MERCURY POLLUTION
Integration and Synthesis

Edited by
Carl J. Watras, Ph.D.
Bureau of Research
Wisconsin Department of Natural Resources
Madison, Wisconsin
&
Center for Limnology
University of Wisconsin-Madison
Trout Lake Station
Boulder Junction, Wisconsin
and
John W. Huckabee, Ph.D.
Electric Power Research Institute
Palo Alto, California

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Sources and Fates of Mercury and Methylmercury in Wisconsin Lakes


Abstract: The mercury cycle in seven northern Wisconsin seepage lakes was characterized by high atmospheric influx, removal by sedimentation and evasive efflux, and by in-lake transformation of Hg to biologically sequestered methyl-Hg species. Direct depositional Hg loading from the atmosphere to lakes was roughly 10 µg/m²/year, with rain and snow the principal delivery vectors. Annual atmospheric Hg deposition exceeded estimated fish bioaccumulation by a factor of roughly 10. The atmospheric Hg influx was roughly balanced by losses to sediments and the return of volatile HgO to the atmosphere. The relative importance of sedimentation and gaseous evasion as Hg loss terms varied from lake to lake, with sedimentation/evasion ratios ranging from 9:1 to 1:1 in the seven lakes studied. Residence times for Hg varied from roughly 125 to 300 days in these lakes.

Methyl-Hg in these lakes also had an atmospheric source, estimated to be roughly 1% of the total Hg inputs. Although the direct atmospheric deposition and sediment accumulation of methyl-Hg roughly balanced, the atmospheric influx of
methyl-Hg was much lower than annual rates of methyl-Hg bioaccumulation. Unless the recycling efficiency of methyl-Hg was extraordinarily high, in situ production was an important source of methyl-Hg species. Most of the methyl-Hg in these lakes was stored in fish tissue. Assuming fish production of 30%/year, the annual bioaccumulation of methyl-Hg exceeded sediment accumulation by a factor of 6 to 7. No dimethyl-Hg has been observed in any Wisconsin lake.

The distribution of Hg species in the study lakes was characterized by very dilute pools that varied seasonally and spatially. Waterborne Hg species had concentrations in the picomolar to femtomolar range, with parts per million to parts per billion concentrations in sediment and organisms. Average waterborne Hg and methyl-Hg concentrations correlated negatively with lake water pH and positively with DOC. Seasonal cycles involved decreasing concentrations under ice cover, followed by build-up during summer. Epilimnetic concentrations ranged from 1 to 3 ng/L Hg and 0.05 to 0.5 ng/L methyl-Hg. Higher mercury concentrations were observed at depth in stratified lakes (Hg >45 ng/L and methyl-Hg >10 ng/L) and Hg maxima were observed near microbial layers in the water column. In anoxic, sulfidic plankton layers, >50% of the Hg may be in the methyl-Hg form (vs. 5 to 15% in the epilimnion).

Methyl-Hg was biomagnified in the foodchain of Little Rock Lake, but there was evidence that nonmethyl-Hg species became more dilute at higher trophic levels. The biomagnification factor for methyl-Hg increased by threefold for each trophic level, approaching 10^3 in fish. The Hg in fish was almost all methylated (>95%), while the Hg in sediments was primarily nonmethyl-Hg (>97%). Since most methyl-Hg in the study lakes appeared to be sequestered by fish biomass, fish contamination could be significantly enhanced by small increases in net rates of methyl-Hg production, recycling, or loading.

I. INTRODUCTION

Reports of Hg-contaminated freshwater fisheries in North America have steadily increased during the past decade (Figure 1). While the issuance of fish consumption advisories reflects both awareness and contamination, there are concerns about disruption of the natural Hg cycle on local, regional, and global scales. Unfortunately, risk assessment, source attribution, and remediation have been hindered by a lack of reliable data on Hg in aquatic environments. Laboratory contamination has compromised much of the data on waterborne Hg.1-4

With new analytical techniques5,6 and the use of "clean" sampling protocols, a more reliable and comprehensive database on environmental Hg is emerging. Mass balances for lakes and watersheds in Wisconsin, Canada, and Sweden indicate that atmospheric deposition is the principal source of Hg.1,2,8 In Wisconsin, the direct deposition of airborne Hg to precipitation-dominated lakes is sufficient to account for annual sediment and fish accumulation.1-9 In Swedish and Canadian drainage lakes, watershed Hg inputs are clearly important,7,10 but ultimately the principal Hg source for remote freshwaters in nonmercury regions appears to be atmospheric deposition, either directly to the water surface or indirectly via export from atmospherically enriched, shallow soil horizons.11-13

Although waterborne mercury concentrations in unpolluted surface waters typically range from about 2 to 20 pM (0.5 to 4 ng/L), mercury is biomagnified to such a high degree that contaminated fish stocks occur even in very remote, northern waters.8,14,15 While geographical gradients in Scandinavia indicate a link between Hg depositional rates and mercury in fish,14 factors such as pH, DOC, and trophic structure further influence bioaccumulation.14,16 Since methyl-Hg seems to biomagnify most strongly in aquatic foodchains, and since almost all of the Hg in fish is methylated,15,16 such mitigating factors could operate by regulating net rates of methyl-Hg formation in the ecosystem.18,19
MERCURY AND METHYLMERCURY IN WISCONSIN LAKES

Figure 1  Number of fish consumption advisories issued for inland lakes in the Great Lakes region of North America during the past decade (1980–1990). Although Michigan issued a blanket advisory during 1989 restricting consumption of fish in all 11,000 lakes within the state, this advisory is counted only once (*). Data obtained from: Jim Amrhein, Wisconsin DNR, Madison; Charles Cox, Ontario Min. Environ., Toronto; Ed Swain, Minnesota PCA, St. Paul; and John Filipus, Michigan DPH, Lansing.

To further our understanding of the mercury cycle in freshwaters and provide a framework for ongoing process-oriented studies, we present here the results of investigations on seven Wisconsin lakes which span gradients of pH and \( \sigma \). We report the concentration and distribution of Hg species in air, precipitation, water, sediments, and biota over seasonal and spatial scales, and we construct comparative mass balances for these lakes. We describe relationships between waterborne Hg species and water quality parameters and we examine differences between lakes in input:output budgets and bioaccumulation patterns. A conceptual model of Hg cycling in Wisconsin lakes is presented. The results of a dynamic modeling study are presented in another chapter in this book.\(^{21}\)

II. METHODS

A. STUDY SITES

Seven lakes in north-central Wisconsin (circa 46°N and 89°W) were sampled routinely between August 1988 and January 1992. This region of Wisconsin is sparsely populated (6.6 people/km\(^2\)) and largely covered with second-growth Great Lakes forest and wetlands. Many of the small lakes in this area can be considered remote from direct anthropogenic influence, with no dwellings or other permanent structures on the shorelines. The study lakes were chosen to span gradients of pH and DOC (Table 1), variables which purportedly influence Hg bioaccumulation.\(^{8,14,16}\) They are all seepage lakes (no permanent surface water inflow or outflow), and most of the lakes were hydrologically mounded above groundwater levels during the study period (except for Pallette Lake and, perhaps, Russett Lake\(^{42}\)). Being isolated from terrestrial watersheds, the lakes were considered model ecosystems for examining atmospheric interactions and in-lake processes.
MERCURY POLLUTION: INTEGRATION AND SYNTHESIS

Table 1 Characteristics of the seven Wisconsin study lakes.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Area (ha)</th>
<th>Mean depth (m)</th>
<th>pH</th>
<th>DOC (mg/L)</th>
<th>SPMa (mg/L)</th>
<th>SO4²⁻ (µequiv/L)</th>
<th>Ca²⁺ (µequiv/L)</th>
<th>Cl⁻ (µequiv/L)</th>
<th>Chl a (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRT</td>
<td>9.8</td>
<td>3.8</td>
<td>4.9</td>
<td>(0.15)</td>
<td>(0.33)</td>
<td>(0.39)</td>
<td>(24.0)</td>
<td>(8.1)</td>
<td>(1.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.5)</td>
<td>(0.33)</td>
<td></td>
<td>(8.1)</td>
<td>(1.8)</td>
<td>(1.8)</td>
</tr>
<tr>
<td>LRR</td>
<td>8.1</td>
<td>3.1</td>
<td>6.0</td>
<td>(0.30)</td>
<td>(0.50)</td>
<td>(0.45)</td>
<td>(7.1)</td>
<td>(4.6)</td>
<td>(0.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.3)</td>
<td>(0.50)</td>
<td></td>
<td>(7.1)</td>
<td>(4.6)</td>
<td>(1.3)</td>
</tr>
<tr>
<td>VAN</td>
<td>43.6</td>
<td>4.7</td>
<td>6.3</td>
<td>(0.37)</td>
<td>(0.65)</td>
<td>(1.00)</td>
<td>(4.8)</td>
<td>(4.6)</td>
<td>(0.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(4.3)</td>
<td>(0.65)</td>
<td></td>
<td>(4.8)</td>
<td>(4.6)</td>
<td>(1.2)</td>
</tr>
<tr>
<td>PAL</td>
<td>70.0</td>
<td>9.6</td>
<td>7.2</td>
<td>(0.22)</td>
<td>(0.98)</td>
<td>(0.37)</td>
<td>(8.5)</td>
<td>(4.2)</td>
<td>(0.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(5.4)</td>
<td>(0.98)</td>
<td></td>
<td>(8.5)</td>
<td>(4.2)</td>
<td>(0.8)</td>
</tr>
<tr>
<td>MAX</td>
<td>9.2</td>
<td>2.9</td>
<td>5.4</td>
<td>(0.22)</td>
<td>(0.98)</td>
<td>(0.37)</td>
<td>(3.5)</td>
<td>(1.0)</td>
<td>(1.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3.3)</td>
<td>(0.98)</td>
<td></td>
<td>(3.5)</td>
<td>(1.0)</td>
<td>(1.0)</td>
</tr>
<tr>
<td>CRY</td>
<td>36.0</td>
<td>10.4</td>
<td>6.3</td>
<td>(0.20)</td>
<td>(0.20)</td>
<td>(0.38)</td>
<td>(5.2)</td>
<td>(5.8)</td>
<td>(0.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.8)</td>
<td>(0.20)</td>
<td></td>
<td>(5.2)</td>
<td>(5.8)</td>
<td>(0.4)</td>
</tr>
<tr>
<td>RUS</td>
<td>19.0</td>
<td>3.9</td>
<td>5.8</td>
<td>(0.26)</td>
<td>(0.20)</td>
<td>(0.38)</td>
<td>(5.2)</td>
<td>(5.8)</td>
<td>(0.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(6.8)</td>
<td>(0.20)</td>
<td></td>
<td>(5.2)</td>
<td>(5.8)</td>
<td>(0.4)</td>
</tr>
</tbody>
</table>

a LRT (Little Rock Lake—treatment basin); LRR (Little Rock Lake—Reference basin); VAN (Vandercook Lake); PAL (Pullette Lake); MAX (Max Lake); CRY (Crystal Lake); RUS (Russell Lake).
b SPM: Suspended particulate matter >0.8 µM.

Note: Water quality data are epilimnetic averages for the study period. Standard deviations are in parenthesis.

B. WATERBORNE Hg SPECIES

Water column samples were collected at roughly 4- to 8-week intervals, targeting events such as peak stratification, overturn, and ice-out. Trace-metal clean protocols based on oceanographic techniques were adapted for sampling mercury in small lakes. Technicians wore lint-free suits, hoods and shoulder-length plastic gloves to reduce the possibility of particulate Hg contamination. Rigorously acid-cleaned sample bottles and equipment (soaked 12 h in hot concentrated HNO₃; boiled 12 h in Hg-free water), sealed in a double layer of plastic bags, were stored in a clean laboratory and removed only for sample collection and transport. Airborne Hg concentrations in the clean lab were about 2 ng/m³.

At the sampling site, field personnel positioned themselves so that wind could not transport contaminants from their equipment or clothing into samples. From a thoroughly cleaned nonmetallic boat or a hole in the ice, multiple samples were collected through the water column at the region of maximum depth in each lake. Typically, three samples were collected from each depth. A peristaltic pump threaded with a 15-cm length of silicone tubing was used to pull water through ½” O.D. Teflon™ tubing held vertical by a weighed Teflon™ torpedo. Whole water samples were dispensed directly into 500 mL Teflon™ bottles. Filtered samples were pumped through preashed (12 h at 550°C) 47 mm diameter quartz fiber filters (Whatman #1851; nominal pore size 0.8 M) housed in Teflon™ holders. The caps of all sample bottles were tightly wrenches after collection to prevent Hg influx during storage.

Filtered and unfiltered aliquots were collected for total Hg, total particulate Hg, total dissolved Hg, total methyl-Hg, particulate methyl-Hg, and dissolved methyl-Hg determinations. Unfiltered samples for Hg determinations were preserved with 10 mL 5 N HCl or HNO₃ at the time of collection. Filtered water for methyl-Hg determinations and seston samples (on filters) were collected and preserved on filters. Frozen samples were preserved on filters until further analysis.

Recently, we have used diatomaceous earth (DE) filters and purged the filters with inert gas (N₂) directly in the field to reduce contamination.

Analytical protocols were performed by analysts using the standard methods of the International Atomic Energy Agency (IAEA) and the National Institute of Standards and Technology (NIST) reference materials.

MERCURY AND MERCURY ANALOGUES

Table 2 Detection limits for mercury species.

<table>
<thead>
<tr>
<th>Mercury species</th>
<th>Detection limits (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>0.1</td>
</tr>
<tr>
<td>Elemental total</td>
<td>0.1</td>
</tr>
<tr>
<td>Particulate total</td>
<td>0.1</td>
</tr>
<tr>
<td>Total methyl</td>
<td>0.1</td>
</tr>
<tr>
<td>Dimethyl</td>
<td>0.1</td>
</tr>
<tr>
<td>Particulate methyl</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Note: Detection limits were determined by the analytical method used.

For total Hg anodic stripping voltammetry (ASV) was used.

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For total Hg anodic stripping voltammetry (ASV) was used.
MERCURY AND METHYL MERCURY IN WISCONSIN LAKES

<table>
<thead>
<tr>
<th>Mercury species</th>
<th>Sample size (mL)</th>
<th>Detection limit (ng/L)</th>
<th>Typical pristine oligotrophic waters (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>100</td>
<td>0.15</td>
<td>1.0</td>
</tr>
<tr>
<td>Elemental</td>
<td>4000</td>
<td>0.006</td>
<td>0.02</td>
</tr>
<tr>
<td>Particulate total</td>
<td>1000</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>Total methyl</td>
<td>50</td>
<td>0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>Dimethyl</td>
<td>4000</td>
<td>0.0006</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Particulate methyl</td>
<td>1000</td>
<td>0.005</td>
<td>0.05</td>
</tr>
</tbody>
</table>

samples (on filters in their Teflon® holders) were preserved by freezing within 6 h of collection. Frozen samples were shipped overnight on dry ice to the analytical laboratory. Approximately 10% of the samples collected were replicates.

Recently, we have sampled using a submersible, nonmetallic pump attached to rigorously cleaned, Silastic® tubing. Samples were collected from depth with flow rates of 5 to 6 L/min directly into clean Teflon® bottles. Filtration was performed in the clean laboratory shortly after collection, using cleaned and blanked disposable filtration units (0.45 μm).23

Analytical protocols for waterborne Hg species followed Bloom and Fitzgerald6 and Bloom.6 All sample handling and analyses were conducted in a dedicated clean laboratory. Typical sample sizes and detection limits are summarized in Table 2. Absolute detection limits for all Hg species were less than 1 pg Hg.

For total Hg analysis, 100 mL aliquots of lakewater were wet-oxidized using BrCl. Following oxidation, samples were prereduced with NH₂OH/HCl, then further reduced with SnCl₂ and purged from solution with nitrogen onto gold traps. Trapped Hg was thermally desorbed into inert carrier gas for analysis by cold-vapor atomic fluorescence spectroscopy (CVAFS) detection. Particulate and dissolved Hg species were defined operationally. Particulate (total) mercury was defined as that fraction recovered after chemical digestion of the in-line quartz fiber filters, followed by the total mercury protocol described above. Dissolved Hg was computed as the difference between total and particulate Hg.

Methyl-Hg determinations were based on the cryogenic GC separation of volatile ethyl analogues.6 Dissolved methyl-Hg was determined by extracting filtered samples from an HCI/KCl matrix into CH₂Cl₂, then back-extracting into pure water by solvent evaporation. The aqueous phase was ethylated with NaB(C₂H₅)₄ and the volatile ethyl analogue was separated from other species using cryogenic GC separation with CVAFS detection. Particulate methyl-Hg was defined as that fraction recovered after chemical digestion (KOH/MeOH) of the in-line quartz fiber filter, followed by the dissolved methyl-Hg protocol. Total methyl-Hg was computed as the sum of dissolved and particulate species.

With the adoption of in-lab filtration protocols mentioned above, the dissolved/particulate fractionation of Hg and alkyl-Hg species are determined in a slightly different way (particulate = total − dissolved).23

Dissolved gaseous Hg (DGM) determinations followed Vandal et al.24 Water samples were collected using an 8-L Teflon®-coated Go-Flo bottle (General Oceanics) which had been thoroughly cleaned and blanked in the laboratory. The sampling protocol was based on Gill and Fitzgerald.23 The bottle was lowered on a clean Kevlar® line by hand and triggered at depth with a clean Teflon® messenger. Analysis was made in a clean laboratory within 3 h of collection. DGM measurements were made by sparging a 4 L sample with Hg-free argon and trapping on either Au or Carbortrap® columns. Detection limits using atomic fluorescence detection were DGM, 1 pg/L; dimethyl-Hg, 0.6 pg/L.24
C. ATMOSPHERIC Hg SPECIES

Atmospheric gaseous and particulate Hg samples were collected routinely from a sampling platform 2 m above the lake surface. Total gaseous Hg (TGM) was trapped on gold columns, while particulate samples were collected using Carbotrap columns. Particulate Hg (PM) was collected using quartz wool plugs. Sample volumes for TGM and speciation determinations were between 0.5 and 2 m³, while larger volumes were needed for particulate measurements (2 to 10 m³). Detection limits were TGM, 0.15 ng/m³; MMHg and PM, 0.005 ng/m³.

Rain and snow samples were collected on an event basis. The rain collector was a glass or Teflon® funnel deployed 2 m above the surface of one of the study lakes. The Teflon® funnel was housed in an acrylic box with a removable lid. The funnel and housing were constructed so that rain entering the funnel contacted only rigorously cleaned Teflon® parts. Prior to each collection, the funnel was rinsed and blanked with clean, acidified water. The funnel was open to the atmosphere only during the rinse and the rain event. Snow samples were collected in clean, 1 L Teflon® jars by scooping snow from the lake surface <12 h after a snowfall. The collector, wearing long plastic gloves, moved forward into the wind scooping the snow from areas free of visible terrestrial inputs (i.e., twigs, needles, etc.). The jars were wrenched tight, double bagged, and stored frozen until analysis in a clean laboratory.

Analytical techniques were similar to those used for lake water samples.

D. BIOTIC Hg SPECIES

Zooplankton samples were collected using a nonmetallic plankton net and then hand picked by species for analysis. After each vertical tow, the net contents were backwashed with surface lakewater into Hg-clean, Teflon® jars which were hermetically sealed and double-bagged in clean, zip-locked plastic bags. Clean protocols were observed throughout sample collection and handling. Within 1 h of collection, individual zooplankton of a given size-class and species were transferred live into small Hg-free, Teflon® vials with rigorously cleaned pipets. Groups of 5 to 20 individuals were immediately frozen in each vial in a small drop of lakewater. Procedural blanks consisted of just the frozen drop of lakewater without zooplankton. For HgT determinations, the zooplankton were first digested in a 200-µL aliquot of 7:2 HNO₃/H₂SO₄, at 70°C for 2 h, and then the entire sample was reduced with SnCl₂ and preconcentrated using dual gold amalgamation. For methyl-Hg determinations, zooplankton were digested in 200 µL of 25% KOH/methanol for 2 h at 70°C followed by aqueous phase ethylation, cryogenic GC separation, and CVAFS detection.

Fish (1-year-old yellow perch, Perca flavescens) were collected using fyke nets or minnow traps. Whole fish were then frozen, lyophilized to constant weight, and ground to a fine powder. Subsamples were digested for 14 h at 220°C in 12 mL of 36% H₂SO₄ and 3 mL of 16 N HNO₃ and analyzed for total Hg by cold vapor AAS following SnCl₂ reduction (modified from Wiener et al9). Precautions were taken to prevent Hg contamination during storage, preparation, and analysis of samples. The accuracy of Hg determinations was verified by analysis of standard reference materials, spiked samples, replicate samples, and procedural blanks with each batch of fish samples. Method limits of detection were 4 ng and limits of quantification were 13 ng for fish. Protocols for determining methyl-Hg in fish are described by Bloom.

E. SEDIMENT Hg

For total Hg determinations in surficial sediment, samples were collected using a diver-operated PVC core sampler (22 cm I.D.) designed to collect the top 5 cm of sediment with minimal disturbance and compaction. Analytical methods for determining total Hg in surficial sediments are described by Rada et al.27 Samples for methyl-Hg analysis were collected from the top 1 cm of profundal cores from Little Rock Lake. Fresh (wet) sediment was
AND SYNTHESIS

ly from a sampling approach on gold columns. Particulate Hg in MMHg and speciation (for particulate Hg in PM, collector was a glass lakes. The Teflon and housing were aned Teflon parts. acidified water. The rent. Snow samples are surface <12 h ward into the wind needles, etc.). The n a clean laboratory.

 added back washed with scaled and double-throughout sample on of a given size- als with rigorously each vial in a small f lakewat without in a 200-μL aliquot reduced with SnCl₂ eterniations, zoo- 70°C followed by on.

To nets or minnow bags ground to a fine 7 H₂SO₄ and 3 mL ng SnCl₂ reduction eterniation during nations was verified ples, and procedural 4 ng and limits of in fish are described

et using a diver-

MERCURY AND METHYL MERCURY IN WISCONSIN LAKES

Table 3  Mean epilimnetic concentrations of Hg species in the seven Wisconsin study lakes.

<table>
<thead>
<tr>
<th>Lake</th>
<th>HgT (ng/L)</th>
<th>Methyl-Hg (ng/L)</th>
<th>Dimethyl-Hg (pg/L)</th>
<th>Hgθ (pg/L)</th>
<th>%S*</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRT</td>
<td>1.11</td>
<td>0.091</td>
<td>ND</td>
<td>17</td>
<td>300</td>
</tr>
<tr>
<td>LRR</td>
<td>1.13</td>
<td>0.075</td>
<td>ND</td>
<td>27</td>
<td>500</td>
</tr>
<tr>
<td>VAN</td>
<td>0.90</td>
<td>0.088</td>
<td>ND</td>
<td>56</td>
<td>1490</td>
</tr>
<tr>
<td>PAL</td>
<td>0.79</td>
<td>0.083</td>
<td>ND</td>
<td>128</td>
<td>3380</td>
</tr>
<tr>
<td>MAX</td>
<td>1.35</td>
<td>0.261</td>
<td>ND</td>
<td>36</td>
<td>950</td>
</tr>
<tr>
<td>CRY</td>
<td>0.72</td>
<td>0.046</td>
<td>ND</td>
<td>157</td>
<td>4100</td>
</tr>
<tr>
<td>RUS</td>
<td>2.10</td>
<td>0.327</td>
<td>ND</td>
<td>34</td>
<td>2250</td>
</tr>
</tbody>
</table>

* %S = Saturation of volatile Hgθ with respect to atmospheric concentrations.
* ND: Not detected, <0.6 pg/L.

leached with 25% KOH in methanol and the leachate was analyzed for methyl-Hg following protocols described above for biotic samples.

II. RESULTS AND DISCUSSION

A. WATERBORNE Hg: VARIABILITY BETWEEN LAKES

Typical epilimnetic concentrations of the Hg species measured in these lakes are shown on Table 3. Annual average [Hg] in all the study lakes was very low (picomolar or parts per trillion) and tended to vary within a narrow range (Ca. 1 to 3 ng/L). Methyl-Hg concentrations were lower by an order of magnitude (ranging from roughly 0.05 to 0.3 ng/L). No alkyl-Hg species other than monomethylmercury have been observed in any of the lakes at a detection limit of about 3 fm. Note that surface waters in all the lakes were supersaturated with respect to Hgθ during summer.

The mercury concentrations observed in these lakes are similar to those reported for open ocean sites and much lower than most of the freshwater data reported in North America before 1989. Clean sampling and novel analytical protocols are primarily responsible for the differences between the old and new freshwater data. Sample contamination has been shown to account for errors of up to 50% in historical data. Even in recent studies, waterborne Hg detection limits often exceed the concentrations typical of many remote northern lakes.

Both [Hg] and [methyl-Hg] tended to increase in the study lakes with increases in both [H⁺] and DOC (Figures 2 and 3). However, because the number of lakes in this study was small, it is not possible to quantify the nature of the pH and DOC dependencies with reasonable confidence.

Most of the waterborne Hg and methyl-Hg tended to be in the dissolved phase (Figures 2 and 3). Although the dissolved/particulate fractionation was highly variable seasonally and spatially, 60 to 90% of the Hg and 40 to 70% of the methyl-Hg was in the operationally defined dissolved pool (>0.2 μm). The average mass of suspended particulate matter (SPM) during midsummer varied from about 0.5 to 3.0 mg/L between lakes. Most of the SPM in these lakes was living and dead plankton, rather than mineralogical particulate.

B. WATERBORNE Hg: SEASONAL VARIABILITY

Although average waterborne [Hg] and [methyl-Hg] varied within a rather narrow annual range, there were detectable seasonal changes. A 2-year time-series for Little Rock lake shows that waterborne Hg concentrations tended to be high during summer and low during winter
Figure 2  Waterborne Hg or methyl-Hg relative to pH in lakes with similar DOC. Data are annual average, volume-weighted concentrations of total Hg (HgT), dissolved Hg (HgD), particulate Hg (HgP), total methyl-Hg (MMHgT), dissolved methyl-Hg (MMHgD), and particulate methyl-Hg (MMHgP). Error bars indicate 2 SD.

(Figure 4). Winter declines in waterborne [Hg] are consistent with the observation that atmospheric inputs are the major source of Hg to these lakes. Under ice cover the lakes are effectively sealed from this external source. During summer, both waterborne [Hg] and [methyl-Hg] tended to increase, reflecting the cumulative effects of increased atmospheric Hg deposition and, perhaps, increased methylation activity due to warmer temperatures.

Following autumn mixis, declines in [Hg] and [methyl-Hg] corresponded to the fall plankton bloom and a period of high sedimentation. During winter, we have observed the gradual decay of an Hg-enriched layer near the sediment surface. We hypothesize that this decay results from the gradual settling of Hg-rich particulate into profundal sediments.

C. WATERBORNE Hg: SPATIAL VARIABILITY
During periods when the watercolumn was well mixed, [Hg] and [methyl-Hg] were relatively uniform from the lake surface to the sediments. However, during stratification there were striking discontinuities in the distribution of Hg species (Figure 5). [Hg] maxima were observed in the metalimnion and hypolimnion—regions where we also observed the development of deep plankton layers (Figure 5A). In these deep plankton layers, most of the Hg was particulate (ca. 80%) and Hg concentrations were up to 10 times higher than those observed in the epilimnion approaching 100 ppm. We hypothesize that upper waters and microbial activity pended Hg burden.

In anoxic/sulfidic environments, or through Partitioning data Little Rock Lake, deepest plankton a function of high
MERCURY AND METHYLMERCURY IN WISCONSIN LAKES

Figure 3 Waterborne Hg and methyl-Hg relative to DOC in lakes of similar pH. Data are annual average, volume-weighted concentrations of total Hg (HgT), dissolved Hg (HgD), particulate Hg (HgP), total methyl-Hg (MMHgT), dissolved methyl-Hg (MMHgD), and particulate methyl-Hg (MMHgP). Error bars indicate 2 SD.

in the epilimnion. In anoxic hypolimnetic plankton layers, [methyl-Hg] increased to levels approaching 100 times those in epilimnetic waters. Similar mercury profiles have been observed in all of the stratified lakes studied, but the absolute [Hg] and [methyl-Hg] associated with plankton layers varied widely between lakes (compare Figures 5A and 5B).

The origin of Hg maxima in the watercolumn of stratified lakes remains uncertain, but their development suggests that newly settled particulate may be an important Hg source. We hypothesize that atmospherically derived Hg may be scavenged by biogenic particles in upper waters and delivered to depth on settling particulate. Upon reaching layers of high microbial activity, decomposition or dissolution reactions may transfer or transform the suspended Hg burden.

In anoxic/sulfidic regions of the watercolumn, complexation with dissolved sulfide, polysulfide, or thiols may increase the dissolved Hg pools relative to the particulate fractions. Partitioning data tend to support this hypothesis. For example, during peak stratification in Little Rock Lake, partition coefficients for Hg and methyl-Hg decrease with depth below the deepest plankton layers (Figure 6). Lowered Kd at depth in Little Rock Lake could also be a function of high concentrations of particulate matter in the 8.5 to 9.5 m depth range.
Figure 4  Seasonal changes in the concentration of waterborne mercury species in the treatment basin of Little Rock Lake. Data are volume-weighted, whole-basin averages.

D. MASS BALANCE FOR TOTAL Hg IN LITTLE ROCK LAKE
The mass balance for mercury in Little Rock Lake (Figure 7a) has evolved as studies progressed from 1988 to 1992.10,26 During this period, airborne Hg was the dominant source to the lake, and sediments were the dominant sink. Inputs from the atmosphere were roughly balanced by sediment accumulation. Data from sediment traps indicated recycling of Hg within the hypolimnion.21

In the atmosphere above the lake, the annual average concentrations of total gaseous and particulate mercury (TGM, TPM) were 1.6 ± 0.4 ng/m³ and 0.02 ± 0.02 ng/m³, respectively.
Figure 5  Vertical distribution of waterborne mercury species in Pallette Lake (A, B) and the treatment basin of Little Rock Lake (C, D).

Figure 6  Particle-water partition coefficients for Hg and methyl-Hg in Little Rock Lake. Kd = log (Cp/Cw), where Cp and Cw are particulate and dissolved concentrations, respectively. CP >0.8 μm (dry wt. basis).
Atmospheric TGM above Little Rock Lake was similar to values reported for air over the North Central Pacific Ocean at similar latitude (TGM: 1.7 ± 0.15 ng/m²), although slightly lower and less variable than TGM values reported for Scandinavia (TGM: 2.5 ng/m²). Thus, presently available data indicate that TGM is rather uniformly distributed for a given latitude in the Northern Hemisphere. This uniformity is consistent with the estimated atmospheric residence time of Hg (6 to 24 months).  

However, for TPM there are comparatively large differences between continental and oceanic concentrations characterized by decreasing TPM concentrations along the gradient from urbanized continental, to remote continental, to remote oceanic regions. This gradient in TPM indicates a continental source, perhaps associated with anthropogenic activity. The gross atmospheric influx of Hg to lakes in this region was estimated to be 10.3 ± 5.0 µg/m²/year: roughly 70% wet Hg deposition and 30% dry Hg deposition. The average [Hg] in rain and snow was 10.5 ± 4.8 ng/L and 6.0 ± 0.9 ng/L, respectively. A scavenging ratio of 437 suggests that Hg in wet deposition was principally derived from the scavenging of particulate Hg in the atmosphere. Calculated leaf-fall Hg inputs to the lake were negligible, due to low mercury concentrations in leaves collected in autumn near the time of abscission (Table 4). Given leaf-litter inputs of 14 g/m²/year, the annual leaf-fall contribution would be 0.6 µg/m²/year Hg and 0.003 µg/m²/year methyl-Hg.

Surface waters of all of the study lakes were supersaturated with TGM during the ice-free season, and this results in an evasive back-flux to the atmosphere. Assuming an average windspeed of 2.5 m/s (LTER database, UW-Trout Lake Station), we calculate an annual Hg efflux of 0.7 ± 0.3 µg/m²/year for Little Rock Lake. The net atmospheric flux of Hg to the lake, then, is about 9.6 µg/m²/year.

Removal of Hg from the watercolumn of Little Rock Lake occurred mainly via sedimentation. Losses to groundwater were calculated at 0.3 µg/m²/year, assuming that groundwater recharge constituted about 47% of the hydrologic losses from the lake and that [Hg] in out-seeping water was the same as lakewater [Hg] (i.e., 1 ng/L). Combined with gaseous evasion (0.7 µg/m²/year) total Hg losses to the airshed and watershed constitute roughly 1 µg/m²/year. The rest (9.3 µg/m²/year, calculated by difference) was carried to sediments on settling particulate.

Our Hg mass balance for Little Rock Lake, then, indicates that net atmospheric inputs to the lake were roughly 1 g Hg annually and that most of this atmosphericy derived Hg (roughly 0.9 g Hg) accumulated in sediments. This estimate of annual Hg accumulation in sediments agrees well with the measured sediment Hg burden (1.1 g Hg in the top 1 mm sediment, Figure 7) calculated from data in Rada et al. A sediment accumulation rate of about 1 mm/year seems reasonable for lakes of this type in the region. Gaseous Hg evasion and groundwater recharge constitute small Hg losses for this lake (roughly 0.1 g/year), but as described below, the relative importance of evasion in the other study lakes varies with pH and DOC.

### Table 4. Mercury in leaves falling into Little Rock Lake.

<table>
<thead>
<tr>
<th>Leaf type</th>
<th>Total Hg</th>
<th>Methyl-Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red maple</td>
<td>0.046</td>
<td>0.00025</td>
</tr>
<tr>
<td>Red oak</td>
<td>0.034</td>
<td>0.00035</td>
</tr>
<tr>
<td>White pine</td>
<td>0.048</td>
<td>0.00007</td>
</tr>
<tr>
<td>Paper birch</td>
<td>0.040</td>
<td>0.00019</td>
</tr>
<tr>
<td>Bigtooth aspen</td>
<td>0.048</td>
<td>0.00020</td>
</tr>
</tbody>
</table>
Figure 7  Mass balances for Hg and methyl-Hg in the treatment basin of Little Rock Lake. All concentrations are in ng/L or ng/g wet weight. Error terms are ±1 SD. Annual sediment Hg accumulation calculated by difference between measured inputs and outputs. Data for bulk sediment Hg calculated from Reference 27 and profundal porewater Hg from Reference 40. Annual methyl-Hg accumulation in sediments is based on the observation that methyl-Hg constituted roughly 1% of HgT in surficial profundal sediment. Dashed line represents the O/A boundary.
Biotic Hg pools in Little Rock Lake were estimated as the product of biomass \( X \) \([\text{Hg}]\). Phytoplankton biomass was assumed equal to suspended seston, and thus included both living and dead cells. Seston mass was measured directly on each sampling date by filtration and weighing. The biomass of crustacean zooplankton was estimated from a vertical series of collections using a Schindler-Patalis trap.\(^{45}\) Fish biomass was estimated from mark and recapture studies.\(^{45}\)

The data for biotic Hg indicated that Hg concentrations increased along the continuum from phytoplankton (seston) to zooplankton to young fish by a factor of two to three per trophic level (Figure 7a). Given the biomass distribution for this lake, the pool of Hg in fish (roughly 0.2 g) was about double that in plankton (0.11 g). The greatest change in Hg concentration occurred between the dissolved phase (roughly 0.9 ng/kg) and the sestonic phase (25 µg/kg, wet weight)—a factor of roughly \(3 \times 10^2\). The largest Hg reservoir in Little Rock Lake was the sediment.

### E. COMPARATIVE Hg MASS BALANCES FOR THE MTL LAKES

Comparative input:output budgets for Hg (Figure 8) were constructed for all seven study lakes using the following criteria:

1. Local atmospheric Hg deposition = 10.3 µg/m\(^2\)/year
2. Ground water discharge = zero, except for Paitene Lake
3. Ground water recharge varied from roughly 18–50% of hydrologic outputs
4. Hg evaporation was a linear function of elemental [Hg] in surface water, extrapolated from the annual rates determined for Little Rock Lake
5. Hg sedimentation was estimated by difference: \[ S = (\text{Hg deposition} + \text{groundwater Hg input}) - \text{(groundwater Hg output + Hg evasion)} \]

Note that groundwater inputs to Russell Lake may be non-zero.\(^{42}\)

The resulting mass balances indicate that direct atmospheric deposition was the dominant Hg input for all the study lakes. However, the relative importance of sedimentation and volatile evasion as Hg loss terms varied from lake to lake. Sedimentation tended to dominate losses in lakes with high [H\(^+\)]\(^-\) and low DOC (Figures 9B and 9D). Hg evaporation assumed greater importance as a loss term in lakes with low [H\(^+\)]\(^-\) and high DOC (Figures 9A and 9C).

The measured sediment Hg burdens observed in the study lakes\(^2\) provide an independent check on our estimates of Hg loss via evaporation and sedimentation. When sediment Hg accumulation rates are calculated both ways (\(S_1\), from the difference between Hg influx and Hg evasion (Figure 9); or \(S_2\), from measured sediment Hg burdens),\(^2\) the agreement is quite good (Figure 10).

There is evidence that the relative importance of evaporation and sedimentation as loss terms may be related to the residence time of atmospherically derived Hg in the upper watercolumn (Figure 11). When evaporation and sedimentation are plotted against epilimnetic Hg residence time, we see two clusters of lakes. Lakes with short epilimnetic Hg residence times have relatively high rates of Hg sedimentation. Lakes with long epilimnetic Hg residence times have relatively high rates of evaporation. Hg residence times are not simply surrogate measures for mean depth or SPM (Figures 11C and 11D).

Hypothetically, the probability of elemental Hg evasion from these lakes would increase with increased Hg residence time in the epilimnion. Provided that elemental Hg does not engage in coordination reactions or absorb strongly to natural organic matter, as indicated by its weak partitioning into organic solvents, all the Hg\(^0\) formed as a result of longer Hg residence in upper waters should be free to volatilize.
Figure 6: Input-output budgets for Hg in the seven Wisconsin study lakes. Sedimentation = (deposition + groundwater discharge) - (evaporation + groundwater recharge). Residence time = (mean areal epilimnetic [Hg] (μg/m²)) / (mean areal Hg influx (μg/m²/d)). Groundwater data for Pallette Lake from Reference 41. LRT: Little Rock Lake—treatment basin; MAX: Max Lake; LRR: Little Rock Lake—reference basin; VAN: Vandercook Lake; PAL: Pallette Lake; CRY: Crystal Lake; RUS: Russell Lake.
The increased sedimentation of Hg with decreasing pH observed in Wisconsin lakes is consistent with observations made during the acidification of Lake 223 in the Canadian ELA.\textsuperscript{30,34} Although acidification increased the solubility of several metals in L223 (e.g., Fe, Zn, Mn, Co), the solubility of Hg decreased with increasing acidity. This behavior has been attributed to the preferential binding of transition metals to acid-soluble oxides and the preferential binding of Hg to acid-insoluble organic substances, such as settling plankton.\textsuperscript{30} Although low pH lakes may have faster sedimentation and lower evasion rates from the epilimnion, waterborne Hg concentrations may still increase with decreasing pH on a whole-lake basis (Figure 2).

\textbf{F. MASS BALANCE FOR METHYL-HG IN LITTLE ROCK LAKE}

This mass balance indicates that atmospheric inputs of methyl-Hg were about 1\% of the Hg\texttext{\texttext{\texttext{$^3$}}} inputs (Figure 7b). We estimate that the methyl-Hg influx was roughly balanced by loss to sediments, based on the observation that the methyl-Hg concentration in surficial, profundal sediments of Little Rock Lake was about 1\% of the total Hg concentration (0.01 g/year, 0.01 g/year).

\textbf{Figure 9} Hg removal via evasion and sedimentation relative to pH and DOC in the Wisconsin study lakes; CRY = Crystal Lake, see text.

\textbf{Figure 10} Independent study lakes. \textit{S}_t = (dep. charge), see Figure 9. assuming 1 mm of sec

Figure 7b). Sedimentation rates higher than the seasonal Hg accumulation rates, Hg within the lake.

In the atmosphere, methyl-Hg fraction varied from 10\% with movement up the fish was methyl-Hg (T: in zooplankton varied: the Hg has been methylized.

Fish constituted the assuming that our estimate about 75\% of the methyl-Hg accumulation.

Accumulation of methyl-Hg (9 mg/yr Hg concentration burden of methyl-Hg: the range reported for

Since methyl-Hg is the measured sedimen Hg to the system. New fraction of the amount demethylated) would observed distributions
Figure 10. Independent estimates of annual Hg sedimentation in the seven Wisconsin study lakes. \( S_a = (\text{deposition} + \text{groundwater discharge}) - (\text{evaporation} + \text{groundwater recharge}) \), see Figure 9. \( S_a \) estimated from measured sediment Hg burdens (\( \mu g/kg/mm \)) assuming 1 mm of sediment accumulation per year.

Figure 7b). Sediment traps indicated a downward flux for methyl-Hg that was roughly 30 times higher than the airborne inputs or sediment accumulation. Although more extensive sediment data (seasonal and spatial) are needed to confirm our estimate of annual methyl-Hg accumulation rates, these data indicate substantial production and/or recycling of methyl-Hg within the lake.

In the atmosphere, <0.5% of the TGM was methyl-Hg. Waterborne methyl-Hg constituted roughly 10% of the total waterborne Hg in the lake. Across lakes, the average methyl-Hg fraction varied from about 5–20% of waterborne HgT. The methyl-Hg fraction increased with movement up the food chain, and in this lake most of the Hg in zooplankton and in fish was methyl-Hg (Table 5). Comparisons across lakes indicate that the methyl-Hg fraction in zooplankton varied substantially (ca. 30 to 90%), but in all fish assayed most (>95%) of the Hg has been methylated.\(^{33,37}\)

Fish constituted the largest methyl-Hg reservoir in the watercolumn of Little Rock Lake. Assuming that our estimates for methyl-Hg in sediment are correct, fish biomass contained about 75% of the methyl-Hg in the entire lake, including freshly deposited sediments (i.e., a 1-year accumulation). Assuming 30% turnover of fish biomass annually, the net bioaccumulation of methyl-Hg in fishes (60 mg/year) exceeded our estimate of annual sediment accumulation (9 mg/year) by a factor of 6 to 7. Although our dataset is limited, the sediment burden of methyl-Hg observed for Little Rock Lake (about 1% of the total Hg) was within the range reported for sediments in other aquatic systems (<0.1–3%).\(^{35}\)

Since methyl-Hg inputs and outputs were small relative to biotic concentrations and to the measured sediment trap flux, in situ production appears to be a major source of methyl-Hg to the system. Nevertheless, precipitation inputs of methyl-Hg can constitute a significant fraction of the amount accumulated annually by fish.\(^{34}\) Highly efficient recycling (i.e., low demethylation) would increase the importance of external input fluxes. In any case, the observed distributions imply rapid transport of methyl-Hg into the foodchain.
Figure 11 Rates of Hg evasion (A) and sedimentation (B) relative to Hg residence time in surface waters of the seven Wisconsin study lakes. Also, relation between Hg residence time and (C) mean depth or (D) suspended particulate mass (SPM). Hg residence times were computed as in Figure 8.

Table 5 Relative concentration of Hg species in phytoplankton, zooplankton, and fish in Little Rock Lake, all on a wet weight basis.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Methyl-Hg</th>
<th>Non-methyl-Hg</th>
<th>%Methyl-Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Phytoplankton</td>
<td>$10^{3.2}$</td>
<td>$10^{3.4}$</td>
<td>35</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>$10^{5.7}$</td>
<td>$10^{5.3}$</td>
<td>70</td>
</tr>
<tr>
<td>Young perch</td>
<td>$10^{6.0}$</td>
<td>$10^{4.7}$</td>
<td>95</td>
</tr>
</tbody>
</table>

Figure 12  Biotic cycling of Hg and methyl-Hg in Little Rock Lake. All rates are g/year. The total biotic flux was computed two ways for each Hg species: (1) assuming all uptake is from water (bold text); (2) assuming all uptake is trophic transfer (standard text). Return from hypolimnion = sediment trap flux - sediment accumulation. (See text for details.)

G. BIOACCUMULATION AND BIOCONCENTRATION OF Hg AND METHYL-Hg

Biotic turnover rates for Hg species in the lake can be estimated using: (1) measured mercury concentrations in water, seston (phytoplankton), zooplankton, and fish; (2) production/biomass (P/B) ratios from the literature for each biotic compartment; and (3) some simplified assumptions about transfer between compartments (Figure 12). For fish, we use a P/B ratio of 0.3/year, for crustacean zooplankton, 10/year (ca. 0.1/d for 100 d), and for phytoplankton, 25/year (0.25/d for 100 d). We assume that the degree of trophic transfer falls between two extremes: (1) 100% direct uptake from water (no trophic transfer), and (2) 100% uptake from the lower trophic level (all trophic transfer). For these extreme cases, we find that 2.5 to 2.7 g Hg cycles through the biota per year. By comparison, 0.5 to 0.7 g methyl-Hg cycles through the biota per year. These biotic fluxes are very close to the turnover fluxes estimated from hypolimnetic sediment trap data: 2.3 g Hg recycled annually; 0.3 g methyl-Hg produced and/or recycled annually (Figure 7).

Bioconcentration factors (Bf) and partitioning coefficients (Kd) measure the tendency of solutes to form solid phase species (biotic and abiotic) in aquatic environments. Computation is similar:

\[ Bf = \frac{Ch}{Cw}; \quad Kd = \frac{Cp}{Cw} \]
Figure 13  Bioconcentration of Hg and methyl-Hg relative to pH in clearwater lakes. Bf = log(Cb/Cw), where Cb and Cw are biotic (wet weight basis). Data are annual epilimnetic averages ±1 SE.

where Cb, Cp, and Cw are concentrations in biota, particulate matter, and water, respectively, (all mass:mass). Since most of the particulate matter in our study lakes was biogenic, we report Bf for seston and for fish—both on a wet weight basis—rather than computing a separate Kd for suspended particulate.

Bioconcentration factors for Hg and methyl-Hg were related to pH in different ways (Figure 13). For both seston and young perch, the Bf (Hg) tended to increase with decreasing pH. This observation is consistent with data from other studies showing increased Hg in fishes from acidic lakes. Over the pH range 5 to 7, young perch bioconcentrated Hg 3 to 5 times more than bulk seston. In contrast to Hg, bioconcentration factors for methyl-Hg were relatively constant over the pH range 5 to 7. Across this pH range, then, [methyl-Hg] in biota and in water increased at similar rates. For bulk seston, the Bf (methyl-Hg) averaged about 5.0, while for young perch it was about an order of magnitude higher. This observation implies that methyl-Hg is bioaccumulated in proportion to supply and that bioaccumulation is greater at higher trophic levels.

The relationships between bioconcentration factors and DOC shows some evidence of an effect working opposite to that of pH (Figure 14). The Bf (Hg) remained relatively constant in both seston and fish across the DOC range 1.5 to 6.5 mg/L. The Bf (methyl-Hg) decreased significantly with increasing DOC in the case of perch (p < 0.05), and there was a similar trend in seston (albeit not statistically significant). Absolute concentrations of Hg and methyl-Hg in both organisms and water are highest in the darkwater lake (Russet Lake, Figures 2 and 3), but a disproportionately higher fraction apparently remains in the waterborne phase.

H. A CONCEPT
At least six proce mercury in the lak ementation, methyl cisn seeage lak ecosystem is ulith inputs follow three (2) conversion to bioaccumulation and the outcome e variables, such as
Sedimentation buried below the exchange or redo also transports Hg boundary. The enhance Hg bu

While methyl of Hg in surface reactions govern separation of the
Figure 14  Bioconcentration of Hg and methyl-Hg relative to dissolved organic carbon (DOC) concentration in lakes of similar pH. BI as in Figure 13. Data are annual epilimnetic averages ±1 SE.

H. A CONCEPTUAL MODEL OF SOURCES AND FATES

At least six processes have an important effect on the concentration and distribution of mercury in the lakes of northern Wisconsin: atmospheric deposition, gaseous evasion, sedimentation, methylation, bioaccumulation, and demethylation (Figure 15). Our studies of Wisconsin seepage lakes, and Scandinavian studies of drainage lakes, indicate that Hg in aquatic ecosystems is ultimately derived from atmospheric deposition. Within lakes, atmospheric Hg inputs follow three main pathways: (1) particle scavenging and transport toward sediments; (2) conversion to elemental Hg and subsequent evasion; or (3) methylation and subsequent bioaccumulation and/or demethylation. These processes may compete for the available Hg and the outcome of this competition seems to be a rather complex function of environmental variables, such as pH and DOC.

Sedimentation appears to be an effective removal mechanism, since Hg is apparently buried below the profundal sediment/water interface and not remobilized by either the cation exchange or redox reactions that liberate other metals such as Fe. However, sedimentation also transports Hg to methylation sites in sediments or in the watercolumn below the O/A boundary. Thus, factors which favor Hg-particle binding, such as decreased pH, may enhance Hg burial and methyl-Hg formation simultaneously.

While methylation seems to occur in anoxic regions of the lake, the supersaturation of Hg in surface waters and undersaturation of Hg in deep anoxic waters indicates that reactions governing the evasion Hg flux occur in the oxic watercolumn but the spatial separation of the evasion and methylation pathways does not rule out competitive interaction
between these processes. In fact, our data indicate that variables which tend to increase Hg residence in the upper water enhance evasive flux at the expense of downward transport to burial or methylation zones. However, it does not necessarily follow that competitive interaction limits rates of methylation. Biotic methylation is also a function of microbial activity. Thus, either the size and physiological status of microbial populations or the availability of Hg substrate may constrain methyl-Hg formation.

The distribution of methyl-Hg in the Wisconsin study lakes indicates that it is effectively bioaccumulated and biologically sequestered. However, we have no data which pertain to the process of demethylation and its importance in the cycling of alkyl-Hg. Since waterborne and sediment pools of methyl-Hg appear to be small, it must either be rapidly shunted back into organisms or demethylated when released via excretion or death. Understanding the bioaccumulation of Hg in these remote lakes clearly will require knowing the environmental dependencies of factors which regulate the formation, destruction, and trophic transfer of methyl-Hg.

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