Mercury Loading Experiments

at the Experimental Lakes Area, northwestern Ontario

also known as

Mercury **E**xperiment **T**o **A**ssess **A**tmospheric **L**oading

In **C**anada and the **U**nited **S**tates

[Updated December 2006]

This one-of-a-kind experiment has been given full approval by Ontario to proceed, and been underway since the spring of 2001. It addresses a need for research that will be useful to the Canadian Council of Ministers of the Environment (CCME) and the United States Environmental Protection Agency (USEPA) for setting regulations on emission levels of mercury to the atmosphere by electrical utilities and others. This is a unique experiment of international scope that can only be carried out at the Experimental Lakes Area, where whole-ecosystems can be manipulated to give understanding of environmental stressors at the ecosystem level.

An ancillary experiment, involving minute additions of mercury to a small stream, was also approved by Ontario. It took place in August of 2005 and investigated the interactions of newly deposited mercury in a flowing system. For more information on this complementary second study, click HERE.

I. **Background and Rationale**

The presence of methylmercury (MeHg) in fish is a natural occurrence, but fish MeHg concentrations in remote lakes in eastern Canada, including Ontario, are often above the 0.5 ppm limit for commercial sale. This is the case even in the absence of direct anthropogenic discharges of mercury to the lakes. Methylmercury is produced from inorganic mercury by bacteria, and is accumulated preferentially by fish. Fish with elevated mercury concentrations are a health concern due to the toxicity of MeHg and exposure via fish consumption. There is a general consensus that elevated MeHg concentrations of fish in remote lakes are influenced by inputs of atmospheric inorganic mercury directly to lakes and indirectly via their watersheds. Furthermore, anthropogenic mercury emissions are likely contributing to mercury loading rates to lakes. Anthropogenic inputs originate as emissions from coal combustion, waste incineration, and as emissions from other industrial and mining processes.

Much research has been undertaken to better understand the impacts of mercury emissions on fish mercury concentrations, and the potential effectiveness of emissions controls. In North America alone, emission controls for electric utilities have been estimated to cost billions of dollars per year. Despite this research activity, a fundamental question remains unanswered: What will happen to fish mercury concentrations if atmospheric mercury deposition is reduced? Uncertainty remains regarding both the magnitude and timing of the response.

The METAALICUS experiment (Mercury Experiment To Assess Atmospheric Loading in Canada and the US) is currently underway at the Experimental Lakes Area (ELA) to examine this issue. METAALICUS involves the addition of stable, non-radioactive, mercury isotopes to a whole ecosystem to see if there is a response in mercury concentrations fish. In 2001, 2002, 2003, and 2004, mercury was added to Lake 658 and its watershed at an annual rate approximately equal to 3 times the annual wet deposition of mercury at the ELA.

Some of the mercury experimentally added directly to the lake water is being measured now in fish, but it is very likely that the mercury concentrations in fish have not yet stabilized in response to the changing mercury load. We cannot yet say what the eventual response of fish mercury concentrations will be following a change in mercury loading. Permission has been obtained to continue mercury additions at the same levels as in the first four years (up to 30 $\mu g/m^2/yr$ of additions) through 2006.

II. **Experimental Objectives**

- To determine the relationship between the atmospheric loading of mercury to lakes and the MeHg concentration of fish.
- To determine the response time of MeHg in a whole ecosystem, including fish, to changes in rate of atmospheric deposition of mercury (HgII).

III. **Participants**

Principle Investigators: Mike Paterson, DFO, and Reed Harris, Tetra Tech Inc.

DFO Participants: P. Blanchfield, C. Podemski.

Other Participants:

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International Advisory Panel:

A. Iverfledt, Swedish Environmental Research Institute (IVL).
J. Munthe, Swedish Environmental Research Institute (IVL).
E. Swain, Minnesota Pollution Control Agency
R. Hesslein, Department of Fisheries and Oceans

IV. **Study Description:**

As described above, METAALICUS is a whole-ecosystem experiment in which mercury loading to a headwater lake and its watershed is being altered experimentally. Lake 658 (Figure 1) at ELA was selected for the study. It is a small (8.3 ha), low productivity, headwater lake on the Canadian Shield and is one of the lakes reserved for

research at the ELA. It has a small drainage basin, including a wetland area, and a diverse fish population. Background studies documenting site conditions prior to the experiment were carried out in 1999-2000.

Figure 1. An aerial view of Lake 658 and most of its watershed. The wetland is to the left, the outflow to the right.

Mercury is being added in the form of stable, non-radioactive isotopes of inorganic mercury (Hg(II)). The power of using isotopes lies in the ability to follow the newly deposited mercury separately from background mercury. Furthermore, different mercury stable (non-radioactive) isotopes are being added to the upland, wetland and lake surface (^{200}Hg, ^{198}Hg and ^{202}Hg respectively) to determine the relative contributions of these sources to fish mercury levels.

The ELA is a low deposition area for mercury, with approximately 7 ug/m^2/yr of wet mercury deposition. The low mercury deposition rate at the ELA means that adding the equivalent of about 1/6th of a teaspoon of mercury per year (approximately 12.5 g) increases wet Hg deposition to the 52 ha Lake 658 ecosystem (lake and watershed) by 3-5 fold. This action results in a wet deposition rate of mercury to the experimental system that is comparable to rates currently observed in some parts of the US Northeast and Florida.

Mercury concentrations are being tracked in all major compartments in the lake, watershed, and atmosphere. Detailed process studies are also being carried out to follow the movement and transformations of mercury through the watershed and lake, as well as air/surface exchange of mercury. This process-based approach will allow us not only to document what happens, but also to understand why. This is essential if we are to use the results of the study to make predictions for other locations. The approach is providing critical information for an existing model that predicts fish mercury concentrations in lakes and the effects of remedial actions such as reductions in mercury loading.

The experiment is being carried out in two phases. Phase I involved pilot and baseline studies in 1999-2000, to prepare for Phase II. The ELA Management Board approved Phase I studies at the February 1999 and February 2000 meetings. Final approval of the full-scale experiment for 2001 through 2003 was obtained in March 2001. The full-scale experiment began in May 2001. Mercury additions have been carried out in 2001, 2002, 2003, 2004, 2005, and 2006. Permission was obtained in 2004 to continue additions until 2006. No further mercury additions are planned for the upland or wetland catchments, but researchers are requesting permission to

continue additions to the Lake 658 water only for up to 3 additional years. This would occur only if deemed necessary to reach equilibrium with existing mercury in the lake.

V. **Milestones:**

- (1999-2000) Two years of pilot scale experiments; pre-addition background monitoring of both candidate lakes.
- (2001-2003) Initial three years of whole-ecosystem isotope additions to upland and wetland areas of the watershed and to the lake surface, and continued pilot studies.
- (2004-2006) Three more years of whole-ecosystem isotope additions, in order to approach an equilibrium state for experimentally added mercury in the Lake 658 ecosystem. An additional
- (2007 and beyond) One to three additional years of mercury addition to the lake water only, as required to reach an equilibrium condition with ambient mercury in the lake. This loading phase of the experiment will be followed by monitoring of the food chain and fish mercury concentrations until conditions return to pre-addition levels.

VI. *Phase One:* Pilot-scale Studies

Pilot-scale studies were carried out from 1999 through 2002. These included:

- Isotopic Hg(II) additions to small upland plots;
- Isotopic Hg(II) additions to a wetland plot; and
- Additions of isotopic mercury to lake enclosures

In 2003, some of the pilot-scale studies done from 1999-2002 were continued or expanded to gain additional knowledge. Monitoring of some of these sites has continued through 2006. Updates to the pilot-scale studies follow:

Pilot Isotopic Hg(II) Additions to Upland and Wetland Catchments

Hg additions to pilot-scale upland plots at ELA were carried out from 1999-2002. These experiments broadened the understanding of mercury behaviour in upland systems, and provided important information when designing a method to apply mercury to the terrestrial system. During simulations of dry deposition or light rain (the conditions under which mercury is being applied for the full scale experiment), little of the mercury applied to upland plots has been exported in runoff since the pilot studies began (up to four years of data for some test areas).

Pilot scale studies from 1999-2002 at a 500 m^2 wetland plot bordering Lake 115 at ELA suggested that the vertical mobility of mercury added to the wetland plot was greater than expected, and confirmed wetlands as active methylation sites.

Additions of Isotopic Mercury to Lake Enclosures

During 2000-2001, a study of isotopic additions of ^{200}Hg(II) to four enclosures was carried out at Lake 239 at the ELA. The enclosure experiments in 2000-2001 confirmed for the first time that the new isotopic analytical methods being used could indeed follow added mercury isotopes through the water, sediments and food web, including fish.

In 2002, 11 enclosures were set up in Lake 240, ELA, and dosed with varying amounts of mercury, up to 15X current annual wet deposition at ELA. In 2003, the enclosures in Lake 240 were dosed a second time but with a different isotope than in 2002.

VII. *Phase Two:* Whole-Ecosystem Mercury Additions at Lake 658

Public Consultation:

During 2000, public information meetings were conducted in Dryden and Kenora to discuss the project with the public. In addition a presentation was made to three NGO's at a meeting in Toronto. Feedback from these presentations was positive. There has been no public opposition or negative media coverage in connection with METAALICUS since permission was originally granted and the project began. Scientific, public, and governmental feedback has been very positive.

Research Activities:

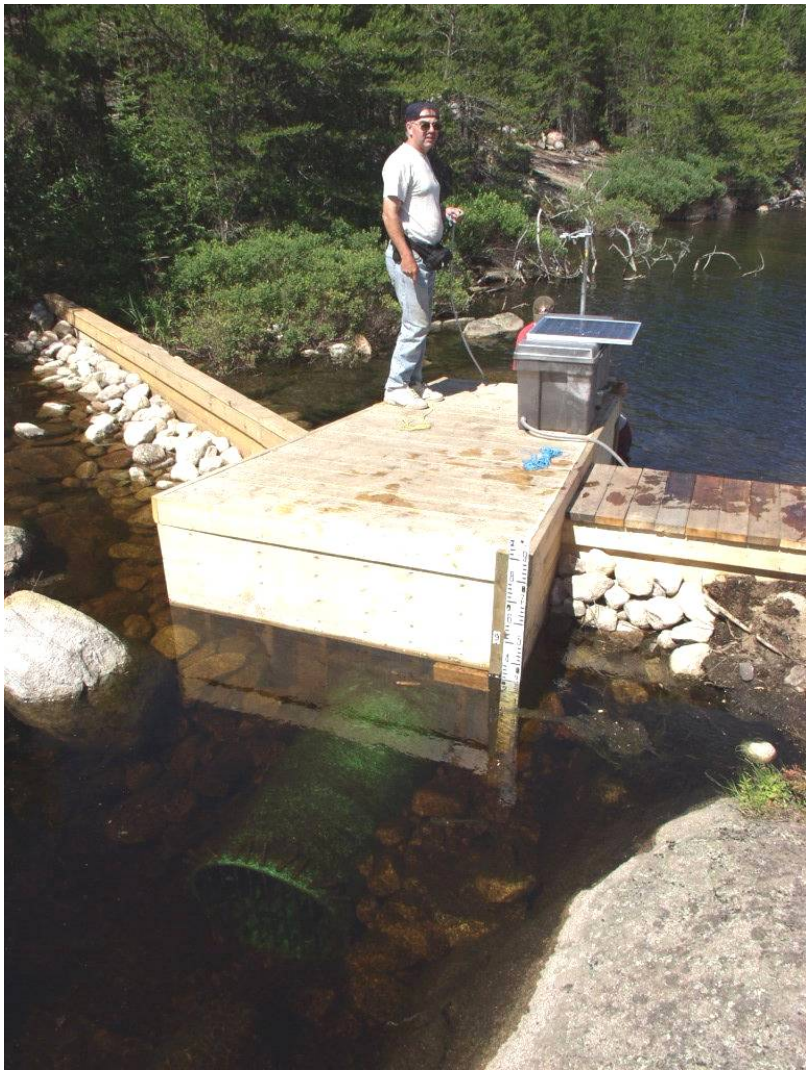
After two years of pilot and baseline studies in 1999-2000, METAALICUS went "full scale" in June 2001. Stable, non-radioactive Hg(II) isotopes are being applied to the upland, wetland, and directly to the lake surface in the Lake 658 (Figure 2)watershed at ELA. The upland, wetland and lake are receiving ^{200}Hg, ^{198}Hg, and ^{202}Hg respectively. In each case the total mercury application rate is approximately 25 $ug.m^{-2}\ yr^{-1}$. Isotopes have been applied during the 2001-2006 field seasons. The upland and wetland areas have been sprayed once per year by an airplane flying low over the canopy. Isotopes were being applied directly to the lake by mixing from a boat at a depth of 0.7 m, over a series of 9 applications during the ice-free season. The mercury loading rate directly to the lake surface was approximately 22 $ug.m^2/yr$.

Figure 2. ELA Lake 658 is the site for the METAALICUS study.

Impact on Downstream Lakes:

Based on pilot-scale studies and our knowledge of the behaviour of mercury in ELA lakes, most of the added mercury will be bound in the upland soils, wetland peat and lake sediments in the long term. Mercury in the Lake 658 outflow (Figure 3) enters a very large downstream lake (Winnange Lake). We expect that the added mercury isotope will not be detected in the Winnange Lake food chain due to the small amount that will be discharged from Lake 658 and the very large volume of Winnange Lake relative to Lake 658 (approximately 1000x larger). Monitoring is being carried out in Winnange Lake to verify that the Winnange Lake food web is not impacted by the experiment. The concentrations of the three different mercury isotopes added to the Lake 658 watershed were examined in young-of-the-year yellow perch and northern pike prior to the addition of isotopes (June 2001) and two years after mercury additions began (May 2003). Tiny amounts of the mercury isotope added to Lake 658 have been detected in some Winnange Lake fish captured near the outflow from Lake 658, but these quantities are small compared to "naturally occurring" mercury in these fish. We are investigating to see if any can be detected in Winnange fish captured farther from the outflow. No experimental mercury has been detected in Winnange Lake sediments. This is not surprising considering that the transport of mercury isotopes out of Lake 658 has been measured and determined to be very small.

Figure 3. This structure is used to monitor flows between Lake 658 and Winnange Lake.



VIII. 2006 Field Season:

The 2006 field season is the sixth field season during which whole ecosystem mercury applications have been carried out. This will be the last year of additions by aircraft to the forest upland and the wetland catchments. Permission has been requested to continue with up to three more years of mercury isotope additions to Lake 658 water only. Detailed monitoring of site conditions, mercury concentrations, and the fate and transport of mercury are continuing. A few pilot-scale studies are also continuing.

Thus far, there is no indication that significant quantities of isotope applied to the upland and wetland have reached the lake and are present in the food web. However, isotope applied directly to the lake now represents a significant portion of the methyl mercury measured in fish in Lake 658. That being said, the methylmercury levels in these fish are still similar to those in fish in other lakes in the region.

IX. Lake Restoration

Prior to the beginning of METAALICUS, it was anticipated that MeHg concentrations in the food web following the mercury additions would be within the range presently observed in remote Canadian lakes that do not receive local anthropogenic mercury sources. This has been the case to date. While some fish mercury concentrations are increasing significantly in Lake 658 as a result of METAALICUS, it is expected that concentrations will return to background levels after mercury additions are stopped. After the experiment has been completed, the study lake will be monitored until fish mercury concentrations return to pre-addition levels and the lake returns to conditions specified in Section VII. 3. of the ELA Memorandum of Agreement. During this recovery period, concentrations of mercury in fish and sediments in Winnange lake will also be monitored every second year.

X. Publications Completed or In Progress:

- Amyot, M., G. Southworth, S.E. Lindberg, H. Hintelmann, J.D. Lalonde, N. Ogrinc, A.J. Poulain and K.A. Sandilands. 2004. Formation and evasion of dissolved mercury in large enclosures amended with 200HgCl2. Atmospheric Environment 38: 4279-4289
- Babiarz, C.L, J.P. Hurley, D.P. Krabbenhoft, C.C. Gilmour, and B.A. Branfireun. 2003. Application of ultrafiltration and stable isotope amendments to the partitioning of mercury in lake water and over land runoff. Science of the Total Environment 304: 295-303.
- Baker R.F., Blanchfield P.J., Paterson M.J., Flett R.J., and Wesson L. 2004. Evaluation of non-lethal methods for the analysis of mercury in fish tissue. Transactions of the American Fisheries Society 133: 568-576
- Branfireun, B. A., D. P. Krabbenhoft, H. Hintelmann, R. J. Hunt, J. P. Hurley, and J. W. M. Rudd. 2005. Speciation and transport of newly deposited mercury in a boreal forest wetland: A stable mercury isotope approach, Water Resour. Res. 41, W06016, doi:10.1029/2004WR003219.
- Eckley, C.S. and H. Hintelmann. Determination of mercury methylation potentials in the water column of lakes across Canada. Submitted to STOTEN, November 2004
- EPRI (2004) METAALICUS Project Interim Report, EPRI, Palo Alto, California, Report # 1005522, 2004. Prepared by Tetra Tech Inc. and Fisheries and Oceans Canada
- Graydon, J.A., V.L. St.Louis, S.E. Lindberg, H. Hintelmann and D. Krabbenhoft. 2006. Investigation of mercury exchange between forest canopy vegetation and the atmosphere using a new dynamic chamber. Environ. Sci. Technol. 40(15): 4680-4688.
- Hintelmann, H. and H.T. Nguyen. Extraction of methylmercury from tissue and plant samples using acid leaching. Submitted to Analytical and Bioanalytical Chemistry, June 2004; Accepted for publication September 2004.
- Hintelmann, H. and R. Harris. 2003. Application of multiple stable mercury isotopes to determine the adsorption and desorption dynamics of Hg(II) and MeHg to sediments. Marine Chemistry 90: 165-173

- Hintelmann, H., R. Harris, A. Heyes, J. Hurley, C. Kelly, D. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K. Scott and V. St. Louis. 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. Env. Sci. Technol. 36: 5034-5040.
- Kelly, C.A., J.W.M. Rudd, and M.H. Holoka. 2003. The effect of pH on mercury uptake by an aquatic bacterium - implications for Hg cycling. Environ. Sci. & Technol. 37:2941-2946.
- Lalonde, J.D., M. Amyot, M-R. Doyon, and J-C. Auclair. 2003. Photo-induced Hg(II) reduction in snow from the remote and temperate Experimental Lakes Area (Ontario, Canada). J. Geophys. Res. 108, No. D6, 4200, doi: 10.1029/2001JD001534.
- Lindberg, S.E., G. Southworth, M. Peterson, H. Hintelmann, J. Graydon, V. St Louis, M. Amyot, and D. Krabbenhoft. 2003. Quantifying reemission of mercury from terrestrial and aquatic systems using stable isotopes: Results from the Experimental Lakes Area METAALICUS study. EOS Trans. AGU 84(46), B31E-0364.
- Ogrinc, N., H. Hintelmann, C. Eckley, and S. Lojen. 2003. Biogeochemical influence on carbon isotope signature in boreal lake sediments. Hydrobiologia 494: 207-213.
- Orihel, D.M., M.J. Paterson, C.C. Gilmour, R.A. Bodaly, P.J. Blanchfield, H. Hintelmann, R.C. Harris, and J.W.M. Rudd. 2006. Effect of loading rate on the fate of mercury in littoral mesocosms. Environ. Sci. Technol. 40: 5992-6000.
- Paterson, M.J., P.J. Blanchfield, C. Podemski, H.H. Hintelmann, C.C. Gilmour, R. Harris, N. Ogrinc, J.W.M. Rudd, and K. Sandilands. 2006. Bioaccumulation of newly deposited mercury by fish and invertebrates: An enclosure study using stable mercury isotopes. Can. J. Fish. Aquat. Sci. 63: 2213-2224.
- Miller, C.M., C.C. Gilmour, A. Heyes, and R.P. Mason. Influence of dissolved organic matter on the complexation of Hg under sulfidic conditions. Environ. Tox. Chem. In press.
- Poulain, A.J., M. Amyot, D. Findlay, S. Telor, T. Barkay, and H. Hintelmann. 2004. Biological and photochemical production of dissolved gaseous mercury in a boreal lake. Limnol. Oceanogr. 49(6): 2265-2275.
- Peterson, M., S. Lindberg, G. Southworth, M. Bogle, J. Graydon. 2004. Investigating mercury re-emission from boreal uplands and wetlands: Latest results from the Experimental Lakes Area, Canada. RMZ-Materials and Geoenvironment 51: 1710-1713.
- Sandilands, K.A., J.W.M. Rudd, C.A. Kelly, H. Hintelmann, C.C. Gilmour, and M.T. Tate. 2005. Application of enriched stable mercury isotopes to the Lake 658 watershed for the METAALICUS project, at the Experimental Lakes Area, northwestern Ontario, Canada. Can. Tech. Rep. Fish. Aquat. Sci. 2597: viii + 48 p.
- Sarica J., M. Amyot, L. Hare, P. Blanchfield, R.A. (Drew) Bodaly, H. Hintelmann, and M. Lucotte. 2005. Mercury transfer from fish carcasses to scavengers in boreal lakes: the use of stable isotopes of mercury. Environmental Pollution 134: 13-22
- Southworth, G., S. Lindberg, H. Hintelmann, M. Amyot, A. Poulain, M.A. Bogle, M. Peterson, J. Rudd, R. Harris, K. Sandilands, D. Krabbenhoft, and M. Olsen. Evasion of added isotopic mercury from a north temperate lake. Environmental Toxicology and Chemistry. In press.
- Southworth, G., S. Lindberg, M. Bogle, M. Amyot, A. Poulain, H. Hintelmann, M. Olson, and K. Sandilands. 2004. Isotopic tracer studies of volatilization of mercury from a north temperate lake. RMZ-Materials and Geoenvironment 51: 1765-1768.
- St. Louis, V.L., J.W.M. Rudd and C.A. Kelly, B.D. Hall, K.R. Rolfhus, K.J. Scott, S.E. Lindberg, and W. Dong. 2001. Importance of the rorest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. Environ. Sci. Technol. 35: 3089-3098.

XI. Feedback

Your feedback regarding this study, or the completed in-stream study, is welcome. We would like to know whether you support, or have concerns about, these experiments, or if you have any unanswered questions. Please contact Dr. Mike Paterson via E-mail to provide your feedback.

Please click on Feedback button to E-mail Dr. Paterson.