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Department of Administration
Division of Energy**

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Reduction in Mercury Loading: Timing and Magnitude of an Ecosystem Response

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Executive Summary

The following report reflects the activities of the Mercury Research Group at the Environmental Chemistry and Technology Program of the University of Wisconsin-Madison (UW-ECT; formerly Water Chemistry Program). The project “Reduction in Mercury Loading: Timing and Magnitude of an Ecosystem Response*” was funded in July, 2003 by Wisconsin Focus on Energy for \$173,190 for the two-year project (July 1, 2003 to June 30, 2005 with a 3-month no-cost extension to September 30, 2005). This is the final report covering the entire duration of the project.

Project Overview

Atmospheric transport, deposition, and reemission of Mercury (Hg) are key processes in the movement of this neurotoxin throughout the globe. Historically, many of the mechanisms that control the cycling of Hg have been obscured by our inability to differentiate between Hg which is new to the system, and that originating from the historic pool. In the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS), stable isotopes of Hg were applied to both the lake and watershed as a tool for identifying key processes that control the environmental fate of Hg. These isotopic techniques have provided the first direct evidence of a whole lake and whole watershed response to “new” atmospheric inputs of Hg. The study takes place at the Canadian Experimental Lakes Area (ELA), located just north of the Minnesota-Ontario border.

Two of the major goals of the project are to determine the fate and transport of the new Hg through the watershed (for example, how quickly the added Hg is transformed and bioaccumulated in fish), and to assess the watershed recovery time due to reductions in atmospheric Hg deposition. As new regulations on atmospheric emissions of Hg from the USEPA approach, it is important that regulatory decisions are based on sound, scientifically defensible data on Hg cycling in the environment.

The specific goal of the work funded through the Environmental Research Program of Wisconsin Focus on Energy was to determine the timing and magnitude of the in-lake response. In particular, our work measured: (a) the speciation (chemical form), (b) partitioning (physical location), and (c) mobility (transport, transformation and bioaccumulation) of Hg within the lake – with special emphasis on the role of the sediment water interface as a removal mechanism for Hg.

In general, project results indicate a rapid response to inputs of new mercury to the lake surface. New inorganic mercury preferentially binds to the particulate phase and is transported to zones of methylation. Most of the inorganic mercury seems to be methylated at the sediment-water interface or in the overlying waters of the hypolimnion. Our research indicates that the hypolimnion plays an important role in the transformation and fate of mercury. Anoxic conditions coupled with the oxidation/reduction cycle of iron influences particle degradation and release of organic matter and mercury into the dissolved phase. Analysis of sediment surveys for mercury and Pb210 indicates a nearly constant net deposition rate and a fairly uniform depositional area. Complete results are being summarized in a series of peer-reviewed journal articles (including one that is reprinted in the appendix). We have endeavored to update the scientific and policy communities through outreach efforts and collaborative work.

** A note on the project title: At the time this work was funded by Wisconsin Focus on Energy, the original phase of isotope addition had come to a close and the recovery phase was expected to begin. Based on the available data, however, the project team for the larger METAALICUS project agreed there was scientific merit in continuing to load the watershed with isotopic amendments of mercury. The main arguments for continuing the loading phase included the lack of steady-state conditions in each compartment; the time-lag in the transport of the terrestrial spike into the lake, and the future ability to observe and interpret the spike. Consequently, isotopes were added to the watershed during each field season encompassed by the work presented here.*

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Table of Contents

Cover page	i
Executive Summary	ii
Distribution List	iv
Table of Contents	v
Introduction	
METAALICUS Project	1
Rationale	
Project-level goals	
Experimental Design	
Participating Institutions & Research Areas	
UW Madison Scope of Work	3
Overview of Research Focus	
Specific actions funded by Wisconsin Focus on Energy	
Organizational Chart	
Methods and fieldwork	
Spike Applications	6
Terrestrial	
Shoreline	
Lake	
Field Apparatus	7
Water Column	
Close Interval Sampler	
Sediment Traps	
Sediment Coring	
Laboratory Methods	8
Isotopic Hg Analysis	
Bioassay Techniques	
Modeling	
Ultrafiltration	
Resin Techniques	
Iron speciation	
Field Campaigns	9
Results and Discussion	10
Mixed-Core Experiments	
Lake Profiles & Sediment Trap Deployment	
Resin, Pigment, Optical, and Size-Fractionation of DOC	
Bioavailability Work	
Value and Transferability	16
Outreach Efforts	16
Bibliography	20
Appendix	
Chadwick et al., 2005	21

Introduction

There is considerable evidence that atmospheric transport, deposition, and reemission of Mercury (Hg) are key processes in the movement of this neurotoxin throughout the globe [1]. Historically, many of the mechanisms that control the cycling of Hg have been obscured by our inability to differentiate between that which is new to the system, and that originating from the historic pool. In the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS), stable isotopes of Hg were applied to both the lake and watershed as a tool for discovering key processes that control the environmental fate of Hg. These isotopic techniques have provided the first direct evidence of a whole lake and whole watershed response to “new” atmospheric inputs of Hg. In this section we describe the major goals of the METAALICUS project and the role of the University of Wisconsin research team.

METAALICUS Project

The overall goal of METAALICUS is to better define the timing and magnitude of the ecosystem response to changes in Hg loading [2]. It is our hypothesis that the sediments will be the ultimate sink for Hg, but the timing of that endpoint will be determined by a complex set of transport and transformation processes within both the lake and the surrounding watershed.

Rationale: Although the presence of methylmercury (MeHg) in fish is a natural occurrence, concentrations are often above the 0.5 ppm health advisory limit. Elevated concentrations are a concern due to the toxicity of MeHg and the exposure to humans and wildlife via fish consumption. Elevated MeHg concentrations have been observed in fish from remote water bodies that lack direct local sources of mercury (either natural or anthropogenic). The likely source of mercury to these remote systems is non-point atmospheric deposition of inorganic mercury. Once deposited, inorganic mercury is converted to MeHg by bacteria and enters the food chain.

The atmospheric pool contains mercury from both natural and anthropogenic sources. Natural sources include volcanoes and mineral deposits. Anthropogenic sources include emissions from coal combustion, waste incineration, mining, and other industrial processes. There has been much research on the impact of mercury emissions on fish mercury concentrations, and the efficacy of emissions controls on anthropogenic sources. In North America alone, emission controls for electric utilities have been estimated to cost billions of dollars per year. Despite this research activity, questions remain about the magnitude and timing the ecosystem response to changing mercury loads. Much of this uncertainty stems from an inability to differentiate between recently deposited mercury and the historic pool.

Recent advances in analytical capability allow the use of stable isotopes as an ambient-level tracer for new mercury in the environment [3, 4]. In addition, the Canadian Department of Fisheries and Oceans (DFO) operates a field station that specializes in watershed-scale experiments, and the principle investigators have obtained the necessary permits to apply the isotopes of mercury. This combination of resources and expertise makes the METAALICUS project a unique opportunity that may not be repeated due to the logistics and expense.

Project-Level Goals: The major goals of the METAALICUS project are to determine the fate and transport of the new Hg through an ecosystem, and to assess the watershed response due to changes in atmospheric Hg deposition. The questions that guided the development of the project were:

- a) *What is the relationship between the amount of Hg in atmospheric deposition and the amount of methylmercury in fish?*
- b) *How quickly will the fish Hg levels respond to a change/reduction in mercury deposition?*
- c) *How will environmental factors affect the magnitude and timing of the response?*

Experimental Design: The METAALICUS project takes advantage of two major assets: (1) highly sensitive isotopic techniques for differentiating between new and old Hg, and (2) a research site that is unparalleled for a project of this scope and relevancy to the effects of power generation and transmission. The METAALICUS project is located within the Lake 658 watershed in the Experimental Lakes Area (ELA; Figure 1) – a research station operated by the Canadian Department of Fisheries and Oceans in northwestern Ontario. Lake 658 is an 8.3 Ha dimictic lake surrounded by a 42-Hectare forested upland, and a 2 Ha wetland on the western reach. There are three major environmental compartments in the study that each received a different isotope of Hg: The upland (^{200}Hg), the wetland (^{198}Hg), and the lake (^{202}Hg). By the end of autumn 2005, the lake and watershed had received 5 years of isotopic Hg additions at a level 5 times background atmospheric deposition. For a detailed description of isotope application methods, please see the Methods and Fieldwork section below.

Note: At the time this work was funded by Wisconsin Focus on Energy, the original phase of isotope addition had come to a close and the recovery phase was expected to begin.

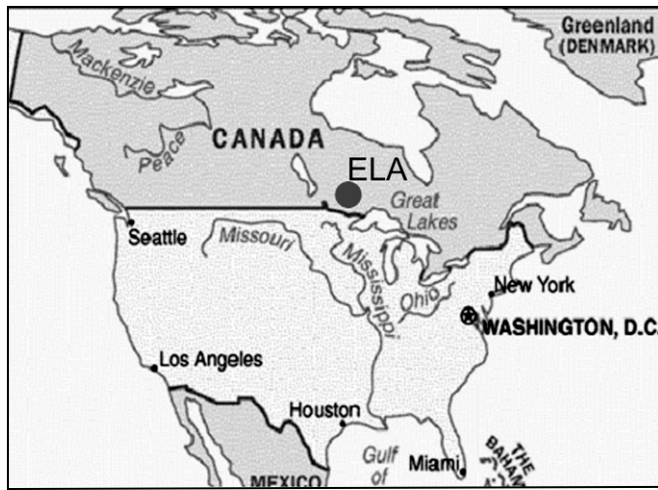


Figure 1. Location of study site

Based on the available data, however, the project team for the larger METAALICUS project agreed there was scientific merit in continuing to load the watershed with isotopic amendments of mercury. The main arguments for continuing the loading phase included the lack of steady-state in each compartment; the time-lag in the transport of the terrestrial spike into the lake, and the future ability to observe and interpret the spike. Consequently, isotopes were added to the watershed during each field season encompassed by the work presented here.

Participating institutions and research areas: Whole-watershed experiments require a diverse array of expertise. The METAALICUS project brought together a multidisciplinary team of 20 principle investigators from 12 US and Canadian institutions (Table 1). Each participating institution has been charged with evaluating a different aspect of the ecosystem response.

Table 1. Areas of specialty for each Institution and Principal Investigator

Institution	Investigators	Specialty
Freshwater Institute; Canadian DFO	Ken Beaty	Hydrology & Meteorology
Freshwater Institute; Canadian DFO	Paul Blanchfield	Fish Ecology
Freshwater Institute; Canadian DFO	Drew Bodaly	Biogeochemistry, Fish Studies
Freshwater Institute; Canadian DFO	Mike Paterson	Water column Invertebrates
Freshwater Institute; Canadian DFO	Cheryl Podemski	Benthic Invertebrates
Freshwater Institute; Canadian DFO	Michael Turner	Littoral Ecology
R & K Consultants	John Rudd; Carol Kelly	Biogeochemistry
Smithsonian Institution	Cindy Gilmour	Meth/Demeth,- Littoral Sediments
Tetra Tech Incorporated	Reed Harris	Whole-Ecosystem Modeling
Trent University	Holger Hintelmann	Water Chemistry, Hg Isotopes
United States Geological Survey	David Krabbenhoft	Hydrology, Upland Geochemistry
US Department of Energy	Steve Lindberg	Atmospheric Chemistry
University of Alberta	Vince St. Louis	Biogeochemistry; Litter-fall, Precip
University of Maryland	Andrew Heyes; Robert Mason	Meth/Demeth -Wetland/Upland Soils
University of Montreal	Marc Amyot	Photoreduction, Oxidation of Hg
University of Toronto	Brian Branfireun	Biogeochemistry, Terrestrial Studies
University of Wisconsin	James Hurley; Chris Babiarz	Hypolimnion Biogeochemistry

University of Wisconsin Scope of Work

In our experience, the strongest approach to research couples seasonal field observations with controlled laboratory experiments to fill gaps in knowledge that will improve our understanding of underlying processes and may also ground-truth environmental modeling efforts. This is an iterative process that builds strong hypothesis for future observation, experimentation, and improved ecosystem management.

Overview of Research Focus: The University of Wisconsin has participated in the METAALICUS project since its inception, and is primarily charged with examining the *hypolimnetic recycling and burial of Hg across the sediment-water interface*. Sediments are a major sink for Hg in the system because settling particles scavenge Hg from the water column. However, redox conditions at the sediment water interface, and in the overlying hypolimnetic waters during anoxia, are sites of intense recycling of Hg before eventual burial [5]. In addition to remineralization of Hg into the dissolved phase as particles fall, sulfur-reducing bacteria that thrive in anoxic conditions convert inorganic Hg(II) into MeHg [6 - 8] – the form of mercury that is bioaccumulative.

In broader terms, our research group addresses several questions that relate to our primary task:

- A) *How quickly will the lake respond to decreased atmospheric deposition?*
- B) *What fraction of the recent Hg will ultimately be buried in the lake sediment and be “permanently” removed from the ecosystem?*
- C) *What is the long-term importance of watershed type on MeHg formation, transport and bioaccumulation?*

Detailed information on the transport and transformation of Hg is needed to understand both the short-term and long-term persistence of the amended isotopes in the watershed and lake. Modeling the fate of Hg in the environment is ultimately tied to the quantification of reaction

rates and the process pathways. Our interest is in the particular processes and pathways that dictate particle-water partitioning. These key focus areas are:

A. Processes at the sediment-water interface. Understanding the mechanisms that control permanent sedimentation and recycling of Hg and MeHg in the bottom waters, and in the neighboring sediment zone, is key to determining the residence time of Hg and MeHg in the lake. Particles reach this zone as either the remains of algae, or other biotic material, or inorganic particles. We need better information on the precise depth of the “active zone” in the sediments, and the key factors that either strip Hg from the lake, or bury it, or enhance its return for possible bioaccumulation.

B. Partitioning to Dissolved Organic Carbon (DOC) in soil water, wetland pore water, and lake water. We have developed state-of-the-art techniques to sample, process, and analyze Hg in the solid, colloidal, and aqueous phase. Our published data strongly identifies DOC as the key phase for transport of Hg from both soil water and wetland water into either groundwater or surface water.

C. Processes controlling initial uptake into algae. While our lake water studies have shown there is a rapid conversion of added isotopes of inorganic Hg to MeHg, a key step for bioaccumulation into higher trophic levels is the sorption of MeHg to algae. We have been interested in this process and have developed a bioassay technique in conjunction with the Wisconsin State Laboratory of Hygiene. We seek to couple that work with the innovative use of stable isotopes, specific isolates of lake DOC, and inorganic ligands to examine the controls on MeHg uptake.

Specific actions funded by Wisconsin Focus on Energy:

The project entitled “Reduction in Mercury Loading: Timing and Magnitude of an Ecosystem Response” was funded by the Wisconsin Focus on Energy to cover four specific actions tied to in-lake processes:

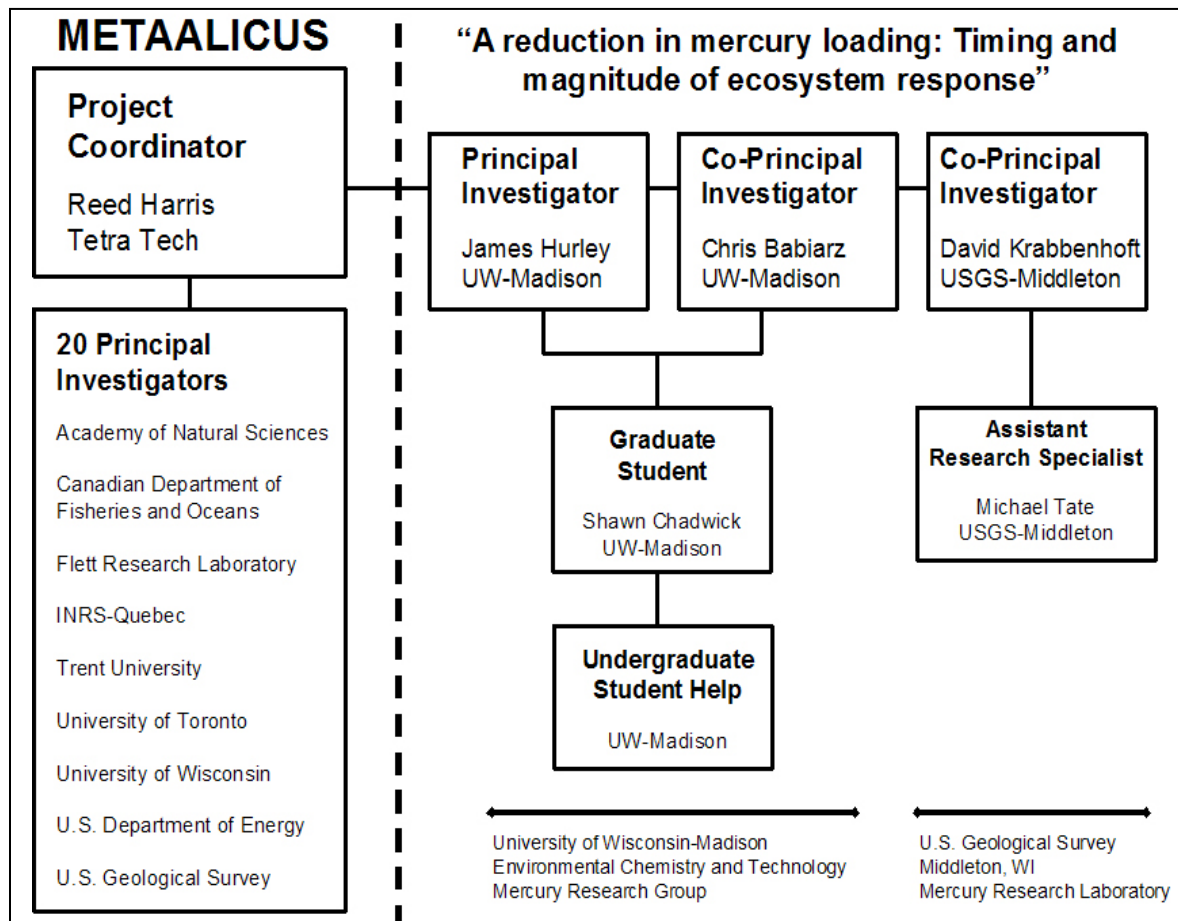
- a) ***Mixed-Core Experiments** to assess post-depositional migration, long-term methylation/demethylation, and estimate net burial rates for Hg in pelagic and littoral sediments.*
- b) ***Lake Profiles & Sediment Trap Deployment** to establish the hypolimnetic mass balance for Hg in the lake. Establish the importance of turnover in redistributing recently deposited Hg throughout the lake.*
- c) ***Resin, Pigment, Optical, and Size-fractionation of Dissolved Organic Carbon (DOC)** to establish the importance of DOC character on Hg transport and transformation.*
- d) ***Bioavailability Work** to determine the changing availability of the spiked Hg over time.*

In addition to these actions, the United States Geological Survey provided in-kind expertise to carry out an action item tied to terrestrial processes: **Soil zone translocation, humus leaching, and methylation experiments.** The purpose of these experiments are three-fold: to determine the factors responsible for the lag in response observed from the terrestrial compartment; to evaluate the relative importance of erosion versus soil-zone mobilization via humic acids on the

long-term transport of Hg from the upland to the lake; and to determine the controlling factors leading to MeHg occurrence in terrestrial soils. This work was not directly supported by Wisconsin Focus on Energy, and is therefore not reported here.

Organizational Chart: Our research group at the University of Wisconsin is one of 12 institutions involved with the larger METAALICUS project (see left hand side of Figure 2). Our work was performed in close cooperation with Dr. David Krabbenhoft and his laboratory at the Middleton office of the United States Geological Survey. Dr Krabbenhoft provided in-kind support for the project through use of the analytical instrumentation to analyze the samples for mercury isotopes. His research group also provided data and expertise regarding the terrestrial component of the project. This information and support was critical for completing and interpreting the results. This report covers the work coordinated by Dr. James Hurley and Dr. Christopher Babiarz at the University of Wisconsin.

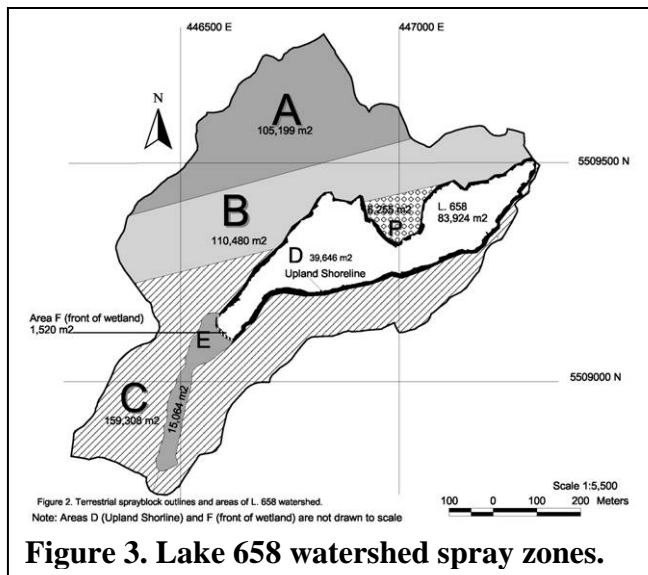
Figure 2. Organizational chart for the University of Wisconsin research group.



Methods and Field Work

Spike Applications

Isotopes of mercury were applied to the lake and watershed using three methods that were tailored to the local terrain and required weather conditions. Each method was used for a different compartment of the L658 basin: terrestrial, shoreline, and lake. In all cases, the target application rate was $25 \mu\text{g}/\text{m}^2/\text{yr}$ (approximately four times the ambient wet deposition rate for mercury at ELA).



Terrestrial: For the terrestrial isotope application, the watershed was split into four areas that were sprayed by airplane (Figure 3): One block for the wetland (E) and three blocks for the upland (A, B, and C). To minimize drift of the spray mist outside of the spray blocks, the spray nozzles were opened and closed by GPS technology. The nozzles were programmed to open 20 meters after entering a spray block and close 20 meters before exiting a spray block. This resulted in 20-meter buffer zone around the outer edge of each block. The buffer zone was sprayed using a different method (see below)

In order to mimic wet deposition and minimize evaporative loss of the isotope, the terrestrial isotope would ideally be applied during a light rain. This is difficult in practice and two criteria were established for the terrestrial application: 1) heavy rainfall should occur within 1 hour of spraying onto dry foliage, and 2) winds should be less than 15 km/hr.

Shoreline: In order to minimize overspray of the terrestrial isotope onto the lake, the 20 meter buffer zone surrounding the shoreline (D and F in Figure 3) was sprayed by fire hose. A 2000 liter plastic tank was secured to a floating barge. The tank was filled with low-DOC water from nearby Lake Winnange because it did not contain the lake isotope. The shoreline was divided into several 20m x 20m plots that were systematically treated as follows: The isotope was mixed into the water stream at the nozzle using a device that diluted 1 liter of spike solution into ~350 liters of lake water. The water was evenly sprayed over the plot, saturating the canopy and ground vegetation. The process was designed to approximate a 1 cm rain event in order to match the precipitation requirement of the terrestrial application (see above). Additional criteria for the shoreline isotope application included low prevailing winds that were in the direction of the shore.

Lake: Application of the lake isotope occurred by boat. The spike solution was mixed into several 20-L carboys of lake water, and the solution was pumped into the wash of a trolling motor. Two small boats were driven around the lake in a random pattern, making sure to cover

the entire surface of the lake. The entire process took several hours to ensure good mixing and minimize the pumping rate. Additional criteria for the lake isotope application included low wind and low light conditions (dusk/night) to avoid photo-reduction and evasion of the isotope.

Field Apparatus

Specialized apparatus required for field sampling was manufactured for this project. All construction material was compatible with trace-metal clean techniques (Teflon, acrylic, polyethylene or polypropylene). All sampling devices and bottles were pre-cleaned using rigorous trace-metal clean protocols.

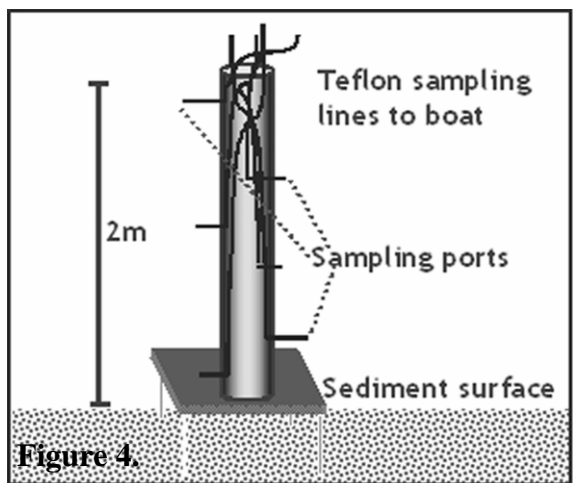
Water Column: Samples were obtained at depth using an all Teflon sampling line and weight connected to a peristaltic pump. The sampling depth was determined by lowering the weight and tubing with a metered Kevlar rope that was pre-cleaned. Samples near the sediment-water interface were collected using a Close Interval Sampler (CIS; see below) that was placed on the sediment surface by a SCUBA diver in June 2001 [5]. Particulate Hg samples were collected in-line on pre-ashed quartz fiber filters rated at a 0.7 μm pore size (Whatman QMA). Filtered Hg samples were collected through in-line polyethersulfone filtration capsules rated at 0.45 μm pore size (Meissner filtration products).

Close Interval Sampler: For accurate sampling of water just above the sediment-water interface, we employed a close-interval sampler. The device holds several Teflon ports at precise depths above the sediment-interface. Long sampling lines connect the ports to outlets at the surface of the lake (see Figure 4). A separate device was placed in each basin of the lake by SCUBA and was allowed to winter-over each season by submerging the outlet ports below the ice line.

Sediment Traps: Acrylic barrels (approximately 81 cm long and 14.5 cm internal diameter) were suspended by Kevlar ropes from a floating array.

Based on the design of Dean et al. [9], the barrels include a funnel to focus material into a bottle. The Trap dimensions are designed to minimize losses and over trapping due to internal lake currents. Traps were deployed in two week intervals to avoid complications from decaying matter and transformation of mercury into methylmercury. Trap material was sieved at 243 microns to remove large particles and biota that would lead to over estimates of the sedimentation flux.

Sediment Coring: To collect sediment cores, we employed short acrylic tubes (approximately 30 cm long by 4.5 cm internal diameter). Cores were collected carefully by SCUBA to ensure that the interface was not disturbed. Cores were extruded on site and sliced at 1 cm intervals into pre-cleaned and pre-weighed vials. Sediments were frozen at the field station at the end of the field day.



Laboratory Methods

We employed state-of-the-art trace level analytical and sampling tools throughout the project.

Isotopic Hg analysis was determined using a Perkin-Elmer Élan 6100 (ICP-MS) that is dedicated for Hg-only analysis. This ultra-sensitive instrument is housed in a state-of-the-art Hg analytical facility operated by Dr. David Krabbenhoft at the USGS in Middleton, Wisconsin. The instrument is fitted with a continuous flow-injector analyzer system, and an inline gold amalgamation system, that allows for rapid sample throughput and low-level detection. The method, modeled after the pioneering work of Hintelmann, et al. [10, 11], has an absolute detection limit of about 1 pg Hg, or about 0.05 ng L⁻¹. The minimum detectable amount of MeHg is also 1 pg.

Bioassay techniques that were developed in conjunction with the Wisconsin State Laboratory of Hygiene (WSLH) were used to assess the bioavailability of old versus new Hg. The WSLH is part of the University of Wisconsin and operates a state of the art biomonitoring facility. In short, cultures of algae (*Selenastrum Capricornutum*) are exposed to test waters that contain a spike of MeHg. Uptake and partitioning of the added mercury is determined after a set incubation time. In essence the exposure is a competitive ligand experiment and gives a relative assessment of the binding strength of the ligands in the test water.

Modeling efforts were supported by providing data from this project to Reed Harris at Tetra Tech Incorporated. Mr. Harris has been instrumental in designing a world-class interactive model of mercury cycling in lakes (the MCM model). The data will improve the calibration of the model for better predictive capacity, and will allow researchers to pose strategic “what if” questions while designing future research studies. At the present time, Tetra Tech is in legal proceedings over ownership of the model. As a result, the MCM model is not presently available for use.

Ultrafiltration techniques were employed to isolate the colloidal-phase. In short, several liters of water are circulated tangentially across a membrane. Some of the water passes through the membrane and is collected as the “permeate.” The remaining water is recirculated until the concentration factor reaches approximately 5. More information on ultrafiltration techniques can be found elsewhere [12].

Resin Techniques

We used Chelex and DEAE resins to determine the portion of weakly-bound Hg(II) in solution. Both techniques offer a standardized method of comparing natural waters against the chelation strength of the resins. Dissolved Hg(II) is retained on Chelex resin, and negatively charged DOC is retained on DEAE.

Iron speciation

We used several techniques to characterize the speciation of iron in natural waters. These include ammonium oxalate extraction (to determine the concentration of amorphous iron) and an optical technique based on phenanthroline chelation (to determine the dissolved phase concentration of Fe(II) and Fe(III)).

Field Campaigns

We completed 12 field campaigns during the course of the project and collected over 1400 individual samples for total and methylmercury analysis. Each campaign usually consisted of four people and three days on site. Table 2 indicates the focus of each field trip. In October 2004 several people joined our field campaign including: geochronology experts Dr. Daniel Engstrom of the Minnesota Science Museum and Drs Edward Swain and Bruce Monson of the Minnesota Pollution Control Agency. These scientists collected and sliced sediment cores from Lake 658 for lead-210 analysis. The results were 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 the project).

Table 2: Summary of Field campaigns for the project.

	2003					2004						2005				
	June	July	Aug	Sept	Oct	May	June	July	Aug	Sept	Oct	May	June	July	Aug	Sept
Lake Profiles	1	1	1	1	1	1	1	1	1	1	1				1	
Sediment Traps		2	2	2	1		3	2	2	2	1					1
DOC SUVA/Pigments	1	1	1	1	1	1	1	1	1	1	1				1	
DEAE/Chelex Resin work		1	1		1				1		1					
Sediment Collection	1				1		1				1					
Mixed-Core Experiments	← Incubation →										1					
Bioavailability Work								1							1	

This table indicates the total number of sampling trips in a given month to collect samples from each row/category.

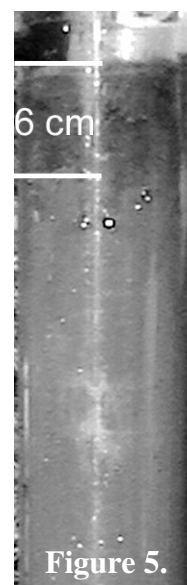
Results and Discussion

Results by our research team indicate that newly deposited Hg is very reactive in each compartment, but the time scale of transport and transformation varies widely. For example, on the short time scale (minutes/hours/days), new Hg is largely bound to particles in each compartment. On the moderate time scale (weeks/months), new Hg is transformed into MeHg (the bioaccumulative form) in the lake and wetland. On the long time scale (years/decades) the effects are difficult to assess given the relatively recent application of the isotopes to the watershed. In the Terrestrial compartment, however, there is some indication of delayed erosion transport of new Hg and/or delayed release of Hg by humic acids (after aging in upland soils). Below we describe the results from each of the key actions funded under this project in more detail.

Action: Mixed-Core Experiments.

Objective: Assess post-depositional processes migration, long-term methylation/demethylation, and estimate net burial rates for Hg in pelagic and littoral sediments.

Methods: Before the first spike was applied to the lake (June 2001), we placed several acrylic barrels at the bottom of the lake that were filled with homogenized sediment and evenly spiked with different isotopes of Hg (^{201}Hg , and Me^{199}Hg). These mixed-cores were incubated in both the pelagic and littoral regions of the lake. The cores were removed from the lake by SCUBA in October 2004 after ~40 months of incubation. Funding from Wisconsin Focus on Energy allowed us to double the incubation time and reduce uncertainty in the results. The sediments were sliced on site and stored frozen for analysis of isotopic Hg, isotopic MeHg, carbon content, water content, and bulk density.



Outcome: 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.

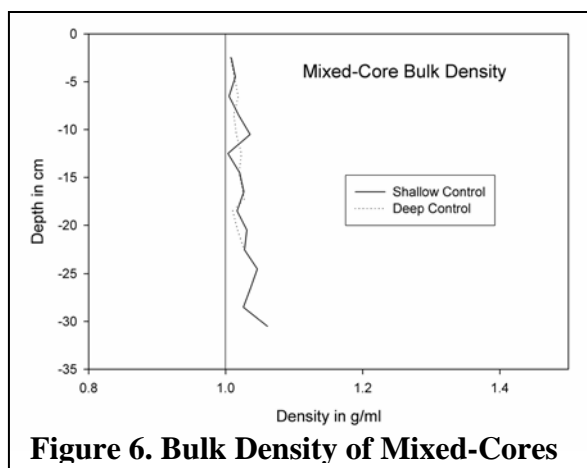


Figure 6. Bulk Density of Mixed-Cores

Changes in the ^{202}Hg or Me^{202}Hg will indicate near surface recycling of new Hg. Samples are currently under analysis but visual inspection indicates a substantial layer of recently deposited flock (see Figure 5). Measurements of bulk density show a slight increase in density with depth, but are effectively uniform throughout (Figure 6). Like the rest of the lake, most of the sediments are composed of soft organic material. The lack of a strong shift in density between the recent accumulation and the mixed sediment indicates good agreement with typical sediment accumulation in the lake.

Action: Lake Profiles & Sediment Trap Deployment.

Objective: Establish the hypolimnetic mass balance for Hg in the lake. Establish the importance of turnover in redistributing recently deposited Hg throughout the lake.

Methods: Water column profiles were collected in both the East and West basins of Lake 658. Typical sampling depths were 2, 5, 7, 9, and 13 m below the water surface. Additional samples were obtained at 5, 10, 20, 40, and 80 cm above the interface to better define important hypolimnetic processes in that region. In addition to Hg samples, we collected ancillary data on temperature, pH, dissolved oxygen, redox potential, conductivity, DOC, suspended particulate matter (SPM), and major ions (primarily Fe and Mn).

Sediment traps were deployed in each basin to collect falling particulate matter. Positioning of the traps was just below the average thermocline (7 m), and just above the sediment water interface (9 m in the east basin, 13 m in the west basin). Differences between upper and lower traps help assess Hg transport, transformation, and dissolution from particles. Traps were deployed during ice-free periods and processed on a bi-weekly basis. Analytes for all samples collected under this action item included total mercury, MeHg and a subset of the following ancillary measurements as appropriate: Major ions, pH, conductivity, temperature, DO, DOC, Redox potential, SPM, LOI, pigments.

Outcome: Native total mercury (HgT) concentrations in the water column were fairly uniform during the 2003 and 2004 field seasons. Concentrations in 2003 ranged from 3 to 9 ng L⁻¹ in the filtered phase. Larger concentrations were observed during the summer months in the hypolimnion. The Lake isotope amendment ranged from 0.2 to 1.7 ng L⁻¹ in the filtered phase. The Wetland and Upland isotope amendment was rarely detectable, but ranged from 0 to 0.1 ng L⁻¹. At times, the Lake isotope amendment was up to 30% of the native pool in the filtered phase. Filtered phase isotopic Hg remained largely in the epilimnion until the thermocline broke down. During most of the year, transport of isotopic Hg from the epilimnion to the hypolimnion was primarily through particulate matter. The concentration of isotopic Hg on falling particles ranges from 0 to 0.88 ng L⁻¹ reaching 141% of the native HgT on particulates (58% of the sum total). Methylated lake isotope reached 180% of the native MeHg concentration on particles (42% of the sum total). These results show that the new Hg is reactive and preferentially binds to particles.

Partitioning of Hg to particles can be expressed as:

$$K_D = 1000 \times \frac{[\text{Hg}]_p}{[\text{Hg}]_f} \quad (\text{units: L/Kg})$$

Where K_D is the partition coefficient; $[\text{Hg}]_p$ is the concentration of mercury on particles (in ng/g); and $[\text{Hg}]_f$ is the concentration of mercury in the filtered phase (in ng/L). As the amount of mercury associated with the particulate phase increases (with respect to the filtered phase) the value for K_D also increases.

The correlation between native and lake-spike partitioning to particles is shown in Figure 7. Any deviation from a 1:1 correlation indicates that the native and lake-spike pools of HgT are

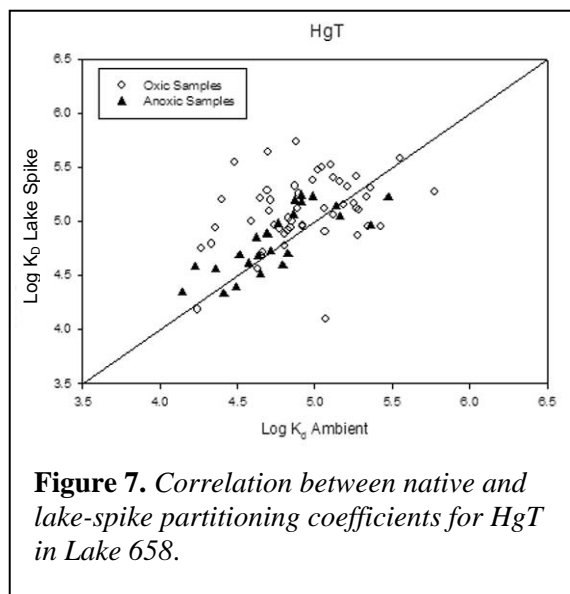


Figure 7. Correlation between native and lake-spike partitioning coefficients for HgT in Lake 658.

behaving differently in L658. The observed shift toward larger partition coefficients for the lake-spike may result from several processes. First, most of the shift occurs in the oxic waters of the epilimnion (open symbols in Figure 7) and may reflect the introduction method. Recall that the isotope is introduced by boat into the top meter of the lake at a rate 5x the annual wet deposition. The partition coefficient is an equilibrium-based concept and the shift may reflect a short-term kinetics-based phenomenon. If so, the shift will likely diminish as the isotope is incorporated into the system after the isotope additions end. This hypothesis is backed by the near 1:1 correlation for hypolimnetic samples which presumably reflects Hg that has been recycled through the ecosystem.

Another hypothesis for the shift is that epilimnetic particles have a different chemical character than hypolimnetic particles. Epilimnetic particles presumably have a larger percentage of living biotic material than those in the hypolimnion. We hypothesize that strong metal-binding ligands are associated with this biotic material. As the biotic particles die and decompose, mercury associated with material is released to the dissolved phase. The near 1:1 correlation in the hypolimnion suggests that the metal-binding ligands associated with the remaining recalcitrant material are relatively weak. As oxygen is depleted in the hypolimnion, lake-spike and native mercury behave similarly with respect to particle partitioning.

The monthly sedimentation flux for mercury in 2003 is presented in Figure 8. Also plotted is the filtered-phase concentration of mercury at the depth of deployment for each set of sediment traps. In general, filtered-phase concentrations are relatively constant at a given depth, varying by only 1-2 ng/L across the field season. This is especially true for the oxic waters in the epilimnion (closed symbols in figure 8). In the suboxic waters of the hypolimnion, there is a general trend toward higher concentrations with time – especially for the lake-spike (open symbols in figure 8). This trend likely reflects the schedule of lake-spike additions that run on 2-week intervals from June through October. As explained further below, however, fall overturn plays an important role in the cycling of mercury in L658 (note the late-October increase in lake-spike HgT concentration on panel C of figure 8).

The flux of particulate mercury to the deep sediment traps is generally larger than that to the shallow traps; this observation is especially true for MeHg (panels B & D in Figure 8). In addition, lake-spike MeHg flux approaches the magnitude of the native MeHg flux throughout most of the year. This observation indicates that the lake-spike is readily available for methylation in the system and may provide anecdotal evidence that all MeHg in the ecosystem is new (or at least behaves as though it is constantly refreshed or recycled).

Calculations of the residence time of Hg in the lake and its long-term fate (i.e. relative proportion buried, bioaccumulated, or evaded) are forthcoming in manuscripts for peer-reviewed journals.

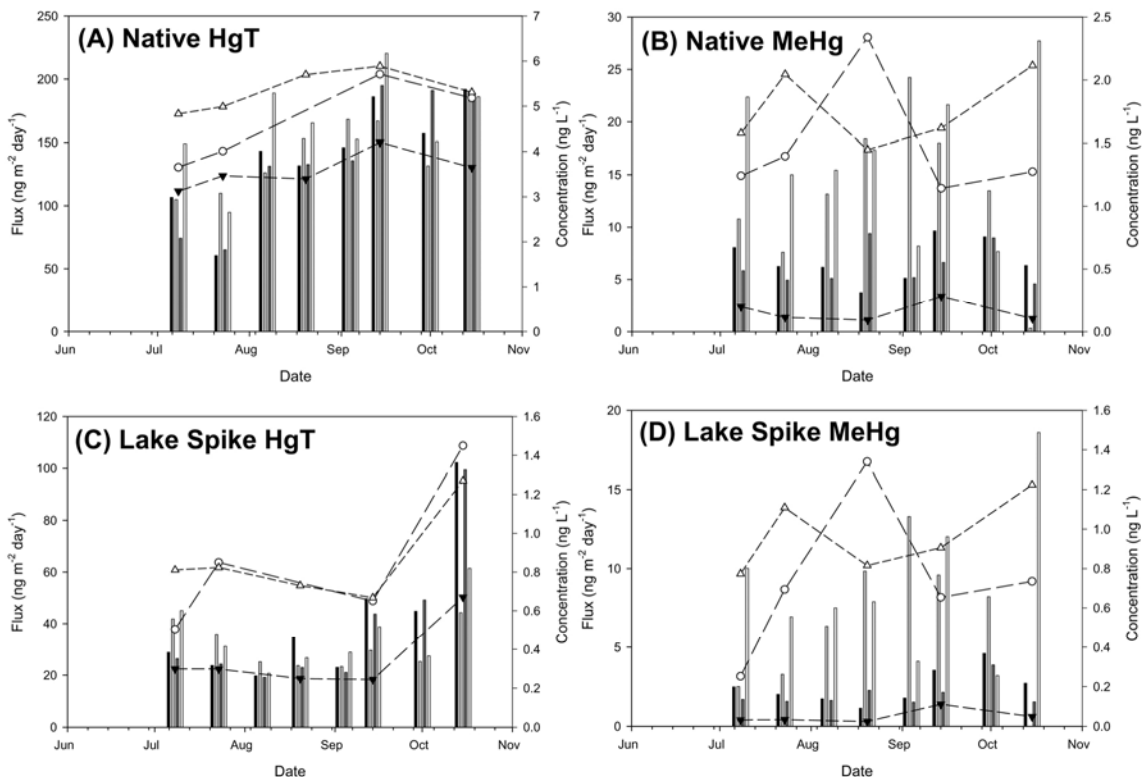


Figure 8. Sedimentation flux of mercury in the east and west basins of Lake 658 for the 2003 field season. Bar groupings are as follows (from left to right): East 7m, East 9m, West 7m, West 13 m. Lines represent the concentration of mercury in the filtered phase ($0.45 \mu\text{m}$) at the depth of trap deployment. Open circles represent the East Basin 9m traps. Open triangles are the West basin 13 m traps. Closed triangles represent the West basin 7 m traps (in 2003, the East basin 7 m traps were not deployed). (A) Ambient HgT; (B) Ambient MeHg; (C) Lake spike HgT; and (D) Lake spike MeHg.

Action: Resin, Pigment, Optical, and Size-fractionation of DOC

Objective: Establish the importance of DOC character on Hg transport and transformation.

Methods: Our lab has been developing methods to better characterize the role of DOC and Fe/Mn redox cycle on cycling of Hg in Lake 658. DOC has long been indicated as a transport vector for Hg in freshwaters [13-15]. The better we can describe the chemical character of DOC, the better we can establish the underlying ligands and mechanisms that control the fate of Hg in freshwater systems. We used Chelex and DEAE resins to assess the binding of mercury to DOC. We also made Specific Ultraviolet Absorption (SUVA) measurements to characterize the relative aromaticity of DOC (an indication of terrestrial vs. in-lake production). Pigment samples also help establish terrestrial versus in-lake carbon sources by identifying and quantifying degradation products. Ultrafiltration was used to isolate the importance of colloidal material in the partitioning and transport of mercury.

Outcome: The results from these experiments suggest a dynamic cycle of mercury transport and transformation in the hypolimnion. Key factors in this cycle include the mineralization of aliphatic particulate matter that settles from the epilimnion, the coupling with the oxidation/reduction cycle of iron, and the association of mercury with colloidal phase organic carbon.

A typical summer profile of DOC is presented in Figure 9. The concentration of DOC increases with depth and the highest concentrations were observed just above the sediment-water interface. This enrichment has been hypothesized to result from mineralization of recently-fallen planktonic particles and the release of DOM associated with iron oxides particles as they dissolve under reducing conditions in the hypolimnion [16] (See reprint in the appendix).

This hypothesis is supported by supplemental information from optical characterization of DOC and analysis of pigments. Our primary optical method was specific UV absorbance (SUVA). Defined as the UV absorbance of a water sample (at a given wavelength) normalized for DOC concentration, it is a useful parameter for estimating the dissolved aromatic carbon content in aquatic systems [17-19]. This is particularly true at 254 nm where SUVA is strongly correlated with percent aromaticity. SUVA can be a semi-quantitative measure of chemical character by expressing the term as a ratio of absorbance at two paired wavelengths.

For example, the E2:E3 ratio is defined as the UV absorbance at 254 nm divided by the UV absorbance at 365 nm. A low value for the E2:E3 ratio is indicative of highly-condensed terrestrial (i.e. allochthonous) carbon while a high ratio is indicative of more aliphatic planktonic (i.e. autochthonous) carbon. The E4:E6 ratio is defined as the UV absorbance at 465 nm divided by the UV absorbance at 665 nm. The E4:E6 ratios for humic acids are usually less than 5.0 while ratios for fulvic acids range from 6.0 to 8.5 [20].

On August 18, 2003, both the E2:E3 and the E4:E6 ratios decreased with depth in Lake 658 (Figure 10). This observation suggests that the molecular weight and aromaticity of DOC increases with depth (a phenomenon described as condensation by Chin *et al.* [17] and Peuravuori *et.al.* [18]). Both the E2:E3 and E4:E6 ratios support the hypothesis that deep hypolimnetic carbon is more terrestrial in nature. However, these results must be viewed in context of additional information. For example, the concentration of iron also increased with depth in the hypolimnion. Both Fe(II) and Fe(III) absorb UV light, and research has shown that

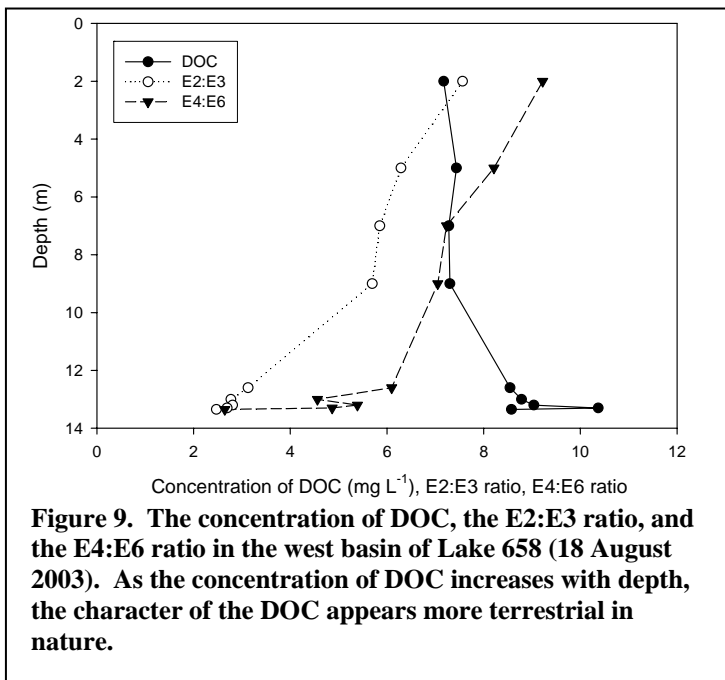


Figure 9. The concentration of DOC, the E2:E3 ratio, and the E4:E6 ratio in the west basin of Lake 658 (18 August 2003). As the concentration of DOC increases with depth, the character of the DOC appears more terrestrial in nature.

Fe can lead to artificially high values for SUVA at 254 nm [19]. In addition, our pigment data suggests that autochthonous carbon is important in the hypolimnion. The highest concentrations of chlorophyll-a, pheophytin-a, and pheophorbide-a (indicators of carbon produced in-lake) were collected from depths just above the sediment-water interface.

In this milieu of organic and inorganic particles, mercury is primarily associated with the organic phase (Figure 10). The association is pronounced in the oxic epilimnion where aliphatic particles are generated and inorganic iron hydroxides are in very low concentration. The importance of these inorganic particles grows in the anoxic hypolimnion where they deliver mercury to the lake bottom. Together these observations suggest that the sediment-water interface is an important site for particle transformation and that mercury will be recycled in the hypolimnion before eventual burial.

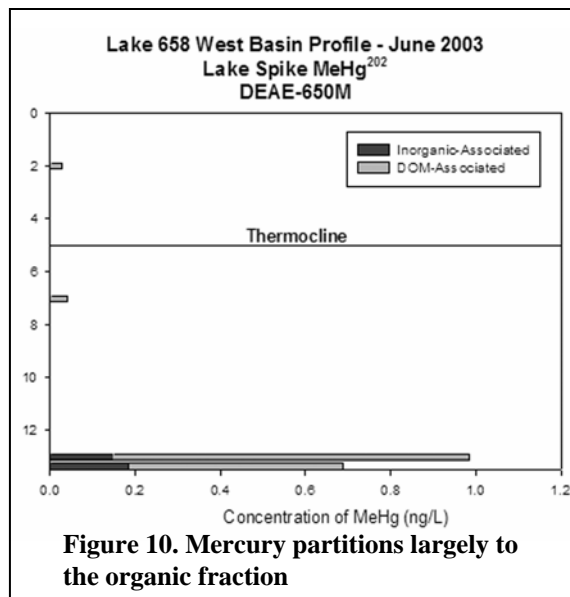


Figure 10. Mercury partitions largely to the organic fraction

Action: Bioavailability Work.

Objective: Determine the availability of the spiked Hg to algae over time.

Methods: Bioassays were conducted in cooperation with the WI State Laboratory of Hygiene Biomonitoring Group using the technique developed by Gorski and Shafer. Dr. Patrick Gorski, Dr Helen Manolopoulos, and Rebecca Moore performed the bioassays on waters from several compartments in Lake 658. These included ELA rain water and water-column samples from the epilimnion and hypolimnion. The bioassay on rain water was conducted under three conditions: full strength rain, 50:50 mixture of rain water and Lake Michigan water, and full strength Lake Michigan water. The idea was to test the change in bioavailability as rain is mixed with receiving waters. Additional water from an ELA stream was collected and ultrafiltered to determine bioavailability from terrestrial waters (a large portion of the overall mercury mass-balance budget)

Outcome: Initial results on the water column samples from 2002 were discarded because the spike levels were too low for the technique to work. Samples were collected again in 2005 and the bioavailability tests are currently in progress. The results will help determine the strength of competitive ligands in ELA lake waters and stream waters. The bioassay on ELA rainwater from 2004 suggests that the receiving water and the 50:50 mixture of rain and receiving water have similar uptake by the algae.

Value and Transferability of the Results

Results from METAALICUS are valuable because the project design is unique and the information obtained is readily transferable to other ecosystems. The project will not likely be repeated due to the cost (\$670,000 USD per year for stable isotopes alone) and the necessary permitting (achieved at ELA). This internationally renowned project brings together top experts in the environmental field and builds upon Wisconsin's proactive approach to better understand complex environmental issues. The use of mercury stable isotopes is a powerful tool that enhances the quality of information obtained by the project. Isotopic techniques allowed us to probe process-level questions and apply the results to other ecosystems. Understanding the factors controlling transport and transformations of mercury is a key to predicting the long-term effects of management decisions regarding Hg emissions.

Among the key findings of this study is the unique behavior of “new” versus “old” mercury. For example, partitioning data suggests that “new” Hg in the epilimnion is more particle reactive than old mercury. Particle transport may then preferentially deliver new mercury to sites of methylation – as supported by the rapid conversion of the inorganic spike to the methylated form within 2-weeks of the initial introduction. As the mercury “ages” the partitioning behavior becomes indistinguishable from the historic pool. These results suggest a rapid response to decreases in atmospheric loading of mercury directly to the lake surface.

This study was not conducted on a lake in Wisconsin, but we are confident that results are directly applicable to many non-calcareous lakes in Wisconsin that derive their mercury load from atmospheric sources. While Lake 658 may have slightly higher epilimnetic DOC levels (6-8 mg/L) than many Wisconsin lakes, the rapid uptake of “new” Hg by plankton suggests that DOC did not inhibit particle uptake. More importantly, the information on processes and rates occurring at the sediment-water interface that rapidly recycle freshly deposited Hg is directly applicable to lakes in Wisconsin that thermally stratify. Information on these rates is critical for predicting the response of Hg reductions to decreased loading of “new” Hg. Further work on the overall MEAALICUS project beyond the scope of this two-year study will allow field validation of rates and mechanisms of watershed and lake responses to reduced loading. Determination of rates of key mercury cycling processes (separating “new” Hg from the historical pool) is vital for models that applied to lakes throughout Wisconsin.

Outreach Efforts

Information obtained from this project has been disseminated through several outreach efforts. These include collaboration with outside scientists, participation and presentations at scientific conferences and workshops, publication of peer-reviewed manuscripts, and reports to funding agencies and stakeholders.

Collaboration: In addition to collaboration with scientists associated with the METAALICUS project, we invited several specialists to join us during our field campaigns or perform cooperative work. This expanded the impact of the project and strengthened the interpretation of the results.

Notable collaboration within the METAALICUS project included close cooperation with the USGS isotope laboratory operated by Dr. David Krabbenhoft (Middleton, WI) and coordinated field campaigns with Cindy Gilmour of the Academy of Natural Sciences in Maryland (presently with the Smithsonian Institution). Dr. David Krabbenhoft graciously offered in-kind support for this project by providing access to specialized analytical equipment for isotope analysis. We have also worked with his research team to accomplish many field tasks that benefited both research groups. Dr. Gilmour was responsible for collecting littoral zone sediment cores that complement those we collected from the hypolimnetic zone. Together we have mapped the deposition of mercury to the sediments across the entire lake.

In February 2004 our research group organized a meeting to discuss the in-lake results. The meeting brought together the principle investigators on the project from at least five institutions to synthesize the data to date. The primary goal was to prepare a mass balance budget for the lake and discuss manuscripts in advance of the annual METAALICUS project meeting.

Notable collaboration outside of the METAALICUS project included Nives Ogrinc of the J. Stefan Institute in Ljubljana, Slovenia, and Dr. Daniel Engstrom of the Minnesota Science Museum. Dr. Ogrinc is an expert in carbon cycling and identifying the origin (i.e. terrestrial vs. in-lake production). In June 2004, 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 was brought on board to determine the historical sedimentation record of Lake 658 and estimate the time-dependant burial of mercury – a critical component of the hypolimnetic mass balance (and a major objective of this project). On December 15th 2005, we held an all-day meeting with Dr. Engstrom at the St Croix Watershed Research Station in Marine on St. Croix, MN. During that meeting we combined and reviewed our data sets on Hg and Pb-210 in sediments of L658. The outcome of the meeting was a framework for describing sedimentation processes and a plan of action for synthesizing the data into manuscript on net accumulation of Hg in L658 sediments.

Workshops:

Dr. James Hurley served on the Steering Committee for the Seventh International Conference on Mercury as a Global Pollutant (June 30 to July3, 2004). He made trips to Ljubljana, Slovenia in 2003 and 2004 to plan the conference. He was instrumental in developing the program and to a lead on providing opportunities for students.

In November 2004, 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. Christopher 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).

Since October 2001, Dr James Hurley, Dr. David Krabbenhoft, and Dr. Christopher Babiarz have served on the Conference Organizing Committee for the Eighth International Conference on Mercury as a Global Pollutant (August 6-11, 2006, Madison, Wisconsin, USA). Dr. Hurley Co-Chairs the conference with Dr. David Krabbenhoft, and Dr Babiarz serves as conference secretariat. The fourth member of the Conference Organizing Committee serves as the technical chair (Dr. James Wiener of the University of Wisconsin – La Crosse). The Conference Organizing Committee has set three principal goals for the conference: to enhance the synthesis of information; to enhance the integration of science and policy concerning environmental mercury pollution; and to increase participation by under-represented groups, including graduate students, beginning professionals, and representatives of developing nations. The conference received nearly 1100 abstracts (a new record for the conference series), and significant progress has been achieved toward each goal. For more information, visit www.mercury2006.org

Presentations:

Graduate student Shawn Chadwick presented a paper entitled: “Speciation controls on the fate and transport of mercury and methylmercury across biogeochemical gradients” at the American Water Resources Association (AWRA) meeting in Wisconsin Rapids (March 4-5, 2004). This meeting brings together environmental scientists and managers in Wisconsin to discuss current research affecting state water resources.

Our research group presented two posters on the METAALICUS project at the 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”

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

Dr. Christopher Babiarz gave an invited presentation on METAALICUS results at the Fall Meeting of the American Geophysical Union (December 14-17, 2004 in San Francisco, CA). The presentation was entitled “Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management.” The presentation 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.

Publications and reports: In addition to quarterly progress reports to the Environmental Research Program of Wisconsin Focus on Energy, we have also prepared manuscripts for peer-reviewed publication. One manuscript written by Shawn Chadwick et al. was recently published in Science of the Total Environment. The paper is reproduced in the Appendix and is entitled “Influences of iron, manganese and dissolved organic carbon on the hypolimnetic cycling of amended mercury.”

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Appendix

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Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury

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Abstract

The biogeochemical cycling of iron, manganese, sulfide, and dissolved organic carbon were investigated to provide information on the transport and removal processes that control the bioavailability of isotopic mercury amended to a lake. Lake profiles showed a similar trend of hypolimnetic enrichment of Fe, Mn, DOC, sulfide, and the lake spike (²⁰²Hg, purity 90.8%) and ambient of pools of total mercury (HgT) and methylmercury (MeHg). Hypolimnetic enrichment of Fe and Mn indicated that reductive mobilization occurred primarily at the sediment–water interface and that Fe and Mn oxides were abundant within the sediments prior to the onset of anoxia. A strong relationship ($r^2=0.986$, $n=15$, $p<0.001$) between filterable Fe and Mn indicated that reduction of Fe and Mn hydrous oxides in the sediments is a common in-lake source of Fe(II) and Mn(II) to the hypolimnion and that a consistent Mn:Fe mass ratio of 0.05 exists in the lake. A strong linear relationship of both the filterable [Fe] ($r^2=0.966$, $n=15$, $p<0.001$) and [Mn] ($r^2=0.964$, $n=15$, $p<0.001$) to [DOC] indicated a close linkage of the cycles of Fe and Mn to DOC. Persistence of iron oxides in anoxic environments suggested that DOC was being co-precipitated with Fe oxide and released into solution by the reductive dissolution of the oxide. The relationship between ambient and lake spike HgT ($r^2=0.920$, $n=27$, $p<0.001$) and MeHg ($r^2=0.967$, $n=23$, $p<0.001$) indicated that similar biogeochemical processes control the temporal and spatial distribution in the water column. The larger fraction of MeHg in the lake spike compared to the ambient pool in the hypolimnion suggests that lake spike may be more available for methylation. A linear relationship of DOC to both filterable ambient HgT ($r^2=0.406$, $n=27$, $p<0.001$) and lake spike HgT ($r^2=0.314$, $n=15$, $p=0.002$) suggest a role of organic matter in Hg transport and cycling. However, a weak relationship between the ambient and lake spike pools of MeHg to DOC indicated that other processes have a major role in controlling the abundance and distribution of MeHg. Our results suggest that Fe and Mn play important roles in the transport and cycling of ambient and spike HgT and MeHg in the hypolimnion, in part through processes linked to the formation and dissolution of organic matter-containing Fe and Mn hydrous oxides particles.

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Keywords: METAALICUS; Mercury; Methylmercury; Cycling; Iron; DOC

1. Introduction

Speciation of mercury (Hg) plays an important role on the fate and transport of mercury in aquatic environments (Miskimmin et al., 1992; Watras et al., 1995; Babiarz et al., 1998; Benoit et al., 1999b) and its subsequent methylation (Compeau and Bartha, 1985;

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Gilmour et al., 1992; Benoit et al., 1999a, 2001a,b; Mehrotra et al., 2003). Detailed information regarding the chemical and physical speciation of Hg and methylmercury (MeHg) can help elucidate the transport and removal processes that control bioavailability of the Hg for methylation and bioaccumulation. The speciation of Hg and MeHg is hypothesized to be controlled by organic and inorganic aqueous-phase speciation (e.g., sulfide, thiol-containing DOM) and solid-phase partitioning (Hurley et al., 1995; Babiarz et al., 1998; Benoit et al., 1999b). Although our understanding of Hg and MeHg cycling in the environment has advanced significantly in recent years, a complete understanding of Hg and MeHg speciation is lacking aside from thermodynamic predictions. Specifically, the relative role of iron/manganese oxides, dissolved organic matter (DOM), and sulfide as ligands in controlling Hg and MeHg speciation and the interaction of these ligand classes are poorly understood.

The fate of Hg introduced into a lake is expected to be linked to both transport and biogeochemical processes. Sedimentation of biogenic organic particles into the hypolimnion of stratified lakes results in an environment of high microbial activity and changing redox conditions, producing ligands that control Hg and MeHg speciation, and subsequent fate, transport, methylation, and bioavailability (Hurley et al., 1991, 1994; Benoit et al., 1999b; Babiarz et al., 2003a,b). The settling particulate organic matter is also a potentially important vector for Hg transport from the epilimnion into the hypolimnion. Microbial respiration of the organic matter produces anoxic conditions at the sediment–water interface and in the overlying hypolimnetic waters, conditions which influence the cycling of mercury prior to burial in the sediments (Hurley et al., 1994; Babiarz et al., 2003a). Anoxic conditions pro-

mote reduction of sediment Fe and Mn hydrous oxides and release of reduced Fe and Mn into the overlying water. Migration to oxic/anoxic boundaries produces Fe and Mn hydrous oxides which incorporate organic matter and inorganic oxide particles/colloids which scavenge trace metals from the aqueous phase in freshwater lakes (Taillefert et al., 2000; Davis, 1984). Specifically, Fe and Mn have large adsorption capacities that can control the concentrations of other ions and dissolved organic matter. Fe and Mn have previously been implicated to be significant in controlling Hg and MeHg distributions (Bloom et al., 1999).

The work presented here is a subproject of the “Mercury Experiment To Assess Atmospheric Loading in Canada and the United States” (METAALICUS), a study designed to better understand the relationship between atmospheric loading of Hg and bioaccumulation in fish. We focused on investigating factors that control the fate and transport of Hg and MeHg across the sediment–water interface. We describe the Fe, Mn, and organic matter cycling in the hypolimnion of Lake 658 and whether relationships to HgT and MeHg suggest an important role of these biogeochemical cycles in controlling the fate and transport of ambient and amended Hg in this experimental lake. We focus on the ambient and lake spike (^{202}Hg , purity 90.8%) Hg and MeHg pools.

2. Site description

Lake 658 (49°43.95' N, 93° 44.20' W) is an 8-ha first-order boreal lake located within the Experimental Lakes Area (ELA) in northwestern Ontario (Fig. 1). Dimictic Lake 658 is separated into two basins with each having a seasonally anoxic hypolimnion (Fig. 1). The maximum depth of the west and east basins are

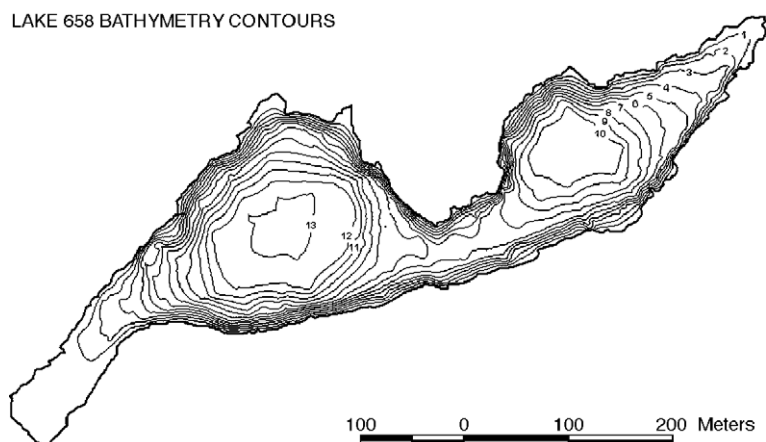


Fig. 1. Bathymetric map of Lake 658 (Middel et al., 2004).

13.4 and 10.9 m, respectively. The lake is connected to Lake 660 (Lake Winnange), and hydrological flows are measured continuously during the ice-free season. The long-term average water residence time of Lake 658 is approximately 5.5 years (Sandilands et al., 2005).

The terrestrial catchment of the watershed is dominated by jack pine (*Pinus banksiana*), black spruce (*Picea mariana*), white birch (*Betula papyrifera*), and trembling aspen (*Populus tremuloides*). Mineral soils within the watershed are thin (usually 1 m or less in depth) and discontinuous over pink Precambrian granodiorite. Soils and bedrock are typically covered with moss (*Spagnum* sp.), club moss (*Lycopodium* sp.), and lichens. Moss (*Spagnum* sp.) reaches depths greater than 0.5 m in the wetland and low-lying areas. Intermittent streamflow drains the uplands and the wetland adjacent to the lake.

3. Methods

3.1. Application of isotopic Hg to Lake 658 and its watershed

Lake 658 was dosed bi-monthly with stable ^{202}Hg nine times during each summer of 2001–2004 at a loading 4 to 5 times the annual wet deposition rate ($\sim 20 \mu\text{g}/\text{m}^2/\text{year}$). In addition, ^{200}Hg and ^{198}Hg were applied annually at a similar loading rate to the 42-hectare upland and 2-hectare wetland portions of the lacustrine watershed, respectively. The total dose over the 2001–2003 period to each part of the ecosystem was $67 \mu\text{g m}^{-2}$ to the upland, $76 \mu\text{g m}^{-2}$ to the wetland, and $66 \mu\text{g m}^{-2}$ to the lake (Sandilands et al., 2005).

Lake spike was added every two weeks from early June until mid-October during the 2002 field season at a loading rate of $22.12 \mu\text{g}/\text{m}^2/\text{year}$ (Sandilands et al., 2005). Prior to spiking, the isotope was pre-mixed with Winnange Lake water in individual 20-L carboys. The lake spiking process involved two boats (one for each basin) powered with electric trolling motors each slowly dispensing the spike into the wake in the epilimnion (Sandilands et al., 2005). The spike solution was administered to the lake at dusk to minimize photo-reduction and evasion. The spike generally resulted in a doubling of the mercury concentration (2 to 3 ng L^{-1}) in the epilimnion of the lake (Hintelmann et al., 2005).

3.2. Sampling methods

All sampling, sample processing, and analysis for Hg and MeHg followed accepted clean techniques to

minimize contamination of samples (US EPA, 1996; Olson et al., 1997; Cleckner et al., 1998). Individual water samples were collected 2, 5, 7, and 9 m from the water surface and 80, 40, 20, 10, and 5 cm from the sediment–water interface. Vertical water column profiles presented here were obtained on the day before each spike (13 days after the previous spike). Six monthly vertical profiles were collected between 31 May 2002 and 22 October 2002. Three vertical profiles are presented here: 15 July 2002, 12 August 2002, and 9 September 2002. Water column samples were obtained by using an all Teflon sampling line and weight connected to a peristaltic pump from a clean boat dedicated to mercury sampling. Filtered samples were collected from acid-cleaned in-line polyethersulfone filtration capsules rated at 0.45- μm pore size (Meissner™ Filtration Products). Samples near the sediment–water interface were collected using a close interval sampler (CIS) constructed of trace-metal compatible materials that allowed us to sample at these fixed depths above the sediment–water interface (Colman, 1979; Babiarez et al., 2003a; Hurley et al., 1994).

Samples for Hg and MeHg analysis were collected in acid-cleaned Teflon bottles, double-bagged, preserved to 1% acid using 50% trace metal grade HCl, and stored at 4 °C until analysis. Major ion samples were collected in acid cleaned PTFE-lined bottles, preserved to 1% acid using 50% trace metal grade HNO_3 , and stored at 4 °C until analysis. DOC samples were collected in 125 mL amber bottles and stored at 4 °C until analysis.

3.3. Analytical methods

All isotopic analyses of Hg and MeHg were performed at the state-of-the-art laboratory operated by USGS in Middleton, WI. Total mercury concentrations were determined using the bromine monochloride (BrCl) oxidation technique followed by stannous chloride (SnCl) reduction, nitrogen purging, gold-trap pre-concentration, and thermal desorption (Gill and Fitzgerald, 1987). Detection was via inductively coupled plasma-mass spectrometry (ICP-MS) on a Perkin Elmer ELAN 6100 (Hintelmann et al., 2002; Babiarez et al., 2003b). MeHg was determined by distillation, aqueous phase ethylation, nitrogen purging, Carbotrap® pre-concentration, thermal desorption, chromatographic separation, and ICP-MS detection (Bloom, 1989; Hintelmann et al., 1995; Hintelmann and Evans, 1997; Babiarez et al., 2003b). The analytical detection limits (three times the standard deviation of the blank) aver-

age 0.1 ng L^{-1} HgT and 0.05 ng L^{-1} MeHg. Our laboratory protocols require the re-analysis of individual samples until the relative standard deviation is within 10% and spike recoveries are within 25%.

Dissolved organic carbon (DOC) was determined using high temperature ($680 \text{ }^{\circ}\text{C}$) catalytic oxidation (Shimadzu TOC-5000) with an analytical uncertainty of $\pm 0.1 \text{ mg L}^{-1}$. Major ion composition (Fe, Mn, Ca, Mg, S, K, and Na) was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer Optima 4300 DV) with an analytical uncertainty typically under 5%. Redox potential, dissolved oxygen, temperature, pH, specific conductance were measured in the field using a multi-parameter sonde (Hydrolab™ Scout II). Total sulfide samples were preserved with sulfide anti-oxidant buffer (SAOB) and analyzed within hours using a specific ion electrode (Benoit et al., 1999a,b). The analytical detection limit for this method was $0.1 \text{ } \mu\text{mol L}^{-1}$. Uncertainties in measurements of dissolved oxygen and temperature were $\pm 0.1 \text{ mg L}^{-1}$ and $\pm 0.1 \text{ }^{\circ}\text{C}$, respectively.

An iron speciation scheme was adopted to better understand oxidative–reductive iron cycling in Lake 658 (Taillefert et al., 2000). In this method, the particulate fraction is determined using the concentration difference between the total and filtered major ion sample. The concentration Fe(II) was determined using a modification of the 1,10-phenanthroline method

(APHA, 1992). Samples were immediately fixed in the field using the colorimetric reagent. Analytical uncertainty for the spectrophotometric determination of Fe(II) was typically less than 5%. The colloidal Fe(III) fraction was calculated as the concentration difference between total Fe and Fe(II) in the filtered major ion sample, assuming that all Fe(II) in the filtrate reacts with the reagent (Taillefert et al., 2000).

4. Results and discussion

4.1. Profile development of temperature, dissolved oxygen, Fe, Mn, DOC, and sulfide

Lake 658 is a dimictic lake that thermally stratifies shortly after ice-out in April or May. Typical water column profiles for the period of summer thermal stratification are shown in Figs. 2 and 3. As the summer progresses, the thermocline eventually deepens to approximately 5 m and gradually becomes shallower in fall until thermal mixing in late October–early November. The thermocline mid-point was positioned at approximately 5 m on 12 August and 9 September profiles (Figs. 2 and 3).

Dissolved oxygen profiles in the west basin of Lake 658 show development of anoxic conditions in the hypolimnion during summer stratification. Oxygen concentrations in the epilimnion ranged from 6.45 to

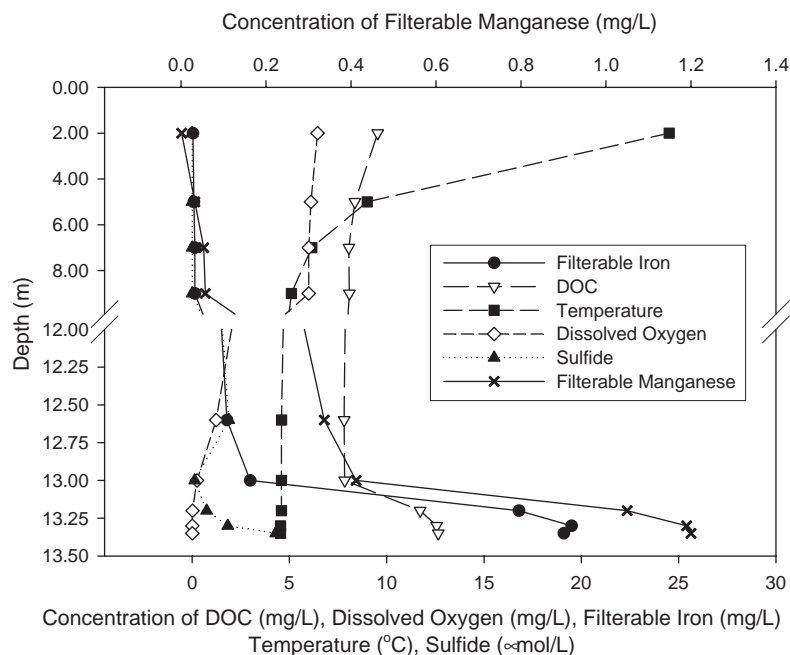


Fig. 2. Profiles of filterable iron and manganese, DOC, dissolved oxygen, sulfide and temperature in the water column of the west basin of Lake 658 on the 12 August 2002.

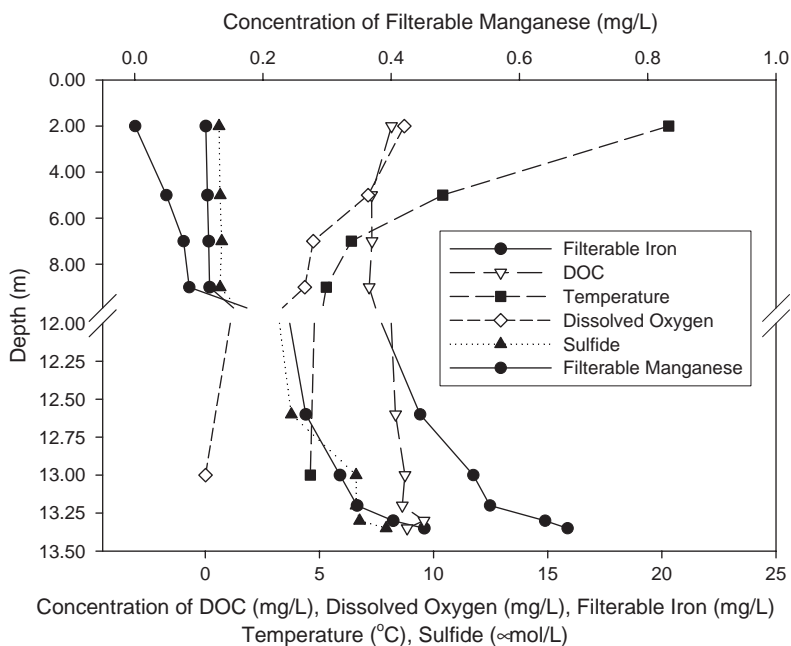


Fig. 3. Profiles of filterable iron and manganese, DOC, dissolved oxygen, sulfide and temperature in the water column of the west basin of Lake 658 on the 9 September 2002.

10.12 mg L^{-1} (77–121% of saturation) in 2002. The maximum is associated with primary production in the epilimnion. Organic particles from primary production, terrestrial transport, and resuspension of littoral sediments settle into the hypolimnion resulting in microbial respiration of the organic matter that produces anoxic conditions at the sediment–water interface and in the overlying hypolimnetic waters. The extent of anoxia in the hypolimnion increases through the late summer months (Figs. 2 and 3) until the breakdown of the thermocline in the fall resulting in rapid reoxygenation of the hypolimnion.

Hypolimnetic anoxia results in a reductive dissolution of Fe(III) and Mn(III, IV) oxide from the sediments followed by diffusion of soluble Fe(II) and Mn(II) to the overlying waters. Concentrations of Fe and Mn in the epilimnion are low and show little temporal variation. The average epilimnetic concentration of filterable Fe and Mn in 2002 were $87.3 \pm 20.8 \text{ ug L}^{-1}$ ($n=6$) and $16.4 \pm 9.0 \text{ ug L}^{-1}$ ($n=6$), respectively. The hypolimnion, on the other hand, shows enrichment in Fe and Mn (up to about 20 and 1 mg L^{-1} , respectively) near the sediment–water interface with increasing anoxia (Figs. 2 and 3). Hypolimnetic enrichment indicates that reductive mobilization occurred primarily at the sediment–water interface and that iron and manganese oxides are present within the sediments prior to the onset of anoxia.

Filterable Mn (as Mn(II)) remained in the water column longer than filterable iron (Figs. 2 and 3). This can be attributed to the higher standard potential of the Mn oxidation reaction and the slower oxidation kinetics of Mn(II) (Davison, 1993). The linear and concave shapes of the overall dissolved iron and manganese profiles near the sediment–water interface during the summer months indicate that the dominant source of dissolved Fe to the hypolimnion is reduction of Fe and Mn oxides in the sediment and diffusion to the overlying water; however, the slight convex shape near the sediment–water interface indicates that the reduction of Fe and Mn oxides associated with settling particles from redox cycling is also important in controlling the distribution of Fe and Mn in the hypolimnion (Davison, 1993; Balistrieri et al., 1992). While recycling from bottom sediments appears to be the dominant source for enrichment of the hypolimnion with Fe and Mn during summer, resuspension of littoral sediments and export from the terrestrial catchment and are likely the main net sources of Fe and Mn to the lake and the hypolimnetic sediments. Diagenesis of settling particulate Fe and Mn from these sources may augment levels of reduced Fe and Mn in the hypolimnion.

Concentration profiles for DOC are very similar to those of Fe and Mn (Figs. 2 and 3). Lake 658 is highly colored due to export of allochthonous organic matter from the surrounding watershed. The concentration of

DOC shows very little temporal variation in the epilimnion during the summer months averaging $8.64 \pm 1.09 \text{ mg L}^{-1}$ ($n=6$). On the other hand, the concentration of DOC increases significantly near the sediment–water interface in the anoxic zone. This enrichment in DOC near the sediment–water interface is often attributed to decomposition of natural organic matter associated with recently fallen particles (Tipping and Woof, 1983; Hamilton-Taylor et al., 1996; Hongve, 1997), but it may also reflect release of sediment-bound DOC associated with dissolution of Fe and Mn hydrous oxides from the sediments.

Concentration profiles for sulfide are also very similar to those of Fe and Mn (Figs. 2 and 3); however, sulfide appears in the hypolimnion after Fe and Mn become enriched. Early in the summer, sulfide is generally detectable only within 10 cm from the sediment–water interface; however, as the summer progresses and extent of anoxia increases, sulfide migrates higher in the water column. On the 12 August 2002, detectable sulfide ranged from 0.14–4.29 $\mu\text{mol L}^{-1}$, and was localized within 1 m of the sediment–water interface (Fig. 2). On 9 September 2002, detectable sulfide ranged from 0.14–7.92 $\mu\text{mol L}^{-1}$, and sulfide had migrated to 6 m above the sediment–water interface (Fig. 3).

Sulfide concentrations are not sufficiently high to control Fe(II) solubility and restrict Fe(II) release from the sediments. However, the concentrations of Fe(II) and sulfide in the hypolimnion during late summer were high enough to cause precipitation of FeS assuming the $\log K_{\text{sp}} = -2.9 \pm 0.1$ for fresh FeS (Berner, 1967; Schoonen and Barnes, 1988; Balistrieri et al., 1992). This formation of FeS in late summer is consistent with visual observations of black particulates and colloids from samples collected near the sediment–water interface. The precipitation of Mn sulfide phases was not thermodynamically favorable in the hypolimnion of Lake 658. Carbonate was also relatively low in the water column (S. Chadwick, unpublished data); therefore, precipitation of FeCO_3 (siderite) and MnCO_3 (rhodochrosite) is insignificant.

4.2. Relationship between Fe, Mn, and DOC

The distribution of DOC is correlated closely with the distribution of filterable iron ($[\text{Filterable Fe}] = 3.305 \pm 0.172[\text{DOC}] - 22.82 \pm 1.681$, $r^2 = 0.966$, $n = 15$, $p < 0.001$) and manganese ($[\text{Filterable Mn}] = 0.162 \pm 0.00867[\text{DOC}] - 0.872 \pm 0.0849$, $r^2 = 0.964$, $n = 15$, $p < 0.001$). This relationship is not surprising for two reasons. First, Mn and Fe hydrous oxides can

serve as electron acceptors in the biological oxidation of organic matter. Thus, settling of particulate organic matter into the hypolimnion leads to release of Fe and Mn from sediments and may promote release of sediment-bound DOC. Through this pathway, organic matter can dictate the chemical and physical form of Fe and Mn (Balistrieri et al., 1992). Second, microscopic investigations have shown that hydrous oxides and high molecular weight natural organic matter (NOM) can form intimate structures (Fortin et al., 1993; Taillefert et al., 2000) at well-defined redox boundaries that can scavenge trace metals during surface complexation and occlusion (Laxen, 1985; Taillefert et al., 2000). These Fe oxide–DOM aggregates were visually observed on particulates collected from the hypolimnion of Lake 658. Dissolution of these aggregates in the anoxic hypolimnion increases the concentrations of both Fe and DOC.

Due to the differences in standard potential, rates of diffusion, and kinetics of oxidation, differences in the water column distribution of Fe and Mn are expected. However, there was also a very strong relationship between filterable Fe and Mn in the water column of Lake 658 ($[\text{Filterable Mn}] = 0.0489 \pm 0.00140[\text{Filterable Fe}] + 0.251 \pm 0.0158$, $r^2 = 0.986$, $n = 15$, $p < 0.001$). This reflects the reduction of Fe and Mn hydrous oxides in the sediments as a common in-lake source of hypolimnetic Fe(II) and Mn(II) and also suggests that the watershed exports a fairly consistent mass ratio of Mn:Fe of 0.05 to the lake.

4.3. Role of reactive iron transport

A model for describing reactive transport of Fe and Mn was originally proposed by Davison (1985). In this conceptual model, Fe and Mn oxides are generated at the oxic–anoxic boundary due to oxidation, and these oxides are vertically transported by diffusion and settling. The result of this process is a generation of a particulate hydrous oxide peak at this boundary above the reduced portion of the concentration profile. The position and magnitude of this peak are dependent on the standard potential for oxidation of the metal and the kinetics of oxidation.

Since the concentration of Fe was generally an order of magnitude greater than the concentration of Mn in the hypolimnion, this conceptual model was applied to the Fe cycling in Lake 658 using an iron speciation scheme adopted by Taillefert et al. (2000), Taillefert and Gaillard (2002). Concentration profiles for particulate Fe, colloidal Fe(II), Fe(II), and dissolved oxygen for the 12 August 2002 are presented in Fig. 4. As in the

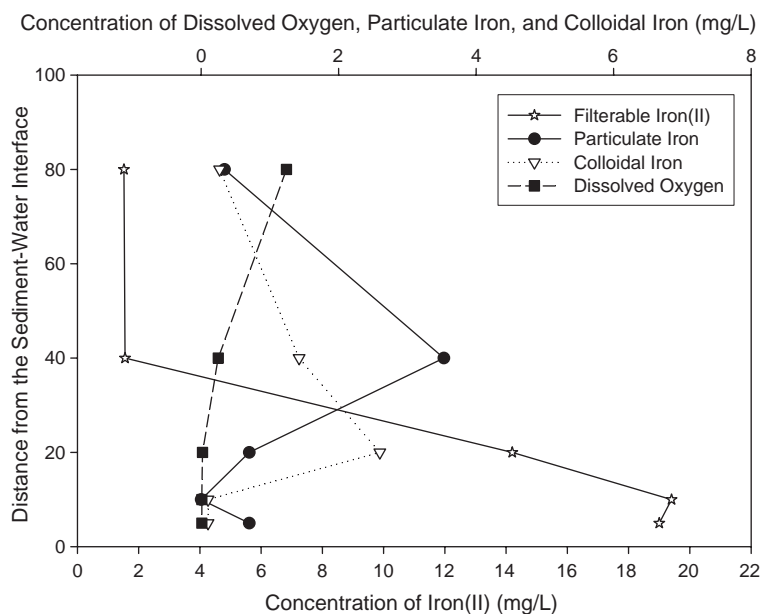


Fig. 4. Profile of dissolved oxygen and iron species in the water column near the sediment–water interface of the west basin of Lake 658 on the 12 August 2002.

conceptual model, a well-defined particulate Fe peak is present at the oxic–anoxic transition in the hypolimnion. This particulate Fe peak settles and persists in the anoxic portion of the hypolimnion. As the particulate Fe is reduced, the Fe becomes colloidal in size. This is consistent with observation of a colloidal Fe(III) peak present further into the anoxic zone (Fig. 4).

Our iron speciation results suggest a persistence of Fe(III) oxide particles in anoxic environments despite thermodynamic predictions as reported previously (Taillefert et al., 2000). Apparently, the rate of settling of particulate Fe is faster than the rate of reduction and dissolution. If DOM and Fe form complex aggregates at the oxic–anoxic transition, particulate Fe could be a vector for transport of DOC to the sediment–water interface.

4.4. Concentration profiles of the ambient and lake spike pools of Hg and MeHg

Concentration profiles for the ambient and lake spike pools of HgT and MeHg on the 15 July 2002, 12 August 2002, and 9 September 2002 are presented in Figs. 5–7. Added isotopic mercury in the filtered phase remained largely in the epilimnion until the thermocline broke down in the fall (Babiarz et al., 2003a). The concentration of filtered ambient and lake spike HgT in the epilimnion ranged from 2.25–2.63 and 0.63–0.94 ng L⁻¹, respectively, from 15 July 2002 to 9 September 2002. Transport of isotopic mercury from the epilimni-

on to the hypolimnion was primarily through settling particulate matter (Babiarz et al., 2003a). Diagenesis of these recently-fallen particles resulted in elevated filterable ambient and lake spike HgT near the sediment–water interface (Figs. 5–7). Filtered ambient and lake spike HgT near the sediment–water interface ranged from 1.53–8.59 and 0.27–2.43 ng L⁻¹, respectively, in the filtered phase from 15 July 2002 to 9 September 2002. Ambient HgT profiles were very similar to lake spike HgT profiles in the hypolimnion indicating similar recycling at or near the sediment–water interface (Figs. 5–7). The historic pool of Hg from the sediments was of minor importance. There does not appear to be a large influence of porewater release from deeper sediments or these profiles would be expected to diverge.

Methylated Hg from the lake spike was first noted in settling particulate matter two weeks after the initial spike in 2001 (Babiarz et al., 2003a). Ambient and lake spike MeHg concentrations in the epilimnion ranged from 0.08–0.20 and 0.01–0.02 ng L⁻¹, respectively, in the filtered phase from 15 July 2002 to 9 September 2002. The MeHg profiles show a low concentration of MeHg in the upper water column with increasing concentrations near the sediment–water interface (Figs. 5–7). MeHg was strongly associated with particles that delivered MeHg to the sediment–water interface (Babiarz et al., 2003a) resulting in enhanced filtered phase MeHg concentrations following diagenesis of these particles in the hypolimnion (Figs. 5–7). Filtered ambient and lake spike MeHg near the sediment–water

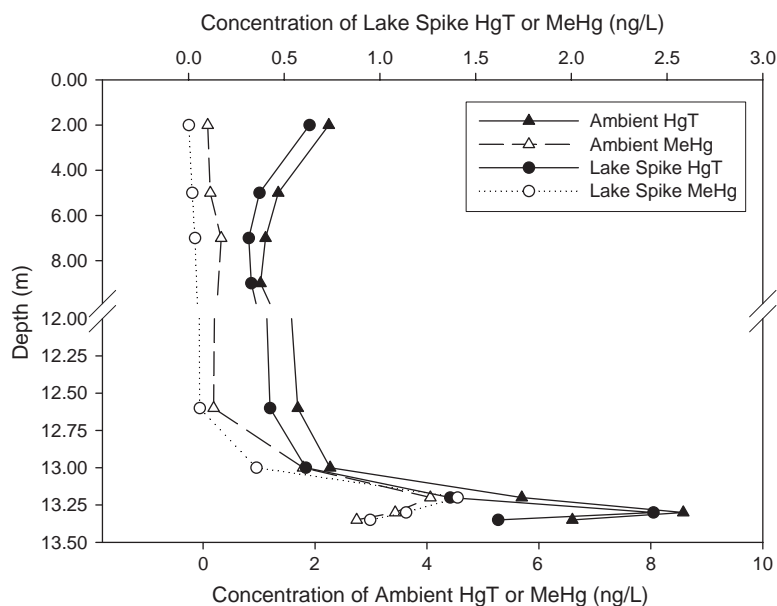


Fig. 5. Profiles of filtered ambient and lake spike HgT and MeHg in the water column of the west basin of Lake 658 on the 15 July 2002.

interface (taken from the CIS) ranged from 0.19–4.06 and 0.06–1.41 ng L^{-1} , respectively, in the filtered phase from 15 July 2002 to 9 September 2002. Similar to HgT profiles, ambient MeHg profiles were also very similar to lake spike MeHg profiles again indicating that deep porewater release of MeHg is probably not important (Figs. 5–7).

The fraction of total mercury as methylmercury in the water column for both the ambient and lake spike

pools on 15 July 2002 and 9 September 2002 are presented in Fig. 8. In the epilimnion, the fraction as methylmercury was slightly greater for the ambient pool than the lake spike pool. However, in the hypolimnion, the fraction of total mercury as methylmercury is usually greater for the lake spike pool than the ambient pool (Fig. 8). This observation suggests that the lake spike may be more reactive to methylation than the ambient pool. We cannot, at this point, deter-

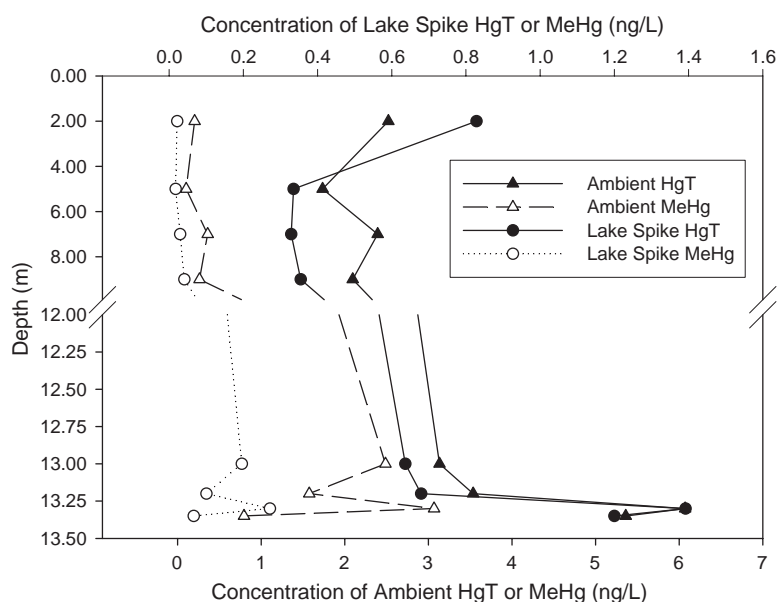


Fig. 6. Profiles of filtered ambient and lake spike HgT and MeHg in the water column of the west basin of Lake 658 on the 12 August 2002.

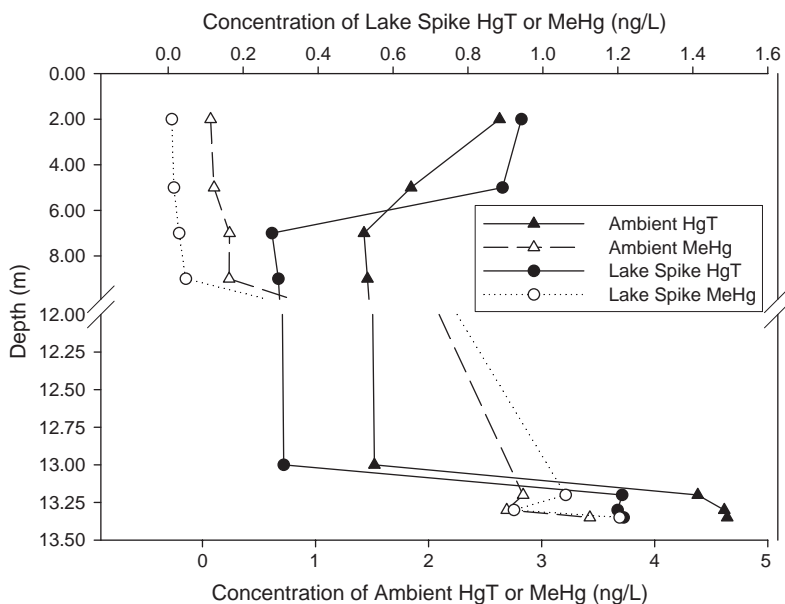


Fig. 7. Profiles of filtered ambient and lake spike HgT and MeHg in the water column of the west basin of Lake 658 on the 9 September 2002.

mine whether MeHg in the hypolimnion is derived from diagenesis of settled particles or from direct methylation in the hypolimnion. However, our CIS sampling shows that very little Hg(II) is present in the filtered phase in the zone directly above the sediment–water interface. The MeHg profile likely reflects production by methylation in the hypolimnion combined with scavenging by Fe-organic particles at the oxic–anoxic boundary that acts to retain MeHg in the hypolimnion.

4.5. Relationship between the ambient and lake spike pools for HgT and MeHg

There is a very strong relationship ($[\text{Lake Spike}] = 0.250 \pm 0.0147[\text{Ambient}] - 0.0934 \pm 0.0594$, $r^2 = 0.920$, $n = 27$, $p < 0.001$) between the lake spike HgT and ambient HgT. Similarly, there is a very strong relationship ($[\text{Lake Spike}] = 0.345 \pm 0.0140[\text{Ambient}] - 0.0594 \pm 0.0280$, $r^2 = 0.967$, $n = 23$, $p < 0.001$) between the lake spike MeHg and ambient MeHg. These two

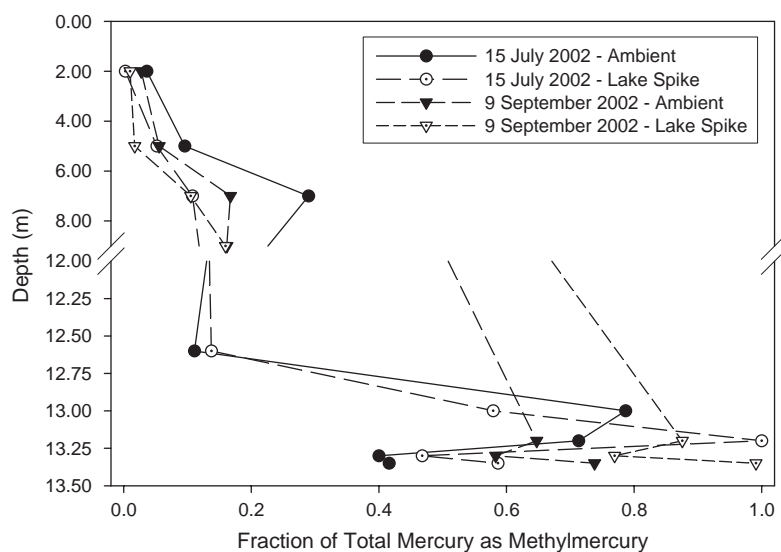


Fig. 8. Profiles of the fraction of HgT as MeHg for the ambient and lake spike pools in the water column of the west basin of Lake 658 on the 15 July 2002 and 9 September 2002.

strong relationships indicate that similar biogeochemical processes are controlling the temporal and spatial distribution of the lake spike and ambient pools of HgT and MeHg in the water column. The epilimnetic samples have the greatest variability in both relationships; however, this variability is expected since the epilimnion was the portion of the lake periodically amended with stable inorganic ^{202}Hg .

4.6. Relationship between DOC and the ambient and lake spike pools of HgT

Dissolved organic carbon has long been implicated as a dominant ligand controlling the fate and transport of Hg and MeHg in aquatic environments (Andren and Harriss, 1975; Babiarz et al., 2001; Amirbahman et al., 2002; Haitzer et al., 2002). A similar positive relationship was found between DOC and the ambient and lake spike pools of filterable HgT. The relationship between filterable ambient HgT and DOC ($[\text{Ambient HgT}] = 0.740 \pm 0.179[\text{DOC}] - 3.144 \pm 1.636$, $r^2 = 0.406$, $n = 27$, $p < 0.001$) is slightly than stronger the relationship between filterable lake spike HgT and DOC ($[\text{Lake Spike HgT}] = 0.169 \pm 0.0501[\text{DOC}] - 0.740 \pm 0.457$, $r^2 = 0.314$, $n = 27$, $p = 0.002$); however, this difference is likely not statistically significant. On the other hand, the concentration of Hg resulting from the lake spike is independent of any addition of DOC from external sources, while the ambient Hg is the result of co-transport of DOC and Hg from the watershed and simultaneous release of DOC and Hg from lake particulate matter. This difference in loading may explain the weaker relationship between lake spike HgT and DOC versus ambient HgT and DOC. The correlation between lake spike Hg and DOC indicates that Hg associates rapidly with natural organic matter (NOM), and it remains distributed with NOM in the water column after particle diagenesis.

The relation between HgT and DOC further suggests that organic carbon plays an important role in the transport of HgT in the hypolimnion. Moreover, the concentration of HgT and MeHg in the hypolimnion is not controlled solely by the redox cycling of Fe and Mn. The variability in the HgT:DOC relation as compared to the Fe:DOC relation indicates that filterable HgT is sensitive to processes that are less important for Fe(II). For example, the speciation of Hg(II) is likely influenced more than Fe(II) by metal-binding organic ligands and sulfide produced in the hypolimnion. Changes in speciation could influence the reactivity and aqueous–solid phase partitioning of Hg(II), causing variability in the HgT–DOC relationship. In addition,

methylation causes changes in the Hg(II)–MeHg ratios, representing another influence on filterable HgT but not on filterable Fe.

There was a very weak relationship ($r^2_{\text{Ambient}} = 0.077$; $r^2_{\text{Lake Spike}} = 0.072$) between MeHg and DOC for the Lake 658 profiles examined (S. Chadwick, unpublished data). Several factors may account for the lack of a strong relationship between the concentrations of filterable MeHg and DOC. The distributions of HgT and MeHg are controlled, in part, by different mechanisms in the hypolimnion. The HgT and DOC increase with depth is likely linked to diagenesis of newly-fallen organic particles, while the distribution of MeHg is also controlled by rates of methylation and demethylation. Similarly to Hg(II), scavenging by Fe-organic particles probably enhances retention of MeHg in the hypolimnion, but the methylation–demethylation cycle is another controlling process. Little non-methyl Hg is present near the sediment–water interface during maximum stratification. Additionally, strong metal-binding ligands (e.g., sulfide) influence the speciation and reactivity of MeHg and the bioavailability of Hg(II) for methylation (Benoit et al., 1999b). For example, high DOC concentrations near the sediment–water interface may reduce the bioavailability of Hg to methylating bacteria due to the large macromolecular size of DOM and strong intrinsic binding to DOM (Miskimmin et al., 1992; Ravichandran, 2004).

4.7. Implications of Fe/Mn/DOC cycling on the biogeochemical cycling of Hg and MeHg

Since DOM is a controlling variable in the distribution of Hg and MeHg in the water column of Lake 658, it is likely that Fe and Mn have an indirect influence in controlling the fate and transport of Hg and MeHg in the hypolimnion. This influence may occur through binding of Hg and MeHg to organic matter associated with Fe and Mn hydrous oxides, through Fe and Mn serving as electron acceptors in the decomposition of particulate organic matter containing Hg(II) and MeHg delivered to the sediment–water interface, and/or by aggregation of DOC–Hg/MeHg species into colloids and particulates at a well-defined redox boundary.

Iron speciation data suggests that of Fe(III) oxide particles persist in anoxic zone of Lake 658 despite thermodynamic predictions (Fig. 4). If Hg is strongly associated with DOC in the water column, and Fe has a controlling influence on the transport of DOC through the generation of DOC–Fe colloids and particulates, Fe is important delivery mechanism of DOC–Hg com-

plexes to the sediment–water interface. This has obvious implications on the long-term fate, transport, and methylation of the amended isotope.

In addition, recent research has shown that Fe can influence on the methylation potential of Hg by controlling the sulfide activity (Mehrotra et al., 2003). This dataset suggests that Fe(II) has a controlling influence on sulfide activity in the hypolimnion of Lake 658 through the precipitation of FeS. Consideration of the role of Fe(II) in the formation of neutral Hg-sulfide complexes (Benoit et al., 1999b) may be important in explaining methylation rates and MeHg distributions in the hypolimnion of Lake 658.

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