Mercury and selenium in fish species in the Idrijca river polluted due to past mercury mining

MILENA HORVAT[1], MIHAEL TOMAN[2], JOŠT STERGARŠEK[2], JOŽE KOTNIK[1], VESNA FAJON[1], DARIJA GIBIČAR[1]

[1]Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia;
E-mail: milena.horvat@ijs.si
[2] Univesity of Ljubljana, Biotechnical Faculty, Slovenia

Abstract: Various fish species were sampled in summer 2003 in the Idrijca river polluted by past mercury mining activity in Idrija, Slovenia. The results obtained showed much lower results as compared to those measured during active mercury mining, however, the concentrations of mercury in fish muscle and liver are still high downstream of the former mercury mine and do not show expected decrease after more than 10 years of the complete of mercury mining.

Keywords: mercury mining, river, fish, total mercury, selenium, muscle, liver

INTRODUCTION

The Idrija mercury mine is situated 50 km west of Ljubljana, Slovenia, 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. The Idrija mine has severely enhanced the mobilization of Hg by mining activities, and Hg-laden material remains in the region. Mercury and methylmercury were measured in various environmental compartments during the period 1995-2004. Some recent measurements of mercury in water, sediments and soil are shown to be very high. Total Hg in the Idrijca river water increased downstream of the mine (from a few ng/L to up to 500 ng/l), with methyl Hg (MeHg) accounting for 1.5 % above the town of Idrija, 0.2 to 0.7 % after Idrija, 2-3 % in river reservoirs and only about 0.2 % in marine waters. 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 (HORVAT ET AL., 2002).

Due to chemical transformation (reduction, methylation, oxidation, demethylation) and 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, in particular fish, produced in contaminated area (HORVAT ET AL., 2004).

EXPERIMENTAL

In this work we collected river fish species at four different locations (Figure 1). The first was above the city of Idrija (reference point), second in the town if Idrija and the third and the fourth location were about 20 and 40 km downstream, respectively. Fish were caught in summer of 2003. At each location several fish of the same species were collected. The following fish species were sampled: marble trout (*Salmo marmoratus*), brown trout (*Salmo trutta*), rainbow trout (*Salmo gairdneri*/*Oncorhynchus mykiss*), European graying (*Thymallus thymallus*), Italian barbell (*Barbus plebejus*), mrenic (*Barbus meridionalis canimus*) and hybrid/crossbreed between marble and rainbow trout (S*almo sp.*). Feeding habits of Italian barbell and mrenic are similar. They feed on insect larvae, crabs, and other insects in water. They are mainly bottom feeders. European graying rainbow and brown trout feed mainly on invertebrates, and insects flying above the water as well as on smaller fish.

Figure 1. Fish sample were taken at location 1 to 4.

Samples of muscle, skin, brain, liver, kidney, gills were collected from fresh fish and stored in deep freezer until further processing. Total mercury and selenium were determined by radiochemical neutron activation analysis (KOSTA AND BYRNE, 1973). Only fish muscle and liver samples has so far been analysed for total Hg and Se, while MeHg has not been analysed as yet.

RESULTS

The results have shown that highest concentrations of mercury in fish muscle and liver are strongly affected by the location and the fish species. As expected, lowest concentrations were found at location 1, upstream the mercury mine. Concentrations of total Hg in fish muscle increased significantly in Idrija, followed by a step decrease at the second station, about 15 km downstream. An increase was observed at the station number 4, close to the inflow of the Idrijca river into the reservoir. Similar trend was also observed for mercury levels in liver, but with much higher concentrations, mainly due to accumulation and retention of inorganic mercury in the fish.

Results are expressed as a mean ±standard deviation based on fresh weight basis. FW.. fresh weight; n.a. not analyzed as yet.Hg in fish muscle.

Table 1. Concentrations of total mercury and selenium in fish muscle and liver samples.

Location	Fish species	Weight (g)	number of fish species	Muscle Hg (mg/kg)	Muscle Se (mg/kg)	Liver Hg (mg/kg)	Liver Se (mg/kg)
1	*Barbus meridionalis caninus*	53 ± 26	5	0.090±0.020	0.48±0.07	0.04±0.01	1.80±0.18
Above	*Salmo gairdneri*	149±125	3	0.15±0.01	0.60±0.06	0.17±0.19	6.66±1.50
Idrija	*Salmo marmoratus*		1	0.10	0.59	0.36	3.35
	Salmo sp.	123±90	5	0.10±0.08	0.59±0.12	0.28±0.19	4.52±0.74
	Salmo trutta fario	80±48	6	0.10±0.07	0.50±0.10	0.20±0.10	4.71±1.09
2	*Salmo gairdneri*	201±64	3	0.29±0.49	0.47±0.1	2.97±0.26	5.29±1.35
In Idrija	*Salmo marmoratus*	999; 80	2	0.56	0.45	3.96; 5.84	2.96; 5.00
	Salmo sp.	206±152	10	0.61±0.87	0.60±0.10	4. 14±7.75	4.74±0.99
	Salmo trutta fario	271±190	4	1.65±2.05	0.95±0.40	4.96±2.83	4.45±3.35
	Thymallus thymallu s	220±208	5	0.50±0.41	1.29±0.39	3.80±1.63	5.06±2.58
	Barbus meridionalis caninus	103±66	6	0.49±0.18	0.428±0.06	0.64±0.59	1.65±0.70
3	*Salmo gairdneri*	332±192	6	0.13±0.040	0.39±0.10	0.22±0.17	3.09±1.15
Kozarska	*Salmo marmoratus*	395±322	3	0.23±0.16	0.50±0.04	0.49±0.17	5.21±1.28
grapa	*Salmo sp.*	531±446	5	0.41±0.43	0.48±0.09	0.45±0.46	9.34±5.80
	Salmo trutta fario	131±24	2	0.26; 0.11	0.91, 0.49	0.32; 0.40	4.34; 4.91
	Thymallus thymallus	305±150	3	0.12±0.03	1.37±0.30	0.37±0.075	5.30±1.25
4	*Barbus meridiona lis caninus*	82±68	5	0.67±0.30	0.42±0.03	0.42±0.19	n.a.
Bača	*Barbus plebejus*	685±204	2	0.54; 0.083	0.34; 0.77	0.30; 4.96	2.63
	Salmo sp.	339±213	7	0.35±0.36	0.60±0.23	0.52±0.64	n.a.
	Thymallus thymallus	547±502	3	1.77±0.48	0.76±0.01	5.59±7.45	n.a.

A positive correlation between total Hg in fish muscle and liver (r^2=0.60) was found. A positive correlation between the size and mercury concentrations in muscle was found only for marble trout (r^2= 0.7614) and European graying (r^2= 0.7206). These two species were caught at a number and size to allow statistical evaluation. Other fish species were of relatively small sizes (young species) and the evaluation of the size vs. Hg concentrations was not meaningful. No correlation between mercury concentration in fish liver vs. size was found. In general, mercury levels in fish liver was higher than in fish muscle, in particular in fish caught in Idrija and downstream from the mercury mine. Further interpretation of the data will be possible when data on Hg speciation is available.

Unfortunately, a very few measurements of mercury in fish was done in the past. A short review of the values reported for the period between 1973 to 1991 are given in Table 2. The highest concentrations of total mercury were reported in fish from Idrija in 1971, which is due to active mercury mining and large inputs of mercury into the river water. In 1980 and 1991 very limited data is available, and it is in the same order of magnitude as in 2003. This means that in recent years, after more than 10 years of closure of mercury mine, Hg concentrations in fish has not decreased as expected, while Hg in sediments and air decreased significantly (HORVAT ET AL., 2002; KOTNIK ET AL., this issue). Comparison with Hg concentrations in other temperate rivers is difficult, as the fish species, size and location might influence Hg levels significantly (BURGER ET AL., 2001). It is interesting to note that the concentrations of mercury in fish muscle in areas after mercury mine are similar to those reported in the Gulf of Trieste (HORVAT ET AL., 1999) and middle Adriatic (HORVAT ET AL., 1987).

Concentrations of Selenium in fish muscle is similar in all fish species, except Europen graying with highest concentrations at all stations. Selenium in liver is significantly higher than in muscle, with higher variations among fish species. There is no correlation between Se and Hg in muscle and liver. Selenium was also analysed in 1980 and the results are comparable with those reported in this study. Selenium concentrations are also similar to those found in marine fish of the Adriatic sea (HORVAT ET AL., 1987).

Table 2. Concentrations of mercury and selenium in Idrijca river over time, expressed on a wet weight basis

Time	Location	Weight (g)	number of fish	Muscle Hg (mg/kg)	Muscle Se (mg/kg)	Liver Hg (mg/kg)	Liver Se (mg/kg)
1971 (Kosta et al., 1974)	Idrija town	Not reported	5	2.6 – 6.6 MeHg 0.16-0.73		29 – 119 MeHg 0.6 – 1.9	
	Kozarska grapa	120-270	5	0.59-1.24 MeHg 0.43-1.08		10-31 MeHg 0.93-2.35	
	Bača	95-520	7	0.30-0.87 MeHg 0.26-0.76		2.73-19.2 MeHg 0.28-1.91	
1980 (Archives, IJS, non-published data)	*Upstream Idrija*	Not reported		0.22	0.47	0.56	3.04
	Idrija town			1.11	0.39	4.72	2.87
	Downstream Idrija, 5 km			0.31	0.43	1.04	2.42
	Idrijca, Stopnik			0.66	0.53	3.77	6.42
	Bača			0.07 0.32	0.43 0.63	0.11 0.90	1.02 3.13
1991 (Stegnar, 1991)	*Lower idrija*	Not reported		1.07-1.82 MeHg 0.61-1.22			

CONCLUSIONS

Mercury concentrations in fish of the Idrijca river is significantly increased after the former mercury mining sites. When the analysis of MeHg in fish muscle are available it will be possible to consider potential concern for those frequently consuming fish from contaminated sites. It is also important to note that Hg in fish may also be of concern for wild life as well as for birds feeding on fish from the river. It will also be of importance to investigate mercury uptake in fish from reservoirs on Soča river and further downstream.

Acknowledgements

This work was supported by the Ministry of Education, Science and Sport of the R Slovenia through a programme P532 and the project Z2-3502. The financial support of the Phare project SLO108.02.0012 is also acknowledged. The technical assistance of Ms. A. Prosenc and the help of fishing associations of Idrija and Tolmin are also acknowledged.

REFERENCES

HORVAT, M., JEREB, V., FAJON, V., LOGAR, M., KOTNIK, J., FAGANELI, J., HINES, M. E., BONZONGO, J.-C. (2002): Mercury distribution in water, sediments and soil in the Idrijca and Soča river systems; *Geochem. Explor. Environ. Anal*. Vol. 2, pp. 287-296.

KOSTA, L., BYRNE, ANTHONY A. R., ZELENKO, V., STEGNAR, P., DERMELJ, M., RAVNIK, V. (1974): Studies on the uptake, distribution and transformation of mercury in living organisms in the Idrija region and comparative areas; *Vestn. Slov. Kem.Druš.*, Vol. 21, pp. 49-76.

HORVAT, M. COVELLI, S., FAGANELI, J., LOGAR, M., MANDIĆ, V., RAJAR, R., ŠIRCA, A., ŽAGAR, D. (1999): Mercury in contaminated coastal environments; a case study: the Gulf of Trieste; *Sci. Tot. Environ.*, Vol. 237/238, pp. 43-56.

PLANINC, R., BAJT, O., HORVAT, M., FAGANELI, J., GORENC, B. (1993): An outline of chemical pollution of the coastal waters of the southeastern (Slovenian) part of the Gulf of Trieste; *Acta Chim. Slov.*, Vol. 40/4, pp. 349-368.

HORVAT, M., ZVONARIĆ, T., STEGNAR, P., PROSENC, A., KONDA, D., SABADIN, A. (1989): Realtionship between total mercury, methylmercury and selenium in fish muscle from the Adriatic Sea; (Ed., J.-P. VERNET) *Heavy metals in the Environment*, Vol. 1, pp. 36-40, Geneva 1989.

BURGER, J. GAINES, K. F., BORING, C. S., STEPHENS, JR. W. L., SNODGRASS, J., GOCHFELD, M. (2001): mercury and selenium in fish from the Savannah River: Species, Trophic Level, and Location Differences; *Environ. Res. Sec. A,* Vol. 87, pp. 108-118.

HORVAT, M., KONTIĆ, B., KOTNIK, J., OGRINC, N., JEREB, V., FAJON, V., LOGAR, M., FAGANELI, J., HINES, M., RAJAR, R., ŠIRCA, A., ŽAGAR, D., PETKOVŠEK, G. AND DIZDAREVIĆ, T. (2004): Remediation of mercury pollution sites, due to mining acrivities; *Crit. Rev. Anal. Chem*., Vol. 33(4), pp. 1-6.

BYRNE, A. R. AND KOSTA, L. (1974): Simultaneous determination of mercury and seleniuem by radiochemical neutron activation analysis; *Talanta*, Vol. 21, pp.1083-1090.

KOTNIK, J., KOCMAN, D., HORVAT, M., LOGAR, M., GIBIČAR, D., FAJON, V. (2004): Distribution in Soča river catchment area; *RMZ*, this issue.

KOTNIK, J., DIZDAREVIČ, T., HORVAT, M. (2004): Current and past mercury distribution in air over Idrija region; *RMZ*, this issue.