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Article

Long-Term Experimental Manipulation of Atmospheric Sulfate Deposition to a Peatland: Response of Methylmercury and Related Solute Export in Streamwater

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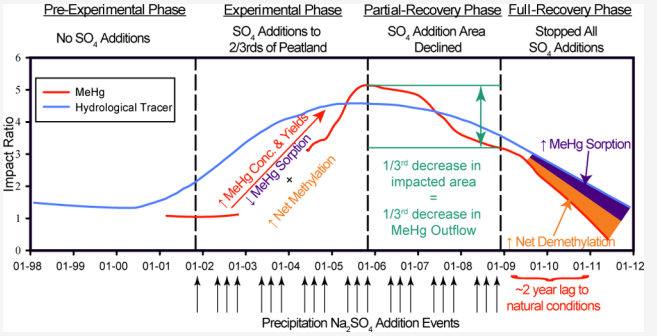
ABSTRACT: Changes in sulfate (SO_4^{2-}) deposition have been linked to changes in mercury (Hg) methylation in peatlands and water quality in freshwater catchments. There is little empirical evidence, however, of how quickly methyl-Hg (MeHg, a bioaccumulative neurotoxin) export from catchments might change with declining SO_4^{2-} deposition. Here, we present responses in total Hg (THg), MeHg, total organic carbon, pH, and SO_4^{2-} export from a peatland-dominated catchment as a function of changing SO_4^{2-} deposition in a long-term (1998–2011), whole-ecosystem, control-impact experiment. Annual SO_4^{2-} deposition to half of a 2-ha peatland was experimentally increased 6-fold over natural levels and then returned to ambient levels in two phases. Sulfate additions led to a 5-fold increase in monthly flow-weighted MeHg concentrations and yields relative to a reference catchment. Once SO_4^{2-} additions ceased, MeHg concentrations in the outflow streamwater returned to pre-SO_4^{2-} addition levels within 2 years. The decline in streamwater MeHg was proportional to the change in the peatland area no longer receiving experimental SO_4^{2-} inputs. Importantly, net demethylation and increased sorption to peat hastened the return of MeHg to baseline levels beyond purely hydrological flushing. Overall, we present clear empirical evidence of rapid and proportionate declines in MeHg export from a peatland-dominated catchment when SO_4^{2-} deposition declines.



KEYWORDS: *inorganic mercury, streamflow, sub-boreal, dissolved organic carbon, sulfate, wetland, flow-weighted, yield, methylmercury*

INTRODUCTION

Atmospheric sulfate (SO_4^{2-}) deposition has been decreasing since restrictions on sulfur dioxide emissions were introduced in the United States and many other countries globally, beginning in the late 1970s.[1−3] Declining SO_4^{2-} deposition has resulted in shifts in catchment-scale biogeochemistry,[4−8] such as increased streamwater dissolved organic carbon (DOC) concentrations and pH, and declining SO_4^{2} concentrations in runoff from catchments.[9−12]

Feedbacks from changing carbon and sulfur cycles may also drive mercury (Hg) cycling, particularly methylmercury (MeHg) production in biogeochemical hotspots such as peatlands and associated laggs.[13−15] Methylmercury, the highly bioaccumulative form of Hg, is produced as a byproduct of anaerobic microbial metabolism, particularly involving SO_4^{2-} reduction.[16−19] In SO_4^{2-} limited systems, such as northern peatlands, MeHg concentrations in both porewater and peat (organic soils >40 cm deep) increase substantially in response to elevated SO_4^{2-} inputs,[13,17,20,21] leading to increased MeHg export from peatland-dominated catchments.[22] The elevated export of MeHg can have deleterious effects on downstream aquatic ecosystems, leading to local or regional fish consumption advisories.[23−25] Even when external SO_4^{2-} inputs decrease, SO_4^{2-} can be regenerated during water table fluctuations, which can continue to stimulate elevated MeHg levels within peat and pore water.[20] It is unknown, however, whether such in situ biogeochemical responses, which could delay recovery from high MeHg levels once SO_4^{2-} inputs decline, are mirrored in catchment runoff.

Here, we report on a long-term (13-year) study of streamwater concentrations and yields of total organic carbon (TOC), SO_4^{2-}, pH, sodium (Na^+), MeHg, and total Hg (THg) at the outflow from a peatland-dominated catchment at

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the USDA Forest Service Marcell Experimental Forest in Minnesota. During this study, portions of the peatland were subjected to experimentally increased SO_4^{2-} deposition (as Na_2SO_4) for approximately 7 years of the overall 13-year study. We compare results with a nearby peatland-dominated catchment with ambient SO_4^{2-} deposition and no experimental manipulation. Previous publications on this experiment have reported a doubling of MeHg production and export during the first year of SO_4^{2-} addition;[22] the longer-term response of MeHg in pore water, peat (solid phase) and mosquito larvae;[13] the role of drought, water table fluctuations, and SO_4^{2-} regeneration on MeHg production;[20] and changes in the peat microbial community.[16] Specifically, we examine how catchment export of MeHg and related solutes changed during both the experimental increase in SO_4^{2-} deposition to the peatland and in the years following termination of the increased SO_4^{2-} deposition. We update previous findings to provide 12 years of new catchment export data beyond that published by Jeremiason et al.[22] and importantly include the 2 year period following the end of the field experiment. Additionally, this study differs from other studies resulting from this experiment, which have more specifically examined processes happening within the peatland porewater, biota, and soil[13,16,20] but not export from the catchment.

METHODS

Study Sites. The peatland of the S6 catchment in the USDA Forest Service Marcell Experimental Forest (47°31′11.8″N 93°28′13.9″W, Minnesota, USA) was the subject of a long-term experiment examining the effects of atmospheric SO_4^{2-} deposition on Hg cycling and transport (herein referred to as the experiment peatland, Figure S1). The experimental (S6) peatland is a 2.0 ha ombrotrophic domed bog formed in a post-glacial ice-block depression, centrally located within an overall 8.9 ha catchment.[26] The peatland is dominated by bog vegetation typical of the region, chiefly *Sphagnum* mosses, ericaceous shrubs, graminoids, and scattered black spruce (*Picea mariana*) and tamarack (*Larix laricina*) trees.[27,28,27,28] The central bog of the experimental peatland is surrounded by an alder (*Alnus incana*) dominated lagg where more minerotrophic water from upland runoff mixes with bog waters.[28,29] The uplands of the S6 catchment surrounding the bog consist of loamy sand outwash soils with forest cover dominated by red pine (*Pinus resinosa*) and white spruce (*Picea glauca*).

The nearby S2 catchment served as a reference system for the experiment. This 9.7 ha catchment includes a central 3.2 ha ombrotrophic domed bog with vegetation similar to the experimental peatland, with an overstory mainly of *P. mariana*.[27,28] The reference peatland is also surrounded by an alder lagg, but with less dense cover and smaller relative area than the S6 lagg at the experimental peatland.[15,28,30,31] The uplands of the S2 catchment are dominated by aspen (*Populus tremuloides*) with other mixed deciduous and coniferous species.[28]

The centrally located peatlands dominate the hydrology of both catchments and all diffuse runoff generated within each catchment is first directed through the peatlands before exiting the catchments.[32,33] The outlet streams of both catchments are monitored for flow at v-notch weirs, with daily total streamflow reported for each catchment.[34] The streamflow responses from both catchments are dominated by inputs from spring snowmelt and storm events, with periods of no flow primarily during winter and many summers. The stream stage has been monitored and daily discharge calculated since 1976 at S6 and since 1961 at S2.[35] The two catchments have similar long-term (1998−2011) annual average runoff, 132 mm $year^{-1}$ from the experimental (S6) catchment and 160 mm $year^{-1}$ from the reference (S2) catchment (Figure S2).[34] Both peatlands are perched above the surrounding groundwater aquifer and therefore isolated from groundwater inflow.[33]

Experimental Design and Sulfate Loading. In 2001, a surface irrigation system was established on the downgradient 1.0 ha of the experimental peatland (Figure S1).[13] The upgradient half (1.0 ha) of the peatland was not irrigated and received only ambient atmospheric SO_4^{2-} deposition. From November 2001 to early 2006 (the "Experimental Phase"), a sodium sulfate (Na_2SO_4) solution, using low conductivity (~10 μS cm^{-1}) and low THg (<1 ng L^{-1}) water from a pond in an adjacent catchment, was distributed across the full extent of the irrigated portion of the peatland three times a year via the irrigation sprinkler system. Using equal additions three times a year (spring, summer, and fall), the system deposited ~200 mg L^{-1} of SO_4^{2-} per addition event, resulting in 32.0 and 15.3 kg ha^{-1} $year^{-1}$ of overall SO_4^{2-} and Na^+ deposition, respectively. This SO_4^{2-} addition represents an approximately 2-fold increase compared to atmospheric loading in the late 1970s, a 4-fold increase compared to the 1990s, and an ~6-fold increase over the 5.5 kg ha^{-1} $year^{-1}$ observed in the mid-2000s.[13]

Between early 2006 and late 2008 (the "Partial-Recovery Phase"), the sprinklers within the upper one-third of the experimentally irrigated area were turned off, and only the sprinklers in the two-thirds nearest the outlet remained in operation.[13] Near the end of 2008, all SO_4^{2-} additions ceased, but streamflow chemistry measurements continued until 2011, with this period designated as the "Full-Recovery Phase" (2009−2011).

Outflow streamwater sampling from both catchments began in 1998 for water quality parameters (major ions, TOC, and pH), while THg sampling was sporadic from 1998 and MeHg sampling began in 2001. This timing resulted in an approximately 3.5 year "Pre-Experimental Phase" for water chemistry parameters and 6 months for Hg prior to any SO_4^{2-} irrigation. From 2001, grab samples were collected at least every 2 weeks when the stream was flowing, resulting in 12−32 samples per year and at least two samples per month. A paired catchment control-impact approach was used to identify experimental effects relative to interannual climate-driven variations, though the short (<1 year) Pre-Experimental Phase for Hg measurement precludes rigorous before-after statistical analyses. To ensure comparable samples between watersheds, days of sampling were paired, except when low- or no-flow conditions precluded collection at either outflow. See the Supporting Information for a more detailed description of the sampling regime.

Chemical Analysis. Aqueous THg concentrations were determined following Environmental Protection Agency method 1631, Revision 3, using a Tekran 2600 Automated Total Mercury analyzer.[36] Methylmercury analysis followed Environmental Protection Agency method 1630[37] up to 2008 after which a modification of this method using isotope dilution and detection by inductively coupled plasma mass spectrometry (ICP-MS; e.g., Hintelmann and Ogrinc[38]) was used for samples through the remainder of the study. Due to the long duration of this study, water samples for Hg

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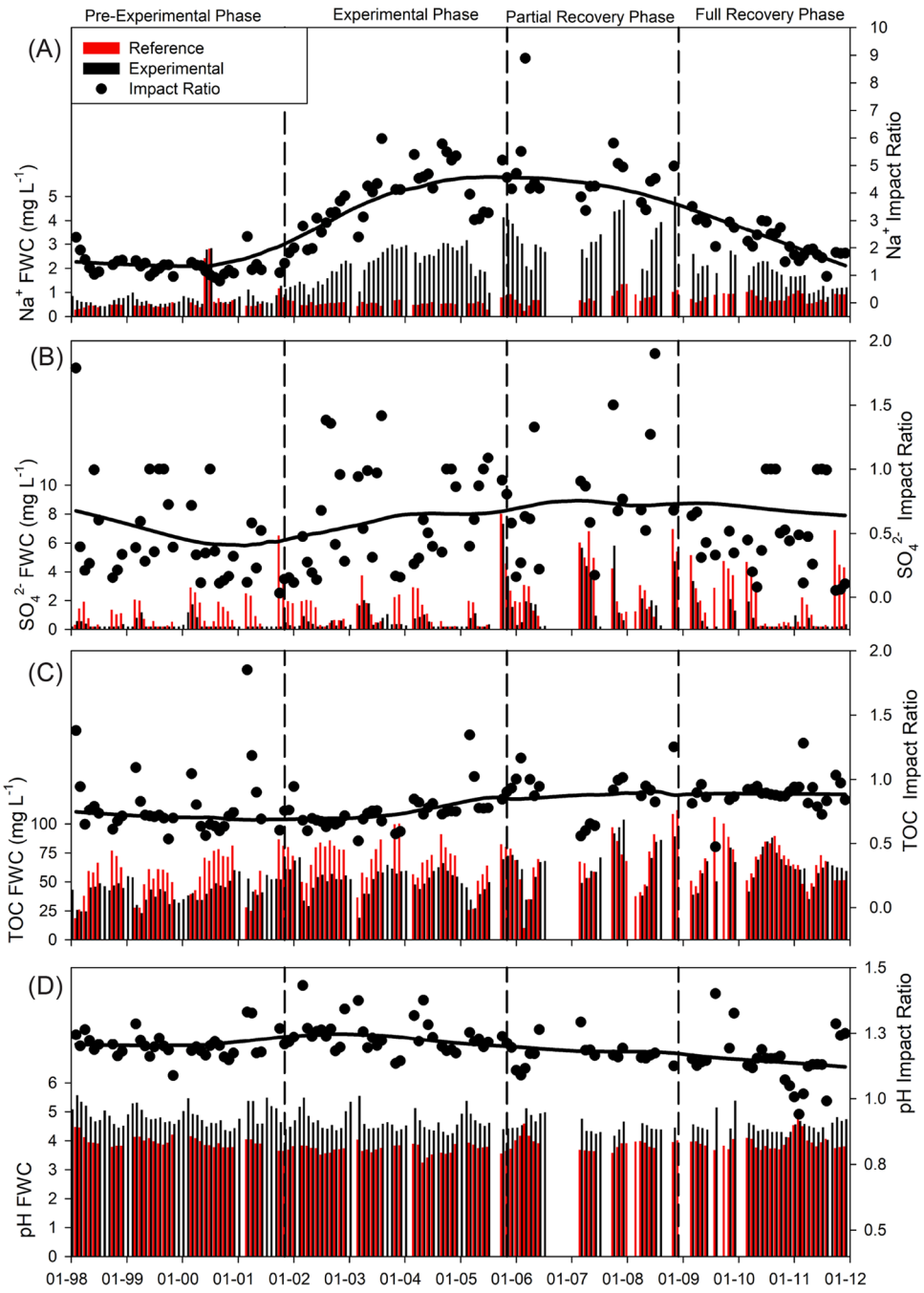

Figure 1. Monthly flow-weighted concentration (FWC) of (A) sodium (Na^+), (B) sulfate (SO_4^{2-}), (C) TOC and (D) pH at the Experimental (S6) and Reference (S2) catchments with the FWC impact ratios (Experimental: Reference) and LOESS fitted line (secondary *y*-axis). The vertical dashed lines indicate transitions between the different experimental manipulations. Sodium sulfate (Na_2SO_4) additions were 3× per year (spring, summer, and fall) between 2001 and 2008. Note the change in scales for the different water quality parameters and impact ratios.

quantification were analyzed at different laboratories over the 13-year study period, though using nearly the same analytical methods throughout, as explained above. Quality control and assurance measurements across the two analytical laboratories were similar and are summarized in Table S1. Notably, between 2003 and 2004, no MeHg samples were processed, nor was THg processed in 2004 due to an eventually resolved analytical laboratory contamination issue. More detailed methods, instruments, and quality control/quality assurance procedures of THg, MeHg, SO_4^{2-}, Na^+, pH, and TOC water samples analysis are detailed in the Supporting Information, Sebestyen et al.,[39] and Sebestyen et al.[40]

Data Analysis. The monthly flow-weighted concentration and total monthly yields for THg, MeHg, inorganic Hg (assumed as the difference between THg and MeHg), SO_4^{2-}, TOC, pH, and Na^+ were determined in the outflow streamflow from both the experimental and reference catchments following Sebestyen and Kyllander.[41] Briefly, daily solute yields were calculated as the product of daily streamflow and the daily concentration of a given species. Concentrations were linearly interpolated between two adjacent concentration values to estimate concentrations on days when no samples were collected. The monthly flow-weighted concentration was then determined by the total monthly yield divided by the total

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monthly volumetric streamflow. Methods to determine the 95% confidence intervals for both monthly flow-weighted concentrations (eq S1) and yields (eq S2) are in the Supporting Information.

The monthly flow-weighted concentrations and yields in the outflow streamwater of the experimental catchment were each divided by the time-matched value from the reference catchment to determine an impact ratio (IR) following,

$$IR_x = \frac{Y_{Exp} \text{ or } C_{FW\ Exp}}{Y_{Ref} \text{ or } C_{FW\ Ref}} \quad (1)$$

where $C_{FW\ Exp}$ (M l^{-3}) or Y_{Exp} (M l^{-2} t^{-1}) is the monthly averaged flow-weighted concentration or yield, respectively, for a given solute at the experimental peatland, and $C_{FW\ Ref}$ (M l^{-3}) or Y_{Ref} (M l^{-2} t^{-1}) is the monthly averaged flow-weighted concentration or yield, respectively, for a given solute at the reference peatland. When concentrations are used in the calculation, this is referred to as a concentration IR, whereas when yields are used in the calculation, this is referred to as the yield IR.

The resultant monthly IRs were used to fit a locally weighted smoothing (LOESS) line with a period weighting of 0.4.[42] This period weighting minimized over-smoothing between the four distinct phases, with each phase accounting for ~20 to 30% of the total observations. Thus, the period weighting would still include any potential lag in the data, while maintaining any effect of a given treatment phase. Using the LOESS smoothed value of the solute-yield IR, the recovery of the added solutes, SO_4^{2-} and Na^+, was determined from the known inputs of Na_2SO_4 (193 and 93 kg of SO_4^{2-} and Na^+, respectively), the measured total atmospheric deposition for the entire S6 catchment (8.9 ha) between 2002 and 2011 (439 and 14 kg of SO_4^{2-} and Na^+, respectively; National Atmospheric Deposition Program (MN16)[43]), and the average Pre-Experimental Phase (1998–2001) IR (eqs S3–S5 in the Supporting Information). By examining differences in IRs between the different phases of the study, impacts related to SO_4^{2-} deposition can be isolated from, for example, inter-annual variations in climate.

RESULTS AND DISCUSSION

Response of SO_4^{2-}, TOC, and pH. Despite several years of experimental SO_4^{2-} additions, neither monthly flow-weighted SO_4^{2-} concentrations (Figure 1B) nor yields (Figure S3B) changed over the 13-year study period. Brief increases in SO_4^{2-} concentrations were observed by Jeremiason et al.[22] after each of the SO_4^{2-} addition events but these relatively short-lived increases in SO_4^{2-} concentrations did not overtly impact the monthly flow-weighted concentrations or yields. In the reference peatland, Urban et al.[44] observed that under ambient conditions sulfur inputs (mostly sulfate) were approximately equal to the outputs and that 33% of total sulfur streamwater export was organic sulfur. The total additional deposition of SO_4^{2-} in this study (32 kg ha^{-1} $year^{-1}$) was 7.4× higher than the total atmospheric sulfur deposition (4.3 kg ha^{-1} $year^{-1}$) reported by Urban et al.[44] and 4.4× higher when accounting for sulfur inputs from both atmospheric and upland runoff. Given that SO_4^{2-} yields were unchanged by the experiment, the experimental peatland must have a large capacity to transform and/or sequester the added SO_4^{2-}. It is likely that the SO_4^{2-} added to the experimental peatland was either incorporated within the peat as organic sulfur or mineral sulfides,[45] taken up by peatland vegetation, emitted to the atmosphere as hydrogen sulfide, or exported in the outflow as organic and/or reduced sulfur species,[44] none of which were measured in this study.

Over the course of the study, average annual pH in the outflow streamwater of the experimental peatland decreased linearly (Figure 2), though a small increase in pH from ~4.7 to

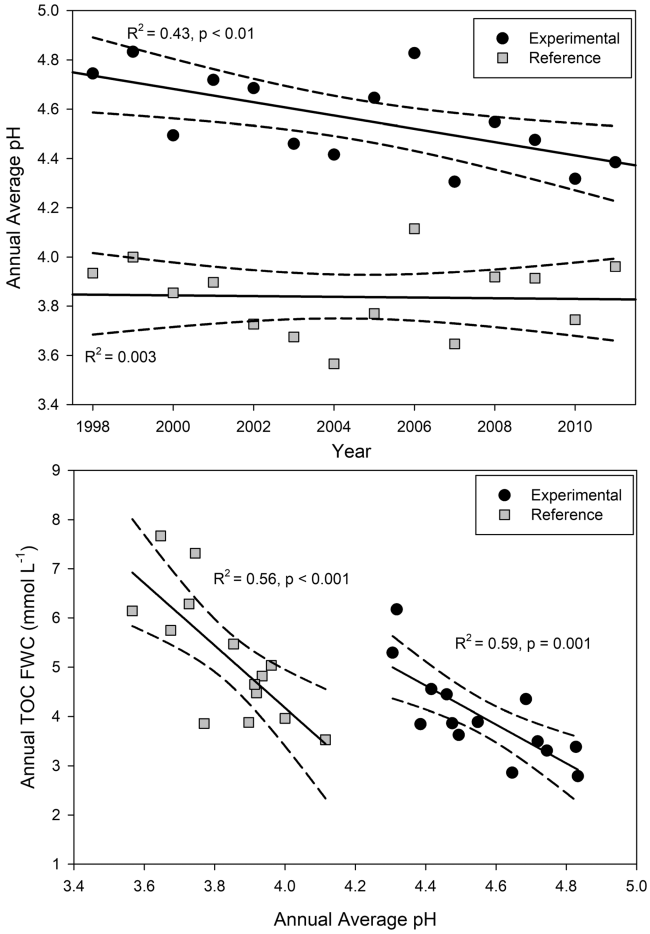

Figure 2. Linear correlations between annual average pH vs year (top) and annual average pH vs annual flow-weighted total organic carbon (TOC) concentration (bottom). Dashed lines are the 95% confidence intervals.

4.8 was observed during 2006. Importantly, the increase in pH during 2006 was observed in the outflow streamwater of both experimental and reference catchments, which resulted in little change in the pH IR in 2006 or anytime during or after the SO_4^{2-} additions (Figure 1D). Thus, any change was not likely due to the experimental SO_4^{2-} additions but rather was modified by landscape and/or climate factors (such as interannual variation in the volume or pH of precipitation) that impacted both peatlands.

Dissolved organic carbon (DOC, here measured as TOC, as particulate concentrations in these systems were negligible[31]) and pH are closely linked biogeochemically (Figure 2) and have been used to infer catchment-scale responses to reductions in anthropogenic SO_4^{2-} deposition.[6,46−48] Annual average pH and TOC concentration were negatively correlated at the outflows of both catchments (Figure 2). During the SO_4^{2-} additions, TOC concentrations increased in the Experimental Phase (2005) and were slightly, but continually, elevated at both the experimental (Pre-Experimental Phase: 43

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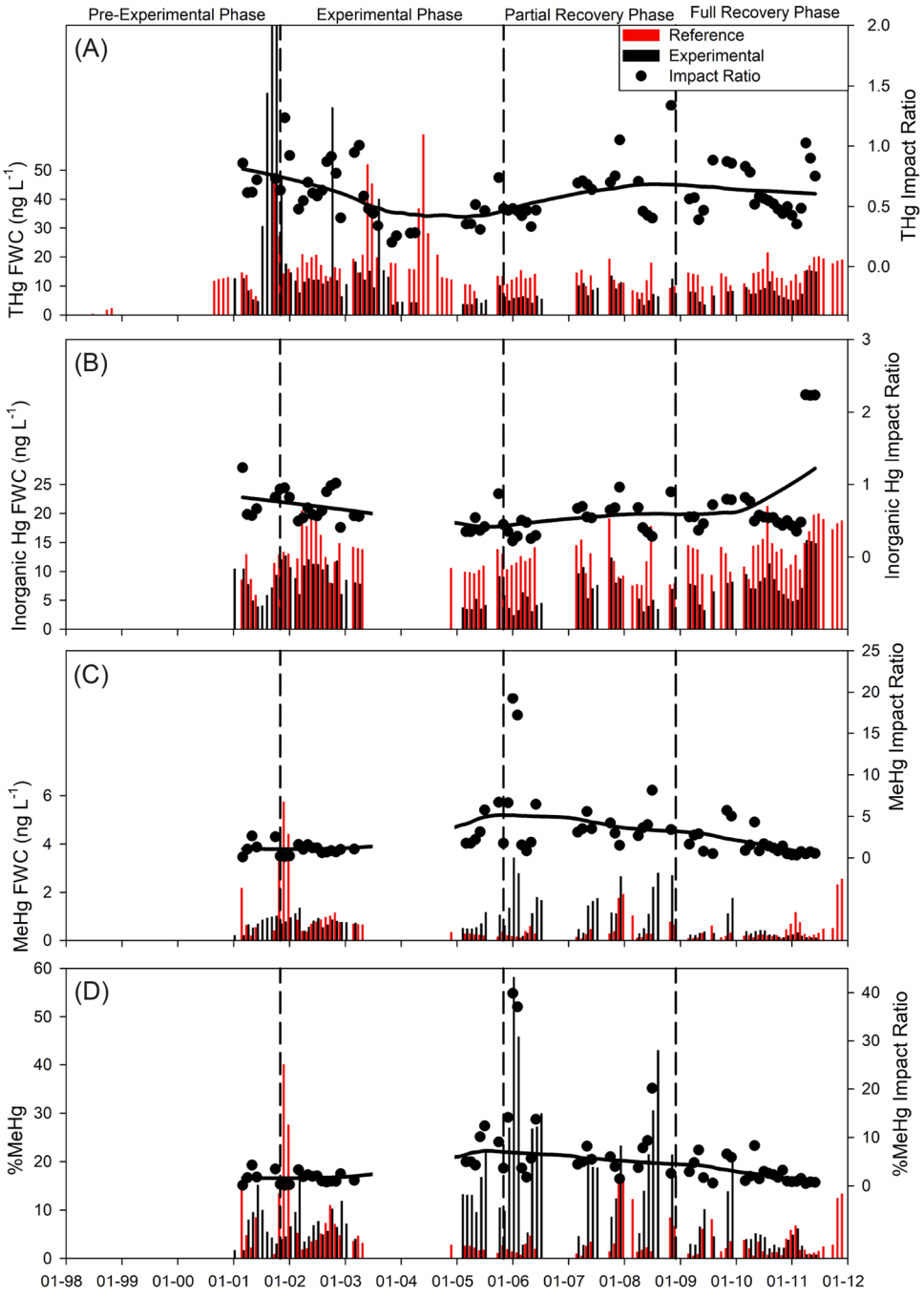

Figure 3. Monthly flow-weighted concentration (FWC) of (A) total Hg (THg), (B) inorganic Hg, (C) methylmercury (MeHg), and (D) proportion of THg found as MeHg (%MeHg) at the Experimental and Reference catchments with the FWC impact ratios and LOESS fitted line (secondary *y*-axis). The vertical dashed lines indicate transitions between the different experimental manipulations. There was a lack of measured data between 2003 and 2005 and to avoid misinterpretation of the LOESS fitted line during that period, it has been removed. Sodium sulfate (Na_2SO_4) additions were 3× per year (spring, summer, and fall) between 2001 and 2008. Note the change in scales for the different Hg species and impact ratios.

mg L^{-1}, Full-Recovery Phase: 62 mg L^{-1}) and reference (Pre-Experimental Phase: 55 mg L^{-1}, Full-Recovery Phase: 68 mg L^{-1}) peatlands until the end of the study in 2011 (Figure 1C). The observed increase in outflow streamwater TOC concentration from the experimental catchment was most likely not a result of the sulfate additions, given that a similar increase was observed from the reference peatland (Figure 1C). Although increased TOC concentrations in outflow streamwater due to increasing pH are commonly observed,[47,49−51] the response in TOC and pH are often conflicting within the literature, related to the confounding impacts of pH and ionic strength on organic carbon solubility.[6,46,47,52,53] At catchment-scales, changes in air temperature, hydrology and vegetation cover have each been linked with increasing DOC concentrations.[47−49,54] Given the lack of a clear systematic change in pH and TOC in the outflow of the experimental catchment, the observed variability in TOC concentration and pH IRs during the experimental additions were likely driven by larger-scale processes (e.g., droughts impacting timing and magnitude of hydrological

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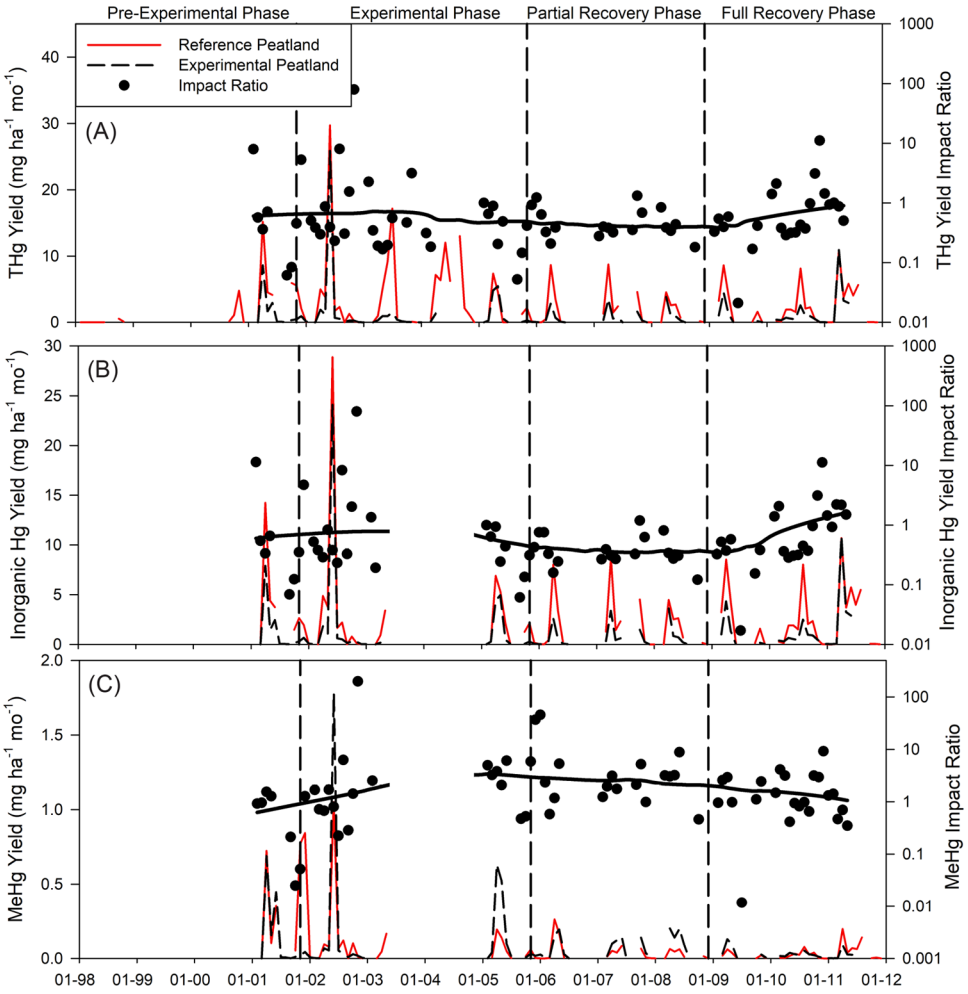

Figure 4. (A) Monthly total Hg (THg), (B) inorganic Hg, and (C) methylmercury (MeHg) yields and yield impact ratios with LOESS fitted line (secondary *y*-axis). The vertical dashed lines indicate transitions between the different experimental manipulations. There was a lack of measured data between 2003 and 2005 and to avoid misinterpretation of the LOESS fitted line during that period, it has been removed. Sodium sulfate (Na_2SO_4) additions were 3× per year (spring, summer, and fall) between 2001 and 2008. Note the change in scales for the different Hg species, as well as the log scale used for all impact ratios.

events[20]) that impacted both peatlands rather than the excess SO_4^{2-} additions.

Hg Response to and Recovery from SO_4^{2-} Additions. Mean monthly flow-weighted concentrations of MeHg from the experimental catchment increased from Pre-Experimental to early Partial-Recovery Phases (2005−2006) from 0.8 ± 0.3 to 1.2 ± 0.9 ng L^{-1}, an ∼50% increase (Figure 3C). By the end of the Full-Recovery Phase (2009−2011), mean monthly flow-weighted concentrations had decreased below Pre-Experimental Phase levels (0.4 ± 0.4 ng L^{-1}). The observed increase in mean monthly flow-weighted MeHg concentrations coincided with a larger decrease in mean monthly flow-weighted inorganic Hg concentrations, decreasing from an average of 9.0 ± 2.7 ng L^{-1} in 2001−2003 to 4.5 ± 1.7 ng L^{-1} in 2005−2006 and returning to approximate pre-experimental concentrations of 8.0 ± 3.4 ng L^{-1} by ∼2010 (Figure 3C). At the reference catchment, mean monthly flow-weighted inorganic Hg concentrations during the same periods followed a similar but more muted trend as at the experimental catchment (13.5 ± 3.9 ng L^{-1} to 11.5 ± 1.5 ng L^{-1} to 14.4 ± 3.5 ng L^{-1}: Figure 3B), while mean monthly flow-weighted MeHg concentrations fluctuated between 1.3 ± 1.5 (2001−2003) and 0.5 ± 0.6 ng L^{-1} (2009−2011; Figure 3C). At both catchments, there was considerable intra-annual variability in all monthly flow-weighted Hg concentrations (Figure 3A−C). However, the proportion of THg present as MeHg (%MeHg) substantially increased from the Pre-Experimental and early Experimental Phases (7 ± 4%, 2001−2003) to the late Experimental and early Partial-Recovery Phase (21 ± 15%, 2005−2006) before declining to 3 ± 2% in 2010−2011 at the experimental catchment. The IRs of THg and inorganic Hg concentrations varied between 0.2−1.3 and 0.2−2.2, respectively, while there was a more substantial range of IRs for MeHg concentration (0.1−19.2) and %MeHg (0.1−40.0; Figure 3C).

The lower inorganic Hg concentrations in 2005−2006 at the experimental catchment can be partly attributed to higher MeHg concentrations during the Experimental and Partial-Recovery Phases as monthly %MeHg increased periodically well above both the Pre-Experimental and Full-Recovery Phases (Figure 3C,D), similar to Jeremiason et al.[22] However, the overall magnitude of changes in inorganic Hg at the experimental catchment during these periods cannot be accounted for by changes in MeHg alone. Given the similar time patterns for inorganic Hg concentrations in runoff from both catchments, it is likely that other, yet unknown hydroclimatic processes, such as the timing and magnitude

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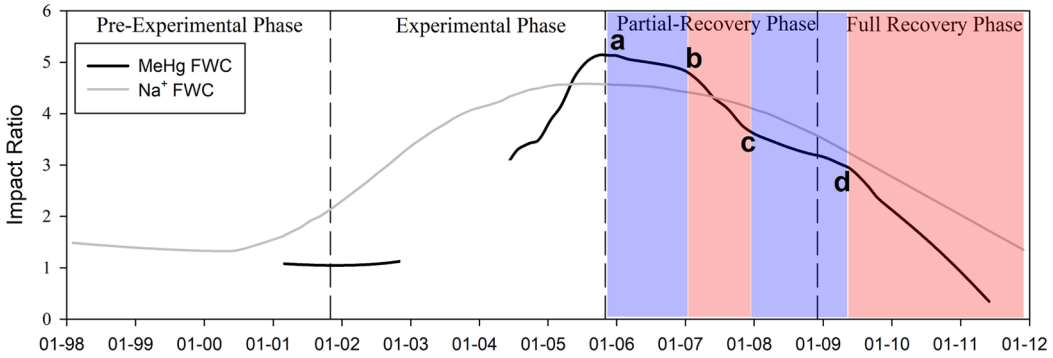

Figure 5. Comparison of LOESS fitted, FWC impact ratios (IR) for methylmercury (MeHg) and sodium (Na^+) during the study period. Four stages are identified based on their relative slopes of the MeHg concentration IR, where the lower rates of decline (blue) preceded periods with higher rates of decline (red). Slopes were similar between corresponding periods of higher and lower MeHg recovery (colors), indicating a systematic response to changes in SO_4^{2-} additions at the catchment scale. Each stage is associated with inflection points in the MeHg slope (a–d) that can designate periods of rapid change in Hg dynamics. The inflection points occur at MeHg concentration IRs of (a) 5.1, (b) 4.9, (c) 3.5, and (d) 3.0. There was a lack of measured data between 2003 and 2005 and to avoid misinterpretation of the LOESS fitted line during that period, it has been removed.

of precipitation or routing of water through the catchment, were partially responsible for the observed time trends in inorganic Hg concentrations. For example, during 2005–2006, the average concentration (10.4 ± 0.3 ng L^{-1}) and total mass (5.4 ± 0.8 $\mu g\ m^{-2}$) of wet deposited atmospheric Hg were lower relative to 2009–2011 (12.5 ± 2.5 ng L^{-1}, 6.0 ± 1.6 $\mu g\ m^{-2}$), and this may be partially responsible for the dip in inorganic Hg concentrations observed in runoff during 2005–2006.[55] Overall, we hypothesize that the observed changes in inorganic Hg in runoff over the experiment resulted from a combination of changes in net MeHg accumulation, changes in wet atmospheric Hg deposition, and possibly, changes in inorganic Hg solubility due to sulfide production and oxidation that were affected by sulfate additions or recovery from sulfate additions.[56]

THg yield in outflow streamwater from the experimental peatland did not systematically change due to the SO_4^{2-} additions (Figure 4A), despite decreased IRs of monthly flow-weighted THg and inorganic Hg concentrations (avg. THg concentration IR 0.98 to 0.48) during the late Experimental Phase (2005) and early Partial-Recovery Phase (2006; Figure 3A). This lack of a clear observable change in THg yield due to the SO_4^{2-} additions was, in part, due to the combined high variability of THg concentrations and streamflow observed during the entire study period. Over these relatively short timescales, the addition of SO_4^{2-} to the experimental peatland did not noticeably change the overall THg yield outside of the observed Pre-Experimental Phase variability, as might have been expected if SO_4^{2} enhanced decomposition of peat released previously bound inorganic Hg.[21,57] It appears that the export of THg, and by extension inorganic Hg (Figure 4B), from these catchments was more strongly controlled by as yet unclear landscape-scale processes.

Despite increases in MeHg production within the peatland[13,20] and the rapid increase in some instantaneous MeHg concentrations during the first year of the study,[22] the monthly flow-weighted MeHg concentration increase at the catchment outlet was not apparent until nearly the end of the Experimental Phase (Figure 3C). This lag in observed change was partly due to the analytical gap from 2003 to 2004, as described in the methods. The monthly %MeHg in outflow streamwater increased dramatically from the experimental catchment by late 2005, suggesting a relatively long lag-time between enhanced SO_4^{2-} amendments and response at the catchment scale but the analytical gap limits ascribing a precise lag-time (Figure 3C). Notably, there were mean monthly flow-weighted %MeHg that exceeded 50% in the outflowing streamwater during the end of the Experimental Phase (early 2005) and, at times, %MeHg of individual streamwater samples was >80% by the second year of SO_4^{2-} additions (Figure 3C). During the Partial-Recovery Phase, the %MeHg of individual samples was often >50%, reaching a maximum of 95% in late 2005 and early 2006. MeHg concentrations and %MeHg were 25× and 40× higher in the streamwater of the experimental catchment compared to the streamwater of the reference catchment during these periods (Figure 3D). Once SO_4^{2-} additions to one-third of the experimental peatland were halted (Partial-Recovery Phase), there was a rapid decline in peatland porewater MeHg concentrations and %MeHg to background levels within one year and in the peat within three years.[13] The response of MeHg in outflow streamwater once all SO_4^{2-} additions ceased (Full-Recovery Phase) did not follow the one-year porewater response nor the three-year peat response, but rather was intermediate between the two rates where MeHg reached ambient concentrations within ∼2 years of ceasing all SO_4^{2-} additions. This intermediate response was likely due to increasing peat MeHg partitioning coefficients (Table S2) after suppression by enhanced sulfide production during the SO_4^{2-} additions.[56] The average ratio between MeHg and TOC increased at the experimental peatland during the Experimental (reference: 0.015, experimental: 0.017 ng-Hg mg-C^{-1}) and Partial-Recovery Phases (reference: 0.008, experimental: 0.021 ng-Hg mg-C^{-1}), respectively, and declined to near pre-experimental (reference: 0.030, experimental: 0.013 ng-Hg mg-C^{-1}) conditions through the Recovery Phase (reference: 0.008, experimental: 0.006 ng-Hg mg-C^{-1}) (Figure S4), driven by increased MeHg concentrations (Figure 3C) and not changes in TOC concentration (Figure 1C). MeHg concentrations, %MeHg, and MeHg:TOC returned to background levels within two-years and were similar to the reference catchment in this study (Figure 3C).

Although it took 2 years for MeHg to return to pre-SO_4^{2-} addition levels, the MeHg concentration IR began to decline approximately 5 months into the Full-Recovery Phase (Figure 5, inflection point d). In contrast, the time-lag at the start of the Partial-Recovery Phase was ∼1.3 years (Figure 5, inflection

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Environ. Sci. Technol. 2022, 56, 17615–17625

point b). During the Partial-Recovery Phase, Coleman Wasik et al.[13] noted that periodic summer droughts (2004−2007) likely led to oxidation of reduced sulfur species to SO_4^{2-}, leading to increased MeHg production within the Recovery Area.[20] Notably, the water table in the experimental peatland was more affected by the drought than was the water table in the reference peatland, though maximum water table changes and the water table position at the end of the experiment were nearly the same (Figure S2). It is therefore possible that the drought-driven re-oxidation of SO_4^{2-} in the experimental catchment may have led to a difference in MeHg export between the study catchments that is beyond the effects of the SO_4^{2-} additions and recovery alone. This SO_4^{2-} from reoxidation of reduced species coupled with the continued SO_4^{2-} inputs to a portion of the peatland closest to the catchment outlet through the Partial-Recovery Phase prolonged elevated MeHg export, in contrast to the more rapid decline in MeHg when all SO_4^{2-} additions ceased. The peatland regeneration of SO_4^{2-} due to drought and subsequent MeHg production,[13,20] and the increased MeHg:TOC during the drought, was evident in the outflow streamwater (Figure 3) at the catchment scale.

Hydrological and Demethylation Influences on the Recovery of Catchment MeHg Export. Because SO_4^{2-} was added in this experiment as Na_2SO_4, Na^+ changes through time provide a means to assess the processes controlling MeHg concentrations in the catchment outflow. There was a clear increase in the monthly flow-weighted concentration and yield of Na^+ in the outflow water of the experimental catchment, corresponding to the addition of Na_2SO_4 (Figures 1A and S3A). Monthly flow-weighted Na^+ concentrations increased rapidly once the additions began, plateauing approximately three years into the study, and were sustained until additions ceased (Figure 1A). Once additions ceased, both Na^+ concentration and yield declined at a relatively constant rate throughout the Full-Recovery Phase, resulting in the return of the concentration IR to pre-experiment conditions after approximately 3 years. By the end of 2011, there was complete recovery (98 ± 43%) of the added Na^+ (~93 kg), when accounting for ambient atmospheric Na^+ deposition.[43]

Sodium is conservatively transported through peatlands when present at similar molar concentrations to other cations in solution.[58,59] In the outflow streamwater of the experimental catchment, calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+) were of similar molar concentrations to Na^+, particularly during the Pre-Experimental and Full-Recovery Phases, (~10 to 240 μmol L^{-1}, Sebestyen et al.[60]), suggesting that it is unlikely that the transport of Na^+ would have been significantly slowed during the Full-Recovery Phase. In many *Sphagnum*-dominated peatlands without comparable major cation concentrations, the transport of Na^+ is slowed by 1.2−2.1× relative to a more conservative tracer, such as chloride, because of adsorption to the peat.[58,61] Because other cations (particularly Ca^{2+} and Mg^{2+}) were of similar molar quantities to Na^+ during the Full-Recovery Phase, the flushing of Na^+ should approximate the hydrological flushing time of the experimental peatland.

Given that Na^+ likely approximates the hydrological flushing time in this instance, deviations between the MeHg and Na^+ concentration IRs indicate additional, nonhydrological processes influencing the MeHg response. For example, if the decline in the MeHg concentration IR followed the decline in the Na^+ concentration IR, the primary control on MeHg export would be hydrological at the catchment scale. Rather, during the initial Partial-Recovery Phase the rate of decline in MeHg concentration IR was slower (Figure 5, shallower slope of segment a−b) than that of Na^+ (Figure 5, the first shaded blue box) because the system was undergoing changes in the rate of net MeHg accumulation in the porewaters of the experimental peatland, as observed by Coleman Wasik et al.[13] During the Full-Recovery Phase after the approximately five-month lag period, the MeHg concentration IR declined at a greater rate (−0.0055 ± 0.003 d^{-1}) than that of Na^+ (−0.0013 ± 0.001 d^{-1}) (Figure 5) suggesting that at the peatland scale, some combination of net demethylation and increased MeHg adsorption to peat was increasing the recovery rate of MeHg observed at the catchment outlet beyond purely hydrological flushing of the experimental peatland. The differences between these slopes (0.004 ± 0.003 d^{-1}) indicates that the recovery rate to pre-experimental levels (IR ≈ 1.0) increased by approximately 75% due to net demethylation and MeHg sorption. The addition of SO_4^{2-} and subsequent production of reduced sulfur species in the Experimental and Partial-Recovery Phases of this study would likely increase the solubility of MeHg,[56] such as through changes to the concentration of aqueous organic sulfur ligands that are able to complex MeHg. Extrapolating a partitioning coefficient (peat MeHg/porewater MeHg) from the average MeHg peat and porewater concentration from Figure 3 in Coleman Wasik et al.[13] and an assumed bulk density of 0.1 g cm^{-3}, partitioning coefficients in the Experimental Area (Figure S1) were 2 to 63% (avg. 29%) lower than the Control Area between 2006 and 2009, while partitioning coefficients in the Recovery Area were similar to the Control Area (Table S2). Once SO_4^{2-} additions ceased, the proportion of MeHg sorbed to peat, rapidly returned to unimpacted conditions (Table S2), explaining approximately one-third of the increased recovery rate. The remaining two-thirds of the increased recovery rate is most likely attributable to net demethylation. Therefore, hydrological processes drove approximately one-quarter of the catchment-scale recovery of both MeHg concentrations (Figure 3C) and yields (Figure 4C) from the experimental catchment.

Overall, through this relatively unprecedented long-term and large-scale experiment, we present clear empirical evidence of relatively rapid declines in MeHg from a peatland-dominated catchment once SO_4^{2-} inputs decline, and importantly, that the declines are also proportional to the area of peatland no longer impacted by excess SO_4^{2-} deposition. In this study, we capitalized on the stepped decrease in contamination to determine how MeHg dynamics change relative to a declining areal extent of excess SO_4^{2-} deposition. In particular, the decrease in IRs for flow-weighted MeHg concentration in experimental catchment outflow streamwater was proportional to the decrease in areal extent of enhanced SO_4^{2-} additions. More specifically, the ~30% decline in the MeHg concentration IR during the first 2 years of the Partial-Recovery Phase (Figure 5) was roughly proportional to the Recovery Area relative to the total treated area. This study therefore provides strong experimental evidence that limiting the extent of SO_4^{2-} contamination will have a proportional impact on decreasing MeHg production and export in peatland-dominated landscapes. Additionally, the inferred proportional responsiveness of causal mechanisms for the MeHg export declines observed in this study (i.e., hydrological flushing and demethylation), which has not been previously quantified, suggests some

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further refinement of the "sulfur rain" hypothesis put forward by Bergman et al.[17] and suggested in the work of a number of studies that have examined SO_4^{2-}-enhanced Hg methylation.[62−64] This hypothesis suggests that MeHg exports are enhanced more strongly by atmospheric SO_4^{2-} deposition than by trends in Hg deposition. Our study provides evidence that this hypothesis is supported for SO_4^{2-} deposition trends in both directions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c02621.

Supplemental Methods for water sampling, analytical QA/QC, data analysis, and comparison of unfiltered versus filter total mercury and methylmercury, maps of the Experimental and Reference peatlands, precipitation and streamflow at both peatlands, monthly yields and yield impact ratios of sodium, sulfate, and total organic carbon, monthly FWC MeHg to TOC ratios, average pore water and peat MeHg concentrations from Coleman Wasik et al.[13] Figure 3, and calculated partitioning coefficients, filtered versus unfiltered streamwater Hg, unique ID numbers for samples from Sebestyen et al.[39] and Sebestyen et al.,[40] and monthly ± standard errors flow-weighted concentrations and yields (PDF)

Sample identification numbers of the Experimental (S6) Reference (S2) catchment samples used for this study (TXT)

Monthly flow-weighted concentrations and yields (± standard error) of MeHg, THg, inorganic Hg, TOC, SO_4^{2-}, and Na^+ (XLSX)

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Notes

The authors declare no competing financial interest.

The data underlying this study are openly available in the Environmental Data Initiative Data Portal at doi:10.6073/pasta/9f8fb5bb7ce3d9549e2cab219fdc65d8 and doi:10.6073/pasta/a47f5019f2ce2aff6cbca0e555939950. To enable easier access to the large amount of study data, a table of unique identification numbers for samples from this study is provided in the Supporting Information.

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