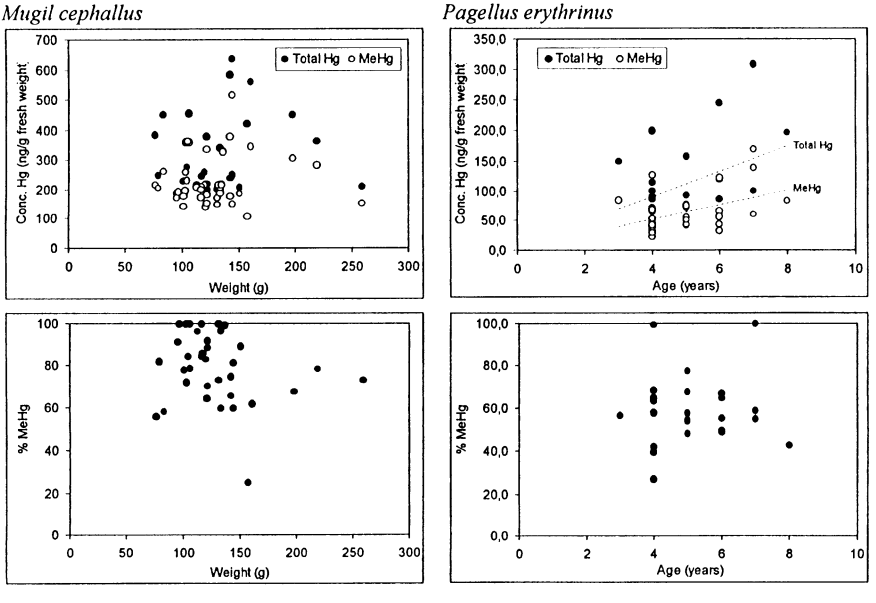


Figure 4. Correlation of total Hg and MMHg concentrations with age (or weight) in two fish species

The results for mixed zooplankton samples are shown in Table 2. Evidently, the concentrations of total Hg and MMHg were 2 to 3 times

higher in June compared to September 1995 and about 10 times higher than in March 1996. The percentage of MMHg was also quite variable being lower in June and September and higher in March. The variability of these data can be related to seasonal biological variations in the Gulf, such as phytoplantonic bloom in May/June compared to low productive periods in March. Most probably the this variability is also related to different planktonic species composition to facilitate the interpretation of the results and for the evaluation of the dynamics of the accumulation and release of total Hg and MMHg in stage of the marine food chain. In general, the concentrations levels observed for both analyses do not significantly differ from other studies in the Mediterranean and similar variability of data have also been reported by other researchers [20].

Table 2. Mercury and methylmercury in zooplankton

Sampling Station/period	Total Hg (ng/g, dry weight)	MMHg (ng/g, dry weight)	% MMHg
D6 June-95	-	-	-
Sept-95	200	19.3	9.65
March-96	30.8	9.08	29.48
A4 June-95	959	65.7	6.85
Sept-95	273	10.1	3.7
March-96	12.8	2.08	16.25
A29 June-95	449	46	10.24
Sept-95	-	-	-
March-96	-	-	-
A20 June-95	501	50.5	10.08
Sept-95	193	8.15	4.22
March-96	17.8	2.13	11.97
CZ June-95	282	23.1	8.19
Sept-95	249	12.2	4.9
March-96	14.2	3.68	25.92
F2 June-95	377	52.3	13.87
Sept-95	56.6	5.31	9.38
March-96	24.2	8.82	10.89
F0 June-95	607	59	9.72
Sept-95	242	8.77	3.62
March-96	24.2	2.1	8.68

5 Mass Balance

In 1996, a provisional annual mercury mass balance was established for the Gulf of Trieste [10, 11]. The sources were 1780 kg of mercury carried to the Gulf by the river Soča, 5 kg coming from the atmosphere and 98 kg arriving by currents from the open sea of the Northern Adriatic. With an annual deposition of 1665 kg of mercury, sedimentation was found to be the major sink while a minor one was

represented by an outflow of 215 kg to the Northern Adriatic. Numerous recent measurements of mercury concentrations at the bottom of the Gulf, in the river Soča (Tables 1 and 3) enabled us to revise and supplement the mass balance, especially for MMHg data.

Using a benthic chamber experiment it was estimated that only 1308 kg (74 %) of the deposited Hg is buried in the sediment annually, while 26% of the total Hg is recycled. Approximately 25% of the recycled Hg is in MMHg form, whereas in the burial part only 1.8 % of total Hg is methylated [20].

Table 3. Concentration of total and particulate Hg and MMHg in the River Soča in Monfalcone (before discharging into the sea)

Sapling period	Total Hg	MMHg
21.Oct.1997 low water discharge; samples were not filtered (less than 2mg/l of the particulate matter, n=2	*Reactive: 0.65; 0,48 ng/l* Total Hg (dissolved+ particulate): 1,87; 1,08 ng/l	0.072;0.070 ng/l
8.Nov. 1997 high water discharge; samples were filtered; n=4	*Reactive: 1.10±0.15 ng/l* Dissolved: 2.98±0.59 ng/l Particulate: 49.6±20.2 mg/kg	0.044±0.010 ng/l 0.092±0.03 ng/g

Measurements of particulate and dissolved mercury during a flood wave with the peak discharge of the last 5-year period in November 1997 (Table 3) confirmed the importance of episodic events on mercury fluxes from contaminated areas to the Gulf of Trieste. With an average of 49.6 μg/g of total Hg content in the suspended matter, an average of 365 g/m^3 of suspended matter and a water volume of 470 million m^3 discharged in 3 days, the total flush of mercury to the Gulf was approximately 8500 kg, which is far above the estimated average annual discharge calculated earlier. The average dissolved MMHg concentrations were around 50 pg/l and particulate bound MMHg around 0.64 ng/g. This means that the total amounts of MMHg in the flood wave was only 0.14 kg . This value is negligible compared to the benthic flux of MMHg into the water column of the Gulf of Trieste, confirming that the main source of MMHg in the Gulf originate from sediment [20].

6 Conclusions

It can be concluded that even though the Hg mine in Idrija was closed completely in 1991, Hg concentrations in sediments and water are still very high and did not show the expected decrease of Hg in the Gulf of Trieste. While some questions have already been answered regarding the main transport mechanisms in the river system and the Gulf of Trieste alone, the main question concerning Hg transformation in the river

systems and Idrija remains unanswered. Further studies are in progress in order to understand basic processes of Hg cycling and to develop models for simulation of future scenarios and plan remediation actions, if necessary.

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