Mercury Contamination: A Nationwide Threat to Our Aquatic Resources, and a Proposed Research Agenda for the U.S. Geological Survey

By David P. Krabbenhoft and James G. Wiener

ABSTRACT

This document describes the national mercury problem, identifies critical data gaps, and proposes the framework for a national mercury investigation. The overall goal of this investigation is to provide scientific information needed by resource managers and environmental planners to identify and evaluate options for reducing exposure of humans and wildlife to this highly toxic metal. Several key questions regarding environmental mercury contamination will be addressed. What are the relative contributions of natural sources and selected human sources to the mercury-contamination problem? What criteria can be used to identify mercury-sensitive ecosystems, in which seemingly small inputs of mercury can cause serious contamination of fish and fish-eating wildlife? What factors and processes control the sensitivity of aquatic ecosystems to mercury? Are there potential ecosystem-management approaches for reducing methylmercury contamination of aquatic biota? What levels of mercury in fish are harmful to fish-eating wildlife? Answers to these questions will provide information critically needed to assess and reduce health and ecological risks of environmental mercury contamination.

INTRODUCTION

Mercury (Hg) is one of the most serious and scientifically challenging contaminant threats to our Nation's aquatic resources. Scientific interest in Hg in aquatic ecosystems has been motivated largely by the health risks of consuming contaminated fish, the primary source of Hg in the human diet. Awareness of the extent of the Hg problem continues to increase as more fish populations are surveyed. For example, the number of Hg-related advisories has grown rapidly, increasing 98% from 1993 (899 advisories) through 1997 (1,782 advisories) (figure 1). Moreover, the number of states issuing advisories for Hg increased from 27 in 1993 to 40 in 1997.

For most ecosystems, atmospheric deposition is the primary Hg source, although there are numerous instances of geologic and anthropogenic point-source contamination problems. Since the industrial revolution, anthropogenic Hg emissions have increased atmospheric Hg levels about three to five fold (Fitzgerald, 1995), and caused corresponding increases in Hg levels in terrestrial and aquatic

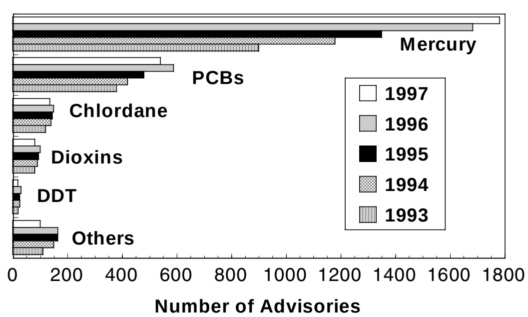

Figure 1. Trends in the number of fish-consumption advisories issued for various pollutants. (source: U.S. Environmental Protection Agency, 1998)

ecosystems. The rate at which rising atmospheric Hg loads translate into increased concentrations in wildlife, however, has remained difficult to predict due to the complex nature of the aquatic Hg cycle.

Toxicologically, the most important process affecting Hg in the environment is methylation, the process by which inorganic Hg is converted to methylmercury (MeHg). Methylmercury is highly neurotoxic, damaging to the central nervous system, and the embryos of vertebrate organisms are much more sensitive than adults (Scheuhammer, 1991; Heinz and Hoffman, 1998). In birds, for example, the effects of MeHg are most severe in embryos and chicks. Low-level dietary exposures that cause no measurable effect in the adults can significantly impair egg fertility, survival of newly hatched chicks, and overall reproductive success. Common loon (*Gavia immer*) chicks reared on low-alkalinity Wisconsin lakes, which contain prey fish with higher Hg concentrations than nearby high-alkalinity lakes, have elevated concentrations of Hg in their blood (Meyer and others, 1995; 1998). Moreover, chick productivity in Wisconsin lakes is inversely correlated with blood-Hg concentrations (Meyer and others, 1998). In Ontario, an estimated 30 percent of the lakes examined by Scheuhammer and Blancher (1994) had prey-size fish with Hg levels considered high enough to impair reproduction of common loons.

Many species of wildlife consume large amounts of fish and can obtain harmful doses of MeHg via dietary uptake. Chicks of common loons, for example, consume more than 50 kg of fish during their first 15 weeks after hatching, whereas adults consume about 1 kg of fish per day (Barr, 1996). If fish consumption is expressed as a percentage of the individual consumer's body mass, rates of fish consumption by common loons exceed those of humans (U.S. population) by a factor of 100 or more (table 1). At these consumption rates, fish considered safe for periodic consumption by humans may contain enough MeHg to adversely affect fish-eating wildlife.

This document describes the framework for a national mercury investigation for the U.S. Geological Survey. The goal of the investigation is to provide scientific information needed by resource managers and environmental planners to identify and evaluate options for reducing exposure of humans and wildlife to this highly toxic metal.

Table 1. Relative Rates of Fish Consumption in Common Loons and Humans

	Daily Consumption of Fish	
Organism	Grams per individual	Percent of body mass
Adult female human (U.S.)[1]		
Median	31	0.06
95th percentile	110	0.22
Common loon[2]		
Chick (first 11 weeks)	400	22-41
Adult	960	19

[1]U.S. Department of Agriculture, Continuing Surveys of Food Intake by Individuals during 1989-1991.
[2]Barr, 1996.

A Critical Assessment of the Mercury Problem Facilitated by the USGS

On July 7-9, 1996, the U.S. Geological Survey (USGS) sponsored a multi-agency workshop on Hg in the environment to transfer information, identify data and information gaps, and identify specific areas of investigation where the USGS could provide scientific and technical leadership. Technical working groups at the workshop achieved general consensus on the state of scientific knowledge and critical information gaps concerning Hg sources and transport, biogeochemical cycling processes of Hg, and MeHg bioaccumulation and effects. The conclusions of the technical working groups were as follows:

<u>Sources</u> The USGS should focus on providing critical quantitative information on Hg point sources and atmospheric loading of Hg. A quantitative inventory of the principal man-related and natural Hg sources could be produced with existing databases and some additional studies. The analysis of dated cores would be particularly useful for determining regional and historical trends in Hg deposition patterns on a national scale.

Biogeochemical Cycling The USGS should focus on providing an improved understanding of the processes controlling MeHg production, destruction, and uptake by organisms in a wide range of environments across the United States. Process-oriented studies are needed to explain the large variation in bioavailability of this toxic metal among aquatic ecosystems. Study sites should span gradients in Hg source types (e.g., atmospheric versus point source dominated), as well as climate, geology, hydrology, and trophic structure.

Methylmercury Bioaccumulation and Effects USGS investigations should focus on environmental factors affecting MeHg exposure to top-level consumers and adverse effects on wildlife.

National Mercury Investigation Study Design

A policy-relevant, national research effort on Hg is needed. The U.S. Geological Survey (USGS) has the multidisciplinary expertise, technical capabilities, and nationally distributed workforce to address many critical information gaps concerning the Hg problem. This investigation would include four coordinated, multidisciplinary components: (1) national information inventories of mercury sources; (2) regional assessments to determine patterns (and controlling factors) of mercury contamination in the nation's aquatic ecosystems; (3) ecosystem investigations to determine the processes and factors influencing methylmercury exposure in aquatic ecosystems; and (4) studies to determine the toxicological significance of methylmercury exposure in fish-eating wildlife, with emphasis on reproductive effects.

National Inventories of Mercury Sources and Deposition

Regulatory and management decisions to mitigate Hg exposure through reductions in emissions requires an understanding of the linkages between sources and ecosystem impacts. Until a more refined assessment of atmospheric-Hg loading (natural and anthropogenic) is achieved, however, the efficacy of anthropogenic emissions reductions as a Hg exposure reduction tool is unknown. Currently, the largest uncertainties in the global Hg mass balance are those associated with natural Hg sources.

The first inventory objective is to quantify Hg releases to the environment from natural and anthropogenic sources. Globally, total emissions (natural and anthropogenic) of Hg to the atmosphere range from 6000 to 8000 metric tons per year, with about half to three quarters coming from man's activities (Nriagu and Pacyna, 1988; Fitzgerald, 1995). However, large uncertainties currently exist for these global Hg fluxes. Estimates from natural sources are particularly poorly documented and further research is required to more accurately define the flux from these sources. Emissions from the ocean are thought to contribute about half of the natural Hg flux to the atmosphere (Mason and others, 1994). Other natural sources, in decreasing order of importance, include: erupting volcanoes, soil vapor flux, geothermal system-hot springs, passively degassing volcanoes and fumaroles, and active faults. A concerted effort to quantify the amount of mercury contributed to the global cycle from these geologic sources would greatly reduce the large uncertainties in global mercury fluxes.

A second contribution the USGS can make toward national information inventories is to improve available databases and estimates of man-related mercury emissions from coal combustion. The USGS has a long data record on the mercury content of various coal beds throughout the United States. Although estimates of man-related mercury emissions are probably more accurate than those of natural emissions, additional efforts are needed to reduce the level of uncertainty in these estimates. As the availability of gas and oil resources become more limited, energy production from coal may increase in the United States and elsewhere, which may have a large impact on the atmospheric mercury loading. Mercury content of coal varies substantially, and how this energy resource is utilized may have significant impact on future mercury emissions and contamination levels of aquatic ecosystems.

The last inventory objective is to document current and historical trends in mercury deposition. Dated sediment cores have been used to estimate current and historical mercury deposition rates (Engstrom and Swain, 1997), but an expanded network of sites is needed to map regional or sub-regional differences in deposition rates. Compiling all the existing data on mercury from dated cores and examining this data set for regional and temporal trends could make an immediate contribution. Ice cores provide an alternative to sediments for estimating historical Hg-deposition rates, and give a direct estimate of atmospheric mercury deposition for a particular locality, but in very few locations is ice coring a viable option. Sediment and peat cores, on the other hand, can be taken from many more locations (deep lakes, reservoirs, and ombrotrophic bogs), but are only an indirect estimator of mercury deposition. Combined use of sediment and ice cores could add valuable information on spatial and temporal trends in mercury accumulation patterns at the national scale.

Regional Assessments

The overall goal of the regional assessments is to identify methylmercury hot spots and ecosystem characteristics associated with high methylmercury levels in aquatic biota. This goal would be accomplished by analyzing and comparing existing and new data on Hg and MeHg in biota, sediments, and water. By collecting and analyzing samples of all three media, more can be ascertained about Hg and MeHg partitioning, accumulation, and bioconcentration. Reliable data on MeHg and Hg from multiple media (biota, sediment, and water) are available for few areas, and large areas of the nation lack data to infer existing or potential methylmercury contamination. West of the Mississippi River and excluding California, reliable data on MeHg in aquatic biota, sediment and water are available for only one site, the Carson River basin. In the eastern half of the country, only about five sites have been intensively studied. Moreover, there are many potentially sensitive, aquatic ecosystems for which little or no comprehensive mercury information are available, including black-water coastal streams; dilute, high-elevation lakes; southwestern reservoirs; watersheds downstream of abandoned mercury-contaminated mines; urban rivers and lakes; playa lakes; and arid basins.

We propose a series of regional-to-national scale, multi-media synoptic sampling efforts be conducted through collaborations between this investigation and other USGS programs and other agencies that desire such information. These assessments should be conducted on a national basis, using consistent sampling and analytical methods to ensure comparability of the results. The general sampling design would include ecosystems that represent diverse environmental settings of climate, geology, soils, land use, and land cover. In addition, the selected sites will span gradients in five primary factors that have consistently been shown to affect mercury abundance, methylation, and bioaccumulation: wetland density, Hg-loading rate, and water-chemistry factors of pH, organic carbon, and sulfate. In 1998, a pilot-scale test of this type of study was conducted collaboratively between the Toxics Substances Hydrology program and the National Water Quality Assessment (NAWQA) program (Krabbenhoft and others, 1999). This study showed several important results, including: (1) effective, Hg-clean sampling for sediment, water, and game fish could be carried out nationally by the USGS; (2) wide ranges of Hg and MeHg concentrations were observed in sediment and water, reflecting ranges of source-load impacts; (3) wetland density was the most important basin-scale factor controlling MeHg production; (4) of the basins sampled, those that favored MeHg production were generally in the eastern United States; (5) mining-impacted sites had the highest Hg concentrations in water and sediment, but the lowest methylation-efficiency in sediments (MeHg/Hg ratio); (6) other Hg sources, such as volcanic activity may be important regionally. Although this pilot study included 106 sites in 21 NAWQA study basins, this sampling density was probably not adequate to make final conclusions about mercury contamination of aquatic ecosystems across the United States. We intend to use what was learned from this pilot study to aid the design of the next synoptic sampling effort. New efforts may include examinations of seasonal differences in Hg and MeHg concentrations and partitioning, information on dissolved and particulate phases, increased spatial resolution from selected basins, controls of sulfur biogeochemistry, information on organic carbon quality as well as quantity, and possibly sampling several levels of each food web.

Ecosystem Investigations

The goal of the ecosystem investigations is to determine the biogeochemical processes that control the production, bioaccumulation, and food-web transfer of methylmercury in aquatic ecosystems. Information from the regional assessments will be used to identify sub-regions or a specific category of ecosystems for the concentrated ecosystem investigations. Priority will be given to areas determined to favor MeHg production and bioaccumulation.

Ecosystem studies will be conducted at about six carefully selected field sites that collectively span gradients of relevant environmental characteristics, including mercury loading rate, bioaccumulation of methylmercury, climate, hydrology, geology, water chemistry, and biology. The level of work envisioned for the ecosystem studies would be similar in scope to the USGS mercury study underway in the Everglades (Krabbenhoft, 1996). Key processes to be studied include species transformations, sediment-water partitioning, bioaccumulation, biomagnification, deposition, sedimentation, and evasion (figure 2). Transformation studies will estimate rates of mercury methylation, demethylation, oxidation, and reduction. We anticipate the relative importance of each of these processes (process rates) will vary among the study basins. A goal of this part of the investigation will be to determine the factors controlling these process rates. In addition, important and related biogeochemical investigations, such as studies on sulfur cycling and other diagenetic sedimentary processes, will be critical elements of these site investigations and often provide the key to understanding the factors controlling mercury cycling at a site.

Considerable ancillary information will be needed to support these detailed investigations. Critical ancillary information includes, but may not be limited to, hydrology, land use, sediment transport and deposition, food-web structure, biological productivity, and geochemistry (dissolved organic carbon, pH, temperature, sulfur chemistry, major ions, and other trace elements). During the selection and screening of candidate study sites, preference will be given to sites for which essential historical and environmental information exist, or to sites where such information can be provided by collaborating with ongoing research or monitoring programs. To the extent feasible, the ecosystem investigations will be conducted at sites of greatest interest to the land-management bureaus of the Department of the Interior.

A numerical mercury cycling model such as that described by Hudson and others (1995) will be used to synthesize the information provided by the ecosystem studies. The model will be used to validate the process rate estimates, make comparisons across study sites, and facilitate hypothesis testing. Important questions, such as what effect Hg-emissions reductions will have on MeHg contamination of aquatic biota in upper trophic levels in various ecosystems nationally, could also be addressed with such a model.

Wildlife Exposure and Effects

The goal of the wildlife exposure and effects component of this investigation is to determine the toxicological significance of methylmercury exposure in selected fish-eating wildlife. Because of the very high neurotoxicity of methylmercury to the developing embryo, these studies will place emphasis on examining effects on reproduction, the biological endpoint most likely to be affected by existing levels of methylmercury exposure in piscivorous wildlife (Heinz and Hoffman, 1998). The threshold concentrations of dietary methylmercury that cause reduced reproductive success and adversely affect the health and survival of developing young will also be estimated. Dose-response relations and threshold dietary concentrations for reproductive effects should be estimated via manipulative experiments in the laboratory and

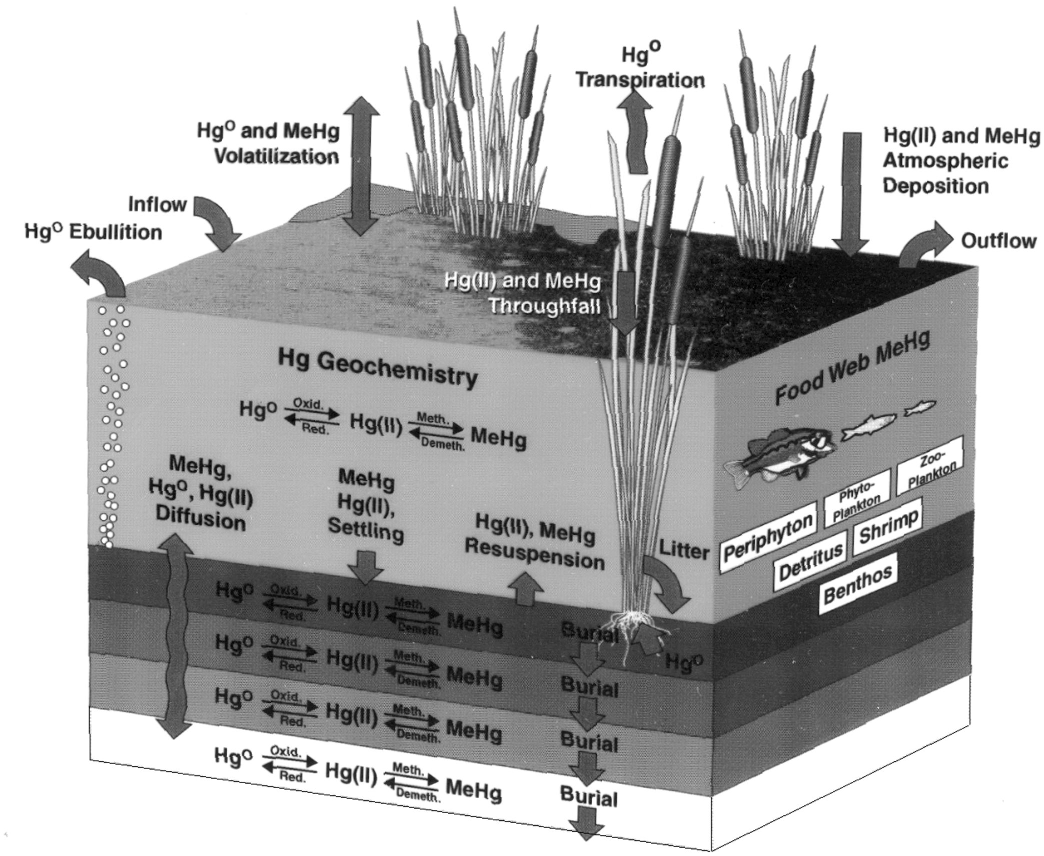

Figure 2. Conceptual model of the mercury cycle and food web for an aquatic ecosystem. Arrows depict various process rates.

field. Laboratory experiments would feature well-defined exposures and control of potentially confounding environmental variables, such as weather, disease, nutrition, and predation. The field experiments would facilitate work with many fish-eating species and analyses of exposure and effects under conditions of varying mercury contamination.

Definition of dietary methylmercury thresholds for reproductive effects should be a primary goal in developing environmental criteria for mercury. Such criteria would give resource managers and regulatory personnel some biologically relevant targets that could be used in environmental decisions regarding mercury. Laboratory and field studies should incorporate a variety of fish-eating and other birds to develop an adequate database for extrapolation to the various groups of birds exposed to methylmercury in natural ecosystems. One of the species recommended for controlled laboratory experiments on the effects of methylmercury on reproductive success is the mallard. Although not a fish eater, the mallard has been used extensively in mercury research and has proven to be a sensitive surrogate for evaluating methylmercury poisoning in other bird species. Large numbers of mallards can be raised and studied to ensure strong statistical defensibility of toxicological results. American kestrels could be used as a surrogate for the effects of contaminants on raptors, such as the bald eagle. A colony of kestrels has been used for many decades at the USGS's Patuxent Wildlife Research Center in studies of reproductive and post-hatching, developmental effects of different classes of contaminants, and the kestrel has proven to be a sensitive species. The Patuxent Center has many years of experience in breeding black-crowned night-herons; the re-establishment of this colony would enable the collection of critical laboratory data on the effects of methylmercury on the reproduction of a fish-eating bird. Other piscivorous birds (adults, chicks, or eggs) to be studied in shorter experiments include double-crested cormorants, common loons, belted kingfishers, and hooded mergansers.

In the laboratory studies, the range of dietary exposures should include environmentally relevant concentrations of methylmercury in prey fish. Reproductive studies should examine endpoints of adult health, fertility, hatching success, growth and survival of young, teratogenic effects, histopathology, and various biomarkers (including nondestructive ones). Mercury concentrations in tissues associated with adverse effects will also be estimated. Other tests will include a comparison of the toxicities of biologically incorporated mercury versus methylmercuric chloride, the interactions of mercury and selenium or other stressors, kinetics, egg injection studies, and behavioral studies.

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AUTHOR INFORMATION

David P. Krabbenhoft, U.S. Geological Survey, 8505 Research Way, Middleton, Wisconsin.

James G. Wiener, U.S. Geological Survey, Upper Midwest Environmental Sciences Center, 2630 Fanta Reed Rd., LaCrosse, Wisconsin.