

# Atmospheric Deposition and Biogeochemistry of Mercury and other Trace Contaminants in Aquatic Ecosystems

Final Project Report  
Part II:

## Mercury Studies 2002-2004

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## 1. Executive Summary.

In 2001, the Forest County Potawatomi Community (FCPC) and the Wisconsin Department of Natural Resources (WDNR) initiated a cooperative research project entitled “Atmospheric Deposition and Biogeochemistry of Mercury and other Trace Contaminants in Aquatic Ecosystems.” This project involved intensive studies of the mercury cycle in Devils Lake and other nearby lakes in northern Wisconsin. The broad research objective was to document similarities and differences between hydrologically different lakes in the region, focusing primarily on the sources and fates of total mercury ( $Hg_T$ ) and methylmercury (meHg - the chemical form of mercury that accumulates in fish and poses a health risk to humans and piscivorous wildlife).

When the planning stage of this project began in 1995, research on mercury contamination in lakes of Wisconsin, Canada and Sweden suggested that the mercury cycles in seepage lakes and drainage lakes might be significantly different (Rudd, 1995). Within the scientific community, it was thought that this difference could help to explain why fish in some lakes were more contaminated than fish in others. At that time, research by the WDNR had focused on the seepage lakes, as exemplified by the well-studied Little Rock Lake (LRL) in Vilas County. Studies of mercury in LRL began in 1984 as part of an EPA-sponsored acid rain project and they continue today (Frost *et al.*, 1999; Watras *et al.*, 2006). Results of the LRL work indicate that the major source of Hg is direct atmospheric deposition to the lake surface, and the major source of meHg is in-lake production in anoxic regions of the water column and sediments. In contrast, studies of drainage systems in Canada and Sweden suggested that the major sources of Hg and meHg in drainage lakes might be the terrestrial watershed – especially areas of the watershed containing wetlands.

In June, 1995 the Director of Natural Resources for the FCPC, Ms Christine Hansen, requested technical assistance on a research project involving mercury studies for Devils Lake on the reservation. Since Devils Lake is a drainage lake, closely coupled to a large wetland, it was jointly felt that this project could potentially enhance our understanding

of the mercury cycle in many lakes and, thereby, benefit all parties involved. A cooperative agreement was formally implemented in February, 2001 and preliminary research on the lake by WDNR began that summer. For each of the next three years, comprehensive studies on the hydrology and biogeochemistry of the Devils Lake watershed were conducted jointly by WDNR and FCPC staff, along with associated scientists and engineers.

Preparation of the Final Project Report began in 2005, under a contract extension agreement signed by the Tribe on 14 September. Pursuant to that agreement, the WDNR submitted Part I of the Final Report in December 2005, summarizing the hydrologic studies conducted in the DL watershed. This present report constitutes Part II of the Final Project Report to the Tribe. Part II summarizes the mercury studies, and it has two main objectives. The first objective is to summarize the findings of biogeochemical investigations conducted in the Devils Lake watershed during 2002, 2003 and 2004 and to compare them to findings for other lakes. The second objective is to compile and tabulate the large amount of mercury data that were collected so that they will be useful to the Tribe in future studies.

Devils Lake is a small (11.7 ha), dystrophic drainage lake in Forest County, Wisconsin (45° 33' N, 88° 50' W) that supports a warm water fishery of perch and bass. The lake is situated in a relatively pristine, forested watershed and it is fed by a small tributary stream that flows seasonally from spring to fall. The tributary stream emanates from a headwater wetland, which accounts for the dystrophic status of the lake (dark, tea-stained water). The lake is drained by a single distributary stream and by seepage to groundwater.

Intensive hydrological investigations of the Devils Lake catchment were conducted in conjunction with the mercury study. These investigations involved measuring or estimating the sources of water to the lake (precipitation, tributary stream flow, non-channelized runoff and groundwater discharge), losses of water from the lake (distributary stream flow, groundwater recharge and evaporation) and the change in the volume of water in the lake (change in water storage) over time. The hydrologic data

were used to construct water budgets for the lake during each year of study. In this second part of the Final Report, the hydrologic data are coupled with chemical data to construct budgets for mercury in the lake. Based on these budgets, the importance of various sources and sinks in the watershed can be assessed.

Annual budgets for total Hg ( $Hg_T$ ) and seasonal budgets for meHg are shown on Table 1 and Table 2 for each of the three studies years. Annual budgets were computed for calendar years, January 1 – December 31. The seasonal budgets were computed for the time period when meHg accumulates in the water column of the lake, generally from the beginning of spring melt to late summer stratification (e.g. April to late August). The annual budgets are useful in assessing the major sources and sinks for waterborne  $Hg_T$ , while the seasonal budgets are needed to identify the major sources of meHg – the chemical form that accumulates in fish. MeHg is produced in anoxic regions of the lake and in anoxic wetland porewaters. A major goal of this research project was to quantify the relative importance of these two sources.

**Table 1.** Annual Budgets for waterborne total mercury ( $Hg_T$ ) in Devils Lake, 2002 – 04

Year	-----Inputs-----			-----Outputs-----			Change in Storage ( $\Delta S$ )
	Precip (P)	Surface Runoff (RO)	Stream Flow ( $Q_{in}$ )	Sedimentation & Evasion (S+E)	Stream Flow ( $Q_{out}$ )	Lake Seepage (GO)	
2002	1.50	0.19	3.27	3.62	0.91	0.11	0.33
2003	1.01	0.05	0.91	1.85	0.62	0.04	-0.52
2004	0.99	0.07	1.18	1.47	0.53	0.06	0.18
<b>mean</b>	1.17	0.11	1.79	2.31	0.69	0.07	0.00
<b>SD</b>	0.29	0.08	1.29	1.15	0.20	0.04	0.46

**Table 2.** Seasonal Budgets for waterborne methylmercury (meHg) in Devils Lake, 2002-04

Year	Precip (P)	Surface Runoff (RO)	Stream Flow (Q <sub>in</sub> )	Net methyl. (M)	Sedimentation (S)	Stream Flow (Q <sub>out</sub> )	Lake Seepage (GO)	Change in Storage (ΔS)
2002	0.012	0.002	0.056	0.408	0.026	0.066	0.004	0.382
2003	0.007	0.001	0.027	0.132	0.009	0.078	0.002	0.078
2004	0.007	0.001	0.023	0.081	0.012	0.048	0.002	0.049
<b>mean</b>	0.009	0.001	0.035	0.207	0.016	0.064	0.003	0.170
<b>SD</b>	0.003	0.000	0.018	0.176	0.009	0.015	0.001	0.184

The mass balances for Hg<sub>T</sub> indicate that the tributary stream was an important external source to the lake, contributing 50% to 70% of the Hg<sub>T</sub> that entered the lake each year. Hg<sub>T</sub> in the tributary stream-water is ultimately attributable to atmospheric Hg deposition onto the watershed as a whole. Given the size of the tributary catchment and the rate of atmospheric Hg deposition, it is clear the terrestrial watershed is a net sink for Hg<sub>T</sub>. In other words, most of the atmospherically-deposited Hg<sub>T</sub> is either sequestered in soils or evades back into the atmosphere, and only a small fraction bleeds out into stream-water and enters the lake.

The mass balances for meHg indicate that the tributary stream contributes more meHg to the lake than does direct precipitation. As such, the tributary stream constitutes the largest external source of meHg to the lake. However, in contrast to Hg<sub>T</sub>, internal sources of meHg are larger than external sources in each year. In other words, more meHg is produced within the lake itself than is derived from the watershed and the airshed combined. Parallel investigations indicate 1) that meHg production rates in Devils Lake are greater than those in Wisconsin lakes that are not connected to wetland; and 2) that the meHg is produced by bacteria that inhabit the anoxic hypolimnion of the lake during summer.

In a comparative study of mercury methylation in the dark-water, wetland-dominated Devils Lake and the clear-water, precipitation-dominated Palette Lake in neighboring Vilas County, Eckley *et al.* (2005) showed that methylation rates in Devils lake were up

to two-fold greater than those in Palette Lake – potentially accounting for the higher concentrations of waterborne meHg in Devils Lake. In both lakes, in-lake methylation was sufficient to account for all the meHg that accumulated during summer.

In a companion study, Kent *et al* (2005a, b, c) showed that similar microbial communities were associated with meHg production in three regional lakes (Devils Lake, Palette Lake and Little Rock Lake). This finding suggests that environmental factors which affect the activity of the resident microbial communities may partly explain the differences in meHg production observed among these lakes. In Devils Lake, the influx of runoff from the headwater wetland may supply nutrient supplements and additional Hg substrate – both of which could result in higher rates of meHg production in this lake.

In conclusion, investigations of the aquatic mercury cycle in Devils Lake indicate that wetland runoff may have both direct and indirect effects that increase the potential for mercury methylation relative to lakes without hydrological connection to wetland. These effects may interact synergistically – producing a larger effect together than either would have separately (*sensu* Watras *et al.*, 2006). Since meHg is the chemical form of mercury that accumulates in fish and poses the major risk to humans and piscivorous wildlife, these findings are directly relevant to the potential for fish contamination in Devils Lake.

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### **3. Methods**

#### ***3.a. Site Description***

Devil's Lake (N 45° 32.954', W 88° 50.040') is a dark-water drainage lake in Forest County, Wisconsin, with a surface area of 11.7 ha, a volume of  $3.5 \times 10^5 \text{ m}^3$ , a maximum depth of 7.6 m, a mean depth of 3.0 m and a water residence time of roughly 1 year. The terrestrial watershed comprises a headwater wetland approximately twice the size of the lake encircled by gently sloping, forested uplands that surround the headwater wetland and the lake itself. A small stream emanates from the headwater wetland and it flows directly to the northeast end of the lake through a narrow valley. Water leaves the lake via a small out-flowing stream to the southwest. A small wetland fringes the down-gradient end of the lake at the mouth of the outlet. A narrow, unimproved, gravel road circumscribes the remaining lake shore, roughly defining a near-shore watershed of 12.3 ha. Further details on the hydrologic setting can be found in Horsley and Witten (2003).

The lake and its forested watershed are situated in thick, unconsolidated glacial till (Simpkins, McCartney and Mickelson, 1987). Groundwater flow directions within the unconfined glacial deposits of the region often follow the land-surface topography, moving from upland to lowland areas and discharging in some lakes, streams, and land depressions. Saturated thickness of the aquifer ranges from 18 m to 49 m in general (Lidwin and Krohelski, 1993). The moderate to low permeability of the glacial till-derived soils that comprise the Devil's Lake surface watershed contributes to a "perched" hydrologic system where surface water elevations sit well above the local groundwater table. The perched nature of the entire Devil's Lake hydrologic system has been demonstrated by surface water levels significantly higher than groundwater levels throughout the system and by a consistent loss of flow volume from upstream to downstream locations in the inlet stream (Horsley & Witten, 2003). This hydrologic setting simplifies construction of water budgets and mercury mass balances since groundwater inputs may be considered negligible.

### **3.b. Sampling and Analysis**

#### **3.b.1. Stream Sampling**

Surface water monitoring was conducted from 1996 through 2001 to roughly characterize the spatial and temporal variability of solutes within the watershed. Stream monitoring was performed routinely at three locations: the Upstream and Inlet sites on the tributary stream and the Outlet (Roadside) site on the distributary stream.

Intensive monitoring of the chemistry and discharge volumes of the tributary and distributary streams was initiated in 2002 and continued through 2004. Stream water samples for chemical analysis were collected weekly beginning at the onset of melt each year. Sampling and analytical protocols were similar to those used during the background monitoring years. Grab samples were obtained at the inlet and outlet sampling sites on the same day that manual hydrologic flow measurements were made (DL Hydrology Report). The stream water samples were shipped on ice in dark coolers. Mercury samples were hermetically sealed in double plastic bags.

At regular intervals (generally each week), stage was determined visually by reading the level of the water surface at each monitoring site on a staff gauge. Concurrently, discharge was estimated using mini (pygmy) Price “AA” flow meters with top-set wading rods. Flow measurement began at the onset of spring melt and continued until the stream stopped flowing in fall. This information was used to compute the stage-discharge rating curves for each site (DL Hydrology Report).

Stream stage was also recorded continuously at 15-minute intervals using baro-compensated, data-logging pressure transducers during the unfrozen portion of the year (early April through November). The logger data were converted to discharge units by applying the rating curves described above. The resultant 15-minute estimates of water discharge were integrated over appropriate time intervals to calculate daily, weekly and annual flow volumes (DL Hydrology Report).

### 3.b.2. Lake Sampling

Lake sampling was conducted at a single mid-lake station, in part because background monitoring had indicated no significant differences between sites L1 and L2 during the period 1996-2001. To obtain vertical concentration profiles, sampling depths were selected after establishing the physical structure of the water column using a SeaBird-19 plus CTD. Prior to profiling, the non-metallic sampling boat was tethered fore and aft to buoys that were permanently anchored to mark the northerly and southerly bounds of the 7 m depth contour. The tethering line thus spanned the lake surface overlying the hypolimnion. The CTD was lowered through the water column at a descent rate of 1 to 2 cm s<sup>-1</sup> at a station located about 3 to 5 m from the southernmost buoy. Data from the sensors were logged at a rate of 4 Hz and graphically displayed in real-time with an on-board laptop computer. In addition to conductivity, temperature and depth, the Seabird unit also measured *in situ* chlorophyll fluorescence, transmissometer beam attenuation, pH and dissolved oxygen so that thermal structure, redox conditions and particle layers could all be used to target the collection of water samples during the second deployment. After obtaining a first Seabird profile, the boat was moved along the tether line toward the northernmost buoy to a second station and an acrylic outrigger was attached to the SeaBird profiler. A submersible, non-metallic pump was fixed to the end of the outrigger so that water could be pumped to the surface through acid-washed C-Flex tubing and collected on deck as described by Watras *et al.* (1998). The collection of water samples began when the unit reached the first target depth. Generally 5 to 7 depths were sampled in the 7 m water column. On every sampling date, the two SeaBird profiles were compared to ensure that the physical, chemical and biological structure of the water column was horizontally uniform across the deep pelagic region of the lake. The single sampling profile was then considered representative of the entire water column. The lake water samples were hermetically sealed in double plastic bags and transported on ice in dark coolers to the UW Trout Lake Clean Laboratory.

### 3.b.3. Precipitation Sampling

Bulk precipitation was sampled continuously and collected weekly from 2002 through 2004 using modified IVL-type collectors (as described by Morrison *et al.* 1995) at two sites. One site was the US NADP/MDN site WI36 located at Trout Lake in neighboring Vilas County (roughly 80 km from Devils Lake) where the deposition of mercury has been monitored continuously since 1995, along with total precipitation amount and ancillary precipitation chemistry (<http://nadp.sws.uiuc.edu/mdn>). A second site was established on the Potawatomi Reservation less than 2 km from Devils Lake. The IVL sampler at this site was maintained by FCPC personnel and operated continuously from May 28, 2002 to August 25, 2004. Duplicate IVL-collectors were operated from May 28, 2002 to September 4, 2002. All IVL samples were stored in the dark and transported to the Trout Lake Clean Laboratory for Hg<sub>T</sub> analysis. The mercury data for the IVL samples collected at the FCPC and Trout Lake air monitoring sites (2002-2004) are presented in **Appendix A3**.

A continuous record of precipitation was not available for the FCPC site for the entire study period. For the purposes of this study, we assumed that mercury concentrations in precipitation were regionally coherent whereas precipitation amount could demonstrate significant local variability. Therefore, we estimated precipitation amount using data from the site with a complete record located nearest to the study site and we estimated Hg<sub>T</sub> concentrations in precipitation from regional means.

The nearest site to the Devils Lake study site with a complete record of precipitation amount for the entire study period was the Laona 6 SW weather station (ID# 474582; Wisconsin State Climatology Office, <http://www.aos.wisc.edu/~sco/>) approximately 13 km due west of DL. Data from this site was used to estimate precipitation amounts for the annual hydrologic budgets reported in the DL Hydrology Report. The use of Laona 6 SW data was validated by comparison with the data collected weekly from the FCPC site for the period May 2002 through August 2004. The similarity of the two records indicated

that the Laona site is a reasonable surrogate for FCPC precipitation (DL Hydrology Report).

**Table 3.** Comparison of atmospheric mercury data collected at DL study site with other sites in region over 117 weeks of parallel collection

	FCPC IVL	TRL IVL	WI36 MDN	WI09 MDN	WI32 MDN
Hg <sub>T</sub> deposition (μg/m <sup>2</sup> )	19.9	17.5	19.5	16.6	19.5
VWA Hg <sub>T</sub> (ng/L)	10.7	9.7	10.9	10.5	12.2
# weeks missing precip data	0	0	0	0	7
# weeks w/o Hg data	0	7	15	23	11
Precip (cm) w/o Hg data	0	0.03	4.2	5.1	5.0

Annual and seasonal Hg<sub>T</sub> concentrations at the DL study site were estimated as the mean of the volume-weighted average (VWA) Hg<sub>T</sub> concentrations from three US NADP/MDN sites. These sites were i) the Trout Lake site (WI36) described above, ii) the Popple River site in Fence, Florence County, WI 50 km northeast of DL (WI32) and the Middle Village site in Shawano County, WI 75 km south of DL (WI09) (<http://nadp.sws.uiuc.edu>). Comparison between the IVL collector at Devils Lake and the mean of the three MDN sites showed that the VWA concentration of Hg<sub>T</sub> differed by roughly 5% during the 117 weeks of parallel sampling in 2002-2004 (10.7 ng/L vs. 11.2 ng/L, respectively), indicating locally coherent Hg depositional regimes (Table 3). The annual and seasonal mean VWA concentrations used to construct the mercury mass balances are shown in Table 4. The mean concentrations were multiplied by the precipitation amounts from Laona 6 SW to estimate Hg<sub>T</sub> deposition at the study site. The atmospheric deposition of meHg to the surface of Devils Lake was estimated to be 1.2% of the atmospheric Hg<sub>T</sub> deposition, based on NADP/MDN data for the Trout Lake site (WI36). During 2002, 2003, and 2004 meHg constituted 0.5%, 1.9% and 1.5%, respectively, of the annual Hg<sub>T</sub> deposition at this site (<http://nadp.sws.uiuc.edu/mdn>). These data agree well with earlier estimates of 1.5% based on measurements at nearby Little Rock Lake (Watras *et al.* 1994, Fitzgerald *et al.* 1991).

**Table 4.** Annual and seasonal VWA Hg<sub>T</sub> concentrations (ng/L) in precipitation from three NADP/ MDN sites (WI36, WI32 and WI10). Values are mean ± SD.

<b>Year</b>	<b>Annual</b>	<b>Seasonal</b>
2002	12.1 ± 0.9	14.0 ± 0.7
2003	11.2 ± 1.9	12.2 ± 1.8
2004	9.1 ± 0.4	12.4 ± 0.8

### **3.b.4. Air Sampling**

A Tekran Model 2537A Mercury Vapor Analyzer was operated at NADP/MDN site WI36 (Trout Lake) from October 3, 2002 until January 20, 2004 taking continuous 5-minute integrated samples. The sampling inlet was connected to a Teflon manifold which also served ozone and sulfur dioxide analyzers maintained by the WDNR Bureau of Air Management. The manifold was connected by ½-inch plastic tubing to an inverted funnel atop a tower which extended above treetops. Airflow was maintained by a vacuum pump and monitored with a flow meter. The Tekran 2537A was equipped with an internal mercury vapor permeation source which was used to perform automatic calibrations at regular intervals. Manual injections of saturated mercury vapor were also occasionally performed.

Daily means of the 5-minute continuous TGM concentrations are compiled in Appendix A4.1. Hourly means of TGM and all of the original TEK files are in Appendices A4.2 and A4.3 (CD only).

### **3.b.5. Aqueous Mercury Analysis**

Samples for mercury analysis collected for background monitoring from 1995 to 2001 were analyzed using purge-trap/CVAFS for Hg<sub>T</sub> (Bloom & Fitzgerald 1988) and ethylation/GC/CVAFS for meHg (Bloom 1989, Liang *et al.* 1994) at Frontier

Geosciences, Inc. (Seattle, WA). Stream samples for mercury analysis collected in 2002 were also analyzed by Frontier Geosciences. Lake samples for mercury analysis collected for intensive monitoring from 2002 through 2004 were analyzed at UW Trout Lake Clean Laboratory where they were analyzed following protocols similar to those used at Frontier Geosciences, *i.e.* EPA Methods 1630 & 1631 (US EPA 2001, 2002). Inter-calibration between these two analytical facilities has shown good agreement for both Hg<sub>T</sub> and meHg analysis in freshwater samples (Bloom *et al.* 1995). Stream samples collected in 2003 were also sent to UW Trout Lake. All UW Trout Lake samples were analyzed in duplicate for Hg<sub>T</sub> and meHg. In 2004, stream samples were analyzed at State Laboratory of Hygiene (Madison, WI).

Mercury data for the tributary and distributary streams are in **Appendix A1**. Data for Devils Lake are found in **Appendix A2**.

### **3.b.6. Ancillary Solutes**

Conductivity and pH were monitored in the field using hand-held meters throughout the study period. Samples for ancillary solutes analyses collected for background monitoring from 1995 to 2001 and stream samples collected in 2002 were sent to ERA Labs, Inc., Duluth, MN. These samples were analyzed for alkalinity, dissolved organic carbon (DOC), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and chlorophyll-a (Chl-a). Results of these analyses are reported in Appendices **A1.1** (stream data) and **A2.1** (lake data).

Lake water samples collected during intensive monitoring 2002 – 2004 and stream samples collected in 2003 were analyzed for pH, DOC, SO<sub>4</sub><sup>2-</sup>, total sulfide, methane, suspended particulate matter (SPM), major cations, anions and metals. SPM, chl *a*, pH, methane and sulfide determinations were performed at Trout Lake lab by WDNR personnel. DOC determinations were performed by UW-Madison personnel at the Center for Limnology. Cations, anions and metals were sent to the State Laboratory of Hygiene

(SLH), Madison, WI. Methods are described by Watras *et al.* (2006) (see Section 5c). Results are reported in Appendices A1.2 (stream data) and A2.2 (lake data).

All ancillary solute analyses on stream samples collected in 2004 were performed by SLH. Results are in Appendix A1.3.

### 3.b.7. QAQC Criteria for Mercury Analyses

Quality control and quality assurance criteria for UW-Trout Lake clean laboratory mercury analyses, 1997 – 2005 with DL site specific values where applicable are as follows:

#### Hg<sub>T</sub> analysis following EPA Method 1631

##### **General Criteria**

- |   |                         |
|---|-------------------------|
| 1. <b>On-going precision</b> (mean ± SD)      | 99.7% ± 6.2%, n=735     |
| 2. <b>Quality control samples</b> (mean ± SD) | 97.6% ± 5.9%, n=158     |
| 3. <b>Bubbler blanks</b> (mean ± SD)          | 3.7 pg ± 3.5 pg, n=1628 |

##### **Aqueous Hg<sub>T</sub>**

- |   |                             |
|---|-----------------------------|
| 1. <b>Reagent blank</b> (mean ± SD)                                   | 15.3 pg ± 6.5 pg, n =228    |
| 2. <b>Daily detection limit</b> (3·sd reagent blanks) (mean, range)   | 0.05 ng/L, 0.01 – 0.18 ng/L |
| 3. <b>Method detection limit</b> (pooled variance of reagent blanks): | 0.05 ng/L                   |
| 4. <b>Method blanks</b> (mean ± SD)                                   | 16.8 pg ± 4.6 pg, n =28     |
| 5. <b>Method detection limit</b> (pooled variance of method blanks):  | 0.04 ng/L                   |
| 6. <b>Lab duplicate RPD</b> (mean ± SD)                               |                             |
| Lake and stream samples   | 4.8% ± 4.4%, n=171          |
| DL Lake and stream samples  | 5.0% ± 4.6%, n=99           |
| Rain samples  | 10.3% ± 9.7%, n=107         |
| 7. <b>Field duplicate RPD</b> (mean ± SD)                             |                             |
| Lake and stream samples   | 4.8% ± 9.1%, n=36           |
| DL Lake and stream samples  | 7.0% ± 7.2%, n=32           |
| DL “A” and “B” rain samples   | 15% ± 15%, n=12             |
| 8. <b>Matrix spike recovery</b> (mean ± SD)                           |                             |
| Lake and stream samples   | 94.8% ± 6.7%, n=111         |
| DL Lake and stream samples  | 92.7% ± 7.2%, n=37          |
| Rain samples  | 103.8% ± 18.4%, n=98        |
| 9. <b>Matrix spike duplicate RPD</b> (mean ± SD)                      |                             |
| Lake and stream samples   | 4.3% ± 5.0%, n=52           |
| DL Lake and stream samples  | 6.6% ± 5.9%, n=22           |
| Rain samples  | 7.2% ± 10.3%, n=128         |



### ***Particulate Hg<sub>T</sub>***

1. <b>Method blanks</b> (mean ± SD)	22.3 pg ± 9.2 pg, n =44
2. <b>Reagent blanks</b> (mean ± SD)	18.2 pg ± 4.1 pg, n =24
3. <b>Filter blanks</b> (mean ± SD)	42 pg ± 32 pg, n =38
4. <b>Yield CRM (DOLT-2)</b> (mean ± SD)	100.6% ± 7.0%, n =18
5. <b>Duplicate RPD</b> (mean ± SD)	27% ± 30%, n =128

## **MeHg analysis following EPA Method 1630**

### ***General Criteria***

1. <b>On-going precision</b> (mean ± SD)	100.4% ± 10.5%, n=609
2. <b>Quality control samples</b> (mean ± SD)	105.7% ± 11.5%, n=78

### ***Aqueous meHg***

1. <b>Reagent blank</b> (mean ± SD)	0.4 pg ± 1.1 pg, n =268
2. <b>Method detection limit</b> (pooled variance of reagent blanks):	0.05 ng/L
3. <b>Distillation blanks</b> (mean ± SD)	0.3 pg ± 0.8 pg, n =123
4. <b>Method detection limit</b> (pooled variance of distillation blanks):	0.03 ng/L
5. <b>Lab duplicate RPD</b> (mean ± SD)	
Lake and stream samples	10.9% ± 9.0%, n=195
DL Lake and stream samples	8.4% ± 7.1%, n=88
6. <b>Field duplicate RPD</b> (mean ± SD)	
Lake and stream samples	7.8% ± 7.7%, n=36
DL Lake and stream samples	7.9% ± 7.7%, n=29
7. <b>Matrix spike recovery</b> (mean ± SD)	
Lake and stream samples	96% ± 11%, n=118
DL Lake and stream samples	93% ± 9%, n=41
8. <b>Matrix spike duplicate RPD</b> (mean ± SD)	
Lake and stream samples	5.4% ± 5.7%, n=39
DL Lake and stream samples	5.3% ± 4.9%, n=19

### ***Particulate meHg***

9. <b>Reagent blanks</b> (mean ± SD)	1.1 pg ± 2.4 pg, n =49
10. <b>Filter blanks</b> (mean ± SD)	1.6 pg ± 2.7 pg, n =69
11. <b>Matrix spike recovery</b> (mean ± SD)	104.3% ± 0.1% pg, n =5
12. <b>Yield CRM (DOLT-2)</b> (mean ± SD)	101.1% ± 0.2%, n =14
13. <b>Duplicate RPD</b> (mean ± SD)	28.2% ± 0.5%, n =92

## **3.b.8. Other analyses**

In addition to sampling Devils Lake for mercury species and ancillary chemical analytes, water samples were also collected to characterize the microbial community and

to estimate methylation and demethylation rate constants at specific depths during peak stratification in 2002. Microbial community composition was characterized with molecular genetic techniques (ARISA and clone libraries). Details of methods and results can be found in Kent *et al.* (2005a, b, c) in Section **5.d**). Rates of mercury methylation and demethylation were measured using stable isotopes of mercury. Methods described in detail and results presented in Eckley *et al.* (2005) in Section **5.a**.

### **3.c. Mass Balance Calculations**

Annual budgets for waterborne Hg<sub>T</sub> in Devils Lake were constructed for years 2002 – 2004. Annual budgets were computed for calendar years, January 1 to December 31. A seasonal mass balance for waterborne meHg for the time period when mercury accumulates in the water column also was compiled for each year. This seasonal period began with the onset of stream flow in spring and continued until peak summer stratification (mid-August). The governing expression was:

$$\Delta S_{\text{Hg}} = (P_{\text{Hg}} + Q_{\text{in-Hg}} + RO_{\text{Hg}}) - (Q_{\text{out-Hg}} + G_{\text{out-Hg}} + E_{\text{Hg}} + S_{\text{Hg}}) + M_{\text{net}}$$

where  $\Delta S_{\text{Hg}}$  is the change in waterborne mercury mass (storage);  $P_{\text{Hg}}$  is the mass deposited atmospherically directly on the lake;  $Q_{\text{in-Hg}}$  is the mass delivered from the upstream wetland via the tributary stream;  $RO_{\text{Hg}}$  is the mass of mercury in non-channelized runoff in the nearshore zone;  $Q_{\text{out-Hg}}$  is the mass lost to the distributary stream;  $G_{\text{out-Hg}}$  is the mass lost to groundwater;  $E_{\text{Hg}}$  is the mass lost by evasion across the air/water interface;  $S_{\text{Hg}}$  is the mass lost to sediments; and  $M_{\text{net}}$  is the mass of meHg in the water column attributable to net in-lake methylation. For the Hg<sub>T</sub> budget,  $M_{\text{net}}$  is zero.

Change in storage ( $\Delta S_{\text{Hg}}$ ) was estimated as the difference in waterborne mass at the beginning and end of the season or water year. The total mass of mercury in the water column was determined as the sum of masses over all depths sampled, according to  $\sum c_i \cdot v_i$ , for  $i = 1$  to  $n$ , where  $c_i$  and  $v_i$  represent the concentration and volume for a given depth stratum ( $i$ ). Midpoints between successive sampling depths were used to bound ( $i$ );

and the lake volume was adjusted for changes in stage. Atmospheric deposition ( $P_{\text{Hg}}$ ) was the product of the volume-weighted average mercury concentration times the amount of precipitation falling directly on the lake (Sec 3.b.3 and Table 4). Stream in-flow ( $Q_{\text{in-Hg}}$ ) was estimated as  $\sum c_t \cdot v_t$ , for  $t = 1$  to  $n$ , where  $c_t$  and  $v_t$  represent the mercury concentration and water discharge volume for a given time interval. Stream sampling dates were used as mid-points between successive time intervals. Non-channelized runoff ( $RO_{\text{Hg}}$ ) was calculated as the product of the runoff coefficient from the hydrologic budget (0.1), precipitation volume and the volume-weighted concentration of mercury in tributary stream water (*i.e.* assuming the same mercury concentration in channelized and non-channelized overland flow). Stream out-flow ( $Q_{\text{out-Hg}}$ ) was estimated as the product of distributary stream discharge volume and the mean epilimnetic concentration of lake over the appropriate time period. Groundwater output ( $G_{\text{out-Hg}}$ ) was the product of groundwater outflow volume times the mean concentration of mercury in the epilimnion (assuming no profundal recharge). Groundwater recharge was seasonally pro-rated from the annual hydrologic budget for the meHg budgets. Evasion and sedimentation were estimated as a pooled residual loss term:  $(E + S)_{\text{Hg}} = (P_{\text{Hg}} + Q_{\text{in-Hg}} + RO_{\text{Hg}}) - (Q_{\text{out-Hg}} + G_{\text{out-Hg}} + \Delta S_{\text{Hg}})$ . For meHg, this term was approximated as 1% of  $(E + S)_{\text{HgT}}$  since meHg constitutes roughly 1% of the  $\text{Hg}_T$  in sediments but it does not evade across the air-water interface to a significant degree (Watras *et al.* 1996, Ullrich *et al.* 2001, Watras *et al.* 1998, Hudson *et al.* 1994). Note that  $(E + S)_{\text{MeHg}}$  is probably a lower limit since demethylation in the sediment is not considered. Net methylation ( $M_{\text{net}}$ ) was calculated according to:  $M_{\text{net}} = \Delta S_{\text{MeHg}} + (Q_{\text{out-MeHg}} + G_{\text{out-MeHg}} + (E + S)_{\text{MeHg}}) - (P_{\text{MeHg}} + RO_{\text{MeHg}} + Q_{\text{in-MeHg}})$ .  $M_{\text{net}}$  is a conservative estimate for the mass in the water column attributable to in-lake production (regardless whether the site of production is in sediments or the water column) if  $(E + S)_{\text{MeHg}}$  underestimates the gross flux to sediments. By definition,  $M_{\text{net}}$  includes demethylation in the water column.

The annual mass balances for waterborne  $\text{Hg}_T$  in Devils Lake, 2002 – 2004, are shown in **Table 1**; the seasonal mass balances for waterborne, meHg are presented in **Table 2**. The annual and seasonal hydrologic budgets upon which the mercury budgets are based are

given in **Tables 5 & 6**. The annual  $Hg_T$  concentrations assigned to hydrologic fluxes are in **Table 7**; seasonal VWA meHg concentrations are in **Table 8**.

**Table 5.** Annual Hydrologic Budgets for Devils Lake, 2002-2004 (from DL Hydrology Report)

Year	-----Inputs-----			-----Outputs-----			Change in Lake Storage ( $\Delta S$ ) ( $m^3$ )
	Precip (P) ( $m^3$ )	Surface Runoff (RO) ( $m^3$ )	Tributary Flow ( $Q_{in}$ ) ( $m^3$ )	Evap (E) ( $m^3$ )	Distributary Flow ( $Q_{out}$ ) ( $m^3$ )	Lake Seepage (GO) ( $m^3$ )	
2002	124,007	16,917	287,331	65,988	318,986	38,474	4,808
2003	90,442	7,589	128,889	65,988	175,704	10,520	-25,293
2004	108,208	7,595	128,990	65,988	163,389	17,167	-1,751
mean	107,552	10,700	181,737	65,988	219,360	22,053	-7,4121
SD	16,792	5,384	91,448	6,243 <sup>a</sup>	86,498	14,604	15,829

**Table 6.** Seasonal Hydrologic Budgets for Devils Lake, 2002-2004

Year	-----Inputs-----			-----Outputs-----			Calc. Change in Lake Storage ( $\Delta S$ ) ( $m^3$ )	Obs. Change in Lake Storage ( $\Delta S$ ) ( $m^3$ )	Residual ( $m^3$ )
	Precip (P) ( $m^3$ )	Surface Runoff (RO) ( $m^3$ )	Stream Flow ( $Q_{in}$ ) ( $m^3$ )	Evap (E) ( $m^3$ )	Stream Flow ( $Q_{out}$ ) ( $m^3$ )	Lake Seepage (GO) ( $m^3$ )			
2002	71394	7482	231360	39593	231182	13914	25547	25547	42373
2003	48858	5121	128888	39593	175704	4208	-36638	-34811	-1827
2004	47427	4971	128990	39593	163389	6679	-28273	-36633	8360
mean	55893	5858	163079	39593	190092	8267	-13121	-29423	16302
SD	13443	1409	59132	-	36114	5044	33748	10947	23146

P calculated from seasonal Laona 6SW precipitation amount and lake area

RO estimated from seasonal precipitation, run-off coefficient = 0.10, and near-shore area = 12.3 ha

$Q_{in}$  estimated as seasonal Inlet discharge (DL Hydrology Report)

E 60% annual evaporation

$Q_{out}$  estimated as seasonal Outlet discharge (DL Hydrology Report)

GO prorated from GO in annual hydrologic budgets

Calc..  $\Delta S$  calculated by difference

Obs.  $\Delta S$  calculated from staff gauge readings and hypsometric curve

Residual Calc  $\Delta S$  – Obs  $\Delta S$

**Table 7.** Hg<sub>T</sub> concentrations (ng/L) used to construct annual budgets for waterborne Hg<sub>T</sub> in Devils Lake, 2002 - 2004

<b>Year</b>	<b>Precip (P)</b>	<b>Tributary Stream (Q<sub>in</sub>) and Surface Runoff (RO)</b>	<b>Distributary Stream (Q<sub>out</sub>) and Lake Seepage (GO)</b>
2002	12.1	11.4	2.9
2003	11.2	7.1	3.5
2004	9.1	9.1	3.2
<b>mean</b>	10.8	9.2	3.2
<b>SD</b>	1.5	2.2	0.3

**Table 8.** MeHg concentrations (ng/L) used to construct seasonal budgets for waterborne meHg in Devils Lake, 2002 - 2004

<b>Year</b>	<b>Precip (P)</b>	<b>Tributary Stream (Q<sub>in</sub>) and Surface Runoff (RO)</b>	<b>Distributary Stream (Q<sub>out</sub>) and Lake Seepage (GO)</b>
2002	0.17	0.24	0.28
2003	0.15	0.21	0.44
2004	0.15	0.18	0.30
<b>mean</b>	0.15	0.21	0.34
<b>SD</b>	0.01	0.03	0.09

## 4. References

Citations of DL Hydrology Report refer to:

*Atmospheric Deposition and Biogeochemistry of Mercury and other Trace Contaminants in Aquatic Ecosystems, Final Project Report Part 1: Devils Lake Watershed Hydrology 2002 – 2004*, prepared by Morrison KA and Watras CJ, December 2005.

The following references are completely cited in Section 5. Complete copies of the published papers and abstracts of the oral presentations are included.

Eckley *et al.* 2005

Watras *et al.* 2005

Watras *et al.* 2006

Kent *et al.* 2005a, b, c

Other works cited:

Frost 1995

Frost T.M., Montz P.K., Kratz T.K., Badillo T., Brezonik P.L., Gonzalez M.J., Rada R.G., Watras C.J., Webster K.E., Wiener J.G., Williamson C.E., Morris D.P. 1999. Multiple stresses from a single agent: diverse responses to the experimental acidification of Little Rock Lake, Wisconsin. Limnol. Oceanogr. **44**(3, part 2): 784-794.

Bloom N.S., Watras C.J. 1989. Observations of methylmercury in precipitation. Sci. Tot. Environ. **87/88**: 199-207.

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Bloom N.S., Horvat M., Watras C.J. 1995. Results of the international aqueous mercury speciation intercomparison exercise. Water Air Soil Pollut. **80**: 1257-1268.

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Hudson R.J.M., Gherini S.A., Watras C.J., Porcella D.B. 1994 Modeling the biogeochemical cycling of mercury in lakes: the Mercury Cycling Model (MCM) and its application to the MTL study lakes. In: Watras C.J. and Huckabee J.W., eds. *Mercury Pollution: Integration and Synthesis*, Lewis Publishers. p. 473-526.

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- Ullrich S.M., Tanton T.W., Abdrashitova S.A. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. Critical Reviews in Environmental Science and Technology **31**(3): 241-293.
- US EPA. 2001. Method 1630: Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS (EPA-821-R01-020). Office of Water, Engineering and Analysis Division, Office of Science and Technology, EPA-821-R01-020. Washington, DC
- US EPA. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (EPA 821-R-02-019). Office of Water, Engineering and Analysis Division, Office of Science and Technology, EPA 821-R-02-019. Washington DC.
- Watras C.J., Bloom N.S., Hudson R.J.M., Gherini S., Munson R., Claas S.A., Morrison K.A., Hurley J., Wiener J.G., Fitzgerald W.F., Mason R., Vandal G., Powell D., Rada R., Rislov L., Winfrey M., Elder J., Krabbenhoft D., Andren A.W., Babiarez C., Porcella D.B., Huckabee J.W. 1994 Sources and fates of mercury and methylmercury in Wisconsin lakes. In: Watras C.J. and Huckabee J.W., eds. *Mercury Pollution: Integration and Synthesis*, Lewis Publishers. p. 153-177.
- Watras C.J., Morrison K.A., Back R.C. 1996 Mass balance studies of mercury and methylmercury in small, temperate/boreal lakes of the northern hemisphere. In: Baeyens W., Ebinghaus R. and Vasiliev O., eds. *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances.*, NATO Advanced Science Institute Series 2: Environment, Kluwer Academic Publishers. p. 329-358.
- Watras C.J., Back R.C., Halvorsen S., Hudson R.J.M., Morrison K.A., Wente S.P. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Sci. Tot. Environ. **219**: 183-208.

## 5. Published works

To date, results of the cooperative FCPC/WDNR project have been published in three peer-reviewed technical papers and three oral papers that were presented at international scientific meetings in the US and Europe. The peer-reviewed technical papers were published in three highly-regarded international journals: 1) The Canadian Journal of Fisheries and Aquatic Sciences, 2) Environmental Science and Technology and 3) Limnology and Oceanography. Those citations, in order of publication are:

Eckley C., Watras C.J., Hintelmann H., Morrison K., Kent A., Regnell O. 2005. Mercury methylation in the hypolimnetic waters of lakes with and without connection to wetlands in northern Wisconsin. Can. J. Fish. Aquat. Sci. **62**: 400-411.

Watras C.J., Morrison K.A., Kent A., Price N., Regnell O., Eckley C., Hintelmann H., Hubacher T. 2005. Sources of methylmercury to a wetland-dominated lake in northern Wisconsin. Environ. Sci. Tech. **39**(13): 4747-4758.

Watras C.J., Morrison K.A., Regnell O., Kratz T.K. 2006. The methylmercury cycle in Little Rock Lake during experimental acidification and recovery. Limnol. Oceanogr. **51**(1): 257-270.

Citations for the oral papers are:

Kent, A.D., C. J. Watras, C. Eckley, O. Regnell, K. D. McMahon and H. Hintelmann. 2005. Microbial community composition and mercury methylation in the anoxic hypolimnia of stratified Wisconsin lakes. ASLO Annual Summer Meeting, June 19-24, 2005, Santiago de Compostela, Spain

Kent, A.D., C. J. Watras, C. Eckley, O. Regnell, K. D. McMahon and H. Hintelmann. 2005 Mercury Methylation Varies with Pelagic Microbial Community



Composition in Lakes Within the Great Lakes Basin. International Association for Great Lakes Research: 48<sup>th</sup> Annual Meeting, Ann Arbor MI, May 23-27, 2005.

Kent, A.D. C.J. Watras, O. Regnell, C. Eckley and H. Hintelmann. 2005. Analysis of microbial community structure associated with mercury methylation in northern Wisconsin lakes. Am. Soc. Limnol Oceanogr. Aquatic Sciences Meeting, Salt Lake City, February, 2005

Complete copies of the technical papers and published abstracts of the oral papers follow.

## **6. Appendices**

### **Appendix A1. DL Stream Data**

#### ***A1.1. H&W data: 1995 - 2002***

- A1.1.1. Tributary Stream (Upstream site)
- A1.1.2. Tributary Stream (Inlet site)
- A1.1.3. Distributary Stream (Outlet site)

#### ***A1.2. TRL data: 2003***

- A1.2.1. Tributary Stream (Inlet site) Summary
- A1.2.2. Tributary Stream (Inlet site) Total mercury data
- A1.2.3. Tributary Stream (Inlet site) Methylmercury data
- A1.2.4. Tributary Stream (Inlet site) pH, SPM and Chl *a* data
- A1.2.5. Distributary Stream (Outlet site) Summary
- A1.2.6. Distributary Stream (Outlet site) Total mercury data
- A1.2.7. Distributary Stream (Outlet site) Methylmercury data
- A1.2.8. Distributary Stream (Outlet site) pH, SPM and Chl *a* data

#### ***A1.3. FCPC data: 2004***

- A1.3.1. Tributary Stream (Upstream site)
- A1.3.2. Tributary Stream (Inlet site)
- A1.3.3. Distributary Stream (Outlet site)

### **Appendix A2. DL Lake Data**

#### ***A2.1. H&W data: 1995-2002***

- A2.1.1. Lake1 site
- A2.1.2. Lake2 site

#### ***A2.2. TRL data: 2002-4***

- A2.2.1. Data summary
- A2.2.2. Total mercury data
- A2.2.3. Methylmercury data
- A2.2.4. pH, SPM and Chl *a* data

#### ***A2.3. FCPC data: 2004***

### **Appendix A3. Precipitation Data: 2002-2004**

#### ***A3.1. FCPC site***

- A3.1.1. FCPC summary
- A3.1.2. FCPC duplicate IVL data

#### ***A3.2. Trout Lake site***

### **Appendix A4. Total Gaseous Mercury Data**

#### ***A4.1. Mean Daily TGM at Trout Lake site***

#### ***A4.2. Mean Hourly TGM at Trout Lake (CD only)***

#### ***A4.3. TEK files (CD only)***