

## Hg distribution in Soča River catchment area

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**Abstract:** Hg values in sediments and soils of Idrija river and Idrija mercury mine influence area have been monitored since 1970. Second source of mercury in Soca River are the remains from I. World War, where mercury was used as mercury fulminate as detonator. Concentration of Hg in sediments of Idrija and lower Soca rivers remains high. Erosion of contaminated river sediments and riverbanks is the main source of Hg in rivers and in the Gulf of Trieste.

**Key words:** Soča catchment, soil, water, mercury

### INTRODUCTION

In the upper part of the Soča river catchment area intensive military operations were performed during I. World War. The result of these operations are elevated Hg levels in whole front line (PIRC, 1996; PIRC ET AL., 1995, 1996), which extended from Gulf of Trieste, Monfalcone, Gorica, Kobarid, Bovec to the current Italian border. Average Hg concentration in top soil was 160 µg/kg, reaching up to 8500 µg/kg in some areas. Southern part of catchment area is heavily polluted by Hg due to 500 years of mining history in Idrija. In the last few years intensive research on Hg in Soca River system



**Figure 1.** Sampling locations.

are on going (RAJAR ET AL., 1997; ŠIRCA, 2000; HORVAT ET AL., 2002; GOSAR ET AL., 1996; HINES ET AL., 2000). Mass balance calculations showed that Soča River is the main source of Hg into the Gulf of Trieste. It yearly contributes about 1780 kg Hg, mainly in particulate form (RAJAR ET AL., 1997; ŠIRCA IN RAJAR, 1997). Hg levels are elevated in both, water and sediments of the lower part of the Soča River. Increased contents of Hg in over bank sediments are probably due to greater wash off and erosion of polluted areas at increased water levels.

## EXPERIMENTAL

Soil samples were collected at 21 locations in the upper part of the Soča catchment area as it is shown on Figure 1 mostly on areas with strong erosion. Only topsoil samples were taken with the exception of the flood plain at the confluence of the rivers Idrijca and Bača where a 1-m-deep profile was also sampled at depths of 50 and 100 cm.

Total Hg concentrations in samples were determined by cold vapour atomic absorption spectrometry according to the procedure described by HORVAT AND LUPŠINA (1991) and HORVAT (1996). Hg in soil was determined

after liophylisation, acid digestion,  $\text{SnCl}_2$  reduction followed by gold amalgamation and detection on an LCD Milton Roy mercury detector. Quality control included reagent blanks to assess contamination, triplicate samples to check precision and certified reference material samples (CRM 320, BCR 580, IAEA 405) to assess accuracy.

## RESULTS AND DISCUSSION

Hg in soils of Soča catchment is shown on Figure 2. Concentrations ranged between 88 and 175 000 ng/g. In upper Soča Valley concentrations were relatively low. Higher Hg levels were found in Cerknica Valley and in Idrijca Valley. The highest Hg concentrations in soil were found in soil of Idrijca River bank near Bača pri Modreju. Hg concentrations increase with depth. This indicates heavier contamination by Hg in the past. Contamination by Hg is consequence of regular flooding of Idrijca River and deposition of contaminated suspended matter during floods. GOSAR ET AL. (1997) reporting extremely high values of Hg in Idrijca River banks which can reach 1000 mg/kg. Erosion of contaminated riverbanks along Idrijca River is the main source of Hg in Idrijca River.

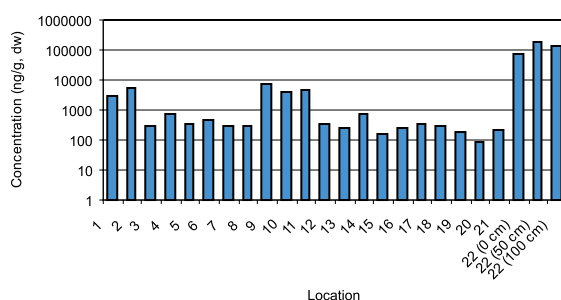


Figure 2. Hg concentration in soils (in ng/g, dry weight).

Many authors (GNAMUŠ ET AL., 2000; ČAR, 1996; BIESTER ET AL., 1999) reported very high concentrations in soils at several areas around Idrija. Recently Hg concentrations have been measured at three locations in Idrija area, at most polluted places (Pront, former smelting plant). Slovenian legislation defines the critical value for total mercury concentrations in soil at 10 mg Hg/kg. Hg concentrations ranged between 47 and 369 mg/kg, which express that Hg is still a problem at certain areas in Idrija as all the samples investigated exceeded the limit value for the total concentrations of Hg in soil. The highest Hg values were measured in the immediate vicinity of the former mine-smelter complex and beneath the mine-smelter on the flood plain of the river Idrija. The origins of mercury at these two locations differ. Mercury in the forest soil close to the smelting house mainly originates from atmospheric deposition of Hg, while in the alluvial ground Hg originates from deposition of particles, in which Hg is present as Hg sulphide. Although the meadow in Idrija at the Pront hill was never under the direct influence of the mine or the smelter, total Hg concentrations at this site are rather high due to native mercury-bearing carboniferous clastic rocks.

Downstream, where the river Idrija merges with the Bača, Hg concentrations are about 3-fold lower than in the town of Idrija but still very high. These very high Hg concentrations reflect active Hg transport from mining sites and recent and past depositions of Hg enriched particles close to the turbulent water flow. The soil depth profile at this location showed an increase of Hg from about 76 mg/kg at the surface to about 175 mg/kg at 50 cm. Farther down at 100 cm depth, the concentrations decreased to around 144 mg/kg. This profile was not deep enough to reach sediments deposited before the beginning of mining operations, hence mercury content was high throughout the profile. It is questionable if this sequence shows sedimentation in chronological order due to erosion and redeposition of sediments typical of fluvial flood plains. However, other cores taken from the same site show a similar course of Hg enrichment.

Hg in water of Soča River is relatively low in its upper flow (0.3 – 4.6 ng/l). More than 50 % of Hg is bounded to particulate matter. Immediately after Idrija River inflow Hg concentration in water increase rapidly and reaches over 10 ng/l. Rapid increase of all Hg species especially DGM can be observed.

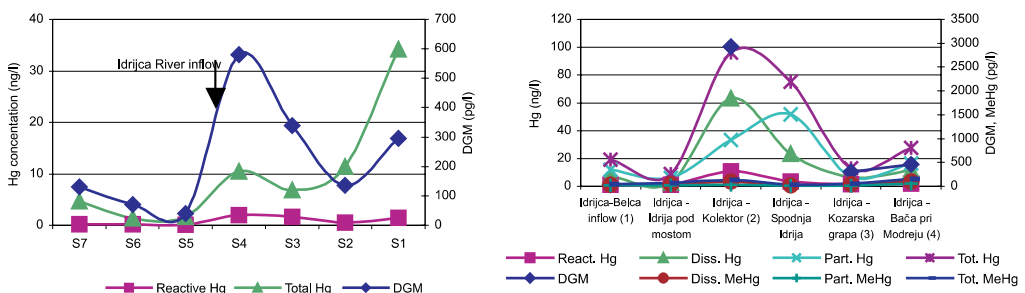


Figure 3. Different Hg species in water of Soca River and Idrija River (ng/l).

Hg also increases in Soča River estuary just before its outflow into Gulf of Trieste. Soča River estuary was more detailed investigated in 2002 and is described elsewhere (COVELLI ET AL., this issue). Similar distribution was observed by other authors (HINES ET AL., 2000; HORVAT ET AL., 1999; HORVAT ET AL., 2002). Hg concentrations in water measured in 2003 are shown on Figure 2.

In Idrija river water concentrations increase immediately after its reach contaminated area (Figure 3). Highest values were observed near Kolektor, near tailings landfill. Downflow to Soča River Hg in water constantly decrease.

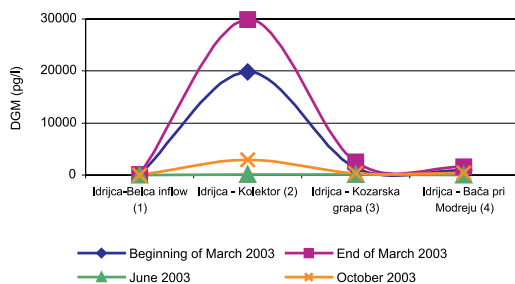


Figure 4. DGM in water of Idrija River.

DGM distribution in Idrija River during different seasons is shown on Figure 4. In spring DGM reaches extremely high values (2933 pg/l) at sampling location near Kolektor (Location 2). High spring concentrations of DGM are consequence of higher biotic activity in river water and lower evaporation to atmosphere due to low water and air temperatures.

## CONCLUSIONS

Water and stream sediments of the Soča River catchment area contain very high concentrations of mercury. In the upper part of the Soča Valley high concentrations are the reflection of the natural background and especially of intensive military operations performed during I. World War. In the lower part of the valley heavily contaminated Idrija region continues to supply Hg in Idrija river system. Hg carried downstream is available for transformation in both the Soča river system and in the marine environment of the Gulf of Trieste. The concentration of mercury in the river sediments and overbank soils varies greatly and does not depend only on the distance from the pollution source but also on hydrological conditions.

Considering the very high Hg concentrations in the Soča river catchment area, the fact that only a part of all available Hg in this area was removed due to erosion and flooding and that natural mercury sources are long lived, it is likely that Soča river catchment area will remain polluted with mercury for quite some time.

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