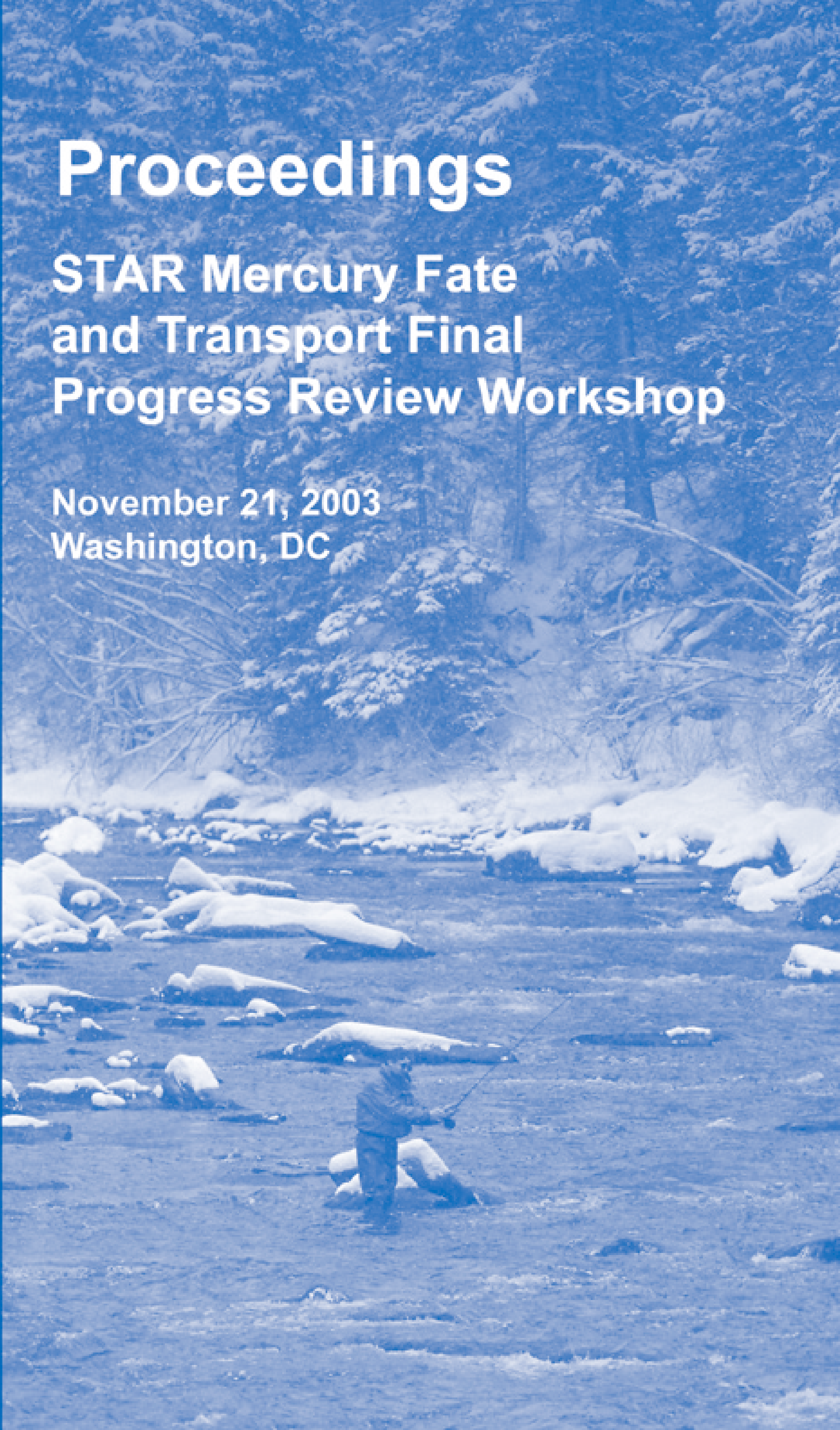
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY



Proceedings

STAR Mercury Fate and Transport Final Progress Review Workshop

November 21, 2003
Washington, DC

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Introduction

In December 1997, the U.S. Environmental Protection Agency's (EPA) Mercury Study Report to Congress identified mercury as a critical human health and environmental problem needing additional scientific and technical research. Mercury poses risks to humans and wildlife, particularly because it concentrates in the tissues of animals as it moves up through a food chain. Observed adverse effects in mammals, fish, and birds have included behavioral and neurological abnormalities, impaired growth and development, reproductive abnormalities such as fetal deformities, and in some cases complete reproductive failure. Fish consumption is the dominant exposure pathway for humans and wildlife. In some cases, mostly in the past, wildlife were killed by extreme environmental concentrations of mercury, for example, from seed grains treated with mercury or from unusually severe instances of waste release. The most pervasive wildlife effects involve reduced breeding success, which now poses severe consequences for water birds throughout North America and some endangered species, including panthers, in the Florida Everglades.

More U.S. waters are closed to fishing because of mercury contamination than any other toxic contamination problem. Because fish consumption can be a significant route of human exposure to toxic chemicals, the U.S. Food and Drug Administration (FDA) issues guidelines to states on fish contamination levels that warrant closures of fishing waters to commercial or recreational fishing. The principal sources of fish contamination, perhaps surprisingly, are air emissions of mercury from coal burning power plants, municipal waste incinerators, and other industrial sources.

This meeting will be the third and final Science to Achieve Results (STAR) Grant Progress Review for the grants from the 1999 Request for Applications (RFA) on Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments. The goal of the review will be to ascertain the progress of the research in addressing the science questions and issues described in the RFA such as: (1) For a given amount of mercury transported into a watershed, what is the predicted concentration of methylmercury in fish? How do mercury and methylmercury spatially distribute across the terrestrial and aquatic components of a watershed? What controls bioavailability of mercury in the food chain? (2) What environmental and biochemical variables control transformation of mercury to methylmercury? What environmental variables control the reduction of divalent mercury to elemental mercury in soils, sediments, and surface waters? (3) How does mercury cycling vary within different geographic regions of the United States (South Florida, Great Lakes, Northeast or West)? How might the variability be accounted for (resource types [wetlands], temperature regimes, microbial communities)? STAR researchers are studying the risks created by mercury in our environment so that we can better understand how to eliminate them.

For further information on the U.S. EPA's STAR Mercury Research Program, please contact William G. Stelz, ORD/NCER, Assistant Center Director for Multimedia, by telephone at (202) 564-6834, or by e-mail at stelz.william@epa.gov.

U.S. EPA National Center for Environmental Research

STAR Mercury Fate and Transport Final Progress Review Workshop

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Executive Summary

OVERVIEW

The U.S. Environmental Protection Agency's (EPA) Science to Achieve Results (STAR) Program's Mercury Fate and Transport Final Progress Review Workshop was held on November 21, 2003. The purpose of this final review was to determine the progress of the research in addressing the science questions and issues described in the Fiscal Year (FY) 1999 Request for Applications (RFA) on Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments. STAR researchers are studying the risks created by mercury in the environment to better understand how to eliminate those risks. Approximately 75 people attended the workshop.

WELCOME AND INTRODUCTORY REMARKS

William Stelz, U.S. EPA

Mr. William Stelz, Office of Research and Development (ORD), Assistant Director for Multimedia at the National Center for Environmental Research, welcomed participants to the final progress review of the STAR Mercury Program. He asked participants to concentrate on findings, results as related to the 1999 RFA, and future research in their areas of expertise. He noted that the STAR 1999 Mercury Solicitation research focused on mercury transport in a watershed context, and that its specific objectives were to: (1) increase our ability to trace mercury from its entrance into the ecosystem, through its biogeochemical cycling, to the concentration of methylmercury (MeHg) in fish tissue; and (2) promote the development of risk management strategies based on sound science. Mr. Stelz gave a brief introduction to the STAR 2001 Mercury Solicitation, which focused on mercury emission sources, atmospheric processes, and deposition. He closed his comments by noting that ORD is focusing its research efforts on the Mercury Multi-Year Plan (MYP), which supports Agency goals. The Mercury MYP aids ORD as a planning and communication tool, and integrates ORD intramural and extramural research efforts. The two long-term goals defined in the MYP are to: (1) reduce and prevent the release of mercury into the environment; and (2) understand the transport and fate of mercury from release to the receptor and its effects on the receptor. The plan can be viewed at: http://www.epa.gov/osp/myp/mercury.pdf.

FORMATION/TRANSPORT OF METHYLMERCURY IN ECOSYSTEMS AND WATERSHEDS

Watershed Influences on Transport, Fate, and Bioavailability of Mercury in Lake Superior

James Hurley, University of Wisconsin

Dr. James Hurley stated that the overall goal of this research is to assess the importance of watersheds in controlling sources, transport, fate, and bioavailability of mercury (Hg) in the Lake Superior basin. The specific research objectives are to: (1) determine the speciation and bioavailability of Hg transported to Lake Superior by rivers that drain representative and contrasting watersheds; (2) determine the watershed-specific characteristics (land cover, land use, surficial deposits) that control physical and chemical forms of Hg transported by rivers; (3) identify key mechanisms controlling Hg bioavailability and speciation in near shore zones relative to open lake regions; and (4) provide process-level information to complement concurrent development of Hg fate and transport models of the Lake Superior ecosystem. The approach combined field and laboratory studies with modeling efforts. The majority of time was spent in the field because there was not a lot of data on Hg cycling in Lake Superior. Field work included sampling within homogenous subwatersheds, riverine mixing zones, and deep water regions of Lake Superior.

This research represents the first comprehensive overview of Lake Superior for Hg. Data indicate that Hg species concentrations are quite low in Lake Superior, similar to Lake Michigan and oceanic waters. Nearshore mixing zones are sites of enchanced bioaccumulation of MeHg for phytoplankton and zooplankton, and in-lake methylation was extremely low for all offshore sediment sites sampled. Watershed export of MeHg may be a function not only of land use/land cover (e.g., there is more transport of MeHg in sandy soils), but also of subsurface flow characteristics. A preliminary mass balance for the lake suggests water retention of 190 years, and that mercury is present for 4.6 years.

Future research will include: (1) atmospheric deposition to explore the effects of local inputs on nearshore (urban) regions and the direct deposition of MeHg in the basin; (2) mixing zones and watershed influences to look at mechanisms for algal and zooplankton uptake and the fate of colloidal MeHg in nearshore zones; and (3) in-lake studies to determine the fate of changing anoxia on MeHg dynamics, mechanics of bioaccumulation in offshore zones, and methylation in deep sediments. The Great Lakes could serve as an excellent site for coastal studies.

In response to an inquiry from Dr. Robert Mason about whether there is direct groundwater input into Lake Superior, Dr. Hurley responded that there have been studies done on the northern shore, although this may be fracture flow. There are sandy areas in nearshore zones as well.

Dr. William Fitzgerald remarked on the utility of comparing work in Lake Superior (e.g., how MeHg is produced) with similar work in regions such as the Long Island Sound.

Understanding the Role of Sulfur in the Production and Fate of Methylmercury in Watersheds

Robert Mason, University of Maryland

Dr. Robert Mason stated that mercury has recently received a great deal of media attention. Methylation is the key process in transforming inorganic Hg that is emitted from various sources into MeHg, the toxic form of Hg that bioaccumulates in fish. The goal of this research is to understand the role of sulfur (especially sulfide) in Hg methylation, and the MeHg fate and transport in watersheds. The specific objectives are to investigate: (1) how Hg complexation with sulfide effects bioavailability of Hg to methylating microorganisms; (2) how MeHg production and accumulation may change for a given change in loading of Hg, sulfur, and other ecosystem constituents; (3) the factors controlling demethylation in environmental matrixes; and (4) the factors controlling Hg bioavailability, methylation, and MeHg fate and decomposition, through laboratory studies and modeling efforts. A novel technique, octanol water partitioning, was refined to measure Hg speciation *in situ* in field samples. This technique can now be used in environments where Hg levels are in the pM range.

Understanding bioavailability to methylation and how net methylation changes over time is important. Factors to consider are speciation effects, the activity of methylating organisms, demethylation (which microbes are involved and the role of speciation), and how Hg recently added to the ecosystem is less bioavailable and less well methylated. Dr. Mason presented a summary of the major findings and future research efforts. The role of sulfide and sulfate in Hg methylation is now well understood. In controlled studies, the methylation rate appears to be directly linked to medium sulfide levels. Further studies need to focus on dissolved organic carbon (DOC) and other parameters and their role in Hg methylation. There is a correlation between short-term Hg methylation and *in situ* MeHg concentrations that makes sense from a thermodynamic and kinetic point of view. Thus, measurements of MeHg in systems where this relationship has been established may provide a reasonable surrogate measure of methylation potential. Modeling suggests that the role of pH in controlling net MeHg in aquatic systems is complex and may be more important than was previously thought. Stable isotope and radioactive addition incubation experiments appear to provide a similar relative measure of methylation potential, but not for demethylation potential. More effort is needed to understand the controls over demethylation. Future work is aimed at demonstrating in the field the presence of neutral Hg species and a relationship between methylation rate and *in situ* Hg speciation, and developing a model that incorporates speciation and other factors to predict Hg bioavailability for methylation and MeHg fate.

Dr. John Sherwell noted that it may not be necessary to know the details of speciation on the input side, because we can measure the total Hg entering the system. Dr. Mason responded that you can get differences in the methylation rate just by spiking Hg into the system in a different form, suggesting that the kinetics of the exchange processes are much slower than one might assume. Thus, measuring only the total Hg input may not provide the necessary information, although speciation measurement may be more critical in Hg reduction than in methylation.

Response of Methylmercury Production and Accumulation to Changes in Hg Loading: A Whole-Ecosystem Mercury Loading Study
Cynthia Gilmour, The Academy of Natural Sciences

Dr. Cynthia Gilmour stated that this study attempts to answer the question: How do ecosystems respond to changes in Hg deposition? The overall objective of this research is to examine the magnitude and timing of the response in net MeHg production to changes in Hg loading. The specific objectives are to: (1) examine the bioavailability of Hg deposited to different types of the watershed, and different watershed components, for methylation through time; (2) use Hg-stable isotopes to elucidate patterns of fate, transport, and bioavailability; and (3) examine the dose-response to Hg loading. Stable Hg isotopes were used to assess old Hg (existing in sediments and soils) versus new Hg (freshly deposited). The analysis was conducted using standard Hg/MeHg techniques, but substituted ICP-MS for CVAF.

In the first study, which is embedded within the Aquatic Cycling of Mercury in the Everglades study, Hg dose-response experiments were conducted with stable isotopes in 1 m diameter mesocosms. The results from the Florida Everglades suggest that: (1) the bioavailability of new Hg for methylation changed rapidly through time; (2) methylation and bioaccumulation of new Hg in the warm shallow water systems occurred in a quick pulse after the Hg spike; and (3) DOC has a strong effect on methylation, and there are interactions between SO_4 and the age of the Hg being methylated. In the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) study, mercury stable isotopes were used to track Hg transport, methylation, and bioavailability for methylation and uptake at the ecosystem level. The key STAR objective of the METAALICUS project was to examine the bioavailability of Hg deposited to different parts of the watershed for methylation through time. Hg stable isotopes have been delivered to the uplands, wetlands, and a first-order drainage lake in northwest Ontario since 2001. Dosing has continued through 2003, at roughly four times the level of atmospheric Hg deposition. A key result from this work is that there is a significant difference between new and old Hg in terms of MeHg production. Other results include: (1) lake budgets show that most of the native and spike MeHg is formed within the lake; (2) surficial sediments, anoxic profundal waters, the adjoining wetland, and epilithon (to a much lesser extent) are sites of MeHg production; (3) lake Hg spike is more dynamic than existing Hg pools; and (4) the time to reach a new equilibrium with the higher Hg deposition rate will be at least 3 years for the Hg spike to the lake, and longer for Hg deposition to the upland and wetland.

The new hypotheses are that ligand exchange rates in natural systems are much slower than expected and influence the availability of Hg for methylation through time, and equilibrium Hg speciation may be inadequate to model MeHg production. The METAALICUS project team will continue with additional years of isotope spike, and would like to address the following questions: (1) How long will it take until a new equilibrium with the new Hg dose is achieved? (2) What will be the time course of ^{200}Hg movement off the wetland, and ^{198}Hg movement in the wetland? (3) How bioavailable for methylation and bioaccumulation will Hg from uplands and wetland be? (4) What biogeochemistry underlies the changes in Hg bioavailability through time and space? As the project moves forward, the third question will be key.

Ms. Kritee asked how the errors in stable isotope measurement were handled in terms of the addition of the ^{202}Hg isotope, which is also present in the ambient environment. Also, how do we know that some isotopes are not preferentially enriched? In response to the first question, Dr. Gilmour stated that the data represents the concentration of excess 202 over natural abundance, which involves matrix algebra and solving simultaneous equations. As to the second question, things as heavy as Hg do not undergo fractionation by enzymatic processes.

Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition?

Edward Swain, Minnesota Pollution Control Agency

Presented by Edward Nater, University of Minnesota

Dr. Edward Nater stated that the objectives of this research are to: (1) determine the relative importance of atmospheric, in-lake, and wetland sources of MeHg to a lake in a forested watershed; (2) determine MeHg net retention and/or source strength of different wetland types; and (3) conduct mesocosm (wetland and lake) and whole wetland experiments to elucidate methylation-enhancing processes. Specifically, it is important to answer two questions. First, in a forested watershed, what is the relative importance of various MeHg sources (in-lake methylation, transport from uplands/wetlands, release from lake sediments, atmospheric deposition)? Second, has MeHg become a larger fraction of the total Hg in aquatic ecosystems because of enhanced methylation rates stimulated as a result of higher rates of sulfate deposition?

Watershed-scale sulfate additions were conducted in the Marcell Experimental Forest, north of Grand Rapids, Minnesota. An irrigation system was built on one-half of a bog, with the upper half as a control and the lower half as the treatment area. The lower portion of the bog received sulfate doses four to five times a year, for a total (addition plus precipitation) of five times the atmospheric deposition. Bog well and weir samples were collected. The following conclusions resulted from the research: (1) enhanced sulfate deposition produces significant increases in MeHg in weir outflow and bog wells; and (2) this ombrotrophic bog is sulfate poor, so results may not transfer well to ground water-influenced wetlands that contain more sulfate. The significance of the findings are that: (1) enhanced sulfate deposition appears to significantly enhance net Hg methylation; and (2) reductions in atmospheric sulfate deposition *may* cause a decrease in environmental MeHg, but because there is no way to reduce the amount of sulfate in the system, this hypothesis cannot be tested empirically.

In spring 2003, there was a 3-week period of high MeHg levels, with hundreds of ng/L MeHg in weir outflows. A next step will be to conduct a laboratory study to examine whether the levels were real, and why this phenomenon occurred. There was an uncommon deep freeze in the bogs, so the hypotheses are that the system produced high MeHg in very cold conditions, or that the freezing resulted in a salt exclusion effect. Also, there are plans to add sulfate to the uplands rather than the bog, and to finish the mass balance for the lakes.

Dr. Gilmour commented that in Florida, reconstructed wetlands that were allowed to dry out produced enormous amounts of MeHg upon rewetting. Her laboratory studies suggest that when the soil is dry, the organic sulfur and inorganic sulfur pools in the soils oxidize; upon rewetting, the sulfate results in rapid production of MeHg. Dr. Nater responded that there is a 1/2-meter zone of dry out every year that refloods in the spring; he has not seen this effect yet, but he will look into it.

BIOGEOCHEMICAL CONTROLS ON MERCURY METHYLATION/DEMETHYLATION RATES

Mercury: Transport and Fate Through a Watershed

Jerome Nriagu, University of Michigan

Dr. Jerome Nriagu stated that the objective of this research is to investigate the role of photochemistry on the cycling of Hg in the Saginaw Bay watershed. Different parts of the Saginaw Bay watershed have different ecosystems (agricultural, wetland, and forested areas), and it is a fairly industrialized area. From the outer bay to Lake Huron there are well-defined chemical gradients, which may play a role in the cycling of Hg in the bay. The ambient airborne Hg levels and fluxes of Hg were measured at more than 40 sites throughout the watershed. Sampling sites included forest soils, agricultural soils, wetlands, city park soils, beach sands, and water samples from different parts of the bay.

Some of the significant results are that: (1) levels of total Hg in the watershed are typically very low; (2) the inner and outer bay differ in their nitrate, sulfate, and chloride concentrations, and this may be affecting Hg cycling in the watershed; (3) there are higher concentrations of total Hg and dissolved gaseous mercury (DGM) in the forested, western areas compared to the agricultural, eastern areas of the bay; (4) diel levels increase during the day in response to solar radiation, and water temperature does not play a significant role; (5) diel changes of DGM vary from day to day and from location to location, raising the question of how to model the production of DGM in a given body of water; (6) there is an increase in DGM production with sunlight upon the addition of ferric ion compared to the dark control, suggesting a link between the organic carbon cycle and the production of DGM; (7) the presence of humic acid increases the production of Hg(0) in the water column; (8) there is higher production of DGM in a closed system compared to an open system, and it cannot simply be concluded that most of the Hg is lost because there are other factors in the lake water that may be affecting production of DGM; and (9) upon heating, the majority of Hg is released below 350 °C, and all Hg is in the form of Hg(0).

The measurements lead to the overall conclusion that little of the mercury that is deposited in the Saginaw Bay is retained in the basin. This leads to the question of what the ultimate sink is for the majority of the Hg that is released in North America. It is possible that Hg is being deposited in the Arctic, a global sink. The next steps will include relating the diel variations to the biological and chemical activities at each location, and working out the photochemical mechanism (including the role of ferric ion) behind the reduction of mercuric ion to elemental mercury in the lake water.

Dr. Fitzgerald commented that although some Hg is going to the Arctic, there are many other contaminated systems (e.g., there is plenty of Hg in areas like the watersheds around mines). Dr. Nriagu agreed, but maintained that this still leaves a lot of Hg to be distributed to the atmosphere, which did not get deposited in the Saginaw Bay watershed. Dr. Fitzgerald added that the residence time for elemental Hg in the air is quite long, so it will be distributed rather broadly. Dr. Mason asked if in the thermal desoprtion experiments, Dr. Nriagu measured the sediment to ensure that all of the Hg had disappeared. Dr. Nriagu replied that a large percentage of the Hg was lost.

Chemical and Biological Control of Mercury Cycling in Upland, Wetland, and Lake Ecosystems in the Northeastern United States

Charles Driscoll, Syracuse University

Dr. Charles Driscoll stated that the objectives of this research are to: (1) quantify patterns of transport and transformations of Hg species in an upland northern hardwood forest through adjacent wetlands to the aquatic environment; (2) evaluate the processes and mechanisms controlling MeHg concentrations and transport in pore waters and surface waters in wetlands; and (3) develop and apply a lake/watershed Hg cycling model to a lake/watershed ecosystem. The Sunday Lake watershed, located in the Adirondack region of New York, was selected because it has different wetland types, and wetlands in the drainage area.

Ten surface-water monitoring sites were sampled at monthly intervals over 3 years at two upland forest sites and wetland sites around the watershed. The upland forest observations are that: (1) hardwood canopy is a sink for total Hg and a source of MeHg; (2) coniferous canopy is a source for total Hg and MeHg; (3) total Hg concentrations are elevated in foliage and litter; (4) concentrations of total Hg are elevated in forest floor solutions and decrease with depth in mineral soil; and (5) there is no soil pattern of MeHg. One focus of this study was the inputs of Hg via vegetation, in terms of the ultimate fate of the Hg (i.e., Is the Hg labile or retained in soil?). Preliminary results suggest that leaf litter is a sink for inputs of inorganic Hg. In the upland studies, the deciduous site has higher levels of Hg per unit carbon than the coniferous site, which is consistent with observations of high inputs of Hg via litter at the deciduous site. In the wetland studies, the highest total Hg concentration was found in *sphagnum spp.*, and Hg increases in the growing season were followed by marked decreases in the fall season prior to die off of the wetland vegetation. Bioconcentration factors in Sunday Lake are slightly lower than what has been reported, most likely due to the higher concentration of DOC at the site. The following overall conclusions were made: (1) wet deposition of total Hg and MeHg are similar to other values reported for eastern North America; (2) it appears that dry Hg deposition (litter + throughfall; 70%) greatly exceeds wet deposition (30%); (3) leaf litter retains total Hg over the short term; (3) the watershed is a sink for total Hg and a source for MeHg, and MeHg production is high in riparian wetlands; (4) the lake is a sink for total Hg and a source for MeHg; and (5) lake and yellow perch Hg concentrations decrease in response to decreasing deposition, according to the results of a watershed mercury model. Future work with the model will examine the difference between changes in mercury deposition and changes in sulfate inputs to the system.

Dr. Nriagu asked if the flux of Hg from the ecosystem to the atmosphere was measured, because he did not see it in the mass balance model. Dr. Driscoll responded that it was not done in this study; the land-atmospheric exchange will be examined in detail in the next study.

Dr. Gilmour inquired about the controls that were put on MeHg production in the model. The response was that there is a functional dependence on a number of parameters, and that the work is quite detailed.

Dr. Patricia Bresnahan asked about what is happening to the mercury being collected in the litter on the leaves, and if measurements were reported based on wet and dry biomass, or dry biomass. Dr. Driscoll responded that measurements were reported based on dry biomass. It is hard to know the ultimate fate of the Hg. Most of the studies in the literature do a single measurement for wetland vegetation over time; he was surprised at how much the concentrations decreased in the fall just before die off. A comparison between wet and dry biomass has not yet been done.

Physical and Chemical Processes Affecting Mercury Cycling

Processes Controlling the Chemical/Isotopic Speciation and Distribution of Mercury From Contaminated Mine Sites

Gordon Brown, Jr., Stanford University

Dr. Gordon Brown stated that mercury contamination is extensive at former Hg and gold mining operations; there is a huge input of Hg into the San Francisco Bay from the California Coast Range mines. An understanding of Hg speciation and sorption processes is critical to predicting the fate, transport, and bioavailability of Hg in mine-impacted regions, and can assist in the design and implementation of effective remediation strategies. The specific objectives of the characterization studies are to: (1) develop a method to determine Hg speciation in natural samples using extended X-ray absorption fine structure (EXAFS) spectroscopy; (2) characterize the effects of a number of variables (geological background, ore processing, particle size, distance from source) on Hg speciation; and (3) determine the macroscopic behavior and molecular-scale modes of Hg(II) sorption to goethite as a function of pH, choride, and sulfate. Different types of Hg deposits (silica carbonate, hot spring) and waste materials (calcines, condenser soot, distributed sediments, floc/precipitates, sieved fractions, waste rock) were sampled. The samples were analyzed in the laboratory using EXAFS and a linear combination fitting procedure, ore roasting, and transmission electron microscopy (TEM).

Conclusions from the speciation experiments are that: (1) EXAFS is an important technique for determining the *in situ* speciation of low-concentration, Hg-bearing samples; (2) mine wastes are composed mainly of HgS, but some contain environmentally-relevant proportions of more soluble Hg phases; (3) Hg speciation is influenced by the geologic origin of the ore, with Hg-chloride phases identified in samples from hot spring Hg ore deposits; (4) the ore roasting process appears to convert cinnabar to metacinnabar; (5) Hg concentration and % Hg-sulfides increase in calcines with decreasing particle size; and (6) Hg in mine wastes remains primarily in the solid phase during transport.

The conclusions for Hg sorption are that: (1) Fe- and Al-(hydr)oxides can play a significant role in the uptake of Hg(II) through direct inner-sphere sorption processes; (2) within the pH range typical of the natural environment, Hg(II) sorption is relatively constant among the substrates studies; (3) the presence of chloride results in reduced Hg(II) sorption, largely through the formation of stable $HgCl_2(aq)$ complexes; (4) the presence of sulfate results in enhanced Hg(II) sorption, largely through the reduction of electrostatic repulsion at positively-charged surfaces; (5) ternary surface complexation has been identified in the presence of chloride and sulfate; and (6) model systems appear to provide good correlates for understanding Hg(II) sorption processes in environmental aquatic systems.

The overall conclusions are that: (1) Hg speciation as determined by XAFS spectroscopy varies from mine site to mine site depending on the mine's geologic history, with some species more soluble and potentially bioavailable than others; (2) laboratory column experiments indicate that colloidal transport of Hg is an important dispersal mechanism for Hg in the environment; (3) Hg colloids identified by XAFS analysis include cinnabar and metacinnabar, those identified by TEM include hematite, jarosite, and a poorly crystalline aluminosilicate gel (the amount of Hg sorbed on these colloids appears to be small); (4) Hg(II) is strongly sorbed by Fe(III)-hydroxides and less strongly sorbed by Al-hydroxides in laboratory experiments (chloride greatly reduces Hg(II) sorption in both cases, while sulfate slightly enhances Hg(II) sorption on these hydroxides); (5) sorption processes involving Hg(II) do not appear to be as important in California Coast Range mine tailings environments as for other heavy metals such as lead or metalloids; (6) the light:dark ratio is greater in samples containing metacinnabar relative to samples containing just cinnabar; (7) flux measurements indicate that non-HgS phases such as HgO (montroydite) and eglestonite may be significantly larger contributors of gaseous Hg than HgS phases; (8) substrate Hg concentration and speciation appear to be dominant factors in controlling Hg atmospheric emissions from mine wastes; (9) ^{201}Hg/^{202}Hg isotopic ratios among Hg minerals from various mines show variations, suggesting that such ratios will not be useful in distinguishing among Hg from different sources; and (1) understanding mercury speciation and sorption processes is critical to predicting its fate, transport, and potential bioavailability in mine-impacted regions and can assist in the design and implementation of effective remediation strategies.

Research already underway includes an examination of particulate Hg to determine if it is a significant source of bioavailable Hg, and the identification of the species of dissolved Hg that are readily methylated by sulfate-reducing bacteria and why these species are preferred. Planned research will examine Hg uptake by plants in the South San Francisco Bay wetlands restoration project.

Dr. Francois Morel asked why Dr. Brown believes that the sorption of Hg on oxides would not stop methylation by bacteria. Dr. Brown responded that he is not certain whether it will stop methylation. He suspects that it will not because Hg is in an ionic form, bound to the surface by two bonds, and a bacterium could remove the Hg from the surface. Dr. Morel inquired about Hg sulfide, and Dr. Brown responded that he suspects a bacterium will have a more difficult time removing Hg from the surface of a sulfide than an oxide, although this could be debated.

Microbiological and Physicochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones

William Fitzgerald, University of Connecticut

Dr. William Fitzgerald stated that consumption of fish is the principal route of human exposure to MeHg. The overall objective of this research is to examine by field and laboratory investigation the physico-chemical/microbiological reactions and processes governing Hg cycling, speciation, and bioavailability in the waters and sediments of the Long Island Sound (LIS) and its watershed/coastal interface. Specifically, the goals of this research are to examine the bioavailability of Hg and its relationship to methylation, *in situ* Hg^0 production and emissions, organic complexation of Hg, sulfur and Hg interactions, and sedimentary Hg methylation. Field collection included an analysis of elemental Hg and sediment samples by electrochemistry measurements. It was determined that Hg emissions from the sound (80 kg/year) are a significant source of Hg to the coastal/continental atmosphere, approximately 35 percent of the Hg entering the sound is volatilized, and these emissions are principally anthropogenic (greater than 75 percent). An expanded spatial and temporal coverage of Hg distribution and speciation is needed, and complementary laboratory investigations of elemental Hg are needed to gain insight into processes and mechanisms.

The LIS MeHg budget suggests that MeHg is carried away from the sound by migrating organisms like fish, implying that the coastal zone can affect more than just the localized region. The following conclusions resulted from the research: (1) Hg methylation in LIS sediments is influenced by the availability of dissolved Hg(II) complexes, which is largely affected by organic matter; (2) seasonal effects on Hg methylation are apparent (e.g., temperature, relative activity of various bacterial groups); (3) bioturbation enhances Hg methylation and may be methylating some portion of the legacy Hg; and (4) much of the MeHg in LIS biota is attributable to sedimentary production. The information and hypotheses generated in this study are being applied to a comprehensive study of MeHg production and mobilization from sediments in the New York/New Jersey Harbor. Future research will involve an examination of MeHg production in sediments on the continental shelf, and an investigation into the significance of MeHg produced in near-shore and shelf sediments to the open ocean and its food web.

Dr. James Hurley asked about atmospheric inputs into the mass balance. Is it just wet bulk deposition, or are there local effects of reactive gaseous mercury (RGM) in the urban area? Dr. Fitzgerald responded that bulk collectors were set up for 14 months, presumably collecting RGM along the coast. There are two sources, local RGM associated with various high-temperature practices and elemental Hg production with RGM generated as a result of interaction with the bromine system. If it were matching with elemental Hg production, a very large increase in localized deposition of Hg in those collectors should be observed, but it was not. If it were relatively modest, like an RGM contribution to the wet deposition of 30 percent, that would be lost in the uncertainty. This is a good mass balance that can be constrained with other data, and the balance suggests that the RGM contribution is not large. However, a 30 or 40 percent addition could not be distinguished. Dr. Hurley said that the waste water inputs are interesting, and asked if it is just aqueous phase coming off, or if sludge inputs are considered. Dr. Fitzgerald responded that the number for the waste water contributions from the LIS is based on the modeling in the sound and an estimate of sewage inputs, and that the scale is huge.

Dr. Arnold Kuzmack commented that he is getting lower values for the amount of Hg in waste water, and he would like to sort out the differences. Dr. Fitzgerald responded that the values are not very high, and the number deals with sewage input into the Long Island Sound and cannot be applied nationally.

The Redox Cycle of Mercury in Natural Waters

Francois Morel and Eileen Ekstrom, Princeton University

Dr. Francois Morel presented a brief description of the redox cycle of mercury in natural waters. He discussed the redox of Hg in surface waters, the source of MeHg in the atmosphere, and the location of Hg methylation in the open ocean. The estimated daytime Hg^0 loss in coastal water is much larger from photo-induced oxidation than volatilization. Cows produce methane, but there is very little MeHg formed; therefore, cows are not important to MeHg budgets. The amount of Hg in yellowfin tuna in 1971 was compared to the amount found in tuna in 1998; over 30 years later, there was the same amount of Hg in tuna in 1998. Hg in tuna does not reflect changes in the atmospheric Hg, suggesting an alternate conclusion that MeHg in the ocean is coming from the deep ocean, and that Hg in tuna may be natural.

Dr. Eileen Ekstrom presented a presentation on the importance of understanding the biochemistry of MeHg. Methylation of Hg by sulfate-reducing bacteria (SRB) is the predominant system for MeHg production in fresh water and coastal systems, yet little is known about the physiology and biochemistry of Hg methylation in bacteria. Biochemical processes control the varying capacity of sulfate-reducing strains to methylate Hg, and may be the rate limiting step(s) in Hg methylation. The objective of this research is to examine the metabolic pathways, enzymes, and coenzymes responsible for Hg methylation in SRB. The research question to be answered is: Is the acetyl-CoA pathway the major route for Hg methylation in SRB? The research approach was toscreen SRB strains for the presence of key acetyl-CoA pathway enzymes and the ability to methylate Hg. Specific inhibitors of the acetyl-CoA pathway were tested to determine their effects on Hg methylation in pure culture. The data show that incomplete-oxidizing strains have CODH enzyme activities below the detection limit, and an inhibitor assay, using an inhibitor of the acetyl-CoA pathway, confirmed that this pathway is not used for Hg methylation. The overall conclusions are that: (1) four incomplete-oxidizing SRB strains do not use the acetyl-CoA pathway for Hg methylation; and (2) three complete-oxidizing strains that require the acetyl-CoA pathway for basic metabolism methylate Hg. In the majority of incomplete-oxidizing SRB strains tested, Hg methylation is independent of the acetyl-CoA pathway, and may not require vitamin B_{12}. It is possible that S-adenosyl-methionine could be the methylating coenzyme for MeHg production in SRB that do not use the acetyl-CoA pathway. Future research will continue to examine the role of methyl-transferring coenzymes, other than vitamin B_{12}, in MeHg production, and the pathways and enzymes responsible for Hg methylation.

Dr. Michael Aucott stated that he suspects that global Hg emissions from the 1970s are not very different from today, and so it is not much of a surprise that the Hg in tuna was the same. Dr. Morel responded that the global Hg emissions may not have changed much, but that this does not apply to the area of study.

Quantifying the Role of Significant Natural Sources and Sinks in the Biogeochemical Cycle of Mercury

Mae Sexauer Gustin, University of Nevada–Reno

Dr. Gustin stated that the objectives of the STAR research are to: (1) develop an understanding of the factors influencing emissions (Hg concentration in substrate, Hg speciation in substrate, light including shading, moisture, temperature) and develop algorithms for scaling; (2) develop a preliminary database on speciation of Hg in air above naturally-enriched sites; (3) develop a database of Hg fluxes for representative source areas for a variety of geologic settings; and (4) develop a framework for scaling up point source measurements to area estimates. The research was conducted by measuring Hg flux from terrestrial sources—including Hg mining districts, recent geothermal areas, sulfur banks, gold mining districts, oil and gas fields, and massive sulfide deposits in Nevada and California—using micrometeorological methods and dynamic field flux chambers, and through controlled laboratory studies using a gas exchange system. The results show that: (1) light, temperature, wind velocity, and precipitation, soil moisture, and shading significantly influence temporal patterns in emissions; (2) geologic factors, such as substrate Hg concentration, hydrothermal alteration, and the presence of heat sources and geologic structures, dictate the magnitude of emissions; (3) Hg emissions applied to natural Hg-enriched substrate in models are underestimated (a database of emissions currently in development for background sites shows fluxes similar to that applied to natural belts in models); and (4) reactive gaseous mercury (RGM) is approximately 1.5 percent of the Hg associated with naturally-enriched areas, is elevated above background concentrations at most sites, and may be directly emitted from the soil. The implications of this research are that naturally-enriched substrate is a more significant source of Hg than previously realized, and that background substrate emissions are similar to that predicted for global Hg belts. RGM is higher in naturally Hg-enriched areas. Also, with the recognition of the importance of atmospheric oxidation of Hg, all forms of Hg released to the atmosphere are significant in terms of potential environmental impacts. In the future, it is important to continue to investigate natural source emissions from geologic sources, fire, and vegetation; the role of background soils; the potential for elemental Hg deposition; re-emission; and the mechanisms controlling emissions.

Research funded by the U.S. EPA’s Experimental Program to Stimulate Competitive Research (EPSCoR) was designed to investigate Hg cycling between plants, soils, and the atmosphere using ecocells and ecopods. The data indicate that as plants leaf out whole ecosystem flux declines, and although the plants are assimilating Hg from the air, shading of the soil is the dominant factor influencing Hg flux. Following the successful demonstration that ecocells can be used to investigate Hg cycling, a grant was awarded by the National Science Foundation to examine vegetation-atmospheric Hg interactions using a tall grass pristine ecosystem. The overall conclusions are that: (1) plants can act as a source and sink of atmospheric Hg; (2) plants can exacerbate Hg emission from the soil to the air (in the tall grass prairie ecosystem, flux associated with vegetation was four to five times greater than soil Hg flux); and (3) shading can significantly reduce emissions and should be included in modeling Hg flux associated with forested systems. Future work will further investigate the role of plants as a sink for atmospheric Hg and a source of Hg to terrestrial and aquatic ecosystems, and the influence of vegetation on air-plant-soil Hg exchange.

Dr. Morel asked about the mechanism of Hg emission, which is season and light dependent. Dr. Gustin replied that with Hg sulfide and other minerals it is most likely photoreduction. Dr. Morel clarified that he would like to know about the mechanisms behind the photoreduction. For example, if there is some sort of temperature effect. Dr. Gustin responded that in plants there is a temperature effect, but with the emissions as a function of speciation, total temperature was controlled.

ADJOURNMENT

Mr. Stelz thanked everyone for their attendance at the conference.

U.S. EPA National Center for Environmental Research
STAR Mercury Fate and Transport Final Progress Review Workshop

Grand Hyatt Washington
1000 H Street, NW
Washington, DC 20001

November 21, 2003

Agenda

Friday, November 21, 2003

8:00 – 8:30 a.m. **Registration**

8:30 – 8:45 a.m. **Welcome and Introductory Remarks—Goals of the Progress Review**
William Stelz, U.S. EPA, Office of Research and Development, National Center for Environmental Research

Formation/Transport of Methylmercury in Ecosystems and Watersheds

8:45 – 9:15 a.m. Watershed Influences on Transport, Fate and Bioavailability of Mercury in Lake Superior
James P. Hurley, University of Wisconsin

9:15 – 9:45 a.m. Understanding the Role of Sulfur in the Production and Fate of Methylmercury in Watersheds
Robert P. Mason, University of Maryland

9:45 – 10:00 a.m. **Break**

10:00 – 10:30 a.m. Response of Methylmercury Production and Accumulation to Changes in Hg Loading: A Whole-Ecosystem Mercury Loading Study
Cynthia C. Gilmour, The Academy of Natural Sciences

10:30 – 11:00 a.m. Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition?
Edward B. Swain, Minnesota Pollution Control Agency
Presented by: Edward Nater, University of Minnesota

Biogeochemical Controls on Mercury Methylation/Demethylation Rates

11:00 – 11:30 a.m. Mercury: Transport and Fate Through a Watershed
Jerome Nriagu, University of Michigan

11:30 – 12:30 p.m. **Lunch**

12:30 – 1:00 p.m. Chemical and Biological Control of Mercury Cycling in Upland, Wetland and Lake Ecosystems in the Northeastern U.S.
Charles T. Driscoll, Syracuse University

Physical and Chemical Processes Affecting Mercury Cycling

1:00 – 1:30 p.m.	Processes Controlling the Chemical/Isotopic Speciation and Distribution of Mercury From Contaminated Mine Sites *Gordon E. Brown, Jr., Stanford University*
1:30 – 2:00 p.m.	Microbiological and Physicochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones *William F. Fitzgerald, University of Connecticut*
2:00 – 2:15 p.m.	**Break**
2:15 – 2:45 p.m.	The Redox Cycle of Mercury in Natural Waters *Francois M. Morel, Princeton University* *Presented by: Eileen Ekstrom, Princeton University*
2:45 – 3:15 p.m.	Quantifying the Role of Significant Sources and Sinks in the Biogeochemical Cycle of Mercury *Mae Sexauer Gustin, University of Nevada-Reno*
3:15 – 4:30 p.m.	**Questions and Discussion**
4:30 p.m.	**Adjournment**

U.S. EPA National Center for Environmental Research
STAR Mercury Fate and Transport Final Progress Review Workshop

Grand Hyatt Washington
1000 H Street, NW
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November 21, 2003

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Watershed Influences on Transport, Fate, and Bioavailability of Mercury in Lake Superior

James P. Hurley*[1, 2]*, Richard C. Back*[3]*, David E. Armstrong*[2]*, Helen Manolopoulos*[2]*,
***and Christopher L. Babiarz*[2]**

[1]*Aquatic Sciences Center, University of Wisconsin-Madison, Madison, WI;* [2]*Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI;*
[3]*Department of Biology, Lake Superior State University, Sault Ste. Marie, MI*

The goal of this study was to assess the importance of watersheds in controlling sources, transport, fate, and bioavailability of mercury (Hg) in a northern temperate lake system. Specific objectives of the study were to: (1) determine the speciation and bioavailability of Hg transported to Lake Superior by representative tributaries/watersheds; (2) determine the importance of watershed-specific characteristics (soil type, land use, surficial deposits) that control physical/chemical forms of Hg transported downstream; (3) identify key mechanisms controlling Hg bioavailability and speciation in nearshore zones relative to open lake regions; and (4) provide process-level information to complement concurrent development of Hg fate and transport models of the Lake Superior ecosystem.

The approach combined field and laboratory studies with modeling to assess the importance of watershed processes in controlling Hg fate and transport in Lake Superior. Each phase of the field studies, laboratory studies, and modeling efforts were strongly linked. Techniques developed and adapted by our group during previous projects ("clean" ultrafiltration, resin techniques, biota processing) were supplemented by newer techniques (stable isotope Hg analysis by ICP-MS; "clean" phytoplankton uptake experiments). Modeling efforts combine ongoing GIS-based watershed yield modeling with the Dynamic Mercury Cycling Model (D-MCM; EPRI, Tetra Tech, Inc.).

Field research focused on three separate efforts—studies in homogenous land cover sites within the watershed, estuarine mixing zone transects, and offshore cruises—to identify key sites for formation and food chain uptake of bioaccumulative methyl Hg in Lake Superior and its watershed. Sampling in contrasting homogeneous watershed subunits identified the importance of the streambed hyporheic zone as a site of methyl mercury (MeHg) formation to headwater streams and eventually transported to mixing zones of tributaries. Three cruises on Lake Superior revealed that Hg species concentrations are quite low in Lake Superior (0.49 ± 0.22 ng L^{-1} HgT), similar to Lake Michigan and oceanic waters. Surface water total Hg samples were elevated along the north shore in April 2000, indicative of river inputs during this high-flow period. During August 2000, methyl Hg (MeHg) averaged 6.4 ± 3.8 pg L^{-1} elevated levels in the western portion of the lake. Phytoplankton Hg analyses showed about a two to threefold enrichment of MeHg in riverine mixing zones versus offshore regions of the lake. Sediment sampling in offshore zones of the lake during 2000 reveal extremely low methylation rates (< 0.1% per day). These studies suggest that in-lake methylation occurred in the warmer, shallow sediments, whereas tributary MeHg was primarily supplied during the spring consistent with observed elevated MeHg in nearshore phytoplankton. Such observations imply that tributary MeHg is more available to the planktonic food Web than is MeHg from *in situ* sources.

Laboratory efforts were dedicated to assessing speciation effects on bioavailability of methyl mercury for planktonic uptake. A culturing and uptake method was developed successfully using "clean" freshwater media, Fraquil, and introduced Hg and MeHg to cultures of Selenastrum in the presence of various ligands and Lake Superior nearshore waters. Finally, the research work will continue with Tetra Tech, Inc., as they develop the EPRI-sponsored Lake Superior Mercury Cycling Model. The model will be calibrated with our results, and simulations will be run to determine long-term trends and various management scenarios for Lake Superior.

This research has allowed a preliminary mass balance of Hg and MeHg and a better understanding of Hg sources and sinks in Lake Superior (see Figure 1). Processes in the Upper Great Lakes appear to be analogous to coastal and offshore processes affecting Hg cycling and allow easier access for process-level work. The research group continues to work with the U.S. Environmental Protection Agency's Great Lakes Program Office on Hg-related issues in the Great Lakes. In addition, preparation is being made to summarize the research results on a Web-based interface that features various video clips of the Lake Superior research cruises.

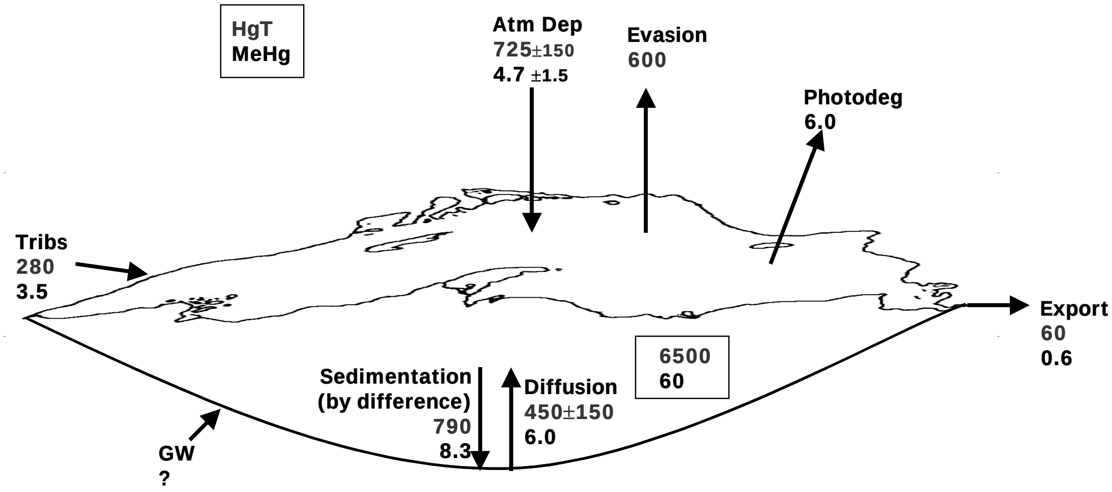

Figure 1. Rolfhus K.R., H.E. Sakamoto, L.B. Cleckner, R.W. Stoor, C.L. Babiarz, R.C. Back, H. Manolopoulos and J.P. Hurley. The distribution of mercury in Lake Superior. Reprinted with permission from *Environmental Science and Technology* 2003;37(5):865-872.

Factors Controlling the Production, Fate, and Transport of Mercury and Methylmercury in Aquatic Systems

Robert P. Mason[1], Andrew Heyes[1], Carrie Miller[1], and Cynthia Gilmour[2]

[1]Chesapeake Biological Laboratory, University of Maryland, Solomons, MD; [2]The Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD

The goals of this project were the careful and detailed examination of the controls over Hg methylation (Hg) and methylmercury (CH_3Hg) fate and transport and demethylation in aquatic systems. Specifically, the role of ligands and Hg complexation, especially the role of sulfide, in influencing Hg methylation was examined in detail. To improve the ability to understand the role of sulfide at low sulfide concentrations found in the environment, it was necessary to develop a new and novel technique of measuring low levels of sulfide (nM-µM) in natural waters. This was accomplished during this study. Overall, experiments have assessed how Hg complexation in solution, and with the solid phase, influences Hg methylation in sediments and, subsequently, how it influences the fate of the CH_3Hg produced (see Figure 1). To measure Hg speciation *in situ* in field samples, the technique of octanol-water partitioning of Hg that had been used previously in estimating bioavailability in laboratory studies at high concentration was refined. By the use of clean techniques and other modifications, it can now be used in environments where Hg levels are in the pM range. In addition, studies have examined the importance of reaction kinetics, in addition to thermodynamic controls, over Hg methylation as aquatic systems are often not at thermodynamic equilibrium. Laboratory studies have focused on determining the binding constants for Hg and CH_3Hg to solid phases, but field studies have measured the distribution of Hg across a diverse range of ecosystems, and the relative methylation potential of these systems. This project's research results have shown that there is a relationship between the measured short-term methylation rate upon spiking samples with Hg and the *in situ* CH_3Hg concentration. This relationship can be demonstrated from consideration of thermodynamic relationships and first-order kinetics. Furthermore, the relationship between Hg methylation and demethylation has been examined from a kinetic standpoint, and this has led to insights into the relative bioavailability of inorganic Hg(II) and $CH_3Hg(II)$ to these microbial processes. The importance of microbial community structure in Hg methylation is another important variable that was investigated using studies across ecosystems, and both spatially and temporally within an ecosystem. The overall focus of the study has been geared toward assessing if and why added ("new") Hg is more bioavailable than the exisiting Hg pool. A model that incorporates speciation and other factors to predict Hg bioavailability for methylation and CH_3Hg fate is being developed.

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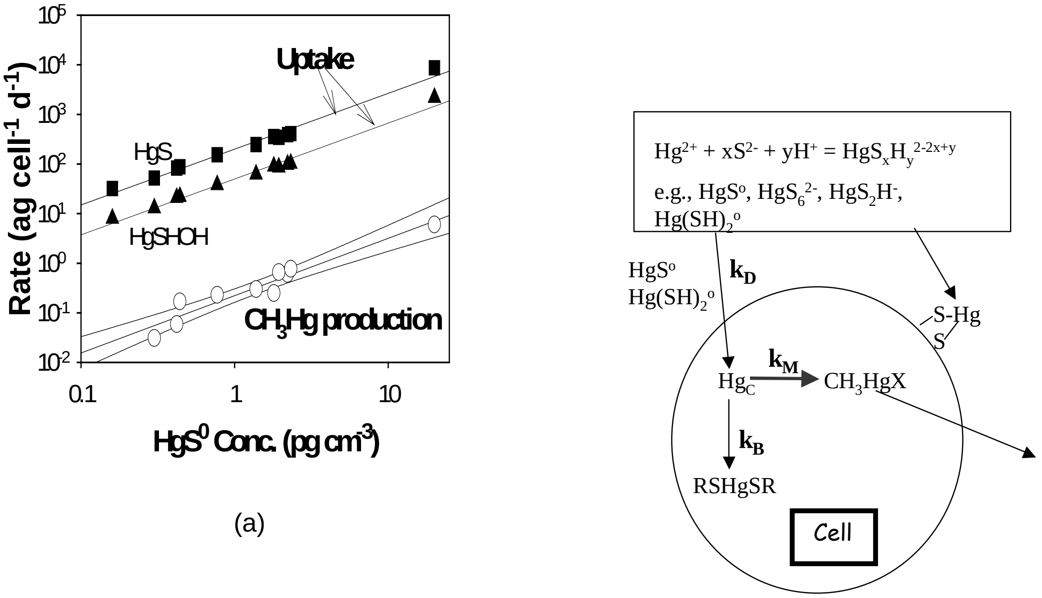

(a)

(b)

Figure 1. **(a)** Comparison of the estimated rate of uptake of neutral Hg sulfide complexes, estimates based on measured K_{OW} values and assuming that the complex is either HgS^0, or as has been suggested, $HgSHOH^0$. Solid symbols indicate estimated rate and concentration based on thermodynamic modeling. Methylation rates are plotted as the open circles. The uptake rate (k_D) is significantly greater than the methylation rate (k_M); **(b)** a diagrammatical representation of the principal processes that govern the rate of methylation by sulfate reducing bacteria exposed to Hg under sulfidic conditions. In this figure, the pathway and rate, k_B, is associated with Hg sequestration reactions within the cell that do not lead to Hg methylation. The overall rate of methylation is determined by the relative rate of these processes. Taken from Benoit et al. (2003).

Response of Methylmercury Production to Changes in Hg Loading: A Comparison of Hg Isotope Addition Studies

Cynthia C. Gilmour[1], Andrew Heyes[2], Robert P. Mason[2], Carrie Miller[2], and Michael Rearick[2]

[1]The Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD;
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This study attempts to answer the question, "How much does methylmercury in ecosystems change in response to a change in mercury loading?" Imbedded in this question are the issues of timing of response, magnitude of response, the influence of scale, and the differences in responses across watershed components. To address this question, two powerful techniques have been used that are novel to the Hg research community: (1) the use of stable Hg isotopes, and (2) the manipulation of systems of various sizes up a boreal lake and its watershed. The use of Hg stable isotopes allows the tracking of Hg spikes separately from Hg already accumulated in ecosystems.

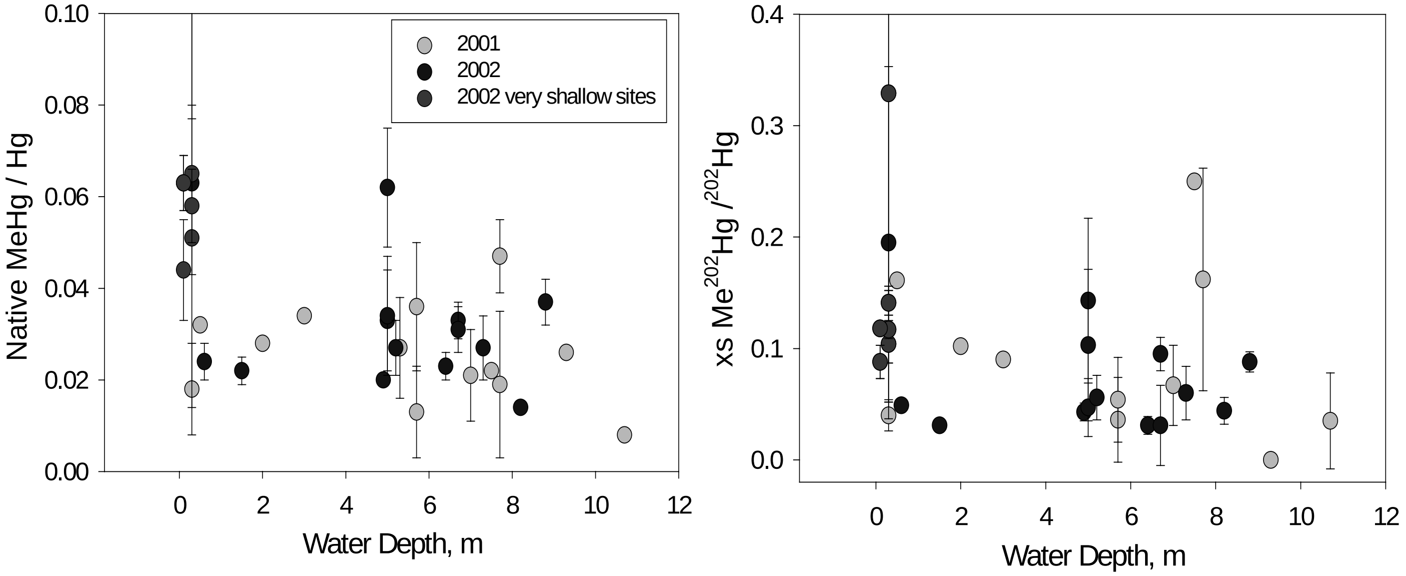
During the course of this study, Hg addition experiments were conducted at different scales and in two different ecosystems, the Florida Everglades and boreal watersheds at the Experimental Lakes Area in northwest Ontario. Some of the studies also examined the influence of sulfate, dissolved organic carbon, and the drying and rewetting of soils on methylation. The main METAALICUS study examined the response to Hg addition at the whole-ecosystem level. Hg stable isotopes were delivered to the entire catchment, including uplands, wetlands, and a first-order drainage lake. The L658 whole-ecosystem Hg addition began in 2001, and has continued with Hg stable isotope dosing at roughly four times the atmospheric deposition through 2003. Upland, wetland, and lake are dosed with separate isotopes to study behavior separately. In both the Everglades and METAALICUS studies, the U.S. Environmental Protection Agency's Science to Achieve Results (STAR) Program has funded the Hg methylation component of large, multi-investigator programs.

A general conclusion from all of the studies is that Hg newly deposited to zones of methylation is more readily converted to methylmercury (MeHg) than existing Hg pools. Mercury spiked into aquatic enclosures, and into L658 directly, was rapidly transported to the primary zone of methylation at the sediment surface. In all of the aquatic studies, a significantly larger fraction of this "new" Hg in surface sediments was found as MeHg relative to existing pools (See Figure 1 for an example from L658). The geochemical behavior of "new" Hg in sediments also is different than that of existing Hg pools, supporting the idea that recently deposited Hg is more bioavailable for methylation. A key question in the L658 study is the timing to reach a new equilibrium concentration of MeHg in sediments and biota. Through 2003, the concentration of $Me^{202}Hg$ (derived from the ^{202}Hg added directly to the lake surface) has continued to increase in surficial sediments, young of the year perch, and other matrices. However, the rate of increase in surface sediments appears to be slowing, suggesting that equilibrium with the new Hg load to the lake surface may be approaching.

The aquatic additions studies at various size scales have shown that the eventual amount of MeHg formed, and the timing of its formation, is highly dependant on the rate and magnitude of Hg delivery to zones of methylation. It appears that the more rapidly Hg is delivered to zones of methylation (generally sediments), the higher the fraction converted to MeHg. In studies where a range of Hg dosing rates were examined, the response in sediment MeHg production to Hg stable isotope doses was generally linear. However, the slope of the response varied dramatically among study sites.

Hg deposited to uplands and wetlands with dry surfaces is deposited away from zones of methylation. Further, Hg deposited to these areas at ELA has been very immobile in the 2 to 3 years since initial dosing. There appears to be little methylation of this Hg, and little or no transport of methylated isotope downslope. Mercury delivered to the surface of the wetland has not yet penetrated into the zone of methylation at the top of the water table, often 10-50 cm below the plant surface. However, Hg delivered to the lake surface has been extensively methylated in the L658 wetland, during times when lake level rise forced lake water horizontally into methylation zones in the wetland.

Overall, these studies show that the change in MeHg production in response to a change in Hg loading depends in large part on the timing and magnitude of transport to sites of methylation. Although little of the isotopic Hg delivered to the L658 uplands and wetlands has moved to date, budgets for ambient Hg strongly suggest that Hg deposited to uplands and wetlands are important contributors to MeHg in lake food webs. It is anticipated that transport and methylation of the Hg isotopes will be delivered to the upland and wetland in future years. The timing and magnitude of the movement, and subsequent bioavailability for methylation in the wetland and in the lake, will be critical to modeling the effects of changing Hg deposition on aquatic food webs.



Native MeHg/Hg

2001 avg = 0.023 +/- 0.009

2002 avg = 0.032 +/- 0.014

$Me^{202}Hg/^{202}Hg$

2001 avg = 0.091 +/- 0.074

2002 avg = 0.073 +/- 0.048

Figure 1. Methylation of newly deposited ^{202}Hg vs. existing Hg pools in L658 surface sediments.

Methylmercury Sources to Lakes in Forested Watersheds: Has Enhanced Methylation Increased Mercury in Fish Relative to Atmospheric Deposition?

Edward B. Swain[1], B.A. Monson[1], J. Jeremiason[2], P.L. Brezonik[3], E. Nater[3], J. Cotner[3], B.M. Johnson[3], N.A. Hines[3], D. Engstrom[4], J. Almendinger[4], and R. Kolka[5]

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[3]University of Minnesota, St. Paul, MN; [4]Science Museum of Minnesota, St. Paul, MN;
[5]U.S. Department of Agriculture, Forest Service, North Central Research Station, St. Paul, MN

This project hypothesizes that after WWII there was increased atmospheric deposition of sulfate enhanced mercury methylation and exacerbated Hg concentrations of fish in sensitive ecosystems. The specific objectives of this study are to: (1) conduct microcosm (wetland and lake sediment) and whole wetland experiments to elucidate the effect of increased sulfate loading; (2) establish the relative importance of atmospheric, in-lake, and wetland sources of MeHg to lakes in forested watersheds; (3) determine the net retention and source strength of different wetland types; and (4) delineate and classify wetlands in other watersheds, and estimate Hg and methylmercury watershed loads to the receiving lakes.

The hypotheses are being addressed in the mercury-sensitive region of north-central Minnesota, where more than 80 percent of assessed lakes are on the U.S. Environmental Protection Agency's list of "impaired waters" due to mercury contamination of fish. Utilizing the facilities of the Marcell Experimental Forest (MEF, USDA Forest Service), net methylation of mercury was compared in a variety of wetlands and in the sediments of Spring Lake. Field sampling was conducted at Spring Lake related to THg and MeHg mass budgets. The exports of THg and MeHg were quantified from six different wetland regimes. Enhanced methylation experiments were conducted in the laboratory. In addition, an irrigation system was constructed in one-half of S6, a black spruce-tamarack wetland to increase atmospheric sulfate deposition four times relative to the control half, and construction of a GIS wetland database was completed in the MEF and in 12 other watersheds.

Sulfate Addition Experiment to Wetland S6. Prior to the first sulfate (SO_4) addition, MeHg concentrations were similar between the control (0.47±0.10 ng*L^{-1}, n=12; mean ± one standard error) and experimental 0.52±0.05 ng*L^{-1}, n=18) halves. Following the first addition in May 2002, MeHg porewater concentrations increased to 1.63 ± 0.27 ng*L^{-1} in 2 weeks after the addition, resulting in a threefold increase. Subsequent additions in 2002 did not further raise porewater MeHg, but MeHg in the experimental half remained elevated relative to the control. MeHg concentrations in flow from the wetland increased following each SO_4 addition (see Figure 1). A second full year of sulfate treatments was completed in 2003.

Spring Lake Mercury Budgets. Quantification and modeling of evasion rates of elemental mercury were made during the daytime, yielding an average loss of 1.1 ng m^{-2} h^{-1} for 2001–2002. Photodegradation rates of MeHg were quantified and yielded loss rates of 0.4 y^{-1} in mid-July and 0.04 y^{-1} in mid-October. Profiles of MeHg in sediment porewater suggest that early in the year, there may be a small diffusive flux of MeHg from sediment to water (0.06 μg m^{-2} yr^{-1}). Several serum bottle experiments were performed with homogenized sediments to further investigate the relationship between net Hg methylation and factors such as carbon, nitrogen, and sulfur. These experiments indicate that in these lake sediments, mercury availability is a major factor in net methylation, based on the addition of mercuric ion or the reduction of Hg availability by the binding with sulfides.

Research results clearly demonstrate that: (1) wetlands are relatively strong sources of methylmercury to lakes, and (2) sulfate additions to wetlands enhance methylation and increase MeHg export from the wetland, suggesting that decreasing sulfate deposition rates would lower MeHg export from wetlands. Lower MeHg export would likely result in lower mercury concentrations in the fish of receiving waters.

The next steps for this research project are to: (1) quantify the effect of chronically increased sulfate loading on net methylation rates; can we predict how much less methylmercury is exported due to post 1990 Clean Air Act reductions in atmospheric sulfate deposition? (2) study the details of how sulfate stimulates net methylation, including methylation, demethylation, sulfate reduction, and the fate of the added sulfur; and (3) utilize the new knowledge on in-lake methylation and methylmercury export from wetlands in computer models of mercury in a variety of lakes; does our new knowledge allow us to better predict which lakes will have elevated mercury in fish?

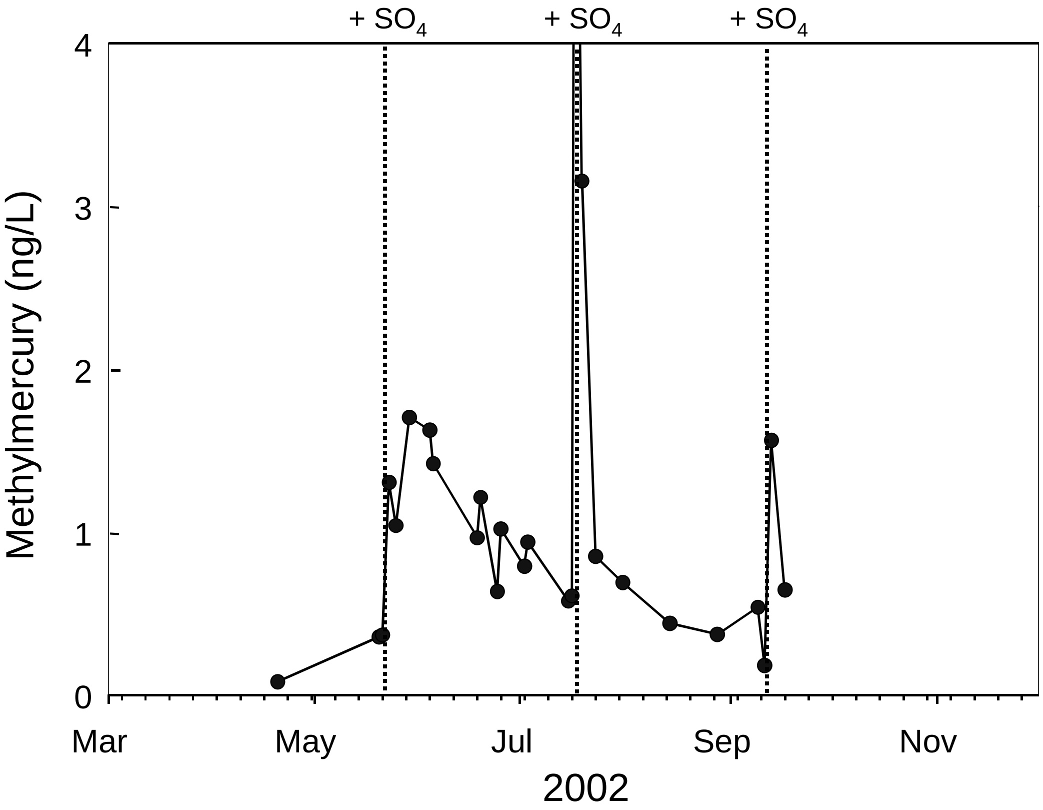

Figure 1. Concentration of methylmercury in water flowing out of the S-6 wetland, half of which had been experimentally treated with sodium sulfate to mimic a 4x increase in atmospheric sulfate deposition. The sulfate doses (vertical dotted lines) were added with an irrigation system.

Cycling of Mercury in Saginaw Bay Watershed

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This project is designed to evaluate the role of photochemistry on the cycling of mercury in Saginaw Bay watershed. Focus of the investigations includes photodependent biotic, abiotic, physical, or chemical processes, and the reaction mechanisms of interest may be homogeneous or heterogeneous. The transect from Saginaw Bay to Lake Huron system has well-defined gradients in chemical parameters (including chlorophyll-α, dissolved organic carbon, phosphorus, nitrogen, chloride, and suspended particulates), trophic conditions, taxonomic composition and biomass, and provides a unique site for the study. The ambient airborne Hg levels and fluxes of Hg were measured at many sites covering forest soils, agricultural soils, wetlands, city park soils, beach sands, and industrial/municipal waste dumps. In addition, the Hg levels were measured in soil samples from the stations and in water samples from the rivers and various parts of the Saginaw Bay. From the survey data, a number of sites were selected, which were intensively monitored over a period of time. This research project focuses on the following: (1) inventory of tributary input of mercury into Saginaw Bay; (2) Diel changes of dissolved gaseous mercury (DGM) in nearshore surface waters of Saginaw Bay; (3) dark oxidation of DGM in the water from surface shorewater of Saginaw Bay; (4) photoreduction of Hg(II) in water samples from Saginaw Bay studied in the laboratory with and without spikes of photoactive chemicals; (5) estimated rates of air/water exchange of Hg in aquatic environments in the watershed; and (6) thermal desorption of Hg from Saginaw Bay area in relation to the likely effects of forest fires on release of Hg from the area. The measurements led us to conclude that little of the mercury that is deposited in Saginaw Bay is retained in the basin. This raises the question, “What is the ultimate sink for much of the mercury that is released in North America?”

Chemical and Biological Control of Mercury Cycling in Upland, Wetland, and Lake Ecosystems in the Adirondack Region of New York

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A detailed study was conducted on the biogeochemistry of mercury (Hg) at Sunday Lake, a forested wetland/lake/watershed in the Adirondack region of New York. The objective of this study was to improve understanding of the inputs, transport, transformations, and fate of Hg in upland forest, wetland, and lake ecosystems. To accomplish this objective, a detailed watershed mass balance study was conducted, including measurements of wet deposition, throughfall, litterfall, soil, soil water, vegetation, wetland porewater, hydrology, surface water chemistry, and aquatic biota. Wet Hg deposition was 10.8 $\mu g/m^2$-yr, with 0.6 percent occurring as methyl Hg. Forest vegetation was important in mediating the inputs of Hg to the forest floor. Inputs of total Hg from litterfall and throughfall greatly exceeded wet Hg deposition, suggesting that dry deposition is the dominant Hg input to this forest ecosystem. Concentrations and fluxes of total Hg were elevated in forest floor leachate, with soil solution concentrations decreasing in the mineral soil. Likewise, soil concentrations of Hg were highest in the forest floor (13-188 ng/g), and decreased with increasing depth in the mineral soil. Concentrations of Hg in surface waters ranged from 1.9 to 4.6 ng/L, with methyl Hg concentrations from 0.2 to 2.53 ng/L. Atmospheric Hg deposition was retained in the watershed.

Sunday Pond is a sink for inputs of total Hg. However, the watershed, particularly riparian wetlands, and the lake were net sources of methyl Hg to downstream surface waters. Concentrations of Hg increased with each trophic level in the aquatic food chain. Mercury bioconcentration factors were lower in zooplankton and in fish than have been reported in other studies, probably due to binding of methyl Hg with high concentrations of organic solutes. The Hg biogeochemistry data have been used to calibrate the Mercury in Adirondack Wetlands Lakes and Terrestrial Systems (MAWLTS) Model for the site. The project team is currently completing the final report and a series of articles for a peer-reviewed journal.

Processes Controlling the Chemical Speciation and Distribution of Mercury From Contaminated Mine Sites

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The major objectives of this project are to: (1) determine the chemical speciation and relative abundance of different forms of Hg in mine wastes from the California Coast Range; (2) investigate the role of colloidal transport as a mechanism for dispersal of Hg from waste sites; (3) identify the mode of Hg sorption in downstream sediments and fine-grained precipitates; (4) determine the effects of complexing ligands on the desorption and sorption inhibition of Hg; and (5) measure and correlate the emission of Hg into the atmosphere with Hg speciation, climate, and geologic factors. A combination of synchrotron-based x-ray absorption fine structure (XAFS) spectroscopy, scanning (SEM) and transmission electron microscopy (TEM), x-ray powder diffraction, and selective chemical extractions have been used to determine the molecular-scale speciation of Hg in different size fractions from mining wastes and in colloidal fractions from column experiments designed to examine the colloidal transport and speciation of mercury (see Figure 1). The speciation of Hg has been determined in mine wastes from a number of abandoned Hg-mines in the California Coast Range, finding that highly insoluble cinnabar and metacinnabar are the primary minerals present. In addition, a number of highly soluble Hg-containing species have been identified, including mercuric chloride ($HgCl_2$), montroydite (HgO), schuetteite ($Hg_3O_2SO_4$), and terlinguite (Hg_2OCl), which may be disproportionately larger contributors of ionic Hg to the surrounding environment than the mercuric sulfides.

One key finding from the laboratory column experiments, coupled with XAFS spectroscopy and TEM, is that most of the colloids are cinnabar or metacinnabar, which is surprising in light of the widely held belief that most heavy metals attach to colloidal particles as sorption complexes. Although Hg(II) forms strong, inner-sphere adsorption complexes on Al- and Fe-oxyhydroxide particles in laboratory sorption/XAFS studies, significant amounts of sorbed Hg(II) have not been detected in natural samples from these mine sites. Potential connections have been explored between Hg speciation and the extent of gaseous Hg emissions from mine wastes employing the spectral databases that we have generated using XAFS spectroscopy (Stanford Group) and controlled flux measurements at a number of localities (University of Nevada, Reno Group). Hg emissions were measured on the same samples on which XAFS measurements were performed at constant temperature under both light and dark conditions based on the known ability of light to increase Hg flux rates. Significant results from the comparisons of Hg speciation and Hg emissions include the finding that the light:dark ratio is greater among samples containing metacinnabar (HgS, cubic) relative to samples containing just cinnabar (HgS, hexagonal) (i.e., light enhancement is more pronounced in samples containing metacinnabar). This finding has implications for the atmospheric release and cycling of Hg from specific types of mine wastes, particularly since our previous XAFS studies have shown that calcines (roasted ore) typically contain high proportions of metacinnabar, which is generated by the ore roasting process. The flux measurements indicate that non-HgS phases such as HgO and $Hg_3Cl_3O_2H$ may be significantly larger contributors of gaseous Hg than HgS phases. Therefore, regions with appreciable Hg-oxides and Hg-chlorides, such as hot-spring type Hg deposits, may be of more concern regarding atmospheric Hg emissions than areas where HgS dominates. The most recent and continuing focus of this project has been on determining the effect of simple low molecular weight organic acids generated by plants in revegetated Hg-mine environments on the dissolution of Hg-containing minerals.

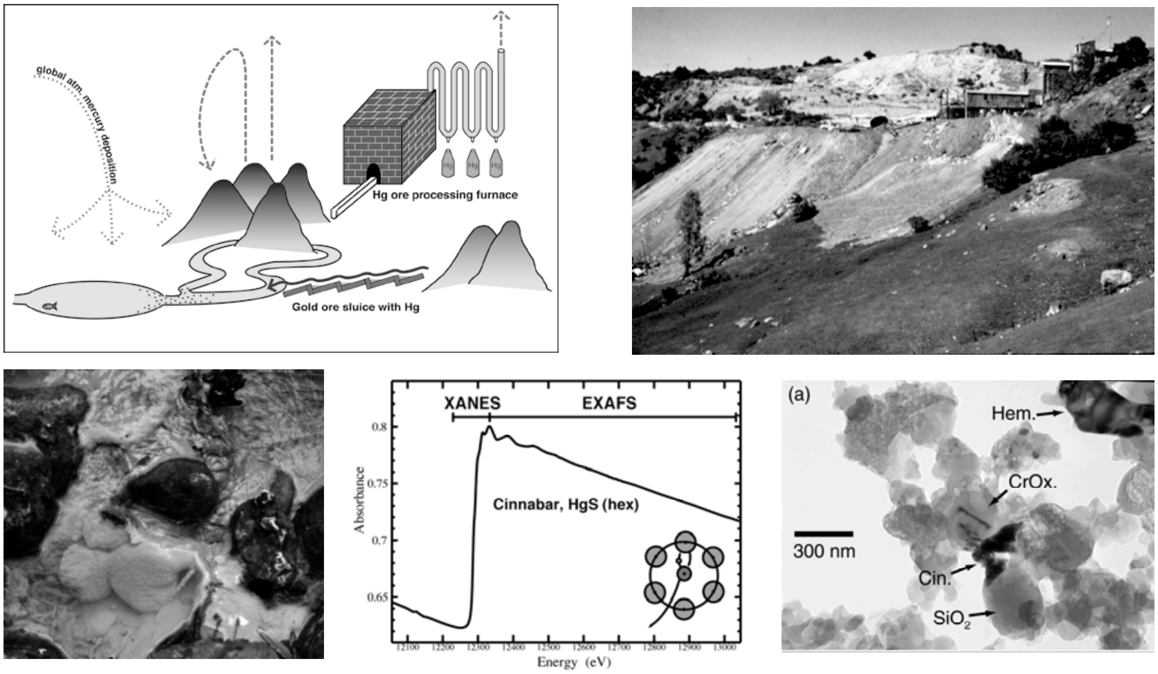

Figure 1. Speciation and distribution of Hg in mine wastes.

Mercury and Methylmercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones

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Consumption of marine fish and seafood products is the principal pathway by which humans are exposed to the very toxic organo-mercurial, methylmercury (MeHg). Thus, biologically productive nutrient-rich nearshore regions, which support major commercial and recreational fisheries, are of special interest. This U.S. Environmental Protection Agency's Science to Achieve Results Hg research project is focused on one of the "Great Waters" of the United States, Long Island Sound (LIS). A comprehensive field and laboratory investigation has been conducted of the physicochemical/microbiological reactions and processes controlling Hg cycling, speciation, and bioavailability in the waters and sediments of LIS and its watershed/coastal water interface (i.e., Connecticut River; East River). The specific objectives are focused on major features of the aquatic biogeochemistry of Hg, particularly MeHg production, elemental mercury (Hg^0) cycling and emissions, interactions between terrestrial watersheds, rivers and nearshore marine waters, and the role of organic matter in governing the bioavailability Hg for competing methylation/reduction reactions. Several important accomplishments will be emphasized, as they affect our understanding of the behavior and fate of methyl and inorganic Hg in the marine environment.

This project hypothesized and confirmed that: (1) *in situ* sedimentary production is the primary source of MeHg to the waters and biota of LIS, and (2) rates of MeHg production depend on the activity of methylating bacteria and availability of inorganic Hg. Potential rates of Hg methylation were greatest in mid-summer (i.e., greatest bacterial activity) and varied spatially in LIS sediments. MeHg production was related inversely to sedimentary organic matter, which is a major control on the partitioning and subsequent bioavailability of inorganic Hg in the low-sulfide pore waters of LIS. Potential rates of MeHg production were related inversely with the distribution coefficient (K_D) of inorganic Hg and positively with the concentration of inorganic Hg in pore waters. Based on diffusional flux estimates, *in situ* sedimentary production is the dominant source of MeHg to LIS (see Figure 1). This flux is likely to be enhanced by infaunal mixing of sediment; a process that we suspect also promotes Hg methylation. Because *in situ* production is the major source of MeHg to LIS, then by extension, it should be the principal source in other comparable near shore systems. In addition, sedimentary methylation can account for most of the MeHg in primary producers of LIS.

This project's research results indicate that most Hg is associated with organic matter in river water and seawater. New and innovative measurements have been conducted to establish the nature and bonding strength of these Hg-organic matter associations. Results indicate that Hg complexing agents are present in the dissolved-phase (< 0.2 µm) at ca. $<$ 1-30 n*N*, with log conditional stability constants (log K') in the range of 22–25. Such ligand characteristics explain why the majority of ionic inorganic Hg dissolved in fresh and saltwaters is associated with organic complexes (> 99% in freshwater, > 50% in seawater). Further, terrestrially derived and marine derived complexing ligands appear to be equally important in LIS.

In addition, the prominent role of Hg^0 production and evasion has been confirmed in an important coastal ecosystem. Annual Hg emissions from LIS are estimated at 80 kg, which is comparable to fluvial inputs. Indeed, about 35 percent of the Hg input (240 kg/y) to LIS is remobilized to the atmosphere. This flux is principally anthropogenic, as most (> 70%) Hg entering LIS has a pollution origin. Production of Hg^0 competes with the *in situ* biological synthesis of MeHg. This work is designed to increase understanding of *in situ* Hg^0 production and emissions and their role in aquatic and atmospheric Hg cycles, which will help constrain Hg biogeochemical cycling and mixing models.

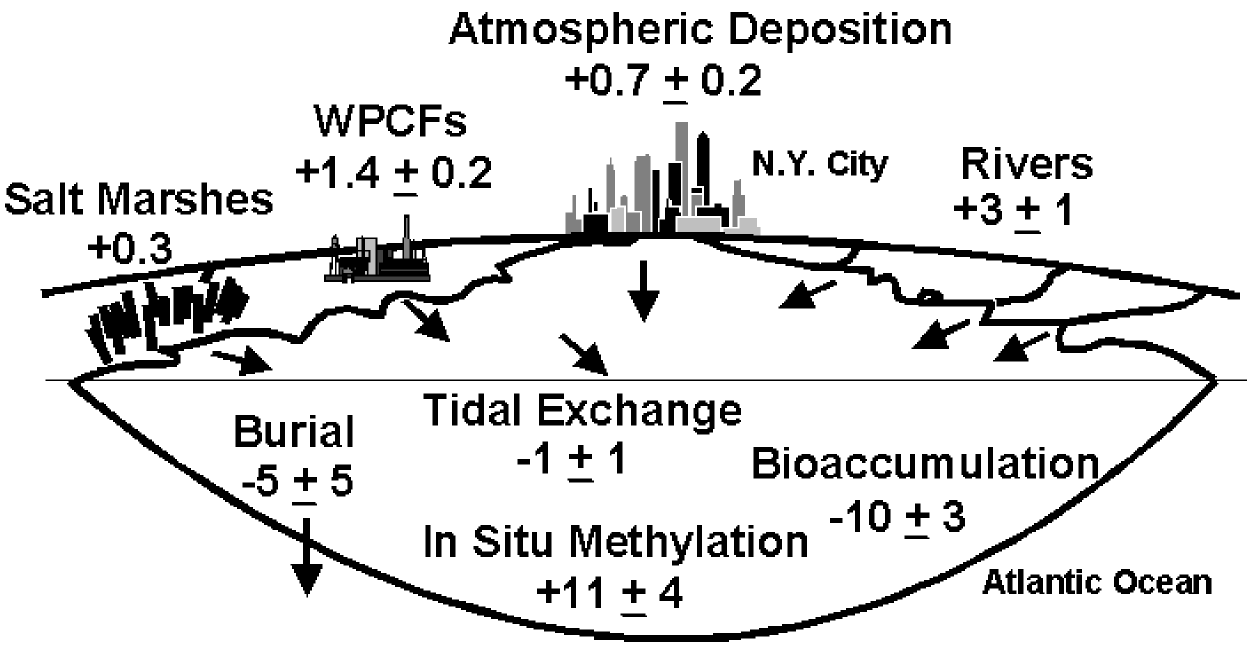

Figure 1. Estimated current methylmercury mass balance for Long Island Sound. In: Balcom, et al. Mercury sources and cycling in the Connecticut River and Long Island Sound. *Marine Chemistry* (Submitted).

Pathways, Enzymes, and Trace Metals: The Importance of Understanding the Biochemistry of Mercury Methylation

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Mercury methylation by sulfate-reducing bacteria (SRB) is the predominant mechanism for methylmercury production in freshwater and coastal systems, yet little is known about the physiology and biochemistry of Hg methylation in SRB. Understanding the metabolic pathways for mercury methylation, the enzymes responsible, and the coenzyme requirements is critical to understanding the basis for methylmercury formation and to designing successful strategies for its mitigation in the environment.

The biochemistry of SRB can vary significantly between groups, with some SRB genera (incomplete-oxidizers) only capable of the catabolic conversion of carboxylic acids to acetate, while complete-oxidizing SRB oxidize reduced carbon substrates all the way to CO_2 via the citric acid cycle or the acetyl-coenzyme A (CoA) pathway. Previous research on one incomplete-oxidizing SRB strain, *Desulfovibrio desulfuricans* LS, implicated the corrinoid-containing enzyme in the acetyl-CoA pathway, presumably a minor biosynthetic pathway in this strain, as being key to mercury methylation. To assess whether the acetyl-CoA pathway is the controlling biochemical process for methylmercury production in SRB, five incomplete-oxidizing SRB strains and two *Desulfobacter* strains that do not use the acetyl-CoA pathway for major carbon metabolism were assayed for methylmercury formation and acetyl-CoA pathway enzyme activities (see Table 1). Three of the SRB strains also were incubated with chloroform to inhibit the corrinoid-containing enzyme in the acetyl-CoA pathway. So far, all species that have been found to have acetyl-CoA activity are complete oxidizers that require the acetyl-CoA pathway for basic metabolism, as well as methylate mercury. Chloroform inhibits Hg methylation in these species either by blocking the methylating enzyme or by indirect effects on metabolism and growth. However, four incomplete-oxidizing strains have been identified that clearly do not utilize the acetyl-CoA pathway either for metabolism or mercury methylation (as confirmed by the absence of chloroform inhibition). Hg methylation is thus independent of the corrinoid-containing enzyme in the acetyl-CoA pathway and may not require vitamin B_{12} in some and perhaps many incomplete-oxidizing SRB strains.

Vitamin B_{12} has been long considered to be the Hg methylating coenzyme in the enzymatic formation of methylmercury, because it was believed to be the only major methylating coenzyme that would donate a methyl–carbanion group able to bind with inorganic mercury. In addition, vitamin B_{12} can methylate mercury abiotically, and a corrinoid compound was found to be important in the methylation of Hg by *Desulfovibrio desulfuricans* LS. Currently, investigation of the role of vitamin B_{12} in mercury methylation is being conducted in the incomplete-oxidizing strain *D. africanus*.

Table 1. Relationship between Hg methylation capacity and presence of the acetyl-CoA pathway.

Genus	Species	Hg Methylation	Acetyl-CoA Pathway[a,b]
Incomplete Oxidizer			
Desulfovibrio	*africanus*	yes	< D.L.
	desulfuricans LS	yes[c]	yes[c]
	desulfuricans subsp. desulfuricans	< D. L.[d]	< D.L.
	vulgaris subsp. vulgaris Marberg	< D. L.	< D. L.
Desulfobulbus	*propionicus 1pr3*	yes	< D. L.
	propionicus MUD	yes	< D. L.
Desulfobacter	*BG-8*	yes[f]	< D. L.
Complete Oxidizer			
Desulfococcus	*multivorans 1be1*	yes	yes
Desulfosarcina	*variabilis 3be13*	yes[d]	yes[e]
Desulfobacterium	*autotrophicum*	yes[d]	yes[e]
Desulfobacter	*hydrogenophilus*	< D. L.[d]	< D. L.[e]
	curvatus	< D. L.	< D. L.

[a] < D. L., less than detection limit.
[b] The presence of the acetyl-CoA pathway determined based on positive CODH activity.
[c] Choi et al., 1994a.
[d] Gilmour et al., in preparation.
[e] Shauder et al., 1986.
[f] King et al., 2000.

Quantifying the Role of Significant Natural Sources and Sinks in the Biogeochemical Cycle of Mercury

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Mercury (Hg) is considered a global pollutant because of its presence as a volatile phase, which facilitates transport and distribution via the atmosphere pathway. To assess the local, regional, and global impacts of atmospheric Hg, significant sources and sinks must be identified and their role quantified. Work associated with two research projects at the University of Nevada (UNR) funded by the U.S. Environmental Protection Agency's (EPA) Science to Achieve Results (STAR) Program on "Light enhanced Hg volatilization from substrate: mechanisms responsible and *in situ* occurrence" and "Processes controlling the chemical/isotopic speciation and distribution of Hg from contaminated mine sites," focused on developing a quantitative understanding of the factors influencing Hg emissions from HG-enriched substrate; developing a database of emissions from representative source areas; developing a preliminary database on the speciation of Hg in the air above Hg-enriched sites; and providing a framework for scaling up Hg emissions for area sources. Research questions were addressed by measuring Hg flux from terrestrial sources using micrometeorological methods and dynamic field flux chambers, and through controlled laboratory studies using a gas exchange system. This work has led to the recognition that broad areas of natural Hg enrichment are a more significant source of atmospheric Hg than previously realized (see Figure 1). Other research has indicated that there are previously unrecognized diffuse sources of atmospheric Hg (landfills, forest fires, sewage sludge amended soils). With this new information on sources, the question arises, "Are there unrecognized sinks?" Research funded by the U.S. EPA's Experimental Program to Stimulate Competitive Research (EPSCoR) at UNR and Desert Research Institute focused on addressing the role of plants in the biogeochemical cycle of Hg using two state-of-the-art 7.3 x 5.5 x 4.5 m (L x W x D) open flow enclosed mesocosms. This project demonstrated that plants can act as a sink for atmospheric Hg and as a pathway by which Hg derived from the atmosphere may be transferred to terrestrial ecosystems.

These three research projects have developed important information that may be applied towards assessing the role of natural sources in the global Hg budget and have advanced the understanding of the biogeochemical cycle of Hg. This information is important for determining the need for and the effectiveness of controls for major anthropogenic sources of Hg such as coal-fired utility boilers.

This work may be and has been used to impact regulatory and management decisions at local and regional scales. In addition, it has been used for assessment of the health hazards for Hg exposures via the atmospheric pathway at Hg-contaminated mine sites; assessment of the impact of releases from Hg-enriched substrate on local ecosystems; and development of remediation strategies for Hg-enriched areas based on quantified Hg releases. The better understanding of the significance of plants as a pathway for Hg to be transferred to terrestrial ecosystems is important information for watershed management decisions associated with Hg-impacted ecosystems and watersheds with fish consumption advisories for Hg.

Research from these projects has significantly furthered the understanding of the role of natural sources in the biogeochemical cycling of Hg and revealed significant data gaps that still need to be addressed. To fill some data gaps, current research at UNR funded by the U.S. EPA STAR program is focusing on generating data that will allow us to develop a natural source emission estimate for the United States and a more complete understanding of atmospheric Hg-lithosphere interactions. Additional work funded by the National Science Foundation is focused on furthering the understanding of plant-soil-atmosphere Hg exchange.

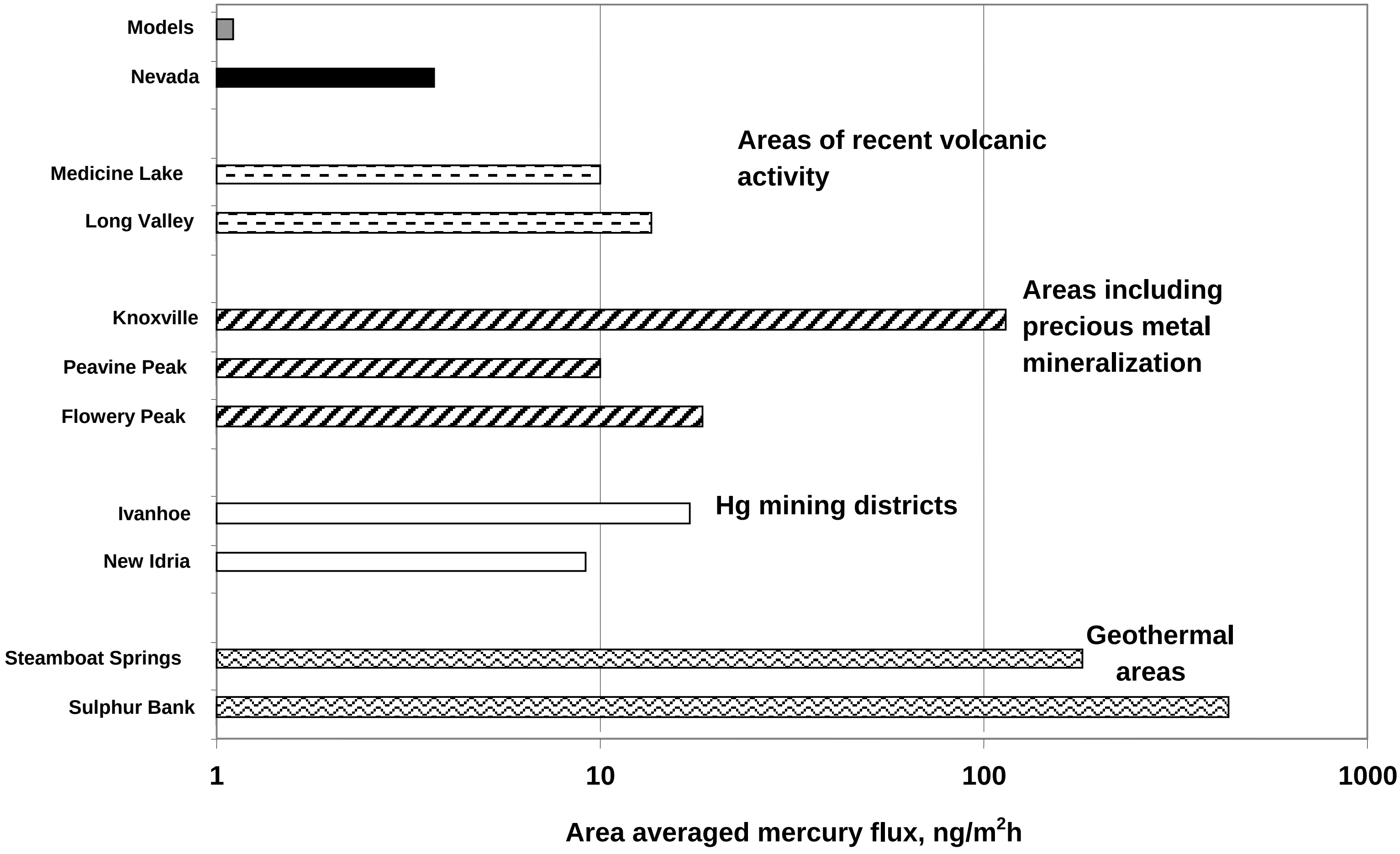

Figure 1. Mercury emissions for a variety of types of natural source areas. The “models” value represents that estimated for global belts of Hg-enriched substrate.

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