

**Inputs, Methylation, Transformation, and Historical Accretion of Mercury
in Northern Freshwater Lakes.**

**A Critical Review of Select Scientific Literature, and Comment on the
Current Direction of New England Freshwater Mercury Research.**

Vermont Department of Environmental Conservation
Water Quality Division
103 S Main St 10N
Waterbury, VT 05671-0408

Prepared by
Neil Kamman, Environmental Scientist
Neil.Kamman@state.vt.us

Foreword:

The primary motivation for the publication of this document is to provide a small review of the primary scientific literature regarding the transportation and fate of the toxic metal mercury through freshwater lake systems. The review is intended to serve primarily as a reference for those persons involved with or interested in current mercury research efforts which are spearheaded by the Vermont Department of Environmental Conservation (VTDEC). Other researchers and citizens are also encouraged to peruse the contents of this review.

VTDEC's mercury research efforts are funded by the U.S. Environmental Protection Agency, through the Regional Environmental Monitoring and Assessment Program (REMAP). The project is being collaboratively executed by the State of New Hampshire, Syracuse University, the Biodiversity Research Institute, the Science Museum of Minnesota, the Vermont Department of Fish and Wildlife, and the US Fish and Wildlife Service. Details about VTDEC's mercury research project are discussed in detail on the World Wide Web at <http://www.anr.state.vt.us/dec/waterq/remap-overview.htm>.

While this review is by no means exhaustive, it does highlight many important contributions to the body of English-language mercury literature available to scientists for lake systems. The review focuses on the biogeochemical movement of mercury into and through lake systems, methods for reconstructing past accretion of mercury to lakes, and present research efforts in New England. The complexities of biotransformation and bioconcentration are not covered in this review document, perhaps to be added as the REMAP project progresses.

VTDEC would welcome any comments or questions stemming from this material. Inquiries can be directed to Neil Kamman, Environmental Scientist, at the address provided above.

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List of Acronyms:

CVAA - Cold Vapor Atomic Absorption

CVAFS - Cold Vapor Atomic Fluorescence Spectroscopy

dw - as expressed on a dry-weight basis

DOC - Dissolved Organic Carbon

ELA - Experimental Lakes Area

Hg - Mercury

HgT - Total Mercury

HgD - Hg, Dissolved Fraction

KaBP - Kilo-annum Before Present

LOI - Loss on Ignition

MeHg - Methylmercury (used to indicate total methylated Hg species unless specifically noted)

ppb - parts per billion

ppt - parts per trillion

ppq - parts per quadrillion

ww - as expressed on a wet-weight basis.

1.0 Introduction:

Mercury (Hg) is naturally occurring element (atomic weight of 200.59) which has been used for centuries in alchemy, traditional and biomedical chemistry, and manufacturing. Research conducted throughout the northern hemisphere strongly suggests that anthropomorphic activities since industrialization have resulted in significant increases in Hg masses and concentrations as measured in a wide variety of environmental sample types (USEPA, 1997). In the preceding two decades, Hg has emerged as a global environmental problem (Fitzgerald et al. 1998, Driscoll et al., 1994).

Hg assumes myriad forms in environmental media, and demonstrates an exceedingly complex biogeochemical cycle (Fitzgerald et al., 1998). From a human and wildlife health perspective, organic Hg complexes (such as methyl-, dimethyl-, and chlorinated monomethyl-Hg) are of chief concern to environmental managers, as these forms are most toxic (USEPA, 1997, NESCAUM, 1998). Exposure of

wildlife to organic Hg complexes is mediated in large part by biomagnification through increasing trophic compartments (Evers et al., 1998, T. Haines, Univ. of Maine, pers. comm.). Exposure of humans to organic Hg complexes is typically via consumption of contaminated fish (ie Minimata Bay, Japan), though well documented historical contamination episodes have also implicated Hg-tainted grains (USEPA, 1995).

In the preceding decade, very significant advances have been made in the ability to detect Hg at extremely low ambient concentrations (Fitzgerald et al., 1998; USEPA, 1995; NESCAUM, 1998; USEPA, 1997). The development of CVAFS (Bloom, 1989) and strict 'ultra-trace level' clean sampling techniques (USEPA, 1996), presently permits MeHg determinations at picogram (parts-per-quadrillion) detection levels. Prior to CVAFS, analyses were limited by the orders-of-magnitude higher detection limits provided by CVAA. The use of CVAFS has increased widely, such that water samples not handled using strict Hg clean collection and analytical protocols are not considered to be sufficiently robust to contribute to the state of the present science (Bloom, 1994). Valid measurements of sediments and fish can still be made using CVAA, as concentrations of HgT in these matrices are typically in the ppb range (Kamman, 1997, Engstrom and Swain, 1992, C.T. Driscoll, Syracuse Univ., *pers. comm.*).

1.1 Review Outline:

This review of current scientific inquiry into the biogeochemistry of Hg in north-temperate and arctic lacustrine systems uses selected literature to focus on the following general areas of research:

Section 2.0) The pathways by which Hg enters north temperate lakes. A brief general discussion regarding global Hg cycling will be followed by an short overview of Hg contributions by precipitation. An investigation of the watershed-level processes governing delivery of Hg to lakes will be presented, with a detailed review of the biogeochemistry of methylation in lake watersheds and waters.

Section 3.0) The role of paleolimnology. Detailed discussion regarding the use of paleolimnological techniques in assessing historical and present accretion of Hg in lakes will highlight selected landmark paleolimnological investigations.

Section 4.0) Current perspectives regarding Hg research in northern New England. While the body of literature regarding the major headings above is voluminous, research is by no means complete. On-going investigations by regional scientists will be discussed in the context of the body of scientific literature.

2.0 The Pathways by Which Mercury Enters Lakes:

2.1 Background:

Mercury is a naturally occurring element which is naturally released to the environment from the earth in a variety of weathering processes as discussed by Rasmussen (1994). Chief among these are the breakdown of cinnabar (HgS) from bedrock, diagenesis and 'degassing' of sediments and wet soils, and release into oceans from deepwater crustal vents. In the former case, Hg thus released can move directly to the atmosphere. In the latter three, Hg thus released cycles through waters before volatilizing from aqueous surfaces into the atmosphere. Taken in aggregate, the release of Hg from geologic settings into the atmosphere can be termed evasion. In the absence of human activity, the global Hg cycle begins with evasion from land and water.

Mercury thus evaded can assume myriad chemical forms. In the atmosphere, elemental Hg vapor {Hg(O)} can be transported vast distances by prevailing currents. In reaction with ozone, Hg(O) is transformed to divalent Hg (HgII). Highly reactive, HgII commonly attaches to particulate carbon (soot), whereupon it settles to the earth's surface (NESCAUM, 1998). Mason et al. (1994) modeled pre-industrial global Hg fluxes. This landmark research identified two major global Hg pools: oceanic, carrying approximately 3.6×10^6 kg HgT; and atmospheric, carrying approximately 1.6×10^6 kg HgT. Mason also elucidated two major flux pathways for the deposition and re-evasion of Hg, and suggested a dynamic balance (ie no net gain or loss of HgT) between each flux direction. Oceanic deposition and re-evasion transport approximately 0.6×10^6 kg per year, while terrestrial deposition and re-evasion transport approximately 10^6 kg per year.

Since industrialization, anthropogenic activities have greatly increased the mass of Hg in the global cycle. Indeed, Mason et al. (1994) employed a mass-balance model, based upon estimates of Hg emissions from various anthropogenic sources, coupled with a complete Hg source inventory. The percent change in the mass of Hg in the pools and fluxes from the pre-industrial to present time periods is astounding. The atmospheric compartment is now estimated to carry 5.0×10^6 kg HgT, while the oceanic pool is estimated at 10.8×10^6 kg HgT. This represents a + 320 and + 333 percent change in the global atmospheric and oceanic compartments, respectively.

Anthropogenic sources of Hg to the environment are manyfold. Major point sources of Hg include combustion (ie. coal, wastes, medical wastes), and manufacturing (ie. chlor-alkali facilities, cement, and pulp and paper) (USEPA 1997). The best point estimates currently available, calculated for the period 1994-1995, suggest that combustion accounts for 87% of annual emissions while manufacturing accounts for an additional 10%. The remaining 3 percent are non-point, or so-called “area” sources.

Tangentially, but nonetheless interesting in a northern New England context, is the fact that nationally, residential fuel-oil boilers are estimated to account for approximately two percent of the total annual point source Hg emissions (USEPA, 1997). Fuel-oil fired boilers are a predominant source of home heating in northern New England, and New England uses a higher proportion of fuel oil per capita than other parts of the United States. As local Hg sources are considered to contribute less than one-half of the total Hg budget for the New England region (NESCAUM, 1998), regulators may consider looking to larger regional cities (Burlington, VT, Rutland, VT, Plattsburg, N.Y.) as potential “area” sources of Hg for reductions. Such a scenario would obviously necessitate that small-scale Hg “scrubber” systems become available for residences at a reasonable cost.

2.2 Mercury in Rainfall:

Mercury in rain and dry-fall has been measured by a variety of researchers in many northern study locations. A landmark early paper by Lee and Iverfeldt (1991) identified a north to south gradient in the concentration of HgT and MeHg in rainfall samples collected from Sweden. This is an older study, and for methodological reasons, the values presented may not be absolutely comparable with those presented in more modern research.

They determined concentrations of HgT and MeHg in rainfall of 10-89 ppt and 0.05-0.59 ppt respectively. Runoff concentrations measured in small streams were 2-12 ppt HgT, with the methyl fraction constituting 0.04-0.64 ppt thereof. Very importantly, Lee and Iverfeldt identified a strong correlation between Hg concentrations and organic constituents (as evidenced by total color) in their samples. This is discussed in detail in Section 2.3 (below). Concurrently, Mierle and Ingram (1991) identified mean concentrations and wet- deposition of HgT as 10.2 ng/l, and 10.2 $\mu\text{g m}^2/\text{yr}$, respectively.

Newer studies have employed modern methods which include all-teflon sampling equipment, collection vessels, and ultra-trace level Hg clean collection and analytical protocols. Dr. G. Keeler (Univ. of Mich.) is a prime figure in the development of such refined air and precipitation monitoring strategies for Hg. In his work with Burke et al. (1995), a mean volume-weighted HgT concentration in precipitation of 8.3 ppt was calculated for a high-elevation study site in Underhill, Vermont. Volume-weighted mean concentrations appeared in their data to be normally distributed. Calculated as wet deposition (an area-based calculation), these authors determined event mean contributions to the landscape of 0.069 $\mu\text{g HgT/m}^2$. Wet deposition was not normally distributed, suggesting a variation in wet deposition of Hg with event size.

Their results are validated in a related study from Michigan by Hoyer et al (1995), who found volume weighted mean HgT concentrations of 7.9-10.8 ppt, but much higher wet deposition (9.5 and 12.7 $\mu\text{g/m}^2$ in 1992 and 1993, respectively). The discrepancy in wet-deposition between these two studies is explained by the results of trajectory analyses, which implicate transport of Hg to the Michigan sampling sites from nearby point sources. Both studies noted a strong seasonality to HgT in precipitation, with peak concentrations and wet-deportation values during summer. Burke forwards this seasonality as the primary factor driving the observed variation in wet deposition of Hg with event size.

Burke further measured Hg(O), dissolved Hg, and particulate Hg in ambient air samples, and reported concentrations in the picogram per cubic meter range (mean HgO and Hg-particulate were 2 and 11 ppq respectively). The investigations by the team of Burke, Hoyer, Scherbatskoy, and Keeler are on-going, and the papers presented here are intended to provide an indication of the types of rainfall and ambient air data that can be expected in the future.

Very new research by Olmez et al. (1998) at MIT is investigating the transport pathways of HgT associated with fine particulate particles ($< 10 \mu\text{m}$). They report that a site very near Vermont (Willsboro Point, Lake Champlain, New York) showed mean HgT associated with fine particulate matter at 40 pg/g . While this value is higher than that noted by Burke (1995) for particulate Hg, Olmez indicated that the values agree with those reported from the Underhill, Vermont site based upon comparison with other publications by Keeler.

2.3 Watershed Level Processes:

As previously stated, Lee and Iverfeldt (1991) conducted an early study identifying relatively strong positive correlations between HgT and MeHg and organic content (as measured by color, $r=0.78$ and $r=0.68$ respectively). They also elucidated a negative correlation between the MeHg and pH in runoff ($r= -0.65$). This relationship was not nearly as strong between HgT and pH. Given that forested lakes typically have greater organic carbon and a lower pH, the authors make the critically important assertion that such a relationship could increase the potential toxicity of Hg in forest lakes with proportionally larger drainage areas. Many of the studies referenced throughout this review cite Lee and Iverfeldt's findings regarding the link between pH, color, and Hg transport in forested watersheds.

Concurrent research by Mierle and Ingram (1991) estimated total Hg concentrations in the tributary streams and open waters of two small forested lakes in Ontario. Methodologically, this study improved upon Lee and Iverfeldt (1991) in that measurements of color as well as dissolved organic carbon (DOC) were made. It falls short of Lee and Iverfeldt in that no attempt was made to measure MeHg. Taken together, the studies are complimentary.

Mierle and Ingram's reported values for HgT in streamflow showed a distinct seasonality marked by higher summer HgT loadings relative to other seasons. This is consistent with precipitation HgT concentrations later reported by Burke (1995) and Hoyer (1995). Corroborating Lee and Iverfeldt, they determined that the export of HgT and DOC was highly correlated in their tributaries, and further substantiated the link between DOC in streams, and humic and fulvic matter in the streams' respective catchments. Importantly, they note that the study watersheds were acting as net sinks for HgT, not net sources, "as would be expected were mineral weathering occurring in the watersheds." This widely

accepted groundbreaking conclusion continues to elicit controversy as evidenced by a vigorous on-going scientific debate which is described in Section 3.2 (below).

In an attempt to look at Hg transport in watersheds of varying land-use types, Hurley et al. (1995) conducted a large-scale monitoring project targeting 39 rivers in Wisconsin. Their sites were selected following a USGS-NAWQA (National Water Quality Assessment Program) protocol which ensures similarity among selected study watersheds. Strict Hg-clean protocols were employed to assess Hg and MeHg in total, particulate, and dissolved phases. This excellent study identified the seasonality reported by the above described research, as well as marked differences in Hg and MeHg export between phases. In every case, MeHg export increased in watersheds with proportionally greater area in forest or wetland. In undisturbed watersheds, HgT was most commonly associated with the filtered phase, but became most associated with particulate matter in agricultural watersheds. The following passage from this study serves to illustrate the importance of strict Hg-clean protocols in the analysis of water samples for any study:

“Our highest value, 42.7 ng/l, was...of similar magnitude to the 34 ng/l reported by Gill and Bruland downstream of a Hg mine effluent. It is interesting to note that even under these perceived ‘contaminated’ conditions, HgT levels did not exceed 50 ng/l, a level frequently reported as ‘below detection limit’ using sampling and analytical techniques frequently used prior to the late 1980’s.”

In the context of this statement by Hurley, the drinking water standard promulgated by the Safe Drinking Water Act for municipal water supplies of 2 µg/l presents a sobering thought indeed.

Balogh et al. (1997) further validate the linking of HgT and particulate matter in their study of the suburban-urban Minnesota River. In this study, the authors identified a very strong correlation between HgT and total suspended solids (TSS). They observed the same seasonality reported by previous researchers in patterns of HgT load in their study sites. This study differentiates itself from prior similar efforts by incorporating measurements of point sources (WWTF’s) of Hg. They found that only one percent of HgT loads could be attributed to point sources. This study design, however, incorporated a potential methodological weakness. Specifically, the samples collected were acquired from a single grab from 0.5m depth, collected at the midpoint of the river. Such a sampling strategy ignores suspended

sediment and flow gradients across the rivers' width and depth. USGS protocols (VTDEC and NYSDEC, 1996) strongly support the use of depth-integrated river samples composited from multiple locations across the width of the river. The effect of this potential methodological problem cannot be quantified without detailed information regarding the sampling sites used by the investigators. In defense of this research, a sufficient number of samples were collected during the course of the study to permit elucidation of flow, TSS, and HgT relationships. The grab sample approach also avoids the complexity of maintaining a strict Hg-clean atmosphere around a depth-integrating sampler; a difficult task.

A similar study incorporating more sophisticated measurements of particulate matter (ie. TSS and particulate organic carbon) by Mason and Sullivan (1998) demonstrated the HgT-TSS link in the urbanized Anacostia River near Washington, D.C. This study showed that sediment-water partitioning (k_d) of both HgT and MeHg strongly and positively correlated with the particulate organic carbon component of TSS. Thus, a clear linking of Hg with organic matter, *in concert with* suspended matter, is established. Interestingly, Mason and Sullivan also found that the urbanized Anacostia retained very little HgT or MeHg, a finding at odds with other similar work (ie. Hurley et al, 1995). The author thus concludes that there are significant non-point contributions of Hg and MeHg, and that MeHg is likely generated within the river system itself.

To complete this review of watershed-level processes, two mechanisms for the linking of Hg with the organic material are presented. In an extremely robust attempt to quantify the amount of Hg transferred from the air to a forested watershed for subsequent processing, Rea and Keeler (1996) made measurements of Hg in leaves, litterfall, and throughfall precipitation at the Underhill, Vermont site previously discussed. Their findings relevant to this review were that: 1) Hg concentrations are higher in throughfall than in precipitation, suggesting that the rain was rinsing Hg from the leaves as it fell through the canopy; and 2) Hg concentrations in leaf matter were lowest after budbreak, increased during the growing season, and were maximal after litterfall. They thus postulated that one major mechanism of Hg deposition to forested watersheds is via the 'scavenging' of ambient Hg by stoma-bearing surfaces, followed either by release to soil-water, or sequestration as the leaves decay after litterfall. Since leaves are one component of the 'raw material' for the development of humic and fulvic acids in tannic-water catchments, this 'scavenging' is one process by which Hg can be bound to organic material for subsequent delivery to downstream waters.

The second process by which Hg becomes associated with organic matter is via bacterial methylation in peatlands or wetlands. Krabbenhoft et al. (1995) conducted an intensive survey of a remote northern Wisconsin watershed. This study found that concentrations of HgT and MeHg were highest in sections of the watershed that were either wetlands, or locations where water passed through peat layers. Their mass-balance calculations suggest that both wetlands and peatlands act as sources of MeHg in watersheds. Branfirun et al. (1996) examined the specific dynamics of MeHg production in a large peatland-lake complex. By performing intensive measurements of MeHg in all hydrologic compartments of the peatland-lake complex, the authors determined that the peatland was a significant, continuing source of MeHg to the down gradient lake.

Research lead by Drs. Charles Driscoll (Syracuse University) and Carl Schofield (Cornell Univ.), in cooperation with various other investigators, the Empire State Electric Research Corporation, and the Electric Power Research Institute (EPRI,) has resulted in excellent papers on Hg dynamics in the Adirondack Mountains, Onondaga Lake, and elsewhere. This body of research, elegant in its simplicity, is referenced by nearly every other subsequently-published study cited in this review. Three landmark studies by the Driscoll team are reviewed favorably herein.

The first of these (Driscoll et al., 1998) strongly validates the findings discussed directly above. In this study, an intensive mass-balance investigation of a small beaver-created wetland complex in the Adirondacks was conducted. Throughout the 15 month period sampled, MeHg was consistently higher in the wetlands outflow than in its inflows. HgT was also higher in the outflow than in the inflows, but that difference was directly proportional to the difference (outflow minus inflow) for MeHg. This suggests that the total Hg added to the system is the result of ontogenic processes within the wetland. Methylation of HgT sequestered in the sediments was suggested as the mechanism of MeHg generation. The period of greatest inferred MeHg production (summer) was marked by highly significant decreases in sulfate and increases in DOC, common correlates of MeHg production in lakes (discussed in section 2.4 below). The authors concluded that, while the watershed studied is a net sink for total Hg (as in Mierle and Ingram, 1991, and Krabbenhoft, 1995), the beaver-pond wetland at the studied watersheds' downstream-most point is a site of significant MeHg production. Based on this conclusion, Driscoll speculated that recent increases in beaver (*Castor canadensis*) populations, and corresponding increases in the areas of watersheds occupied by beaver impoundments, could have resulted in greater MeHg export

from such watersheds to downstream lakes, and a subsequent increase in fish-tissue Hg burdens in the Adirondacks.

2.4 In-Lake Processes:

Characterization of the partitioning of Hg and organic Hg complexes in lakes is a difficult task to which researchers in this arena have applied two general approaches. This first approach, field studies, constitute a minority of the literature regarding Hg in lakes. The reasons for this are clear. Field studies are expensive to conduct, and control over the variables which influence the outcomes under evaluation is difficult to achieve. The second approach, benchtop experiments using lake sediments and waters collected from the field, is much more common in the reviewed literature. In the following section of this review, field and bench studies are used to identify those factors which are demonstrated to mediate methylation of Hg in lakes. The very strong contribution by Swedish scientists to this field of study can not be understated.

In conjunction with their research on watershed transport, Lee and Iverfeldt (1991) collected Hg and MeHg samples, as well as ancillary data, from eight Swedish lakes of varying morphometry. They reported in-lake HgT and MeHg concentrations of 1.3-15ng/l and 0.04-0.8 ng/l respectively. Their data showed very clear and statistically significant relationships between HgT and MeHg, and color, pH, watershed-lake area ratio, retention time, and HgT in northern pike (*Esox lucious*). As expected from their watershed-level work, HgT and MeHg increased with increasing color and decreasing pH in lake waters.

Most interestingly, mean MeHg proportion (MeHg/HgT) was strongly and positively correlated with watershed-lake area ratio, and strongly and negatively correlated with retention time. The authors attributed this to the relative preference of MeHg to bind to organic fractions of “lower molecular weight.” The unstated underlying hypothesis that Lee and Iverfeldt make in their statement is that lakes with proportionally larger watersheds, or faster flushing rates, have a relatively higher proportion of “lower molecular weight” compounds to which MeHg can bind. Moreover, it would be expected that lakes with shorter retention times and larger watershed ratios would have a greater proportion of settling matter present than in lakes with longer flushing rates. The settling inorganic particulate matter in lakes

of larger watersheds can be expected to have iron and other earth metals adsorbed thereto, compounds of *higher* molecular weight than the humic fractions the authors contend preferentially hold HgT. Thus, while the relationship they observed is no doubt real, and it is supported by Mason and Sullivan's (1998) findings, their proposed explanation would benefit from validation with data.

An excellent laboratory assay by Regnell and Tunlid (1991) involved the use of sediment cores from the deep hole of a eutrophic lake. In this experiment, the authors spiked the cores with radiolabeled $^{203}\text{HgCl}$, and measured bacterial and abiotic (in a 'killed' core) methylation under varying dissolved oxygen regimes. Other factors such as temperature and light were held constant at expected in-lake values. $^{203}\text{MeHg}$ and ^{203}HgT were measured in both water and sediment. Methylation increased over threefold in cores held in an anoxic state. Moreover, their experiments indicated that the sediments were a source of ^{203}HgT under anoxic conditions, while they were considered a sink under aerobic conditions. Microbiological assays were also conducted for bacterial activity and generation of cobalamin, a vitamin B derivative commonly associated with methylating activity by bacteria. These data suggested that increased bacterial activity under anoxic conditions was responsible for the observed increase in $^{203}\text{MeHg}$ concentrations.

In order to validate their hypothesis that bacterial activity indeed increased methylation, and to ascertain the effect of pH on methylation activity, Regnell (1994) conducted what could be considered a benchtop microcosm - whole lake experimental manipulation study. To begin, Regnell installed 4 limnocorrals in an oligotrophic lake, acidifying two to a pH of 4.4 (from 6.9), and retaining 2 as control. Multiple sediment-water cores were collected from each corral. At the time of core collection, pH in the acidified corrals was 5.8, while the pH in the control was 6.6.

In the laboratory, cores from each corral were treated similarly to the experiment described above (Regnell and Tunlid, 1991). After initiation of anoxia, a subset of the cores was given additions of *triptic soybroth* to stimulate bacterial growth and reproduction, effectively increasing the bacterial population, and thus, the hypothesized methylation potential. As found previously, sediments were found to be a ^{203}HgT source in anaerobic microcosms. Moreover, this study's design permitted the authors to observe that the anoxia-induced increase in methylation observed in the 1991 effort was not merely an artifact of eutrophic lake sediment chemistry. The effects of pH were partially masked by high nitrate levels which

developed over the course of the experiment (in-lake acidifications used a mix of nitric, sulfuric, and hydrochloric acids). Significantly higher methylation rates were observed in microcosms containing experimentally enhanced bacterial populations, validating hypotheses stated in 1991. Regenells' research was further enhanced (Regnell et al., 1996) by additional microbiological assays which strongly implicated *Desulfobacter spp.* in the production of MeHg in sediments.

Independent validation of Regenell's work can be inferred from a study by Zhang and Planas (1993). In this research, the authors incubated sediment-water cores both with and without bacterial colonies. Those cores supporting bacterial colonies produced higher measured MeHg concentrations than did sterile cores. Sterile cores did, however, demonstrate methylation. Demethylation only occurred in non-sterile sediments, leading the authors to conclude that demethylation is wholly a biological process, while methylation has an abiotic component. Zhang and Planas likely had fluorescent lights in their laboratory, for their finding was directly refuted by Sellers et al. (1996), who, in a simple benchtop experiment, discovered that methylmercury indeed is abiotically demethylated, *via photodegradation*. In further experiments using waters from an ELA lake, they conducted a mass-balance accounting of methylmercury inputs excluding sediments, and found that MeHg was degraded at twice the rate that externally-derived MeHg was deposited. This research provides a fundamental validation of the role of sediments as the major source of methylmercury in lakes suggested by Driscoll et al. (1998).

A similarly executed series of benchtop experiments used sediment-water cores collected from the moderately acidic Quabbin Reservoir, Massachusetts, to investigate the effects of sulfate on MeHg production (Gilmour et al., 1992). In this study, cores were collected, sectioned, and analyzed for MeHg and HgT. Core incubation systems were then constructed using Quabbin water and sediments, and MeHg production under various controlled sulfate concentrations was evaluated.

In the incubated cores, increasing sulfate concentrations resulted in increased MeHg production, and a net movement of Hg from HgT in sediment, to MeHg in water. Sulfate concentrations declined in direct proportion to MeHg increases, strongly implicating sulfate-reducing bacteria as mediating methylation. In incubated cores where bacterial sulfate reduction was inhibited (by the addition of 2 bromoethane-sulfonic acid), MeHg production was reduced. In incubated cores where sulfate reduction was blocked entirely (by the addition of sodium molybdate), methylation ceased altogether.

HgT and MeHg stratigraphy was measured downcore in several Quabbin cores from littoral to hypolimnetic locations. Sediment concentrations (as wet weight) were low, as would be expected in large, rapidly flushed reservoir systems (Kamman, N. Vermont Department of Environmental Conservation, unpublished data). Unfortunately, while organic sediment fractions are reported (as LOI), no sediment percent solids data are presented, precluding comparison of their sediment Hg data with that of other studies which reported Hg concentrations as dry-weight. Dating profiles for the cores would also have been useful. Surficial sediment MeHg concentrations were highest in littoral muds.

The connection between organic matter and methylation potential was explored further by Miskimmin (1991) on sediments acquired from ELA Lake 239. In this project, using $^{203}\text{HgCl}$, the author demonstrated that: 1) after a fixed period of time (24hr), aqueous $^{203}\text{MeHg}$ concentration increased with increased DOC concentration, while sediment $^{203}\text{MeHg}$ concentrations were unaffected; and 2) after incubation for 7 days, solubility of MeHg increased with increasing DOC. Unfortunately, this particular study demonstrated some methodological shortcomings, including a lack of trace-metals clean techniques for sample acquisition and analysis, lack of experimental control, and failure to account for the sediments oxygenation state. Nonetheless, Miskimmin's work suggested that DOC plays a role in the partitioning of MeHg between sediments and waters, and allowed the notion that sediments are a source of MeHg.

Ralmal et al. (1993) explored methylation and demethylation rates in the epilimnion and hypolimnion of four northwest Ontario lakes. They found that early-mid summer temperature increases stimulated methylation, and that fall temperature declines retarded demethylation. This was attributed to enhancement of microbial communities at increased temperatures. In a key finding, the authors report that methylation rates from epilimnetic sediments were 20-40 fold higher than in hypolimnetic sediments. However, the relatively low concentrations of HgT in epilimnetic sediments as compared to those in hypolimnetic sediments may reduce the relative importance of the increased rates when total MeHg mass produced is considered. Laboratory-measured methylation/demethylation (M/D) was compared to in-lake concentrations of MeHg. Agreement between the ^{203}Hg inferred (M/D) and in-lake MeHg concentration was very good. Interestingly, ambient MeHg data showed a clear bimodal pattern of concentration through time, with peaks early and late summer observed in all of the lakes. The significance of this pattern was not discussed in text.

Matilainen and Verta conducted a very well executed study of methylation and demethylation in aerobic waters of five Finnish lakes. They found that methylation and demethylation were positively correlated with temperature, and demethylation was positively correlated with DOC (as inferred by color). This latter point suggests perhaps a scavenging of MeHg at high DOC concentrations. Finally, they noted that methylation rates were inversely correlated to the proportion of HgT in particulate phase.

Rada et al. (1993) conducted an interesting effort to quantify whole-lake burdens of Hg in the sediments of six Wisconsin seepage lakes (including the experimentally acidified Little Rock Pond). In this project, 50 cores were collected from randomly selected locations from the lakes using a spatial algorithm designed to equalize the number of cores acquired across varying sediment depths. They found a wide range in HgT concentrations in sediments, and a wide range in whole-lake HgT sediment burdens. While clean techniques were not employed for this effort (they used CVAA), the authors achieved an impressively low quantitation limit (0.7 ng/g-dw), far below that typically achieved with CVAA. While these authors preferred to make their calculations using a wet-weight sediment concentration, both wet and dry-weight values were reported. A very strong negative correlation between pH and sediment HgT burden was observed, which was speculatively attributed to pH-driven evasion of elemental Hg (HgO) from the lake surfaces.

A 19-lake winter study by Watras et al. (1996) further validated the relationship between HgT, MeHg, and DOC and pH. Ambient concentrations ranged from 0.3-5.3 ng/l HgT, and 0.01-2.8ng/l MeHg. MeHg concentration was positively correlated with HgT. Statistically significant relationships were observed between HgT and MeHg, and DOC, and pH. Weaker but significant relationships were observed with dissolved oxygen, iron, and manganese.

In a pair of papers from the same field effort, Driscoll et al. (1994 and 1995) explored the relationship of ambient HgT and speciated MeHg, physico-chemical parameters, and HgT in yellow perch (*Perca flavescens*) in 16 Adirondack lakes. First reported as a full-feature article in *Environmental Science and Technology*, and subsequently revised for *Water, Air and Soil Pollution*, this research portrays the highly complex and quite devious interaction between Hg, methylation, DOC, organic ligands, fish uptake, and other metals typically present in tannic and acid-stressed lakes.

This is one of the first research projects to measure species of MeHg in ambient waters. In lake HgT concentrations were reported in the 1-5ng/l range, the majority of which were in the dissolved fraction. One-meter MeHg concentrations ranged from 0.068 ng/l to 0.61 ng/l (about 10% of HgT), and were highly variable across the limited sampling conducted. In all cases epilimnetic MeHg concentrations were elevated in lakes with anoxic hypolimnia, strongly suggesting that lake sediments represented a majority of the MeHg source. Increased HgT and MeHg were observed in lakes of higher DOC. Increased DOC was observed in lakes with larger proportions of nearshore wetlands, as was increased HgT and MeHg. All of these findings are consistent with many of the studies cited above (Regnell et al. 1991, 1992, and 1996; Matilainen and Verta 1995; Miskimmin, 1991; Lee and Iverfeldt, 1991).

Yellow perch Hg concentration was found to increase predictably with fish age, and this trend compared well with a similar study from the Upper Peninsula of Michigan (actual fish-tissue concentrations in the Adirondack study were significantly higher). Surprisingly, however, simple regression models indicated that fish tissue HgT did not increase significantly with increasing MeHg, pH, or DOC, though monomeric aluminum did. To assess the interrelationship between DOC and aluminum, a multiple regression procedure was employed, which demonstrated that fish-tissue HgT indeed increased strongly with pH, DOC, and MeHg, but only up to a threshold DOC concentration of 8mg/l. Beyond this DOC concentration, fish-tissue Hg is actually reduced. The authors infer convincingly that the cycling of aqueous aluminum leached from the soils of anthropomorphically acidified lake catchments has a strong effect on the availability of aqueous MeHg, through competition for organic ligand and organic acid binding sites. This inference is well supported by their data, although an absolute test would necessitate a large mesocosm or multiple whole-lake manipulation study.

Thus emerges the complex dual role of DOC in the Adirondack study lakes. First, DOC is primarily responsible for the transport of HgT and MeHg from nearshore wetlands. Once in-lake, DOC simultaneously fosters methylation at the sediments (Miskimmin, 1991), and inhibits MeHg uptake in biota by binding (Driscoll et al., 1994 and Driscoll et al., 1995), or by reduced aqueous MeHg concentrations from demethylation (Matilainen and Verta, 1995). In the presence of monomeric aluminum such as would be found in an anthropomorphically acidified lake, aluminum, having a higher organic affinity than MeHg, outcompetes MeHg for binding sites on such fractions of DOC as organic acids or ligands. Once sufficient DOC exists to complex an acid lakes entire aluminum burden, mono-

MeHg is in turn bound, and thus less available for bioaccumulation. In sum, the presence of aluminum in acid lakes exacerbates the bioaccumulation of MeHg into fish by keeping DOC from binding the MeHg.

3.0 Historical Deposition of Mercury to Lakes as Evidenced by Sediment Reconstructions:

As the biogeochemistry of Hg has become increasingly well studied and understood, a clear question has emerged: to what extent do the concentrations and cycles of mercury exceed background, or pristine levels? Indeed, some of the highest toxic Hg concentrations for non-industrially impacted lakes are found in remote, forested or mountainous areas (Driscoll et al., 1994). Rasmussen (1994) has suggested that this Hg is perhaps of geologic origin, the by-product of weathering or diagenesis. At face value, this appears a reasonable hypothesis, strongly supported by Coker et al. (1995), who conducted an investigation of sediment HgT concentrations along a geologic gradient on the Canadian Shield. The following section of this review discusses briefly the admittedly short-term history behind paleolimnological investigations of HgT accumulation to lakes, and describes an ongoing controversy between two ‘schools of thought’ regarding Hg biogeochemistry. Specifically, those who purport that problems associated with Hg cycling are due to geologic processes, and are thus not really problems per-se, are at odds with those who feel that the Hg cycles have been greatly affected by anthropogenic Hg additions to the global biosphere. Their battle of scientific logic is fought in the pages of *Environmental Science and Technology*; their casualties, the research conducted by many of the authors cited in this volume and elsewhere.

3.1 The Role of Paleolimnology:

Paleolimnological techniques to infer historical water chemistry status of lakes using sedimented diatoms were developed during the 60's and 70's, but ‘came of age’ in their application to acidified lakes during the early 1980's (Ouellet and Jones, 1983, Oldfield and Appleby, 1984, Charles and Norton, 1986, Charles and Whitehead, 1986). Many of these projects analyzed their sediments for trace-metals, but only for use as ancillary data in the interpretation of diatom-inferred historical water quality predictions.

Such projects are telling. Ouellet and Jones (1983) measured increasing enrichments (above background) of sediment HgT with increased watershed disturbance in 26 Canadian Shield lakes. Charles and Norton (1986) documented enrichment of sediments with HgT, and attributed this to atmospheric deposition. The large-scale Paleocological Investigations of Recent Lake Acidification project (PIRLA, Charles and Whitehead, 1986) assessed historical and present water chemistry conditions in 35 lakes across the United States. This broad interdisciplinary project spawned new directions for paleolimnological research.

Typical paleolimnological investigations using Hg are conducted as follows. A sediment core or series of cores is collected from the sediments of a study lake. These sediments are sectioned at coarse (10cm) to fine (0.5cm) intervals. Date values are associated with depths down-core by radiometric measurement of gamma-emissions from radioactive isotopes of Pb (as ^{210}Pb), Cs (as ^{137}Cs), and Am (as ^{141}Am) (Oldfield and Appleby, 1984). Historical timeframes for emissions of these radioisotopes are understood. For example, down-core peaks in ^{137}Cs are attributed to late-1950's nuclear testing, while precipitous declines in ^{210}Pb are attributed to the banning of lead in gasoline. Dating of sediments is critical to the interpretation of sediment HgT concentrations to account and correct for normal sediment focusing, which varies with individual lake bathymetry. Sediment sections are analyzed for HgT using methods appropriate to expected concentrations (CVAA for HgT, CVAFS for MeHg). Sediment accretion rates are then used in conjunction with HgT measurements to calculate a flux of HgT to a lake for a given period of time.

Early in the 1990's, Swain et al (1992) and Engstrom et al. (1994) reported on the first study specifically reconstructing HgT accumulations in 7 Minnesota and Wisconsin lakes. Their research indicated that HgT fluxes to lakes became and remained elevated above baseline fluxes beginning 1800-1850, and increased again beginning 1930 to 1950 to a much greater degree. By regressing the flux of Hg against watershed:lake area ratio, the authors determined that slope of the regression was significantly greater for modern fluxes, and that the intercept was also higher (Figure 1). This important point merits the elegantly simple text from Swain et al (1992):

“The slope of the linear relation represents the incremental increase in Hg accumulation per unit increase in the ratio between the catchment and lake areas. If all the Hg deposited to the catchment were transported to the lake, the slope would be equal to the

rate of atmospheric deposition. On the other hand, if the slope were zero, direct deposition to the lake surface would be the only significant source.”

In a significant enhancement of their collaborative research, Engstrom and Swain (1997) expanded their study set to include urban lakes in Minneapolis, western Minnesota lakes, and a set of remote lakes in southeast Alaska. In this project, their new and re-cored lake stratigraphies suggested declines in fluxes to urban lakes and the remote 1992 lake set beginning in approximately 1972, while fluxes continued to increase in the western Minnesota and Alaskan lake sets. Note that overall HgT concentrations in

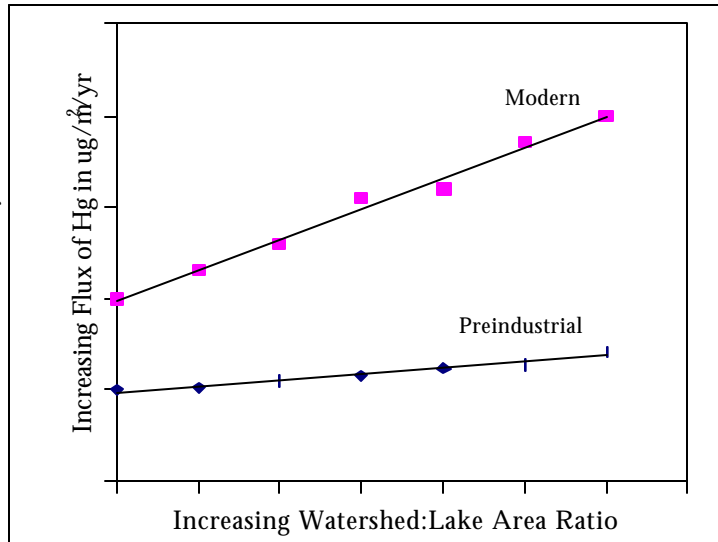


Figure 1. Theoretical representation of the modern and pre-industrial relationship between watershed:lake ratio and HgT flux. Adapted from Swain et al., 1992.

the western MN and AK lake muds were lower than the urban and remote MN lakes, an observation which testifies to the importance of dating. The inferred HgT fluxes were then paired against estimated US industrial Hg emissions from a variety of sources, with striking results. Indeed, decreases in Hg production and usage in the US were coincident with the decreases observed in fluxes to the urban and eastern Minnesota lake sets. The continued increase in fluxes to the western Minnesota and Alaskan lakes was attributed to global Hg usage, which has continued more or less unabated.

McIntosh et al. (1994) conducted a comprehensive evaluation of the toxic constituents in Lake Champlain, Vermont and New York. The second, intensive phase of this two-phase assessment involved paleolimnological determination of HgT stratigraphy at 10 sites throughout the lake. Coring locations were sited to correspond to locations which had high surficial HgT concentrations measured during an earlier whole-lake screening. This is the only study in this review which employed CVAFS, due to anticipated low background (deep-core) HgT concentrations. In nine of the 10 sites, HgT stratigraphy followed the pattern described by Engstrom and Swain (1997) for the eastern Minnesota and urban lake sets.

One site, located adjacent to an offshore oil tanker pumping terminal, displayed a pattern of very high HgT concentrations until recent sediments, followed by precipitous HgT declines. Lakewide, the highest surficial sediment HgT concentrations were observed at this site. Grain-size distributions in this core are used to argue that this particular core represents a particularly good record of atmospheric deposition to Burlington Harbor. This allows the reader to infer that excessively high *background* HgT at this site, which precipitously drops by 1µg/g *above* the 20-21 cm 'cookie' downcore, can be explained by atmospheric deposition or runoff reductions from adjacent Burlington. Two alternate explanations are also possible. First, this structure is near the vicinity of the City of Burlington WWTF. This plant was upgraded from primary to secondary treatment in 1953, and it is thus plausible that the onset of plant operation significantly reduced HgT discharges to the lake. The drastic HgT decrease from 21-20cm supports this explanation. Alternately, oil off-loading at the terminal was halted by 1971. One can speculate that the period 1970-1971 corresponds with the 20 cm sediment subsample. While fuels and oil are not known to carry great amounts of Hg, an on-going addition of oil into the waters at this site due to routine small spills could very likely account for the high concentrations noted below 21cm. The latter alternate explanation is less likely since it would require a 0.74cm annual sediment accretion rate (not accounting for focusing), which seems very high indeed. The truth likely incorporates elements from both of these alternate hypotheses, though it is impossible to suggest which, since dating profiles are not provided for this most interesting site. Throughout the lake, background HgT concentrations were noted to be 30-50 ng/g (as dw).

In discussion, McIntosh indicates that it is unknown whether the majority of HgT in deepwater Lake Champlain sediments is atmospherically deposited, or the result of either sediment organic fraction binding, or diagenetic or bedrock weathering processes. Shanley et al. (*in press*) states categorically that Hg-bearing bedrock in the Lake Champlain basin is essentially nonexistent. As described below (Fitzgerald et al., 1998), diagenesis from sediments is unlikely. Thus atmospheric deposition, superimposed over the variety of small industrial facilities which produce may produce Hg in their waste and/or emissions, is implicated.

Hermanson (1998) conducted a paleolimnological investigation of two low-arctic lakes in the vicinity of southeastern Hudson Bay. One of these lakes is affected by a WWTF discharge, while the other is assumed to be of pristine status. The pristine lake experienced a sixfold increase in inferred HgT flux

during the period 1750-1980. Modern flux rates to this lake are estimated at 15 to 18 $\mu\text{g}/\text{m}^2/\text{yr}$, which is consistent with the range reported by Engstrom and Swain (1997) for Alaskan lakes. In the WWTF-impacted lake, HgT fluxes increased very dramatically beginning approximately 1960, coinciding with the establishment of the treatment facility. Prior to 1960, HgT fluxes to this lake compared well with the other, pristine lake, indicating significant WWTF-derived HgT loading.

In this study, three cores were collected in tight proximity, at the lakes deep hole. These cores were sectioned, the sections composited, and the composites analyzed for ^{210}Pb , percent solid, organic carbon (as LOI) and HgT, as well as other trace metals (ie. Pb, Cd). No reason is given for the compositing procedure, which is not reported in the methods of other studies. Most likely, the compositing provided Hermanson sufficient sediments to conduct all intended analyses. Mixing of multiple cores in this fashion can be acceptable provided one has certainty that the cores are of equal depth, and that the corer has entered the sediments *vertically* for each core. Both issues are important. For the core depth issue, core tubes which penetrate deeper into the sediments produce an artifact known as ‘core compaction,’ such that for each additional centimeter penetrated into the muds, the deeper sediments are progressively compacted by the weight of the overlying muds in the core (D. Engstrom, Univ. of Minnesota, *pers. comm.*). Compositing three cores of unequal length, while providing good matches in shallow sediments, could mix very age-dissimilar sediments deeper. In lakes where sedimentation rates are low (ie. low-arctic lakes), the age difference could be considerable. This can be overcome by the use of a piston-style corer, but it is not stated in text what type of corer was used. The result of such a compositing procedure is difficult to predict, except that ‘noisy data’ would be expected, both in dating values and HgT stratigraphy. Such noise does appear to challenge Hermanson’s data. Nevertheless, there exists sufficient elevation in flux rates above background such that the trends reported in this research appear valid.

Von Gunten et al. (1998) reported trace metals concentrations, including HgT, in sediments from the Zurichsee (Zurich, Switzerland). A “long core” was hammer-piston collected from the deep hole of the lake (136m), extending to a depth of 200m below the sediment-water interface. A parallel gravity core was obtained from the same proximal location to a depth of 70cm for detailed 200-year sediment chronology reconstruction. Data from a depth of 40 meters (approx. 15 KaBP) in the long core are used as background concentrations, against which recent 200 year depositions are assessed.

Mercury concentrations in their sediments were extremely high compared with North American and arctic lakes, with pre-1800 concentrations of 0.4 µg/g or greater. Sediment HgT concentrations increased until approximately 1970, and declined to pre-industrial levels. No Hg data were provided (most unfortunately) from the 15 KaBP sediments. Coincident increases and subsequent decreases of Cu, Zn, and Cd were also reported. The 1935-1970 HgT sediment concentrations warrant scrutiny. Indeed, values of as high as 1 µg/g were reported, which approach NOAA moderate effects toxicity concentrations (Long and Morgan, 1990). These high concentrations are consistent with the Lake Champlain oil tanker terminal site discussed in McIntosh (1994).

This study may is not absolutely comparable to others presented in this review for the following reasons. The authors used atomic emission for HgT determinations instead of CVAA or CVAFS. Further, the chemists in this study used an extremely aggressive extraction procedure involving HNO₃, HClO₄, and HF. While likely appropriate for coarse mineral material such as would be expected 20m downcore, such aggressive extractions can result in the formation of interfering substances when used with the high organic content sediments typical of hypolimnetic gyttja. Indeed, HNO₃-H₂SO₄ is typically sufficient to digest most lake sediments. No information is given as to the trace-metals cleanliness of the chemical analyses. Also the large difference in lake geochemistry between Zurichsee and North American lake sets likely plays a role in HgT deposition to these sediments. The hardness of the alkaline Zurichsee is certainly higher than midwestern, northeastern, low arctic, and Alaskan lakes, which might lead to a greater potential for Hg precipitate formation in the lake. The net result of this would be to transfer greater quantities of HgT from solution into sediments. Fluxes of HgT were not calculated, so absolute comparison of these data with other studies in this review is impractical.

Lockhart et al. (1998) reports on an 18 lake paleolimnological survey of Canadian lakes. The lakes selected for analysis ranged in size from the 3.7 ha Far Lake, to the 3.1 x 10⁶ ha Great Bear Lake. Two locations of the Hudson Bay were also included in this study. This is indeed a wide variation in study sites. In an enhancement in study design over other paleolimnological surveys, the investigators assessed HgT in soil profiles in selected locations around each study lake to determine potentially available watershed-delivered Hg.

As in other locations, they found low background, and elevated modern sediment concentrations, and calculated flux patterns similar to the Engstrom and Swain (1997) Alaskan lake set (ie, no decrease in HgT flux at the most modern sediments). Sediment HgT concentrations were low in this study set, with modern mean concentrations ranging from 0.025 to 0.155 $\mu\text{g/g dw}$. Modern fluxes ranged from 2.1 to 51 $\mu\text{g/m}^2/\text{yr}$ (excluding the south Lake Winnipeg site, which is subject to anthropogenic loadings from by nearby Winnipeg). One of the lakes in this study, ELA Lake 375, has been the subject of a mass-balance Hg budget study. Modern flux rates calculated from the Lake 375 core were in good agreement with the anthropogenic inputs estimated in conjunction with the mass balance study.

In an effort to capitalize on the long-completed PIRLA project (Charles and Whitehead, 1986), Lorey and Driscoll (*in review*) have acquired archived sediments for 7 PIRLA lakes in the Adirondacks. The sediments were analyzed for HgT by CVAA. Deep-core concentrations ranged from 0.02 to 0.2 $\mu\text{g/g-dw}$, while modern sediments ranged from 0.18 to 0.50 $\mu\text{g/g dw}$. These are among the highest concentrations for remote lakes of all papers reviewed, but appear consistent with HgT concentrations from a set of relatively undisturbed Vermont lakes (N. Kamman, Vermont Department of Environmental Conservation, unpublished data). Decreases in concentrations and fluxes are apparent in the top-most strata of the PIRLA cores, suggesting that reductions in anthropogenic HgT loadings were just becoming manifested in the cores as of the PIRLA collections. The authors analyzed their data using the technique of Swain and Engstrom (1992, Figure 1), and determined that current flux to the geographic study area has increased from 5.0 $\mu\text{g/m}^2/\text{yr}$ during the preindustrial period to 8.9 $\mu\text{g/m}^2/\text{yr}$ as of 1983 (the year the PIRLA cores were collected).

3.2 Controversy in the Scientific Community:

In the final analysis, the reduction of Hg in the global reserve will depend on reductions of Hg sources. When suggestions are made regarding alteration of mining methods, or reductions in the number of planned hydropower projects, things very quickly become political. Rasmussen (1994), with funding from the Ontario Hydro Research Division (Acknowledgments, Rasmussen, 1994), prepared a comprehensive critical review in *Environmental Science and Technology*. The goal of this critical review was to suggest that the apparently elevated Hg concentrations reported among multiple biogeochemical compartments were actually the result of natural processes. Mineral weathering, diagenesis, sediment

degassing, oceanic venting of high Hg-bearing waters, and the high organic affinity of Hg as a transport mechanism are all cited as examples of why elevated Hg observations should be considered 'natural.' Rasmussen provided examples from the worldwide literature on geothermal exploration, volcanology, and seismicity including many international studies, in support of her contentions. Specific studies regarding Hg concentrations in soils, vegetation, peatlands, lake sediments, and oceans are discussed. It is noteworthy that of the 130 citations used in support of the Rasmussen review, only 28 are from research conducted since 1990. Thus, Rasmussen relies heavily on conclusions generated from other fields of study using what are now considered outdated methods (Fitzgerald, 1998). In her own conclusions, Rasmussen stated:

“Studies of this type are presented as evidence that long-range transport of anthropogenic Hg is responsible for elevated Hg concentrations in fish and other wildlife in remote areas. As these conclusions hold serious implications for government and industry, the underlying assumptions deserve careful scrutiny. An examination of the sampling and calculation methodologies used in these studies reveals a lack of attention to geological factors which affect natural distribution patterns of Hg in soil, atmosphere, vegetation, and sediments.”

A vast majority of the studies employing Hg clean technology were in-press or in-review when the Rasmussen review was written. Correspondingly, those (many) scientists expressing unfavorable opinions of Rasmussens review were forced to await the final publication of their own research before responding. In a direct rebuttal, Fitzgerald et al. (1998) stated:

“The purpose of this review is to provide the careful scrutiny that such controversial conclusions demand. It is our contention that the case for atmospheric Hg contamination in remote areas is stronger than ever, having been advanced by worldwide improvements in analytical methods, sampling techniques, and experimental design over the past decade.”

Fitzgerald et al. (1998) provided point-by-point rebuttal of every argument made by Rasmussen (1994). Regarding deep-ocean venting as a source of Hg, authors stated that open ocean profiles of aqueous Hg

do not reveal a pattern of increasing Hg with depth, as would be expected under the deep-ocean venting hypothesis, suggesting that such a source is not sufficient to overcome the oceanic rate of vertical mixing. With respect to diagenesis of lake sediments, the reviewers point to the fact that within every well dated core reported in the literature, there is a nearly synchronous rise in Hg in sediments, beginning in the early 1900's. Many other observations from the paleolimnological literature reviewed in this volume are used to further make the case for atmospheric deposition. With respect to organic affinity, the authors argue that for all sediment cores analyzed from lakes, while organic content remains stable below the first few centimeters beneath the microzone, Hg is not stable, declining with time to a background concentration. Example after example of erroneous data reported in the older studies cited by Rasmussen are highlighted, including a complete lack of critical dating data. The authors were wise to await publication of the body of their respective research. Indeed, in the 1998 reviews reference list, 63 of 104 studies date 1990 or after. Finally, it is singularly telling that the authorship list of the Fitzgerald et al. review draft submission to *Environmental Science and Technology* included **twenty-two** authors of worldwide repute (D. Engstrom, *pers. comm.*). When asked to pare down their list to 4, the reviews acknowledgments section grew exponentially.

4.0 Current Perspectives in Northeastern Mercury Research:

The job of characterizing Hg cycling in northeastern lakes and lake watersheds is incomplete. The author of this review is familiar with many of the studies and monitoring efforts described below. Unless referenced to a specific publication, information regarding these studies has been acquired by personal communication described projects respective principal investigators.

For approximately the past decade, many northeastern states have developed fish-tissue Hg datasets. These data are analyzed using risk assessment models to develop estimates of allowable fish consumption. More often than not, these efforts are conducted on shoestring budgets, and are discontinuous in nature. Rhode Island has few lakes, and correspondingly little developed fish-tissue contamination data. Vermont and New Hampshire have small fish contaminant datasets (fish from 40+ and 60+ lakes, respectively), collected as cooperative ventures between those states' environmental and fisheries agencies. Massachusetts has a fairly robust contamination dataset, with smallmouth bass as its primary focus.

Connecticut allocated considerable State funds to conduct a comprehensive survey of fish-tissue Hg in Connecticut lakes. The Connecticut data can be considered the most robust fish-tissue Hg database in the Northeast, in that they have the greatest number of lakes with fish-tissue data available.

However, Maine is indeed a northeastern stronghold of Hg research. This comes as no surprise, as Maine has over 1000 'Great Ponds' (10ac). In 1993, the State of Maine, in cooperation with Dr. Terry Haines (Univ. of Maine., USFWS), was awarded a USEPA grant to collect fish from a spatially randomized selection of lakes, using the EPA-EMAP lake selection protocol. This protocol is designed to assure that the lakes from which samples are collected are representative of the population of lakes from which the sample was drawn. Accordingly, the results of standardized surveys in these study lakes can be projected to the whole population of lakes. By collecting select species of fish using this protocol, Maine clearly has developed a very robust dataset for use in risk assessment. This Maine effort also assessed sediment HgT and other in-lake parameters to predict the lake types which would be expected to have elevated Hg in fish. Lacking MeHg values for waters and sediments, and selected water chemistry parameters, this element of the Maine project was not entirely successful.

Present University of Maine investigations by Dr. Haines and others include assessments of, in-lake MeHg and sediment MeHg, paleostratigraphy on select Maine ponds, toxicological assessments of chronic MeHg exposure in forage fish, and the pathways through which MeHg accumulates in bald eagles (*Haliaeetus leucocephalus*). Dr. Haines has a Hg-clean CVAFS laboratory at the Univ. of Maine.

A small group of researchers with a keen interest in the chronic toxicity of MeHg to loons (*Gavia immer*) are currently involved in a variety of multi-co-authored, collaborative projects. Known as the BioDiversity Research Institute, this group, under the leadership of D. Evers and P. Reaman, have successfully elucidated continent-wide variation in the Hg content of loon eggs, blood, and feathers. These observations are tied directly to anthropogenic sources of Hg (Evers et al., 1998). They have also identified significant variation in loon Hg burdens which are attributable to specific in-lake factors including DOC and the 'degree of artificiality' of a waterbody (ie. reservoir or lake). The BioDiversity Research Institute is truly interested in advancing the state of the science regarding Hg and loons (and other piscivorous birds), and work with a great many researchers to accomplish the job.

In Vermont, a pre-existing NADP/NAPAP precipitation station located at the Underhill State Forest has been instrumented by Dr. T. Scherbatskoy (Univ. Of Vermont) to collect Hg samples from air and precipitation since 1992. Research on watershed level processes, including the effects of litterfall and throughfall (Rea et al., 1996), HgT concentrations in precipitation and air (Burke et al., 1995), and stream and groundwater flow (Shanley et al., *in press*), are based at the Underhill site. In conjunction with this research, a limited number of observations regarding HgT and MeHg in Lake Champlain water and biota (plankton) have been measured (Shanley et al., *in press*, M. Watzin, Univ. of Vermont, *pers comm.*). The Underhill station is currently involved in the NESCAUM air and precipitation monitoring network described below. The USGS is also active in measurement of Hg in conjunction with its NAWQA and other activities. Dr. J. Shanley (USGS, Montpelier, VT) is cited in this review as an active collaborator with Dr. Scherbatskoy and others studying the transport of Hg in streamflow. Other USGS activities include assessment of Hg and other trace metals, as well as PCB's, in tributaries to Lake Champlain in Vermont and New York (Coleman and Clark, 1994).

In the Adirondack mountains, Dr C.T. Driscoll (Syracuse Univ.) and Dr. D.R. Engstrom (Univ. of Minnesota) are collaborating to re-core the PIRLA lakes discussed in Lorey and Driscoll (*in review*). Cores for this effort were collected during September, 1998. Results of this investigation will be interesting in that the ca. 1983 cores analyzed by Lorey and Driscoll were just beginning to show the decline in fluxes of Hg to surface sediments. The intervening 15 years should provide sufficient sediment to categorically state whether HgT fluxes to Adirondack lakes are in decline. These results could provide very strong corroboration of the conclusions in Engstrom and Swain (1997), and further rebuttal of Rasmussen (1994), by validating the points raised in Fitzgerald et al. (1998).

With the initiation of the Maine Regional-EMAP (REMAP) study, USEPA-Region 1 became very interested in developing a broad approach to Hg assessment in waters New England-wide. To this end, Region 1 has cooperated with the USEPA Office of Science and Technology to launch a broad inquiry into Hg biogeochemical cycling in New England. Funded under the umbrella of the REMAP program, this coordinated set of projects is aimed at developing New England specific Hg cycling information. The REMAP project has two overall components: air monitoring coordinated by NESCAUM; and a lakes assessment component coordinated by the Vermont Department of Environmental Conservation (VTDEC).

The NESCAUM component has initiated sampling at locations across New England, with air monitoring equipment deployed in strategic locations. These highly sophisticated monitoring stations are measuring HgT and HgD in precipitation, as dry deposition on coarse and fine particulate matter, and as Hg(O). The NESCAUM network went on-line in December of 1997, and is in operation presently.

The VTDEC component (Kamman, 1997; <http://www.anr.state.vt.us/water1.htm>) has four project elements:

- C Assessment of HgT and MeHg, and factors known to mediate methylation and bioaccumulation, in waters and surficial sediments of 90 spatially randomly-selected lakes across Vermont and New Hampshire. Collaborating co-investigators include C.T. Driscoll and the New Hampshire Department of Environmental Services;

- C Assessment of Hg burdens in loons and other piscivorous birds of 90 lakes. BioDiversity Research Institute is primary investigator for this component;

- C Comprehensive paleolimnological assessment of 13 lakes. Collaborating co-investigators include D.R. Engstrom, C.T. Driscoll and New Hampshire Department of Environmental Services;

- C Investigation of bioconcentration factors for multiple trophic compartments (fish, benthos, plankton) on a subset of the study lakes. Collaborating co-investigators include Vermont Department of Fish and Wildlife and New Hampshire Department of Environmental Services.

The REMAP studies bring together the considerable expertise of well-known regional and national scientists, and talented field personnel. These studies interface well with the body of Hg literature as described in this review. Successful completion of the field programs will produce a dataset describing:

- C Gradients in atmospheric deposition of Hg across New England, and correlation of these gradients with gradients in surficial HgT concentrations in VT and NH lakes;

- C Estimates of the methylation potential of the population of lakes 20 acres or greater in size (excluding Lakes Champlain, Memphremagog, Winnepesaukee, Squam, and Connecticut River Reservoirs) across VT and NH;
- C Estimated HgT bioconcentration of up to 4 trophic compartments on a subset of the study lakes (plankton, benthos, fish, piscivorous birds);
- C Detailed estimated of present and historical fluxes of HgT to lakes across VT and NH, including an investigation of flux gradients across the study area as they relate to measured deposition of Hg.

5.0 Conclusions:

The body of literature regarding Hg biogeochemistry in aquatic systems is voluminous. Only recently, by capitalizing on significant advances in analytical technology, have scientists accurately described Hg cycling in lakes. Subsequently, many recent studies specific to north-temperate lakes and lake watersheds have been executed, providing the following broad conclusions.

- C There exist measurable amounts of Hg in precipitation in all geographic areas tested. Measurements thereof have been used to infer fluxes of Hg to broad geographic areas. Variation in Hg in precipitation appears to be driven by proximity to anthropogenic sources. Hg is transported in the air on fine particulate matter, including organic particles (soot).
- C Hg in the landscape has a very strong affinity for organic complexes, and transport through watersheds is mediated primarily by these substances. In more developed areas, Hg associates more strongly with suspended sediments. Hg is known to evade from terrestrial and aqueous surfaces.
- C The toxic form of Hg most commonly found in the environment is MeHg. Biotic and abiotic MeHg production in aquatic systems far outweighs depositional sources. This production is

mediated by dissolved oxygen, pH, sulfate, and DOC. Wetlands and peatlands, and lake sediments, are primary sites of methylation in fresh waters. Photodegradation may provide a significant mechanism for demethylation of Hg.

- C In lakes, MeHg complexes strongly with humic and fulvic acids, and other related ligands. Hg bioaccumulates strongly in lakes which possess these compounds. It has been shown that other trace metals compete with MeHg for binding sites on organic acids and ligands. This competition plays a key role in bioavailability of MeHg.

- C Current fluxes of Hg to lakes, as determined using paleolimnological techniques, are as much as an order of magnitude greater than those prior to the onset of industrialization. Modern inferred fluxes compare well with flux estimates from concurrent mass-balance studies, supporting the use of paleolimnological techniques as a valid method of reconstructing historical Hg deposition.

- C The highly technical nature of measuring and tracking Hg through its biogeochemical cycles results in expensive and difficult research projects. Controversy has grown over the use and comparison of older research with modern research.

Research into Hg biogeochemical cycling in the northeastern United States is on-going, and there exist gaps in the current knowledge. Fertile grounds for additional research are manyfold. Our understanding of the mechanisms behind methylation would benefit from *in-situ*, as opposed to benchtop experiments, like those executed by Regnell. The mechanisms behind competition between MeHg and other trace metals for organic binding sites have been explored only by Driscoll and his associates. Well designed *in-situ* experiments using labeled Hg could permit an evaluation of biogeochemical and trophic-level interactions in lakes, yielding actual biomagnification estimates. A deeper understanding of these mechanisms is critical to understanding bioaccumulation of MeHg in fish. Such research would require the use of limnocorral or whole-lake manipulation approaches, and could only be conducted in an area where such an environmentally invasive approach would be acceptable. A more environmentally-friendly approach could employ stable isotopes of Hg to assess biomagnification, but such methods are as of yet

undeveloped. Finally, continued paleolimnological investigations are critical, as these will permit evaluation of the efficacy of Hg emission controls.

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