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Lacustrine Responses to Decreasing Wet Mercury Deposition Rates—Results from a Case Study in Northern Minnesota

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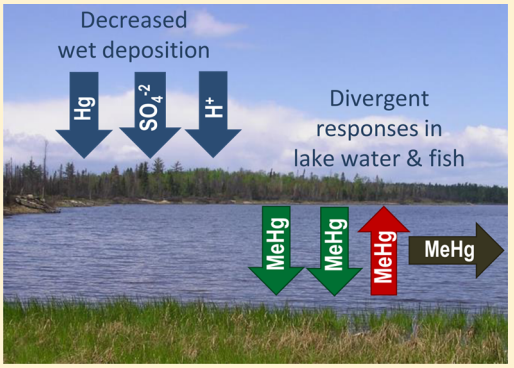
Supporting Information

ABSTRACT: We present a case study comparing metrics of methylmercury (MeHg) contamination for four undeveloped lakes in Voyageurs National Park to wet atmospheric deposition of mercury (Hg), sulfate (SO_4^{-2}), and hydrogen ion (H^+) in northern Minnesota. Annual wet Hg, SO_4^{-2}, and H^+ deposition rates at two nearby precipitation monitoring sites indicate considerable decreases from 1998 to 2012 (mean decreases of 32, 48, and 66%, respectively). Consistent with decreases in the atmospheric pollutants, epilimnetic aqueous methylmercury ($MeHg_{aq}$) and mercury in small yellow perch (Hg_{fish}) decreased in two of four lakes (mean decreases of 46.5% and 34.5%, respectively, between 2001 and 2012). Counter to decreases in the atmospheric pollutants, $MeHg_{aq}$ increased by 85% in a third lake, whereas Hg_{fish} increased by 80%. The fourth lake had two disturbances in its watershed during the study period (forest fire; changes in shoreline inundation due to beaver activity); this lake lacked overall trends in $MeHg_{aq}$ and Hg_{fish}. The diverging responses among the study lakes exemplify the complexity of ecosystem responses to decreased loads of atmospheric pollutants.



INTRODUCTION

Atmospheric transport and deposition of mercury (Hg) has elevated Hg levels in aquatic ecosystems worldwide.[1] Some of the Hg entering aquatic ecosystems is converted to methylmercury (MeHg), a toxic form that accumulates and biomagnifies in aquatic food webs. As a result, widespread fish-consumption advisories meant to protect human health have been issued in the United States[2] and elsewhere. Furthermore, piscivorous wildlife also are subject to toxic effects of Hg.[3] Hg levels in fish (Hg_{fish}) from many lakes in Voyageurs National Park in northern Minnesota exceed concentrations at which sublethal reproductive effects have been observed in fish.[4]

Mercury levels in fish vary greatly among aquatic ecosystems; this variability is affected by numerous factors including the load of Hg to an ecosystem; factors that affect Hg methylation and delivery to the base of the aquatic food web; and factors that affect biomagnification to game fish.[1,5,6]

Mercury accumulation rates in lacustrine sediments have declined since peaking in the mid to late 20th century in many inland lakes in forested watersheds in the north-central United States,[7,8] including lakes in Voyageurs National Park.[9] These declines are attributed to removal of Hg from products, industrial processes, and waste streams[7] and to decreasing anthropogenic Hg emissions on the continent.[10] Furthermore, in the United States, emission controls related to the Clean Air Act have resulted in decreases in wet deposition rates of sulfate (SO_4^{-2}) and hydrogen ion (H^+).[11,12] The interactions of SO_4^{-2}, acidic precipitation, and organic carbon are complex and likely vary among ecosystems,[13] which has implications for Hg cycling.[14]

We present a case study of trends in key measures related to Hg in atmospheric deposition, lakes, and lacustrine food webs in northern Minnesota. As with much of the Northern Forests ecoregion,[15] northern Minnesota contains many Hg-sensitive lakes with high Hg_{fish} levels.[16,17] We examine trends in atmospheric deposition of key contaminants (Hg, SO_4^{-2}, H^+), trends in Hg and MeHg in lake water in four lakes, and trends in Hg in age-1 yellow perch (*Perca flavescens*) from those same four lakes. Although our study is small in scale, we are

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unaware of other attempts to examine relationships among trends in atmospheric inputs, water-column Hg concentrations, and Hg_{fish} concentrations in a single region.

There is considerable variability in Hg_{fish} concentrations among lakes within Voyageurs National Park.[17] Two lakes in the park have northern pike (*Esox lucius*) with the highest Hg levels measured in the State of Minnesota (one of these lakes, Ryan Lake, will be considered herein). As with most lakes in the region, lakes in Voyageurs National Park lack substantial geologic or local industrial point sources of Hg. Atmospheric transport and deposition of Hg emitted from both anthropogenic and natural sources is likely the only substantial source.[17,18] Within the park and throughout northeastern Minnesota, Hg levels in fish are highest in lakes with low acid-neutralizing capacity (ANC), pH, and nutrient concentrations; high color and dissolved organic matter (DOM); and abundant hydrologically connected wetlands.[17,19]

MATERIALS AND METHODS

Study Area. Voyageurs National Park, an 883 km^2 park in northeastern Minnesota, contains numerous lakes and wetlands (Figure 1). The land cover is largely boreal forest, with thin soils, and common outcrops of Precambrian bedrock.[20] The lakes in this region are generally low-ANC, low-productivity lakes, with MeHg and dissolved organic carbon (DOC) levels that are strongly correlated to abundance of wetlands within a lake's watershed.[17] Four small lakes in Voyageurs National Park (Table 1) have been sampled for epilimnetic lake water and fish since 2000 (Shoepack Lake) or 2001 (Brown, Peary, and Ryan lakes), as part of earlier studies.[17,21]

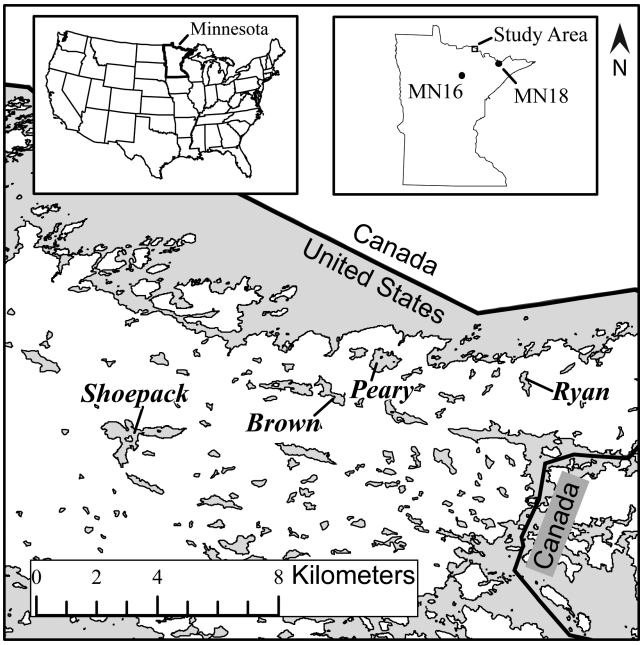

Figure 1. Location of four study lakes within Voyageurs National Park, and nearby National Atmospheric Deposition Program precipitation monitoring sites MN16 and MN18.

Wet Deposition. Although both wet and dry deposition are important in the mercury cycle,[22] consistent long-term data for dry Hg deposition are lacking in the region; we focus analysis of atmospheric inputs on wet deposition. The two closest National Atmospheric Deposition Program (NADP) sites in northern Minnesota (Figure 1) are collocated Mercury Deposition Network (MDN) and National Trends Network (NTN) sites,[23] which were examined for trends in wet Hg, SO_4^{-2}, and H^+ deposition. Although lake sampling began in 2000, Hg deposited to upland and wetland environments may take years (or decades) to be transported to the lake.[24] Therefore, we include deposition data collected during 1998–2012. Site MN16 (Marcell, Minnesota) is approximately 120 km south–southwest of Voyageurs National Park, and MN18 (Fernberg, Minnesota) is 120 km southeast of Voyageurs National Park. Methods for sampling and analysis of Hg in wet deposition have been fully described elsewhere.[25] (and references therein) Briefly, weekly composited precipitation samples are collected and analyzed using modifications of U.S. Environmental Protection Agency (U.S.EPA) Methods 1669[26] and 1631;[27] precipitation samples for Hg were analyzed at Frontier Global Sciences in Seattle, Washington. Data considered herein met the NADP's acceptance criteria (generally described in refs 25 and 28). Site MN18 Hg deposition data for 2002 were excluded because NADP criteria for calculating annual deposition rate were not met for that year. Thus, trend analyses for Hg are based on 14 complete years at MN16, and 13 of 14 years at MN18. We assumed that short-term (intra-annual) variations in wet deposition were unimportant in assessing multiyear trends in lake water and fish tissue Hg concentrations, and focus solely on annual precipitation chemistry (annual wet deposition rate and precipitation-weighted mean concentration) as a potential driver of in-lake trends.

Precipitation was collected and analyzed for SO_4^{-2} by ion chromatography and for H^+ by ion selective electrode, following NADP's published field and laboratory methods.[29,30] Laboratory-determined H^+ (rather than field determinations) was used for H^+ deposition trends reported herein. Data were considered acceptable for all years for SO_4^{-2} and H^+. Extensive documentation of NADP's methods, quality assurance plans, and quality assurance reports is available online.[23]

Table 1. Selected Lake Characteristics;[17,20] and Selected Water Measurements from near Centroid of Each Lake (Means from This Study, Based on *n* Samples Per Lake over Study Period, Where *n* = 7–10 for ANC; 13–16 for DOC; and 24–28 for pH and Secchi Transparency)

lake name	lake area (ha)	watershed area (ha)	wetlands (percentage of watershed area)	lake volume (10^6 m^3)	maximum depth (m)	mean depth (m)	pH	ANC (μeq L^{-1})	DOC (mg L^{-1})	Secchi transparency depth (m)
Brown	30.8	158.9	9.9	1.3	8.2	4.2	7.0	129	9.4	2.7
Peary	45.3	734.6	19.8	1.2	4.6	2.6	7.2	195	10.1	2.4
Ryan	14.2	86.9	6.4	0.3	3.7	2.1	6.9	130	12.7	2.8
Shoepack	123.8	1735	25.8	3.6	7.3	2.9	6.5	114	15.5	1.3

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LAKE WATER

Aqueous Hg analyses were measured on unfiltered, epilimnetic lake water, which was sampled two to three times per year, between May and September, during most years of the study period. This sampling regime was assumed to be representative of lake water conditions during the growing season. U.S. Geological Survey (USGS) personnel collected samples during 2000−2006, generally during the months of May, July, and September. No sampling was conducted in 2007. Beginning in 2008, National Park Service (NPS) personnel collected Hg samples from the four study lakes, in addition to performing routine water-quality monitoring during June, July, and August. Trace-metal clean sampling protocols were detailed previously.[31] Briefly, water samples were collected from approximately 5 cm depth, in the middle of each lake. Mercury samples were collected by dipping precleaned (in 4 *N* HCl at 65 °C) Teflon bottles off the bow of a windward-heading canoe; preserved by acidification with HCl to a final normality of approximately 0.02 *N*; and analyzed at the USGS Wisconsin Mercury Research Laboratory in Middleton, Wisconsin. Total Hg determinations in lake water (THg_{aq}) also used U.S.EPA method 1631.[27] Methylmercury in lake water ($MeHg_{aq}$) was determined by ethylation, followed by gas chromatographic separation and cold vapor atomic fluorescence detection.[32,33] Concentrations of THg_{aq} in field blank samples ranged from <0.04 (the detection limit) to 0.31 ng L^{-1} (maximum likelihood mean = 0.093 ng L^{-1}, n = 17; one outlier, 0.79 ng L^{-1}, excluded). $MeHg_{aq}$ was detected at the detection limit (0.04 ng L^{-1}) in two field blank samples, and was <0.04 ng L^{-1} in the remaining blank samples (n = 16). Sixteen sets of duplicate and triplicate lake water samples collected throughout the course of study yielded pooled coefficients of variation (CV) of 11% for THg_{aq} and 19% for $MeHg_{aq}$.

During 2000−2006, unfiltered samples for total organic carbon (TOC) were collected in borosilicate vials, and TOC was determined by high-temperature combustion, and a carbon analyzer (model 1010, OI Analytical, College Station, Texas) using Standard Method 5301B.[34] Starting in 2008, DOC was measured in filtered-water samples (0.7 μm glass-fiber filters), using a comparable U.S.EPA method.[35] TOC and DOC were similar in these low suspended-particulate-matter lakes, and are treated as the same measurement (DOC) herein. Field blank samples yielded minimal DOC contamination (<0.1−0.3 mg L^{-1}), and the pooled CV across five sets of replicate samples was 1.9%.

Fish. Yellow perch were sampled during the month of May, within 2−4 weeks after ice melt, by methods of Wiener and others.[17] Generally, 20−30 fish were sampled each year from each lake, and analyzed individually; however, fewer fish (8−16) were sampled during five of the sampling events and one event was represented by five fish. Fish age was estimated by analysis of scales,[36] and by examination of frequency distributions of fish length within each lake and sampling year. Age-1 fish (approximately one year since hatching) were targeted, and are assumed to integrate basal (water column and lower trophic level) MeHg over the preceding year. Although some larger (>age-1) perch were captured, they were excluded from the analysis presented herein. Fish were measured (total length, mm), weighed (g), and lyophilized to a near constant dry weight. Lyophilized perch obtained in 2000 were digested whole. In subsequent years, lyophilized whole perch were pulverized and homogenized with a mortar and pestle or stainless steel blender. For fish collected during 2000−2006, a 50-mg sample of the homogenate from each fish was digested in strong acid and analyzed by flow injection cold-vapor atomic absorption spectrophotometry with a PerkinElmer FIMS 100 (2000−2002)[37] or by cold-vapor atomic fluorescence spectroscopy with a Lehman Laboratories Hydra AF Gold Plus analyzer (2003−2006).[38] For fish collected during 2009−2012, 40- to 50-mg subsamples of dried, homogenized whole fish were analyzed by thermal decomposition and atomic absorption with an automated Milestone DMA-80 Direct Mercury Analyzer.[39] Precision and accuracy of total mercury in fish were quantified by the analyses of (1) analytical and procedural blanks, (2) replicate samples, (3) spiked samples, and (4) certified reference materials from the National Institute of Standards and Technology (NIST; Albacore Tuna, Mussel Tissue) and the National Research Council of Canada (NRCC; DOLT-4, DORM-1, DORM-3, TORT-1, TORT-2). Mean CV for triplicate samples were less than 10%. Mean recovery of spiked samples ranged 90−110%, and mean concentrations of reference materials were within the certified ranges.[17,40,41] Nearly all (≥95%) of the Hg in whole yellow perch is MeHg.[37,42,43] Thus, the measured concentrations of THg in yellow perch provide valid estimates of their MeHg concentrations.[42,43]

Trend Tests. Testing for temporal trends was done with SAS/STAT software (version 9.3),[44] generally using the GLM (for analysis of covariance) or REG (for simple linear regression) procedures. For precipitation chemistry trends, data from sites MN16 and MN18 had similar patterns over time, and were analyzed together by analysis of covariance (ANCOVA). Annual wet deposition rates (for Hg, SO_4^{-2}, and H^+) and annual precipitation-weighted mean concentrations (Hg only) were regressed against year, using the sampling site as a class variable. Lake water-column data were log-transformed to remove heteroscedasticity of residuals, and regressed against time (in years, using sampling date). For epilimnetic $MeHg_{aq}$ concentrations, which occasionally were less than the detection limit (left-censored), we used maximum likelihood regression using the LIFEREG procedure in SAS, assuming a normal distribution of $\log[MeHg_{aq}]$ (the Shapiro-Wilk test for normality indicated that distributions of $\log[MeHg_{aq}]$ were not significantly different from the normal distribution for the two lakes with no left-censored data). Significant slopes ($p < 0.05$) indicate trends in concentration or deposition rate. An outlier value for $\log[MeHg_{aq}]$ in Brown Lake, identified as an outlier with Grubbs' test,[45] was not included in trend tests.

For yellow perch, within the fairly narrow length and age range sampled for most fish, Hg_{fish} was not significantly correlated with fish length. For age-1 yellow perch, $\log[Hg_{fish}]$ was regressed against year. Regression residuals showed modest departures from normality; therefore, trend analyses also were performed using the nonparametric Mann-Kendall test, with the Sen's slope to assess trend magnitude.[46] The significance and magnitude of trends from nonparametric analysis were similar to the linear regression results, and we focus on regression-based results herein. As noted in the Materials and Methods section, typically 20−30 fish samples were collected each year from each lake, with a few years being relatively undersampled. Omitting each year's data from the regression analysis had no effect on significance and direction of trends, and only modest effects on the slope for the three lakes with

significant trends in Hg_{fish} (see SI Table S1); thus, the relatively undersampled years had minimal effect on the trend results.

Trend magnitudes are expressed as a percentage change in expected values (EV) over the periods 2001−2012 for lake water and fish and 1998−2012 for wet Hg deposition. Expected values were exponentiated from the log-transformed regression predictions, and multiplied by the mean of the exponentiated residuals to adjust for back-transformation bias (the Duan smearing estimate; see p. 256−257 of ref 46).

RESULTS

Wet Deposition. From 1998 to 2012, rates of wet Hg deposition decreased by approximately 32% at sites MN16 and MN18 (Figure 2A; Table S2 in SI). Similarly, annual precipitation-weighted Hg concentrations decreased by approximately 28% (Figure 2B; $p < 0.01$). During the same period, no trend was apparent in annual precipitation depth ($p = 0.33$). Annual deposition of SO_4^{-2} and H^+ declined by means of 48% and 66%, respectively, from 1998 to 2012 (SI Table S2, Figure S1).

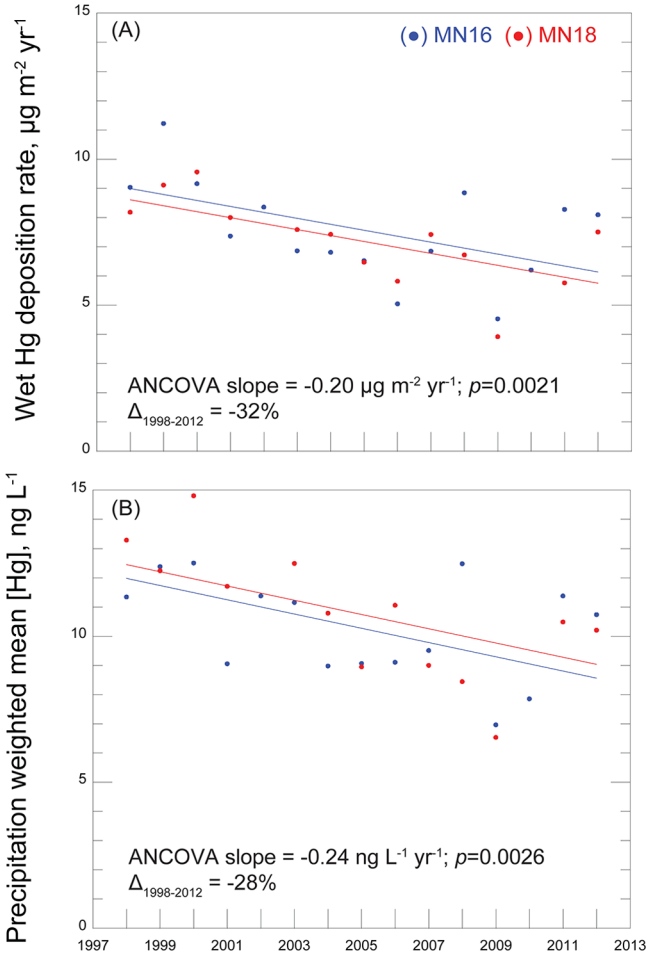

Figure 2. Trends in annual (A) wet total Hg deposition rate and (B) precipitation-weighted total Hg concentrations, for two northern Minnesota Mercury Deposition Network sites (MN16, Marcell, Minnesota; MN18, Fernberg, Minnesota). $\Delta_{1998-2012}$ is the percent change in mean expected values from analysis of covariance, for the respective years.

Lake Water. Trend results were mixed for epilimnetic lake water THg_{aq}, $MeHg_{aq}$, and DOC (Figure 3, SI Table S2). In Brown Lake, $MeHg_{aq}$ increased by 85% and DOC increased by 30% from 2001 to 2012. In contrast, $MeHg_{aq}$ in Peary and Ryan lakes decreased by 50% and 43%, respectively (mean decrease = 46.5%), whereas DOC and THg_{aq} had no trends. In Shoepack Lake, both THg_{aq} and DOC had modest increases over the study period (27% and 25%, respectively). Although the overall trend in epilimnetic $MeHg_{aq}$ in Shoepack Lake was not significant (Figure 3), $MeHg_{aq}$ decreased from 2000 to 2006,[21] then subsequently rebounded with measurements since 2008 frequently exceeding 0.4 ng L^{-1}, among the highest epilimnetic $MeHg_{aq}$ levels for all Voyageurs lakes (cf. refs 21 and 31). Epilimnetic pH appeared to be increasing in all four study lakes, although trends were significant for only one of the lakes (SI Figure S2).

Yellow Perch. Trends in Hg concentrations in fish varied among lakes, but paralleled the trend in epilimnetic MeHg within each of the four lakes (SI Table S2). Hg_{fish} increased in Brown Lake by 80% from 2001 to 2012. In Peary and Ryan Lakes, Hg_{fish} decreased 37% and 32%, respectively (mean decrease = 34.5%) (Figure 4). Shoepack Lake had no significant trend in Hg_{fish}, but was sampled less frequently than the other lakes, particularly in the latter years of this study (SI Table S1, Table S2).

DISCUSSION

A spatiotemporal analysis of monitoring data from 845 lakes across Minnesota (including two lakes from this study, Ryan and Peary) shows an overall downward trend in $MeHg_{fish}$ from 1982 to 1992, but an upward trend from 1992 to 2006.[47] Not all individual lakes exhibit this overall trend. Hg_{fish} levels in some lakes have decreased while others in the region have increased,[47] and monitoring data generally are not collected in sufficient temporal detail to examine within-lake Hg_{fish} trends, or trends in causative factors such as aqueous MeHg.

The 32% decrease in wet Hg deposition in northern Minnesota from 1998 to 2012 (Figure 2A; SI Table S2) is of considerable magnitude. Previous trend analyses of MDN wet Hg deposition across shorter time intervals for this region indicated differing results. For example, there was no change in wet Hg concentration and deposition from 1996 to 2005 or from 2002 to 2008,[25,48] whereas 1998−2005 data indicated significant decreases.[49] Previous studies[25,49] reported decreases in Hg deposition at several sites in the northeastern United States—east of Minnesota, where a greater number of Hg emissions exists. The significant decrease in the annual precipitation-weighted mean concentration of total Hg, in the absence of a trend in annual precipitation depths, is consistent with the substantial (59%) reduction in U.S. mercury emissions from 1990 to 2005.[50]

The decreases in SO_4^{-2} and H^+ deposition reported here are similar to previously reported decreases for sites MN16 and MN18 for 1985−2009,[11] and reflect widespread decreases in both SO_4^{-2} and H^+ deposition in response to air pollution controls.[11] Decreases in SO_4^{-2} loading also may cause Hg methylation to decline. The addition of SO_4^{-2} to wetlands has been shown to exacerbate MeHg production.[51,52] Decreases in SO_4^{-2} inputs have been experimentally linked with decreased MeHg production,[53] and a long-term decrease in Hg_{fish} from lakes on Isle Royale (a northern forests ecosystem, about 300 km east of Voyageurs National Park) has been attributed to decreased SO_4^{-2} deposition, in the absence of a concomitant decrease in Hg deposition.[54]

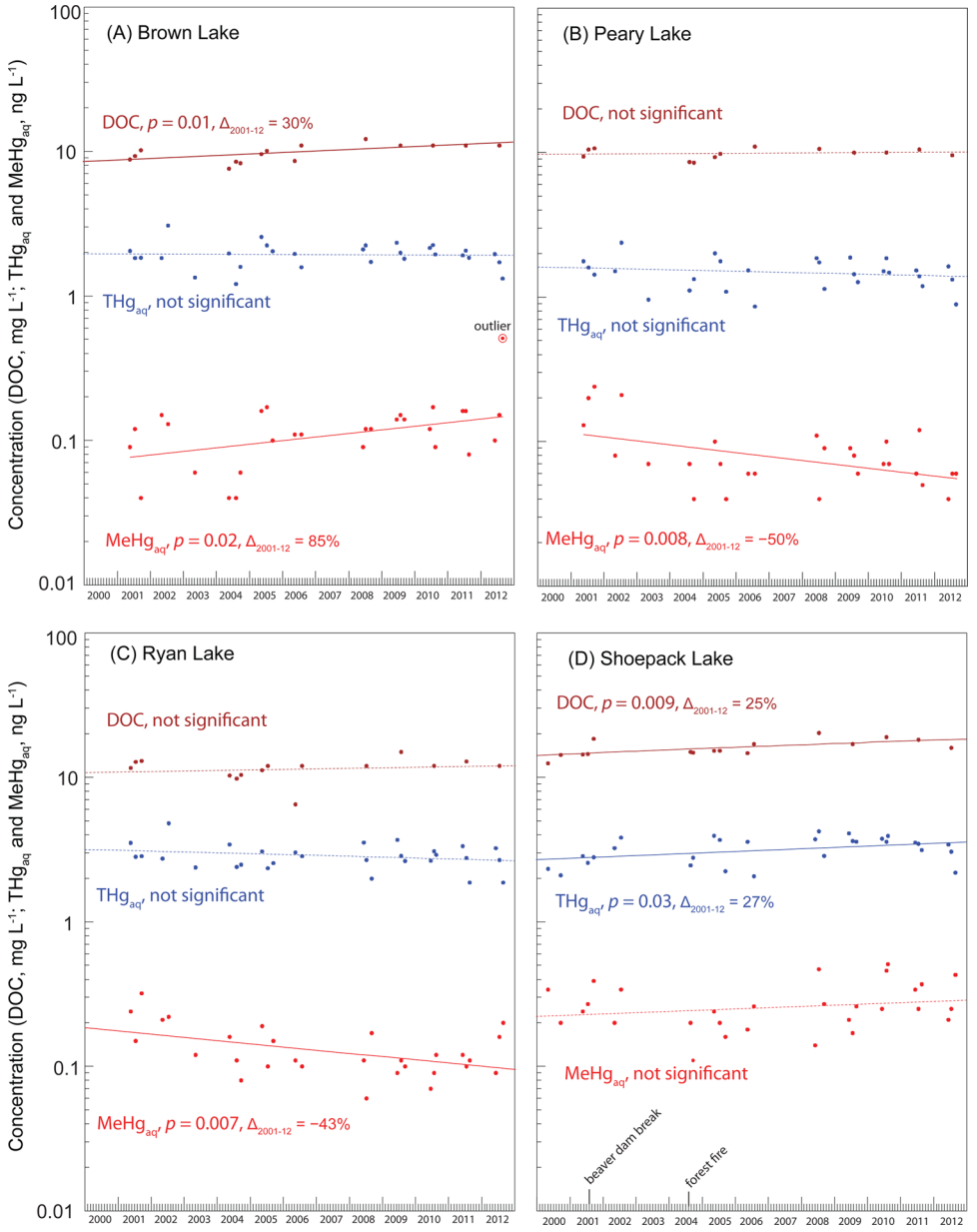

Figure 3. Dissolved organic carbon (DOC), total mercury (THg_{aq}), and methylmercury ($MeHg_{aq}$) concentrations in epilimnetic water for four Voyageur's National Park lakes, 2000−12 (Shoepack Lake) and 2001−12 (Brown, Peary, and Ryan Lakes). An outlier value for $MeHg_{aq}$ in Brown Lake (graph A) was not included in the trend analysis. $\Delta_{2001-12}$ is the percent change in expected values from regression analysis, for the respective years.

Similarly, the prevailing literature indicates a strong influence of H^+ on Hg cycling. Controlled experiments have found substantially higher Hg methylation rates, and lower MeHg demethylation rates, at pH 5.0 versus pH 7.0.[55] Several surveys in the Upper Midwest[19,56] and elsewhere[57] have shown negative correlations between lake pH and Hg_{fish}. Consequently, reduced H^+ loading from emission controls[58] also has the potential to reduce MeHg production and availability to aquatic biota.

Kallemeyn and others[20] previously reported that pH and ANC increased, while SO_4^{-2} decreased in several lakes within Voyageurs National Park, from 1978 to 2000, in response to reduced acidic deposition. The trends we observe in epilimnetic pH (SI Figure S2) are consistent with reduced acidic deposition during our study period, and appear to be a continuation of longer-term increases in lake pH in response to reduced acidic deposition. Epilimnetic SO_4^{-2} and ANC were not collected with sufficient frequency in our study to assess trends.

Lakes are expected to exhibit both a rapid reduction in MeHg in water and fish in response to reduced Hg deposition directly to the lake surface; and a slow response (on the order of decades) to Hg deposited on wetland and upland compartments because of the storage of Hg in vegetation, organic matter, and soils and the long lag times between reduced Hg deposition rates and decreases in Hg in catchment runoff.[5,24] The mixed results for the four study lakes exemplify the complexity of whole-ecosystem responses. The upward $MeHg_{aq}$ and Hg_{fish} trends for Brown Lake are supported by an increase in DOC—a strong covariate[17] but are counter to the trends in wet Hg, SO_4^{-2}, and H^+ deposition. Increases in DOC in remote catchments have been attributed to numerous factors, including decreases in SO_4^{-2} deposition, changes in land cover, and

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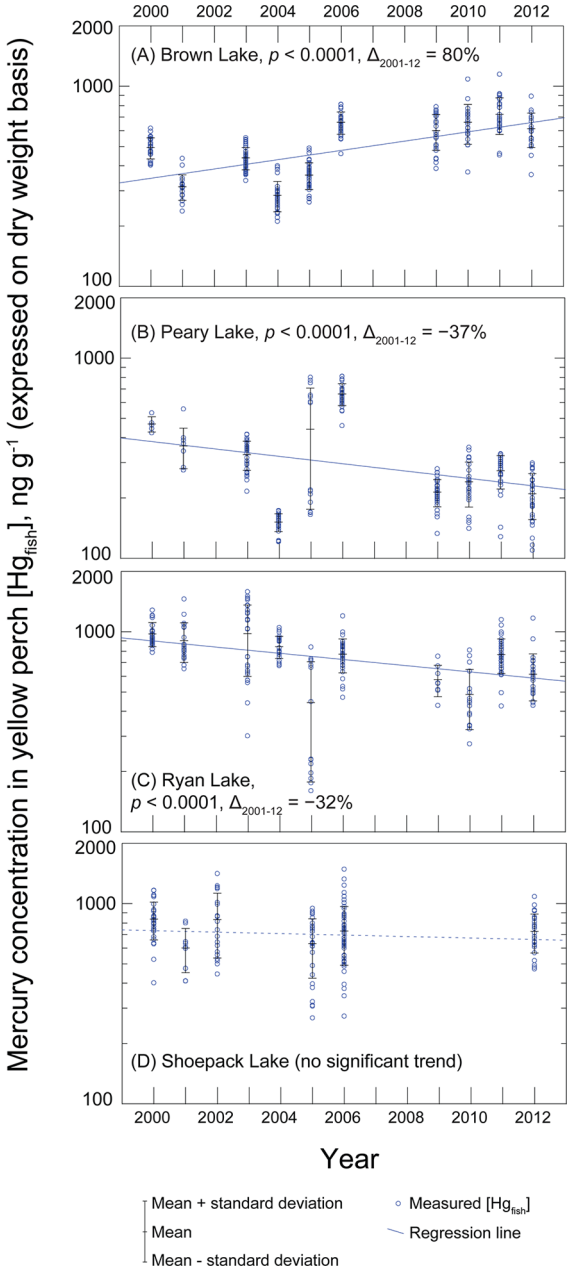

Figure 4. Trends in mercury concentrations in whole yellow perch from four lakes in Voyageurs National Park, 2000–2012. Trends in three lakes (Brown, Peary, and Ryan) were highly significant. $\Delta_{2001-12}$ is the percent change in expected values from regression analysis, for the respective years.

changes in temperature and precipitation.[13] There is evidence that elevated DOC, in response to reduced acid and SO_4^{-2} deposition, may exacerbate MeHg levels in some ecosystems.[14] However, decreased SO_4^{-2} loading is not a likely explanation of increases in DOC, $MeHg_{aq}$, and Hg_{fish} in Brown Lake; if it were, we would expect Peary and Ryan Lakes to respond similarly to Brown Lake. Instead, increased inflow from an upstream lake with higher $MeHg_{aq}$ and DOC is a more likely source for increased MeHg loading to Brown Lake. During 2001–2002, a lake directly upstream from Brown Lake (Oslo Lake) had higher epilimnetic $MeHg_{aq}$ than Brown Lake in four out of five sampling events, and all sampling events where DOC was sampled.[31] Lake levels in all study lakes increased from 2006 to 2012 (SI, Figure S3), which supports the hypothesis that increased inflows of water with higher MeHg affected the trend in Brown Lake. Additional research on MeHg production and fluxes in Brown Lake and its catchment would be needed to definitively ascribe cause to the observed increase in MeHg.

Trends in Peary and Ryan Lakes (downward $MeHg_{aq}$ and Hg_{fish}) are broadly consistent with trends in wet deposition. Decreased $MeHg_{aq}$ levels likely reflect decreased MeHg production, which is consistent with lower wet Hg deposition,[59] and lower wet SO_4^{-2} deposition.[51]

Shoepack Lake experienced two disturbances during the study period. A beaver dam on the lake's outlet failed in 2001, resulting in partial drawdown of the lake.[60] This reduced lake surface area by 47%,[60] and exposed previously inundated wetland soils. Water levels have since partially rebounded. Although data for the complete study period are lacking, the National Park Service has measured an increase in water level of 0.9 m from 2006–2012 (SI Figure S3). Drawdown and reflooding exacerbate mercury methylation,[61−64] and is a plausible explanation for the apparent trend reversal in Shoepack Lake $MeHg_{aq}$ levels. The other disturbance was a 2004 forest fire, which burned about 20% of Shoepack Lake's catchment, including nearly 80% of its shoreline. Although significant losses of soil Hg occurred in burned areas, no short-term changes on MeHg in water or fish were observed.[21] The literature on the effect of forest fires on the mercury cycle is mixed, and includes studies that found no effect of fire on in-lake MeHg (e.g., boreal Precambrian Shield lakes in Quebec, Canada[65]) and studies that indicated short-term increases in Hg and MeHg in runoff (e.g., Moab Lake in alpine Alberta, Canada[66]).

Understanding changes in MeHg contamination of aquatic food webs, in response to changes in key factors of methylmercury production, is critical to assess the efficacy and benefits of emissions reductions. This case study—the first we are aware of to report a >10-year trend in $MeHg_{aq}$ and THg_{aq}—shows diverging responses among the study lakes and exemplifies the complexity of ecosystem responses to decreased loads of atmospheric pollutants. Although we cannot establish causation, the downward trends in $MeHg_{aq}$ and Hg_{fish} in two of our four study lakes are consistent with decreases in atmospheric loading of mercury, as well as SO_4^{-2} and H^+, which indirectly affect the mercury speciation and bioavailability. However, the mixed results from the remaining two lakes exemplify that recovery will vary among ecosystems, and may be affected by watershed-specific hydrologic conditions and disturbances.

Marked decreases in wet Hg deposition[25,67] and Hg_{fish}[67] in the northeastern United States have accompanied regional reductions in Hg emissions. Although our study area is more remote, compared with the northeastern United States, regional- to national-scale reductions in Hg emissions appear to be resulting in decreased Hg deposition in northern Minnesota as well. Protected areas, such as national parks, provide optimal natural settings for monitoring and assessing responses of aquatic systems and food webs to changes in atmospheric deposition of Hg.[68] On unprotected landscapes, the effects of land use and related human disturbances, such as those associated with forestry and agriculture, can greatly affect the transport of THg and MeHg from the terrestrial catchment to aquatic systems[69,70] and the concentration of MeHg bioaccumulated near the base of the aquatic food web.[71] The cycling of Hg—including the microbial production of MeHg—

also can be affected by natural disturbances, such as beaver activity[72] and fire.[73] One of the four lakes in the present 12-year study was affected by two such disturbance events. Thus, the interpretation of Hg trends can be complicated by the confounding effects of on-site natural disturbances, even within a protected area such as Voyageurs National Park.

We conclude that multiple study sites are desirable when assessing ecosystem responses to changes in atmospheric deposition of Hg. In the absence of a nationally coordinated program to assess mercury trends, which has been proposed but not yet implemented,[74] case studies such as this provide valuable insights on trends in mercury in aquatic ecosystems. Whole ecosystem mass balance studies in multiple watersheds in the same region are needed to fully understand how changes in deposition affect MeHg levels in lake water and fish.

■ ASSOCIATED CONTENT

Supporting Information

Regression-based data for temporal trends, including mercury, sulfate, and hydrogen ion in wet deposition; methylmercury, total mercury, and dissolved organic carbon in lake water; and mercury in age-1 yellow perch. Relative water levels in study lakes during 2006−2012. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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