Significant Research Findings:

Impacts of Atmospheric Deposition and Lake and Watershed Processes on Mercury Exposures of Fish and Piscivorous Wildlife in New England Lakes

Scientific Problem and Policy Issues	The atmospheric deposition of mercury (Hg) to watersheds worldwide has emerged as a major environmental problem. Environmental Hg contamination poses threats to humans through the consumption of Hg-tainted fish, to the fish themselves, and to piscivorous wildlife owing to a high bioaccumulation potential. The United States Environmental Protection Agency (EPA) has recently promulgated a revised fish tissue methylmercury (MeHg) criterion of 0.3 µg g^{-1} as dry weight (d.w.) under §304(a) of the Clean Water Act.
	Atmospherically-derived Hg is emitted from the combustion of fossil fuels and medical and municipal wastes, from landfill emissions, and from accidental releases such as the breakage of thermometers or fluorescent lamps. Once deposited on the landscape, Hg is transported/sorbed onto particulate matter and/or complexed with high molecular weight dissolved organic carbon (DOC) species, ultimately accumulating in watershed soils and in wetlands and lakes. In anaerobic systems, Hg is bacterially methylated to form toxic methylmercury (MeHg). MeHg has been shown to accumulate in the food chain. In lakes, numerous investigators have noted that total Hg (HgT) in fish tissue is elevated in lakes of lower pH and of higher terrigenous DOC content. Other important water chemistry parameters which mediate MeHg availability include sulfate, dissolved oxygen, redox potential, sulfides, and soil-derived aluminum. The trophic structure of lakes mediates Hg bioaccumulation to upper trophic levels. Recent findings indicate that lake trophic status influences bioaccumulation of Hg to fish tissues in potentially conflicting ways. While the body of Hg-related literature in fresh water continues to grow, numerous studies have focused on the processes mediating Hg bioavailability. Fewer rigorous, statistically-designed initiatives to ascertain the generalized Hg contamination across landscapes are available.
Research Approach	The purpose of this research was to provide scientific information and technical data needed to help reduce uncertainties that limit EPA's ability to assess and manage Hg and MeHg risks. This was performed via two parallel projects. First, the concentrations of HgT and MeHg in waters and sediments were characterized for a representative set of Vermont (VT) and New Hampshire (NH) lakes. These concentrations were related to easily measured water column chemical parameters and watershed-level physical attributes. A primary research goal was to identify

specific lake types in which elevated MeHg is formed and in which this toxin is accumulated into middle and higher trophic-level organisms. The study was designed specifically to determine the generalized level of Hg contamination in sediment, water, and biota of multiple trophic levels across the VT-NH region, using a geographically randomized approach. This type of approach ensures that results provide a statistically valid representation of regional conditions.

Second, the Regional Mercury Cycling Model (R-MCM), a well-recognized developmental model, was applied to the set of VT and NH lakes using available water column chemical parameters and watershed level physical attributes. R-MCM was evaluated as a predictive tool by comparing simulated mercury concentrations with the observed Hg concentrations. Of particular interest was its ability to adequately capture and simulate the governing fate and transport processes of mercury in a number of watersheds and their associated water bodies with minimal site-specific information. A realistic evaluation of the R-MCM should lead to a better understanding of its strengths and weaknesses, and highlight ways to improve this and similar modeling systems. This is an important step toward the ultimate goal of improving the assessment tools needed to successfully manage mercury exposure and risk.

| **Results and Impact** | The first part of this work summarizes findings of a three-year field study of Hg in freshwater lakes of VT and NH. The study was designed specifically to determine the generalized level of Hg contamination in sediment, water, and biota of multiple trophic levels across the VT-NH region, using a geographically randomized approach. Hg was detectable in waters of all lakes sampled. The average water-column HgT concentrations were 1.78 ($\pm$ 0.1) parts per trillion (ppt) for shallow-water samples and 11.52 ($\pm$ 0.81) ppt in deep lake waters. MeHg averaged 0.299 ($\pm$ 0.018) ppt in shallow waters and 0.829 ($\pm$ 0.092) ppt in deep waters. The increased deepwater Hg and MeHg concentrations suggest accumulation in bottom waters, which may be due to losses from upper waters and/or releases from deepwater sediments. The average Hg concentration in sediments was 0.240 ($\pm$ 0.01) parts per million (ppm), which agrees well with previous studies. Sediment MeHg averaged 1.7% ($\pm$ 0.1%) of sediment HgT. Sediment HgT concentrations were most elevated in lakes in the most remote and forested regions of VT and NH and were lowest in lakes with the greatest levels of watershed development. |

The historical deposition of Hg to the study region was reconstructed using paleolimnological techniques. Hg presently accumulates in lake sediments at a rate 3.7 times that of the period 1825 and before. The rate of sediment Hg accumulation is presently declining region-wide, and the onset of this decline is generally coincident with implementation of the 1990 Clean Air Act Amendments. Net atmospheric deposition to lakes across VT and NH is estimated to be 21 μg m^{-2} yr^{-1}. The paleolimnological analysis suggested that a lag can be expected between reductions in emissions of Hg, and reductions in Hg accumulation to lake sediments, owing to Hg currently accumulated in watershed soils.

This study evaluated the accumulation of Hg in the tissues of yellow perch (*Perca flavescens)* and common loons (*Gavia immer*), a threatened obligate fish-eating bird. Hg concentrations in yellow perch fillets averaged 0.239 ($\pm$ 0.007) ppm and ranged from a low of 0.051 ppm to a maximum of 1.3 ppm, which is quite

elevated for yellow perch. Nearly 100% of the Hg in perch tissues was in the MeHg form. Yellow perch fillets from NH lakes were significantly higher in Hg than the yellow perch from VT lakes. Results of the loon tissue analyses suggest that across the region, 50% of VT lakes and 70% of NH lakes had loons with tissue Hg concentrations that placed those animals in a "moderate" or higher risk category. These perch and loon tissue data indicate that Hg contamination is readily bioaccumulated in most lakes across the VT-NH region. Further statistical analyses indicate that Hg and MeHg derived from watersheds, and contributing to shallow lake waters, are more likely to be the main Hg source to fish and other biological tissues than are Hg and MeHg derived from lake sediments.

The eutrophic lakes displayed very low levels of tissue Hg contamination. This suggests that fish tissues of biologically-productive lakes may have far lower Hg concentrations than is currently presumed by existing fish tissue advisories. Various criteria exist for Hg to protect human health and aquatic life. The most conservative legal water quality criterion for Hg in VT waters is 12 ppt, to protect aquatic biota subject to chronic, low-level Hg exposure. The most conservative standard in NH is 51 ppt, to protect against bioaccumulation of Hg in game fish. In this study, no shallow lake waters violated the VT water column criterion, and only 16% of lakes across the region showed violations in the deep water portions of the lakes. No lakes exceeded the NH water column criterion. However, tissue contamination in excess of criteria limits was found in many lakes and most lake types. Thirty percent of lakes sampled had perch fillet means in excess of the EPA criterion and 60% of lakes had perch fillet tissues exceeding 0.2 ppm. Ninety percent of lakes displayed sediment Hg concentrations in excess of the NOAA sediment quality guideline of 0.15 ppm, above which a low or greater risk of impact to sediment-based biota is considered likely. These findings clearly indicate that the existing numeric water column criteria within the VT and NH standards are not sufficiently conservative to limit accumulation of Hg to sediments, or to limit risks to humans due to fish consumption, and to limit risks to wildlife.

A statistical model was developed to predict the likelihood that tissue MeHg concentrations of yellow perch would exceed the EPA MeHg criterion, using data from the study lakes. This model uses simple measures of water chemistry (lake buffering capacity, conductance, acidity, organic content, and flushing rate) and is applicable to VT and NH lakes 20 acres in size or larger. Based on the model results, 29% of all VT lakes and 62% of all NH lakes are likely to violate the EPA criterion. This model can be used as a screening tool to identify lakes in need of additional fish tissue sampling.

The second part of this work presents our R-MCM modeling application and evaluation. Our primary determination is that the R-MCM is not currently at a level where it can be directly applied to a new region or series of lakes without calibration. The R-MCM captured specific trends observed in the general mercury literature, such as the correlation of higher fish tissue Hg concentrations with lower pH. Using various visual and statistical analyses, we found that simulating mercury concentrations was no more predictive than simply using the mean of observed values from the regional dataset. Through a rigorous separation technique of evaluating only specific lake characteristics, we concluded that there

was not a lake type that the R-MCM predicted better. The default level input parameterization was found to have the largest amount of random scatter for the data points. The scatter was greatly reduced by specifying lake-specific values for the default level characteristics, suggesting that the greatest improvement in the R-MCM's predictive capability might be gained by gathering precise data on such general lake characteristics as pH, size, trophic status, and stratification.

Further comparison of the R-MCM simulated versus observed Hg concentrations revealed these important results: (1) HgT concentrations were generally under-predicted, (2) percent MeHg in the epilimnion was generally under-predicted, (3) percent MeHg in the sediment was generally over-predicted, and (4) increasing the outflow of MeHg from the watershed improved the model's predictive ability. These results suggest that the challenges with implementing the R-MCM and similar models may lie more in the difficulties of modeling the loading of Hg and MeHg to the water body than modeling its internal Hg cycling. Our results imply the importance of accurate modeling of both the mercury cycle in watersheds and the loading from these watersheds into the water body of concern.

Research Collaboration and Research Products	This research is the result of collaboration among staff from the Vermont Department of Environmental Conservation, the New Hampshire Department of Environmental Services, Syracuse University, Biodiversity Research Institute in Falmouth, ME, Ecosystems Research Inc. in Norwich, VT, EPA Region 1 in Boston, MA, and the U.S. EPA National Exposure Research Laboratory in Athens, GA. Publications from this study include: Kamman, N.C., Driscoll, C.T., Estabrook, R., Evers, D.C., and Miller, E.K., Biogeochemistry of Mercury in Vermont and New Hampshire Lakes, An Assessment of Mercury in Waters, Sediments and Biota of Vermont and New Hampshire Lakes - *Comprehensive Final Project Report*. U.S. EPA, National Exposure Research Laboratory, Athens, GA, 2004. Kamman, N.C., Lorey, P.M., Driscoll, C.T., Estabrook, R., Major, A., Pientka, B., and Glassford. E., "Assessment of mercury in waters, sediments and biota of New Hampshire and Vermont lakes sampled using a geographically randomized design," Environ. Toxicol. Chem. 23(5): 2004. Kamman, N.C. and Engstrom, D.R., "Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from 210Pb-dated sediment cores," Atmos. Environ. 36, 1599-1609, 2002. Knightes, C.D. and Ambrose, R.B. Analysis of Mercury in Vermont and New Hampshire Lakes: Evaluation of the Regional Mercury Cycling Model. U.S. EPA, National Exposure
Future Research	This project completes the evaluation phase of the NERL watershed mercury research program. Future research activities will focus on improvements to watershed and water body mercury cycling models, and linkage with regional atmospheric mercury models.

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