Report for 2000WI8G: Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study

- Articles in Refereed Scientific Journals:
    - Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott and V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology. 36(23):5034-5040.
    - Babiarz C.L, J.P. Hurley, D.P. Krabbenhoft, C.C. Gilmour, and B.A. Branfireun. 2003. Application of ultrafiltration and stable isotope amendments to the partitioning of mercury in lake water and over land runoff. Science of the Total Environment. 304: 295-303
    - Babiarz, C.L., J.P. Hurley, D.P. krabbenhoft, T.R. Trinko, M. Tate, S.P. Chadwick and D.E. Armstrong. 2003. A hypolimnetic mass balance of mercury from a dimictic lake: results from the METAALICUS project. Journal de physique IV. 107:83-86.
    - Chadwick, S.P., Babiarz C.L., Hurley J.P., and Armstrong, D.E. (In Press) Biogeochemical cycling of iron, manganese and dissolved organic carbon in a seasonally anoxic lake amended with stable isotopes of mercury. Science of the Total Environment.
    - Babiarz, C. L., J. P. Hurley, D. P. Krabbenhoft, S. P. Chadwick, T. R. Trinko, and M. Tate. (2004) Towards a hypolimnetic mass balance of Hg in a dimictic lake: Early results from the METAALICUS project. RMZ Materials and Geoenvironment 51:778-782.
    - Branfireun, B.A., D.P. Krabbenhoft, H. Hintelmann, R. J. Hunt, J.P. Hurley, and J.W.M. Rudd. 2005. The transport and speciation of atmospheric mercury in a Boreal forest wetland: A stable mercury isotope approach. In Press, Water Resources Research.
- Conference Proceedings:
    - Harris, R.C., J.W.M. Rudd, M. Amyot, C. Babiarz, K. Beaty, P. Blanchfield, A. (Drew) Bodaly, B. Branfireun, C.C. Gilmour, A. Heyes, H. Hintelmann, J. Hurley, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, K. Rolfhus, K. Sandilands, K. Scott, G. Southworth, V. St. Louis. 2001. METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and MeHg Concentrations of Fish. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments Sponsored by the U.S. Environmental Protection Agency. West Palm Beach, Florida. May.
    - Hurley, J.P., M. Amyot, M., K. Beaty, K., P. Blanchfield, R.A. Bodaly, B. Branfireun,, C.Gilmour, R.C. Harris, A. Heyes, H. Hintelmann, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, J.W.M. Rudd, K. Sandilands, G. Southworth, V. St. Louis. 2003. Watershed-level Addition of Mercury Stable Isotopes: A Tool for Understanding Processes from Deposition to

Bioaccumulation. Conference on Frontiers in Assessment Methods for the Environment (FAME). Minneapolis, MN. August. (Invited).

- Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. An overview of the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States. American Water Resources Association. Minocqua, Wisconsin. February 27 & 28, 2003.
- Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. A Hypolimnetic Mass Balance of Mercury from a Dimictic Lake: Results from the METAALICUS Project. 12th International Conference on Heavy Metals in the Environment. Grenoble, France. May 26-30, 2003.
- Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS). Experimental Lakes Area, Canadian Dept of Fisheries and Oceans. June 24, 2003.
- Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft. Early results from the mercury experiment to assess atmospheric loading in Canada and the United States. Environmental Chemistry & Technology Program, University of Wisconsin. September 19, 2003.
- Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS). 26th Midwest Environmental Chemistry Workshop. Iowa City, Iowa. October 10-12, 2003.

Report Follows

Project Update: 6-15-05

Project Title:
Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study

Project Investigators:
James P. Hurley, University of Wisconsin Water Resources Institute, David P. Krabbenhoft, U.S. Geological Survey, Kristofer R. Rolfhus, University of Wisconsin

Background

Problem and Research Objectives
Fish consumption advisories have been issued in 40 states in the U.S. and all provinces of Canada due to deleterious health effects associated with ingesting fish of high Hg concentrations. Nearly all of the mercury in fish is methylmercury (MMHg), a neurotoxin that biomagnifies to high concentrations toward the top of aquatic food webs. Small quantities of methylmercury in the diet can adversely affect wildlife and humans. Human and wildlife exposure to methylmercury is almost entirely through the consumption of fish. Thus, the greatest present research need is to further understand what drives this widespread contamination problem and to unravel the complex set of processes that link nonpoint mercury loading to bioaccumulation in fish.

There is a general consensus that, in the absence of direct point-source discharges, the primary source of Hg that bioaccumulates to upper trophic levels is atmospheric deposition. The U.S. EPA's Science Advisory Board identified in The Mercury Report to Congress (EPA 1997) several gaps regarding our current understanding of Hg cycling. In particular, they pointed to ecosystem cycling of atmospherically derived Hg, including post-depositional transport pathways, rates of transport, and biogeochemical transformation processes (methylation/demethylation and reduction/evasion).

Watershed characteristics (such as land cover patterns, soil type and glacial deposits) exert a strong influence on export, partitioning and speciation of Hg_T and MMHg from watersheds. These characteristics directly affect the types and amounts of suspended particulate matter (SPM), colloids, forms of dissolved organic compound (DOC), and other ligands transported within and from terrestrial portions of catchments to down-gradient aquatic ecosystems where bioaccumulation of Hg in the food web begins. Elucidating the connections between atmospheric Hg loading and various watershed components (forest soils and vegetation, bedrock, wetlands, streams and lakes) and bioaccumulation in the food web is the general scope of the Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S. (METAALICUS) project.

METAALICUS is a large, multidisciplinary, multi-investigator project, with an anticipated four-year budget totaling approximately nine million dollars (including the purchase of isotopes). The project is a whole-watershed application of stable-Hg isotopes at the Experimental Lakes Area (ELA), near Kenora, Ontario. The ELA is one of the very few places where direct application of contaminants in field studies is allowable, and emphasizes the unique opportunity that this study provides.

Overall Objectives of the METAALICUS Project

1. Provide direct information on the effects of nonpoint atmospheric Hg deposition on bioaccumulation in predatory fish
2. Determine the relative importance of the watershed (including upland and wetland portions) and direct deposition in determining bioaccumulation of Hg in predatory fish of a lacustrine environment.
3. Provide (for the first time) direct measurement of ecosystem response times between Hg deposition and transport, and provide a direct comparison of the reactivity of Hg added via "new deposition" and Hg considered as the historic pool within the watershed.
4. To more definitively trace Hg processes and pathways at the ecosystem scale using near-ambient levels of isotopes.
5. Provide information on rates and pathways of Hg cycling to support a watershed-based Hg cycling model

Objectives for University of Wisconsin-USGS Subproject of METAALICUS

Because METAALICUS is a large project, principal investigators have been assigned various focus areas to ensure complete coverage of the major Hg transformation and transport studies. The investigators associated with our subproject will be specifically addressing upland and wetland Hg-cycling processes and pathways that contribute to Hg accumulation in aquatic food webs. Our efforts within this subproject support overall objectives 2 through 5 above.

Our objectives for this subproject are to:

1. Determine the fraction of a watershed Hg yield that is "new" versus that derived from the historic pool of Hg in the soils and vegetation.
2. Provide direct observations of the extent of mobility of new Hg in upland soils and wetland peat.
3. Isolate and quantify transport vectors (dissolved organic carbon, colloids, particulates) leading to export from different watershed components.
4. Assess the effects of partitioning and pathway in influencing bioavailability of Hg derived from uplands and wetlands to the study lake.
5. Elucidate the contribution of new versus historic Hg to the formation and optimal locations for methylation of Hg and relative mobility for transport from the watershed to the lake.

Methodology

The experimental design consists of both loading and tracer experiments. Mercury has an ideal distribution of stable isotopes that are all readily available from specialized distributors. We will increase Hg loads using 95% pure stable (nonradioactive) isotope of mercury [e.g., $^{198}Hg(NO_3)_2$, $^{200}Hg(NO_3)_2$, $^{202}Hg(NO_3)_2$] using the techniques in Hintelmann et al. 1995 and Hintelmann and

Evans 1997. The spike will be delivered to upland/wetland plots and mesocosms by diluting the mercury isotope into rainfall collected on site. During full-scale ecosystem addition of spike-equilibrated water, we will add separate isotopes to the upland, wetland and lake components of the watershed. The use of enriched stable isotopes of Hg allows for the analytical discrimination of new "labeled" Hg and background Hg at trace concentrations. Ratios of isotopic Hg to ambient Hg in the same samples can be analyzed to determine the relative availability of "old" versus new Hg inputs. Isotopic Hg can also be used to follow Hg through different watershed transformation and transport processes and subsequently through different compartments of the lacustrine food web.

During both pilot scale and full-scale implementation, we will use physical and chemical fractionation techniques (developed at the University of Wisconsin) to describe the composition and chemical lability of organic-Hg complexes in runoff and wetland discharge. These methods serve to separate aqueous Hg species by size and their ability to form complexes with competing solid phase ligands attached to resins, creating both concentrated ligand and ligand-free test solutions. Ultrafiltration methods will characterize the importance of sub-particulate fractions (colloids and truly dissolved species) to the transport and bioavailability of upland and wetland Hg. For example, we have observed that inorganic Hg in the <100 kD fraction of inundated ELA forest soil extracts are the most readily available for uptake to aquatic bacteria, using the *mer-lux* bioreporter assay (K. Scott, pers. comm.). The Chelex studies allow for kinetic and thermodynamic evaluation of Hg binding strength and reactivity, and directly addresses whether weakly-bound Hg complexes are biogeochemically important. The XAD treatments will further characterize the organic ligands to which Hg is bound, including hydrophobicity, acidity, and molecular weight. We will also be conducting reactive Hg measurements to operationally determine chemical lability of Hg-DOC fractions.

This project utilizes the cooperative efforts of the University of Wisconsin Water Chemistry Program (UWWCP) Mercury Laboratory and the USGS Mercury Research Laboratory (both in Madison, Wisconsin). Groups at both laboratories have specialized facilities and instrumentation for trace metal research. Each laboratory has dedicated clean room facilities developed for low-level Hg processing and analysis. The UWWCP facility has three Hg analytical systems (Tekran, Brooks-Rand) as well as supporting instrumentation such as a Perkin-Elmer Plasma II ICP-OES; Waters 600 HPLC with 991 Diode Array Detector; PE 5100Z GFAA; Shimadzu TOC-500 with a particulate carbon analyzer. Modern shop facilities located in our UW building allows for fabrication of specialized equipment. The USGS facility houses the main instrumentation for isotopic analyses for this study, a new Perkin-Elmer Elan 6000 that is dedicated for mercury-only isotopic analysis. In addition, the USGS lab has four Tekran Hg analytical systems, and an OI TOC-1010 carbon analyzer.

1. **Project Update:**

2004 Sampling Strategy and Field Campaigns

Our 2004 field-season strategy focused on the construction of a well-constrained hypolimnetic mass balance for mercury in the hypolimnion of the lake. We also committed resources to specific experiments designed to understand the underlying processes: Sediment accumulation

rates (including the historic depositional record for mercury), the kinetics of mercury partitioning to lake particles, and the retrieval of a mixed-core incubation experiment.

We completed six monthly field campaigns from May to October 2004. Our standard sampling protocol included water-column sampling and sediment-trap processing to establish the hypolimnetic mass-balance for mercury in the lake. The water column samples are used to estimate the standing pool of mercury in the hypolimnetic water column, and the sediment trap samples are used to estimate particle transport into and out of the hypolimnion. We also measured mercury in pore-waters of freshly fallen particulate matter that lies on the surface of the sediments. This pore-water data is important for calculating the flux of mercury out of the sediments from diffusion. Initial data suggests this term is large and may account for the buildup of MeHg in the hypolimnion. We also collected sediment cores on a regular basis (July, August, and October) to document the net storage of mercury in the lake sediments. This data will be combined with previous data to track seasonal changes in mercury content, and will also be combined with detailed geochronology information from Dr. Daniel Engstrom of the Science Museum of Minnesota (see collaboration section below).

In addition to the standard sampling protocol, we collected samples for specific experiments designed to look at the reactivity and biouptake of Hg in the watershed.

- In July, we collected extra surface water from the west basin to conduct a particle scavenging experiment for mercury. The kinetics of Hg sorption to particles was investigated using ^{201}Hg(II) as a tracer in a time series experiment. Additional experiments were performed to determine the role of Hg loading on the partition coefficient.
- In August we collected rain water from ELA to be used in a parallel biouptake project in collaboration with Dr. Patrick Gorski (see collaboration section below).
- Also in August, we collected hypolimnetic water to conduct an experiment on sample storage methods for DOC. Anoxic waters with high iron content can result in flocculation of DOC if the samples are frozen. Flocculation interferes with the analysis resulting in artificially low concentrations.
- In September we collected extra water at the sediment-water interface to verify and expand the experiment on sample storage methods for DOC.
- In October, we retrieved a mixed-core sediment incubation experiment that was initiated before the first addition of the lake isotope in June 2001. The goal of the incubation was to assess post-depositional migration of mercury (up or down a sediment core) and post depositional methylation/demethylation of mercury (conversion between the inorganic and organic forms). This experiment will be the first insitu experiment to test an important assumption of sedimentation models (that mercury is inactive once buried at depth). In short, sediments from Lake 658 were homogenized, spiked with ^{201}Hg and Me^{199}Hg and placed in both the littoral and pelagic areas of the lake. Because the original cores were well mixed, any change to the native Hg profile will indicate the mobility of old Hg. Changes to the ^{201}Hg and Me^{199}Hg profiles will either indicate methylation/demethylation or post-depositional migration of recently deposited Hg with depth. Changes in the ^{202}Hg or Me^{202}Hg will indicate near surface recycling of new Hg. The retrieved sediments will be analyzed for isotopic Hg, MeHg and ancillaries (major ions, carbon, water content/porosity, etc…).

Sample Analysis and Data Reduction

In 2004 we completed the analysis for our standard suite of water column and sediment trap samples through the end of the 2003 field season. For the 2004 field season, approximately one third of our aqueous total-mercury samples have been analyzed and 75% of our aqueous methylmercury samples have been analyzed. Remaining mercury samples include solid-phase sediment transects from each field season and sediment samples from the mixed-core experiment. Less than 20% of all non-mercury samples remain to be analyzed. In addition, our entire data base was updated to match reporting standards set by METAALICUS principal investigators at the 2002 annual meeting. The reporting standards allow data sets to be compared across all participating METAALICUS research groups.

Outside Presentations

Our research group presented several papers on the METAALICUS project in 2004.

7th International Conference on Mercury as a Global Pollutant in Ljubljana, Slovenia, June 27- July 2, 2004. This conference is the preeminent international forum for dissemination of scientific advances on mercury. Four hundred and fifty scientists from 47 countries attended the 5-day conference. Our contributions focused on the transformation and fate of mercury in the hypolimnion of Lake 658.

- Christopher Babiarz presented early results from our overall scientific approach in a poster entitled: *Towards a Hypolimnetic mass balance: Early results from the METAALICUS project.*
- Shawn Chadwick presented the partitioning behavior of mercury at the oxidation/reduction boundary in a poster entitled: *Speciation controls on the fate and transport of mercury and methylmercury across biogeochemical gradients.*

27th Midwest Environmental Chemistry Workshop (MWECW) in Madison, Wisconsin, October 15-17, 2004. The MWECW has become the preeminent venue for Midwestern graduate students in environmental science to discuss their research among colleagues. Shawn Chadwick gave a presentation entitled *Kinetic studies of mercury (II) speciation with dissolved organic matter*.

Fall Meeting of the American Geophysical Union in San Francisco, California, December 14-17, 2004. Dr. Christopher Babiarz was recruited to give an invited presentation on *Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management*. This was the only talk on mercury in a session entitled *Soil Retention of Atmospheric Solutes.* The session also included presentations on sulfate, nitrate, and aluminum that allowed for strong cross-disciplinary discussion.

Collaboration and Outreach

Our research group continues to collaborate with other researchers on the METAALICUS project. In addition to performing specialized isotopic mercury analysis with the USGS isotope

laboratory operated by Dr. David Krabbenhoft (Middleton, WI), we collaborated with the following scientists during the last year:

Dr. Nives Ogrinc of the J. Stefan Institute in Ljubljana, Slovenia. Dr. Ogrinc is an expert in carbon cycling and its sources (i.e. terrestrial vs. in-lake). In June, we prepared and delivered subsamples from our archived sediment trap material to Dr. Ogrinc. Her analysis will help us interpret the recycling and remineralization of carbon at the sediment water interface.

Dr. Daniel Engstrom of the Minnesota Science Museum. Dr. Engstrom is an expert on sedimentary record of freshwater lakes. He and his team joined us on a field campaign in October to collect and slice sediment cores for lead-210 analysis. The results will be used to determine the historical sedimentation record of the lake including focusing factors. This information will help us estimate the time-dependant burial of mercury in the sediments of the lake – a critical component of the hypolimnetic mass balance (a major objective of this project). Dr. Engstrom reports that lead-210 analysis and loss-on-ignition (LOI) analysis are both progressing smoothly. We expect the results in summer 2005 along with sub-samples of sediment for mercury analysis in our laboratory.

Dr. Patrick Gorski of the University of Wisconsin. Dr. Gorksi is an expert on bioaccumulation of mercury in the lower food web. In December, he conducted a bioassay on ELA rain water in cooperation with the WI State Laboratory of Hygiene Biomonitoring Group. The results of this experiment will help determine the availability of mercury in rain as it mixes with lake water.

We also participated in two outreach projects:

- In November, Dr. James Hurley served on the Science Advisory Council of the Collaborative Mercury Research Network (**COMERN**) in Gimli, Manitoba. The goal of COMERN is to integrate research toward a better understanding of processes ruling mercury exchange and accumulation in wide-scale ecosystems in the northern part of the American continent. The meeting provided an opportunity for multidisciplinary discussion and integration of METAALICUS results.
- On March 3, 2005, Dr. Babiarz participated in a one-day workshop comparing results from the METAALICUS project with those of the ACME project (Aquatic Cycling of Mercury in the Everglades).

Project Completion Timeline

To date we have made significant progress toward the specific goals outlined in our research plan. The field component of the project is complete, and we have strong data sets that include: a mixed sediment core experiment, seasonal lake profiles, sediment trap deployment, and experiments investigating iron and DOC controls on mercury speciation. With the exception of sediments, all samples from 2003 (and earlier) have been analyzed, and we anticipate finishing the analysis of 2004 water column samples by September 30, 2005. We expect analysis of sediment samples to be completed by December. We have one manuscript in press, and we expect to submit three more by the end of the year (not including a lake chemistry overview paper that includes our data but is being written by a colleague at the Smithsonian Institution).

1) *Speciation controls on the partitioning of HgT and MeHg in lake amended with stable isotopes.* Target Journal: Biogeochemistry
2) *Isolation of DOM species of HgT and MeHg using diethylaminoethyl cellulose.* Target Journal: Environmental Science & Technology
3) *A Hypolimnetic mass balance of mercury in a seasonally anoxic lake amended with stable isotopes of mercury.* Target Journal: Environmental Science & Technology
4) *Role of iron, manganese, and organic carbon on the sedimentation of amended mercury.* Target Journal: Water research, Biogeochemistry, or Canadian Journal of Fisheries and Aquatic Sciences
5) *Post-depositional methylation, demethylation, and migration of mercury in carbonaceous lake sediment.* Target Journal: Environmental Science & Technology (To be submitted in 2006).

2. **Notable Achievements and Awards**:

Dr. Christopher Babiarz was recruited to give an invited presentation on METAALICUS results at the Fall Meeting of the American Geophysical Union (December 14-17, in San Francisco, CA). The presentation was entitled *Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management*, and was the only talk on mercury in a session about *Soil Retention of Atmospheric Solutes.* The session also included presentations on sulfate, nitrate, and aluminum that allowed cross-disciplinary discussion.

3. Publications:

Chadwick, S.P., Babiarz C.L., Hurley J.P., and Armstrong, D.E. (In Press) *Biogeochemical cycling of iron, manganese and dissolved organic carbon in a seasonally anoxic lake amended with stable isotopes of mercury.* Science of the Total Environment.

Babiarz, C. L., J. P. Hurley, D. P. Krabbenhoft, S. P. Chadwick, T. R. Trinko, and M. Tate. (2004) *Towards a hypolimnetic mass balance of Hg in a dimictic lake: Early results from the METAALICUS project.* RMZ Materials and Geoenvironment **51**:778-782.