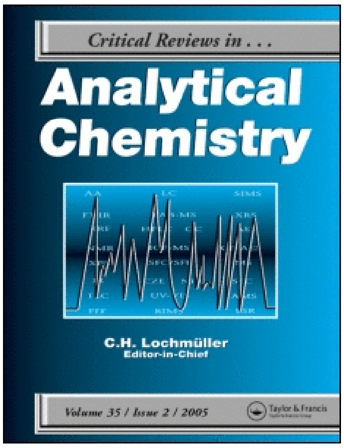

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Remediation of Mercury Polluted Sites Due to Mining Activities

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ABSTRACT: During the 500 years of mercury mining in Idrija, large quantities of Hg were released into the environment. Due to chemical transformation (reduction, methylation, oxidation, demethylation) and the transport of mercury enriched particles into the river system and the Gulf of Trieste, the mercury problem is of local, regional, and global concern. The results of some studies indicate that Hg is actively accumulated in terrestrial and aquatic food webs, which leads to an increased exposure of inhabitants frequently consuming food, particularly, fish produced in a contaminated area. In order to understand the impact of mercury mining on the environment and human health, it is necessary to integrate the experience of various disciplines (e.g., chemists, biologists, geologists, hydrologists, epidemiologists, economists, etc.). Political support at the local and regional level in Slovenia and Italy is as well an ultimate requirement for the successful implementation of remediation, based on scientifically based criteria.

1. INTRODUCTION

Mercury is widely considered to be among the highest priority environmental pollutants of continuing concern on the global scale. Although there is a continuous problem of occupational exposure to inorganic Hg, predominantly elemental Hg, possible effects on broader segments of the population, due to widespread dispersal of Hg in the environment has become the major concern in recent years. Mercury is among the most highly bioconcentrated trace metals in the human food chain, and many national and international agencies and organizations have targeted mercury for possible emission control. Mercury toxicity depends on its chemical form, among which alkylmercury compounds are the most toxic. The biogeochemistry of mercury has received considerable attention, because of the toxicity of methylmercury compounds (MeHg), the accumulation of Hg in biota, and its biomagnification in aquatic food chains. Concerns about Hg are based on its effects both on 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 bioaccumulated through the food chain is as MeHg. Therefore, knowledge of the concentration, transport, transformation, and dynamics of MeHg in aquatic ecosystems is needed to predict its potential impact on humans, as well as on aquatic life.

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One of the most comprehensive reviews for a current understanding of mercury is summarized in the USA Environmental Protection Agency's (EPA) Mercury Report to Congress that is available on the internet: http://www.epa.gov/tnn/uatw/112nmerc/mercury.html and the report prepared by the National Research Council of the USA [1], and the European Union Position paper "Ambient Air Pollution by Mercury." http://europa.eu.intIcomm/environment/air/background.htm#mercury.

2. MERCURY MINE IN IDRIJA, SLOVENIA

The Idrija mercury mine is situated 50 km west of Ljubljana, Slovenia (Figure 1), and it is a site of the second largest Hg mine in the world which was in operation continually for 500 years until about 20 years ago. Over five million metric tonnes of Hg ore were 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. One unfortunate outcome of centuries of Hg mining activity has been the constant exposure of the inhabitants of the area to Hg poisoning, including high Hg levels in miners. The Idrija mine has severely enhanced the mobilization of Hg by mining activities, and Hg-laden material remains in the region. Most importantly, the processing of Hg ore over the centuries and the venting of the mine shaft, which releases naturally occurring native Hg (Hg^0), caused extremely elevated levels of airborne Hg. Concentrations of Hg in air samples exceed 2.5 $\mu g/m^3$, during active mining periods; yet, even today, airborne Hg levels near the abandoned smelter and around the mine shafts are very high at over 300 ng/m^3 [2, 3].

3. MERCURY TRANSPORT AND TRANSFORMATION

The tailings and contaminated soils in the Idrija region are continuously eroded and serve as a continuous source for the river, the flood plains, and the Gulf of Trieste. This is confirmed by the fact that even after 10 years after closing the Hg mine, Hg concentrations in river sediments and water are still very high, and there are no signs of the expected decrease of Hg in the Gulf of Trieste [4–10]. Recent

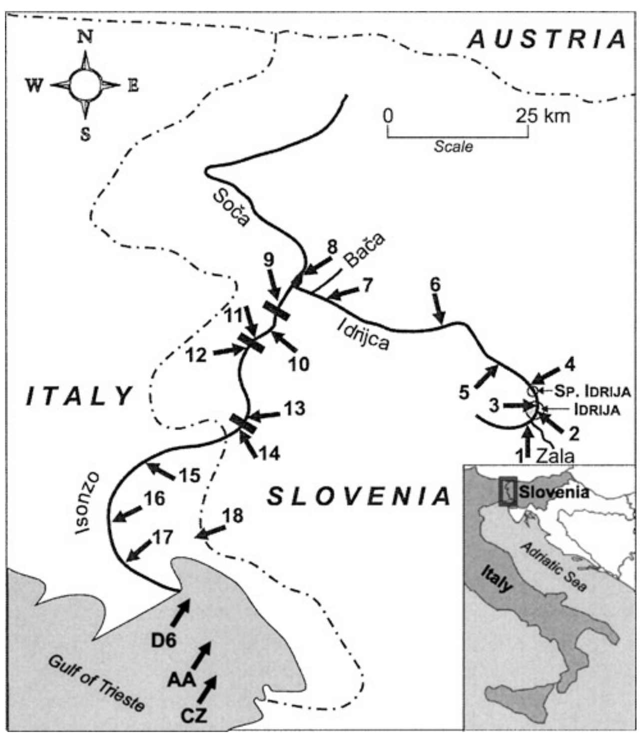

FIGURE 1. The areas directly impacted by the mercury mining activity and the identification of sampling points.

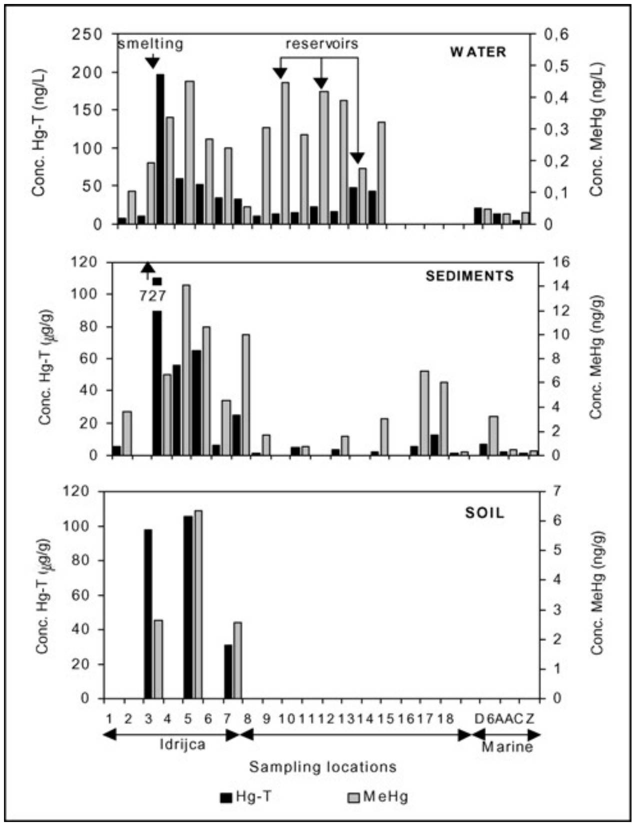

FIGURE 2. Concentrations of total and MeHg in water, sediments, and soils [12, 13].

studies in the Idrijca, Soca, the Gulf of Trieste region are mainly directed towards the quantification of Hg fluxes and better understanding of the fate of mercury, its accumulation in the flood plain, and its final input to the marine environment. An assessment of the extent of contamination in the Gulf of Trieste, after the closure of the Hg mine, was also made [9, 11–19].

Mercury and methylmercury were measured in various environmental compartments during the period 1995–97. Some recent measurements of mercury in water, sediments, and soil are shown in Figure 2. Total Hg in the idrijca river water increased by a factor of 4 downstream of the mine, with methyl Hg (MeHg) accounting for 1.5% above the town of idrija, 0.2–0.7% after idrija, 2–3% in river reservoirs and only about 0.2% in marine waters. This clearly shows the important role of reservoirs in MeHg dydnamics. Concentrations of Hg in sediments and flood plain soils also increased by several fold downstream, with MeHg ranging from 0.01 to 0.1% in riverine and marine sediments, and less than 0.01% of MeHg in flood plain soil.

Hg methylation and MeHg demethylation seem to be active in all compartments of the study area, and must, therefore, be studied together in order to properly assess the fate, mass balances, and fluxes of Hg. The data obtained thus far show that even 10 years after the 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 [11]. Recent estimates on the Hg balance in the Gulf of Trieste have shown that the annual input through the Soca River discharge is about one ton and a half [14, 15]. The major source of inorganic mercury is still the Soca River, while the major source of methylmercury is the bottom sediment of the Gulf, which enters bottoms waters and presumably the marine food chain (Figure 3) [9, 16–19].

As a consequence Hg in fish frequently exceed the value of 0.5 mg/kg, which is set as the maximum permissible level in a number of countries. In addition, a mathematical model of mercury transport and cycling in the Gulf of Trieste was also developed in order to simulate future scenarios [15].

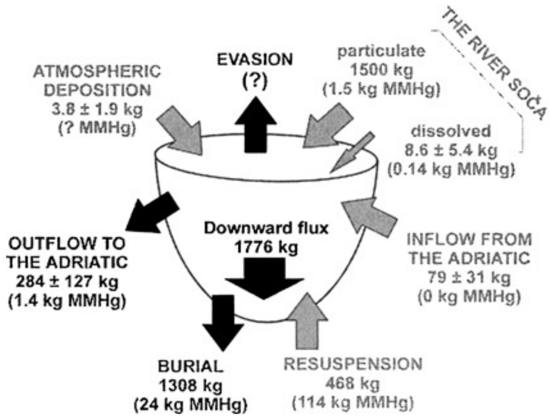

FIGURE 3. Mass balance of mercury in the Gulf of Trieste [14].

4. AIR

Mercury concentrations in air in the town of Idrija are still very high. They vary from 0.01 to about 0.490 $\mu g \cdot m^{-3}$ and did not show a significant drop during the last ten years, however, they are much lower than during the active period of the mining (0.1 to 10 $\mu g \cdot g^{-1}$). The air concentration depends on the weather conditions, direction of winds, and sampling locations. There are two major sources: one is close to former smelter, and the other is close to the ventilation shaft from the mercury mine. Biomonitoring of Hg air contamination, using epyphitic lychens, was developed and is succesfully used to estimate average air mercury concentrations in the study area [2, 3, 21].

5. TERRESTRIAL ECOSYSTEM

Mercury distribution and uptake by plants, including mushrooms, and various organisms of the contaminated Idrija region and control areas in Slovenia has been the subject of various studies [22, 23]. The results confirmed the effective transfer of Hg from soil (and air) to vegetation, herbivores, and carnivores further up the food web. Interestingly, a higher accumulation of MeHg was observed in those environments polluted with high concentrations of inorganic mercury, compared to less contaminated and control areas [24, 25].

6. HUMAN EXPOSURE

Mercury concentrations in drinking water (surface and groundwater) are below 0.1 $\mu g \cdot l^{-1}$ and are even lower away from the Idrija region [2, 18, 26]. These values are far below the permissable level of 1 $\mu g \cdot l^{-1}$. This also indicates that the total intake of Hg by humans through water consumption is low. The mercury concentration in foodstuffs in the Idrija region varies considerably, depending on location and type [10, 27, 28]. However, Hg is elevated in almost all food products, including meat. The highest concentrations were found in fish caught in the Idrijca and Soca rivers and vary from 1.07 to 1.87 mg/kg, f.w., where the percentage of MeHg in fish increases with distance from the town of Idrija [2].

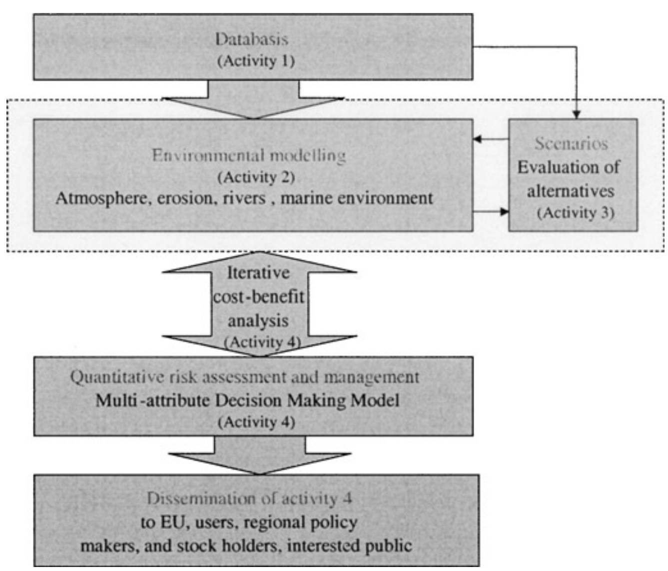

FIGURE 4. An integrated approach for science based management of the study area.

TABLE 1
An Estimated Daily Intake of Mercury in Humans, Expressed as μgHg per kg of Body Weight

	Idrija Region		The Gulf of Trieste	
	Total Hg	MeHg	Total Hg	MeHg
Air (inhalation)	0.05–0.10	—	0.001–0.005	—
Fish (100 g/day)	0.20–3.33	0.18–3.20	0.18–1.35	0.17–1.33
Other food	0.66	0.132	0.05	0.01

There are two major exposure pathways for the local population. One is the exposure to atmospheric Hg in Idrija and nearby surroundings, and the other is exposure through food consumption, including fish in the coastal area of the Gulf of Trieste. Today, the highest values of Hg in air are still close to the US EPA reference concentrations for chronic inhalation exposure of 0.4 $\mu g \cdot m^{-3}$. This indicates that some inhabitants, in more exposed areas of the town of Idrija, are potentially at risk, due to exposure to elemental mercury through inhalation. Exposure to inorganic Hg through food consumption other than fish is not considered to pose significant problems. On the contrary, the coastal population shows increased values of Hg in hair [29, 30], as an indication of exposure to MeHg, due to fish consumption (Table 1). Further comprehensive studies conducted in the region will provide more information about possible health effects.

7. CONCLUSIONS AND RECOMMENDATIONS

It is generally accepted that the formation and bioaccumulation of methylmercury is the most critical point of environmental quality in mercury contaminated sites. The reduction of methylmercury in seafood can, therefore, be defined as the priority objective with regard to the mercury contamination problem in the wider Idrija area and in the Gulf of Trieste. To reach this target two principal strategies exist:

- reducing the input of mercury to the system
- changing the conditions to reduce the formation of methylmercury

Due to the highly complex biogeochemistry of mercury, measurement campaigns and models that address the mentioned subjects (riverine transport, atmospheric transport, marine transport, species transformation and so on) are required. Further, the development of an integrated model approach, which will combine all these individual subjects is required (Figure 4). To fulfil this, well tested and approved models for single compartments should be adapted and linked to an integrated natural science-based model of mercury transport or fate in the wider Idrija region and the Gulf of Trieste.

All the relevant data for the project should be compiled, including socio-economic data, mercury levels in all environmental compartments, GIS information layers, and data for remediation options and its cost benefit. An integrated environmental model of transport and the fate of mercury should include different models: atmospheric, erosion and riverine transport, marine transport and dispersion, and biogeochemical models. The integrated model would then be used as a management tool and should be capable of quantifying the responses of the entire air-land-river-sea-biota system to specific measures or abatement activities, and alternatives for economic development should include an assessment of reliable alternatives for economic development in the region. The quantitative risk assessment and management should include evaluation of the spatial variability of contaminants, probabilistic risk analysis, risk perception, extended cost-benefit analysis, integral environmental impact assessment, and multi-attribute decision tree analysis, leading to final decision-making options. Therefore, the researchers in the region are focusing their efforts to achieve the above objectives.

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