

Sources of Methylmercury to a Wetland-Dominated Lake in Northern Wisconsin

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Several lines of evidence suggest that wetlands may be a major source of methylmercury (MeHg) to receiving waters, perhaps explaining the strong correlation between concentrations of waterborne MeHg and dissolved organic carbon (DOC) in regions such as northern Wisconsin. We evaluated the relative importance of wetland export in the MeHg budget of a wetland-dominated lake in northern Wisconsin using mass balance. Channelized runoff from a large headwater wetland was the major source of water and total mercury (Hg^T) to the lake during the study period. The wetland also exported MeHg in high concentrations (0.2–0.8 ng L⁻¹), resulting in an export rate similar to those reported for other northern wetlands (ca. 0.3 μg MeHg m⁻² y⁻¹). Yet, based on intensive sampling during 2002, the mass of MeHg that accumulated in the lake during summer was an order of magnitude greater than the export of MeHg from the wetland to the lake. Hence, a large in-lake source of MeHg is inferred from the mass balance. Most of the accumulated MeHg built-up in anoxic hypolimnetic waters; and the build-up was roughly balanced by losses of inorganic Hg (Hg^(II)) implying a chemical transformation within the anoxic water column. An abundance of sulfate-reducing bacteria (SRB) in hypolimnetic waters, established by DNA analysis of the pelagic microbial community, along with a previous report documenting high methylation rates in the hypolimnion of this lake (ca. 10% d⁻¹), suggest that this transformation was microbially mediated. These findings indicate that the direct effect of wetland runoff may be outweighed by indirect effects on the lacustrine MeHg cycle, enhancing the load of Hg^(II),

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the activity of SRB, and the retention of MeHg, especially in northern lakes with flushing times longer than six months.

Introduction

Methylmercury (MeHg) production underlies the global problem of mercury contamination in freshwater fish because it is the chemical form of Hg that accumulates in aquatic food webs and poses the greatest risk to humans and piscivorous wildlife. For remote and otherwise pristine lakes, the methylation of atmospherically deposited Hg^(II) is mediated by bacteria that inhabit anoxic sediments, hypolimnetic water, and associated wetlands (4, 11–15). Although the relative importance of these methylation sites may vary seasonally and spatially, several studies suggest that wetlands are the principal source of MeHg to lakes when wetland runoff dominates the catchment hydrology (2, 4, 6, 16). Water discharged from wetlands is generally enriched in MeHg relative to precipitation or water flowing through uplands (2, 9, 10, 17); and the concentration of MeHg in lakes or rivers is often related to the amount of wetland in their catchments (6, 18, 19). While wetlands are geochemical sinks for most contaminants, including Hg^(II), wetlands are often net sources of MeHg, especially during periods when hydrologic discharge occurs as overland flow (9, 10, 16). The biogeochemical process governing MeHg production in wetlands appears to be similar to that observed in the sediments and anoxic waters of lakes—i.e. microbially mediated methylation associated with dissimilatory sulfate reduction (14, 20).

Among lakes in northern Wisconsin, the strongest environmental correlate of waterborne MeHg is dissolved organic carbon (DOC, $r^2 = 0.85$) (18). For these lakes, the concentration of waterborne MeHg varies by more than 10-fold; and the standardized concentration of MeHg in yellow perch (*Perca flavescens*) varies by a similar amount (21). Since the DOC is mainly of wetland origin, and since wetlands are known to be net sources of MeHg, it seems clear that wetland runoff has an impact on the lacustrine MeHg cycle. However, it is not clear whether the impact arises directly from enhanced MeHg loading or indirectly from some other property of wetland runoff. In addition to exporting MeHg, wetland runoff also exports Hg^(II), inorganic nutrients, and organic matter—thereby providing substrates that could stimulate microbially mediated methylation within the lakes themselves, as implied by high specific rates of methylation in dark water versus clear water Wisconsin lakes (3). DOC of wetland origin also has light attenuating properties which would retard the photodestruction of MeHg (*sens. Sellers (1)*); and as a strong metal-binding ligand, DOC would help to retain MeHg in the water column. In either case, one might expect a greater accumulation of MeHg in lakes influenced by wetland runoff.

There are few published studies which provide sufficient detail to establish the relative importance of various MeHg sources to any given lake. A notable exception is the MeHg budget for Lake 240 in the Canadian Experimental Lakes Area (L240, ELA) (1). For L240, the net accumulation of MeHg in the water column during summer was large relative to external sources; and when gross internal methylation was estimated by accounting for all other sources and sinks, including photodemethylation, it was 20-fold larger than the sum of pluvial and fluvial MeHg sources. Similar conclusions were drawn from the early mass balance for MeHg in precipitation-dominated Little Rock Lake (LRL) (7). But the

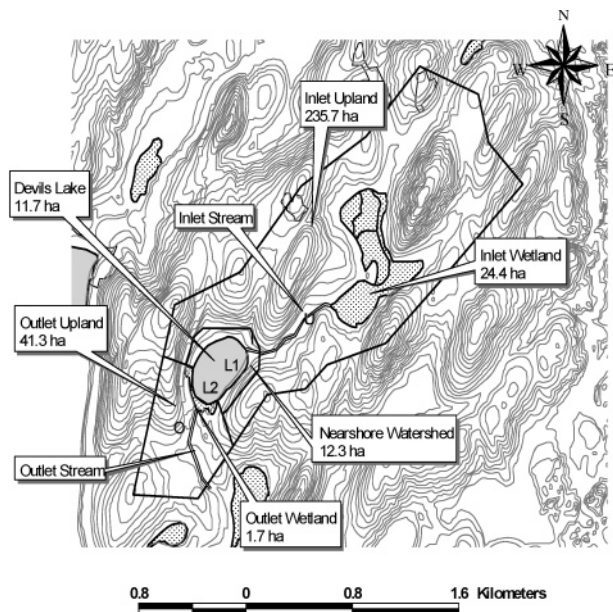


FIGURE 1. Devils Lake watershed, Forest County, WI (N 45° 32.954', W 88° 50.040'). Watershed boundaries delineated topographically. Contour interval = 10 ft. Direction of water flow from northeast to southwest. Sampling sites: U, upstream (wetland outfall); I, inlet; L1, lake 1; L2, lake 2; O, outlet (below outlet wetland).

hydrologic influence of wetland on both L240 and LRL was moderate to low; and modeling studies have indicated that the relative importance of wetland MeHg export should be proportional to the amount of wetland in the contributing catchment (4). For hypothetical lakes, modeling has shown that internal production could dominate the MeHg budgets of lakes without significant wetland influence; but for lakes with strong hydrologic connection to wetland, watershed inputs of MeHg are more likely to be the principal source.

To empirically test this hypothesis, a mass balance study of Hg_T and MeHg was conducted in a small, dark-water drainage lake situated in a well-defined, forested watershed containing a relatively large headwater wetland that discharged directly to the lake via a short stream. For several years prior to the mass balance study, the lake and its watershed were monitored seasonally to roughly constrain the hydrologic budget and the range of solute concentrations in the wetland runoff, the water column of the lake, and in the distributary stream. Then during 2002, intensive sampling of the entire drainage was conducted and a mass balance was constructed by coupling the hydrologic budget with frequently measured concentrations of Hg_T and MeHg—focusing on the summer period when MeHg accumulates in the water column. During peak stratification, the pelagic microbial community was also investigated, focusing on the distribution of sulfate-reducing bacteria (SRB) in the water column, since SRB are generally considered to be the principal methylators of mercury in aquatic ecosystems (11, 13, 22–27).

Methods

Study Site. Devils Lake (N 45° 32.954', W 88° 50.040') is a dark-water drainage lake in Forest County, Wisconsin, with a surface area of roughly 12 ha, a volume of $3.5 \times 10^5 \text{ m}^3$, a maximum depth of 7.6 m, a mean depth of 3 m, and a water residence time of roughly 1 year. The terrestrial watershed comprises a headwater wetland roughly twice the size of the lake encircled by gently sloping, forested uplands that surround the headwater wetland and the lake itself (Figure 1). 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 (28).

The lake and its forested watershed are situated in thick, unconsolidated till deposited as glacial ice advanced and retreated several times across the area between approximately 22 000 and 12 000 years BP (29). Devils Lake is most likely perched in till of the youngest of the lithostratigraphic till units in the area (the Nashville Member of the Copper Falls Formation) (28). 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 to 49 m in general (30). The moderate to low permeability of the glacial-till-derived soils that comprise the Devils 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 Devils 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 (28). This hydrologic setting simplifies construction of a water budget since groundwater inputs may be considered negligible.

Hydrologic Budget. Hydrologic inputs and outputs to the lake and changes in lake stage were directly measured or estimated for water year 2002 (October 1, 2001–September 30, 2002). Because the lake is perched above the surrounding groundwater system, inputs were limited to direct precipitation (P), surface runoff (RO) from the near-shore watershed, and surface water flow via the tributary stream that emanates from the headwater wetland (Q_{in}). Outputs were from evaporation (E), outflow through the distributary stream (Q_{out}), and seepage (G_{out}) through the lake bottom. The resulting lake water balance equation was

$$\Delta S = (P + RO + Q_{in}) - (E + Q_{out} + G_{out})$$

where ΔS represents the change in lake storage. Inflow to the lake as subsurface flow in the unsaturated zone and outflow due to aquatic plant transpiration were considered to be negligible.

Weekly precipitation amounts for the full 2002 water year were obtained from the National Climatic Data Center for the Laona 6 SW weather station located less than 20 km from the study area (31). These data were compared to on-site precipitation data collected weekly beginning in May 2002. Agreement between the two sites was good, with roughly 51 and 54 cm of precipitation falling between May and October (28).

Streamflow-in and streamflow-out were calculated from continuous stage recordings and stage–discharge relationships that were established following the standard USGS protocol (32, 33) using mini (pygmy) Price “AA” flow meters with top-set wading rods. Stage measurements at both the inlet and outlet streams were made at 15-minute intervals using baro-compensated, data-logging pressure transducers for the unfrozen portion of the year (early April through November). The resultant 15-minute estimates of water discharge were later integrated over appropriate time intervals to estimate weekly, monthly, or seasonal discharge amounts.

Lake storage volume was calculated as a function of lake stage and lake bathymetry. Lake stage was measured at 15-

minute intervals with an electronic data logger, as with stream stages. Lake bathymetry was measured in the autumn of 1995 with sonar equipment and the gathered depth data were plotted and contoured to create a representative bathymetric map of the lake. On the basis of the lake bathymetry and the record of stage changes, a hypsographic expression was developed to estimate the volume of the lake at successive depth intervals.

Nonchannelized runoff from the unmonitored portion of the near-shore watershed was estimated by applying a runoff coefficient of 0.10 to the 12.3-hectare area of forest that lies between the lakeshore and the encircling gravel road. This runoff coefficient was derived from the water yield estimated for the full inlet upland (Figure 1) by comparing total precipitation load to total streamflow volume for the water year. Thus, it accounts for the loss of runoff due to infiltration and evapotranspiration.

The annual evaporation rate (mm y^{-1}) for Devils Lake was assumed to be the same as that developed by the USGS for Little Rock Lake in neighboring Vilas County, which borders Forest County to the northwest (34). These rates were based on Class-A evaporation-pan data converted to lake evaporation by applying lake-pan coefficients developed from data collected at Rainbow Reservoir, which lies between Little Rock Lake and Devils Lake. For Devils Lake, the mean evaporation rate estimated for a 7 year period that covered both wet and dry years ($564 \pm 20 \text{ mm y}^{-1}$, se) was used (34). Out-seepage from the lake to groundwater (G_{out}) was determined in the water balance equation by difference, once values for all other variables were input.

Background Water Quality Monitoring. Surface-water monitoring was conducted from 1996 through 2001 to roughly characterize the spatial and temporal variability of solutes within the watershed. Five sampling stations were established along a transect from the headwater wetland through the lake to the outlet stream just below the outlet wetland (Figure 1). Grab samples were collected at these stations 3–4 times each year during spring, summer, and fall. Conductivity and pH were monitored in the field using hand-held meters. Samples were analyzed for alkalinity, dissolved organic carbon (DOC), total Kjeldahl nitrogen (TKN), total phosphorus (TP), and chlorophyll-a (Chl-a) at ERA Labs, Inc., Duluth, MN.

The collection of samples for mercury analysis followed clean techniques as in USEPA Method 1669 (35). Duplicate whole water samples were collected by immersing acid-cleaned Teflon bottles just below the water surface taking care not to disturb sediments or collect surface film. The bottles were rinsed three times to condition the bottle walls prior to final sample collection. The mercury samples were hermetically sealed and double-bagged for transport on ice by overnight express to Frontier Geosciences, Inc. (Seattle, WA) where they were analyzed using purge-trap/CVAFS for Hg_T and ethylation/GC/CVAFS for MeHg (5, 36, 37).

Intensive Surface-Water Sampling for Mercury Budgets during 2002. Intensive monitoring of the streams, lake, and local precipitation began in 2002 at the start of the spring melt. Streamwater samples were collected weekly beginning at the onset of melt using sampling and analytical protocols 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 with the pygmy meters. The streamwater samples were shipped on ice in dark coolers to Frontier Geosciences by overnight express, where they were analyzed for Hg_T and MeHg.

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 nonmetallic 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 $1\text{--}2 \text{ cm s}^{-1}$ at a station located about 3–5 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, nonmetallic 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. (21). The collection of water samples began when the unit reached the first target depth. Generally 5–7 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 where they were analyzed following protocols similar to those used at Frontier Geosciences, i.e., EPA Methods 1630 and 1631 (38, 39). Inter-calibration between these two analytical facilities has shown good agreement for both Hg_T and MeHg analysis in freshwater samples (40). All samples were analyzed in duplicate for Hg_T and MeHg.

Analytical protocols for ancillary analytes (pH, DOC, SO_4^{2-} , total sulfide, suspended particulate matter, major cations, anions, and metals) in lake water profiles followed methods described by Watras (18).

Precipitation Sampling. Bulk precipitation was sampled continuously with weekly integrated collections during 2002 using modified IVL-type collectors (41) at two sites. One site was the US NADP/MDN site No. 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. Duplicate IVL-collectors were operated continuously at the Devils Lake site beginning in May 2002. Comparison between the IVL collectors at Devils Lake and Trout Lake showed that the volume-weighted average concentration of Hg_T differed by roughly 7% during the 18 weeks of parallel sampling in water year 2002 (10.7 vs $10.0 \text{ ng Hg}_T \text{ L}^{-1}$, respectively), indicating locally coherent Hg depositional regimes.

The direct atmospheric deposition of MeHg to the surface of Devils Lake was estimated to be 1.3% of the atmospheric Hg_T deposition during water year 2002, based on NADP/MDN data for the Trout Lake site. During 2002 and 2003, MeHg constituted 0.5% and 2%, respectively, of the annual Hg_T 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 (7, 42).

Although bulk, open-field depositional estimates probably underestimate the total atmospheric deposition of Hg_T and MeHg to the Devils Lake watershed (due to throughfall and litterfall effects), they provide a reasonable estimate of direct pluvial inputs to the surface of the lake. Furthermore, the estimates of loading to the lake via streamflow and nearshore runoff would by definition integrate the watershed yield of Hg_T and MeHg from all sources combined.

Quality Control and Quality Assurance Criteria for Aqueous Mercury Determinations. QA/QC criteria for Hg_T and MeHg in rain, stream, and lake water closely followed those specified in EPA Methods 1630 and 1631. For samples analyzed at the Trout Lake facility, the method detection limits were 0.05 ng Hg_T L⁻¹ (estimated from the pooled variance of method blanks, *n* = 225) and 0.03 ng MeHg L⁻¹ (pooled variance of distillation blanks, *n* = 123). Ongoing precision was 99.7% ± 6.3% for Hg_T (mean ± SD, *n* = 707) and 100.6% ± 10.2% for MeHg (*n* = 570). Lab duplicate and field duplicate RPDs (relative percent difference between duplicates) averaged 5% ± 5% (*n* = 99) and 7% ± 7% (*n* = 32) for Hg_T; and they averaged 8% ± 7% (*n* = 88) and 8% ± 8% (*n* = 29) for MeHg in Devils Lake and streamwater samples. Lab duplicate and field duplicate RPDs for Hg_T in precipitation samples were slightly higher, averaging 10 ± 10% (*n* = 107) and 15% ± 15% (*n* = 12), respectively.

Mass Balance Calculations. Seasonal mass balances for waterborne Hg_T and MeHg in Devils Lake were constructed for the period from spring overturn to peak summer stratification when mercury accumulates in the water column (May 30 to August 19, 2002). Mercury budgets were also compiled for the entire water year. The governing expression was

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

where ΔS_{Hg} is the change in waterborne mercury mass (storage); P_{Hg} is the mass deposited atmospherically directly on the lake; $Q_{\text{in-Hg}}$ is the mass delivered from the upstream wetland via the inlet stream; RO_{Hg} is the mass of mercury in nonchannelized runoff in the nearshore zone; $Q_{\text{out-Hg}}$ is the mass lost to the outlet stream; $G_{\text{out-Hg}}$ is the mass lost to groundwater; E_{Hg} is the mass lost by evasion across the air/water interface; S_{Hg} is the mass lost to sediments; and M_{net} is the mass of MeHg in the water column attributable to net in-lake methylation. For the Hg_T budget, M_{net} is zero.

Change in storage (ΔS_{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 $\sum c_i v_i$, 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_{Hg}) was the product of the volume-weighted average mercury concentration in bulk deposition times the amount of precipitation falling directly on the lake. Stream in-flow ($Q_{\text{in-Hg}}$) was estimated as $\sum c_t v_t$, 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 midpoints between successive time intervals. Nonchannelized runoff (RO_{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 streamwater (i.e., assuming the same mercury concentration in channelized and nonchannelized overland flow). 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). Ground-

water recharge was seasonally pro-rated from the annual hydrologic budget. Evasion and sedimentation were estimated as a pooled residual loss term: $(E + S)_{\text{Hg}} = (P_{\text{Hg}} + Q_{\text{in-Hg}} + \text{RO}_{\text{Hg}}) - (Q_{\text{out-Hg}} + G_{\text{out-Hg}} + \Delta S_{\text{Hg}})$. For MeHg, this term was approximated as 1% of $(E + S)_{\text{HgT}}$ since MeHg constitutes roughly 1% of the Hg_T in sediments but it does not evade across the air-water interface to a significant degree (8, 15, 21, 43). Note that $(E + S)_{\text{MeHg}}$ is probably a lower limit since demethylation in the sediment is not considered. Net methylation (M_{net}) was calculated according to: $M_{\text{net}} = \Delta S_{\text{MeHg}} + (Q_{\text{out-MeHg}} + G_{\text{out-MeHg}} + (E + S)_{\text{MeHg}}) - (P_{\text{MeHg}} + \text{RO}_{\text{MeHg}} + Q_{\text{in-MeHg}})$. M_{net} is a conservative estimate for the mass in the water column attributable to in-lake production (regardless of 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_{net} includes demethylation in the water column.

Microbial Community Composition. In addition to sampling Devils Lake for mercury species and ancillary chemical analytes, water samples were also collected to characterize the microbial community at specific depths during peak stratification in 2002. These samples were filtered through 0.2- μm filters during collection and the filters were then preserved at -80 °C until processed. To obtain a DNA "fingerprint" of the diversity of bacteria at each depth, the PCR-based terminal restriction length polymorphism (T-RFLP) technique was used on 16S rDNA from each sample (44, 45). Reaction conditions have been previously described (46). A web-based resource for analysis of T-RFLP profiles (<http://trflp.limnology.wisc.edu>) was used to compare the resulting DNA fragment patterns with terminal restriction fragment (T-RF) lengths predicted from known 16S rDNA sequences, allowing phylogenetic assignment of individual fragments resolved from the digested PCR products (46). Of primary interest was the distribution of sulfate-reducing bacteria (SRB) in the anoxic hypolimnetic waters, since SRB have been implicated as the principal methylators of mercury in aquatic systems.

Results and Discussion

Background Surface Water Monitoring. Seasonal sampling of surface waters along the longitudinal transect from the headwater wetland through the outflowing stream indicated that the wetland was a potentially important source of several solutes to the lake. Data collected from 1996 through 2002 show that the inlet stream had consistently lower pH and higher concentrations of DOC, major ions, and nutrients than the surface water of Devils Lake (Table 1, Figure 2). Concentrations of Hg_T and MeHg were also higher in the inlet stream than in the lake surface water, by factors of roughly 4-fold for Hg_T and 1.6-fold for MeHg on average (Table 1, Figure 3).

Along the course of the inlet stream, concentrations of the measured solutes did not change substantially indicating that there was no preferential gain or loss of dissolved substances as the stream flowed through the short stretch of upland to the lake. These results strongly suggest that export from the headwater wetland was the major source of the solutes measured in streamwater. Background hydrologic studies suggested that the stream lost water to the upland water shed rather than gaining water as it flowed toward the lake, based on a decrease in discharge between the upstream and inlet stations (28). This observation is consistent with the hydrologic setting of the lake and stream described as perched above the local aquifer. Although the hydrologic loss may have been small, all ensuing budgets were based on measurements of water flow and solute concentrations made at the inlet site, near the entry point to the lake.

In the out-flowing stream, the concentration of several solutes increased relative to epilimnetic lake waters at certain

TABLE 1. Chemical Characteristics of Surface Waters in the Devils Lake Catchment along a Transect from the Headwater Wetland through the Outlet Stream^a

variable	units	method	sampling site				
			upstream	inlet	lake 1	lake 2	outlet
pH		field	3.7 (0.3,17)	3.8 (0.3,16)	5.3 (0.5,24)	5.3 (0.6, 18)	4.8 (0.3, 11)
Alkalinity	mg L ⁻¹ as CaCO ₃	SM 2320b 18th ed.	<1 (_,17)	<1 (_,16)	1.9 (0.9,16)	2.1 (1.1,10)	4.0 (2.0,3)
DOC	mg L ⁻¹	EPA 415.1	58.8 (19.1,16)	56.5 (18.8,15)	9.0 (1.8,23)	8.5 (1.5,17)	9.7 (3.0,10)
Hg _T (unfiltered)	ng L ⁻¹	EPA 1631	12.4 (10.1,32)	12.1 (5.5,31)	2.8 (1.7,24)	3.0 (2.0,20)	4.4 (1.3,26)
Hg _T (filtered)	ng L ⁻¹	EPA 1631	10.9 (8.5,22)	10.3 (3.6,23)	4.3 (1.1,11)	3.4 (3.7,7)	3.3 (1.0,20)
MeHg(unfiltered)	ng L ⁻¹	ref 5	0.50 (0.20,32)	0.45 (0.17,31)	0.31 (0.21,24)	0.29 (0.17,20)	1.09 (1.39,26)
MeHg (filtered)	ng L ⁻¹	ref 5	0.43 (0.20,22)	0.40 (0.16,23)	0.30 (0.24,10)	0.34 (0.20,7)	1.03 (1.27,20)

^a Sampling sites shown on Figure 1. Data are mean (SD, *n*) for all samples collected, 1996 through 2002. Lake 1 and lake 2 are epilimnetic waters.

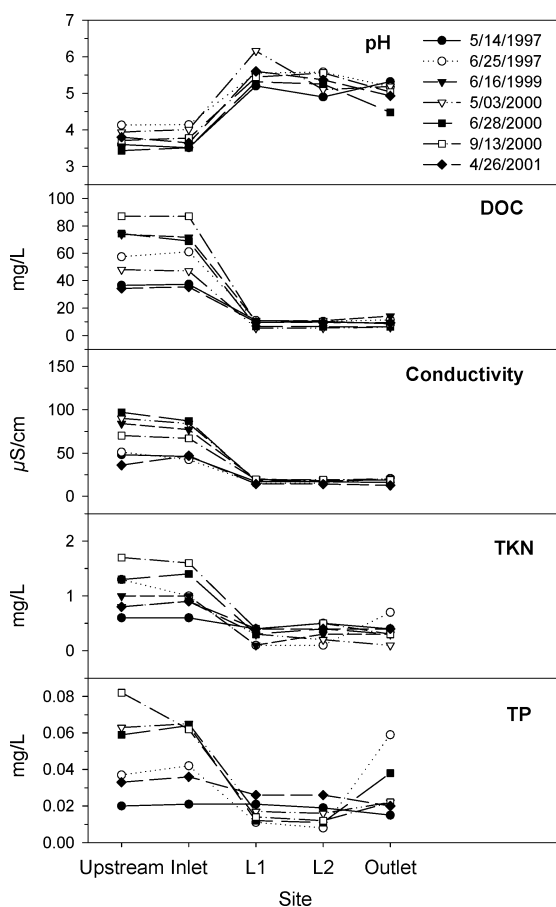


FIGURE 2. Spatial and temporal changes in water quality along transect from headwater wetland to outflow stream in the Devils Lake catchment. Sampling sites shown in Figure 1. Data only for dates on which all stations were sampled for all analytes.

times of year (Table 1, Figures 2 and 3). The observed increases were likely due to contributions from the small wetland that borders the upper-most reach of the outlet stream (Figure 1). Although the contribution was relatively small for most solutes, it was substantial for waterborne Hg species. The contribution of MeHg from the outlet wetland was occasionally large during mid-summer, as indicated by high variability in outlet streamwater (Figure 3; Table 1). This observation is consistent with the general notion that wetlands are a net source of MeHg to receiving waters. To

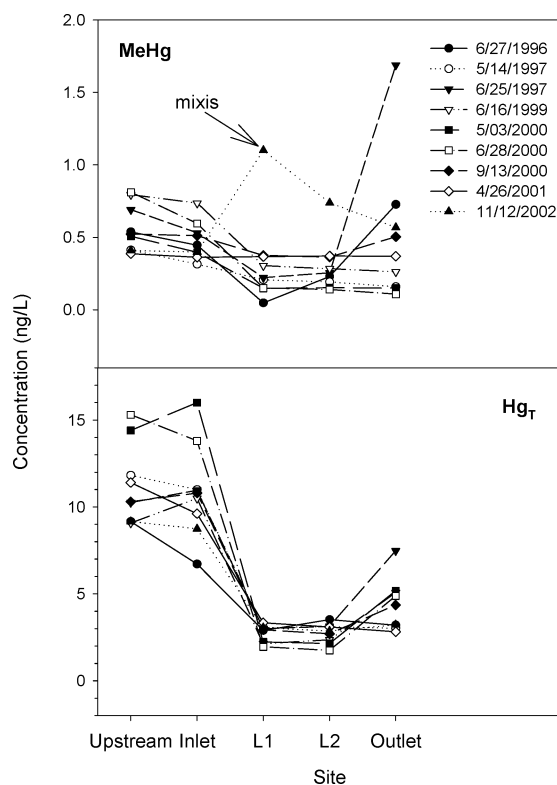


FIGURE 3. Spatial and temporal changes in the concentration of methylmercury (MeHg) and total mercury (Hg_T) along the transect from headwater wetland to the outflow stream in the Devils Lake catchment. Sampling sites as described for Figure 2.

compensate for this riparian wetland source, fluvial export from the lake was calculated using solute concentrations measured in epilimnetic lake water multiplied by the hydrologic discharge measured in the outlet stream.

Within the lake, background monitoring indicated seasonal pulses of MeHg in surface waters. Following mixis in autumn, the concentration of MeHg in epilimnetic lake water increased substantially, reaching concentrations >2-fold higher than those in inflowing streamwater (Figure 3). The autumn pulse of elevated epilimnetic MeHg was observed after mixis in November 2000, November 2001, and in October and November, 2003. The phenomenon is consistent with the entrainment of MeHg-rich profundal waters (see below).

TABLE 2. Hydrologic Budget for Devils Lake

water budget	Inflow (I) (10 ³ m ³)			Outflow (O) (10 ³ m ³)			storage change (ΔS) (10 ³ m ³)
	precipitation (P)	nearshore runoff (RO)	streamflow (Q _{in})	evaporation (E)	streamflow (Q _{out})	seepage (G _{out})	
annual ^a	130	14	200	66	150	120	8
seasonal ^b	44	5	58	40	33	56	-22

^a Annual budget: October 1, 2001 to September 30, 2002. ^b Seasonal budget: May 30 to August 19, 2002.

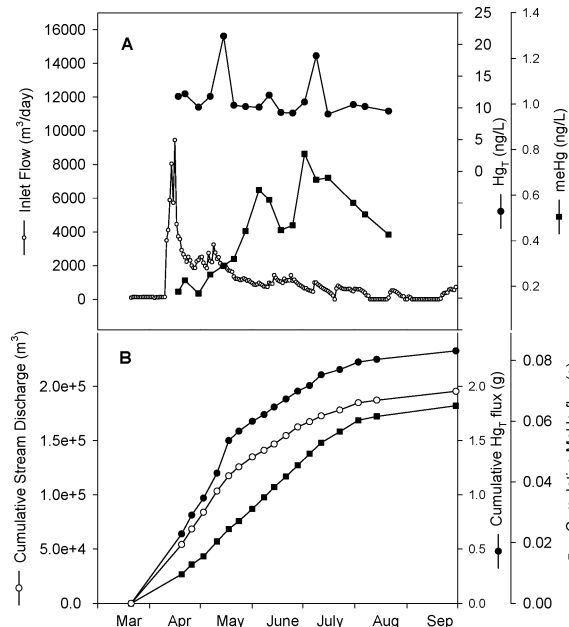


FIGURE 4. Inputs of water and mercury to Devils Lake via the inlet stream during 2002. Cumulative fluxes estimated as the product of weekly water discharge times the weekly mercury concentration, summed over time. Points in A and B do not line up because concentrations were measured at the midpoint of each flux interval. September flux based on August concentration.

Overall, the solute concentration gradients observed along the transect from headwater wetland to lake outlet indicate that the wetland was potentially an important source of H⁺, DOC, major ions, nutrients, Hg_T, and MeHg to the lake.

Water Budget. The hydrologic budget for 2002 indicated that the major sources of water to the lake were runoff emanating from the headwater wetland and direct precipitation onto the lake surface (Table 2). Tributary flow, direct precipitation, and diffuse runoff in the near-shore zone accounted for 58%, 38%, and 4% of the hydrologic budget over the full water year, respectively. The major losses of water occurred through distributary streamflow and out-seepage, which accounted for 45% and 36%, respectively, of the annual water outflow. During summer, however, evaporation and outseepage accounted for larger shares of the outgoing water; and as the inflow stream subsided there was a net loss of water from the lake that constituted roughly 8% of the mean lake volume, or 24 cm of depth, due largely to evaporation (Table 2).

The hydrograph for the inlet stream was characterized by high discharge from the melting snowpack during early spring, which is typical for northern watersheds (Figure 4A). Consequently, roughly half of the cumulative stream discharge to the lake occurred from the onset of spring melt in mid-March to early May (Figure 4B). Discharge from the inflowing stream declined until early autumn when the stream stopped flowing. The hydrograph for the outlet stream was similar to that of the inlet stream, with the majority of water flow occurring in early spring (Figure 5).

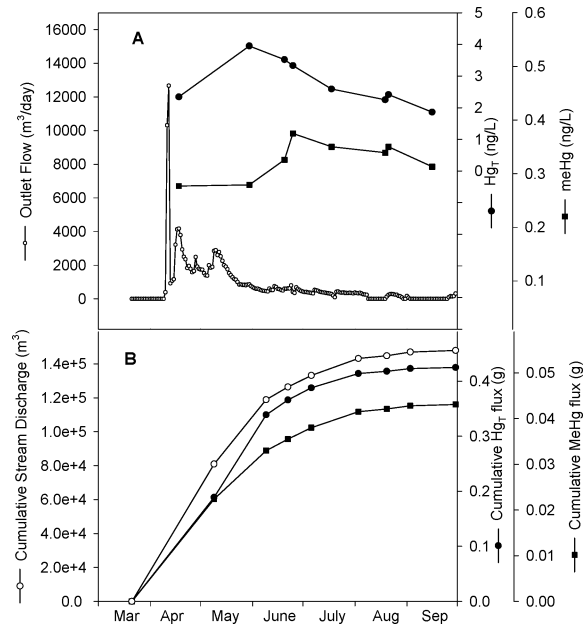


FIGURE 5. Outputs of water and mercury from Devils Lake via the outlet stream during 2002. To avoid chemical contributions from the outlet wetland, the mercury out-flux was estimated as the product of streamwater discharge (m³) times the concentration of Hg_T or MeHg in surface lake water (g/m³).

On the basis of the water budget for 2002, the hydrologic residence time in Devils Lake was estimated to be roughly 1 year (lake water volume/annual water input volume).

Total Mercury Budget. During spring and summer 2002, the concentration of Hg_T in the tributary stream varied from roughly 10 to 20 ng L⁻¹ (mean 11.6 ± 3.3 ng L⁻¹, SD) with a slight declining trend over time as streamflow subsided (Figure 4A). As a result of the relatively constant concentration over time, the cumulative fluvial flux of Hg_T to the lake paralleled the cumulative flux of water (Figure 4B). Roughly 60% of the tributary input of Hg_T to the lake occurred during spring runoff.

The mean concentration of Hg_T in precipitation falling directly on the lake was similar to that observed in the tributary stream, averaging roughly 11 ng L⁻¹ (Figure 6). Precipitation Hg_T increased during summer and declined in autumn, as observed at other sites in Wisconsin and elsewhere in North America (47). During the ice-free period, direct pluvial loading to the lake averaged roughly 3.5 μg Hg_T m⁻² week⁻¹ (Figure 6).

Since tributary flow was the largest single source of water to the lake, it was also the dominant source of Hg_T, delivering more than 60% of the Hg_T load annually and seasonally (Table 3). The other fluvial source, nearshore runoff, contributed an additional 4% of the total Hg_T load. Combined, these two fluvial sources constituted roughly two-thirds of the external Hg_T input. Direct pluvial inputs of Hg_T to the lake surface accounted for the remaining one-third (Table 3).

Within the lake, the concentration of Hg_T was relatively low and uniform throughout the water column during early

TABLE 3. Annual and Seasonal Mass Balances for Hg_T in Devils Lake during Water Year 2002

budget period	Inputs (mg)			Outputs (mg)			change in storage (ΔS) (mg)
	precipitation (P)	nearshore runoff (RO)	streamflow (Q _{in})	evasion & sedimentation (E + S)	streamflow (Q _{out})	out-seepage (G _{out})	
seasonal ^a	450	50	630	920	110	180	-80
annual ^b	1,260	160	2,380	2860	420	350	170

^a Seasonal budget period: May 30 to August 19, 2002. ^b Annual budget period: October 1, 2001 to September 30, 2002.

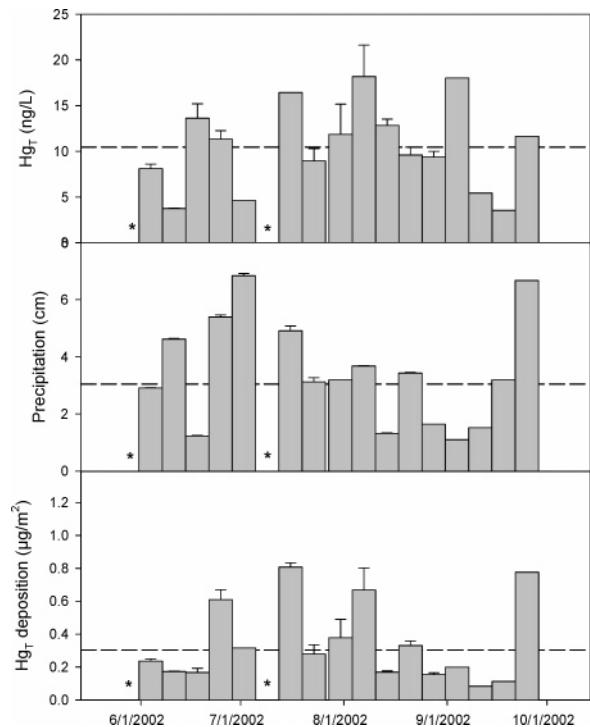


FIGURE 6. Pluvial inputs of water and Hg_T to Devils Lake from May to October 2002. Error bars indicate range of duplicate collectors. Asterisks indicate weeks with no precipitation. Dashed lines are mean values.

spring mixis; but as fluvial inputs flowed to the lake during spring melt, the waterborne concentration of Hg_T roughly doubled (Figure 7A). As summer stratification developed, the concentration of Hg_T declined progressively in the epilimnion while it increased progressively in the hypolimnion (Figure 7A)—suggesting that epilimnetic Hg_T was scavenged by particulate matter settling into profundal water. After autumn mixis, the concentration of Hg_T was again relatively uniform with depth (Figure 7B). Under ice-cover, when the lake was sealed from both fluvial and pluvial inputs, the concentration of waterborne Hg_T remained relatively steady.

The seasonal increase and decrease of waterborne Hg_T in Devils Lake is evident when changes in storage (mass Hg_T) are plotted over time (Figure 8). The whole-lake mass of waterborne Hg_T increased rapidly during spring melt, remained relatively constant during summer and declined again during fall and winter. A similar annual cycle has been observed for Hg_T in nearby Little Rock Lake, which is dominated by pluvial inputs (47). In Little Rock Lake the strong impact of spring melt was absent and the increase due to summer rain was more gradual.

The remaining terms of the Hg_T budget are shown in Table 3. As observed in other Wisconsin lakes, the major losses were attributable to sedimentation and evasion across the air–water interface. The individual magnitude of these two major loss processes was not quantified, since the primary

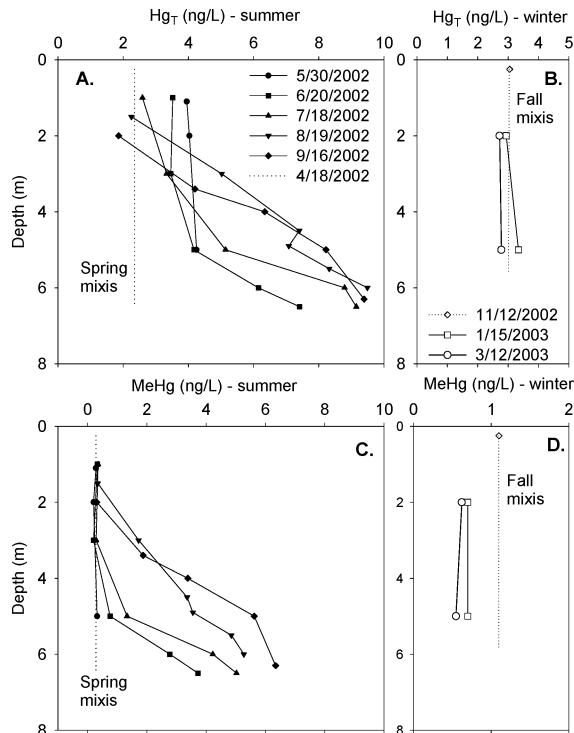


FIGURE 7. Seasonal depth profiles of Hg_T (A and B) and MeHg (C and D) in the water column of Devils Lake during spring–summer 2002 and the ensuing winter.

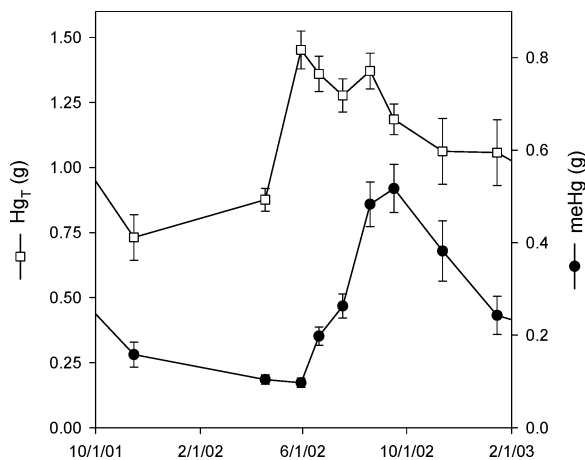


FIGURE 8. Annual cycles of waterborne Hg_T and MeHg in Devils Lake. Error bars indicate range of duplicates.

focus of this investigation was on MeHg rather than Hg_T. Nonetheless, the relative importance of the major loss processes for Hg_T operating in Devils Lake were similar to those previously observed in two nearby seepage lakes despite large differences in the water residence times (Table 4). In all three lakes, the estimated residence time for waterborne Hg_T (pool/influx) was shorter than the water residence time (<1 year, as observed for many lakes ranging in size from

TABLE 4. Comparison of Hg_T Loss Processes in Three Small Wisconsin Lakes

	Little Rock Lake ^a	Russett Lake ^a	Devils Lake
hydrology	seepage, clear water	seepage, dark water	drainage, dark water
Water residence time	4 y	4 y	1 y
Hg _T residence time ^b	149 d	296 d	96 d
Hg _T loss process			
sedimentation	82%	68%	79%
evasion	15%	28%	
groundwater recharge	3%	4%	10%
stream outflow	0	0	11%
total	100%	100%	100%

^a From refs 7 and 8. ^b Pool/flux.

small kettle lakes to large drainage lakes such as Lake Michigan (48)).

Methylmercury Budget. Waterborne MeHg also exhibited a strong annual cycle in Devils Lake, but the phases of the waterborne MeHg cycle were shifted in time relative to the annual Hg_T cycle (Figure 8). For MeHg, the spring increase began later and it built more gradually to a shorter-lived peak. As shown in Figure 7C, the spring melt did not deliver a large pulse of MeHg to the epilimnion. Instead, the concentration of MeHg gradually increased in the hypolimnion during summer stratification while epilimnetic concentrations remained relatively constant. By late summer, MeHg constituted 50–70% of the Hg_T at depth, reaching concentrations >6 ng L⁻¹ in the anoxic hypolimnion (c.f. Figure 7A and C). After autumn mixis the concentration of waterborne MeHg in the epilimnion increased dramatically as profundal water was entrained into the epilimnion (Figures 7D and 3). Then under ice-cover, waterborne MeHg concentrations declined to values close to those observed in spring (Figures 7D and 8). The winter decline suggests that sedimentation and/or demethylation dominate the MeHg cycle in the water column at this time of year. Since MeHg rarely constitutes more than 1% of the Hg_T in lake sediments (15)–1 or 2 orders of magnitude lower than the percentage in settling particles and macrobiota (21)—demethylation also appears to be an important process at the sediment surface.

The concentration of MeHg in wetland runoff averaged 0.45 ng L⁻¹ (± 0.19, SD) at the inlet site and it increased progressively from about 0.2 to 0.8 ng L⁻¹ between spring and midsummer (Figure 4A). As a result, MeHg loading via streamflow was relatively constant between April and August, as increasing concentrations offset decreasing flow (Figure 4B). For the spring–summer season, the average MeHg concentration at the inlet was about 50% higher than that observed in epilimnetic waters of the lake (0.30 ng L⁻¹ ± 0.05 ng L⁻¹, SD) and about 5-fold higher than MeHg concentrations in precipitation (0.1 ng L⁻¹ ± 0.05 ng L⁻¹, SD).

Thus, the external input/output budget for MeHg in Devils Lake during 2002 indicated that the major external source of MeHg was wetland runoff—as observed for Hg_T (Table 5). The inlet stream accounted for 76% of the externally supplied MeHg during the course of the year. Direct precipitation was the second largest source, contributing 18% of the annual MeHg load to the lake. On an areal basis, MeHg was exported from the wetland at a rate of 0.27 μg m⁻² y⁻¹, which is near the upper end of the ranges reported for northern temperate/boreal wetlands (Table 6).

The total mass of MeHg exported from the headwater wetland (67 mg) was potentially large enough to contribute to fish bioaccumulation in a significant way. Assuming that the rate of MeHg accumulation by the DL fish community was similar to that estimated for Little Rock Lake (which is

TABLE 5. Annual External Input/Output Budget for MeHg in Devils Lake during Water Year 2002

	budget term	MeHg mass (mg)
inputs	precipitation	16
	streamflow	67
	nearshore runoff	5
	total	88
outputs	streamflow	43
	groundwater recharge	35
	net sedimentation	29
	total	107

similar in surface area and volume, and supports a similar warm-water fishery of perch and bass), MeHg export from the wetland could potentially account for as much as half of the MeHg accumulated by fish annually (i.e., assuming a total of 200 mg MeHg in the fish pool turning over at a rate of 0.3 y⁻¹) (7).

Yet, when the external loads of MeHg are compared to the seasonal build-up of MeHg within the lake (ΔS_{MeHg}), the biogeochemical significance of wetland MeHg export becomes minor. The seasonal mass balance indicated that the internal production of MeHg was an order of magnitude larger than the external contribution from wetland runoff (Table 7). To account for the 385 mg MeHg that accumulated in the water column during summer, a net internal production of 382 mg was needed after taking all external sources and sinks into account. Given the balance between external inputs and losses, almost all of the observed change in MeHg storage can be attributed to internal production during summer.

Observed changes in the chemical speciation of waterborne Hg support the conclusion that MeHg was produced internally at high rates. During summer, MeHg accumulated in the water column at an average rate of 4.2 mg MeHg d⁻¹ while Hg^(II) was being depleted at a similar rate (5.5 mg d⁻¹; Figure 9A, Table 8). This similarity suggests that Hg^(II) was depleted mainly because of its transformation to MeHg. Within the epilimnion, Hg^(II) was lost at an average rate of 1.4 mg d⁻¹ while epilimnetic MeHg remained relatively constant, suggesting that Hg^(II) was removed from the epilimnion by processes such as evasion and sedimentation and that methylation took place elsewhere (Figure 9B, Table 8). Most of the MeHg increase within the lake occurred in the anoxic hypolimnion, where MeHg increased at nearly the same rate that Hg^(II) was depleted (ca. 4 mg d⁻¹) (Figure 9C, Table 8). These observations suggest that the summer build-up of MeHg in the hypolimnion resulted from the in situ transformation of Hg^(II) entering from above. It seems less likely that Hg^(II) was depleted from the hypolimnion entirely by sedimentation since this loss would need to be balanced almost exactly by the diffusion of MeHg from profundal sediments. Previous experimental studies in Wisconsin and Canada have indicated that profundal sediments do not methylate Hg^(II) at high rates (12, 49). Chemical modeling suggests that most of the Hg^(II) in these anoxic, sulfidic waters may be present as soluble Hg–S complexes, which may be highly bioavailable to methylating microbes in the water column (43, 50, 51). The high percentage of Hg_T being present as MeHg in the hypolimnion (68%) suggests that the availability of Hg^(II) for methylation, once it enters the anoxic hypolimnion, is indeed high (c.f. Figure 7A and C).

The Hypolimnetic Microbial Community. Fine-scale biological profiles mapped by the SeaBird sonde indicate that layers of anaerobic microbes inhabited the water column below the oxic/anoxic boundary, as evidenced by sharp peaks in the in vivo fluorescence signal (bacteriochlorophylls) and

TABLE 6. Export Rates for MeHg from Various Watersheds Containing Wetlands

location	watershed type	annualized export rate ($\mu\text{g MeHg m}^{-2} \text{ y}^{-1}$)	reference
ELA, Ontario	wetland	0.18 to 0.55	2
ELA, Ontario	upland/riparian wetland	0.03–0.1	4
ELA, Ontario	upland/headwater wetland	0.1 to 0.24	4
ELA, Ontario	basin wetland	0.08 to 0.25	6
Adirondacks, NY	upland/riparian wetland	0.17	9
Sweden	upland/5% to 16% wetland	0.03 to 0.11	10
Sweden	swamp forest	0.16	10
Northern Wisconsin	headwater wetland	0.27	this paper

TABLE 7. Seasonal Mass Balance for MeHg in Devils Lake, May 30 to August 19, 2002

component	mass (mg)	areal flux ($\mu\text{g m}^{-2}$)
change in storage (ΔS)	385	3.3 ^a
external inputs	42	
wetland runoff (inlet) (Q_{in})	33	0.13 ^b
nonchannelized runoff (RO)	3	0.02 ^c
precipitation (P)	6	0.05 ^a
losses	39	
outflow stream (Q_{out})	11	0.09 ^a
groundwater recharge (G_{out})	19	0.16 ^a
evasion + net sedimentation ($E + S$)	9	0.08 ^a
internal input		
net methylation (M_{net})	382	3.3 ^a

^a Normalized to lake area. ^b Normalized to wetland area. ^c Normalized to adjacent watershed area (see Figure 1).

in horizontal beam attenuation (pigmented and nonpigmented microbes) (Figure 10A). T-RFLP analysis of bacterial DNA in these layers indicated the presence of SRB throughout the hypolimnion during peak stratification (Figure 10B and Table 9). The diversity of T-RFs assigned to SRB genera was greatest at 4.5 and 6.0 m. Although T-RF signal strength may not exactly reflect the initial stoichiometry of 16S rDNA templates due to PCR bias, we note that the signal intensity of SRB T-RFs are also greatest at these sample depths, which implies greater SRB biomass in these samples.

The presence of SRB in the hypolimnetic water column is consistent with the observed decline in waterborne sulfate, which decreased from roughly 30 μM in surface waters to 9 μM in the hypolimnion (Figure 10B). As sulfate declined, the concentration of sulfide increased from $<0.1 \mu\text{M}$ to 30 μM as a product of sulfate reduction. The inexact stoichiometry between sulfate depletion and sulfide accumulation results in part from continued inputs of SO_4^{2-} from the epilimnion and from H_2S consumption by photosynthetic sulfide oxidizing bacteria (PSB) which occupied the upper hypolimnion, as indicated by the fluorescence peaks in Figure 10A. Overall, the spatial patterns of solutes and microbes are similar to those observed in earlier studies of nearby Little Rock Lake and Palette Lake where hypolimnetic $\text{Hg}^{(II)}$ methylation was demonstrated (12, 52).

The presence of SRB in the hypolimnetic waters is also consistent with a previous report of high methylation rates in the hypolimnion of Devils Lake (3). In that experimental study, specific rate constants for methylation and demethylation in the water column were determined using stable $\text{Hg}^{(II)}$ isotopes as tracers during incubation experiments conducted under ambient conditions for 24 h time periods using the technique of Hintelmann et al (53). The objectives were to determine whether the rate constants varied with the spatial distribution of MeHg and to determine whether the measured rates were sufficient to account for the observed ΔS_{MeHg} in

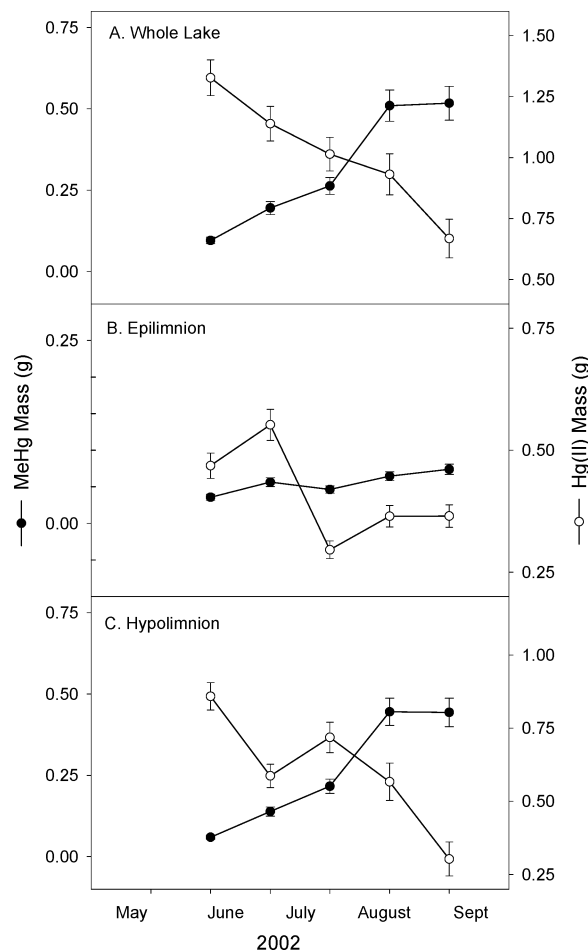


FIGURE 9. Changes in the mass of waterborne MeHg and $\text{Hg}^{(II)}$ in Devils Lake during summer. $\text{Hg}^{(II)}$ = Hg_T - MeHg. Error bars indicate range of duplicates.

TABLE 8. Seasonal Rate of Accumulation or Depletion for Waterborne MeHg and $\text{Hg}^{(II)}$ in Devils Lake (May 30 to September 16, 2002)^a

lake stratum	rate of accumulation or depletion (mg d^{-1})	
	MeHg	$\text{Hg}^{(II)}$
whole lake	4.2 (0.94)	-5.5 (0.96)
epilimnion	0.3 (0.79)	-1.4 (0.38)
hypolimnion	3.9 (0.94)	-4.0 (0.74)

^a $\text{Hg}^{(II)}$ Calculated as Hg_T - MeHg. Rates estimated by linear regression of data on Figure 9 (r^2 in parentheses).

the lake during the summer of 2002. Eckley et al. constructed a simple model using the measured rates which yielded a net production of MeHg in the hypolimnion sufficient to account for the observed accumulation during summer (3).

TABLE 9. SRB Genera Identified in Devils Lake Hypolimnetic Waters Using T-RFLP as Described in Text

sample depth	genus	class	family
1.5 m	<i>Desulfotomaculum</i>	Firmicutes	Peptococcaceae
	<i>Desulfitobacterium</i>	Firmicutes	Peptococcaceae
3.0 m	<i>Desulfotomaculum</i>	Firmicutes	Peptococcaceae
4.5 m	<i>Nitrospina</i>	δ-Proteobacteria	Nitrospinaceae
	<i>Desulfomicrobium</i>	δ-Proteobacteria	Desulfomicrobiaceae
	<i>Desulfovibrio</i>	δ-Proteobacteria	Desulfovibrionaceae
	<i>Desulfobacterium</i>	δ-Proteobacteria	Desulfobacteraceae
	<i>Desulfotomaculum nigrificans</i>	Firmicutes	Peptococcaceae
4.9 m	<i>Nitrospina</i>	δ-Proteobacteria	Nitrospinaceae
	<i>Desulfuromonas</i>	δ-Proteobacteria	Desulfuromonaceae
5.5 m	<i>Nitrospina</i>	δ-Proteobacteria	Nitrospinaceae
	<i>Desulfuromonas</i>	δ-Proteobacteria	Desulfuromonaceae
6.0 m	<i>Desulfotomaculum</i>	Firmicutes	Peptococcaceae
	<i>Nitrospina</i>	δ-Proteobacteria	Nitrospinaceae
	<i>Desulfovibrio</i>	δ-Proteobacteria	Desulfovibrionaceae
	<i>Desulfobacterium</i>	δ-Proteobacteria	Desulfobacteraceae
	<i>Desulfotomaculum</i>	Firmicutes	Peptococcaceae

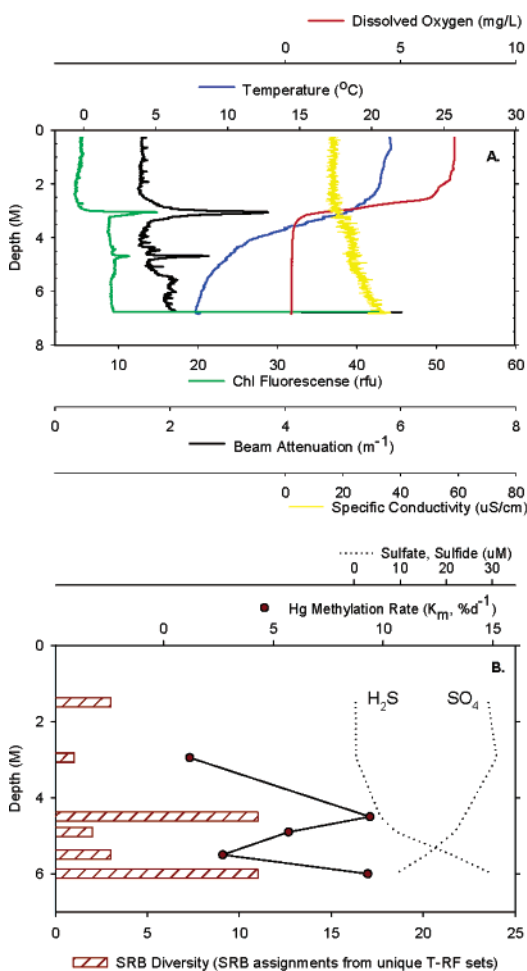


FIGURE 10. Stratification of Devils Lake during August 2002: (A) data from SeaBird 19Plus CTD; (B) SRB diversity; methylation rate constants reported previously (3); and the concentrations of total sulfide and sulfate.

As shown in Figure 10B, Eckley et al. (3) reported high rates of methylation in the anoxic hypolimnetic water column, ranging from 2.4 to 9.7% d⁻¹. The highest methylation rate constants were found at depths where we found the diversity and detection of SRB T-RFs to be highest. These were also the only depths where SRB genera within the *Desulfovibrionaceae* and *Desulfobacteriaceae* were detected (4.5 and

6.0 m; Table 9). At depths where SRB signal strength declined and no *Desulfovibrionaceae* or *Desulfobacteriaceae* were detected, the reported methylation rate declined as well. Pure cultures and sediment slurries containing these two SRB groups are known to methylate Hg^(II) (26, 54) and methylation activity has been correlated with their distribution in sediments (27, 55, 56) although the relationship to a particular metabolic pathway remains unclear (57).

Wetland Impact. Results of the mass balance and microbial community analysis indicate that despite a substantial output of MeHg from the headwater wetland (ca. 0.3 μg MeHg m⁻² y⁻¹), the dominant process governing the high MeHg concentrations and accumulation observed in this wetland-dominated lake was in-lake MeHg production, hypothetically mediated by SRB in the anoxic hypolimnetic waters. Although the wetland contributed 56% of the Hg_T that entered the lake during summer, the influx of wetland-derived MeHg constituted only 8% of the MeHg that accumulated in the water column. Wetland MeHg export would need to increase by more than 10-fold during summer to equal the estimate for net in-lake production. When external losses of MeHg are considered, the relative importance of wetland runoff diminishes further.

Two scenarios can be used to explore the sensitivity of these findings to different environmental conditions. One scenario considers the potential impact of storm events during summer; the second considers the impact of a larger contributing wetland. For scenario one, assuming that the average concentration of MeHg in runoff could be maintained at 1 ng/L during summer storms, episodic runoff events totaling roughly 4 × 10⁵ m³ (more than the total volume of the lake) would be needed to match the in-lake MeHg production observed in 2002. This additional runoff is almost 7 times the volume delivered to the lake during the summer of 2002, an unrealistically large amount. For scenario two, given the reported range of MeHg export rates from temperate/boreal wetlands (0.1–0.5 μg MeHg m⁻² y⁻¹; Table 6), a contributing wetland that was 3-fold to 17-fold larger could theoretically deliver enough MeHg to match in-lake production. However, the watershed yield of water would need to increase proportionately, reducing the water residence time in the lake from 1 year to between 0.06 and 0.3 years. This result implies that the relative importance of wetland export may be proportional to the flushing rate of the receiving lake, all other things being equal. For wetland-dominated lakes with water residence times longer than 6 months, in-lake production would hypothetically dominate the MeHg budget.

TABLE 10. Summer Mass Balances for MeHg in Three Small, Northern Lakes with Different Degrees of Wetland Influence^a

	LRL	L240	DL
hydrology	seepage	drainage	drainage
surface area (ha)	9.8	44.1	11.7
wetland influence	low	moderate	high
Mass Balance			
δ storage	66 ± 30	220	385
pluvial input	5 ± 2	13 ^b	6
fluvial input	0		36
outflow	1 ± 0	3	30
demethylation	?	54 ^c	?
methylation (net)	(65 ± 30)	264	(382)
net sedimentation	3 ± 2	?	9

^a Little Rock Lake treatment basin during de-acidified years 1998–2002 (Watras et al., unpubl. data). L240, Canadian ELA (1). DL, Devils Lake (this paper). Units are mg MeHg (mean ± SD where multiple years available). Estimates of methylation are gross or (net). ^b Total external input. ^c Photodegradation.

Although there are few detailed mass balances for MeHg in lakes during the summer accumulation phase, the mass balance for Devils Lake can be placed in the context of two previous field studies. As indicated in Table 10, Little Rock Lake in northern WI, Lake 240 in the Canadian ELA, and Devils Lake differ in the degree to which wetland runoff influences lacustrine hydrology. Nonetheless, internal methylation dominates the seasonal mass balances of all three lakes. Although this limited comparison suggests that external MeHg loading increases with increasing wetland influence, the direct effect of wetland on all three budgets is relatively minor.

However, the indirect effects of wetland runoff on the lacustrine MeHg cycle may be large and they may account for the strong correlation between waterborne MeHg and DOC observed across northern Wisconsin lakes (18). Indirect wetland effects could include (1) increasing the input of Hg^(II); (2) stimulating microbial activity via inputs of organic matter, SO₄²⁻, and other nutrients; (3) inhibiting the photodestruction of MeHg; and (4) enhancing the retention of MeHg in the water column through chelation by dissolved and colloidal organic matter.

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