

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231277086>

Decreasing Mercury in Northern Wisconsin: Temporal Patterns in Bulk Precipitation and a Precipitation-Dominated Lake

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · AUGUST 2000

Impact Factor: 5.33 · DOI: 10.1021/es000991g

CITATIONS

34

READS

42

5 AUTHORS, INCLUDING:



Carl Watras

Wisconsin Department of Natural Resources

66 PUBLICATIONS 2,596 CITATIONS

SEE PROFILE



Robert J M Hudson

University of Illinois, Urbana-Champaign

49 PUBLICATIONS 2,651 CITATIONS

SEE PROFILE



Timothy K Kratz

University of Wisconsin-Madison

79 PUBLICATIONS 5,485 CITATIONS

SEE PROFILE

Decreasing Mercury in Northern Wisconsin: Temporal Patterns in Bulk Precipitation and a Precipitation-Dominated Lake

C. J. WATRAS,^{*,†,‡} K. A. MORRISON,[†]
R. J. M. HUDSON,[§] T. M. FROST,[‡] AND
T. K. KRATZ[‡]

Environmental Contaminants Section, Wisconsin Department of Natural Resources, Trout Lake Station, Center for Limnology, University of Wisconsin—Madison, 10810 CTY N, Boulder Junction, Wisconsin 54512, and Department of Natural Resources and Environmental Sciences, University of Illinois at Champaign—Urbana

Long-term monitoring of a precipitation-dominated lake in northern Wisconsin indicates decreasing mercury concentrations over the past decade. In the surface waters of Little Rock Lake, aqueous Hg_T has decreased at an average rate of 0.04 ng/L/y—or roughly 40% from 1988 to 1999. The concentration of aqueous $meHg_T$ in Little Rock Lake has decreased too—at an average rate of 0.004 ng/L/y (roughly 50% since 1988). Atmospheric monitoring also indicates decreased mercury in bulk precipitation. For those years when we have a continuous data record (1994 through 1999), the annual Hg cycle in bulk precipitation has been damped and the average rate of bulk atmospheric Hg deposition decreased by roughly 50% (from 11.2 ug/m²/y to 5.5 ug/m²/y). These trends suggest that the lake waters have responded to decreased atmospheric Hg deposition—perhaps driven by reduced anthropogenic emissions in the region. Ancillary data and mass balance modeling are used to more fully investigate recent changes in the aquatic mercury cycle.

Introduction

Atmospheric deposition is the major source of mercury to many aquatic ecosystems, particularly in remote regions of the Northern Hemisphere (1, 2). Several lines of evidence indicate that depositional rates and atmospheric burdens of Hg increased globally with increasing industrial activity during the last century (3–8). However, there is growing evidence that this trend has reversed in recent years. The evidence includes decreased Hg accumulation in the surficial sediment of Minnesota lakes (9), lower concentrations of gaseous Hg in the atmosphere over the Atlantic Ocean, southern Germany, and southwestern Scandinavia (10, 11), and reduced rates of wet Hg deposition in Sweden (10). Taken together, these observations indicate that a decrease of 20% to 50% occurred during the early 1990s.

* Corresponding author phone: (715)356-9494; fax: (715)356-6866; e-mail: cjwatras@facstaff.wisc.edu.

[†] Environmental Contaminants Section, Wisconsin Department of Natural Resources.

[‡] Trout Lake Station, Center for Limnology, University of Wisconsin—Madison.

[§] University of Illinois at Champaign—Urbana.

Recent Hg decreases have been attributed to pollution abatement practices involving various combustion sources as well as reductions in the industrial use of Hg. According to the inventory of Engstrom and Swain (9), industrial uses of mercury in the U.S. dropped from > 2500 metric tons in the 1960s to roughly 600 metric tons in 1993, largely due to the elimination of mercury in paint products and electrical apparatus. However, since a vast reservoir of historically deposited Hg remains in sediments and terrestrial watersheds, the projected impact of any depositional decline on lake waters is uncertain. The continued mobilization and transformation of historically deposited Hg in sediments and soils could buffer the response of aquatic ecosystems for decades.

Here we examine the temporal trend for mercury in the surface waters of a small seepage lake in northern Wisconsin during the past decade (Little Rock Lake, 1988–1999). Since atmospheric deposition is the principal source of Hg to the lake, we also examine temporal patterns for Hg in bulk precipitation and compare trends in the lake to trends in bulk atmospheric deposition. We then use mass balance modeling to assess changes in the aquatic Hg cycle over recent time.

Methods

Study Sites. Surface water monitoring was conducted at Little Rock Lake (LRL), an 18 ha precipitation-dominated seepage lake situated in an undisturbed watershed in Vilas County, WI (46°N, 89°42' W). This region is remote from heavy industrial activity, and it is sparsely populated (ca. 7 people/km²). LRL is regionally representative of lakes that are highly sensitive to direct atmospheric inputs (12, 13), and it is one of the first aquatic ecosystems for which detailed mass balances of Hg_T and $meHg$ were successfully constructed (14, 15). The data we report are for samples collected in the southern-most basin of the lake between 1988 and 1999. LRL was the site of a whole-ecosystem acidification experiment (13), but the south basin served only as a reference during the manipulation. This basin, which is physically separated from the rest of the lake, has a surface area of 8.1 ha and a maximum depth of 6 m. It does not thermally stratify or develop an anoxic hypolimnion.

All atmospheric samples were collected at the National Atmospheric Deposition Program (NADP) station located near the eastern shore of Trout Lake and within 7 km of LRL. The NADP site is a 40 m × 55 m grassy opening in a red pine forest. The site is accessed via footpath.

Clean Technique. Throughout the 12-year study period, all mercury samples were collected, handled, and analyzed using ultraclean techniques to avoid contamination with extraneous Hg (16, 17). Analytical detection limits (defined as 3 sd of procedural blanks) for aqueous Hg_T and $meHg$ have ranged unsystematically from 0.03 to 0.18 ng/L and 0.01 to 0.09 ng/L, respectively, over the study period. Details of the methods used to determine mercury species and ancillary constituents in lake water, precipitation, and air are well documented (18–22). All the protocols had consistently high sensitivity, and they were periodically intercalibrated throughout the period of study. As a result, the 12-year data set is not obviously biased by successive methodological improvements that could artificially create the appearance of trends with time (23, 24).

Atmospheric Sampling. NADP monitoring of wet SO_4 , pH, and Ca began in 1980. Samplers for PM_{10} and ozone

TABLE 1. Temporal Trends in the Concentration of Hg and Related Constituents in Lake Water, Air, and Precipitation from Northern Wisconsin^a

constituent	period	n	slope	SE	P	% change
Lake Water						
Hg	1988–99	55	$-0.040 \text{ ng}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.015	<0.01	–39
meHg	1988–99	47	$-0.004 \text{ ng}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.001	<0.01	–53
sulfate	1988–99	59	$-0.16 \text{ mg}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.035	<0.001	–51
DOC	1988–99	95	$0.15 \text{ mg}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.018	<0.001	58
H ⁺	1988–99	199	$-0.081 \mu\text{M}\cdot\text{y}^{-1}$	0.028	<0.01	–64
Air						
PM ₁₀	1995–99	254	$0.33 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{y}^{-1}$	0.13	0.02	18
ozone	1995–99	244	$3.3 \times 10^{-4} \text{ ppm}\cdot\text{y}^{-1}$	2.3×10^{-4}	0.001	5
Precipitation						
Hg	1995–99	259	$-1.23 \text{ ng}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.21	<0.001	–50
H ⁺	1988–99	611	$-0.34 \mu\text{M}\cdot\text{y}^{-1}$	0.07	<0.001	–24
	1995–99	250	$-1.2 \mu\text{M}\cdot\text{y}^{-1}$	0.2	<0.001	–35
sulfate	1988–99	611	$-0.055 \text{ mg}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.005	<0.001	–45
	1995–99	250	$-0.01 \text{ mg}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.01	0.5	–5
calcium	1988–99	611	$-0.003 \text{ mg}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.001	<0.05	–15
	1995–99	250	$0.010 \text{ mg}\cdot\text{L}^{-1}\cdot\text{y}^{-1}$	0.004	0.2	30

^a For lake water, linear regressions were performed on the data from Figures 1 and 2. For precipitation and air, linear regressions were performed on the seasonal moving averages computed weekly. Precipitation data span two time periods (1988–99 and 1995–99) to allow direct comparison with lake water and air.

were co-located at the site in 1992 by the Wisconsin Department of Natural Resources (WDNR) (21). Atmospheric monitoring of Hg in bulk precipitation began in 1993 (19). Precipitation samples for Hg determination were collected using an all-glass, bulk deposition collector. The collector was deployed continuously, and the NADP station monitor retrieved samples weekly. Details of the sampler design, construction, deployment, and performance were described previously (25, 19). Details of the aerosol and ozone monitoring are described in ref 21. Aerosol mass was determined at ground level for one continuous 24-h sampling period each week. For aerosol < 10 μm (PM₁₀), preweighed quartz fiber filters (8 × 10 in.) were placed in a high-volume air sampler with a flow rate of 0.8 to 1.4 m³/min. Ozone was monitored continuously every day from a 10 m tower using a UV absorption monitor and the data were recorded hourly. Wet SO₄, wet Ca, precipitation pH, and precipitation amount were determined according to standard NADP methods by the Illinois State Water Survey, University of Illinois, Champaign–Urbana (22).

Lake Water Sampling. Since the chemistry, hydrology, and biology of Little Rock Lake have been monitored since 1983 as part of ongoing investigations of acid rain and mercury cycling, protocols for sample collection and analysis have been thoroughly documented (12, 13, 15, 26, 27). For mercury and other aqueous analytes reported here, surface water samples were collected by pumping water from a depth of 1 or 2 m. The trace-metal-clean collection protocol followed EPA Method 1669 (28).

Data Reduction and Statistical Analysis. To explore annual cycles, weekly data were smoothed by computing seasonally moving averages (13 weeks) with each week receiving equal weight. All wet concentrations were volume-weighted during smoothing. Spectral analyses were performed on the smoothed data by Fast Fourier Transform after removal of the mean and trend (SYSTAT). Long-term trends and correlation between variables were investigated using linear regression of the smoothed and raw sets of data as specified below. Regression analyses used SigmaPlot and SigmaStat (SPSS, Inc).

Results and Discussion

Temporal Trends in Lake Water Chemistry. The data for Little Rock Lake indicate that there has been a significant

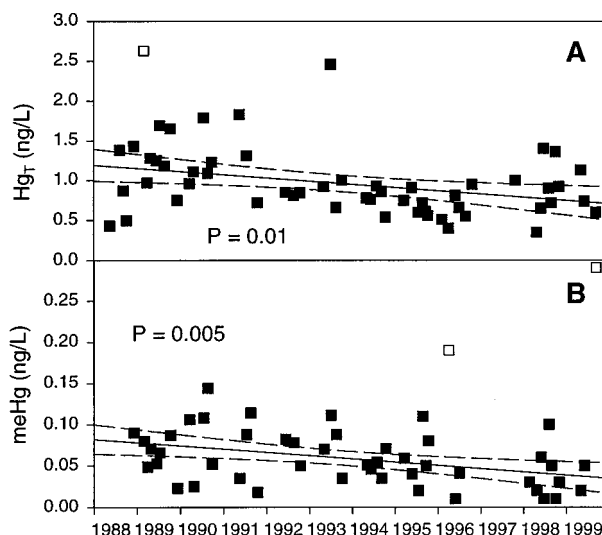


FIGURE 1. Temporal trends for aqueous Hg_T (A) and meHg_T (B) in the surface waters of Little Rock Lake (reference basin). Solid line shows linear regression with 95% confidence interval. Open squares indicate outliers that were not included in the linear regression

decrease in the aqueous concentration of Hg_T in surface waters during recent years ($p < 0.01$). When averaged over the entire period of study (1988–1999), the rate of decrease is -0.04 ng/L/y (Figure 1A). The total change constitutes a 39% decline for the decade (Table 1). Aqueous meHg has also decreased significantly in LRL and at an average rate of -0.004 ng/L/y (a 53% change from 1988 through 1999, Figure 1B and Table 1).

Information on other variables monitored along with Hg in the lake and region during the study period provides an opportunity to evaluate potential biogeochemical mechanisms that underlie observed changes. We first examined the historical precipitation record, since atmospheric deposition is the primary source of Hg to the lake and since deposition is directly related to the amount of precipitation received (15, 29). Because there was no detectable trend in precipitation amount over the period 1988–1999 (Figure 2A), the observed declines in lake water Hg_T and meHg cannot be attributed simply to a trend in the amount of precipitation received. Nor can the declines be attributed to a major change

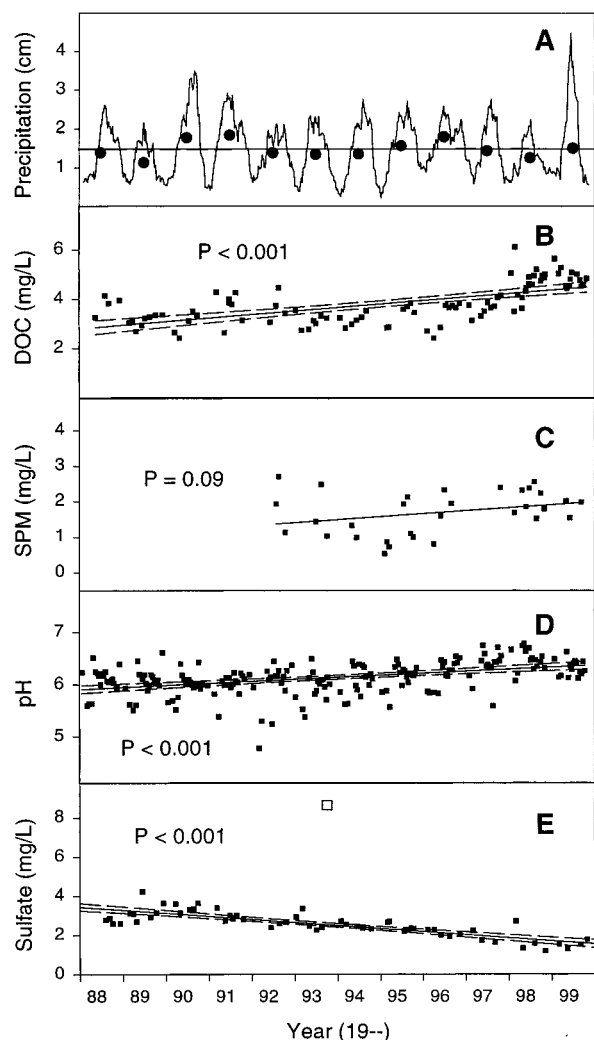


FIGURE 2. Temporal trends for precipitation amount (A) and selected analytes in the surface waters of Little Rock Lake (reference basin): (B) dissolved organic carbon; (C) suspended particulate matter; (D) pH; (E) sulfate. Solid lines indicate linear regressions, with 95% CI for those analytes where $p < 0.05$ (dashed line). In (A) data are plotted as the seasonal running average calculated weekly and the closed circles show the annual means: the horizontal line is both the linear regression and the long-term mean.

in the chemical speciation of mercury in surface waters. Organic complexation is the dominant factor affecting mercury speciation in lake waters of northern WI, as evidenced by the strong positive relationship between mercury concentration and DOC (30–32). The data provide no evidence that binding to dissolved organic ligands has declined in LRL. In fact, given the historical trend for DOC in surface waters, one would expect an increase in waterborne mercury concentrations rather than a decrease (Figure 2B; Table 1). Likewise, there is no strong evidence for an increase in the rate of mercury removal to sediments due to an increase in settling particles (Figure 2C). Hence, none of these three mechanisms (decreased amounts of precipitation, decreased organic complexation, or increased sedimentation) provides a simple explanation for the observed decline in aqueous mercury.

However, the declining trends in Hg_T and $meHg$ are mechanistically consistent with observed trends in lake water pH and sulfate (Figure 2D,E; Table 1). The reduction of Hg^{II} to Hg^0 and the subsequent evasion of dissolved gaseous mercury across the air–water interface have been shown to

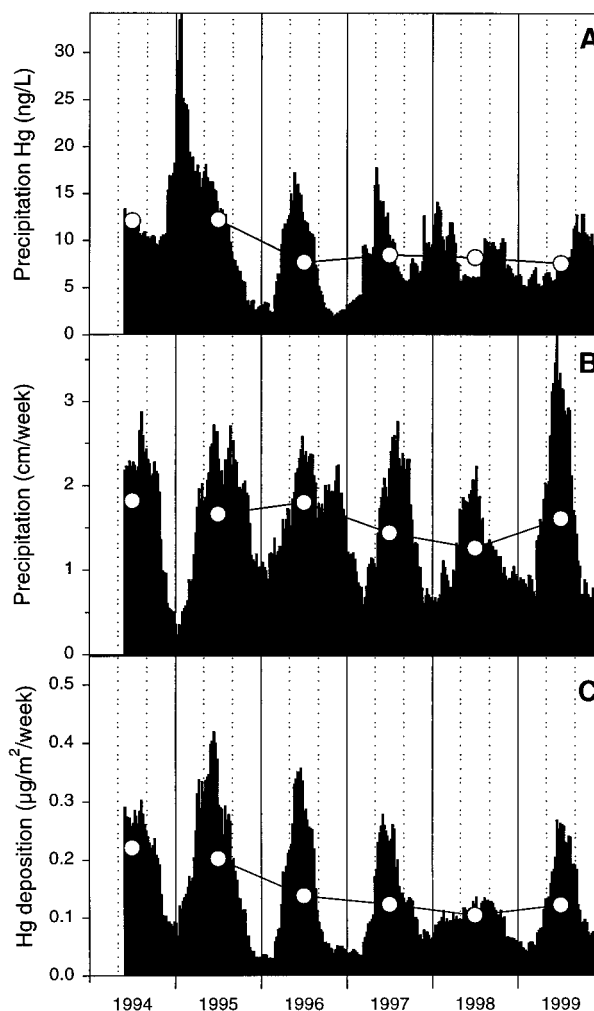


FIGURE 3. Annual cycles of Hg in bulk precipitation (volume-weighted, A), precipitation amount (B), and atmospheric Hg deposition (C) at Trout Lake in northern Wisconsin, expressed as the seasonal moving average calculated weekly. Open circle indicates the annual mean.

increase with increasing pH in circumneutral lakes (30, 33). Thus, one would expect a decline in the aqueous pool of Hg as the specific rate of evasion increased with pH between 1988 and 1999. Since the methylation of Hg^{II} is related to the activity of sulfate reducing bacteria in natural waters (34), one would also expect a decrease in the aqueous pool of $meHg$ as SO_4 declined between 1988 and 1999. Although an increase in Hg^{II} reduction and a decrease in methylation are consistent with the observed trends in Hg and $meHg$, the effects of pH and SO_4 alone are not sufficient to explain the time trends observed in LRL ((30)—see below). Additional changes in mercury sources or sinks would be required.

Temporal Changes in Precipitation Chemistry and Atmospheric Deposition. Since atmospheric deposition is the major source of mercury to LRL, we examined the variability of Hg in bulk precipitation for indications of change with time. Strong seasonality was evident in the smoothed data for the Hg concentration in precipitation, precipitation amount, and the weekly depositional rate (Figure 3). Although the seasonally averaged value for each of these three variables was relatively high during summer and low during winter (Table 2), the annual cycles were not strictly in phase with each other. Regression analysis of the data from Figure 3A,B indicated no significant relationship between precipitation Hg and precipitation amount. However, Hg concentration and precipitation amount were correlated negatively when

TABLE 2. Seasonal Concentration of Hg in Precipitation, Precipitation Amount, and the Deposition Rate at Trout Lake, Northern Wisconsin (1994–1999)^a

season	N	vol-weighted Hg concn (ng/L)	precipitation amt (cm/week)	Hg deposition rate ($\mu\text{g}/\text{m}^2/\text{week}$)
spring	67	12.4	1.71	0.213
summer	77	9.6	2.45	0.234
autumn	57	6.1	1.59	0.096
winter	84	6.7	0.88	0.059

^a Data are means and N is number of weeks with data. Concentration data are volume-weighted. Seasons start on April 1 (spring), July 1 (summer), October 1 (autumn), and December 1 (winter). All winter samples are snow.

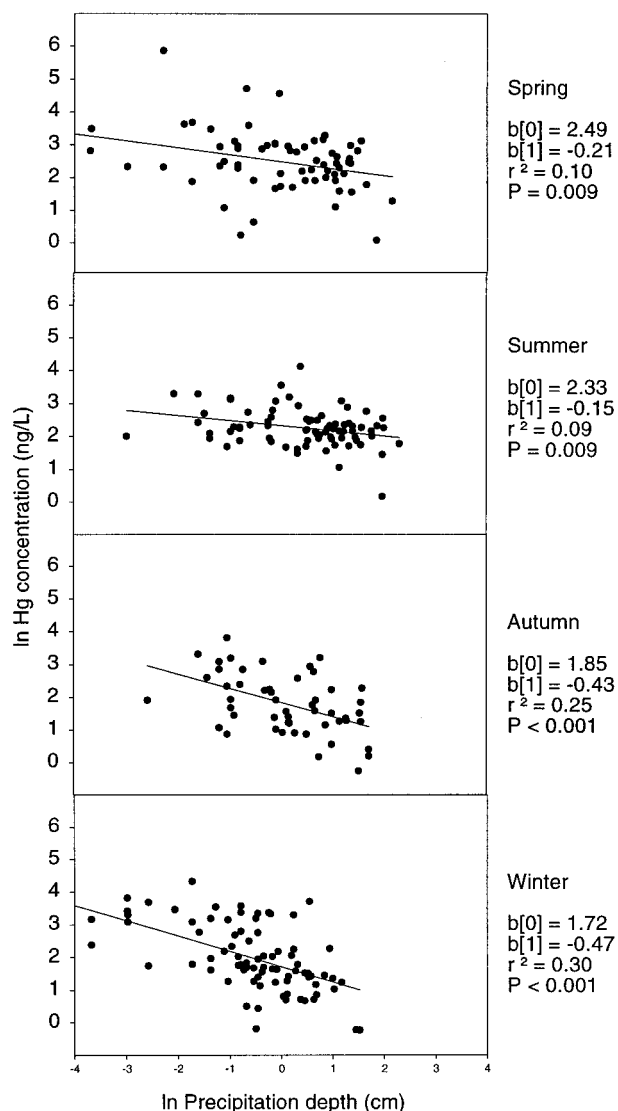


FIGURE 4. Relationship between the concentration of Hg in precipitation and the amount of precipitation received during a given week for each season. Data comprise all original determinations from 1993 through 1999.

weekly observations were parsed by season (Figure 4). In all seasons, higher Hg concentrations were associated with lower volume precipitation events, but the functional relationship between concentration and volume varied between seasons.

A similar annual Hg cycle has been reported in several other North American regions that differ in climate, meteorology, and proximity to anthropogenic sources of Hg (e.g. northern Vermont (35), Minnesota (29, 36), and Florida

(37)). Although the common factor or factors driving the seasonal pattern are not clear, observations from subtropical Florida indicate that a transition from rain to snow is not a necessary condition or sufficient explanation for the cycle.

We compared the Hg cycle to the annual cycles for ozone, aerosol mass, wet sulfate, calcium, and H^+ as an initial step toward evaluating some of the factors potentially regulating Hg in precipitation over a time scale of one year. At our Wisconsin site, the annual cycles of O_3 and PM_{10} were most similar to the annual cycle for Hg concentration (Figure 5A,B—see ref 38). Spectral analysis clearly showed a dominant frequency of one cycle per year for all three analytes, but visual inspection indicates that phase alignment was not consistent over time. Regression analysis indicated that no single variable explained more than 5% of the total variance in Hg concentration.

In addition to the strong annual cycle, there is also evidence of a recent decrease in the concentration of Hg in precipitation and the rate of atmospheric Hg deposition in this region (Tables 1 and 3). During the period for which we have complete annual data, the Hg concentration decreased by 1.2 ng/L/y, and the rate of Hg deposition decreased by 0.02 $\mu\text{g}/\text{m}^2/\text{wk}/\text{y}$. Neither trend was attributable to a decrease in precipitation amount (Figure 1A) or a change in the seasonal distribution of precipitation received at the site (Table 4).

The observed decrease in Hg concentration and deposition parallels a recent decrease in SO_4 and H^+ in precipitation, declines which are widely attributed to reduced emissions of SO_2 from coal-fired facilities (39). In Wisconsin, the recent decrease in SO_2 emissions is primarily due to coal switching (to western coals with low sulfur content (40)). Even though more coal is burned annually, SO_2 emissions have dropped almost 50% since the onset of state-mandated controls (39). Since there is evidence, albeit scant, that low-sulfur, western sub-bituminous coal also contains lower amounts of Hg (41), it is possible that the observed decrease in precipitation Hg is related to burning cleaner coal.

Alternatively, decreased precipitation Hg may be attributable to recent pollution controls that specifically target Hg emissions. There have been sharp reductions in the industrial and commercial use of Hg in applications such as control instruments, electrical apparatus, chlorine gas production, batteries, and paint products over the past decade (9). Another contributory factor may be the closure of the nearby Copper Range smelter. Located roughly 100 km north of our study site, the smelter was potentially a large regional source of atmospheric Hg. Analysis of wind speed and direction indicates that winds from the northern quadrant impacted LRL roughly 30% of the time during the 1990s (42). It was recently demonstrated that a significant decrease in the Hg content of aerosol at remote sites in New York State was due to reduced emissions from Canadian smelters (43).

Mass Balance Models and Biogeochemical Mechanisms.

To examine the observed trends in mercury more fully, we constructed Hg mass balances for LRL in 1995 and 1999—spanning the period when we have measurements both in the lake and in atmospheric deposition. The new budgets build upon an earlier mass balance for the lake (15, 30) using the linearized trends from Table 1. The results indicate a modest decrease in the evasion rate between 1995 and 1999 (1.2 $\mu\text{g}/\text{m}^2/\text{yr}$ to 1.0 $\mu\text{g}/\text{m}^2/\text{yr}$) and a relatively large decrease in the net accumulation of Hg in sediments (8.1 $\mu\text{g}/\text{m}^2/\text{yr}$ to 4.2 $\mu\text{g}/\text{m}^2/\text{yr}$) (Figure 6A).

According to these budgets, atmospheric Hg deposition and Hg accumulation in sediments both declined by roughly 50%, while lake water Hg declined by roughly 20%. One mechanism that could explain a slower decline in lake water is Hg remobilization from sediments. A remobilization flux

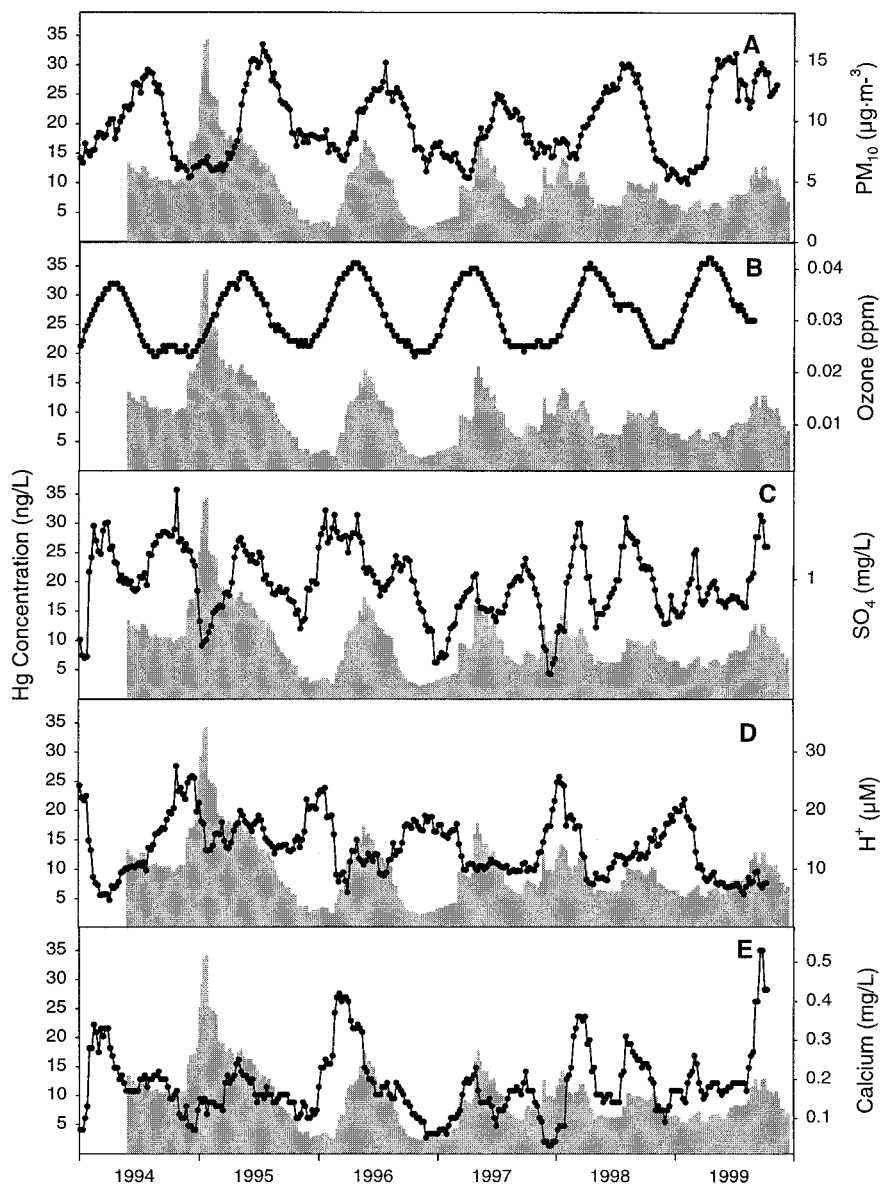


FIGURE 5. Annual cycles of atmospheric aerosol $< 10 \mu\text{m}$ (A), ozone (B), wet sulfate (volume-weighted (C)), wet H^+ (volume-weighted (D)), and wet Ca (volume-weighted (E)) at Trout Lake in northern Wisconsin, expressed as the seasonal moving average calculated weekly, superimposed on the annual cycle of Hg in bulk precipitation (bars).

TABLE 3. Temporal Trends in Deposition of Hg and Related Constituents in Northern Wisconsin^a

constituent	period	n	slope	SE	P	% change
Hg	1995–99	259	$-0.020 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{week}^{-1}\cdot\text{y}^{-1}$	0.004	<0.001	-52
precipitation amt	1995–99	259	$-0.04 \text{ cm}\cdot\text{week}^{-1}\cdot\text{y}^{-1}$	0.03	0.2	-12
H^+	1995–99	250	$-25 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{week}^{-1}\cdot\text{y}^{-1}$	3	<0.001	-46
sulfate	1995–99	250	$-0.5 \text{ mg}\cdot\text{m}^{-2}\cdot\text{week}^{-1}\cdot\text{y}^{-1}$	0.3	0.14	-14
calcium	1995–99	250	$0.09 \text{ mg}\cdot\text{m}^{-2}\cdot\text{week}^{-1}\cdot\text{y}^{-1}$	0.07	0.2	17

^a Linear regressions were performed on the seasonal moving averages computed weekly.

of roughly $6 \mu\text{g m}^{-2} \text{yr}^{-1}$ from surficial sediments could buffer the lake's response to decreased atmospheric deposition in a manner consistent with these observations (Figure 6B).

Comparable budgets for meHg have not been attempted because none of the major fluxes were quantified. We note, however, that the decrease in waterborne meHg was greater than the decrease in Hg_T (Figure 1, Table 1). This observation is consistent with the observed trends in H^+ and SO_4 , factors that have been shown to affect methylation rates and concentrations of meHg in nature (34, 44).

In conclusion, observations over the past decade indicate decreasing mercury in bulk precipitation and in a precipitation-dominated lake in northern Wisconsin. These changes are consistent with recent inventories of anthropogenic emissions for the region. They suggest that pollution abatement policies can have an effect over a short time scale—despite large stores of Hg in the watershed and lake sediments. These Hg stores may provide some buffering, but they do not over-ride substantial changes in depositional rates, at least in the case of a model seepage lake.

TABLE 4. Seasonal Distribution of Precipitation at the Trout Lake Monitoring Site

year	precipitation	
	% falling as snow	% in autumn and winter
1995	12.9	38.0
1996	27.3	49.8
1997	15.6	32.2
1998	16.7	34.1
1999	14.7	23.2

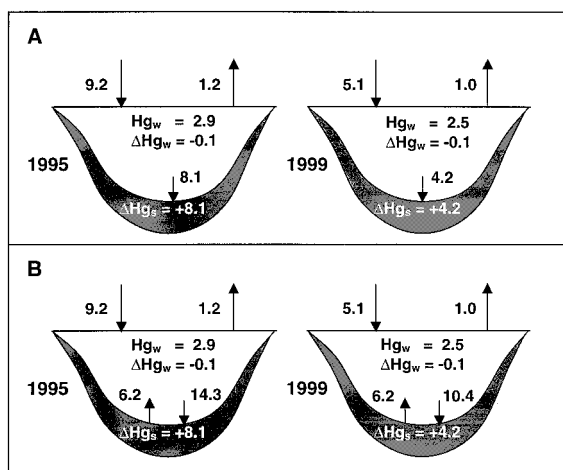


FIGURE 6. Estimated annual Hg balances for Little Rock Lake in 1995 and 1999. (A) Only net rate of sedimentation (S_{net}) is shown. (B) Gross sedimentation (S_{gross}) and remobilization (R) fluxes are shown. Fluxes (arrows) and rates of accumulation (ΔHg_s , ΔHg_w) have units of $\mu g m^{-2} yr^{-1}$. Total Hg in water column (Hg_w) has units of $\mu g m^{-2}$ and was computed for a 3.1-m average lake depth. Annual deposition fluxes and ΔHg_w are estimates from linear trends (Table 1). Evasion derived from measured value for 1989 (15) and assumption that Hg^0 production is proportional to dissolved Hg. (Note that a mechanistic model developed from lakes in this region (30) predicts the specific rate of Hg^0 production remains constant for the trends in lake water chemistry reported here.) ΔHg_s computed from: $\Delta Hg_s = \text{deposition} - \text{evasion} - \Delta Hg_w$. Remobilization flux (assumed constant 1995–1999) estimated by applying ($\Delta Hg_s = S_{gross} - R$) in 1995 and 1999 and assuming S_{gross} changed in proportion to Hg_w with adjustments for effects of DOC trend on K_d (30).

Acknowledgments

Research was supported by the Wisconsin Department of Natural Resources, the Electric Power Research Institute, The Lake Superior Basin Trust, and the US National Science Foundation. We thank Bruce Rodger and Tom Sheffy (Bureau of Air Management, WI DNR), Nicolas Bloom (Frontier Geosciences, Inc) and Lian Liang (Cebam, Inc.) for their assistance. This is a contribution from the Trout Lake Station, Center for Limnology, University of Wisconsin-Madison.

Literature Cited

- (1) Lindqvist, O. *Water, Air, Soil, Pollut.* **1991**, 55, 1–261.
- (2) Baeyens, W., Ebinghaus, R., Vasiliev, O., Eds.; *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*; Kluwer Academic Publishers: Netherlands, 1996; 561 pp.
- (3) Rada, R. G.; Wiener, J. G.; Winfrey, M. R.; Powell, D. E. *Arch. Environ. Contam. Toxicol.* **1989**, 18, 175–181.
- (4) Verta, M.; Tolonen, K.; Simola, H. *Sci. Tot. Environ.* **1989**, 87/88, 1–18.
- (5) Swain, E. B.; Engstrom, D. R.; Brigham, M. E.; Henning, T. A.; Brezonik, P. L. *Science* **1992**, 257, 784–787.
- (6) Slemr, F.; Langer, E. *Nature* **1992**, 355, 434–436.
- (7) Johansson, K. *Verh. Internat. Verein. Limnol.* **1985**, 22, 2359–2363.

- (8) Norton, S. A.; Dillon, P. J.; Evans, R. D.; Mierle, G.; Kahl, J. S. The history of atmospheric deposition of Cd, Hg, and Pb in North America: evidence from lake and peat bog sediments. In *Acidic Precipitation: Sources, Deposition, and Canopy Interactions*; Lindberg, S. E., Page, A. L., Norton, S. A., Eds.; Springer-Verlag: New York, 1990; pp 73–102.
- (9) Engstrom, D. R.; Swain, E. B. *Environ. Sci. Technol.* **1997**, 31, 960–967.
- (10) Iverfeldt, A.; Munthe, J.; Pacyna, J.; Brosset, C. *Water, Air, Soil Pollut.* **1995**, 80, 227–233.
- (11) Slemr, F.; Junkermann, W.; Schmidt, R. W. H.; Sladovic, R. *Geophys. Res. Lett.* **1995**, 22, 2143–2146.
- (12) Rose, W. J. *Hydrology of Little Rock Lake in Vilas County, North Central Wisconsin*; 93-4139; U.S. Geological Survey: Madison, WI, 1993.
- (13) Brezonik, P. L.; Eaton, J. G.; Frost, T. M.; Garrison, P. J.; Kratz, T. K.; Mach, C. E.; McCormick, J. H.; Perry, J. A.; Rose, W. A.; Sampson, C. J.; Shelley, B. C. L.; Swenson, W. A.; Webster, K. E. *Can. J. Fish. Aquat. Sci.* **1993**, 50, 1101–1121.
- (14) Fitzgerald, W. F.; Mason, R. P.; Vandal, G. M. *Water, Air, Soil Pollut.* **1991**, 56, 745–768.
- (15) 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. Sources and fates of mercury and methylmercury in Wisconsin lakes. In *Mercury Pollution: Integration and Synthesis*; Watras, C. J., Huckabee, J. W., Eds.; Lewis Publishers: 1994; pp 153–177.
- (16) Patterson, C. C.; Settle, D. M. The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting, handling, and analysis. In *Accuracy in Trace Analysis: Sampling, Sample Handling and Analysis*; LaFleur, P., Ed.; National Bureau of Standards: Washington, DC, 1976; pp 321–351.
- (17) Fitzgerald, W. F.; Watras, C. J. *Sci. Tot. Environ.* **1989**, 87, 223–232.
- (18) Watras, C. J.; Morrison, K. A.; Back, R. C. Mass balance studies of mercury and methylmercury in small, temperate/boreal lakes of the northern hemisphere. In *Regional and Global Mercury Cycles: Sources, Fluxes and Mass Balances*; Baeyens, W., Ebinghaus, R., Vasiliev, O., Eds.; Kluwer Academic Publishers: Netherlands, 1996; pp 329–358.
- (19) Morrison, K. A.; Kuhn, E. S.; Watras, C. J. *Environ. Sci. Technol.* **1995**, 29, 571–576.
- (20) Bloom, N. S.; Horvat, M.; Watras, C. J. *Water, Air, Soil, Pollut.* **1995**, 80, 1257–1268.
- (21) Wisconsin Department of Natural Resources. *Wisconsin 1997 Air Quality Report*; PUBL-AM-278-98; Bureau of Air Management: Madison, 1998.
- (22) Illinois State Water Survey. *Standard Operating Procedures for the Initial Sample Processing of National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) Precipitation Samples at the Central Analytical Laboratory (CAL) at the Illinois State Water Survey*; Version 2.0; Illinois State Water Survey: Champaign, IL, 1993. (<http://nadp.sws.uiuc.edu/nadpdata/siteinfo.asp?id=W136&net=NADP>).
- (23) Bruland, K. W. Trace metals in seawater. In *Chemical Oceanography*; Riley, J. P., Chester, R., Eds.; Academic Press: London, 1983; pp 157–220.
- (24) Flegal, A. R.; Coale, K. H. *Water Resources Bulletin* **1989**, 25, 1275–77.
- (25) Iverfeldt, A. *Water, Air, Soil Pollut.* **1991**, 56, 251–265.
- (26) 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. *Limnol. Oceanogr.* **1999**, 44, 784–794.
- (27) Watras, C. J.; Frost, T. M. *Arch. Environ. Contam. Toxicol.* **1989**, 18, 157–165.
- (28) U.S. EPA. *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*; EPA 821-R-95-034; Office of Water, Engineering and Analysis Division (4303): Washington, DC, 1995.
- (29) Sorenson, J. A.; Glass, G. E.; Schmidt, K. W. *Environ. Sci. Technol.* **1994**, 28, 2025–2032.
- (30) Hudson, R. J. M.; Gherini, S. A.; Watras, C. J.; Porcella, D. B. Modeling the biogeochemical cycling of mercury in lakes: the Mercury Cycling Model (MCM) and its application to the MTL

- study lakes. In *Mercury Pollution: Integration and Synthesis*, Watras, C. J., Huckabee, J. W., Eds.; Lewis Publishers: 1994; pp 473–526.
- (31) Watras, C. J.; Morrison, K. A.; Host, J.; Bloom, N. S. *Limnol. Oceanogr.* **1995**, *40*, 556–565.
 - (32) Watras, C. J.; Back, R. C.; Halvorsen, S.; Hudson, R. J. M.; Morrison, K. A.; Wente, S. P. *Sci. Tot. Environ.* **1998**, *219*, 183–208.
 - (33) Vandal, G. M.; Mason, R. P.; Fitzgerald, W. F. *Water, Air, Soil Pollut.* **1991**, *56*, 791–803.
 - (34) Gilmour, C. C.; Henry, E. A.; Mitchell, R. *Environ. Sci. Technol.* **1992**, *26*, 2281–2287.
 - (35) Burke, J.; Hoyer, M.; Keeler, G.; Scherbatskoy, T. *Water, Air, Soil Pollut.* **1995**, *80*, 353–362.
 - (36) Glass, G. E.; Sorenson, J. A. *Environ. Sci. Technol.* **1999**, *33*, 3303–3312.
 - (37) Guentzel, J. L. Ph.D. Thesis, Florida State University: Tallahassee, FL, 1997.
 - (38) Munthe, J. Thesis, Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-142 96; Göteborg, Sweden, 1991; 51 pp.
 - (39) Stoddard, J. L.; Jeffries, D. S.; Lukewille, A.; Clair, T. A.; Dillon, P. J.; Driscoll, C. T.; Forsius, M.; Johannessen, M.; Kahl, J. S.; Kellog, J. H.; Kemp, A.; Mannio, J.; Monteith, D. T.; Murdoch, P. S.; Patrick, S.; Rebsdorf, A.; Skelkvale, B. L.; Stainton, M. P.; Traaen, T.; van Dam, H.; Webster, K. E.; Wieting, J.; Wilander, A. *Nature* **1999**, *401*, 575–578.
 - (40) Wisconsin Department of Natural Resources. *Sulfur Dioxide and Nitrogen Oxides Emissions Report*; PUBL 290-99; Bureau of Air Management: Madison, WI, 1999.
 - (41) Bloom, N. S.; Prestbo, E. M. A new survey of mercury in U.S. coals; *Proceedings of the 11th Annual Coal Conference*; Center for Energy Research, University of Pittsburgh: 1994.
 - (42) Kratz, T. K. Meteorological Data Set, North Temperate Lakes Long-Term Ecological Research program (<http://www.limnology.wisc.edu>); NSF, Center for Limnology, University of Wisconsin—Madison.
 - (43) Olmez, I.; Ames, M. R.; Gullu, G. *Environ. Sci. Technol.* **1998**, *32*, 3048–3054.
 - (44) Rudd, J. W. M. *Water, Air, Soil Pollut.* **1995**, *80*, 697–713.

Received for review February 10, 2000. Revised manuscript received July 12, 2000. Accepted July 17, 2000.

ES000991G