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Deposition and Cycling of Sulfur Controls Mercury Accumulation in Isle Royale Fish

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Mercury contamination of fish is a global problem. Consumption of contaminated fish is the primary route of methylmercury exposure in humans and is detrimental to health. Newly mandated reductions in anthropogenic mercury emissions aim to reduce atmospheric mercury deposition and thus mercury concentrations in fish. However, factors other than mercury deposition are important for mercury bioaccumulation in fish. In the lakes of Isle Royale, U.S.A., reduced rates of sulfate deposition since the Clean Air Act of 1970 have caused mercury concentrations in fish to decline to levels that are safe for human consumption, even without a discernible decrease in mercury deposition. Therefore, reductions in anthropogenic sulfur emissions may provide a synergistic solution to the mercury problem in sulfate-limited freshwaters.

Introduction

Anthropogenic emissions of mercury have contaminated ecosystems on a global scale (*1*). In aquatic ecosystems, microbes transform deposited inorganic mercury into methylmercury (*2*) which biomagnifies in food webs (*3*), resulting in high concentrations in fish (*4*). Consumption of contaminated fish is the major route of methylmercury exposure in humans and is detrimental to health (*5*). The Clean Air Mercury Rule, issued by the U.S. Environmental Protection Agency in 2005, and other similar initiatives aim to reduce anthropogenic mercury emissions and thus atmospheric mercury deposition. Considerable effort is now being spent to determine how mercury concentrations in fish will respond to reductions in mercury deposition, but other factors may also be important for the bioaccumulation of methylmercury in fish (*6*, *7*). Since preindustrial times in northeastern Minnesota, mercury deposition has increased three-fold, while the concentrations of mercury in fish have increased ten-fold (*8*). In the nearby boreal lakes of Isle Royale, Michigan, we studied temporal trends of mercury concentrations in fish in relation to atmospheric mercury deposition and other factors.

Isle Royale is an island ecosystem in Lake Superior (Figure 1A) far removed from industrial and urban centers, but it is plagued by air pollution (e.g., *9*, *10*). Mercury, perhaps the most prevalent of these pollutants, has been documented in high concentrations in fish from lakes on the island (*11*−*14*). Indeed, concentrations in the mid-1990s were high enough in several lakes to elicit fish consumption advisories for humans and to raise serious concerns about toxicological effects to fish and fish-eating wildlife (*12*). We returned to Isle Royale in 2004−2006 and, to our surprise, discovered mercury concentrations in northern pike (*Esox lucius*) substantially declined during the past decade. This decline is good news for the ecosystem, and we focused on finding its cause. Three plausible hypotheses were identified: (i) atmospheric mercury deposition has declined, reducing the amount of inorganic mercury available for methylation, (ii) changes in the ecology of northern pike or its underlying food web have occurred, reducing the bioaccumulation or biomagnification of methylmercury, or (iii) environmental factors that stimulate net methylation have lessened, reducing the amount of methylmercury available for bioaccumulation. We address each of these hypotheses in turn and, finally, point to reduced rates of sulfate deposition as the primary cause.

Materials and Methods

We used live and museum-preserved fish, sediment profiles, water, and archived data to reconstruct temporal trends of mercury concentrations in fish, atmospheric mercury deposition, and other factors. The fish species of most interest was northern pike because they are ubiquitously distributed among the island's lakes and are the predominant species in the fishery (*12*). Northern pike ($n = 124$) were collected from a total of eight lakes: two non-advisory "reference" lakes (Richie and Siskiwit) and six "advisory" lakes (Angleworm, Eva, Intermediate, Sargent, Shesheeb, and Wagejo). Walleye (*Sander vitreus*, from Lake Whittlesey) and coregonids (*Coregonus artedii* and *Coregonus clupeaformis*, from Siskiwit Lake) were also collected. Sediment cores and epilimnetic water were collected from four lakes (Richie, Sargent, Siskiwit, and Whittlesey). Physical, chemical, and biological characteristics of the study lakes are described by Kallemeyn (*12*). Studies of mercury biogeochemistry in Lake Richie and Sargent Lake are reported by Gorski et al. (*13*).

Fish. Live fish were collected by gill net or hook-and-line and sacrificed according to protocols approved by the Miami University Institutional Animal Care and Use Committee.

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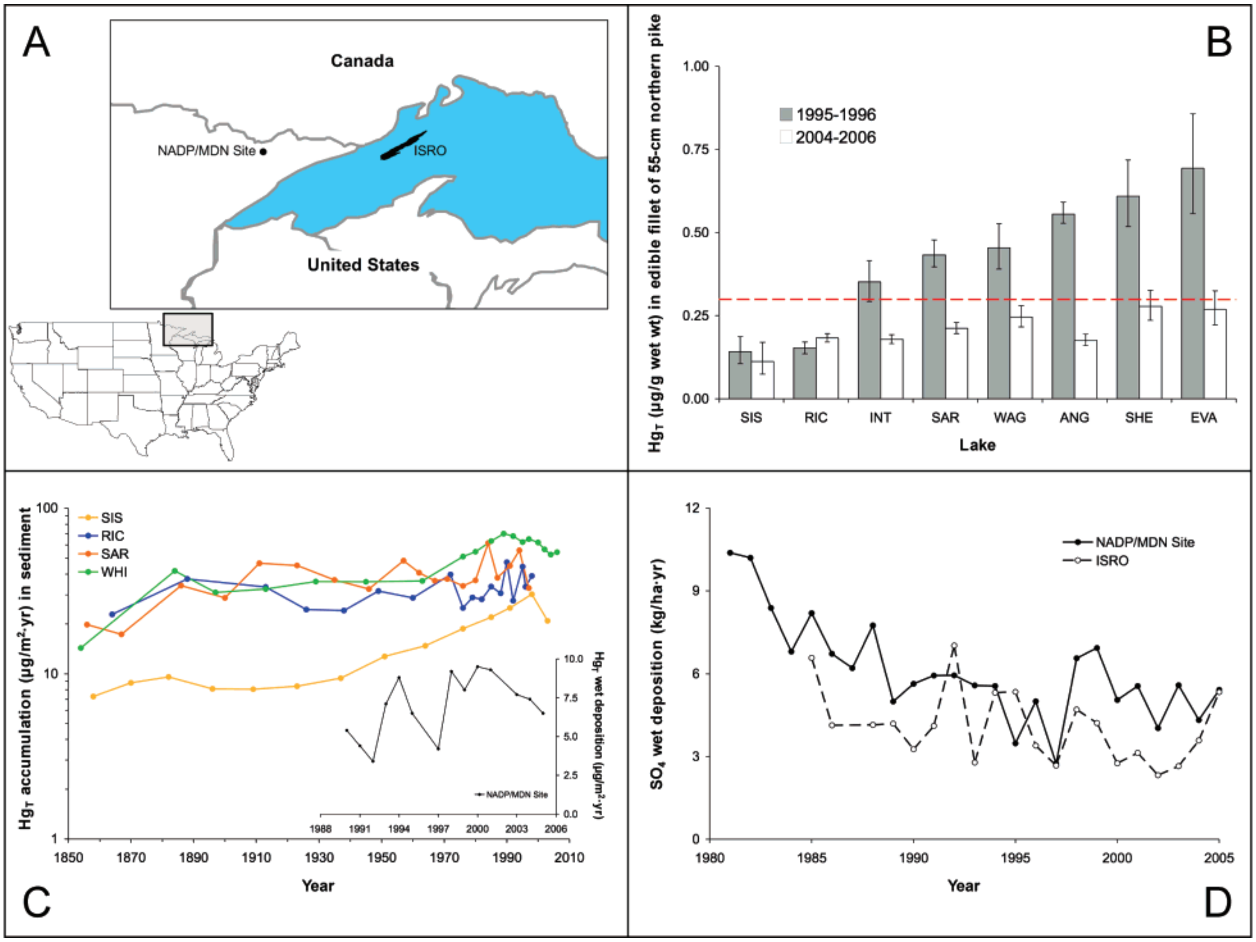

FIGURE 1. Isle Royale, mercury, and sulfate. (A) Location of Isle Royale (ISRO) and the nearest National Atmospheric Deposition/Mercury Deposition Network (NADP/MDN) site. (B) Concentrations of total mercury (Hg_T) in edible fillets of 55 cm northern pike (*Esox lucius*) collected from eight lakes at Isle Royale during 1995–1996 (gray bars) and 2004–2006 (white bars). Lakes include Siskiwit (SIS), Richie (RIC), Intermediate (INT), Sargent (SAR), Wagejo (WAG), Angleworm (ANG), Shesheeb (SHE), and Eva (EVA). The red, dashed line represents the U.S. Environmental Protection Agency fish tissue criterion for methylmercury to protect human health. Error bars represent 1 SE. (C) Accumulation of Hg_T in sediment from four lakes at Isle Royale. Lakes include Siskiwit (dark red), Richie (blue), Sargent (orange), and Whittlesey (WHI, green). Inset graph shows wet deposition of Hg_T at the nearest NADP/MDN Site. (D) Wet deposition of sulfate (SO_4) at Isle Royale (open circles, dashed line) and the nearest NADP/MDN site (filled circles, solid line).

Preserved fish were obtained from the University of Michigan Museum of Zoology. Since 1920, the museum's protocol for preserving fish has involved fixation in 10% formalin for up to 1 week, washing in water for 1 d, and storage in 70% ethanol. It is possible that a different method was used to preserve the fish from 1905. Live and preserved fish were sexed, measured for total length, and sampled for scales and skin-on edible fillets. At least two scales from each fish were examined to determine age (*15*) and back-calculated total length at age (*16*). Skin-on edible fillets were analyzed for carbon and nitrogen stable isotopes and total mercury. For carbon and nitrogen stable isotopes, fillet subsamples were dried, ground, packaged into tin capsules, and sent to the University of California, Davis, CA, Stable Isotope Facility for analysis (*17*). Laboratory standards for carbon (Pee Dee Belemnite) and nitrogen (atmospheric N_2) were analyzed before and after every twelve samples and were within 0.1‰ of known values. Ten percent of samples were analyzed in duplicate. The mean relative standard deviations for the duplicates were 0.3% for carbon and 2.3% for nitrogen. To adjust for effects of museum preservation on the $\delta^{13}C$ and $\delta^{15}N$ values of preserved fish, correction factors were applied according to the meta analysis performed by Kelly et al. (*18*). For total mercury, fillet subsamples were acid digested according to U.S. EPA method 245.6 (*19*) and analyzed by cold-vapor atomic absorption spectroscopy. Duplicate samples, spiked samples, and certified reference materials (TORT-2, DORM-2) were digested and analyzed with each batch of samples. Mean relative standard deviation for duplicate samples was 6.0%. Mean recovery of spiked samples was 94.2%. Mean measured concentrations of reference materials were within (TORT-2) or 4.0% below (DORM-2) the certified ranges. It is unlikely museum preservation affected total mercury concentrations of preserved fish because total mercury was not detectable in preservation fluids before or after use (*11*). We did, however, account for the dehydration of preserved fish with the methods of Swain and Helwig (*8*). Briefly, fillets from preserved fish were dried before analysis of total mercury. Separately, "wet" fillets sampled from fresh fish were dried to determine conversion factors between dry and wet weights. Conversion factors for northern pike and coregonids were 0.208 and 0.197 g dry/g wet weight, respectively. All data for preserved walleye are from a previous publication (*11*). Concentrations of total mercury were standardized to a chosen total length for northern pike, walleye, and coregonids for each lake from regressions of log-transformed data (*20*).

Sediment. Sediment cores were obtained with piston or gravity corers from depositional basins within lakes. Cores were sectioned and freeze-dried. Analysis of ^{210}Pb was performed on each core to determine age and sedimentation rates (*21*). Except for Siskiwit Lake, sedimentation rates were

TABLE 1. Mean (1 SE) Stable Carbon (δ^{13}C) and Nitrogen (δ^{15}N) Isotope Compositions in Edible Fillets of Northern Pike in Lakes of Isle Royale, 1905, 1929, 1998−1999, and 2004−2006

	1905			1929			1998−1999			2004−2006		
lake	*n*	δ^{13}C (‰)	δ^{15}N (‰)	*n*	δ^{13}C (‰)	δ^{15}N (‰)	*n*	δ^{13}C (‰)	δ^{15}N (‰)	*n*	δ^{13}C (‰)	δ^{15}N (‰)
ANG				3	−25.27 (0.10)	8.47 (0.20)				12	−28.20 (0.22)	9.10 (0.15)
EVA				3	−28.51 (0.51)	9.76 (0.30)				12	−29.59 (0.27)	9.73 (0.11)
INT				3	−24.44 (0.77)	8.84 (0.11)				20	−27.13 (0.12)	10.21 (0.12)
RIC				2	−25.99 (0.36)	9.98 (0.19)	11	−26.06 (0.34)	9.99 (0.14)	16	−26.50 (0.25)	9.70 (0.28)
SAR	1	−24.39 (na)	9.49 (na)	3	−25.97 (0.35)	9.80 (0.32)	14	−27.90 (0.17)	10.29 (0.14)	20	−26.95 (0.14)	10.58 (0.16)
SHE				3	−28.79 (0.16)	8.17 (0.48)				14	−30.92 (0.11)	9.57 (0.08)
SIS				1	−22.02 (na)	8.39 (na)				11	−23.18 (0.50)	8.48 (0.17)
WAG				5	−26.61 (0.29)	8.28 (0.13)				19	−28.63 (0.40)	8.47 (0.12)

multiplied by a correction factor (calculated as the atmospheric ^{210}Pb flux divided by the core-specific ^{210}Pb flux) to adjust for focusing. Analysis of total mercury was performed on each core according to previously published methods (*22−24*). As for fish, duplicate samples, spiked samples, and certified reference material (PACS-2) were digested and analyzed with each batch of samples. Mean relative standard deviation for duplicate samples was 6.0%. Mean recovery of spiked samples was 96.4%. Mean measured concentration of PACS-2 was within the certified range. Values for total mercury accumulation were calculated by multiplication of the focusing-corrected sedimentation rates by total mercury concentrations. Analysis of diatoms (*25*, *26*) was performed on cores from Lake Richie and Sargent Lake to reconstruct lake productivity (as total phosphorus). Total phosphorus was inferred from diatom assemblages by comparison with a calibration data set from 64 lakes in northern Wisconsin (*27*). Analysis of total sulfur (TS) and chromium-reducible sulfur (CRS) was performed on each core according to Aspila et al. (*28*) and Canfield et al. (*29*), respectively. Ten percent of samples were analyzed in duplicate. Mean relative standard deviation for duplicates was 10.5% for TS and 13.1% for CRS. Values for non-CRS were derived by subtracting CRS from TS.

Water. Epilimnetic water was collected by hand into polyethylene cubitainers, filtered through 0.45 μm membranes, and analyzed for sulfate according to standard methods (*30*). One of four samples was analyzed in duplicate with a relative standard deviation of 1.7%.

Statistics. Data were analyzed with paired t-tests, least-squares regression, and analysis of variance (ANOVA) with SAS or SPSS. Assumptions of statistical tests were validated before analysis. Because of inherent variability in the monitoring data (*31*), a type I error (α) of 0.1 was used to judge the significance of all statistical tests.

Results and Discussion

Decline in Mercury Concentrations of Northern Pike. In comparison to data from Isle Royale a decade ago (*12*), concentrations of total mercury in edible fillets of 55 cm northern pike (Figure 1B) remained essentially the same in reference lakes (paired t-test, $t_1 = 0$, $p = 1$) but declined substantially in advisory lakes (paired t-test, $t_5 = 6.90$, $p = 0.001$) to levels considered by the U.S. Environmental Protection Agency as safe for human consumption ($<0.3\ \mu$g/g wet weight) (*32*). Similar declines have been reported for lake trout (*Salvelinus namaycush*), northern pike, and walleye in likewise semipristine boreal lakes of adjacent northwestern Ontario, Canada, westward into Manitoba, Canada (*33*). The cause of these declines was not determined. To the south of Isle Royale and nearer to industrial and urban centers, mercury concentrations of yellow perch (*Perca flavescens*) in Little Rock Lake, northern Wisconsin, declined by 30% between 1994 and 2000 because of reduced rates of atmospheric mercury and sulfate deposition (*34*). A follow-up study of twelve lakes in northern Wisconsin indicated this decline may have also been associated with increased dissolved organic carbon (DOC) concentration (*35*).

Multiple Working Hypotheses. The source of mercury to Isle Royale is unequivocally atmospheric (*36*), but deposition has not abated in recent years and, therefore, the amount of inorganic mercury available for methylation has not declined. Sediment records from lakes on the island, data from the Mercury Deposition Network (linear regression, $r = 0.500$, $p = 0.069$, $n = 14$) (*37*), and literature sources (*38−40*) all indicate a century-long trend of stable or increasing rates of atmospheric mercury deposition at or near Isle Royale (Figure 1C). On the basis of observed total mercury accumulation in surface sediment from four lakes and best estimates from the literature, we estimate that, on average, about 2/3 of the mercury entering the lakes at Isle Royale is mobilized from atmospheric deposition to the watershed and about 1/3 is from direct deposition to the lake surface. Wet plus dry deposition (12.5 μg/m^2 year) (*41*) minus evasion (0.7 μg/m^2 year) (*42*) equals 1/3 of the flux to sediments (mean 36 μg/m^2 year). Watershed inputs (5−43 μg/m^2 year) (*43*) can account for the other 2/3. This partitioning, however, is unlikely to have changed with time, and we conclude that the deposition of mercury to the lakes has not decreased over at least the past decade, and therefore, changes in mercury source cannot explain the dramatic decline in mercury concentrations we observed in fish.

We next considered whether changes in the ecology of northern pike or its underlying food web have occurred, influencing changes in the bioaccumulation of methylmercury. Methylmercury is primarily taken up by fish in their food (*44*). Because aquatic food webs biomagnify methylmercury (*3*), lake productivity (*45*) and trophic position (*46*, *47*) affect uptake. Sedimentary diatom records since 1850 indicate a slight increase in productivity in a reference lake, Lake Richie (linear regression, $r = 0.544$, $p = 0.077$, $n = 11$), but no change in productivity of an advisory lake, Sargent Lake (linear regression, $r = 0.133$, $p = 0.733$, $n = 9$) (Supporting Information, Figure S1).

Analyses of stable carbon and nitrogen isotopes indicate no meaningful change in trophic position of northern pike in any study lake since at least 1929 (Table 1). We did observe statistically significant differences in δ^{13}C and δ^{15}N among years (randomized complete block ANOVA for δ^{13}C, $F_{3,7} = 31.2$, $p < 0.001$ and δ^{15}N, $F_{3,7} = 5.69$, $p = 0.001$), but the differences were subtle and not consistent with trends in mercury concentrations in fish. Post-hoc pairwise comparisons revealed no changes in δ^{13}C ($t_7 = -0.960$, $p = 0.338$) and δ^{15}N ($t_7 = -0.380$, $p = 0.708$) during the past decade, which is the period of most interest. However, significant changes occurred between historic and recent samples (e.g., 1929 versus 2004−2006 for δ^{13}C, $t_7 = 8.93$, $p < 0.001$, and δ^{15}N, $t_7 = -3.88$, $p < 0.001$). For δ^{13}C and δ^{15}N, recent values are on average 1.81‰ lower and 0.564‰ higher, respectively, than historic values. These are rather subtle changes because the range for δ^{13}C in northern pike among study lakes is greater than 12‰, and Vander Zanden and Rasmussen (*48*) reported an enrichment of 3.4‰ per trophic level for δ^{15}N. Further, we cannot reasonably explain the differences in δ^{13}C and δ^{15}N among years. Differences could be an artifact from the preservation of museum specimens. Preservation with formalin and ethanol significantly affects δ^{13}C and δ^{15}N values in fish tissue, and if possible, species-specific correction factors should be applied to adjust for these effects (*18*). Northern pike were preserved with both formalin and ethanol, but we know of no correction factors for this species. Instead, we used correction factors from the meta-analysis performed by Kelly et al. (*18*). Otherwise, changes in δ^{13}C and δ^{15}N have been described in lakes following the introduction of non-native species (*49*). However, introductions of non-native species to the inland lakes of Isle Royale have not occurred (*12*). It is also possible that source values for δ^{13}C and δ^{15}N have changed over time because of atmospheric pollution (*50*). Regardless of possible causes, the changes in δ^{13}C and δ^{15}N are not consistent with the observed decline in mercury concentrations in northern pike from 1929 to the present. Lower δ^{13}C values indicate a shift toward food of pelagic origin. In oligotrophic lakes such as the inland lakes of Isle Royale, pelagic food webs tend to bioaccumulate contaminants to a higher degree than benthic food webs (*51*). Higher δ^{15}N values indicate increasing trophic status. Mercury concentrations in fish increase with increasing trophic status (*46*, *47*). Therefore, as Swanson et al. (*52*) conclude, subtle changes in trophic position may not result in changes in mercury bioaccumulation.

Fish growth also affects methylmercury bioaccumulation (*53*), but as expected with little or no change in lake productivity and trophic position, growth rates of northern pike have also not changed (randomized complete block ANOVA, $F_{1,14} = 0.010$, $p = 0.936$, with linear trend test over time for males, $t_{14} = -0.540$, $p = 0.597$, and females, $t_{14} = -0.660$, $p = 0.523$) (Supporting Information, Table S1). We therefore reject the hypothesis that changes in the food web or the ecology of northern pike have influenced the biomagnification or bioaccumulation of methylmercury into these fish.

Finally, we examined the role of environmental factors in the reducing the amount of methylmercury available for bioaccumulation. Changes in climate, landscape, and water quality could influence the net methylation of mercury in lakes (*6*). However, the environment of Isle Royale is remarkably stable. The local climate, moderated by Lake Superior, is becoming more variable with fluctuations in the North Atlantic Oscillation (*54*), but the annual average temperature and precipitation have not significantly changed (*55*). Designations as a national park, a wilderness area, and an international biosphere reserve have prevented major landscape alterations for more than 50 years. With the exception of sulfate, water chemistry has not appreciably changed in lakes on the island since at least 1980−1981 (*56*). For example, pH and the concentration of DOC, factors often correlated with mercury concentrations in fish (*6*), have exhibited no significant annual trends (*55*, *56*). Atmospheric sulfate deposition, however, has exhibited a downward trend at Isle Royale since monitoring began in 1985 (linear regression, $r = -0.389$, $p = 0.090$, $n = 20$; Figure 1D) (*37*). Like many areas affected by high sulfate deposition (*57*), watershed outputs of sulfate to the lakes at Isle Royale have significantly exceeded inputs to the watershed from wet deposition because of desorption from soil of sulfate deposited in past years (*55*). This excess sulfate watershed source has likely delayed recovery of lake sulfate concentrations (*57*), but because sulfate deposition has remained relatively low now for several years (*37*), watershed outputs have declined to nearly equal inputs from wet deposition (*55*). Consequently, lake sulfate concentrations have declined (randomized complete block ANOVA, $F_{2,18} = 85.2$, $p < 0.001$, with linear trend test over time, $t_{18} = -9.38$, $p < 0.001$) (Supporting Information, Table S2). Similar trends have been reported across North America and Europe and are ultimately caused by decreased sulfur dioxide releases from anthropogenic sources such as coal combustion and metal smelting (*58*).

The microbial cycling of sulfur exerts a strong control on mercury methylation in lakes (*7*). Sulfate-reducing bacteria are known to methylate mercury (*59*), but also of importance in freshwaters, their metabolic byproduct, sulfide, may form a neutral complex with inorganic mercury that is readily bioavailable to a host of methylating microbes (*60*). Therefore, mercury methylation appears to be dependent on the activities of sulfate-reducing bacteria. The metabolic activity of sulfate-reducing bacteria is first order with respect to sulfate concentration at low sulfate concentrations, as typically found in most lakes (*61*). Thus, sulfate availability limits mercury methylation. Several independent investigations have demonstrated this relationship (*62*−*66*). Most notably, additions of sulfate to a treatment basin of Little Rock Lake stimulated sulfate reduction and mercury methylation (*66*) and ultimately caused increased total mercury concentrations in fish (*34*).

We tested whether recent declines in sulfate deposition to the lakes of Isle Royale have lowered rates of sulfate reduction resulting in less methylation of inorganic mercury and thus less methylmercury in fish. We reconstructed the history of sulfate reduction by examining the concentrations of sulfur in sediment profiles (Figure 2) (*67*). Before industrialization, low rates of sulfate deposition (*68*) limited sulfate reduction in lakes, as indicated deep in sediments by relatively constant and low concentrations of CRS (the ultimate end product of sulfide produced from sulfate reduction, *29*). With industrialization, rates of sulfate deposition increased steadily to a maximum of six times pre-1890 levels (*68*) in 1976. These rates have since declined in response to implementation of the U.S. Clean Air Act of 1970 (*58*, *68*). This depositional history is recorded in the sediment of Sargent Lake, where the maximum CRS concentration is six times that of deep sediment and is reached at a depth (7 cm) corresponding to 1976. Thereafter, CRS concentrations decrease in accordance with declining rates of sulfate deposition to the lake. The top few centimeters of the CRS profile could also, in part, reflect the early diagenetic addition of sulfur into organic matter through sulfate reduction. However, with low lake sulfate concentrations, most sulfate reduction and CRS formation would be expected to occur in the upper 1−3 cm of sediment (*67*, *69*) and therefore would not likely contribute to a CRS increase below this depth range.

In Lake Richie, the historic trends in CRS concentration parallel those in Sargent Lake, but the magnitude of change is much smaller (Figure 2). This implies that rates of sulfate reduction in Lake Richie were consistently suppressed compared to Sargent Lake, which in turn would yield lower rates of methylmercury production and explain the lower concentrations of total mercury in northern pike from Lake Richie (Figure 1B). The recent decrease in sulfate reduction rates in Sargent Lake (and presumably the other advisory lakes on Isle Royale) would also explain why fish now contain mercury below the advisory limit. Without further study, it is not immediately apparent what is causing the difference in sulfur cycling between these two lakes.

We further tested the relationship between sulfate reduction rate (as reconstructed through CRS concentration) and mercury accumulation in fish by analyzing total mercury in museum specimens of fish collected as far back as 1905 from four lakes on Isle Royale. When linear regreassion is used to compare concentrations of total mercury in fish to time-equivalent sediment CRS concentrations, strong positive relationships emerge (Figure 3). Indeed, for northern pike,

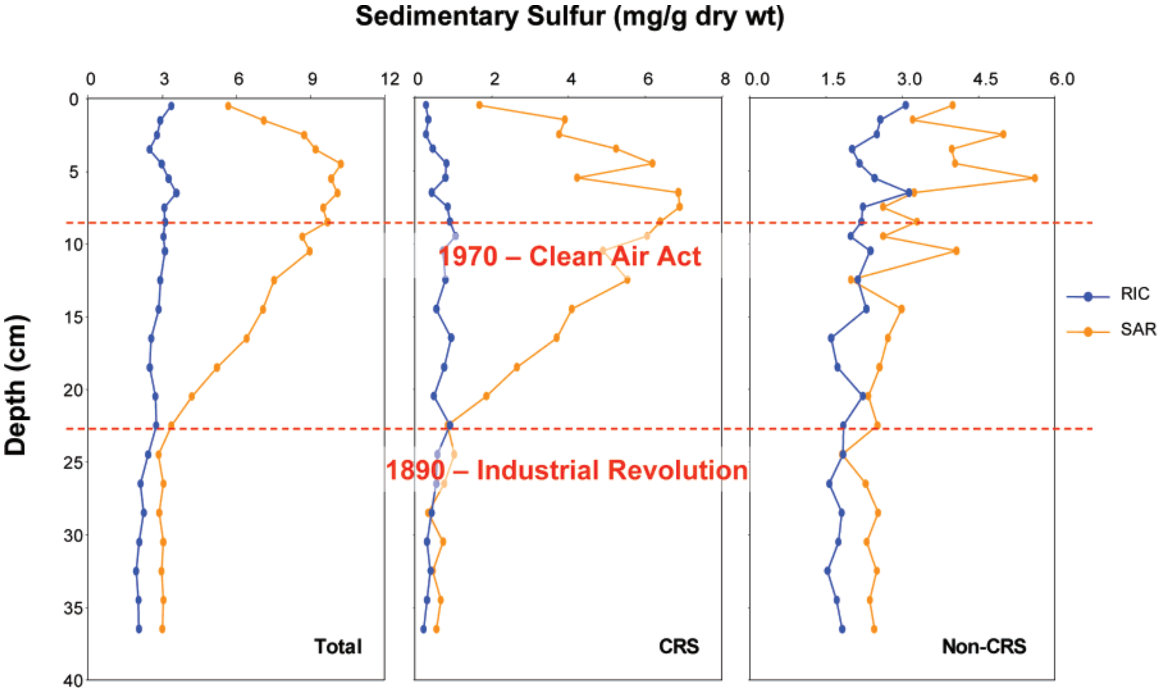

FIGURE 2. Concentrations of total sulfur, chromium-reducible sulfur (CRS), and non-CRS in sediment profiles from Lake Richie (RIC, blue) and Sargent Lake (SAR, orange), Isle Royale. The red, dashed lines represent 1890 (Industrial Revolution) and 1970 (U.S. Clean Air Act).

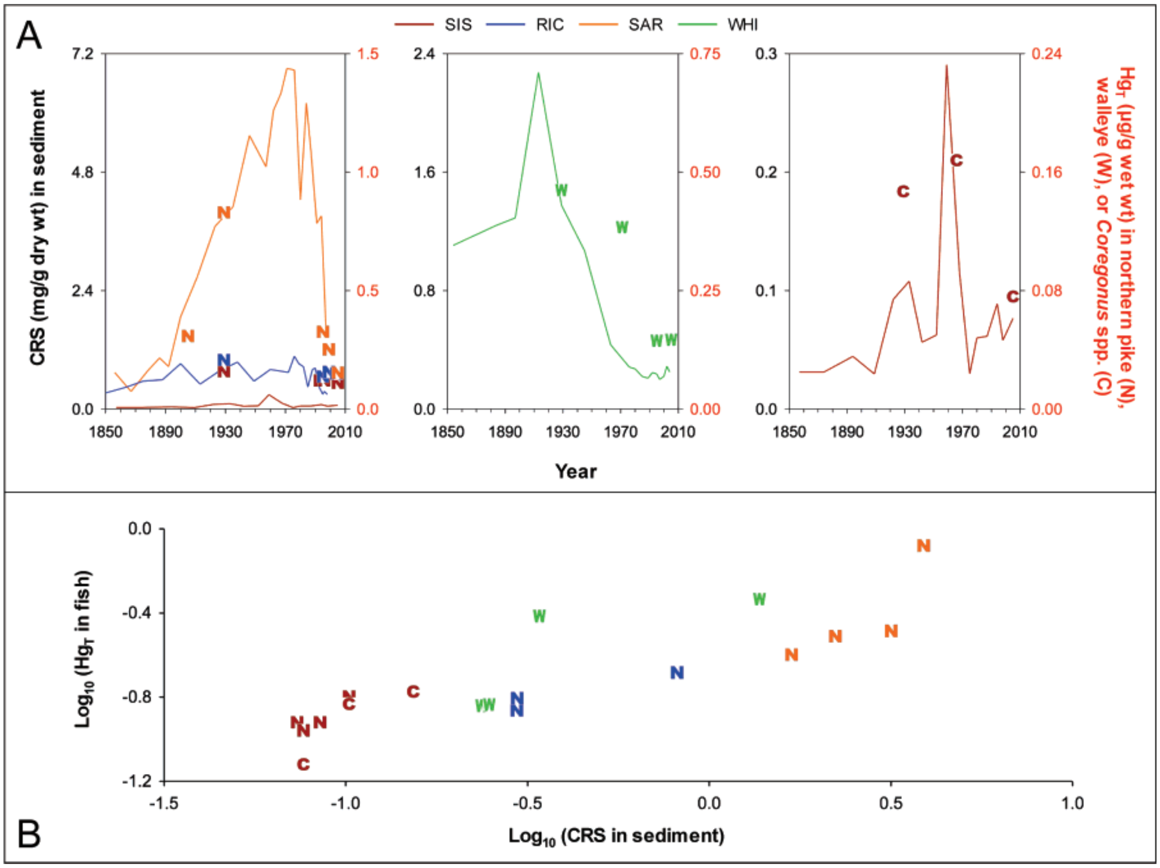

FIGURE 3. History of sulfate reduction in sediment and mercury in fish at Isle Royale. (A) Concentrations of chromium-reducible sulfur (CRS) in sediment (lines) and total mercury (Hg_T) in edible fillets of 50 cm northern pike (N; *Esox lucius*), 30 cm walleye (W; *Sander vitreus*), and 19 cm *Coregonus* spp. (C; *Coregonus artedii*, *Coregonus clupeaformis*) from four lakes at Isle Royale. Lakes include Siskiwit (SIS, dark red), Richie (RIC, blue), Sargent (SAR, orange), and Whittlesey (WHI, green). Total lengths for standardization of Hg_T in fish were chosen to overlap among years. (B) Scatterplot of log-transformed data for CRS in sediment and Hg_T in fish.

walleye, and coregonids, respectively, CRS concentration explained 79 ($r^2 = 0.794$, $p < 0.001$, $n = 11$), 65 ($r^2 = 0.650$, $p = 0.196$, $n = 4$), and 80% ($r^2 = 0.801$, $p = 0.294$, $n = 3$) of the variability in mercury bioaccumulation during the past century, albeit the latter two relationships are not statistically significant because of small sample sizes. In comparison, time-equivalent sediment total mercury accumulation rates explained only 40% of the variability in mercury bioaccumulation in northern pike during the past century ($r^2 = 0.399$, $p = 0.224$, $n = 11$) and were actually negatively related to total mercury in walleye ($r = -0.920$, $p = 0.080$, $n = 4$) and coregonids ($r = -0.658$, $p = 0.542$, $n = 3$). It appears that the deposition and cycling of sulfur has primarily controlled mercury accumulation in fish at Isle Royale for at least the past century.

Taken together, our results indicate that reductions in methylmercury contamination of fish have occurred in the absence of any change in atmospheric mercury deposition. In sulfate-limited freshwaters, such as the lakes of Isle Royale and other boreal lakes that contain much of the earth's unfrozen freshwater, reductions in methylmercury contamination of fish are possible solely through reductions in sulfate deposition. Existing acid rain programs and other sulfate deposition control efforts have had the unintentional additional benefit of controlling methylmercury bioaccumulation in these freshwater systems. Any significant increase in the atmospheric loading of sulfur, such as the proposed use of sulfur dioxide to slow climate change (*70*), could reverse this positive effect. On the other hand, the eventual implementation of mercury control measures in the U.S. and globally should work synergistically with existing sulfate controls to further reduce methylmercury contamination of fish at Isle Royale and elsewhere (*71*).

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Supporting Information Available

The Supporting Information for this manuscript includes one figure and four tables containing a historical reconstruction of total phosphorus in water of Lake Richie and Sargent Lake, mean back-calculated total lengths of northern pike, sulfate in epilimnetic lake water, and all original data for fish and sediment. This material is available free of charge via the Internet at http://pubs.acs.org.

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