RESEARCH ARTICLE

Key Points:
- Examined effects of variable hydrology and sulfate inputs on sulfur and mercury cycling
- Sulfate inputs to peatlands create more effective methylating environments
- Drought enhances methylmercury production within and release from peatlands

The effects of hydrologic fluctuation and sulfate regeneration on mercury cycling in an experimental peatland

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Abstract A series of severe droughts during the course of a long-term, atmospheric sulfate-deposition experiment in a boreal peatland in northern Minnesota created a unique opportunity to study how methylmercury (MeHg) production responds to drying and rewetting events in peatlands under variable levels of sulfate loading. Peat oxidation during extended dry periods mobilized sulfate, MeHg, and total mercury (Hg_T) to peatland pore waters during rewetting events. Pore water sulfate concentrations were inversely related to antecedent moisture conditions and proportional to past and current levels of atmospheric sulfate deposition. Severe drying events caused oxidative release of MeHg to pore waters and resulted in increased net MeHg production likely because available sulfate stimulated the activity of sulfate-reducing bacteria, an important group of Hg-methylating bacteria in peatlands. Rewetting events led to increased MeHg concentrations across the peatland, but concentrations were highest in peat receiving elevated atmospheric sulfate deposition. Dissolved Hg_T concentrations also increased in peatland pore waters following drought but were not affected by sulfate loading and did not appear to be directly controlled by dissolved organic carbon mobilization to peatland pore waters. Peatlands are often considered to be sinks for sulfate and Hg_T in the landscape and sources of MeHg. Hydrologic fluctuations not only serve to release previously sequestered sulfate and Hg_T from peatlands but may also increase the strength of peatlands as sources of MeHg to downstream aquatic systems, particularly in regions that have experienced elevated levels of atmospheric sulfate deposition.

1. Introduction

Peatlands are sites of active biogeochemical cycling for many elements, including sulfur and mercury, because they provide a gradient in oxidation-reduction potentials that are exploited by different microbial communities to gain metabolic energy from chemical transformations [*Blodau et al.*, 2007; *Bottrell et al.*, 2007; *Deppe et al.*, 2010]. Peatlands, and wetlands in general, are considered to be sinks for atmospherically deposited sulfate, in part because sulfate-reducing bacterial (SRB) communities consume incoming sulfate [*Pester et al.*, 2012; *Spratt et al.*, 1987; *Urban et al.*, 1989]. However, there is a significant body of literature showing that drought cycles can alter this function and make peatlands sources of sulfate to downstream aquatic environments [*Bayley et al.*, 1986; *Dillon et al.*, 2007; *Eimers et al.*, 2004; *Mitchell and Likens*, 2011]. Therefore, predicted changes in climate that promote drought conditions [*Sheffield and Wood*, 2008] could have the secondary effect of recycling sulfate previously sequestered in peatlands and increasing sulfate inputs to downstream aquatic systems.

While sulfate release from peatlands following drought has been widely investigated, little research has been conducted on the response of mercury biogeochemistry to drought and drought-induced sulfate release. Mercury is a contaminant of great concern in many freshwater systems, particularly because the most common organic form of mercury, methylmercury (MeHg), is biomagnified in aquatic food chains, putting humans and piscivorous wildlife at risk to its neurotoxic effects [*Mergler et al.*, 2007; *Munthe et al.*, 2007]. Peatlands are generally considered to be sinks for total mercury inputs (Hg_T) from atmospheric deposition

and upland runoff but sources of MeHg to downstream aquatic systems [*Branfireun et al.*, 1998; *St. Louis et al.*, 1994]. The transformation of inorganic mercury to MeHg in the environment is predominantly an anaerobic process carried out by bacterial groups that carry the *hgcAB* gene cluster [*Parks et al.*, 2013], particularly SRB [*Gilmour et al.*, 2013]. Because mercury methylation can be stimulated by sulfate addition to sulfur-limited aquatic systems [*Branfireun et al.*, 1999; *Gilmour et al.*, 1992; *Jeremiason et al.*, 2006] drought-induced sulfate release represents a potential mechanism whereby peatlands could become even larger sources of MeHg in the landscape.

Most research investigating the effect of hydrology on mercury cycling has focused on reservoir creation (i.e., inundation/flooding) [*Bodaly et al.*, 1997; *Hall et al.*, 2005; *St. Louis et al.*, 2004], export from watersheds [*Babiarz et al.*, 1998; *Balogh et al.*, 2006; *Bushey et al.*, 2008; *Mitchell et al.*, 2008b], and cascading effects on biota [*Bodaly and Fudge*, 1999; *Bodaly et al.*, 1984; *Evers et al.*, 2007] but not the direct effects of drought on MeHg production/release within peatlands. *Gilmour et al.* [2004] performed rewetting incubations on dried Everglades sediment in the laboratory and observed both sulfate release and a consequent rise in mercury methylation, while *Feng et al.* [2014] found that drying and rewetting cycles within wetlands constructed for water treatment resulted in sulfate release and downstream increases in MeHg production. A recent series of studies in California, USA, also highlighted the importance of drying and rewetting to MeHg production within and export from agricultural and wetland systems managed for rice production and waterfowl habitat [*Alpers et al.*, 2014; *Marvin-DiPasquale et al.*, 2014; *Windham-Myers et al.*, 2014]. A few studies have specifically addressed the issue of drought influence on mercury bioaccumulation. *Snodgrass et al.* [2000] found that a drying period was important in explaining higher fish mercury levels in South Carolina depressional wetlands, and *George and Batzer* [2008] invoked drought conditions to explain elevated invertebrate mercury levels in the Okeefenokee Swamp. *Ackerman and Eagles-Smith* [2010] and *Feng et al.* [2014] likewise cite drying and rewetting patterns as an important control on Hg_T body burdens in caged fish experiments in agricultural and constructed wetland systems receiving elevated sulfur inputs.

The study reported here was part of an 8 year whole-ecosystem experiment on the effects of elevated sulfate deposition on MeHg production in a boreal peatland [*Coleman Wasik et al.*, 2012; *Jeremiason et al.*, 2006]. Two severe droughts occurred during the course of that study, effectively overlaying a drying and rewetting manipulation onto the sulfate addition experiment. The purpose of this paper is to describe the effects of these drought events on mercury cycling in the context of the depositional history of sulfate. The experimental peatland was divided into treatments that received differing sulfate loads, and intensive pore water sampling was used to monitor dissolved sulfate, Hg_T, and MeHg concentrations before, during, and after drought. Solid phase (peat) samples were also collected over the course of the experiment and are discussed in greater detail elsewhere [*Coleman Wasik et al.*, 2012]. In addition, water levels were experimentally manipulated in mesocosm enclosures to simulate natural drought-induced changes in sulfur and mercury cycling. Our main objectives were to (1) determine whether differential atmospheric sulfate loading affected sulfate release following drought, (2) understand how the oxidizing effects of drought affected mercury cycling, and (3) explore the interaction between drought-induced sulfate release and MeHg production.

2. Materials and Methods

2.1. Field Site Description

The study was conducted in the S6 peatland located within the Marcell Experimental Forest (MEF), a unit of the Chippewa National Forest in northern Minnesota (Figure 1). The 2.0 ha S6 peatland occupies an elongate, ice-block depression common in the glacial landscape surrounding the MEF [*Sebestyen et al.*, 2011]. The raised ombrotrophic center of the S6 peatland is dominated by an overstory of mature black spruce (*Picea mariana*) and tamarack (*Larix laricina*) and an understory of ericaceous shrubs (e.g., *Chamaedaphne calyculata* and *Ledum groenlandicum*), herbaceous forbs (e.g., *Cypripedium acaula* and *Menyanthes trifoliata*), and *Sphagnum* spp. [*Marcell Experimental Forest (MEF)*, 2013]. Alder (*Alnus rugosa*) along the peatland margin delineates the minerotrophic lagg, which receives runoff from a 6.9 ha white spruce (*Pinus glauca*) and red pine (*Pinus resinosa*) upland [*MEF*, 2013].

The regional climate at the MEF is continental, with annual precipitation averaging 710 mm between 2000 and 2008 (Table 1). A significant portion of the precipitation is received during the winter months, and because hydrology in the S6 peatland is driven by precipitation, spring snowmelt is typically the largest
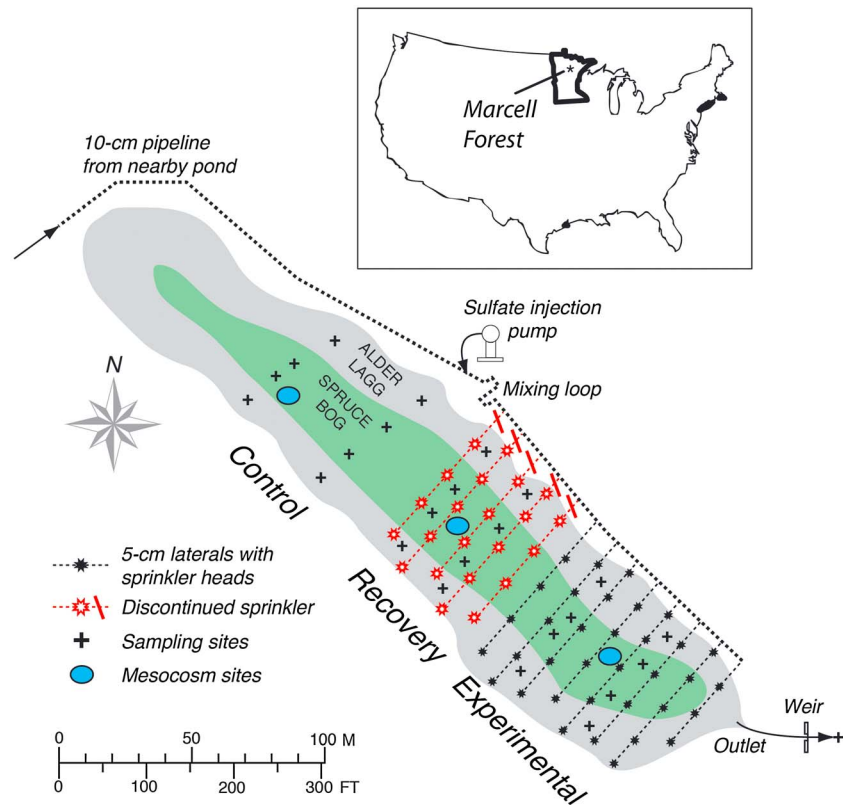
Figure 1. A schematic of the experimental design within the S6 peatland illustrating the PVC rainfall simulator, location of sampling sites, and experimental mesocosm locations. See text for details. The inset map shows the location of the Marcell Experimental Forest in Minnesota.

hydrologic event of the year [*Nichols and Verry*, 2001]. The S6 peatland is hydrologically perched above the regional groundwater table, and therefore, its water table elevation (WTE) and outflow are heavily dependent on precipitation. The lagg margin represents the dominant flow path for both the central bog and upland catchment, with the central bog generally contributing most of the total outflow [*Rauneker*, 2010]. WTE and outflow are monitored continuously by the United States Forest Service Northern Research Station at a centrally located bog well and a 120° V notch weir, respectively. Upland near-surface flow and interflow collectors are used to estimate hydrologic and chemical inputs from the uplands.

2.2. Sulfate Deposition Experiment

Results reported here were obtained during a long-term study (2001–2008) of the effects of elevated atmospheric sulfate deposition on MeHg production in a sulfur-limited peatland. Ambient sulfate deposition, recorded since 1977 at the MEF (National Atmospheric Deposition Program site MN16) [*National Atmospheric Deposition Program*, 2014] decreased by 50% from 11 kg ha^{-1} yr^{-1} in the early 1980s to approximately 5.5 kg ha^{-1} yr^{-1} in the mid-2000s. Sulfate deposition to the experimental treatment in this study was increased by 32 kg ha^{-1} yr^{-1} (~4X the ambient 1990s rate) to simulate late twentieth century sulfate deposition rates experienced across much of eastern North America.

Table 1. Average Annual Precipitation, Outflow, and Water Table Elevation (WTE) in the S6 Peatland for the Periods 1964–2008, 2000–2008, and 2005–2007[a]

	Precipitation mm	Outflow mm (m^3)	WTE Mean (m asl)	WTE Min (mm)	WTE Max (mm)	Median Δ WTE (mm)	Max Δ WTE (mm)
1964–2008	773	155 (13,832)	422.675	−475	+442	360	660
2000–2008	710	110 (9,766)	422.696	−414	+421	400	620
2005–2007	660	91 (8,128)	422.634	−352	+95	550	620

[a]WTE Mean represents the mean for the period of record indicated. WTE Min and WTE Max are the difference in mm between the WTE mean and the WTE Min or Max. Δ WTE is the difference between the annual maxima and minima WTE in the peatland.

The experimental design of the overall study has been described previously [*Coleman Wasik et al.*, 2012; *Jeremiason et al.*, 2006]. Briefly, in 2001 the S6 peatland was divided roughly in half into control and experimental treatments, and a PVC rainfall simulator was constructed across the experimental portion. This system consisted of a 10 cm main pipeline that ran along the northern edge of the peatland and 13 5 cm lateral lines extending across the original experimental treatment, each with rotating sprinkler heads mounted on 1 m vertical risers spaced at regular intervals. Dilute surface water (specific conductivity = 20 μS cm^{-1}) was drawn from a nearby pond, and a concentrated sodium-sulfate solution was injected into the main pipeline at a point downgradient of the control treatment. A mixing loop in the main pipeline ensured that the concentrated sulfate was thoroughly mixed with the source water. Sulfate was added in three simulated rainfall events each year (spring, summer, and fall). Each sulfate addition was followed by a rinsing period to wash sulfate off the vegetation, resulting in a total of 6–8 mm of simulated rainfall. In the spring of 2006 a new recovery treatment was established by discontinuing sulfate addition to the upgradient, one third of the original experimental treatment. A bromide tracer was added during each application to monitor movement of application water. However, bromide was not conservative in the peat and so served instead as a presence/absence indicator rather than a quantitative tracer.

2.3. Water Table Mesocosm Experiment

Twelve water table mesocosms were installed across the peatland in July of 2007 to experimentally manipulate hydrologic fluctuations and measure the effects on sulfur and mercury cycling. Four 75 cm lengths of 30.5 cm (ID) PVC pipe were driven into homogeneous lawn areas of the central bog within each treatment (control, recovery, and experimental). Each mesocosm was allowed to equilibrate overnight, and pore waters were sampled the next day to capture mercury and sulfate concentrations prior to water table manipulation. Deionized water was then added to each mesocosm until the water table was approximately 1 cm above the peat surface. Not all mesocosm installations were successful in maintaining experimental water levels above the peatland water table. If water levels in mesocosms fell by more than 5 cm overnight (owing to leakage out the bottom), the PVC pipe was repositioned and again monitored for leaks. Mesocosms were reset up to 2 times before abandoning the effort at that location. Once mesocosms were successfully installed, pore waters were sampled on days +1, +2, +3, +7, +9, +11, and +13 after raising the water table. Deionized water was added periodically to maintain water levels at the peat surface as sampling and evaporative losses caused declines. The mesocosm experiments were initiated 1 week prior to the summer 2007 sulfate addition. Mesocosms located in the experimental treatment were covered during the sulfate application, following which 130 mg of Na$_2$SO$_4$ was added directly to each in a dilute, deionized water solution. This application rate was comparable to the amount added to the S6 peatland during the summer sulfate addition.

2.4. Pore Water Sampling

The short-term effects of sulfate addition were monitored through intensive sampling of peatland pore waters before and after each addition. Initially, two transects were established in the control and experimental treatments, and four 1 m^2 sampling plots were evenly distributed among the central bog and lagg margins along each transect. Sampling plots were preferentially located in lawn areas [*Branfireun*, 2004]. In 2006 two transects were established in the newly created recovery treatment, and the original experimental treatment transects were relocated further downgradient to ensure that sampling occurred within the treated area. At the same time instrument sites housing a pressure transducer and nested temperature and oxidation-reduction potential electrodes (at 10, 20, and 30 cm depths) interfaced to a Campbell data logger were also installed in the central bog along the southernmost transect in each treatment. These sites were used to monitor the interaction between local water table elevation and redox conditions in the peat. Pore water samples were collected in triplicate from bog plots located next to the instrument sites in order to increase sample numbers and assess the local heterogeneity in pore water chemistry. Pore waters were collected from each plot on days −1, +1, +3, and +7 relative to each sulfate addition as well as on day +14 for every spring and fall addition. Beginning in 2006 pore waters were sampled with greater frequency in the spring, either starting with snowmelt or beginning soon thereafter, and an additional sampling day was added 1 week prior to the fall sulfate additions. In the fall of 2007 pore waters from each plot were also sampled on days +2, +4, +9, +14, +18, and +27 after a large rainfall event on 6 September.

Pore waters were collected using a portable peristaltic pump and a 1.9 cm ID, Teflon probe with a 5 cm perforated tip. The probe was inserted into the peat 5–10 cm below the water table surface [*Branfireun et al.*, 2001; *Branfireun et al.*, 1999]. Pore waters were then drawn through 0.64 cm ID Teflon tubing by a peristaltic GeoPump and passed through acid-washed 47 mm Teflon filter holders (Savillex Co.) prefitted with ashed, 0.7 μm, glass-fiber filters into sample bottles. Samples for dissolved Hg_T, MeHg, and major anions were collected from each plot on every sampling day. Samples for dissolved organic carbon (DOC) were collected from each plot 1 day prior to sulfate additions in 2005 and 2006 and on each sampling day in 2007 and 2008. All mercury samples were collected directly into new, 125 mL PETG bottles using accepted, clean sampling techniques [*Bloom and Fitzgerald*, 1988] and preserved by acidifying to 0.5% (vol/vol) with high-purity HCl. Field duplicates and equipment blanks accounted for 10% of all samples.

2.5. Analytical Methods
2.5.1. Anions
Pore water samples were analyzed for anions (SO_4^{2-}, Cl^-, and Br^-) by ion chromatography on a Dionex DX-500 according to standard methods. Each run included 10% deionized water blanks, 10% sample duplicates, and check standards. Check standards and duplicates were within 10%, and detection limits for each anion were 0.01 mg L^{-1} in each year.

2.5.2. Dissolved Organic Carbon
Pore water samples were analyzed for DOC according to standard methods by either a UV-persulfate oxidation method on a Tekmar-Dohrmann Phoenix 8000 or by catalytic combustion on a Shimadzu carbon analyzer. All samples were analyzed in duplicate. Check standards and equipment blanks accounted for 10% of analyzed samples. Sample replicates and check standards were within 10%, and equipment blanks were generally less than 1 mg L^{-1} DOC each year.

2.5.3. Mercury
Dissolved Hg_T was analyzed according to Environmental Protection Agency (EPA) method 1631, Revision E on a Tekran 2600 Automated Total Mercury Analyzer. Samples were allowed to oxidize overnight with bromine monochloride to convert all mercury species to Hg^{2+} and then neutralized with hydroxylamine prior to analysis. Mercury was converted to Hg^0 using stannous chloride reduction, purged from solution, and trapped on gold traps. Mercury was then thermally desorbed in a stream of argon and analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS). The instrument was calibrated daily, and each analytical run included 20% deionized water blanks, 10% sample duplicates, and 5% matrix spikes. In all years spike recoveries were between 78 and 114%, relative percent differences between duplicates were less than 10%, and method blanks were below 1 ng L^{-1}.

Dissolved MeHg was analyzed according to methods described in *Bloom* [1989] and *Liang et al.* [1994]. Samples were first distilled with 8 M H_2SO_4 and 20% KCl (wt/vol) in an extraction manifold using acid-cleaned Teflon vessels. Distillates were refrigerated and analyzed within 48 h. All mercury species in solution were ethylated using sodium tetraethylborate, purged from solution in a stream of nitrogen, and trapped on Tenax traps. The trapped mercury species were thermally desorbed in a stream of argon or helium and separated during passage through a chromatographic column. The separated mercury species were then converted to Hg^0 in a pyrolytic trap and analyzed by CVAFS on a Tekran 2500 or Brooks Rand Model III spectrometer. The instruments were calibrated daily, and each analytical run included 5% deionized water blanks, 10% sample duplicates, and 5% matrix spikes. In all years spike recoveries were between 98 and 103%, relative percent differences between duplicates were less than 12%, and method blanks were below 0.15 ng L^{-1}.

Poor calibration curve linearity, high blanks, or quality control samples more than 15% deviation from expected concentrations in any Hg_T or MeHg analysis precluded sample analysis until the analytical issue was resolved. Quality assurance and control results for total and methyl-mercury analyses for each year can be found in Tables S1 and S2 in the supporting information.

2.6. Numerical Analyses
All statistical analyses were performed using the statistical software R [*R-Development-Core-Team*, 2011]. The Wilcoxon rank-sum analysis was used to compare mean sulfate and mercury concentrations between two treatments at a time on each day and within each treatment before and after sulfate additions or storm events. Kruskal-Wallis analyses were used to (1) assess differences in sulfate and mercury concentrations in
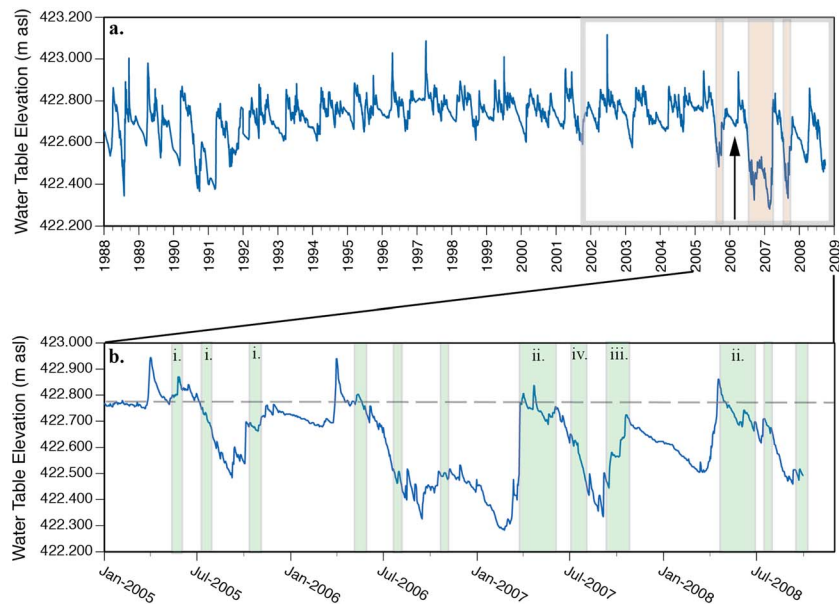
Figure 2. (a) Twenty-year record of water table elevation in the S6 peatland (1988–2008). The gray box bounds the study period. The arrow indicates the start of the recovery treatment. The brown-shaded bands denote the severe droughts that occurred during the course of the sulfate addition experiment. (b) This period of recent variability is magnified, and sulfate additions and sampling periods in each year are indicated by the green-shaded bands. The average elevation of the peat surface is indicated by the dashed horizontal line. Roman numerals denote sampling periods highlighted in Figure 4 (i), Figure 5 (ii), Figure 6 (iii), and Figure 7 (iv).

the spring of 2007 and the spring of 2008 that resulted from very different antecedent moisture conditions and (2) assess the effect of water-level manipulations in the experimental water table mesocosms. Statistical analyses of mesocosm data were conducted separately for Hg_T, MeHg, %MeHg, SO_4^{2-}, and DOC within each treatment. The day relative to experimental water table rise was considered as a nominal variable in the analysis. A P value less than or equal to 0.05 was considered significant.

A series of multiple regression analyses was performed to ascertain correlation between the magnitude and duration of fluctuations in WTE and sulfate concentrations within each treatment. Sulfate data were averaged by treatment for each sampling day and then natural log transformed prior to regression analyses to normalize residual error. Sulfate values from the experimental treatment that were collected within 1 week of sulfate addition were not included in the analysis to avoid bias in the data set. To isolate the influence on observed pore water chemistry of the magnitude and duration of the water table fluctuations, we calculated the maximum change in the water table and the duration of that change for each of five different periods (10, 20, 30, 60, and 90 days) preceding each pore water sampling date.

3. Results

3.1. Drought in the S6 Peatland

3.1.1. Effect on Water Table Elevation

The S6 peatland is considered to be a poor fen with little or no connection to the regional groundwater table [*Sebestyen et al.*, 2011]. The center of the peatland is raised relative to its margins creating an ombrotrophic system that relies predominantly on atmospheric precipitation for water and nutrient inputs. The lack of a moderating, regional hydrologic influence results in relatively large interannual and intraannual variations in water table elevations (WTEs) and outflow (Table 1). Water levels and outflow generally reach peak values during and after spring snowmelt, decline over midsummer to late summer, and usually rebound during the fall after vegetation senescence (Figure 2). This general pattern varies from year to year. For example, during abnormally wet years there may be no summer decline, while during abnormally dry years there may be no fall rebound (e.g., 1999 and 2006, respectively; Figure 2a). Severe droughts have occurred at the MEF several
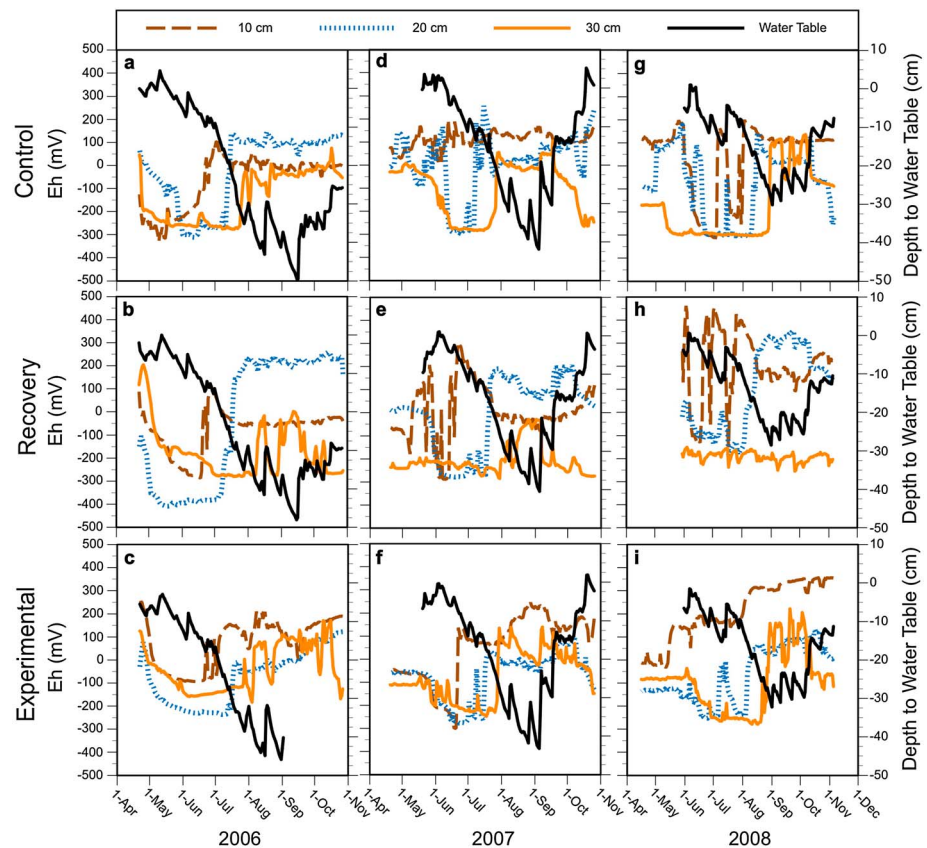
Figure 3. Eh profiles at 10, 20, and 30 cm depths and depth to water from the peat surface in the control, recovery, and experimental treatments in 2006, 2007, and 2008.
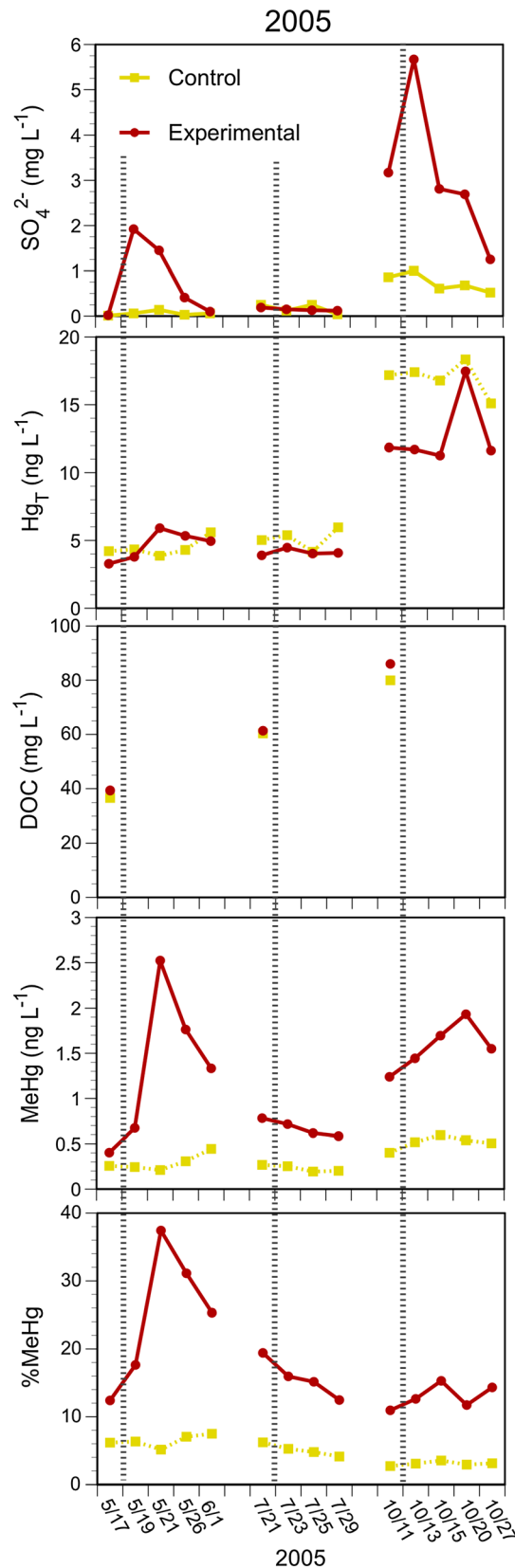
times over the nearly 50 years of data collection (1967–1968, 1976–1977, 1990–1991, and 2006–2007) and were initiated by a year in which the area received less than 600 mm of precipitation.

The most recent drought occurred during the course of the 8 year sulfate addition experiment in S6 (Figure 2b). In 2006 the MEF received 561 mm of precipitation. The WTE reached its annual maximum of 422.94 m above sea level (asl) on 31 March during the spring snowmelt and then declined to a minimum of 422.33 m asl on 15 September. The water table rebounded slightly in late September/early October but then resumed a slow decline until snowmelt the following spring.

In February 2007 the WTE in S6 reached 422.28 m asl—the lowest level measured in 30 years—and then rebounded more than 550 mm during the snowmelt period in late April, resaturating peat that had been dry for nearly 9 months. The S6 WTE remained relatively stable throughout May and then began a decline through the summer, similar to that seen the previous year. In September several large rain events over the MEF raised the WTE 390 mm over the course of 6 weeks (6 September to 19 October). The water table began another decline in late October that lasted through the winter. However, the wetland froze in a saturated condition as opposed to the very desiccated state of the previous year. In 2008 the WTE resumed a more historically typical pattern.

3.1.2. Effect on Oxidation-Reduction Potential

The oxidation-reduction potentials measured within each treatment at three different depths in 2006, 2007, and 2008 provided insight on the depth of oxygen penetration into the peat as water tables rose and fell (Figure 3). Generally, redox conditions were moderately elevated in the early spring of each year and then became more negative as the peatland thawed and warmed. As the water table fell past each probe depth during the summer the corresponding redox potentials jumped to very positive values indicating the intrusion of oxygen. When the water table rebounded in the fall redox potentials declined slowly toward their previous levels, presumably as oxygen was consumed.

Figure 4. Pore water chemistry in the S6 peatland in 2005 (May–October). Dashed lines indicate experimental sulfate additions. DOC samples were collected only on the day prior to each sulfate addition in 2005.

The peat at 10 cm in each treatment was often subject to oxidizing conditions regardless of whether the peatland was experiencing drought or not (Figure 3). Strongly negative redox values were primarily observed at 10 cm depth during the spring when the water table was at or near the peat surface. The peat at 20 cm depth experienced larger changes in redox conditions over the course of each year in response to declining water tables and large rainfall events. Strongly negative values prevailed during the spring and early summer periods while the late summer and fall were characterized by positive redox values. Large rainfall events on 1 July 2007 and 13 July 2008 caused transient increases in redox values at 20 cm depth (Figures 3d–3i), possibly owing to downward percolation of oxygenated rainwater. Shortly, thereafter the WTE continued its steep summer decline, and redox potentials spiked upward and remained there well into the fall of both years. Redox conditions were most consistent at 30 cm depth among treatments and years, declining to low steady values in spring or early summer and then spiking upward as WTE fell below the probe depth in midsummer. Because water tables fell particularly low in 2006 and 2007, oxygen was able to penetrate to 30 cm depth for extended periods of time (Figures 3a–3f).

3.2. Response of Pore Water Sulfate and Mercury to Drying Events
3.2.1. Water Table Elevation and Sulfate Addition
Sulfate was added to the experimental treatment 3 times during each field season between 2002 and 2008 to observe possible stimulation of mercury methylation. The effectiveness of each sulfate addition was influenced by the position of the water table, as

exemplified by trends in pore water %MeHg and sulfate concentrations in 2005 (Figure 4). Over the sulfate addition and sampling period in spring of 2005 the WTE was high, averaging 422.825 m asl. Sulfate concentrations in experimental treatment pore waters increased nearly 2 orders of magnitude from near detection before the sulfate addition to 1.92 ± 0.03 mg L^{-1} after the addition. Three days after the sulfate addition, as sulfate concentrations were declining, %MeHg rose by 3X (from 12 ± 9% to 39 ± 18%). Because concurrent Hg_T concentrations remained constant in the experimental treatment, this MeHg rise is attributed to increased production. Sulfate and Hg_T concentrations and %MeHg in the control treatment were stable (<0.14 mg SO_4^{2-} L^{-1}, <5 ng Hg_T L^{-1}, and 5–8% MeHg) throughout the spring period.

By the time of the summer sulfate addition water tables had fallen 130 mm since the spring addition. In contrast to the spring period sulfate concentrations did not increase in the experimental treatment, but instead remained similar to control treatment levels, likely because added sulfate did not reach the water table. Experimental treatment %MeHg levels also remained stable over the period but were elevated 2–3 times above control treatment levels. Again, Hg_T concentrations in the control and experimental treatments were stable and consistently low over the monitoring period (4–5 ng L^{-1}; Figure 4). DOC levels during the summer application period were 50% higher than spring concentrations.

In the fall of 2005 sulfate concentrations were already elevated in both control and experimental treatment pore waters (0.86 ± 1.39 and 3.17 ± 1.83 mg L^{-1}, respectively; Figure 4) prior to the sulfate addition, which itself was preceded by an 80 mm rain event. Sulfate concentrations in experimental treatment pore waters increased to 5.67 ± 1.83 mg L^{-1} following the addition, while %MeHg increased only modestly (from 11 ± 6% to 15 ± 4%), despite sulfate concentrations that were nearly 3 times those that were associated with a 3X increase in %MeHg after the spring addition. Moreover, %MeHg levels in the control treatment were stable over the sampling period and lower than during either the spring or summer sulfate additions (3–4%). Hg_T concentrations in both treatments were 3–4X higher than at any time during the previous spring or summer (Figure 4), and DOC concentrations were 2X spring concentrations.

3.2.2. Rewetting Events
The severe droughts in 2006 and 2007 and the rewetting events that followed caused large swings in WTE and highlighted the effects of hydrologic fluctuations on sulfur and mercury biogeochemistry in the S6 peatland.

3.2.2.1. Spring Thaw Period
The 2006 drought persisted into the winter causing the upper 30–40 cm of the acrotelm in the S6 peatland to freeze in an oxidized state. Therefore, an extensive sampling campaign was undertaken in the spring of 2007 to monitor sulfur and mercury cycling as the peatland resaturated. On 26 March pooled snowmelt was sampled from the frozen peat surface, and water chemistries were found to be uniform among treatments (2–3 mg SO_4^{2-} L^{-1}, 4–8 ng Hg_T L^{-1}, 0.14–0.18 ng MeHg L^{-1}, and 1.7–3.9% MeHg; Figure 5). As the peat slowly thawed over the next 6 weeks a "natural" sulfate addition ensued. Sulfate concentrations peaked at very high levels for this peatland (3.20 ± 3.54, 5.72 ± 8.54, and 7.89 ± 2.58 mg SO_4^{2-} L^{-1} in the control, recovery, and experimental treatments, respectively). As sulfate concentrations declined MeHg concentrations and %MeHg reached peak levels that were significantly higher than early season lows ($P < 0.05$; Wilcoxon rank sum) and were significantly different among treatments ($P < 0.05$; control = 1.18 ± 1.53 ng MeHg L^{-1}, 10 ± 10%; recovery = 2.06 ± 2.34 ng MeHg L^{-1}, 16 ± 6%; and experimental = 2.60 ± 2.06 ng MeHg L^{-1}, 25 ± 14%). Hg_T concentrations increased significantly in the control and recovery treatments to 12 and 16 ng L^{-1}, respectively ($P < 0.05$; Wilcoxon rank sum), and more than doubled relative to levels observed during the first sampling in each treatment. However, Hg_T concentrations did not show any systematic differences among treatments over the monitoring period. DOC concentrations rose steadily over the entire spring thaw period and were not significantly different among treatments ($P > 0.05$; Wilcoxon rank sum).

The sampling schedule developed for the spring of 2007 was followed in the spring of 2008 because antecedent moisture conditions prior to the spring of 2008 (described above) were opposite those in the spring of 2007 and provided a natural, experimental comparison (Figure 5). Sulfate concentrations were again near 2 mg L^{-1} in snowmelt water pooled on the frozen peat surface in all three treatments. However, in 2008 sulfate concentrations remained nearly identical among treatments over the entire sampling period and declined steadily over the thaw period to near-detection limits just prior to the spring 2008 sulfate addition. Despite much lower sulfate concentrations during the spring thaw period, MeHg concentrations
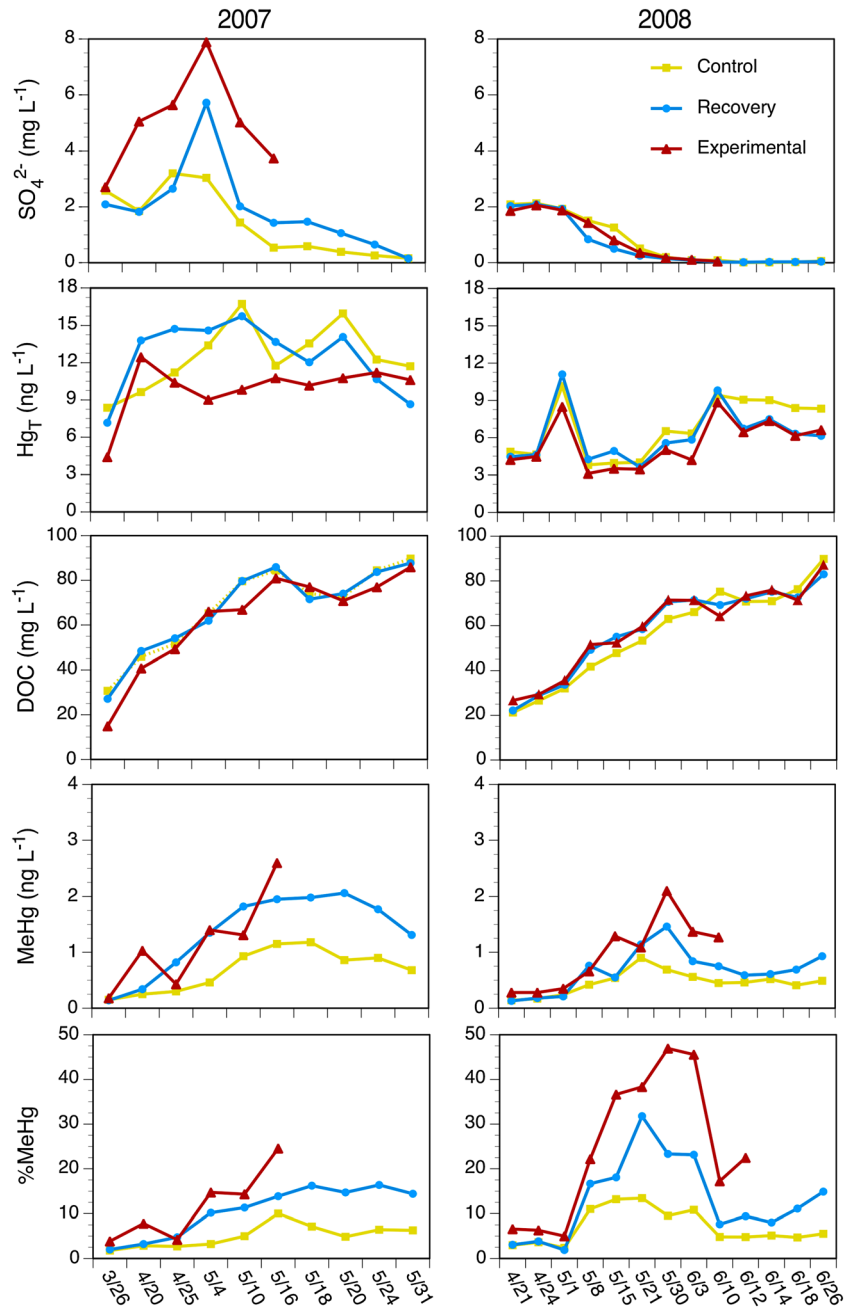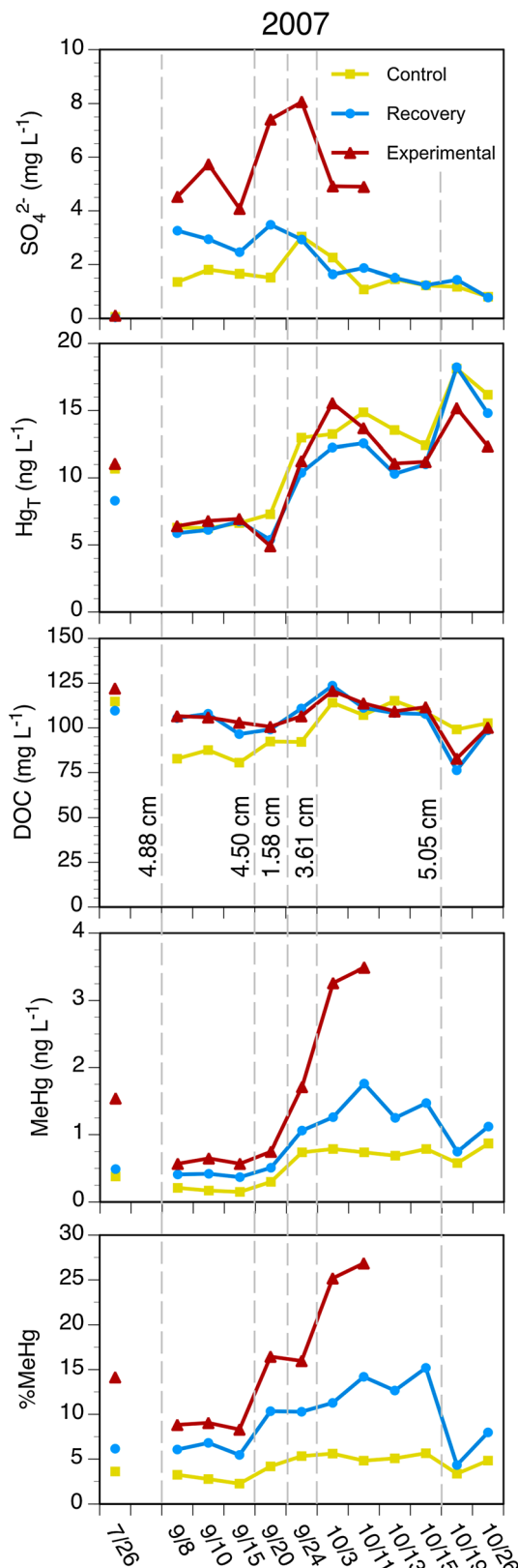
Figure 5. Pore water chemistries in each treatment of the S6 peatland over the spring-thaw and sulfate addition periods in 2007 and 2008. Only preaddition data are shown for sulfate, MeHg, and %MeHg levels in the experimental treatment.

followed a similar pattern to that observed in 2007 (Figure 5). Peak MeHg concentrations were somewhat lower than those seen in 2007 (0.90 ± 0.80, 1.46 ± 1.51, and 2.10 ± 0.72 ng L^{-1} in the control, recovery, and experimental treatments, respectively), but %MeHg levels appeared to be higher in 2008 (13 ± 8, 32 ± 6, and $47 \pm 22\%$ in the control, recovery, and experimental treatments, respectively), and the difference between the control treatment and the recovery and experimental treatments was more pronounced than in 2007 (Figure 5). Hg$_T$ concentrations were generally lower than in 2007; again, there were no significant differences in Hg$_T$ concentrations among treatments ($P > 0.05$; Wilcoxon rank sum). Dissolved organic carbon concentrations rose steadily again over the entire 2008 spring thaw period and were not significantly different among treatments ($P > 0.05$; Wilcoxon rank sum).

2007

Figure 6. Pore water chemistries in each treatment of the S6 peatland over the fall water table rise in 2007. Only preaddition data are shown for sulfate, MeHg concentrations, and %MeHg levels in the experimental treatment. Major rainfall events are indicated by dashed lines and depths (cm).

3.2.2.2. Fall Water Table Rise

In September 2007 a series of large rainfall events drove a relatively rapid water table rise and relieved the severe summer drought. As was seen during the rewetting event in the spring of 2007, sulfate concentrations rose significantly from late July values as the peat resaturated (Figure 6; $P < 0.05$; Wilcoxon rank sum), and significant differences existed in peak sulfate concentrations among the treatments ($P < 0.05$; Wilcoxon rank sum; 3.04 ± 3.58 mg SO_4^{2-} L^{-1}, 3.48 ± 2.58 mg SO_4^{2-} L^{-1}, and 8.06 ± 4.86 mg SO_4^{2-} L^{-1}, in the control, recovery, and experimental treatments, respectively). In early September following the first rainfall event, average MeHg concentrations, and %MeHg in the control and recovery treatments were comparable with late July values (Figure 6), while in the experimental treatment MeHg concentrations were significantly lower ($P < 0.05$; Wilcoxon rank sum). Subsequently and over the course of three additional rain events, MeHg concentrations and %MeHg rose significantly ($P < 0.05$; Wilcoxon rank sum), reaching peak levels by early October (control = 0.87 ± 0.63 ng MeHg L^{-1} and $6 \pm 4\%$ MeHg; recovery = 1.76 ± 0.90 ng MeHg L^{-1} and $15 \pm 6\%$ MeHg; experimental 3.49 ± 1.69 ng MeHg L^{-1} and $27 \pm 15\%$ MeHg). Hg_T concentrations were also significantly lower in early September relative to late July ($P < 0.05$; Wilcoxon rank sum), then rose significantly by late September ($10–13$ ng L^{-1}; $P < 0.05$; Wilcoxon rank sum) and were similar among treatments throughout the entire water table rise. Fall DOC concentrations were comparable to late July levels and remained relatively constant over the entire monitoring period.

3.3. Experimental Water Table Manipulation

A series of water table mesocosms was used to experimentally simulate a water table rise after a period of low WTE in mid-July 2007. Hg_T, MeHg, sulfate, and DOC concentrations in pore waters were measured 1 day prior to the experimental WTE rise and for up to 2 weeks thereafter. The effects of the water table experiments varied by
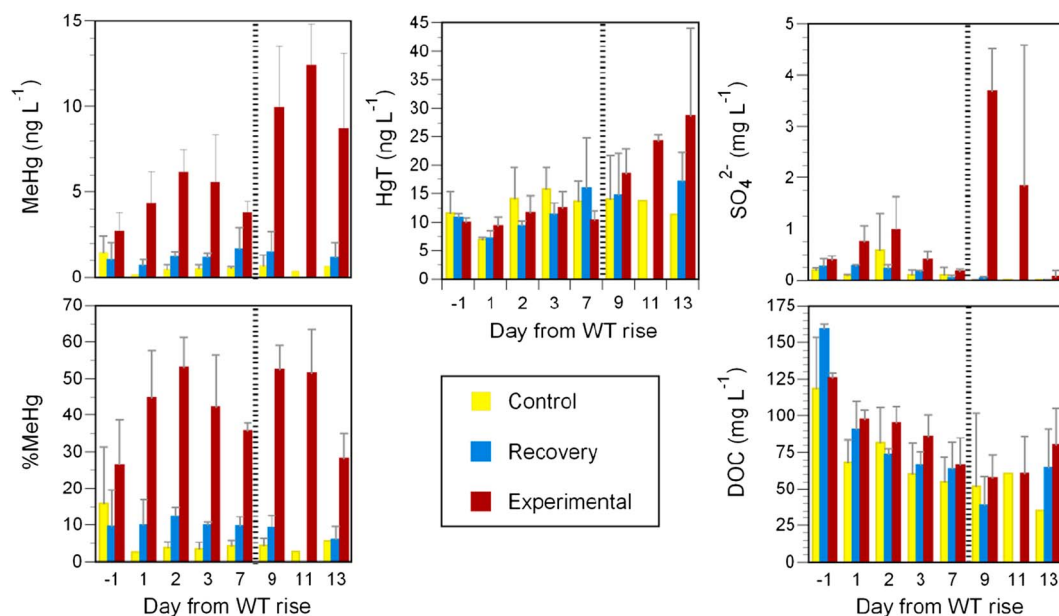
Figure 7. Pore water chemistries in the water table mesocosms in each treatment. The dashed lines indicate experimental sulfate additions to the experimental treatment.

treatment and by chemical constituent (Figure 7). In the control and recovery treatments the water table rise did not have a significant effect on any of the chemical constituents measured ($P > 0.05$; Kruskal-Wallis), whereas in the experimental treatment the water table rise significantly affected all measured constituents ($P \leq 0.05$; Kruskal-Wallis). Hg_T concentrations rose over the duration of the experiment while DOC concentrations fell. Sulfate, MeHg, and %MeHg each peaked 2 days after the water table rise and then declined until day 8. Because summer sulfate additions in 2005 (Figure 4) and 2006 did not cause any measurable changes to sulfate or mercury in experimental treatment pore waters, the experimental treatment water table mesocosms were also used to determine whether sulfate applied during high WTE in the summer would cause similar MeHg responses to those measured during the spring. Sulfate was applied to the water table mesocosms in the experimental treatment 1 week following the WTE manipulation. In contrast to trends observed during the summer sulfate additions in 2005–2007, sulfate concentrations peaked in the experimental treatment mesocosms 1 day following the sulfate addition (day 9 after the water table rise), while MeHg and %MeHg peaked 3 days after sulfate addition (day 11).

4. Discussion

4.1. Sulfate Release After Drought

4.1.1. Sulfate and Antecedent Moisture Conditions

The sulfate concentrations measured in S6 pore waters were similar to those reported for other boreal peatlands [*Mitchell et al.*, 2008a; *St. Louis et al.*, 1994] as well as for peatland mesocosms experimentally amended with sulfate [*Bergman et al.*, 2012; *Branfireun et al.*, 1999]. However, the sulfate concentrations in this study tended to be much lower than those measured in areas that are currently, or were historically, impacted by high levels of atmospheric sulfate deposition, such as the northeastern United States [*Mitchell and Likens*, 2011; *Selvendiran et al.*, 2008] and eastern Canada [*Eimers and Dillon*, 2002; *Eimers et al.*, 2007; *Warren et al.*, 2001]. Sulfate concentrations in S6 pore waters rose following each extended dry period in this 8 year study, which is consistent with observations in other peatland, temperate wetland, and stream systems [*Bayley et al.*, 1986; *Bayley et al.*, 1992; *Devito and Hill*, 1999; *Eimers and Dillon*, 2002; *Eimers et al.*, 2007; *Kerr et al.*, 2012; *Mitchell and Likens*, 2011; *Warren et al.*, 2001].

In this study the average sulfate concentration for each sampling date (excluding experimental treatment values immediately following sulfate addition) appeared to be inversely related to antecedent moisture

Table 2. Regression Statistics for the Sulfate Concentrations in the Control, Recovery, and Experimental Treatments Against the Maximum Change in WTE (ΔWTE) Over the Preceding 10, 20, 30, 60, and 90 Day Periods and the Duration of That Change (Δt)[a]

Treatment	Preceding Period	Max ΔWTE Coefficient	Max Δt Coefficient	Max ΔWTE* Max Δt Coefficient	Model RSE (d.f.)	r^2	F Statistic P value
Control	10 day	17.29	0.20	−0.83	2.28 (113)	0.09	0.01
	20 day	28.57***	0.16***	−1.43***	2.15 (113)	0.19	<0.01
	30 day	7.99*	0.04	−0.19	2.31 (113)	0.06	0.07
	60 day	5.71*	0.08***	0.003	2.03 (113)	0.28	<0.01
	90 day	2.74	0.05***	0.007	2.18 (113)	0.16	<0.01
Recovery	10 day	10.81	0.09	−0.61	1.59 (51)	0.10	0.14
	20 day	12.03	0.08	−0.41	1.54 (51)	0.17	0.02
	30 day	8.88	0.04	−0.18	1.49 (51)	0.22	<0.01
	60 day	2.51	0.03	0.03	1.40 (51)	0.32	<0.01
	90 day	−8.37*	0.004	0.15**	1.57 (51)	0.14	0.05
Experimental	10 day	21.72*	0.10	−2.02	1.87 (44)	0.20	0.02
	20 day	19.26*	0.11	−0.83	1.87 (44)	0.20	0.02
	30 day	5.87	0.01	−0.06	1.93 (44)	0.15	0.07
	60 day	3.95	0.06*	0.01	1.79 (44)	0.27	<0.01
	90 day	4.09	0.08***	−0.01	1.63 (44)	0.40	<0.01

[a]Multiple regression equation: $\log [SO_4^{2-}] = \max \Delta WTE * \max \Delta t + b + \varepsilon$. Significance codes.
***$Pr(>|t|) < 0.001$.
**$Pr(>|t|) < 0.01$.
*$Pr(>|t|) < 0.05$.

conditions. Pore water sulfate concentrations were lowest when the water table had been high over the preceding time period and were highest when the water table had been low (Figure S1 in the supporting information). Furthermore, the relationship between pore water sulfate and changes in WTE became stronger with greater amplitude of fluctuation and increasing length of the drawdown period as indicated by the higher r^2 and lower P values for the 60 and 90 day WTE regressions as compared to the 10 day WTE regressions (Table 2). Longer drought appears to result in greater mineralization of the peat. The increasing strength of the relationship between sulfate concentrations and the length of the drawdown period is not surprising given that other studies have found that the sulfate that appears during a rewetting event comes from the oxidation of organic sulfur compounds stored in the peat [*Eimers et al.*, 2003; *Mandernack et al.*, 2000; *Mörth et al.*, 1999]. Isotopic studies of sulfur cycling in peat have found that sulfate added to peatland mesocosms is predominantly incorporated into the organic-sulfur fraction of the peat matrix through bacterial sulfate reduction and plant uptake [*Bartlett et al.*, 2009; *Chapman and Davidson*, 2001] and that the sulfate released during rewetting events has a light isotopic signature relative to atmospheric deposition, suggesting reoxidation of sulfur from the "lighter" carbon-bound sulfur pool [*Mandernack et al.*, 2000; *Mörth et al.*, 1999].

The precipitation-driven hydrology of the S6 peatland allowed water tables to decline as much as 50 cm in particularly dry years, causing desiccation and oxidation of deep peat layers that normally experience strongly reducing conditions (Figure 3). Dramatic hydrologic fluctuations coupled with the high organic content of the peat make it likely that the sulfate released during rewetting events in this peatland comes from the carbon-bound sulfur pool. Furthermore, inorganic sulfur concentrations were low across the peatland (3 ± 2%), making readily oxidized sulfur compounds like acid-volatile sulfides an unlikely source of recycled sulfate.

4.1.2. Sulfate Release After Elevated Sulfate Deposition

For any given drying event more sulfate was mobilized into pore waters in the experimental treatment than in either the control or recovery treatments. Following rewetting events in the spring and fall of 2007, sulfate concentrations in experimental-treatment pore waters were more than twice that in the control treatment, while sulfate concentrations in the recovery treatment were intermediate between the control and experimental treatments (Figures 5 and 6). Because sulfate disappeared from pore waters following sulfate additions and rewetting events, and because no significant differences were found in the solid total-sulfur pool among the treatments [*Coleman Wasik et al.*, 2012], it appears that a greater fraction of the organic sulfur pool was available for release in peat that had recently experienced elevated sulfate loading. Furthermore, the

finding that sulfate release was greater in the recovery treatment than in the control treatment 2 years after sulfate additions had ended indicates that this more labile organic sulfur pool persisted for some time after elevated sulfate deposition had ceased. These observations provide support for our previous hypothesis [*Coleman Wasik et al.*, 2012] that newly added sulfate gradually becomes incorporated into more recalcitrant forms of organic sulfur over time.

The water table mesocosm experiments confirmed both the differential remobilization of sulfate among treatments and the importance of the duration of WTE drawdown and peat oxidation. Mesocosms in the experimental treatment experienced a significant increase in sulfate concentrations following the water table manipulation (increased WTE). No such sulfate rise was detected in the control or recovery treatments, and the rise that did occur in the experimental treatment was much lower than that observed following the 2006 and 2007 droughts. Average peak sulfate concentrations in the experimental treatment following each drought were roughly $8 \, mg \, L^{-1}$ as compared to $1.0 \, mg \, L^{-1}$ in experimental-treatment mesocosms following the WTE manipulation. The muted release in the mesocosms was likely a result of the short oxidation period experienced by the peat prior to mesocosm installation. The peat was not as desiccated as it had been during the 2006 and 2007 droughts—only the top 10–15 cm of peat experienced oxidizing conditions for approximately 3–4 weeks. Shorter-duration drawdowns likely affect loosely bound sulfate and labile organic sulfur compounds, whereas during extended droughts microbial communities and physical processes may begin to break down more recalcitrant pools of organic sulfur leading to greater sulfate remobilization.

The finding that sulfate is remobilized from wetlands following drought is not unique to this study. However, most previous research has involved ecosystems that were experiencing concurrent changes in ambient sulfate deposition and regional hydrology (drought cycles). The experimental design of the study presented here elucidates the additive effect of past and current sulfate deposition levels on the naturally occurring release of sulfate caused by drought cycles and provides insight into the mechanisms whereby sulfate release from historically impacted peatlands may decline.

4.2. Effect of Drought on Mercury Cycling

4.2.1. Total Mercury

Total mercury (Hg_T) concentrations in S6 pore waters averaged between 3 and $12 \, ng \, L^{-1}$ during most sampling periods, which is similar to values reported for other peatlands [*Heyes et al.*, 2000; *Mitchell et al.*, 2008a; *Regnell and Hammar*, 2004; *Selvendiran et al.*, 2008]. However, during the fall of 2005 and the spring and fall of 2007, average Hg_T concentrations in pore waters jumped to $12–20 \, ng \, L^{-1}$ (Figures 4–6). These three sampling periods coincided with rewetting events in S6, likely indicating oxidative release of Hg_T from peat. The spring of 2007 and 2008 present a natural experimental contrast between dry and wet antecedent moisture conditions and its effect on Hg_T release. Over the entire spring thaw period in 2007 (26 March to 16 May) average Hg_T concentrations were 109–142% higher than the hydrologically similar period in 2008 (21 April to 30 May). It is interesting to note that Hg_T and sulfate release were very different following water table rise in the fall of 2007. Whereas sulfate concentrations 2 days after the initial fall water table rise were an order of magnitude higher than they had been on the last sampling day of the summer addition, Hg_T concentrations were 20–50% lower than they had been on the last sampling day of the summer addition. Furthermore, Hg_T concentrations remained stable for more than a week after the first major rain event that initiated the water table rise. Once Hg_T concentrations did start to rise, they more than tripled over the following 4 weeks. These observations suggest that peatlands have the potential to become large, short-term sources of mercury to downstream systems if mercury binding within the peat is disrupted by drought-induced oxidation.

The observed Hg_T releases were not necessarily controlled by DOC mobility. Given the close association between mercury and organic matter [*Dittman and Driscoll*, 2009; *Driscoll et al.*, 1995; *Kolka et al.*, 2001], it might be expected that the amount of Hg_T released would remain stable relative to DOC during peat oxidation and resaturation following a drought. However, we found that Hg_T concentrations in pore waters were substantially elevated relative to DOC 1 month following rewetting events in the fall of 2005 and 2007, indicating that short-term release of Hg_T following drought is more pronounced than for DOC (Figure S2 in the supporting information). Furthermore, whereas pore water Hg_T concentrations in the early spring of 2007 were 2–3X those measured in the early spring of 2008, the trend in DOC concentrations was consistent from year to year, rising slowly from $\sim20 \, mg \, L^{-1}$ to $\sim80 \, mg \, L^{-1}$ over the 2 month period following snowmelt.

The finding that Hg_T concentrations can vary independently of DOC concentrations in peatland pore waters warrants further investigation in light of the proposed use of continuous, in situ DOC measurements as a proximal indicator of mercury export from watersheds [*Dittman et al.*, 2009; *Burns et al.*, 2013].

Sulfate additions did not appear to affect pore water or solid-phase Hg_T concentrations during wet or dry periods, contrary to observations of *Åkerblom et al.* [2013], who found that long-term sulfate addition ($10–20\,kg\,ha^{-1}\,yr^{-1}$ for 14 years) to peatland mesocosms caused declines in solid phase Hg_T. In our study the inventory of Hg_T in the top 8 cm of peat in the experimental treatment was generally lower than that in the control treatment each year (with the exception of 2005), although the differences were not significant, nor was there a trend in the experimental treatment over the course of the 8 year study [*Coleman Wasik et al.*, 2012]. Sulfate addition might have been expected to mobilize mercury from the peat if that mercury was released from the carbon utilized by bacterial communities or if sulfides generated by the activity of sulfate-reducing bacteria (SRB) caused mercury to be stripped from the solid phase [*Skyllberg*, 2008]. There was no evidence of this, as Hg_T concentrations in the control treatment pore waters were generally higher than those in the experimental and recovery treatments on a given sampling day, and there was no systematic trend in pore water Hg_T in the recovery treatment that would otherwise indicate a lingering effect of previous sulfate additions. Perhaps no effect was observed because the large pool of mercury present on the solid phase was a more important control on pore water Hg_T concentrations than the enhancement of microbial activity due to sulfate addition [*Coleman Wasik et al.*, 2012].

4.2.2. Methylmercury

MeHg concentrations and %MeHg observed in this study ($0.1–4.0\,ng\,L^{-1}$ and 2–50%, respectively) fall within the ranges reported in other boreal peatland studies [*Bergman et al.*, 2012; *Branfireun et al.*, 1999; *Heyes et al.*, 2000; *Mitchell et al.*, 2008a]. The MeHg present in peatland pore waters can come either from physical release (desorption) from the solid phase (where >99% of MeHg is found) or from net methylation. To support the elevated SRB-mediated production of MeHg observed in this system, sources of carbon, sulfate, and inorganic mercury must be available to microbes [*Benoit et al.*, 2002]. Because MeHg and the substrates required for SRB-mediated mercury methylation can all be released from the solid phase through peat oxidation, it is difficult to know whether simple oxidation or sulfate-stimulated methylation is more important in controlling MeHg flux from wetlands following drought. In this study both mechanisms (release and production) were observed to occur.

As described above, sulfate concentrations rose dramatically in all treatments in the spring of 2007 as the S6 peatland resaturated after a 9 month drought. Given that spring sulfate additions during the entire 8 year study consistently induced large methylation events in the experimental treatment [*Coleman Wasik et al.*, 2012; *Jeremiason et al.*, 2006], we expected that this large drought-induced pulse of sulfate in peatland pore waters would have a similar effect on MeHg production across treatments. Indeed, average pore water MeHg concentrations were significantly higher (29%, 146%, and 80% in the control, recovery, and experimental treatments, respectively; $P < 0.01$; Kruskal-Wallis) during the snowmelt period in 2007 (26 March to 25 April) than in the hydrologically similar period in 2008 (21 April to 1 May). On the other hand, %MeHg levels during snowmelt were statistically the same between the 2 years ($P = 0.54$; Kruskal-Wallis), suggesting that release of MeHg (and Hg_T) from the solid phase occurred as the peat was resaturated following drought. However, as sulfate concentrations began to decline, MeHg concentrations and %MeHg levels rose further, while Hg_T concentrations remained relatively stable, likely indicating new MeHg production as a result of SRB activity. The same trend was observed when the WTE was manipulated in the water table mesocosm experiments providing further confirmation that a pulse of sulfate to pore waters during rewetting events can stimulate mercury methylation (Figure 7).

Despite significantly higher MeHg concentrations in the spring of 2007 as compared with 2008 ($P < 0.01$; Kruskal-Wallis), %MeHg levels in 2007 were significantly lower than in 2008 ($P < 0.005$; Kruskal-Wallis). That is, a larger fraction of pore water Hg_T was methylated in 2008 relative to 2007. This difference may be a function of the stable hydrologic conditions (consistently high WTE) present during the spring of 2008 as opposed to the spring of 2007 (initially low WTE). Because SRB activity requires anoxia, sulfate reduction and Hg methylation may have been inhibited for a period of time in 2007 by elevated oxygen in the peat profile. This idea is supported by the observation that sulfate concentrations continued to increase beyond the initial mercury release in late April of 2007. It is less likely that this delayed effect was a result of temperature

because in each spring sulfate concentrations began to decline well before the peat had thawed completely (Coleman Wasik, St. Croix Watershed Research Station, unpublished data, 2008).

The fall rewetting event in 2007 provided further confirmation that drought can cause not only MeHg release but also stimulate MeHg production. The largest rise in Hg_T concentrations occurred between 20 September and 24 September, and thereafter Hg_T concentrations stabilized. On the other hand, MeHg concentrations and %MeHg levels in the recovery and experimental treatments continued to increase beyond 24 September coincident with declining sulfate concentrations. These sustained increases likely represent new MeHg production caused by the drought-induced sulfate pulse.

This study allowed us to observe the effect of different atmospheric sulfate deposition rates on MeHg release and production in the context of hydrologic variability. More MeHg was produced and released in experimental and recovery treatments than in the control treatment following each drought. We previously reported [*Coleman Wasik et al.*, 2012] much higher MeHg concentrations in the solid phase within the experimental and recovery treatments relative to the control treatment and suggest here that a larger pool of MeHg is available for drought-induced release in peat that has experienced elevated rates of sulfate deposition. Furthermore, because the organic sulfur pool formed from recent sulfate deposition is more susceptible to oxidation and mobilization following drought, the potential exists for greater MeHg production from the activity of SRB as peat is resaturated. Finally, it appears that recent exposure to elevated sulfate deposition may have "primed" SRB communities in the experimental and recovery treatments because of either changes in the bacterial community itself or changes in their geochemical environment. In the spring of 2008 sulfate concentrations in peatland pore waters were the same among treatments after snowmelt and over the entire spring thaw period. However, MeHg concentrations and %MeHg levels increased to a much greater degree in experimental and recovery treatments relative to the control treatment. The observation that greater methylation ensued in treatments exposed to elevated rates of sulfate deposition—despite having, for a period of time, similar concentrations of pore water sulfate—may indicate that the bacterial community in treated peat was more able to efficiently reduce added sulfate and as a result methylate more mercury.

5. Conclusions

This study provides important insights on the effects of drought and subsequent water table fluctuations on sulfur and mercury cycling in a boreal peatland. Because two severe droughts occurred during the course of an experimental manipulation of atmospheric sulfate deposition, we were able to examine the in situ interaction of hydrologic fluctuations with varying sulfate loads on sulfur and mercury biogeochemistry. Sulfate concentrations in peatland pore waters were a function of antecedent moisture conditions in combination with experimental manipulations. Because the sulfate that reappeared in pore waters during rewetting events likely came from the large pool of organic sulfur in the peatland, prolonged water table drawdowns lead to greater sulfate release in all treatments. However, sulfate mobilization was highest and most responsive to drying conditions in the experimental treatment where recently added sulfate had become incorporated into the organic sulfur pool, yet was still relatively labile compared with organic sulfur in the control treatment.

The effect of antecedent moisture conditions on mercury biogeochemistry was more complicated. Although Hg_T concentrations increased significantly in peatland pore waters during rewetting events following drought, Hg_T release was not always immediate. Despite the common finding that peatlands are sinks for Hg_T in the landscape, the large release of mercury from the peat following drought provides evidence that peatlands can also be short-term sources of inorganic mercury to downstream aquatic systems under these specific hydrologic conditions.

In contrast, wetlands are well-known sources of MeHg to downstream aquatic systems [*Babiarz et al.*, 1998; *Bushey et al.*, 2008; *St. Louis et al.*, 1994], and sulfate stimulation of in situ methylation has almost certainly contributed to the flux of MeHg from the S6 peatland [*Jeremiason et al.*, 2006]. Based on findings from the full 8 years of sulfate addition [*Coleman Wasik et al.*, 2012], it was expected that the high pore water sulfate observed following the 2006 and 2007 droughts would significantly stimulate mercury methylation in peatland pore waters. Although there was evidence of increased MeHg production as the drought-induced sulfate was consumed, our results also demonstrate the potential for drought to further elevate MeHg flux from peatlands because of oxidation and desorption of MeHg from the solid phase.

This study was equally revealing regarding the effects of elevated sulfate deposition on mercury biogeochemistry beyond stimulation of mercury methylation. Although mercury export from the S6 peatland was not examined in this study, peatland pore waters represent an important component of outflow from this system under the right hydrological conditions [*Mitchell et al.*, 2008b]. In our experimental treatment, sulfate release following drought was greater than that in the control treatment. Not only was that sulfate then available to drive SRB activity and Hg methylation but it was also available for export to downstream aquatic systems (e.g., lakes and other wetlands) that could be equally susceptible to in situ net methylation. Drought-induced MeHg release in the experimental treatment was also greater relative to the control treatment during rewetting events because a larger pool of MeHg had built up in the solid phase of the experimental treatment as a result of chronically elevated sulfate loading [*Coleman Wasik et al.*, 2012]. This observation implies the potential for greater MeHg export from sulfate-impacted peatlands to downstream aquatic systems relative to unimpacted peatlands. Finally, the observation in the spring of 2008 that net methylation (as inferred from changes in % MeHg) was greater in the experimental treatment relative to the control—despite similar concentrations of pore water sulfate—indicates that chronically elevated sulfate deposition had increased the methylation efficiency of the SRB community. The cumulative effect of elevated sulfate deposition to peatlands is to create more effective conditions for methylation and stronger sources of MeHg within a landscape. Furthermore, the fact that changes in sulfate, MeHg, and %MeHg in recovery-treatment pore waters were always intermediate between those in the control and experimental treatments demonstrates that the effect of elevated sulfate deposition on peatlands persists for some period of time after sulfate deposition has declined.

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