

Chemical and Biological Control of Mercury Cycling in Upland, Wetland and Lake Ecosystems in the Northeastern U.S.
EPA Grant Number: R827633 Title: Chemical and Biological Control of Mercury Cycling in Upland, Wetland and Lake Ecosystems in the Northeastern U.S.

Project Period: November 1, 1999 through October 31, 2002 (Extended to October 31, 2003)

Description:

Widespread contamination of mercury in remote aquatic environments due to atmospheric deposition, and consequent high concentrations in the biota, demand an improved understanding of the mechanisms of mercury transformations and cycling in lake/watershed ecosystems. Previous studies have reported elevated concentrations of mercury in the water column and in fish in lakes in the Adirondack region of New York. Concentrations of mercury in fish tissue have been shown to increase with decreasing pH, suggesting a link between mercury accumulation and surface water acidification. Lakes which receive drainage from wetlands are characterized by high concentration of methylmercury because of elevated rates of methylation that occur in these environments but low bioconcentration of mercury in fish due to the supply of dissolved organic carbon which decreases the bioavailability of methylmercury. Recent paleolimnological studies have shown marked (3.5x) increases in sediment mercury deposition since 1850, suggesting that increases in atmospheric mercury deposition have contributed to the regional contamination of mercury. Moreover, these studies suggest that watershed retention of mercury has decreased markedly over the last 60 years, from 95% retention of atmospheric mercury deposition in the 1930s to 75% retention today. As a result there is an acute need to clarify the chemical and biological processes regulating the transport, fate and bioavailability of mercury in soft-water lake/watersheds of the northeastern U.S., and to develop and apply a simulation model to depict these processes.

Objective:

A detailed project was conducted on the biogeochemistry of mercury (Hg) at Sunday Lake, a forested wetland/lake/watershed in the Adirondack region of New York. The overall objective of this study was to improve understanding of the inputs, transport, transformations, and fate of Hg in upland forest, wetland, and lake ecosystems. The specific objectives of the research project were to: (1) quantify patterns of transport and transformations of mercury species in an upland northern hardwood forest through adjacent wetlands to the aquatic environment; (2) evaluate the processes and mechanisms controlling methyl Hg (CH₃Hg⁺) concentrations and transport in pore water and surface water in wetlands; (3) evaluate historical patterns of Hg dynamics in soft-water lakes; and (4) develop and apply a lake/watershed Hg cycling model to a lake/watershed ecosystem.

Summary/Accomplishments:

Watershed measurements were taken, and a 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. Sediment cores also were collected from eight lakes in the region to investigate historical patterns of Hg deposition. Finally, a Hg cycling model was developed and applied to Sunday Lake watershed.

Wet Hg deposition was 10.3 µg/m²-year, 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 70 percent of the total Hg input to this forest ecosystem. The pathway of Hg inputs differed between coniferous and deciduous plots. Total Hg inputs at the coniferous plot largely occurred via throughfall, whereas litterfall dominated Hg inputs at the hardwood plot. 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. 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.

Concentrations of total Hg and ²¹⁰Pb date were determined in sections of sediment cores collected from eight lakes in the Adirondacks. Although there were lake-to-lake variations, on average, sites showed a 5.8-fold increase in sediment Hg deposition from background values (before 1900) to peak values. Hg deposition peaked (from 1973 to 1995) and decreased in recent years. Current sediment Hg deposition is 3.5 times background values. For a given year, sediment Hg deposition increased with increasing watershed area to lake surface area. Conducting this analysis for preanthropogenic conditions, we estimated the deposition of Hg to the surface of a perched seepage lake (i.e., watershed area to lake surface area of one) was 3.4 + 1.0 µg/m²-year. For modern conditions, we determined the deposition of Hg to the surface of a perched seepage lake was 8.6 + 2.4 µg/m²-year; a value similar to current estimates of wet Hg deposition. Using sediment deposition data across the project lakes, it appears that the retention of Hg in Adirondack lakes and watersheds has been decreasing over the past 200 years. The mechanism responsible for this decline is unclear.

The Hg biogeochemistry data collected in this project were used to develop and calibrate the Mercury Cycling Model for headwater drainage lakes. Hypothetical calculations have been conducted to evaluate the response of Sunday Lake to decreases in atmospheric Hg deposition.

The Redox Cycle of Mercury in Natural Waters

EPA Grant Number: R827915 Title: The Redox Cycle of Mercury in Natural Waters Investigators: Morel, Francois M. Institution: Princeton University EPA Project Officer: Stelz, Bill Project Period: October 11, 1999 through October 10, 2002 (Extended to October 10, 2003)

Description:

The objective of this project is to elucidate the parameters that control the flux of elemental mercury from natural waters to the atmosphere. To this end it is proposed to undertake a series of iterative laboratory and field experiments focused on the principal chemical and biological redox mechanisms that transform mercury between its divalent, Hg(II), and elemental, Hg(0), forms. The experimental plan is designed to test three complementary hypotheses based on preliminary data and the literature.
Hypothesis 1. Biological reduction of Hg(II) to Hg(0) is normally effected as a two electron transfer reaction by transmembrane metal reductases in photosynthetic microorganisms, phytoplankton, and cyanobacteria.

Hypothesis 2. Chemical reduction of Hg(II) occurs in two distinct one-electron transfer reactions: i) reduction of Hg(II) to Hg(I) which requires a high energy reductant (typically formed in the light) such as the superoxide anion or an organic radical (probably a semiquinone); ii) reduction of Hg(I) to Hg(0) by organic matter.

Hypothesis 3. Likewise, the oxidation of elemental mercury requires first oxidation of Hg(0) to Hg(I), likely effected by the same radicals, superoxide or semiquinones, and then oxidation of Hg(I) to Hg(II) by oxygen which is facilitated by chloride complexation of the ionic mercury species.

Final Report

Summary/Accomplishments:

The ultimate question in mercury research is how biogeochemical processes and transformations help influence methylmercury exposure to humans and wildlife. We have responded to this challenge by studying three poorly understood processes critical in determining mercury levels in aquatic organisms. Primarily, we studied water column photooxidation, a mechanism that can cause an increased retention time for mercury in the waterbody, leading to an increased likelihood for it to be methylated. Our laboratory also focused on better understanding the physiology and biochemistry of mercury methylation in sulfate-reducing bacteria, the key organisms in freshwater and coastal systems that create the bioaccumulating neurotoxin, methylmercury. Finally, we have sought to better understand the possible sources of methylmercury to open ocean fish, the prime exposure route of mercury to humans.

The oxidation of volatile aqueous Hg(0) in aquatic systems may be important in reducing fluxes of mercury out of aquatic systems. Through laboratory and field experiments on St. Lawrence River water samples, we identified parameters (i.e., chloride concentration, semiquinone inclusion) that regulate the photooxidation of Hg(0). Elemental mercury oxidation was found to be mediated chiefly by ultraviolet (UV) radiation as: (1) "dark" oxidation was not found to be statistically significant; (2) visible light induced a significant but slow photooxidation ($k=0.09\text{h}^{-1}$); and (3) visible plus UV radiation led to a faster photooxidation ($k=0.6\text{--}0.7\text{h}^{-1}$), mainly because of UVA induced reactions. Doubling UV radiation did not increase the reaction rate of Hg(0) photooxidation in natural water samples, indicating that some factor other than photon flux was rate limiting and suggesting that the reaction involves intermediate photo produced oxidant(s). The addition of methanol, a OH scavenger, decreased mercury photooxidation rates by 25 percent in brackish waters and by 19 percent in artificial saline water containing semiquinones, indicating that OH may be partially responsible for Hg(0) oxidation. Photooxidation rates were not affected by oxygen concentrations and did not decrease when samples were heat-sterilized, treated with chloroform, or filtered prior to exposure to light. In the St. Lawrence River, a typical photooxidation flux rate would be $300\text{ pmole m}^{-2}\text{ h}^{-1}$, compared to volatilization flux of $7\text{ pmole m}^{-2}\text{ h}^{-1}$. In coastal waters, the dominant Hg(0) sink is likely to be photooxidation rather than volatilization from the water column during summer days, even in periods of high winds.

Sulfate-reducing bacteria (SRB) in anoxic waters and sediments are the major organisms that transform inorganic mercury –which otherwise would be buried and removed from the watershed– into the bioaccumulating neurotoxin, methylmercury. Although a considerable amount of work has addressed the environmental factors that control methylmercury formation and the conditions that control inorganic mercury bioavailability to SRB, little work has been undertaken analyzing the biochemical mechanism of methylmercury production. The acetyl-CoA pathway has been implicated as key to mercury methylation in one SRB strain, *Desulfovibrio desulfuricans* LS, but this result has not been extended to other SRB species. To probe whether the acetyl-CoA pathway is the controlling biochemical process for methylmercury production in SRB, five incomplete-oxidizing SRB strains and two *Desulfovibrio* strains that do not use the acetyl-CoA pathway for major carbon metabolism were assayed for methylmercury formation and acetyl-CoA pathway enzyme activities. Three of the SRB strains also were incubated with chloroform to inhibit the acetyl-CoA pathway. All species that have been found to have acetyl-CoA activity, including complete oxidizers that require the acetyl-CoA pathway for basic metabolism, methylate mercury. We have identified, however, four incomplete-oxidizing strains that clearly do not utilize the acetyl-CoA pathway for mercury methylation. Mercury methylation is independent of the acetyl-CoA pathway and may not require vitamin B12 in some and perhaps many incomplete-oxidizing SRB strains.

Although the bulk of human exposure to mercury is through the consumption of marine fish, most of what we know about mercury methylation is from studies of freshwaters. We know little of where and how mercury is methylated in the open oceans, and there is currently a debate whether methylmercury concentrations in marine fish have increased along with global anthropogenic mercury emissions. Measurements of mercury concentrations in Yellowfin tuna caught off Hawaii in 1988 show no increase compared to measurements of the same species caught in the same area in 1971. On the basis of the known increase in the global emissions of mercury over the past century and of a simple model of mercury biogeochemistry in the equatorial and subtropical Pacific Ocean, we calculate that the methylmercury concentration in these surface waters should have increased between 9 and 26 percent over this 27 year span if methylation occurred in the mixed layer or in the thermocline. Such an increase is statistically inconsistent with the constant mercury concentrations measured in tuna. We conclude tentatively that mercury methylation in oceans occurs in deep waters or in sediments.

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

EPA Grant Number: R827635 Title: Microbiological and Physicochemical Aspects of Mercury Cycling in the Coastal/Estuarine Waters of Long Island Sound and Its River-Seawater Mixing Zones Investigators: Fitzgerald, William F. , Visscher, Pieter T. Institution: University of Connecticut EPA Project Officer: Stelz, Bill
Project Period: October 1, 1999 through September 30, 2002

Description:

The primary exposure of humans to methylHg (MMHg) is through the consumption of marine fish and fish products, yet the marine environment has been largely ignored and under sampled. Estuaries and adjacent coastal waters are major repositories for riverborne/watershed derived Hg species. Increased knowledge and understanding concerning the biogeochemical behavior and fate of Hg in important productive nearshore regions such as Long Island Sound (LIS) is a critical need. One of the most striking findings from our preliminary work is the presence of significantly large emissions of elemental Hg (Hg⁰) from the waters of LIS to the local/regional atmosphere. We postulate that Hg cycling in natural waters (i.e., LIS) plays a key or governing role in controlling the overall aquatic biogeochemistry of Hg and the bioavailable Hg species. We are proposing a three-year comprehensive physicochemical and microbiological marine program to investigate reactions and processes controlling Hg emissions, cycling, and bioavailability in Long Island Sound and its watershed/coastal water interface. Using prior Hg mass balance studies as a framework, we are proposing a experimental (large field and laboratory effort) and theoretical design (modeling) that will allow the results to be applicable to other regions of the coastal zone.

Objective:

Consumption of marine fish and seafood products is the principal pathway by which humans are exposed to the very toxic organomercurial, monomethylmercury (MMHg). Consequently, there is an urgent need for increased knowledge and understanding of the marine biogeochemical cycling of mercury (Hg) and the impact of anthropogenically related Hg inputs. Biologically productive, nutrient-rich near-shore regions, which support major commercial and recreational fisheries, are of special interest. Accordingly, our U.S. Environmental Protection Agency Science to Achieve Results (STAR) Hg research was focused on Long Island Sound (LIS), its watershed, and river-seawater mixing zones. This major natural resource provides a valuable analog for other near-shore/urban marine ecosystems. Our process reaction-focused investigations will allow the results to be applied in other marine regions. Such an approach was essential, given the complexity and variability of fertile estuaries and adjacent coastal waters, which are major repositories for natural and pollutant riverborne/watershed-derived substances such as Hg. The specific objectives of this research project were concerned with several major features of the aquatic biogeochemistry of Hg, particularly elemental mercury (Hg⁰) cycling and emissions, MMHg production in sediments, interactions between terrestrial watersheds, rivers, and near-shore marine waters, and the role of organic matter (OM) in governing the availability of Hg for competing methylation/reduction reactions. Our work was conducted in the local coastal waters of LIS, a large (3,200 km²) embayment in the northeastern United States. LIS is the subject of numerous biogeochemical investigations and a long-term monitoring program of its waters (Connecticut Department of Environmental Protection [CT DEP], 2003). Current and historic pollution, including sewage (Buchholtz ten Brinck, et al., 2000), has perturbed LIS significantly. As a consequence, it has longitudinal gradients in pollutant Hg (Varekamp, et al., 2000; Hammerschmidt and Fitzgerald, 2004), dissolved oxygen and nutrients (CT DEP, 2003), as well as sediment geochemistry and microbial activities (Knebel and Poppe, 2000; Mccray and Buchholtz ten Brinck, 2000; Poppe, et al., 2000). Such gradients in LIS are expected to encompass the range of water column and sediment characteristics found in most other coastal regimes. Thus, information on the biogeochemistry of Hg and MMHg in LIS is directly applicable to comparable coastal marine sediments and systems.

Previous measurements of sources and sinks of Hg in LIS have been validated by several independent measurements, resulting in well-constrained mass balances for total Hg and MMHg in LIS (Vandal, et al., 2002; Balcom, et al., submitted, 2003). The principal sources of total Hg (241 kg yr⁻¹) to LIS are rivers (~136 kg yr⁻¹; 56 percent of total inputs), water pollution control facilities (WPCFs) (~11 kg yr⁻¹; 5 percent), the East River (~68 kg yr⁻¹; 28 percent), and direct atmospheric deposition (~26 kg yr⁻¹; 11 percent). Principal external sources of MMHg to LIS (~5 kg yr⁻¹) include rivers (~3 kg yr⁻¹), the East River (~1.4 kg yr⁻¹), and direct atmospheric deposition (~0.7 kg yr⁻¹). In situ sedimentary production was predicted to be the major source of MMHg in LIS (Langer, et al., 2001), and Hammerschmidt, et al. (submitted, 2003) have estimated a sediment-water flux of 11 ± 4 kg MMHg yr⁻¹ (65 percent of total inputs). Although direct atmospheric Hg deposition to LIS is small (~26 kg yr⁻¹), modest leaching (25-30 percent watershed delivery; 90-108 kg Hg yr⁻¹) of the LIS-wide atmospheric deposition normalized to its watershed area accounts for 65-80 percent of river Hg inputs (Balcom, et al., submitted, 2003).

Summary/Accomplishments:

Hg-Organic Interactions

Spring runoff contributes large amounts of Hg to rivers (watershed leaching) that is tightly bound to dissolved and colloidal organic ligands and particulate matter, which are largely unreactive (not reducible with Sn[II]; Rolfhus, et al., 2003; Lamborg, et al., 2003). Complexation of inorganic mercury cations (Hg[II]) by natural organic compounds has been posited as an influential and often controlling feature of the aquatic biogeochemical cycling of this toxic metal and was one of the working hypotheses for the present study. The high affinity of Hg for OM is characterized by stability constants that are typically five or more orders of magnitude greater than most other metals (e.g., Mantoura, et al., 1978). Complexation of Hg by organic ligands exerts control on important, speciation-dependent, biogeochemical transformations such as methylation, reduction/evasion, and solubility/adsorption (e.g., Barkay, et al., 1997; Benoit, et al., 1999a; Benoit, et al., 2001a; Rolfhus and Fitzgerald, 2001; Turner, et al., 2001; Lamborg, 2003). Although many studies suggest that the majority of Hg present in natural waters is complexed with organic ligands, little quantitative information currently exists regarding the abundance and strength of such Hg-complexing agents in natural waters. We have developed a new method for the determination of the concentration and conditional stability constants of dissolved organic matter (DOM) towards Hg using an in vitro reducible-Hg titration approach (Lamborg, et al., 2003).

Long Island Sound. We found the concentration of Hg-binding organic ligands in LIS and its environs to range from less than 1 to greater than 60 nN, and that the conditional stability constants (affinities of the OM for Hg) are very high ($\log K' = 21-24$; Lamborg, et al., 2003). Only one ligand class was found in the natural waters tested (i.e., rivers, seawaters, bog waters, sewage, and sedimentary porewaters). Concentrations, affinities, and kinetics implicate multidentate binding sites as the principal chelation moieties for Hg. Recent spectroscopic investigations of Hg binding to soil organic material have pointed to multidentate associations involving sulfur and oxygen bonds to Hg (Xia, et al., 1999; Hesterberg, et al., 2001). In freshwaters, greater than 99.9 percent of Hg is found in organic complexes (Lamborg, et al., 2003), and although the fraction of Hg in organic complexes varies in salt waters, coastal waters also are dominated (> 50 percent) by organic forms. These findings are significant, as the organically complexed pool is likely to have much different biogeochemical reactivity, and can, therefore, affect Hg biogeochemistry on local, regional, and global scales.

Ligand activity through the salinity gradient of the Connecticut River (CTR) indicated that a majority of the ligands in LIS would be of terrestrial origin. Ligand distributions through the CTR estuary suggest pseudoconservative mixing (higher concentrations in fresher waters) of ligand derived from the CTR watershed (Lamborg, et al., 2003). Furthermore, the ligand:dissolved organic carbon (DOC) ratios for a variety of end member waters for LIS indicate that offshore (continental shelf) waters and sewage (East River) possess very ligand poor DOC. Therefore, a substantial percentage of the Hg binding compounds present in the coastal waters of LIS are allochthonous in origin (Lamborg, et al., 2003). We have constructed a first-order mass balance for ligand and DOC in LIS (Lamborg, et al., submitted, 2003), based on measurements of ligand concentrations, DOC analyses, and some estimated DOC fluxes. The principal sources of ligands to LIS are riverwater (47 percent; terrestrial OM) and phytoplankton DOC exudation (31 percent), and the only significant loss term identified is tidal exchange with the low DOC/low ligand waters of the continental shelf. The seasonal variations in ligand abundance (lowest during winter and highest during summer and spring) are a reflection of the importance of river flow and primary production, as these sources are strongest in the spring and summer in LIS (Lamborg, et al., submitted, 2003).