

# Methylmercury Declines in a Boreal Peatland When Experimental Sulfate Deposition Decreases

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## Supporting Information

**ABSTRACT:** Between 2001 and 2008 we experimentally manipulated atmospheric sulfate-loading to a small boreal peatland and monitored the resulting short and long-term changes in methylmercury (MeHg) production. MeHg concentrations and %MeHg (fraction of total-Hg ( $Hg_T$ ) present as MeHg) in the porewaters of the experimental treatment reached peak values within a week of sulfate addition and then declined as the added sulfate disappeared. MeHg increased cumulatively over time in the solid-phase peat, which acted as a sink for newly produced MeHg. In 2006 a “recovery” treatment was created by discontinuing sulfate addition to a portion of the experimentally treated section to assess how MeHg production might respond to decreased sulfate loads. Four years after sulfate additions ceased, MeHg concentrations and %MeHg had declined significantly from 2006 values in porewaters and peat, but remained elevated relative to control levels. Mosquito larvae collected from each treatment at the end of the experiment exhibited  $Hg_T$  concentrations reflective of MeHg levels in the peat and porewaters where they were collected. The proportional responses of invertebrate  $Hg_T$  to sulfate deposition rates demonstrate that further controls on sulfur emissions may represent an additional means of mitigating Hg contamination in fish and wildlife across low-sulfur landscapes.



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## INTRODUCTION

Atmospheric sulfate deposition increased dramatically with the advent of the industrial period, ultimately causing widespread ecosystem acidification, especially downwind of large population centers in North America and Europe.<sup>1,2</sup> Regulatory efforts aimed at controlling sulfur dioxide emissions were very successful at reducing sulfate deposition,<sup>3–5</sup> but ecosystems have responded variably depending on landscape and climatic factors.<sup>6</sup> Whereas most research in sulfate-impacted systems has focused on recovery from environmental acidification,<sup>7,8</sup> sulfate deposition is also of considerable consequence to the production of methylmercury (MeHg),<sup>9</sup> the predominant form of mercury that bioaccumulates in food webs.

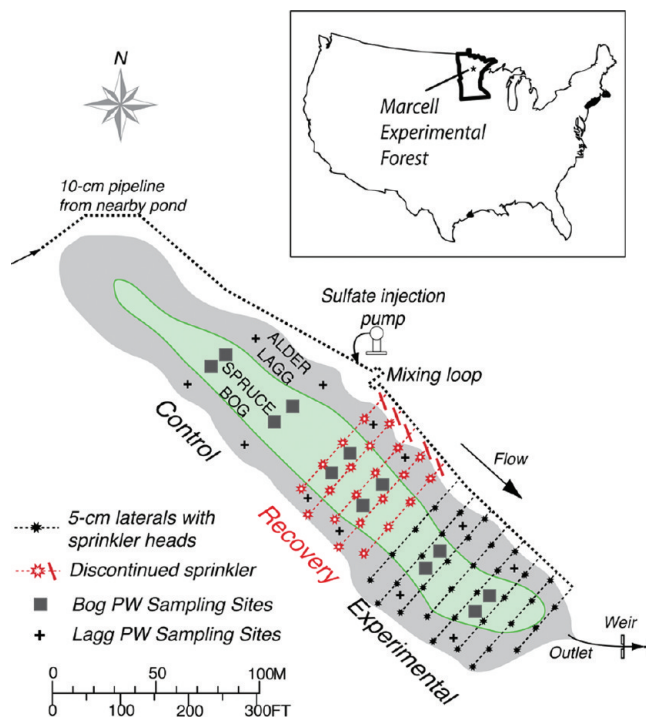
Wetlands are a major linchpin in the coupled biogeochemical cycles of sulfur and mercury and serve two potential countervailing roles in ecosystem recovery from sulfate deposition. They are sites of active sulfate reduction and so provide an important sink for legacy sulfate leaching from upland soils toward downstream aquatic systems.<sup>10</sup> Wetlands are also important sites of mercury methylation in the landscape.<sup>11</sup> Augmented sulfate inputs can stimulate MeHg production in sulfur-limited systems due to the increased activity of sulfate-reducing bacteria (SRB), which are known mediators of the methylation process.<sup>9,12–16</sup> Therefore continued inputs of sulfate from uplands may prolong elevated MeHg production in, and export from, wetland systems.<sup>17</sup> Our understanding of how MeHg production in ecosystems responds to declining sulfate deposition, and the subsequent effects on mercury concentrations in biota, is limited to a handful of largely correlative studies in lakes.<sup>18,19</sup> We therefore lack an experimental basis for predicting the rate of ecosystem recovery, the factors that enhance or inhibit it, or the biogeochemical mechanisms involved.

To investigate the in situ response of net MeHg production as an ecosystem recovers from elevated sulfate deposition, we experimentally amended a peatland in northern Minnesota with sulfate for four years and then monitored the system over an equivalent period after sulfate additions ceased. Changes in porewater, peat, and biotic MeHg levels across treatments with differing sulfate depositional histories were used to (1) understand the impacts of increasing and decreasing sulfate deposition on net MeHg production within the peatland, (2) identify mechanisms that promote and inhibit recovery of systems previously impacted by elevated levels of sulfate deposition, and (3) connect changes in sulfate deposition to mercury levels in biota. The extended nature of this project provided an opportunity to study wetland recovery processes against a backdrop of variable climate and hydrology.

## MATERIALS AND METHODS

**Study Site.** This study was performed in the S6 watershed of the Marcell Experimental Forest (MEF), a field-research facility of the Northern Research Station of the USDA Forest Service (Figure 1). The 2.0-ha S6 peatland has an overstory of mature black spruce (*Picea mariana*) and tamarack (*Larix laricina*) within a central bog area and is dominated by alder (*Alnus rugosa*) within its lagg margin.<sup>20</sup> The perched water table in the central bog is hydrologically isolated from the uplands and the lagg, creating a mineral-poor, ombrotrophic system ideal for experimental manipulation of atmospheric deposition.

**Sulfate Additions.** Long-term atmospheric deposition records from the National Atmospheric Deposition Program (NADP) site (MN-16) at MEF show that sulfate deposition



**Figure 1.** Schematic of the sulfate delivery system illustrating the experimental design within the S6 peatland. Porewater (PW) sampling sites in the bog (■) and lagg (+) were located along transects within each treatment. The first 5 lateral pipelines encompass the recovery treatment. See text for further details. The inset map shows the location of the Marcell Experimental Forest.

decreased by roughly 50%, from 11 kg ha<sup>-1</sup> yr<sup>-1</sup> in the early 1980s to approximately 5.5 kg ha<sup>-1</sup> yr<sup>-1</sup> in the mid-2000s (Supporting Information Figure S1).<sup>21</sup> Our experimental additions increased sulfate loading to 32 kg ha<sup>-1</sup> yr<sup>-1</sup>, or approximately 4× the average ambient 1990s deposition rate at MEF. This rate is representative of late 20th-century sulfate deposition across large areas of eastern North America, and thus provides an appropriate model for the effects of increasing sulfate deposition on MeHg production as well as the recovery processes that a sulfate-impacted peatland would experience as sulfate deposition declined.

The specific details of the initial experimental design and sulfate delivery system for this study were described previously by Jeremiason et al.<sup>9</sup> Briefly, in the summer of 2001 the peatland was divided into control and experimental sections, and a sulfate delivery system was constructed of PVC pipe across the down-gradient experimental half (Figure 1). Source water was pumped from a nearby, dilute pond (specific conductivity = 20 μS cm<sup>-1</sup>), a concentrated sodium sulfate solution was injected into the 10-cm main pipeline just above the experimental treatment, and the sulfate-enriched solution was sprayed onto the peatland surface via sprinkler heads atop 1-m risers. Sulfate amendments began in the fall of 2001 and continued three times each year (spring, summer, and fall) through 2008. Each sulfate addition simulated approximately 6–8 mm of rainfall, which did not significantly alter the peatland water table. In the early spring of 2006 a recovery treatment was created by discontinuing sulfate addition to the up-gradient, one-third of the original experimental treatment (Figure 1).

**Field Sampling. Porewaters.** Two porewater sampling transects were established in the control and experimental treatments, with four 1-m<sup>2</sup> sample plots distributed evenly across the



central bog area and lagg margins along each transect (Figure 1). To isolate the effect of atmospheric sulfate deposition on MeHg production from effects caused by upland inputs, only data from the central bog sites were considered for this paper. In 2006 two additional transects were established in the newly created recovery treatment, and transects located in the experimental treatment were repositioned down-gradient to ensure sampling occurred well within the treated area. Peat porewater samples were collected from each plot on day -1, +1, +3, and +7 relative to each sulfate addition. Extra sampling days were added to spring and fall samplings on days -7 and +14.

Porewater samples were collected by portable peristaltic pump through a 1.9-cm ID, Teflon probe with a custom-machined tip perforated with 5-mm holes. The probe was inserted into the peat to a depth approximately 5 cm below the water table and porewater was pumped via Teflon tubing through acid-washed, 47-mm Teflon filter-holders (Savillex Co.) pre-loaded with ashed, 0.7- $\mu\text{m}$ , glass-fiber filters directly into new, 125-mL PETG bottles. Bottles were rinsed in triplicate with porewater prior to filling, and samples were preserved with high-purity HCl to 0.5% (v/v). Samples were collected for dissolved  $\text{Hg}_\text{T}$ , MeHg, and major anions on each sampling day throughout the course of the project.  $\text{Hg}_\text{T}$  and MeHg samples were collected using accepted clean sampling techniques.<sup>22</sup> Field duplicates and equipment blanks accounted for 10% of samples.

**Peat Samples.** Surficial peat cores were collected annually from each treatment in 2003, 2005–2007, and 2009 by coring or cutting and hand-collection (SI Table S2). All peat samples were kept in frozen storage and freeze-dried prior to analysis of  $\text{Hg}_\text{T}$  and MeHg.

**Invertebrate Samples.** In late spring 2009, near the end of the study, mosquito (*Culex* spp.) larvae were collected in triplicate batches from each treatment by netting with vinyl-coated aquarium nets. Mosquito larvae were hand-picked at the MEF laboratory, placed in vials of deionized water overnight to purge gut contents, and then frozen. Samples were freeze-dried prior to analysis of  $\text{Hg}_\text{T}$  content. Where enough mass remained, samples were also analyzed for MeHg content.

**Laboratory Analyses. Porewaters.** Aqueous  $\text{Hg}_\text{T}$  was analyzed according to EPA method 1631 Revision E.<sup>23</sup> Samples were oxidized overnight with BrCl and then neutralized with  $\text{NH}_2\text{OH}$ . Stannous chloride reduced the oxidized mercury species to  $\text{Hg}^0$ , which was purged and trapped on gold traps. Mercury was thermally desorbed from the traps in a stream of Ar and analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) on a Tekran 2600 Automated Total Mercury Analyzer. Daily calibrations were checked with lab-made standards. Each run included 20% deionized-water blanks, 10% sample duplicates, and 5% sample matrix spikes.

Aqueous MeHg was analyzed according to methods described in Bloom<sup>24</sup> and Liang et al.<sup>25</sup> at the Branfireun laboratory (2005 samples), the Jeremiason laboratory (2006 samples), or the Balogh laboratory (2007 and 2008 samples). Samples were distilled with 8 M  $\text{H}_2\text{SO}_4$  and 20% KCl in an acid-cleaned, Teflon, extraction manifold and distillates were analyzed within 48 h. Mercury species were ethylated with sodium tetraethylborate and then purged from solution and trapped on Tenax traps. Mercury species were thermally desorbed from the traps and carried in a stream of Ar or He through a short chromatographic column. The separated mercury species passed through a pyrolytic trap where they were thermally transformed into

$\text{Hg}^0$ , and analyzed by CVAFS on a Tekran 2500 spectrometer (Branfireun and Jeremiason laboratories) or a Brooks Rand Model III (Balogh laboratory). Each run included 5% deionized-water blanks, 10% sample duplicates, and 5% sample matrix spikes.

Water samples for major anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ) were analyzed on a Dionex DX-500 ion chromatograph according to standard methods by the USFS Northern Research Station laboratory in Grand Rapids, Minnesota. Each run included 10% deionized-water blanks, 10% sample duplicates, and check standards. Replicate standard measures and lab duplicates were within 10% and method detection limits were 0.1  $\text{mg L}^{-1}$  each year.

**Peat Samples.** For  $\text{Hg}_\text{T}$  analysis, peat samples were microwave digested in concentrated  $\text{HNO}_3$  and diluted prior to analysis by dual gold-trap amalgamation CVAFS, as described above for porewaters. For MeHg analysis, peat samples were distilled as outlined for porewaters, but with the inclusion of a known mass spike of enriched  $\text{Me}^{199}\text{Hg}$  in each vessel. Samples were analyzed by isotope dilution–gas chromatography–inductively coupled plasma mass spectrometry (ID-GC-ICPMS) with mercury detection on an Agilent 7700 ICPMS according to the methods of Hintelmann et al.<sup>26</sup> In addition to blanks and duplicates, certified reference materials (MESS-3 for  $\text{Hg}_\text{T}$ ; ERM-CC580 for MeHg) were analyzed in 10% of samples.

Quality assurance and control results for aqueous and solid phase  $\text{Hg}_\text{T}$  and MeHg for each year can be found in Tables S2–S4 of the Supporting Information.

**Mosquito Larvae Samples.** For  $\text{Hg}_\text{T}$  analysis, mosquito larvae samples were microwave digested in concentrated  $\text{HNO}_3$  and diluted prior to analysis by dual gold-trap amalgamation CVAFS, as described for porewaters. MeHg in mosquito larvae samples was heat extracted in a solution of 25% KOH in methanol, with a known mass spike of enriched  $\text{Me}^{199}\text{Hg}$  in each vessel. Samples were analyzed by ID-GC-ICPMS. In addition to blanks and duplicates, the certified reference material DORM-3 was analyzed in 10% of samples.

**Numerical Analysis.** Weighted means were calculated for annual porewater results because sampling dates were not evenly distributed throughout the season. Annual porewater values from each treatment were calculated by multiplying the mean result on each sampling day within a treatment by a weighting factor and then summing. The weighting factor was equal to the fraction of the season represented by a sample since the previous sampling date (e.g., the day - 1 sample collected for a summer addition had a much larger weighting factor than a sample collected 2 days later on day +1). The season began on the first date on which peat soil temperatures at 10-cm depth were greater than 1 °C, and ended with the last sampling date each year. Bulk density of the peat did not change appreciably within the top 8 cm (one-way Anova,  $p = 0.18$ ), and so mean results for each peat core were calculated by multiplying concentrations for each interval by a weighting factor related to interval thickness (2 or 4 cm) and summing. Treatment means were then calculated from the weighted averages. Mosquito larvae results from each sample batch were averaged for each treatment.

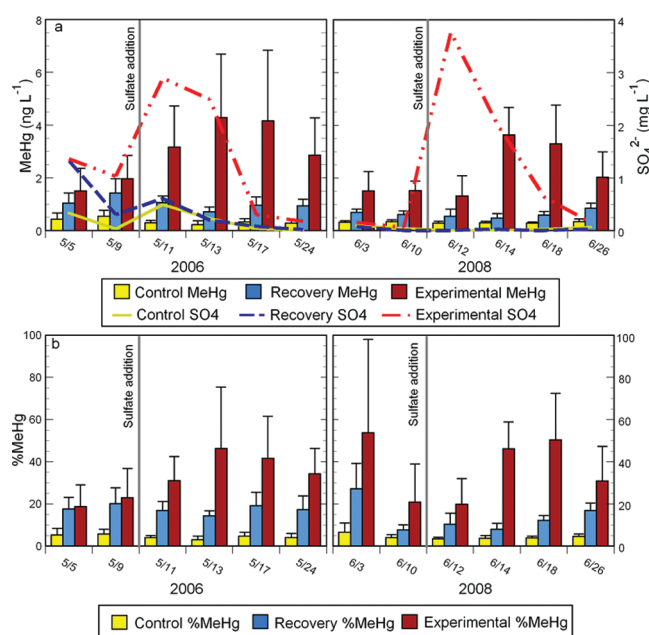
The program R was used for all statistical analyses.<sup>27</sup> The distributions for both porewater and solid data were right-skewed, so each data set was natural-log-transformed prior to statistical analyses to obtain a normal distribution. A linear-least-squares model of the transformed data was fit on treatment and year factors. Residual plots of the transformed data

did not show any systematic bias. General linearized hypothesis tests were used to compare the estimated slopes for each treatment in each year and generate  $p$ -values. A  $p$ -value  $<0.05$  was considered significant.

## RESULTS AND DISCUSSION

**MeHg Response to Sulfate Applications.** The short and long-term processes whereby elevated sulfate deposition affected MeHg production within the S6 peatland were explored through intensive sampling of porewaters and periodic collections of peat cores, respectively (Figure 1). Although the MeHg pool in porewaters can be affected by factors other than methylation, such as changes in water chemistry, partitioning between the aqueous and solid phases, and the character and abundance of organic ligands,<sup>13,28,29</sup> MeHg in porewater nevertheless represents the most dynamic and mobile MeHg pool and is thus important for considering downstream effects. The solid peat represented the major sink for MeHg and  $\text{Hg}_\text{T}$ —of the total mercury mass in the upper 8 cm of peat matrix,  $>99.7\%$  of MeHg and  $>99.8\%$  of  $\text{Hg}_\text{T}$  was bound to the peat.

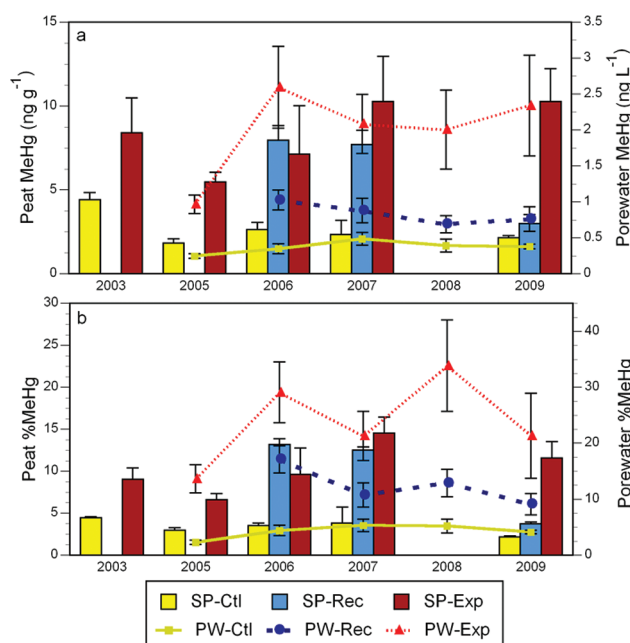
**Porewaters.** An increase in porewater MeHg concentration in response to sulfate addition was clearly evident following spring sulfate application to the central-bog as illustrated here for the spring of 2006 and 2008 (Figure 2), the first and last year of



**Figure 2.** (a) Sulfate and MeHg concentrations ( $\pm 1$  s.d.), and (b) %MeHg (the ratio of MeHg to  $\text{Hg}_\text{T}$ ;  $\pm 1$  s.d.) in control, recovery, and experimental treatment porewaters of the S6 peatland over the period of spring sulfate addition in 2006 and 2008. The spring 2006 and 2008 addition periods were chosen because they illustrate patterns in the first and last year of recovery, respectively.

recovery, respectively. In each year porewater sulfate concentrations in the experimental treatment peaked one day following the additions ( $2.9 \pm 2.1$  mg L<sup>-1</sup> in 2006 and  $3.8 \pm 2.2$  mg L<sup>-1</sup> in 2008). As sulfate concentrations declined, the porewater MeHg pool increased dramatically (Figure 2a). MeHg concentrations peaked by the third day post-addition in each year ( $4.3 \pm 2.1$  ng L<sup>-1</sup> in 2006 and  $3.6 \pm 1.0$  ng L<sup>-1</sup> in 2008). MeHg as percentage of  $\text{Hg}_\text{T}$  (%MeHg) followed a very similar pattern, peaking at  $46 \pm 29\%$  three days after the addition in 2006 and at  $50 \pm 22\%$

seven days after the addition in 2008 (Figure 2b). In contrast, mean sulfate and MeHg concentrations and %MeHg in the control area were consistently low each spring ( $<0.5$  mg L<sup>-1</sup>,  $<0.6$  ng L<sup>-1</sup>, and  $<7\%$ , respectively). MeHg concentrations and %MeHg were significantly higher in the experimental treatment than in the control on each day shown in Figure 2 ( $p < 0.05$ ). Peak MeHg concentrations and %MeHg in the experimental treatment, postaddition, were significantly higher than preaddition levels ( $p < 0.05$ ). Annual, seasonally weighted, average porewater MeHg concentrations and %MeHg in the experimental treatment were 4–9 $\times$  higher than corresponding levels in the control section (Figure 3).



**Figure 3.** (a) MeHg concentrations and (b) %MeHg levels in the solid peat (SP; interval-weighted average values) and porewaters (PW; annual, seasonally weighted average values) in the control, recovery, and experimental sections of the S6 peatland 2003–2009. Error bars for peat are standard errors of weighted treatment means. Error bars on porewaters are standard deviations calculated from weighted annual means.

The order-of-magnitude increases in MeHg concentrations and %MeHg in porewaters of the experimental treatment following sulfate application are of similar magnitude and timing to the responses reported by Jeremiason et al.<sup>9</sup> for the first year of this study and other mesocosm-scale studies in nutrient-poor, boreal peatlands.<sup>14,30</sup> Our interpretation of these results is that the added sulfate stimulated SRB activity resulting in a net increase in Hg methylation. The steady buildup of a large pool of solid-phase MeHg in the peat matrix (see below) provides strong evidence for this *de novo* production of MeHg.

An alternative explanation for the observed increase in porewater MeHg is a change in partitioning of MeHg and  $\text{Hg}_\text{T}$  between the aqueous and solid phase resulting from an increase in the dissolved sulfide pool.<sup>28</sup> We modeled mercury speciation in response to increasing dissolved sulfide concentrations and found that the molar ratio of MeHg to  $\text{Hg}_\text{T}$  peaked at  $0.3 \mu\text{M}$  sulfide and subsequently decreased, which is similar to previously reported findings (model parameters shown in SI Table S6).<sup>28</sup> However, at low sulfide concentrations the model did not accurately predict MeHg and  $\text{Hg}_\text{T}$  concentrations in the

dissolved phase possibly because of uncertainty in the log  $K$  value for the reaction between MeHg and thiol groups or because of kinetic limitations controlling adsorption/desorption of MeHg. Many studies have demonstrated the difficulty of accurately representing mercury speciation in the presence of high DOC.<sup>29,31–33</sup> Although we can not rule out the possibility that sulfide-driven changes in solid-phase partitioning caused porewater MeHg to increase, the weakness of the simple equilibrium model and the fact that the total pool of MeHg in the experimental section increased progressively over time argues strongly that increased MeHg production, rather than sorption/desorption reactions, is responsible for the MeHg patterns seen following sulfate addition.

**Peat.** The solid-phase data integrate the responses to sulfate additions that were noted above for porewater MeHg concentrations and %MeHg in the experimental treatment (Figure 2). In the control section, MeHg concentrations and %MeHg remained consistently low in both peat and porewaters (Figure 3). Average MeHg concentrations and %MeHg in the peat of the experimental treatment were 4–9× greater than the corresponding values in the control section. There was no significant effect of treatment on  $Hg_T$  concentrations in peat, which ranged between 63 and 110 ng g<sup>-1</sup> across the peatland over the 5-year period.

The MeHg pool within a peatland represents a dynamic equilibrium between MeHg production, predominantly through biotic methylation, and removal processes, including biotic and abiotic demethylation, bioaccumulation, and advective transport.<sup>13,14,34</sup> In sulfur-limited systems, such as the experimental peatland in this study, sulfate addition represents an important factor influencing MeHg production and contributes to higher MeHg concentrations in wetland porewaters and soils than would be expected based on atmospheric Hg inputs alone.<sup>12–14,35</sup> The increases in %MeHg in peat and porewaters of the experimental treatment relative to those in the control indicate that experimentally increasing sulfate loads shifts that equilibrium toward greater MeHg production.

**Recovery from Elevated Sulfate Deposition. Porewaters.** The recovery treatment—a subsection of the experimental treatment to which sulfate application was halted—was created in the spring of 2006. Sulfate concentrations in recovery porewaters declined almost immediately thereafter, generally remaining low and following a temporal pattern similar to that of the control in each year (Figure 2a). In contrast to sulfate, MeHg concentrations and %MeHg in recovery treatment porewaters remained elevated well above control levels during the first year of recovery ( $p < 0.001$ ). In 2007 annual, seasonally weighted %MeHg declined 37% from 2006 levels ( $p < 0.001$ ), but then held steady between 2007 and 2009. MeHg concentrations fell more gradually over the recovery period, declining 32% between 2006 and 2008 ( $p < 0.001$ ). Both MeHg concentrations and %MeHg in the recovery section remained elevated relative to control values through the end of the study (Figure 3). The continued difference in porewater MeHg between the control and recovery treatments likely reflects equilibrium with the peat rather than continued elevation of MeHg production.

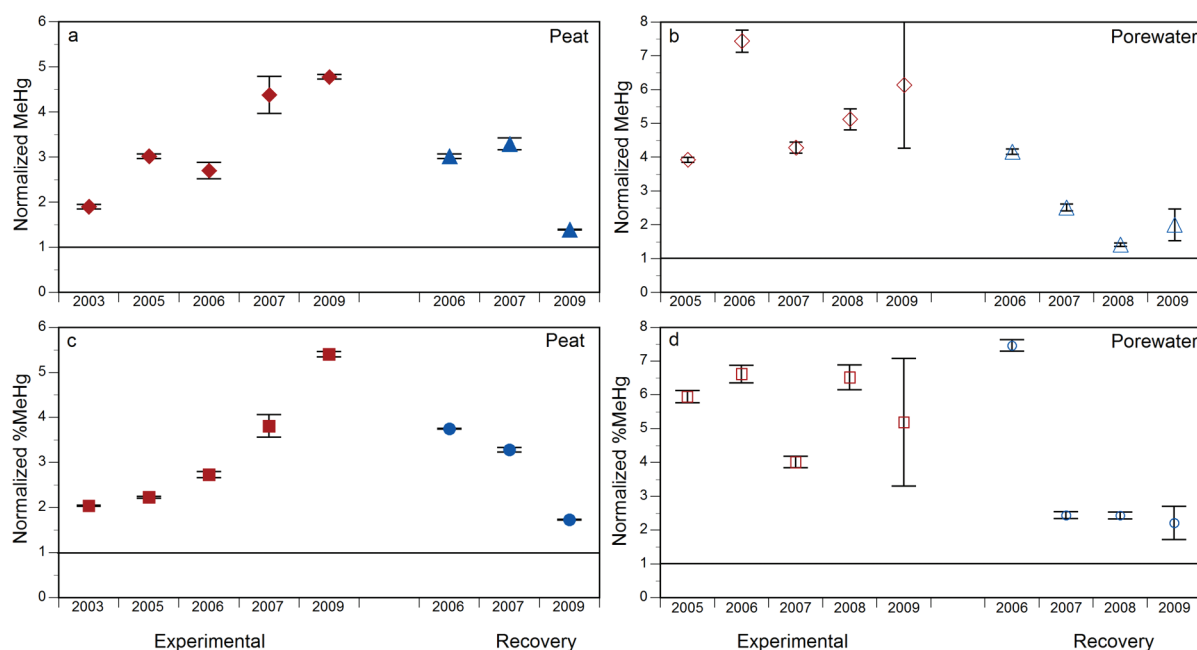
**Peat.** MeHg concentrations and %MeHg in recovery treatment peat declined by 62% and 76%, respectively, between 2006 and 2009 ( $p < 0.005$  and  $p < 0.02$ ). Demethylation was a more important MeHg loss process than desorption coupled with advective transport out of the system. This conclusion follows from the observation that concentrations of MeHg in porewaters were too low to account for the mass of MeHg lost from the recovery-section peat. Jeremiason et al.<sup>9</sup> found that

nearly 1800  $\mu$ g MeHg was exported from the S6 peatland in 2002. The mass of MeHg lost in the top 8 cm of the recovery treatment alone between 2006 and 2009 was approximately 120 mg, or more than 65× the amount exported in outflow in 2002 from the entire peatland.

Methylmercury concentrations in the peat of the recovery treatment did not show significant declines within the first two years after sulfate additions were halted. This could either imply that the kinetics of desorption of the newly accumulated MeHg from the peat was much slower than the decreases in methylation rates in porewaters, or that elevated MeHg production was sustained for a period of time by internal recycling of the previously added sulfate. Such recycling has been proposed by others<sup>13,14</sup> and would also explain our observed short-term response to sulfate addition in which sulfate disappeared from experimental porewaters within three days of application, while porewater MeHg levels remained elevated two weeks later (Figure 2). Urban et al.<sup>10</sup> investigated sulfur biogeochemistry in a small peatland 1 km from the S6 site and determined that annual recycling of sulfur was equivalent to annual external sulfur inputs. Blodau et al.<sup>36</sup> found evidence that an anaerobic sulfur cycle sustained SRB activity under reducing conditions in an ombrotrophic peatland, providing an explanation for the high sulfur recycling rates observed by Urban et al.<sup>10</sup> Thus one possible mechanism for recovery following the cessation of sulfate addition to the S6 peatland is that sulfur compounds within the peat become more recalcitrant over time. That is, as the pool of added sulfur is repeatedly turned over, labile sulfur compounds are preferentially consumed and progressively converted into refractory organic forms, which are much more slowly cycled by anaerobic and aerobic processes. In line with this hypothesis, differential sulfate release was observed among treatments in the S6 peatland following drying events, which can expose reduced sulfur moieties to oxygen (SI Table S5). The highest sulfate release into porewaters occurred in the experimental treatment, and the lowest release was observed in the control section. Because there was no significant difference among treatments in size of the total sulfur pool in the peat, these results suggest that the newly added sulfate was more susceptible to release/recycling than the pre-existing pool of ambient sulfur.

**Interannual Variability.** Despite the significant trends in peat MeHg concentrations and %MeHg (increases in the experimental treatment and decreases in the recovery treatment), there is some unexplained variability in the data—for example, the decrease in peat %MeHg between 2003 and 2005 and the fluctuating porewater values in the experimental treatment (Figure 3). These variations are likely the result of year-to-year differences in precipitation and hydrology, such as the series of summer droughts that persisted at the MEF from 2005 to 2007. Hydrologic variability can affect mercury cycling in peatlands by altering peat accumulation and decomposition, redox conditions, and methylation potentials.<sup>37–40</sup> Such effects are most clearly evident in the S6 control treatment where interannual fluctuations in both porewater and peat MeHg cannot be the result of sulfate manipulation. In the experimental and recovery treatments the effects of these large-scale physical processes are superimposed on trends due to sulfate addition alone. For example, the 2007–2009 decline of MeHg in the recovery section can be explained, at least in part, by the cessation of sulfate amendments, but this should not be the case for the experimental treatment where sulfate additions continued. Thus it appears that some of the interannual variability in MeHg



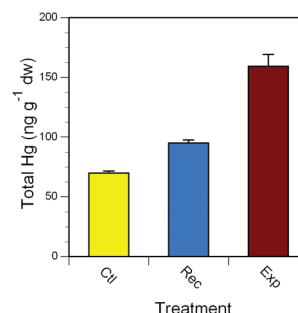


**Figure 4.** Ratio of [MeHg] and %MeHg in recovery and experimental treatments to [MeHg] and %MeHg in the control treatment in the peat (a and c) 2003–2009 and porewaters (b and d) 2005–2009 ([MeHg] experimental peat (◆), [MeHg] experimental porewater (◇), %MeHg experimental peat (■), %MeHg experimental porewater (□), [MeHg] recovery peat (▲), [MeHg] recovery porewater (Δ), %MeHg recovery peat (●), %MeHg recovery porewater (○)). Peat error propagated from standard errors of mean [MeHg] and %MeHg in control and respective treatment (experimental or recovery). Porewater error propagated from standard deviations for control and respective treatment. The horizontal line at  $y = 1$  in each figure represents a ratio of 1:1 or a return to control levels in the treatments.

concentrations and %MeHg in each treatment (Figure 3) was the result of overriding climatic and/or hydrologic effects.

To remove the influence of natural hydrologic variability from the longer-term effects of experimental sulfate addition, we normalized MeHg concentrations and %MeHg in the experimental and recovery treatments to corresponding values in the control treatment for porewaters and peat in each year (Figure 4). Normalized MeHg concentrations and %MeHg in the experimental peat increased cumulatively with time such that by 2009 these values in the experimental treatment were 5–6× higher than those of the control ( $p < 0.005$ ). In the recovery treatment the opposite trend occurred, and by 2009 normalized MeHg concentrations and %MeHg approached a value of 1, indicating a near-return to control levels. However, the trend was not significant ( $p = 0.28$ ) owing to small sample sizes ( $n = 4$ ) from each treatment. Normalized MeHg concentrations in the porewaters of the experimental treatment did not show any discernible trend with time, presumably because most newly produced MeHg accumulated in the peat. The large loss of MeHg from the recovery-section following the discontinuation of sulfate addition indicates that reductions in sulfate deposition could produce a relatively rapid decline in MeHg export to connected lakes and streams.

**Biotic Response.** In the spring of 2009 mosquito larvae (*Culex* spp.) were collected in the S6 peatland to compare mercury concentrations in biota among treatments, as mosquitoes are sensitive indicators of mercury loading to, and MeHg production within, aquatic systems.<sup>41</sup> Dry-weight,  $Hg_T$  concentrations in *Culex* spp. larvae mimicked %MeHg trends in peat samples, with experimental-treatment larvae having significantly elevated mercury concentrations relative to those found in the control and recovery sections ( $p < 0.05$ ; Figure 5). Significant differences in mosquito-larvae  $Hg_T$  also persisted between the control and recovery sections ( $p < 0.05$ ). Although sample masses were



**Figure 5.** Dry-weight,  $Hg_T$  concentrations ( $\pm 1$  s.d.) in mosquito larvae (*Culex* spp.) in control (Ctl), recovery (Rec), and experimental (Exp) treatments in spring 2009.

insufficient to allow MeHg analysis of all mosquito larvae samples, for the six samples measured for both  $Hg_T$  and MeHg in this study, MeHg comprised  $62 \pm 19\%$  of  $Hg_T$  in mosquito larvae, and  $Hg_T$  explained 75% of the variability in MeHg concentrations (SI Figure S2).

These biotic results provide direct evidence that increasing/decreasing sulfate loading to peatlands translates into significant increases/declines in biotic mercury concentrations. Whereas MeHg in experimental-treatment peat was  $>4.5\times$  that in the control by 2009,  $Hg_T$  in mosquito larvae from the experimental treatment in the same year was just over  $2\times$  the levels found in the control. Apparently some of the MeHg produced as a result of sulfate-stimulation became less bioavailable with time. This finding agrees with other studies which have found that recently produced MeHg is more available to biota than older MeHg.<sup>42,43</sup>

Because detritivorous mosquito larvae spend a short time in their aquatic habitat, they present a snapshot of mercury bioaccumulation in the season during which they hatch. Mercury bioaccumulation within sulfate-impacted peatlands may be even

greater for invertebrates with long aquatic larval stages and those higher in the food chain, such that recovery from sulfate deposition may take longer than for mosquito larvae. Although the S6 wetland does not itself support fish, its outflow contributes to the MeHg load of downstream lakes that have susceptible fish populations. Moreover, direct transfer of MeHg to terrestrial foodwebs through the emergence and predation of aquatic insects has been identified as an important trophic pathway that may contribute to lowered reproductive success for insectivorous birds that exploit riparian and wetland habitats.<sup>44,45</sup>

**Broader Impacts.** Our long-term sulfate-loading experiment created an opportunity to observe the in situ processes whereby sulfate deposition enhanced MeHg production within a peatland, MeHg declined once sulfate additions were discontinued, and mercury levels in biota mirrored changes in sulfate inputs. Increasing sulfate deposition by 4X led to a MeHg increase of similar magnitude in both porewaters and peat. These changes in MeHg production occurred despite flat trends in Hg deposition over the study period.<sup>46</sup> The steady accumulation of MeHg in the peat over time, relative to the control, suggests sustained disequilibrium between methylation and demethylation over the course of the experiment. At what point equilibrium between MeHg production and removal processes would be achieved at these elevated levels of sulfate deposition is an open question. The finding that most of the MeHg lost from the recovery treatment was likely due to in situ demethylation rather than export from the system implies that the majority of the MeHg produced in response to elevated sulfate deposition may not be transported to downstream aquatic systems. This is supported by the finding that peat and porewater MeHg increased by ~4X in response to a 4X increase in sulfate deposition but MeHg flux from the wetland in the first year of this study only increased by 2X.<sup>9</sup>

The proportional, synchronous decreases in mosquito-larvae mercury with cessation of sulfate addition indicate that declines in sulfate deposition can directly reduce MeHg in biota. Wetland recovery from elevated, anthropogenic sulfate deposition may explain some of the downward trends seen in fish and wildlife mercury across North America and Europe in the late 20th century as regulations on sulfur emissions took effect.<sup>19,47–49</sup> It is important to note that atmospheric mercury deposition declined concurrently with the reductions in sulfate deposition in many areas<sup>50</sup> and may also be responsible for declining mercury concentrations in biota.

In this study MeHg responses to climatic variability were superimposed on the trends caused by sulfate addition alone. The fluctuations in peat MeHg seen in the control section, and the declines in MeHg concentrations in the experimental treatment over the periods 2003–2005 and 2007–2009, demonstrate that physical processes can also alter the balance between methylation and demethylation from year to year. Climatic events such as severe droughts, which lead to oxidation of reduced sulfur species and sulfate formation, may slow or reverse declining MeHg levels in wetlands. The influence of drought on sulfate release from wetlands and sulfate export from watersheds are well documented.<sup>5,51–54</sup> Altered sulfur cycling consequent to climatic shifts may thus explain some of the recently reported reversals in downward fish mercury trends noted above.<sup>49,55</sup>

Sulfate deposition to ecosystems downwind of industrial centers increased by more than an order of magnitude over natural background rates by the mid-20th century.<sup>21</sup> It is reasonable to infer that such large increases in sulfate loading

caused comparably large increases in MeHg production in sulfur-limited peatlands—increases above and beyond those arising from the 3–4X rise in mercury deposition during that same time period.<sup>56,57</sup> Subsequent regulations of sulfur emissions, such as the 1970 Clean Air Act and its 1990 amendments in the United States, led to substantial reductions in sulfate deposition across regions once affected by very high levels of atmospheric loading.<sup>5</sup> As of 2009 sulfate deposition across eastern North America remained well above background levels<sup>21</sup> highlighting the potential benefits to additional reductions. Our finding that peatland MeHg responds rapidly to reductions in sulfate inputs implies an opportunity to mitigate mercury contamination through policies aimed at further reducing sulfur emissions and deposition.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Information regarding peat sample collection, quality control data for aqueous and solid total- and methyl-mercury analyses, average sulfate concentrations in porewaters during a water table rise in 2007, annual sulfate deposition rates at the Marcell Experimental Forest, the correlation between Hg<sub>T</sub> and MeHg concentrations in invertebrates samples, and equilibrium model parameters. This information 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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