

Proceedings of the U.S. Geological Survey 2004 Mercury Workshop: Mercury Research and Its Relation to Department of the Interior Resource Management

Edited by John A. Colman

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Executive Summary

The Mercury Workshop was sponsored by the U.S. Geological Survey (USGS), Eastern Region, under the U.S. Department of Interior (DOI) Science on the DOI Landscape Initiative, on August 17-18, 2004, in Reston, Virginia. The workshop was convened to (1) summarize information on mercury sources and cycling on DOI lands in the eastern United States, (2) learn the perspectives of the DOI bureaus regarding mercury on DOI lands, (3) provide information to DOI land managers about monitoring mercury and minimizing mercury accumulation in wildlife and humans, and (4) consider future directions for mercury monitoring and research on DOI lands. This information was conveyed through invited oral presentations, a panel discussion by DOI bureau scientists, and contributed posters. These workshop proceedings present a summary of information on this complex subject, as well as a synopsis of concerns about mercury as expressed by researchers and land managers. All of the presentations were videotaped and are available at the following URL, along with the slides presented: <http://www.usgs.gov/mercury/2004workshop/>

Presentations on the effects of mercury on humans and wildlife indicate the magnitude of the problem. An estimated 600,000 human newborns per year in the United States have levels of mercury in blood in excess of the U.S. Environmental Protection Agency reference dose, the amount estimated to be without an appreciable risk of deleterious effects. The effect on wildlife is equally compelling, likely contributing to population decreases of many threatened fish-eating species—including fish, birds, and mammals. Methylmercury is the major mercury chemical species affecting humans and wildlife; it is brought to higher predators, including people, through the aquatic food web and fish. Thus, mercury methylation rates in the environment and mercury deposition rates from the atmosphere are important factors in understanding the effects of mercury on humans and wildlife.

Most oral presentations at the workshop concerned investigations on DOI lands. These lands are widely distributed on the continent and offshore, and include most types of environments where biogeochemical processes generate methylmercury from mercury deposited from the atmosphere. The presentations indicated that land-management practices, such as burning, flooding, tilling or other ground disturbance, and fertilizing (including sulfur application), affect mercury cycling and the generation of methylmercury. The mechanisms for land-management effects likely involve alteration of surface-water pH, sulfide and sulfate concentrations, and dissolved organic carbon concentrations, which have been determined in many of the studies to influence the generation of methylmercury and the accumulation of methylmercury in aquatic food webs.

The panel of DOI bureau scientists expressed concerns about mercury contamination in national parks and wildlife refuges, including effects on wildlife and sport fishing from atmospheric deposition of mercury that originates from emission sources off public lands. A need was expressed for site-specific instructions accessible to managers of the individual parks and refuges on monitoring and managing the mercury problem. Concerns on American Indian lands include the effects of mercury on human health from consumption of fish, which is a traditional food source among tribes in the Eastern Region of the USGS, and the effects on wildlife. For example, of the 180 pounds of fish consumed per adult per year that is traditional among the Minnesota Chippewa Tribe population, only 5 percent (9 pounds) can be consumed by women of child-bearing age or by children, if mercury consumption restrictions are followed. Concerns for offshore resources (marine environment) relate to basic mercury research questions. There is a need to define accurately the relative importance for mercury accumulation in the marine food web of various mercury sources, including sources associated with mineral exploration, fossil fuel combustion, and natural emissions from volcanoes. The source, whether anthropogenic or natural, of substantial amounts of mercury that can be found in marine fish is presently unknown.

The concluding session of the workshop, with general discussion on future monitoring and research, pointed to the use of the location and environmental circumstance of public lands for establishing expanded monitoring of mercury deposition and mercury biogeochemical cycling investigations. National Park Service (NPS) and Fish and Wildlife Service (USFWS) officials expressed the need to package information in forms readily understood by land managers and by the public. Despite substantial progress in mercury research, significant questions remain. During the discussion, managers encouraged scientists to continue mercury research but also asked for interim products for use in land management, such as maps, databases, and site-specific recommendations that would lessen the effect of land-management practices on mercury accumulation.

The direction of future research, as indicated through the discussion, could include studies of the relation between mercury sources and mercury receptors. Progress has been made on the question of why adjacent lakes with presumably similar deposition rates of mercury from the atmosphere have substantially different concentrations of mercury in fish. In these lake systems, many environmental factors, such as pH, dissolved organic carbon (DOC) concentration, sulfur compound concentration, proximity of wetlands, trophic state, and water clarity, mediate overall microbial methylmercury production (methylation and demethylation of mercury by bacteria). Variability among sites associated with these factors slows the progress of matching the proximity and size of mercury sources with effects at receptor sites, and makes forecasting the results of emission remediation uncertain. Monitoring ecosystems for changes in mercury occurrence and concentrations that result from decreases in mercury sources following remediation would help establish the relationship between source and receptor. A poster and several comments addressed strategies for establishing a network to monitor change.

Other research questions that relate to possible remediation strategies include the extent to which "old mercury" (previously deposited mercury) continues to be available for microbial methylmercury production. Understanding of the processes and controls of atmospheric deposition of mercury is incomplete in that known deposition rates from the Mercury Deposition Network cannot be simulated very closely with models of mercury deposition. Other uncertainties include determining the correct deposition rate (or atmospheric mercury residence time) resulting from the background global mercury pool, and determining whether the rate of background mercury deposition is sufficient to support substantial rates of methylation. Finally, there are many species that have not been evaluated with respect to mercury accumulation and effects. Wading birds, insectivorous birds, and other animals were mentioned in this regard during the discussion session.

Many questions for which there are answers in freshwater environments remain unanswered in marine environments. In the Gulf of Mexico, for example, the source of mercury in marine fish remains unknown. Is it of anthropogenic or natural origin? What is the relative importance of mercury from the Mississippi River compared to other sources? How do the very low concentrations of methylmercury in ocean water get concentrated to high levels in marine fish? What are the principal locations of mercury methylation in the marine system? How does mercury accumulation and elimination in marine fish compare to these processes in freshwater species? What are the relative amounts of methylmercury and total mercury in marine species? Answers to these and other questions about mercury in marine environments will require future research.

Environmental research on mercury has produced compelling evidence on the detrimental effects of mercury deposition from the atmosphere to the landscape. More investigations would be needed to determine how best to mitigate the effect of mercury already deposited on the landscape and to regulate mercury emissions to the atmosphere so that deposition will decrease to acceptable levels.

concentrations of Ba and total Hg in sediments from near-field stations, coupled with the high levels of Ba as barite in these sediments, support the contention that barite was the primary source for anthropogenic mercury in these sediments. Concentrations of methylmercury ranged from 0.11–1.05 ng/g with a mean of 0.44 ± 0.27 ng/g for all far-field sediments and ranged from <0.03 –2.7 ng/g with a mean of 0.45 ± 0.41 ng/g for all near-field sediments. In contrast with results for total mercury, this study showed that concentrations of methylmercury in sediment from all six drilling sites did not vary significantly between near-field and far-field stations. However, considerable variability was observed in concentrations of methylmercury at several sites and was partly related to local variability in redox state in the upper 10 cm of sediment. Low to non-detectable levels of methylmercury were observed in near-field stations where the redox potential (Eh) was <-100 mV (anoxic and highly reducing) in the presence of abundant total H₂S (>1 millimolar). Higher values of methylmercury were found in a few near-field stations where levels of total organic carbon were higher and where Eh values were about 0 mV (anoxic, moderately reducing). These observations are consistent with studies showing that optimum conditions for methylmercury formation are in anoxic sediment with sulfide-poor interstitial water and sufficient levels of biodegradable organic matter and nutrients. With respect to the role of petroleum drilling fluids as a source of total mercury to Gulf of Mexico, the estimated input of mercury from drilling discharges is 300 kg/yr, ~1 percent of the total inputs from the Mississippi River (21,000 kg/yr with particles and 1,500 kg/yr dissolved) and the atmosphere (5,100 kg/yr).

Session 6: Influence of Ecosystem Setting on Mercury and Mercury Management

Moderator: Adria Elskus, University of Kentucky

Session Summary

This session was an extension of the case-study session (Session 2). These presentations added more detailed information about the factors influencing mercury methylation described in the case-study session and described some strategies for controlling mercury mobilization as well as for long-term mercury monitoring. Although recently deposited mercury may be most bioavailable, mercury deposited in the past, as described in one presentation, may be remobilized through soil disturbances such as erosion or burning. Salt and freshwater wetlands are ecosystems long associated with generation of methylmercury. Methylation in wetlands of the Everglades, the Gulf coast, and San Francisco Bay were compared in a presentation that concluded that more research would be needed to predict methylation rates in these environments. A detailed mercury investigation of paired watersheds in Acadia National Park pointed to long-term effects of land management on mercury cycling, including changes in plant

species and related changes in dry-deposition rate resulting from burned watersheds.

Abstracts

Mercury Bioaccumulation in Stream Ecosystems—Detailed Studies, Spatial Assessments, and Trend Monitoring

By M.E. Brigham¹

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Management of ecosystems that contain mercury-sensitive waters (lakes or streams with relatively high levels of mercury in fish or other biota) may benefit from consideration of research on mercury cycling, bioaccumulation, and related environmental issues. Mercury stored in soils from past deposition represents a notable environmental pool of mercury. Retaining this mercury in upland portions of watersheds, rather than promoting its transport to aquatic ecosystems, is one strategy that may help ameliorate mercury bioaccumulation in some ecosystems. Activities that exacerbate erosion of surficial soils or weathering of soil-organic carbon may greatly increase loading of mercury to aquatic ecosystems. Other land-based influences, such as increases in impervious areas resulting from urbanization or low-intensity fires, also may exacerbate transport of mercury from uplands to aquatic ecosystems. Land-management practices that restore soil-organic carbon, such as certain soil conservation measures, may help retain atmospherically deposited mercury on the land surface.

In addition to the transport of mercury, mercury methylation—a critical step in the mercury bioaccumulation cycle—can be influenced by environmental processes that intersect with human activities. Creation of reservoirs or impoundments promotes methylation of mercury. Methylation of mercury also has been exacerbated in many ecosystems by repeated wetting and drying cycles, which may be influenced by hydrologic modifications; and inputs of sulfate from atmospheric, agricultural, or other sources.

To improve understanding of mercury bioaccumulation in stream ecosystems, the U.S. Geological Survey is conducting detailed studies at two streams in Oregon, three in Wisconsin, and three in Florida. In general, atmospheric deposition of mercury increases along this west-to-east gradient, and methylmercury production and bioaccumulation in fish is more prominent in low-relief, high-wetland stream basins. Study streams drain a range of settings—reference areas, with minimal human disturbances, to highly urbanized settings. These studies aim to describe concentrations and fluxes of mercury in key components of the stream ecosystem: water, streambed sediment, porewater, and biota. Detailed studies are supplemented by spatial assessments of variations in mercury bioaccumulation through one-time (synoptic) sampling of mercury and methylmercury in water, sediment, and fish tissues at several hundred streams across the nation, covering a diverse

led to higher measured rates of MeHg production in the former wetland type. Comparing ecosystems, MeHg production rates from Lake Pontchartrain wetlands were of similar range and magnitude to those from the estuarine portion of the SFB, and both were higher than the Everglades and delta and freshwater wetlands of the SFB. It remains a difficult problem to predict MeHg production rates in various wetland types; the long-term goal of this research is to develop an understanding of the relative rates of sediment MeHg at various spatial scales, which may ultimately assist resource managers in designing wetland restoration strategies that minimize net MeHg production and bioaccumulation.

Landscape Control on Mercury Biogeochemistry in Gauged Paired Watersheds at Acadia National Park

[Title in agenda: Mercury Biogeochemistry in Two Gauged Watersheds, Acadia National Park]

By Steve Kahl¹, Sarah Nelson², Ken Johnson², Katherine Sheehan², Ivan Fernandez, Aria Amirbahman², Terry Haines³, and Robert Lent⁴

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Two upland watersheds at Acadia National Park (Acadia NP), U.S. (44° 20' N latitude; 68° 15' E longitude) were instrumented in 1998 to provide a long-term foundation for ecological and watershed research at Acadia NP, representative of coastal ecosystems of the Gulf of Maine. The research was initiated as part of USEPA/NPS PRIMENet (Park Research and Intensive Monitoring of Ecosystems Network), a system of UV-monitoring stations and long-term watershed research sites located in U.S. national parks. A main goal was to address watershed research questions about mercury, based on natural differences in forests and soils induced by an intense wildfire in one watershed in 1947. The unburned 47-hectare (ha) Hadlock Brook watershed is 70 percent spruce-fir mature softwood forest. In contrast, the nearby burned 32-ha Cadillac Brook watershed is 20 percent regenerating mixed northern hardwoods and 60 percent shrub/rocky balds.

Mercury (Hg) deposition is higher in the unburned Hadlock watershed (10.2 $\mu\text{g}/\text{m}^2/\text{yr}$) than Cadillac (9.4 $\mu\text{g}/\text{m}^2/\text{yr}$) because of the greater scavenging efficiency of the softwood vegetation in Hadlock. As is typical in other studies around the world, methylmercury (MeHg) is less than 1 percent of the total deposition to the landscape, underscoring that there is little justification for the high cost of monitoring MeHg in deposition. A marine re-volatilization source of Hg in deposition does not appear to be a major factor, because Cl and Hg concentrations in deposition are out of phase. Mercury export is lower in Cadillac Brook (0.4 $\mu\text{g}/\text{m}^2/\text{yr}$) than in Hadlock Brook (1.3 $\mu\text{g}/\text{m}^2/\text{yr}$) because of elemental volatilization during the fire that reduced total Hg in soils, along with subsequently lower rates of atmospheric re-deposition in a watershed with more bare soil and bedrock, and regenerating vegetation. In

laboratory experiments, Hg has been shown to be less mobile in soils from the burned watershed. The results also show that Hg flux per hectare is greater from wetlands, but Hg flux per unit carbon is greater from uplands. Methyl-mercury was consistently less than 10 percent of total Hg flux in streamwater, regardless of streamflow or total Hg concentration. MeHg flux was not correlated with total Hg soil pools, suggesting that the mobile, bioavailable Hg pool is much smaller than total soil pools. If true, then decreases in total Hg from the atmosphere should result in decreased bioavailability of Hg.

These data show that 50 years following a wildfire there was lower atmospheric deposition due to changes in forest species composition, lower soil pools, and greater ecosystem retention for Hg in the burned watershed. We propose that one of the controlling factors to explain the wide variation in Hg bioaccumulation in seemingly similar and adjacent lakes may be the fire or other disturbance in the local landscape.

Session 7: Moderators' Summaries and Suggested Future Research Directions for the DOI Landscape Mercury Initiative

Moderator: Sarah Gerould, U.S. Geological Survey

Session Summary

Summaries of each session were presented at the end of the workshop by the session moderators. Included with these science summaries were appeals by the session moderators for more research products in forms that are useful to, and understandable by, land managers. Map products, for example, of mercury deposition, mercury methylation susceptibility, or mercury concentrations in fish, were suggested as particularly useful. Moderators also expressed a need for greater synthesis of data as a goal for future research.

After the summaries by moderators, discussion with conference participants began regarding the elements needed in a long-term strategy for mercury research that would increase communication between the mercury research community and DOI resource managers who deal with mercury effects. Land managers asked for research products that would be specific to their land areas on such topics as recommended land-management procedures for mitigating effects of mercury, monitoring strategies for mercury, and the criteria for judging necessity of a risk analysis. Scientists were encouraged, in the discussion, to pursue continued research but also were requested to produce interim products, so informed management can go forward with information that is already known.

An interesting example of a site-specific question on land management was given to illustrate the lack of improvement from management of the Cape Sable seaside sparrow. At least two management techniques, wet and dry cycling, and burning, are being done to enhance habitat, but these techniques may be increasing mercury methylation in the process. Population models (that do not include mercury effects) for

out of the affected streams? What are net mercury methylation rates? What are the relative contributions of bioavailable mercury? To answer these questions, major data gaps will need to be filled. The most important data gaps involve methylmercury concentrations in surface water and near-stream sediments. Mercury concentrations in ground water will also need to be measured. The goal of the study is to answer these questions with as much certainty as possible and to better understand why mercury concentrations in fish tissue remain high 40 years after the mercury waste disposal stopped.

An Assessment of Risk of Methylmercury Exposure to Fish-Eating Birds Foraging at a Constructed Wetland in South Florida

By Darren G. Rumbold¹

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Stormwater Treatment Area - 2 (STA-2) was designed with three independent treatment marshes to remove phosphorus in agricultural runoff and reduce eutrophication in the northern Everglades. However, there was a concern that, in doing so, STA-2 might inadvertently worsen the existing mercury problem in the Everglades. Accordingly, operating permits required start-up monitoring of total mercury and methylmercury (MeHg) and authorized flow-through operation only after concentrations in the interior marsh were not significantly greater than concentrations in the supply canal. This case study summarizes an assessment of the risk of MeHg exposure to fish-eating birds required as a permit modification to authorize flow-through operation of Cell 1 without it first satisfying this start-up criteria. The assessment estimates the risks posed by MeHg to the great egret (*Ardea alba*) and the bald eagle (*Haliaeetus leucocephalus*). Exposure models were based on literature-derived life-history parameters combined with site-specific MeHg concentrations in water, sediment, and fish. To assess risk, daily MeHg intake by females and cumulative MeHg consumed by nestlings were compared to literature-derived effects thresholds. The results indicated a low likelihood that MeHg exposures to birds foraging throughout STA-2 would exceed effects thresholds at the time of this assessment. Birds foraging exclusively from Cell 1 or the small discharge canal were predicted to experience greater exposures and could be at potential risk. However, this worst case risk was comparable or lower than risk levels encountered in nearby water conservation areas or in Everglades National Park. Due to limitations in published effects thresholds, confidence in the risk characterization was lower for older eaglets remaining near their natal nest in the STA. Finally, there was no evidence that discharges from STA-2 have increased the risk of MeHg exposures immediately downstream of the STA above those of background risk levels.

Mercury Bioaccumulation in Lotic Salamanders: A Review and Assessment

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Mercury (Hg) bioaccumulation in salamanders has received little attention despite widespread Hg contamination of aquatic ecosystems and worldwide amphibian declines. Here we report a review of Hg contamination in larval northern two-lined salamanders (*Eurycea bislineata bislineata*) collected from streams in Acadia National Park (ANP), Maine, and Bear Brook Watershed, Maine (BBWM)—a paired, gauged watershed treated with bimonthly applications (25 kg/ha/yr) of ammonium sulfate [(NH₄)₂SO₄] since 1989—and Shenandoah National Park (SNP), Virginia. Our results suggest that watershed-scale attributes including fire history, whole-catchment (NH₄)₂SO₄ additions, wetland extent, and forest cover type influence Hg bioaccumulation in two-lined salamanders inhabiting lotic environments. We also discuss future research directions to evaluate Hg bioaccumulation in stream ecosystems at existing long-term ecological research sites in the northeastern United States. Long-term, broad-scale studies that address variation in Hg cycling across a wide gradient of physical, climatic, and biotic conditions will allow researchers to develop a more synthesized perspective on patterns and processes related to fate, transport, and bioavailability of Hg in aquatic ecosystems.

Mercury Emissions and Lake Deposition: A Qualitative Model and Its Application to Lake Whatcom, Washington

By Anthony J. Paulson and Dale Norton

A simple atmospheric deposition model was developed that allowed comparisons of the deposition of mercury (Hg) to the surfaces of lakes in Whatcom County, Washington. The model required wind data, Hg emission rates from each source, an estimate of the speciation of Hg in the emissions (particulate, reactive, or vaporous Hg) of each type of Hg source, and the atmospheric residence time of each Hg species. Of all the lakes examined, basin 1 of Lake Whatcom would have been most affected by the Hg emissions from the chlor-alkali plant that operated in the City of Bellingham until 2000. The down-lake decrease in estimated atmospheric deposition to Lake Whatcom was not reflected in the enrichment of Hg in the sediments above pre-industrial concentrations. The enrichment ratios of 2 to 3 in the sediment from throughout Lake Whatcom were on the lower end of values of enrichment ratios found across the U.S. The length-adjusted concentrations of Hg in largemouth and smallmouth bass were not related to estimated deposition rates of Hg to the lakes from local atmospheric sources. Estimates of Hg deposition derived from the model indicated that the most significant deposition