

## Bioaccumulation of mercury in benthic communities of a river ecosystem, affected by mercury mining

SUZANA ŽIŽEK<sup>1</sup>, MILENA HORVAT<sup>1</sup>, MIHAEL JOŽEF TOMAN<sup>2</sup>

<sup>1</sup> Department of environmental sciences, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

<sup>2</sup> University of Ljubljana, Biotechnical faculty, Department of Biology, Večna pot 111, SI-1000 Ljubljana, Slovenia

### INTRODUCTION

Idrijca river is situated in the western part of Slovenia. This is a region between the Alps, Karst and the Adriatic sea. The climate is predominately temperate with slight submediterranean and alpine influences. The annual precipitation is very high. Due to very steep mountain slopes, there is also strong erosion, causing important sediment transport (RAJAR, 2001). In the town of Idrija a mercury mine was operating for 500 years. The outflow from the mine was polluting the Idrijca river. Mining activities ceased in 1994, but the levels of mercury are still elevated in Idrijca river (HINES ET AL., 2000; HORVAT ET AL., 2002), as well as in the gulf of Trieste (HORVAT ET AL., 1999). This study was interested in how total mercury (Hg-T) and methyl mercury (MeHg) build up in benthic communities (periphyton and macroinvertebrates).

The primary producers in river ecosystems are unicellular and filamentous algae and blue-green bacteria in the periphyton layer. They represent food for grazing macroinvertebrates (snails, mayflies, some caddis flies etc.), which in turn are food to predatory macroinvertebrates (stoneflies, damself-

lies, leaches etc.). LAWRENCE and MASON (2001) discovered that the intake of mercury in benthic invertebrates is affected by mercury concentrations in the sediments, the physical and chemical properties of the sediments and on the concentrations of mercury in organisms of lower levels in the food chain.

### METHODS

Four sampling sites were chosen on the Idrijca river, so that the first one was before the Idrija mine, near the inflow of Belca river. The second site was in the town of Idrija, where the effluents from the mercury mine flow into Idrijca., two more sites were chosen downstream from Idrija.

Samples were collected during spring, summer and autumn 2003. Of the primary producers, filamentous green algae were sampled in spring and periphyton s.str. in summer and autumn. Macroinvertebrates were sampled at random, those that could be found during the sampling. They were mostly caddis flies (*Trichoptera*) and mayflies (*Ephemeroptera*). Samples of water were also collected.

All the samples were freeze-dried. Total mercury concentrations were determined using the cold vapour atomic absorption (CV AAS) after acid digestion (HORVAT ET AL., 1991). MeHg concentrations were measured using two different methods, depending on the nature of the sample. In plant samples and all the samples from the first sampling site, MeHg was determined using solvent extraction, aqueous-phase ethylation, gas chromatographic separation, pyrolysis and CV AFS detection (LIANG ET AL., 1994). For the rest of the samples, MeHg was measured using solvent extraction, gas chromatographic separation and the electron capture detection (GC ECD) (HORVAT & BYRNE, 1990).

## RESULTS AND DISCUSSION

Figure 1 shows mercury concentrations in periphyton. The only organisms that were sampled on all occasions were caddis flies. Their Hg-T and MeHg concentrations are shown in Figure 2.

This investigation has shown that the concentrations of mercury in benthic organisms of the Idrija river downstream from the mine are elevated compared to their environment. The Hg-T concentrations in sediments are comparable to those in the organisms, whereas MeHg concentrations are much higher in the biota. The highest concentra-

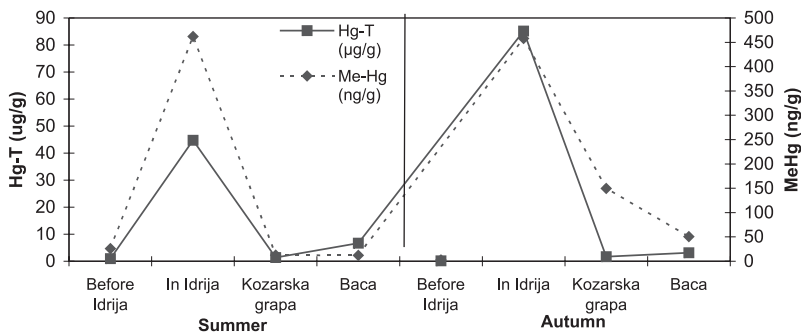


Figure 1. Hg-T and MeHg concentrations in periphyton of the Idrija river

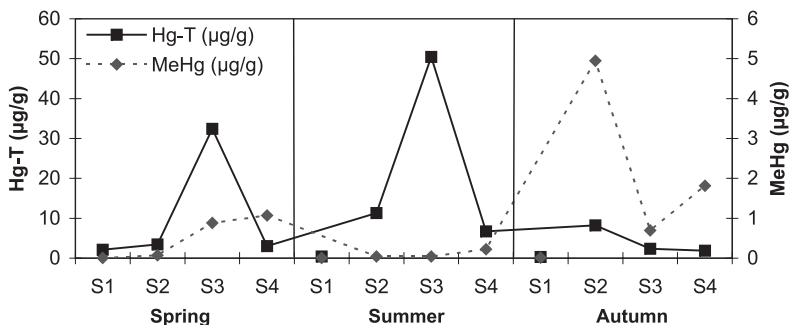


Figure 2. Hg-T and MeHg concentrations in caddis flies (Trichoptera) of the Idrija river. S1=before Idrija, S2=in Idrija, S3=Kozarska Grapa, S4=Baca

tions were measured in the town of Idrija. The mercury concentrations in benthic organisms thus reflect to some extent the concentrations in water and sediments. However, more should be known about the ecology, physiology and metabolism of these organisms to be able to interpret the measured concentrations. In order to do that, sampling of macroinvertebrates should not be random, but performed in such a way that the position of the organism in the river food web would be known.

In the case of caddis flies, some seasonal differences were observed (Figure 3). The most important difference between the autumn sample and the prior two samplings was in the organisms obtained. In the spring and summer samplings, the collected organisms were case-dwelling, whereas in autumn the samples were made of members of the Hydropsychidae family, which do not make a case and are filter feeders. It seems that this difference in ecology could account for the differences in caddis flies mercury concentrations on different sites.

The percent of MeHg is lower in primary producers (algae and periphyton s.str.) than in animals. It may have happened that during periphyton collection, some inorganic particles adhered to the organisms were also present in the samples. That would explain some high results obtained for periphyton and algae. The organic content of this kind of samples is known to be very low and it should be measured in the future.

## CONCLUSIONS

This study is a preliminary investigation of mercury in benthic communities of river Idrija and will hopefully be a contribution to our knowledge of mercury cycling in the biota of mercury-contaminated rivers. It has shown that the effects of mercury reach into every compartment of the river ecosystem.

## REFERENCES

- CLECKNER, L.B., GARRISON, P.J., HURLEY, J.P., OLSON, M.L., KRABENHOFT D.P. (1998): Trophic transfer of methyl mercury in the northern Florida Everglades. *Biogeochemistry*, 40, 347-361.
- HINES, M.E., HORVAT, M., FAGANELI, J., BONZONGO, J.-C., BARKAY, T., MAJOR, E.B., SCOTT, K.J., BAILEY, E.A., WARWICK, J.J., LYONS, W.B. (2000): Mercury Biogeochemistry in the Idrija River, Slovenia, from above the Mine into the Gulf of Trieste. *Environmental Research Section A*, 83, 129-139.
- HORVAT, M., BYRNE, A.R. (1990): A modified method for the determination of methylmercury by gas chromatography. *Talanta*, 37, 207-212.
- HORVAT, M., COVELLI, S., FAGANELI, J., LOGAR, M., MANDIČ, V., RAJAR, R., ŠIRCA, A., ŽAGAR, D. (1999): Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *The Science of the Total Environment*, 237/238, 43-56.
- HORVAT, M., JEREB, V., FAJON, V., LOGAR, M., KOTNIK, J., FAGANELI, J., HINES, M.E., BONZONGO, J.-C. (2002): Mercury distribution in water, sediment and soil in the Idrija and Soča river systems. *Geochemistry: Exploration, Environment, Analysis*, 2, 287-296.

- HORVAT, M., LUPŠINA, V., PIHLAR, B. (1991): Determination of total mercury in coal fly ash by gold amalgamation cold vapour atomic absorption spectrometry. *Analytica Chimica Acta*, 243, 71-79.
- LIANG, L., HORVAT, M., BLOOM, N.S. (1994): An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. *Talanta*, 41, 371-379.
- LAWRENCE, A.L., MASON, R.P. (2001). Factors controlling the bioaccumulation of mercury and methylmercury by the estuarine amphipod *Leptocheirus plumosus*. *Environmental Pollution*, 111, 217-231.
- RAJAR, R. (2001): Hydrology of the Idrijca and Soča Rivers and the Gulf of Trieste. *RMZ – Materials and Geoenvironment*, 48, 49-55.
- ULLRICH, S.M., TANTON, T.W., ABRASHITOVA, S.A. (2001): Mercury in the Aquatic Environment: a Review of Factors Affecting Methylation. *Critical Reviews in Environmental Science and Technology*, 31(3), 241-293.