Indicators of Mercury Reactivity and Bioavailability in the Environment; a Search for Cost-effective Monitoring Strategies

M. Horvat

Department of Environmental Sciences, "Jožef Stefan" Institute, Jamova 39, 1000 Ljubljana, SLOVENIA, milena.horvat@ijs.si

Abstract
To understand and monitor the ecosystem responses to various contaminant loadings related to anthropogenic activities and/or climate change requires an integrated approach employing a network of indicators. In order to demonstrate the complexity of the issue a case study presented in this work is related to mercury loading in an area impacted by the past mercury mining activity in Slovenia. Numerous studies have been implemented in the area to search for the best indicators of changes in mercury loading in air, the catchment and coastal waters, and the terrestrial environment. One of the important conclusions of these studies is that environmental biomonitoring, including human biomonitoring, offers a convenient and cost-effective way to assess spatial and temporal trends of mercury pollution and represents a good measure of mercury reactivity and availability in the environment. It can also be used as early warning systems for humans and other organisms in this ecosystem. Therefore, further efforts should be spent on standardization of the methodologies so that biomonitoring can widely be applied and the international comparability of data secured.

Key words: mercury analysis and speciation, indicators, biomonitoring

Introduction
Mercury and its compounds are highly toxic, persistent and bio-accumulative and therefore it is of special concern for wild life and humans. It is therefore important to design an observation system that provides relevant and trustworthy information on the state of the environment in an integrated network of indicators as presented in Figure 1.

**Figure 1.** Integrated network of indicators for mercury loading (adopted from Harris et al., 2007).
It has to be mentioned that the presence of mercury in environmental compartments does not necessarily mean that it can readily enter biological systems. Chemically and biologically mediated transformation processes transform mercury into bioavailable forms. The most important process is the formation of monomethylmercury (MeHg) which can easily enter biological systems, where it is biocumulated and bioaccumulated. Therefore to follow the formation and fate of MeHg represents the main quality objective in mercury pollution studies. Early warning systems, including specific indicator organisms have been extensively studied in different environmental compartments [Harris et al., 2007].

Biomonitoring refers to the use of a biological entity as a detector and its response as a measure to determine environmental conditions. It represents the best approach to assess exposure and potential effects and is an indispensible part of risk analysis, particularly when enlarged to biomonitoring of effects and susceptibility. It has been widely accepted in large scale biomonitoring programmes in Europe to assess spatial and temporal trends of exposure to chemicals [PHIME-www.phime.org, ESBIO and COPHES - www.eu-humanbiomonitoring.org, ICP Vegetation, http://icpvegetation.ceh.ac.uk/].

Case Study
In order to demonstrate the usefulness of biomonitoring, a case study of the former mercury mine, Idrija, Slovenia will be used in this presentation. A number of environmental aspects have been studied in the area, including the main transport, fate and mass balance of mercury in the catchment [Horvat et al., 2002, Hines et al., 2000, 2006, Kocman, et al. 2006, 2010, Kotnik et al. 2005, Kocman, 2009]. Modelling tools were developed and validated in support of proper planning for remediation [Kocman, 2008, Žagar et al., 2006]. Environmental monitoring has been implemented for a number of years [Horvat et al. 2002], including measurements in air [Kotnik et al., 2005; Grönlund et al., 2005], soil [Kocman et al., 2004, 2010] and in the river Idrija and Soča/Isonzo [Hines et al., 2000, 2006; Horvat et al., 2002; Kocman et al., 2004, 2010; Žižek et al., 2007], and the Gulf of Trieste [Horvat et al., 1999, Lipej]. Mercury enters the river in inorganic form and then undergoes various chemical and biological transformation processes, such as oxidation, reduction, methylation, demethylation, adsorption and desorption [Hines et al., 2006]. A few of the studies have also addressed the bioavailability of mercury and the transfer of mercury and its compounds into biological organisms and the man. Some of the results are presented below.

Air
Mercury concentrations can be accurately measured by sensitive and automated instrumentation. [Grönlund et al. 2005, Kotnik et al., 2005], which provide good quality data with high time resolution. Mercury in contaminated sites is variable and depends on the wind direction, temperature, moisture and of course the vicinity of major mercury sources. Although these methods are characterized by high accuracy and time resolution, such measurements are relatively expensive due to regular maintenance and power demands.

Alternatively, a methodology employing epiphytic lichens and/or mosses has shown to be very suitable to assess mercury levels in air over longer periods of time [Horvat et al., 2000, Jeran et al. 2002]. The use of lichens in biomonitoring have proven to be suitable to assess spatial and temporal trends of mercury concentrations in air. As evident from Figure 2, average mercury concentrations in air and mean values in lichens are in excellent correlation.

Aquatic Environment
Mercury accumulation and speciation in the river food chain included filamentous algae, periphyton, macroinvertebrates and fish. The results have shown that highest total Hg concentrations in biota correlate well with total Hg levels in sediments and water [Žižek et al., 2007]. The level of MeHg is spatially and seasonally variable, showing higher values at the most contaminated sites during the summer and autumn periods. The percentage of Hg as MeHg increases with the trophic level from water (0.1-0.8%), algae (0.5-1.3%), periphyton (1.6-8.8%) to macroinvertebrates (0.1-100%) and fish (40-100%) which indicates active transformation, accumulation and magnification of mercury in the benthic organism of this heavily contaminated torrential river.

Fish seem to be among the most suitable bioindicator organisms in the river ecosystem [Horvat et al., 2004, Munthe et al., 2007], as they represent the top of the aquatic food chain.
Fish eating cormorants are at the top of the food chain could also be useful, but no studies have been performed so far. There is an additional added value of using fish for potential human exposure assessment [Scheuhammer et al., 2007].

A number of biomonitoring studies have also been performed in the coastal environment and have been included in compliance monitoring implemented by coastal sites [Lipej et al. 2010]. For the purpose of this paper the usefulness of mussels (M. Galloprovincialis) in active and passive biomonitoring may be particularly emphasized [Kljakovič et al., 2006]. These approaches have been developed to the standardization level and have already been used as an early warning system [Sericano, 2000].

**Terrestrial Environment**

Total mercury and MeHg concentrations from long-term monitoring of the terrestrial soil-vegetation-herbivore-carnivore food chain with regard to accumulation and
transformation processes were studied over a period of 5 years (1997-2001) in areas contaminated with mercury to differing degrees, as well as uncontaminated areas [Gnamuš et al. 2000] Assessment of the inhaled and ingested contribution of mercury from the environment in roe deer (Capreolus capreolus L.), the selected wild mammal species living in these areas, showed that while the ratio between these two routes of uptake is relatively constant, intake of mercury with food in roe deer is much more important than inhaled mercury, which represents only up to 0.2% of ingested Hg. Although the plant species comprising roe deer foodstuffs were not active accumulators of mercury from soil or air, vegetation mediates significant transfer of Me-Hg to herbivores, and this becomes subject to further accumulation in the higher trophic levels of this food chain. Besides roe deer other bioindicators such as chamois (Rupicapra rupicapra L.) were selected to confirm the uptake of mercury from plants. Though the conclusions drawn from the carnivorous predators lynx (Felis lynx L.) and wolves (Canis lupus L.) are limited due to the limited number of animals shot [8 and 2, respectively], the results and their comparison to other environmental data showed the transfer of Hg from soil (and air) to vegetation, herbivores and thus to carnivores further up the food chain. The results of the measurements, as well as the concentration factors (CF) and bio-accumulation factors (BAF), show appreciable accumulation of Me-Hg and less marked accumulation of T-Hg at higher trophic levels of this terrestrial food chain. Interestingly, higher accumulation of Me-Hg was observed in those environments polluted with high concentrations of inorganic mercury compared to less contaminated and control areas.

A number of studies have also been conducted on a potential use of terrestrial isopod Porcellio scaber (Isopoda, Crustacea) as an indicator of mercury load in terrestrial systems [Nolde in sod. 2005, 2006]. These studies have uncovered the importance of long-term Hg pollution in induction of Hg tolerance in the terrestrial isopod. The lysosomal membrane stability, hepatopancreas epithelium thickness, feeding activity and animal bacterial gut microbiota composition were determined. The results confirm the hypothesis that the response to short-term Hg exposure differs in animals from Hg polluted and unpolluted field locations. The animals and their gut microbiota from the Hg polluted location were less affected by Hg in a short-term feeding experiment than those from the unpolluted environment. The pollution-induced population tolerance of isopods and their gut microbiota as a measure of the effects of long-term environmental pollution have been addressed in recent work of Lapanje and coworkers (Lapanje et al, 2008).

![Figure 4. Correlation between frequency of fresh fish consumption and THg levels in human hair (Miklavčič et al. 2010).](image-url)
**Human Biomonitoring**

Human biomonitoring refers to monitoring activities using biomarkers that focus on environmental exposures, damage, diseases and/or disorders and genetic susceptibility, and their potential relationships.

In general population, hair and blood are used as biomarkers of exposure for MeHg. Concentrations in hair are proportional to simultaneous concentrations in blood but are about 250 times higher. They are also proportional to concentrations in the target tissue, the brain. Total Hg levels in 485 pregnant women (most sensitive population strata) presented in Figure 4 show that even at low level MeHg intake hair can successfully be used as a biomarker of exposure.

**Conclusions**

The results of measurements in various environmental compartments show that mercury is present in very high concentrations in soils and sediments. Active transport of inorganic mercury is taking place. The expected reduction of mercury concentrations in biota since the Mercury Mine was closed was not observed. The concentrations of mercury found in bioindicators is elevated in the near Idrija region, but not to the extent to cause noticeable adverse effects. It has to be mentioned, however, that change in land use and water management (such as construction of a new hydropower dam in the river Idrijca) may seriously change the reactivity and formation of MeHg. An optimized monitoring programme should therefore be implemented using physical, chemical and biological methods and in particular appropriate biomonitoring to detect changes in mercury mobility, reactivity and bioavailability.

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**References**


