Historical Mercury Mass Balance of the Idrijca and Soča River Catchment

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Abstract: In the town of Idrija, Slovenia, the world's second largest mercury mine has been active for 500 years. During its activity about 37.000 tons of mercury has been lost in the environment. Historical mercury mass balance in the Idrijca and Soča River catchment was established from measurements and by use of a mathematical model. Atmospheric transport was estimated and transport of particulate and dissolved mercury by Idrijca and Soča River was taken into account by use of a 1-D aquatic model MeRiMod. Different, mostly high discharges, were simulated as mercury is mostly bound to suspended matter, which is transported in high quantities by flood waves. Sediment core data from the Gulf of Trieste and measured concentrations from floodplains were used to verify and calibrate the model. Relatively high discrepancy between mercury lost from mining and smelting process and the amount of mercury in the nearby environment was found, which leads to conclusion, that not all processes were taken into account correctly. Additional measurements and improvement of the model are necessary to determine the exact reason of discrepancy.

Key words: mercury cycling, mass balance, mathematical modelling, Idrija, Soča catchment

Introduction

The Idrija mine, second largest mercury mine in the world was in exploitation for about 500 years. According to official data, about 107,000 tons of mercury was produced until 1988, when production was reduced to a few hundred kilograms per year. Production stopped in 1995. It has been estimated that more than 34 % of mercury, approximately 37,000 tons has been dissipated into environment (Dizdarević et. Al., 2002; Gosar, 1997). During smelting high concentrations of mercury in the air were measured, locally

reaching even 4000 ng/m3, and the total evasion to atmosphere exceeded 20 kg/day of mercury. Significant quantity of mercury, bound to smelting remains, which were deposited along the banks of the Idrijca River, has been washed away and, mostly in its particulate form, transported downwards the Idrijca / Soča River system. Almost 10 years after closure of mine, the amount of mercury transported to the Gulf of Trieste (about 1500 kg/year) is not decreasing, as significant quantities are still deposited in flood plain areas (Horvat et al., 1999; Rajar et al., 1999; Rajar et al., 1999; Rajar et al., 2002).

The Idrijca / Soča catchment has an area of about 3300 km². In the upper (Slovenian) part both rivers mostly flow through narrow valley with some floodplains. Near the town of Idrija mercury contents in riverbed and overbank sediment reach from 100 to 1000 mg/kg. Downstream concentrations are lower, 5 to 680 mg/kg (Gosar, 1997).

Annually averaged discharge of the River Soča at its mouth is about 160 m³/s, during autumn flood-wave discharge reaches up to 2000 m³/s. Concentrations of suspended sediment in flood-wave reach up to 500 g/m³ with Hg concentrations up to 50 mg/kg (RAJAR ET AL., 2001).

One-dimensional model MeRiMod (CARROLL ET AL., 2000; CARROL & WARWICK, 2001), a combination of modified US-EPA models RIVMOD, WASP5 and MERC4 was further used to simulate river-bank erosion and transport of mercury. River topography without present-time dams was used, together with official data about concentrations of mercury in smelting remains.

RESULTS AND DISCUSSION

Atmosphere. The data (DIZDAREVIĆ ET AL., 2002) for the last period of smelting (recovery rate between 85 and 92 %) estimate more than 20 kg/day of mercury emissions to the air. It can be assumed that in the past, with lower recovery rate (65 to 75 %), but also lower production, mercury emissions were somewhat higher. It was estimated, that about 3000 tons of Hg was lost in the atmosphere. It is not known how much of this mercury has been transported out of Idrija region, as

the valley is narrow and closed by steep hills and mountains. Considering long-distance air transport of about 50 %, 1500 tons of mercury has left the catchment.

Soil, riverbed and overbank sediment: The remaining part of air-transported mercury has settled to nearby area, polluting soil. Also, smelting remains were deposited along the Idrijca River, washed away by flood-waves. Measured concentrations in riverbed and overbank sediment reach up to 1000 mg/kg near the mining area and decreases downstream to about 50 mg/kg at the Soča River mouth. Taking into account the area of both riverbeds and flood-plains, and the average concentration of 100 mg/kg the amount of mercury deposited in the area is about 10,000 tons.

Water and suspended sediment transport:

It was found that in about 1500 kg Hg/year that reach the Gulf of Trieste, only about 10 kg/year are in dissolved form (ŽAGAR & ŠIRCA, 2001). High water events participate more than 80 % of sediment and mercury transport; therefore we were mainly focused on discharges with higher recurrence. A scenario of such events for 500 years was made and model simulations were performed. It was determined that about 2500 tons of mercury has entered the Gulf of Trieste during the last 500 years. This result is also confirmed by sediment corer data from the Gulf, where the estimated quantity of mercury is about 2000 tons. Considering outflow from the Gulf of about 500 kg/year (RAJAR ET AL., 2004) and taking into account expected exchange with the atmosphere of the same order of magnitude, we can get approximately the same number.

Summing all calculated and estimated values, we get an amount of about 15,000 tons. All estimated and simulated results are, by our opinion, rather overestimated and the discrepancy between mercury lost from the excavating and smelting process and mercury that has entered air, soil and water was still found to be over 60 %, which leads to conclusion that either not all transport processes were taken into account correctly or the data about losses during exploitation of the Idrija mercury mine are also overestimated. Additional measurements of mercury concentrations in different compartments and further improvement of the model are necessary to determine the exact reason of discrepancy.

Conclusions

A historical mass balance for the Idrijca / Soča Rivers catchment has been established. High discrepancy of about 60 % between the quantity of mercury lost from the Idrija mercury

mine and calculated and simulated results has been found. Additional measurements, as well as further improvement of mathematical models used is necessary to determine the exact reason of discrepancy. Although the agreement of results is not very good, it can be seen that the quantity of mercury in the soil, riverbed and overbank sediment significantly exceeds the quantity of mercury that has already left the catchment. Therefore, we cannot expect significant decrease of mercury transport along the river system to the Gulf of Trieste in the near future.

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