Gaseous mercury fluxes in peatlands and the potential influence of climate change

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HIGHLIGHTS

• Measured total gaseous mercury fluxes in peatlands simulating climate change impacts.
• Strongest depositional trend with lower water table and sedge-dominated cover.
• Surface sorption and stomatal uptake of mercury stronger in shrub than sedge foliage.
• Marginal influence of 2 m deep peat warming on peatland gaseous mercury flux.

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ABSTRACT

Climate change has the potential to significantly impact the stability of large stocks of mercury (Hg) stored in peatland systems due to increasing temperatures, altered water table regimes and subsequent shifts in vascular plant communities. However, the Hg exchange dynamics between the atmosphere and peatlands are not well understood. At the PEATcosm Mesocosm Facility in Houghton, Michigan, total gaseous Hg (TGM) fluxes were monitored in a subset of 1-m³ peat monoliths with altered water table positions (high and low) and vascular plant functional groups (sedge only, Ericaceae only or unmanipulated control) above the Sphagnum moss layer. At the SPRUCE bog in north-central Minnesota, TGM fluxes were measured from plots subjected to deep peat soil warming (up to +9 °C above ambient at a depth of 2 m). At PEATcosm, the strongest depositional trend was observed with the Low WT e sedge only treatment mesocosms with a mean TGM flux of $-73.7 \pm 6.3$ ng m⁻² d⁻¹, likely due to shuttling of Hg to the peat at depth by aerenchymous tissues. The highest total leaf surface and tissue Hg concentrations were observed with the Ericaceae shrubs. A negative correlation between TGM flux and Ericaceae total leaf surface area suggests an influence of shrubs in controlling Hg exchange through stomatal uptake, surface sorption and potentially, peat shading. Surface peat total Hg concentrations are highest in treatments with greatest deposition suggesting deposition controls Hg accumulation in surface peat. Fluxes in the SPRUCE plots ranged from $-45.9 \pm 93.8$ ng m⁻² d⁻¹ prior to the implementation of the deep warming treatments to $-1.41 \pm 27.1$ ng m⁻² d⁻¹ once warming targets were achieved at depth.

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1. Introduction

In addition to natural sources such as volcanic emissions, anthropogenic sources including coal burning, gold mining, and waste incineration have contributed to significantly increase mercury (Hg) in global terrestrial, atmospheric pools (Selin, 2009). Atmospheric deposition via either wet or dry processes represents the dominant input of Hg to the Earth’s surface (Fitzgerald et al., 1998; Driscoll et al., 2007). Wetlands are particularly important sinks of atmospherically-deposited Hg in the landscape (Wallschläger et al., 2000; Zilliioux et al., 1993). Following deposition, Hg is subjected to numerous hydrological and biogeochemical influences, which might either incorporate it into soil and vegetation stocks (Hintelmann et al., 2002), or lead to its release from soil, water and/or vegetation back to the atmosphere following reduction to its elemental form, Hg(0) (Poissant et al., 2004a). Total gaseous mercury (including all forms of gaseous Hg, the majority of which is typically Hg(0)) fluxes have been monitored in freshwater wetlands (Poissant et al., 2004a, b; Zhang et al., 2006; Lindberg and Zhang, 2000; Marsik et al., 2005). However, only a few more recent studies have focused on soil-air exchange dynamics in boreal peatlands (Kyllönen et al., 2012; Fritsche et al., 2014; Osteroth et al., 2016) despite the large amounts of Hg stored in these systems (Grigal, 2003).

Peatlands are immense stores of organic matter in the landscape (Gorham, 1991) and may represent a significant source of Hg to the atmosphere (Grigal, 2003). Climate change has the potential to significantly impact the hydrology, biogeochemistry and ecology of peatland ecosystems due to increasing temperatures and changes in precipitation patterns (Kunkel et al., 2003; Groisman et al., 2005; Bridgham et al., 2008). Enhanced variability in precipitation, with less frequent and more intense events anticipated across the northern continental United States (Kunkel et al., 2003; Groisman et al., 2005), may have direct impacts on the hydrology of peatlands with the potential for prolonged periods of water table recession and greater variability throughout the summer months (Thomson et al., 2005; Whittington and Price, 2006). Subsequent changes in the dominant vascular plant functional groups may occur as a result of prolonged dry periods and warming temperatures in peatlands (Weltzin et al., 2003; Strack et al., 2006; Breuwer et al., 2009; Dieleman et al., 2015). Due to their ability to reach deeper water stores, regulate water loss through stomata and oxygenate the rooting zone by shuttling oxygen via aerenchymous tissue, sedges may have a competitive advantage over shrub vegetation and Sphagnum mosses during periods of water stress (Dieleman et al., 2015). However, several studies (i.e. Weltzin et al., 2000; Breuwer et al., 2009) including the PEATcosm mesocosm experiment (Potvin et al., 2015) have observed a shift towards increasing Ericaceae shrub abundance and productivity under drier conditions. Therefore, plant communities in both bogs and fens are likely to change with the increasing temperatures and enhanced water stress resulting from climate change, although the direction of this change is not clear (Weltzin et al., 2003). Changes in plant community composition in concert with alterations to the hydrology and redox condition of the peat may have profound effects on peat decomposition and therefore the carbon storage abilities of peatlands (Waddington et al., 2015). Given the strong relationship between Hg and organic matter, the potential changes in water table recession and variability, dominant vascular plant communities, peat mineralization and shifting carbon balances resulting from hydrological, ecological and biogeochemical changes may affect the dynamic exchange of total gaseous Hg (TGM) fluxes between the peat and the atmosphere.

Total gaseous Hg exchange with background soils is often well correlated with meteorological variables (Gustin et al., 2006; Lin et al., 2010). Air and soil temperatures are important thermodynamic controls on Hg reduction and emission from soils (Edwards et al., 2001), as is solar radiation because of the importance of photoreduction processes in controlling Hg emissions (Moore and Carpi, 2005). These factors act to influence Hg emissions by effectively lowering the activation energy required for Hg reduction (Carpi and Lindberg, 1998). Changes in soil moisture significantly impact Hg fluxes from mineral soils (Gustin and Stamenskovic, 2005; Song and Van Heyst, 2005). Wetting of the soil surface by precipitation increases Hg emissions from initially dry soils, with spikes in fluxes following the rain event and decreasing fluxes as the soil dries (Gustin and Stamenskovic, 2005; Mazur et al., 2015). The mechanisms governing this increase with wetting may involve desorption of Hg from the soil particles and subsequent displacement of the Hg from the soil pores. However, emissions from saturated soils are often suppressed, potentially due to the slow diffusion of Hg(0) through water (Bahlmann et al., 2004; Gustin and Stamenskovic, 2005; Song and Van Heyst, 2005). Enhanced evaporation coincident with increasing atmospheric temperatures may also affect the dynamic exchange of Hg by transporting Hg to the soil surface via capillary action (Briggs and Gustin, 2013). Therefore, altered water table position and variability in precipitation patterns may have a direct impact on seasonal Hg emission and deposition patterns in peatlands resulting from changes in soil moisture and redox conditions. Assuming similar mechanisms to those observed in mineral soils (Bahlmann et al., 2004; Gustin and Stamenskovic, 2005; Song and Van Heyst, 2005), episodic re-wetting of the peat following prolonged water table drawdown may enhance TGM fluxes from peatlands. Once saturated however, significant emission of Hg to the atmosphere may be inhibited. Periods of wetting may provide the necessary redox conditions to promote Hg(II) reduction (Moore and Castro, 2012) to Hg(0) and subsequent release from the peat. Taken together, the direct and indirect influences of increasing temperatures and altered precipitation regimes on peatland TGM fluxes clearly warrant further investigation.

The shifting composition of the vascular plant community may also affect the exchange of Hg through stomata and the potential liberation of Hg from soil via the roots (Rea et al., 2002; Leonard et al., 1998a, b). Sedges with deep roots and aerenchymous tissues (Breuwer et al., 2009) may affect the magnitude and direction of TGM fluxes depending upon root depth and Hg concentrations within the soil profiles, as has been observed with other wetland
vegetation (Lindberg et al., 2005). Lindberg et al. (2005) determined that the source of TGM emissions from aquatic macrophytes was the rhizosphere. However, translocation of Hg between the roots and the foliage of forest canopies is minimal (Ericksen et al., 2003). Although several studies of soil-air Hg dynamics have been conducted over bare soil (e.g. Carpi and Lindberg, 1997; Poissant et al., 2004b; Miller et al., 2011), vegetation in both forests and wetland systems plays an important role in controlling the exchange of Hg with the atmosphere via both stomatal and non-stomatal pathways including leaf surface sorption (Lee et al., 2000; Rea et al., 2002; Ericksen et al., 2003; Marsik et al., 2005; Stamenkovic and Gustin, 2009; Laacouri et al., 2013). Evaporation of morning dew from the surface of vegetation has also been identified as a potential source of Hg to the atmosphere (Marsik et al., 2005). Stomatal exchange was observed to be an instrumental process governing net TGM emission from the canopy of a mixed sawgrass-cattail wetland in the Everglades as Hg emission coincident with stomatal uptake of carbon dioxide (Marsik et al., 2005). The manner in which climate change-induced shifts in vascular plant community composition affects the direction and magnitude of TGM fluxes between peatlands and the atmosphere remains unclear and therefore requires further study.

The overall objective of the PEATcosm study was to characterize diurnal TGM fluxes in peatlands and to investigate impacts on TGM fluxes due to changes in vascular plant community composition, water table position, and peat warming, using two field-scale peatland climate change simulation experiments. Diurnal fluxes were measured in a subset of the PEATcosm (Peatland Experiment at the Houghton Mesocosm Facility) peat monoliths, manipulated to simulate climate-induced changes in vascular plant functional groups and water table position and variability. To assess the potential effects of soil warming, TGM fluxes were also measured in the SPRUCE (Spruce and Peatland Responses Under Climatic and Environmental Change) experimental peatland prior to and throughout a large-scale manipulation of deep (2 m) peat temperatures. It was hypothesized that 1) peatland plant functional groups would differentially affect TGM fluxes due to differences in vascular structures 2) increased sedge cover would increase TGM deposition to peatlands due to incidental shuttling of Hg via aerenchymous tissue and 3) increased soil temperatures would enhance TGM fluxes from the peat to the atmosphere.

2. Methods

2.1. PEATcosm site description

The PEATcosm experiment was located at the United States Forest Service Houghton Mesocosm Facility, at the Forestry Sciences Laboratory in Houghton, Michigan, USA (47.11469°N, 88.54787°W). The regional climate is humid continental with typical annual precipitation of approximately 870 mm. Mean temperatures range from -13°C in January to +24°C in July (30 year means at Houghton County Airport; Potvin et al., 2015).

The Mesocosm Facility houses 24 intact 1 m³ (1 m x 1 m x 1 m) peat monoliths open to the air on top and inserted into a climate-controlled tunnel which allows belowground access to each of the bins and the simulation of natural peat temperature gradients with depth. The monoliths were harvested from an ombrotrophic peatland located in Meadowlands, MN, USA in May 2010 and transferred into individual Teflon-coated, stainless steel mesocosm bins, preventing metal transfer to the peat. Vegetation manipulations were initiated in 2011, and full water table manipulations were initiated in 2012. At the conclusion of the experiment in July 2015, the monoliths were destructively harvested. The full description of the PEATcosm experiment can be found in Potvin et al. (2015), including peat monolith harvest, facility details and experimental design.

The PEATcosm study comprises a full-factorial experimental design, with two water table (WT) prescriptions crossed with three different plant functional group treatments, simulating potential climate change outcomes. Each treatment combination is replicated across four mesocosms, in a randomized complete block design, for a total of 24 experimental units. The water table treatments were based on long-term (approximately 50 years) data from the Marcell Experimental Forest in north-central Minnesota (47.51907°N, 93.45966°W), located near the peat monolith harvest site. The two WT treatments were modelled after years with: 1) typical variability and average WT position (referred to as ‘High WT’) and 2) comparably high variability and low WT position (referred to as ‘Low WT’). These target WT profiles were maintained through a combination of artificial precipitation additions, rain-exclusion covers and regulated outflow from approximately the acrotelm-catotelm boundary during the snowmelt period from each of the bins (see Potvin et al., 2015 for details). The three plant functional group treatments, simulating likely community composition alterations resulting from climate change (Strack et al., 2006; Weltzin et al., 2000; Chapin et al., 1996), are as follows: 1) all Ericaceae removed (referred to as ‘sedge only’ treatment), 2) all sedge removed (‘Ericaceae only’ treatment) and 3) both sedge and Ericaceae present (‘unmanipulated control’ treatment). The dominant sedge species present in the bins was Carex oligosperma Michx., while the dominant Ericaceae shrubs included Chamaedaphne calyculata (L) Moench., Calamia polifolia Wangenh., and Vaccinium oxyccos L. The dominant moss species in the peat monoliths were Sphagnum rubellum Wilson, S. magellanicum Brid., S. fuscum (Schimp.) Klinggr and Polytrichum strictum Brid. Polytrichum commune Hedw., Eriophorum vaginatum L., Andromeda polifolia L. var. glaucophylla (Link) DC., Rhododendron groenlandicum (Oeder) Kron and Judd, and Drosera rotundifolia L. were also present in the mesocosms.

2.2. SPRUCE site description

The SPRUCE experimental peatland is an 8.1 ha ombrotrophic, spruce-Sphagnum bog (known locally as “S1”), located within the Marcell Experimental Forest (MEF) in north-central Minnesota (47.51907°N, 93.45966°W). Typical annual precipitation for the MEF is approximately 780 mm. Mean temperatures at the MEF range from -15°C in January to +19°C in July (Sebestyen et al., 2011). The overstory is dominated by two tree species: Picea mariana (Mill.) B.S.P. and Larix laricina (Du Roi) Koch. The understory consists primarily of Ericaceae shrubs including Chamaedaphne calyculata, Calamia polifolia, Vaccinium angustifolium Aiton, Vaccinium oxyzuccos, and Rhododendron groenlandicum as well as sedges Eriophorum spp. and the lily Maianthemum trifolium (L.) Sloboda. The dominant bryophyte present on hummocks is Sphagnum magellanicum, while hollows are mainly colonized by S. angustifolium (C.E.O. Jensen ex Russow).

The SPRUCE study (http://mspruce.ornl.gov/) is a climate change field experiment that will involve the long-term (10-year) manipulation of both soil and air temperature, and atmospheric carbon dioxide (CO₂) concentrations within open-top, approximately 12 m diameter, enclosures along three transects within the S1 bog. Prior to the full initiation of the SPRUCE experiment in 2016, an approximate one-year, deep (2 m below the peat surface) soil warming experiment was conducted from June 2014 through the end of July 2015. This study describes TGM fluxes before (May 2014), during (August 2014), and following prolonged deep peat warming (June 2015). The heating infrastructure utilized to warm the peat at depth within the experimental enclosures is similar to
that described in Hanson et al. (2011).

2.3. Experimental design and mercury flux measurements

Subsets of the total number of experimental treatments in each experiment were monitored for TGM flux using dynamic flux chambers (DFCs). Despite their limitations (Wallslager et al., 1999; Gillis and Miller, 2000), DFCs were the only appropriate method given the size and scale of the experimental mesocosms and plots. These measurements were taken over individual 24-h periods. This was necessary as similar meteorological conditions (i.e. no rain, with similar cloud cover and incoming solar radiation) could only be achieved within relatively short (4–6 days) time-frames. Similar ambient conditions were necessary to discern potential treatment effects. At PEATcosm, TGM fluxes were measured on a subset of 8 of the mesocosm bins in July 2014 at the peak of the growing season. Simultaneous measurements were taken on two mesocosms in each 24-h period. In all, duplicate mesocosms of the following experimental treatment pairings were monitored for TGM fluxes: High WT — control vegetation, Low WT — control vegetation, Low WT — Ericaceae only, and Low WT — sedges only. These treatments span the range of vascular plant functional group treatments with the Low WT prescription representing the greatest anticipated hydrological changes in peatlands due to climate change. The High WT — control vegetation treatment acts as the unmanipulated, control scenario. The duplicate mesocosms for each treatment were not measured during the same 24-h period. Mean water table positions during the flux measurement period were 37 ± 5 cm below the peat surface (mean ± standard deviation) for the Low WT treatments and 15 ± 0.1 cm below the peat surface for the High WT treatment.

At the SPRUCE site, TGM fluxes were measured in six experimental enclosures, focusing on duplicates of deep soil warming treatments with target temperature differentials of +0, +4.5 and +9°C above ambient soil temperatures at 2 m depth. These target differentials were achieved at 2 m depth within 60 days of the June 2014 initiation, but were not similarly observed nearer the surface. Due to the considerable distance between SPRUCE plots and equipment availability, two replicate locations within each experimental plot were measured simultaneously. Flux measurements at SPRUCE were performed in May 2014 prior to the initiation of the deep soil warming treatments, August 2014 once soil warming target temperatures were achieved at depth and June 2015 following prolonged deep soil warming. Due to an equipment malfunction, one +0 and one +4.5°C plot (Plots 4 and 6, respectively) could not be monitored in June 2015.

Ambient TGM fluxes were measured using two transparent Teflon DFCs (0.036 m² footprint, 6.5 cm height and 2.0 L volume with 1 cm diameter inlet holes every 2.5 cm around the perimeter and a 5 cm wide bottom flange as per Eckley et al., 2010) placed on the peat surface and connected to a Tekran 2537A Gaseous Mercury Analyzer. The DFCs were placed on hummock microtopographic forms within each plot and mesocosm. Standing vegetation was present beneath the footprint of each DFC. Weighted rings (clear plastic tubing filled with small ball bearings) were placed on the DFC bottom flange to ensure a tight seal to the peat surface. The sampling flow rate of the analyzer was 1.5 L min⁻¹. A soda lime trap was connected in the sampling inlet line just prior to introduction into the analyzer to prevent passivation of the gold traps by acid aerosols (Erickson et al., 2006; Miller et al., 2011). A four-port sampling manifold/switching unit (Tekran 1115 Synchronized Multi-Port Sampling System) connected to the analyzer facilitated the alternation of air accumulation among four Teflon lines, an inlet and outlet for each of the two DFCs, each fitted with a 0.2 μm disposable particulate syringe filter (PTFE-membrane in a polypropylene housing, Cole-Parmer). The manifold allowed nearly simultaneous duplication of measurements (Carpi and Lindberg, 1997). One complete flux measurement for one DFC was achieved every 20 min. Fluxes were calculated using the equation:

\[ F = \frac{Q}{A} \frac{(C_o - C_i)}{A} \]

where \( F \) is the total flux (ng m⁻² h⁻¹), \( Q \) is the chamber flushing flow rate (m³ h⁻¹), \( C_o \) is the Hg concentration measured at the chamber outlet (ng m⁻³), \( C_i \) is the Hg concentration measured adjacent to one of the chamber inlet holes (ng m⁻³), and \( A \) is the footprint area of the chamber (m²). Quality control of the calculated fluxes was based on the determination of the inter-cartridge concentration difference for each of the TGM fluxes measured using the Tekran 2537A according to the method described by Eckley et al. (2011). Calculation of daily TGM fluxes was achieved by integrating the area under the 24-h curve of all valid measurements for each DFC. Positive flux values represent emission from the soil surface to the atmosphere, while negative values signify TGM deposition to the soil.

To ensure consistent conditions in each DFC and its inlet and outlet lines while not being measured, a secondary bypass vacuum pump was attached to the four-port manifold to draw ambient air through the lines at the 1.5 L min⁻¹ sampling rate (Mazur et al., 2014). This flushing flow rate was applied to prevent artificial concentration gradients over the soil and vegetation surfaces within the DFCs and as a consequence induce higher fluxes due to exceedingly high flow rates, erring on the side of a lower flow rate as suggested by Eckley et al. (2010). A bubble flow calibrator (mini-Buck Calibrator M-5) was connected to each of the inlet and outlet lines prior to each sampling campaign to ensure the rate of air flow facilitated by the secondary pump. The analyzer was calibrated prior to each 24-h cycle measurement using the internal mercury permeation source. Each of the two DFCs were soaked in a 10% hydrochloric acid bath for 24 h and rinsed thoroughly with deionized water prior to sampling. To ensure the cleanliness of the DFCs prior to and throughout each monitoring campaign, blank measurements were performed in the field for approximately 24 h by placing each DFC on clean polycarbonate sheeting on the ground surface adjacent to the plots or mesocosms (0.04 ± 0.16 ng m⁻² h⁻¹, mean ± standard deviation, \( n = 123 \) 20-min fluxes) and were not subtracted from flux measurements as is consistent with other published work (e.g. Eckley et al., 2010; Mazur et al., 2014). Condensation occurred on the inside of the DFCs during the experiments, which could not be mitigated through an increase in DFC flushing flow rate. To assess if Hg(0) accumulation occurred in the condensation, samples were collected by rinsing each DFC following the measurement cycle using a known volume of deionized water (18 MΩ cm) as has been previously done by Briggs et al. (2012). The collected rinse water was acidified with 0.5% trace-metal grade HCl and stored in darkness at 4°C until total Hg analysis. Mean TgH concentrations of these unfiltered DFC condensation rinses were low, representing approximately 1.2 ± 1.2% (mean ± standard deviation) of the mean daily TGM fluxes.

Incoming solar radiation as well as air and surface peat temperature were recorded at 5-min intervals on a Campbell Scientific CR1000 data logger during the Hg flux measurements. A pyranometer (Kipp and Zonen SP-Lite 2 Silicon Pyranometer) was placed mid-way between the two DFCs being monitored for each 24-h cycle. Surface peat temperature adjacent to each of the monitored DFCs (to prevent disturbance under the DFC) was measured using temperature probes (109 Temperature Probes) inserted approximately 2 cm below the peat surface. Ambient air temperature outside of the chambers was also measured using a shielded
thermocouple throughout the flux measurements.

2.4. PEATcosm vegetation and surface peat Hg

To determine the relative influences of TGM uptake through the stomata of vascular vegetation as compared to sorption to leaf surfaces, foliar rinsing was performed similar to the methods conducted by Rea et al. (2000), Erickson et al. (2003) and Laacouri et al. (2013). Following the completion of the PEATcosm experiment in July 2015, vascular vegetation was collected from each of the mesocosm bins that were monitored for TGM fluxes. The vegetation from each bin was separated according to species: Carex oligosperma (n = 5), Eriophorum vaginatum (n = 3), Kalma polifolia (n = 6), Chamaedaphne calyculata (n = 6). The leaves of each species collected from each bin (ranging from 170–500 leaves) were placed in a known volume of deionized water and gently shaken for five minutes using a horizontal shaker. The rinse solution was decanted into a new polyethylene terephthalate glycol (PETG) bottle and a second DI water rinse was sequentially performed on each leaf sample. These rinses were followed by two sequential rinses using a dilute (pH 4) trace-metal grade nitric acid solution to ensure all surface-deposited Hg was removed. All samples were stored in darkness at 4 °C until THg analysis the following day. Surface Hg loads are expressed both by dry weight (ng g−1 dry wt.) and by one-sided surface area (ng m−2) similar to Rea et al. (2000) and Laacouri et al. (2013). An average leaf surface area for each species was determined by measuring the length and width of a subset of leaves and assuming the leaves to be oval in shape (one-sided surface area = (½ length) * (½ width) * n). This average was multiplied by the number of leaves counted for each species to estimate a total area of leaves rinsed. To estimate the amount of Hg sorbed to the vascular vegetation under each DFC, the number of leaves and an average leaf length and width for each species present under the footprint of each DFC was counted in the field following the TGM flux measurement period. The coverage of vascular vegetation was not consistent across the bins and therefore by counting the leaves under each DFC and applying a mean leaf area, an estimate of total leaf area (in cm2) could be made. After rinsing, the leaf samples were frozen and subsequently lyophilized. The dried samples were ground prior to THg analysis to determine the amount of Hg found within the leaf tissue following surface rinsing as compared to that resulting from the leaf rinses and therefore sorbed to the leaf surface. To assess the possible relationship between TGM fluxes and peat Hg concentrations, surface peat (0–10 cm) samples were collected from each of the eight monitored mesocosms using a clean stainless steel corer. Peat samples were immediately frozen and lyophilized prior to analysis for THg concentrations.

2.5. Analytical methods

Total Hg concentrations of the DFC condensation rinses, foliar rinses, lyophilized vegetation and peat were determined using a Tekran Model 2600 automated Total Mercury Analyzer, using cold vapor atomic fluorescence spectroscopy (CVAFS) according to US EPA Method 1631. Freeze-dried vegetation and peat samples were digested in hot nitric acid. All Hg in the condensation and foliar rinses as well as the diluted peat and vegetation digestates was oxidized by reaction with bromine monochloride (BrCl) overnight prior to analysis. Recovery of a THg spike was 96 ± 5% (mean ± standard deviation, n = 6), replication of duplicates was 2.0 ± 1.6% (n = 6) and the detection limit for water samples, calculated as three standard deviations of matrix blanks, was 0.16 ng L−1 (n = 23). Recovery of standard reference material (MESS-3) following digestion was 97 ± 2% (n = 2). The detection limit for solid material was 0.01 ng g−1 (n = 6).

2.6. Statistical analyses

All statistical analyses were performed using R statistical software (R Development Core Team, 2014) with α = 0.05. For the PEATcosm measurements, only a qualitative assessment of TGM flux trends among the four crossed water table and plant functional group treatments were considered since only two replicate mesocosms per treatment were measured and statistical power of duplicates is low. Correlative relationships using Pearson correlation were investigated between hourly TGM fluxes and incoming solar radiation as well as surface peat soil temperatures among the four treatments. Only non-zero solar radiation values (i.e. daylight) were included in these correlative relationships. The correlative relationships between daily TGM fluxes and surface peat THg concentrations, total leaf area beneath each DFC, and Hg sorbed to the vegetation surfaces in each of the eight monitored mesocosms were also examined. The relationship between the number of sedge stems present beneath each DFC and the daily TGM fluxes was investigated collectively for the PEATcosm and SPRUCE sites. Significant differences in THg concentrations on the surface of the different vascular plant species, as well as that within the vascular plant tissues were assessed using a one-way analysis of variance (ANOVA), followed by post-hoc testing with Tukey adjustments. Differences in daily TGM fluxes among SPRUCE treatment plots throughout the course of the deep soil warming experiment were assessed using regression analysis with mean daily surface peat temperatures for each of the three sampling campaigns. Significant changes in the slope of this regression over the three sampling events of the deep warming experiment were assessed using an analysis of covariance (ANCOVA) with the surface peat temperature as the covariate.

3. Results

3.1. PEATcosm — water table and plant functional groups influence

The crossed water table position and vascular plant functional group treatments influenced the dynamic exchange of TGM between the peat monoliths and the atmosphere (Fig. 1). Consistent evasion of TGM from the peat was observed in both of the High WT control mesocosms over the course of the 24-h periods with a mean (± standard deviation) daily flux of +35.2 ± 10 ng m−2 d−1. In contrast, strong deposition of TGM to the peat was observed in the
Low WT sedge only bins, with a mean daily TGM flux of $-73.7 \pm 6.3$ ng m$^{-2}$ d$^{-1}$. Total gaseous Hg was deposited to one of the Low WT Ericaceae only bins ($-69.1$ ng m$^{-2}$ d$^{-1}$), while slight emission of TGM was observed from the other bin ($+4.2$ ng m$^{-2}$ d$^{-1}$). Two contrasting flux directions were also observed for the Low WT control mesocosms with one strongly emitting TGM to the atmosphere ($+144.5$ ng m$^{-2}$ d$^{-1}$) while TGM deposition occurred in the other mesocosm ($-35.2$ ng m$^{-2}$ d$^{-1}$; Fig. 1). There was a significant, positive, but weak correlation ($R^2 = 0.10, p < 0.001$) between the mean inlet TGM concentrations and the corresponding 20-min TGM fluxes measured during daylight hours across the treatments (Fig. S1).

Sedges were present beneath the DFC placed on the peat surface of the Low WT — control monolith exhibiting deposition throughout the 24-h monitoring cycle. Although sedges were present beneath the DFC at both the PEATcosm (closed red circles) and SPRUCE (open black circles) sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

When considering the foliar rinses of the Ericaceae and sedge vegetation, the highest surface THg concentrations were washed from the *Chamaedaphne calyculata* (leatherleaf) leaves. This shrub had significantly higher THg sorbed to the leaf surfaces on a dry mass basis than *Kalmia polifolia* (bog laurel) as well as both sedges, *Carex oligosperma* and *Eriophorum vaginatum* (Fig. 5a). *Carex oligosperma* had the lowest surface THg concentrations; significantly lower than either of the Ericaceae shrubs. These patterns were also consistent, although not significant on a per area basis, wherein *C. calyculata* and *K. polifolia* had slightly higher THg concentrations than both of the sedges (Fig. 5b). When considering the amount of THg in the leaf tissue, both *C. calyculata* and *K. polifolia* had significantly higher tissue THg concentrations than either of the sedges (Fig. 5c).

Among leaf area, the amount of Hg sorbed to the vegetation under each DFC, and THg in surface peat, only peat THg concentrations were significantly correlated with mean daily TGM fluxes (Fig. 6). A negative, but not significant correlation was observed between the measured TGM daily fluxes and the estimated Ericaceae total leaf area present beneath each DFC (Fig. 6a; $R^2 = 0.44$, $p = 0.15$). A marginally significant negative correlation was observed between the estimated amount of leaf-sorbed Hg on Ericaceae shrubs under each DFC and measured TGM fluxes (Fig. 6b; $R^2 = 0.54$, $p = 0.09$). A significant negative correlation ($R^2 = 0.82$, $p < 0.01$) was observed between the PEATcosm TGM fluxes and the surface (0–10 cm) peat THg concentrations (Fig. 6c).

### 3.2. SPRUCE bog TGM fluxes

In May 2014 before the onset of experimental warming, 24-h TGM fluxes measured across all plots had an average daily flux of $-45.9 \pm 93.8$ ng m$^{-2}$ d$^{-1}$ (mean ± standard deviation). These fluxes ranged from deposition at an average rate of $-158.8$ ng m$^{-2}$ d$^{-1}$ to evasion of $+199.1$ ng m$^{-2}$ d$^{-1}$ (Fig. 7). In August 2014 once the deep soil warming treatments had been achieved at depth, the minimum TGM flux recorded was $-38.5$ ng m$^{-2}$ d$^{-1}$ while the maximum TGM flux observed was $+59.2$ ng m$^{-2}$ d$^{-1}$ with a mean TGM daily flux rate of $-1.41 \pm 27.1$ ng m$^{-2}$ d$^{-1}$. Following a prolonged period under deep soil warming conditions, the mean daily TGM flux measured in June 2015 was $+10.2 \pm 44.6$ ng m$^{-2}$ d$^{-1}$, ranging from deposition at a rate of $-42.6$ ng m$^{-2}$ d$^{-1}$ to evasion at a rate of $+107.4$ ng m$^{-2}$ d$^{-1}$ (Fig. 7).

### 3.2.1. Influence of deep peat warming

In May 2014, prior to the implementation of the deep warming treatments, no significant correlation was observed between the mean TGM fluxes and the mean daily surface peat temperatures ($p = 0.23$). Similarly, no relationships were observed in August 2014 ($p = 0.55$) once the warming targets in the deep peat layers had been achieved nor in June 2015 ($p = 0.69$) following prolonged deep warming. No significant correlations were observed between the TGM fluxes and the peat temperatures at a depth of 2 m for the August 2014 ($p = 0.78$) or June 2015 ($p = 0.46$) samplings, both of which achieved the target temperature differentials.

When comparing the slopes for the relationships between surface peat temperature and TGM flux, the slope of the May 2014 data collected prior to deep soil warming is significantly different from those collected in August 2014 and June 2015 under warming conditions (Fig. 8; $p = 0.04$). Deep warming may therefore influence the amount of Hg emitted from the peat as there is a transition in the slope of the relationship from strongly negative in May 2014 prior to the initiation of the deep warming treatments, to moderately negative once warming target differentials were achieved at depth in August 2014, and to slightly positive in June 2015 following prolonged deep warming (Fig. 8). This trend in TGM flux may not be strongly reflected in relation to surface peat temperature as target temperature differentials were not achieved nearer the surface of the peat profile as air warming was not initiated for this one-year experiment. However, this progressive change in
slope throughout the deep warming experiment under warming conditions suggests some influence of deep soil warming on TGM flux from the peatland.

4. Discussion

4.1. PEATcosm peat monoliths – influence of vascular plant community on TGM fluxes

The relatively strong depositional trends observed when sedges were present under DFCs, both as the sole surface vascular cover and with other vegetation present (Figs. 1 and 2), suggest a significant role for vegetation type in controlling TGM fluxes. Foliage may interact with atmospheric Hg in multiple ways including exchange of Hg through stomata (Ericksen and Gustin, 2004; Hanson et al., 1995; Lindberg et al., 1998), wet and dry deposition of Hg onto foliar surfaces (Stamenkovic and Gustin, 2009) as well as uptake of Hg into vascular vegetation from soil water transported to the foliage via transpiration (Graydon et al., 2006; Rea et al., 2002). Rooting structures of vascular vegetation may also be important conduits for the dynamic exchange of Hg between the atmosphere and soil (Leonard et al., 1998a, b). Since the sedge species (*C. oligosperma* and *E. vaginatum*) present in the mesocosm bins had generally both the lowest surface-sorbed and leaf tissue THg concentrations, it is unlikely that sorption to sedges or uptake by sedges is the mechanism by which they enhance TGM deposition. Rather, the impact is more likely a function of increased shuttling of TGM from the atmosphere, coincident with oxygen transport to the peat via aerenchymous tissues (Breeuwer et al., 2009) under low water table conditions.

Relative to the role of sedges, Ericaceae shrubs appear to influence gaseous Hg exchange dynamics through sorption onto foliar surfaces and/or uptake through stomata and accumulation in leaf tissue. Greater sorption of Hg to the foliar surfaces of Ericaceae shrubs as well as stomatal uptake into the shrub leaf tissue is associated, albeit weakly, with reduced emission and some depositional fluxes (Fig. 6a and b). Mercury sorbed to the surface of Ericaceae leaves, particularly that which is exposed to incoming solar radiation on the top of the leaves, may likely be photoreactive (Laacouri et al., 2013). Once deposited, this surface-sorbed Hg may undergo considerable re-emission to the atmosphere and contribute to the predominantly emissive fluxes from the Ericaceae-dominated treatments. Increased leaf area will also result in more stomata present and therefore the potential for greater Hg uptake, likely in the form of gaseous Hg(0), while stomata are open during daylight hours for the process of photosynthesis (Lindberg et al., 2002; Marsik et al., 2005; Laacouri et al., 2013). Increased uptake of Hg through stomata may account for the increased
accumulation of Hg within the leaf tissues of the Ericaceae shrubs, as translocation of Hg from the roots to the leaves is often observed to be negligible in vascular plants (Ericksen et al., 2003) and therefore contribute to the diminished emissions from the monoliths with greater Ericaceae leaf area coverage.

The relative importance of surface Hg sorption for different plant functional groups may depend upon such factors as surface roughness (Rea et al., 2000) as well as any potential chemical compounds present on the vegetation or in the atmosphere which may promote TGM sorption and the subsequent potential for Hg reduction and re-emission back to the atmosphere (Hanson et al., 1995; Marsik et al., 2005). Sedge leaves are sleek and glabrous as compared to the scabrous and leathery surfaces of *C. calyculata* and *K. polifolia* leaves. These differences may influence the strength of Hg deposition and the potential re-emission from the plant surface. In addition to exposure to solar radiation, leaf surface texture may contribute to the observed differences in TGM flux dynamics between treatments as well as the leaf surface Hg concentrations between vascular functional groups. Rea et al. (2000) suggested that the rough surface of birch leaves with small hairs may more efficiently trap dry deposition as compared to the smooth surface of maple leaves. The form of Hg deposited to the leaf surfaces may also be influenced by the texture of the leaves. Reactive and water-soluble Hg(II) and aerosol Hg were the likely forms of Hg rinsed from foliar surfaces in the study by Rea et al. (2000). Comparatively, gaseous elemental Hg(0) is more likely to be quickly re-emitted to the atmosphere following deposition to foliar surfaces due to its minimal solubility in water, but may also be taken up through stomata or oxidized to soluble Hg(II) (Hanson et al., 1995; Rea et al., 2000). Leaves are considered dynamic surfaces for Hg exchange acting as either sites of deposition or emission depending upon the prevailing conditions such as temperature and moisture (Hanson et al., 1995). Therefore, leaves may contribute to the predominant emission observed in the Ericaceae-dominated PEATcosm peat mesocosms, although this flux may vary depending upon the amount of leaf area.

The observed differences in the strength of the relationships between TGM fluxes and solar radiation and soil temperature (Fig. 4) among the treatments may be due to differences in vegetative coverage among the plant functional groups, which results in

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Fig. 4. Relationship between PEATcosm hourly TGM fluxes (ng m⁻² h⁻¹) and a) soil temperature (in °C) and b) solar radiation (kW m⁻²) among the four crossed water table and vascular plant functional group treatments.
differential peat shading. Reduced emissions occurred in mesocosms with greater cover of Ericaceae shrubs which, in addition to the influence of TGM sorption to and potential re-emission from foliar surfaces, may be the result of diminished solar radiation reaching the peat surface because of higher leaf area (Fig. 6a). In forested environments, canopy cover influences Hg fluxes from the forest floor due to shading and shade impacts on solar radiation and soil temperatures; with soil temperature becoming an increasingly stronger control as canopy cover inhibits solar radiation penetration to the forest floor (Choi and Holsen, 2009a). A reduction of incoming solar radiation reaching the peat surface may reduce the amount of photoreduction of Hg(II) to Hg(0) available for re-emission as seen in a harvested forest system with varying degrees of biomass removal (Mazur et al., 2014). Shading variations as a result of seasonal progression from leaf-out to leaf-off periods in a forested system significantly affect the magnitude of Hg flux with the highest fluxes occurring prior to leaf-out (Choi and Holsen, 2009a). Therefore, shading by the Ericaceae vegetation may also contribute to the decreased emissions of Hg from the peat surface by potentially inhibiting photoreduction and Hg re-emission. Shading by shrub cover in bog systems is therefore an important potential control on TGM fluxes and may influence the relative contributions of soil temperature and solar radiation in governing Hg exchange dynamics.

The trend in TGM fluxes across the PEATcosm treatments is reflected in the THg concentrations in the surface 0–10 cm of peat, with higher peat THg in monoliths with stronger deposition, suggesting that the deposited Hg is retained in the surface peat. This is a rather novel finding since higher surface soil concentrations typically correspond to higher TGM emissions, particularly in polluted sites (Gustin et al., 2003; Miller et al., 2011), but also less distinctively in background soils (Gustin et al., 2006; Kuiken et al., 2008). In some low Hg soils (i.e. less than 100 ng g⁻¹) no relationship between soil Hg concentrations and TGM fluxes may be observed (Ericksen et al., 2006). The observed negative relationship between flux and surface Hg deposition may provide further support for the shuttling of Hg from the atmosphere and its deposition to the peat by the sedge vascular vegetation. The strength of the correlation may also suggest that there is minimal re-emission of Hg from the peat surface once deposited.

4.1.1. Potential climate change implications for TGM fluxes

Global climate change has the potential to significantly affect the dominant vascular plant functional groups present in peatlands due to changes in hydrology (Welzlitz et al., 2003; Strack et al., 2006; Breeuwer et al., 2009; Dieleman et al., 2015; Potvin et al., 2015). Regardless of the direction of shifting plant communities, the exchange of TGM with the atmosphere will likely be affected. Dominance of Ericaceae shrubs may result in a greater proportion of atmospheric Hg being sorbed to the leaf surfaces of these plants. This pool of Hg sorbed to the surface of vegetation may be susceptible to reduction mechanisms including photochemical and subsequent re-emission to the atmosphere, although Ericaceae leaf coverage will likely reduce emissions from the peat due to shading. If increased temperatures and elevated atmospheric CO₂ concentrations in concert with prolonged periods of water table recession do indeed promote the establishment of sedges in peatlands (Fenner et al., 2007; Dieleman et al., 2015), enhanced deposition of TGM to the peat may occur. This deposited Hg may then be bound to the soil organic matter or contributed to pore water due to changes in hydrology (Weltzin et al., 2003; Strack et al., 2006; Breeuwer et al., 2009; Dieleman et al., 2015; Potvin et al., 2015). Regardless of the direction of shifting plant communities, the exchange of TGM with the atmosphere will likely be affected. Dominance of Ericaceae shrubs may result in a greater proportion of atmospheric Hg being sorbed to the leaf surfaces of these plants. This pool of Hg sorbed to the surface of vegetation may be susceptible to reduction mechanisms including photochemical and subsequent re-emission to the atmosphere, although Ericaceae leaf coverage will likely reduce emissions from the peat due to shading. If increased temperatures and elevated atmospheric CO₂ concentrations in concert with prolonged periods of water table recession do indeed promote the establishment of sedges in peatlands (Fenner et al., 2007; Dieleman et al., 2015), enhanced deposition of TGM to the peat may occur. This deposited Hg may then be bound to the soil organic matter or contributed to pore water due to the favourable redox environment of the soil, particularly with aerated surface peat as a result of lowered, fluctuating water tables (Waddington et al., 2015), promoting the oxidation of gaseous Hg(0) to Hg(II) (Moore and Castro, 2012). Increased provision of Hg to peatlands by sedge vegetation may have important implications in terms of both availability for inorganic Hg methylation and inorganic Hg and methylmercury (MeHg) mobility. Peatlands are ideal environments for MeHg production with predominantly saturated soils and favourable redox conditions for sulfate and iron-oxidation as well as methanogenic bacteria to carry out this reaction (Branfireun et al., 1996; Tjerngren et al., 2012). Previous research at the PEATcosm experimental mesocosms demonstrated that the highest THg and MeHg concentrations in pore water and snowmelt runoff were consistently in the Low WT – sedge only monoliths (Haynes et al., 2017). With greater Hg deposition in these sedge-dominated wetlands, more Hg is available for the conversion to MeHg and subsequent export to downstream aquatic ecosystems. Although each of the four treatment combinations were only
monitored for TGM fluxes on two separate 24-h periods, the mechanisms postulated to account for the observed magnitude and direction of these fluxes provide an important first look at how these influences simulating climate change may impact TGM fluxes within peatland ecosystems.

4.2. SPRUCE bog fluxes — deep soil warming influence on TGM fluxes

Warming of peat soils at depth influenced TGM fluxes in the SPRUCE bog with a statistically significant increase in the slope of the surface peat temperature-TGM flux relationship in response to warming conditions (Fig. 8). Although consistent temperature differentials of +4.5 and +9 °C above ambient throughout the peat profile could not be achieved in this initial SPRUCE deep warming manipulation experiment due to the lack of added air warming, differences were observed in the surface peat temperatures among the treatment plots (Fig. 8). Gustin et al. (1997) concluded that heating of the air above the soil had a greater impact on Hg flux than heating of the soil itself in contaminated tailings soil cores. Even without added air warming to the enclosures, a slight warming of the surface peat does appear to result in an increase in TGM emission to the atmosphere. Previous studies have observed correlative relationships between both air and soil temperatures and TGM fluxes from background soils including wetlands (e.g. Poissant and Casimir, 1998; Edwards et al., 2001; Marsik et al., 2005). Increased temperatures result in enhanced TGM fluxes due to a lowering of the activation energy for Hg reduction (Carpi and Lindberg, 1998; Kim et al., 2012; Moore and Castro, 2012). Biotic influences on TGM emissions including microbially-mediated reduction of Hg may also be accelerated by warming influences by augmenting microbial activity, although they exert less control than abiotic factors (Choi and Holsen, 2009b). Deep warming within the peat profile does indeed result in enhanced TGM fluxes from the peatland, suggesting either that the slight warming observed at the surface enhanced reduction processes or that greater warming at depth resulted in Hg reduction at depth, with only small proportions able to diffuse to the surface for evasion. With increasing air and soil temperatures as a result of global climate change, TGM fluxes from peatland ecosystems may be enhanced, but confidence in this conclusion would be enhanced by further, longer term research at the SPRUCE project, including
4.3 Peatland TGM fluxes compared to other wetland environments

Only two published studies have previously examined soil-air Hg dynamics in boreal peatland systems using DFCs (Kyllönen et al., 2012; Fritsche et al., 2014). However, the measurements in these studies were not conducted continuously throughout 24-h diurnal cycles, which integrate both daytime and nighttime fluxes. The magnitude of the fluxes recorded for the ombrotrophic, spruce-Sphagnum, SPRUCE bog is similar to that of other studies of boreal peatlands as well as other freshwater wetlands. For example, Kyllönen et al. (2012) observed mean hourly fluxes of 0.2 ng m⁻² h⁻¹ with values ranging from −0.3 to +0.6 ng m⁻² h⁻¹ in a boreal Sphagnum and grass-dominated wetland. Measured in August under shaded plots within a mixed acid peatland, Fritsche et al. (2014) observed TGM fluxes of 1.39 ± 2.3 ng m⁻² h⁻¹. In a marsh with vegetation removed from beneath the DFCs, TGM fluxes ranged from 0.35 ± 0.15 ng m⁻² h⁻¹ measured in cloudy conditions to 1.03 ± 0.79 ng m⁻² h⁻¹ recorded in sunny conditions (Zhang et al., 2006). Using a relaxed eddy accumulation system, Osterwalder et al. (2016) observed mean fluxes of 3.0 ± 3.8 ng m⁻² h⁻¹ from a boreal peatland during the spring snowmelt period. Collectively, these studies demonstrate that peatlands and some freshwater wetlands represent nearly neutral fluxes.

The diel pattern in TGM fluxes observed for both the PEATcosm (Fig. 3) and SPRUCE peatland sites, with peak fluxes occurring in concert with peak solar radiation and surface soil temperatures shortly after midday due to radiative heating, is similar to the trends observed over both mineral soil and open water sites (Poissant and Casimir, 1998) as well as boreal forest soils (Kyllönen et al., 2012). This trend has similarly been observed for most soils with both contaminated and background Hg levels (e.g. Poissant and Casimir, 1998), as well as in a boreal wetland environment (Kyllönen et al., 2012). Despite the moderate TGM fluxes observed in peatlands as compared to upland, mineral soils, the congruence in diurnal trends suggests that influences such as solar radiation and soil and air temperatures may similarly affect peat soils. Other meteorological variables such as precipitation patterns and soil moisture (Gustín and Stamenkovic, 2005) as well as wind speed and direction (Marsik et al., 2005), which are important controls on TGM exchange dynamics in other environments, may also play key roles in peatland TGM flux. Given the likely impacts of climate change on the hydrology, ecology and biogeochemistry of peatland systems, further study on the influence of these factors is warranted.

5. Conclusions

Combined changes in water table position and variability, and vascular plant functional groups may significantly alter TGM deposition to peatlands. Aboveground and belowground biomass of vascular vegetation is instrumental in controlling TGM dynamics via stomatal exchange, surface sorption and vascular aerenchyma tissues. Increased Ericaceae shrub abundance with climate change (Potvin et al., 2015) may alter the dynamic exchange of gaseous Hg via leaf surface sorption and reduction, leading to more positive (surface to air) emission fluxes. A shift in dominant vascular plant functional group towards sedges under a changing climate may result in greater deposition of gaseous Hg to these systems via vascular shuttling under low water table conditions. This deposited Hg may sorb to the organic matter increasing the amount of Hg available for methylation or be mobilized in peat pore waters (Haynes et al., 2017). From this study, the potential impact of increasing peat temperatures on TGM flux is still equivocal. Inter-site variability was too great to make a strong conclusion about temperature impacts. The deep-peat-only warming in the current experiment is unlikely to adequately represent future peat temperature scenarios, particularly at the surface. Still, the significantly shifting trend between flux and soil temperatures throughout the deep-peat warming experiment is suggestive of a developing temperature influence on increasing TGM flux. Given the potential antagonistic impacts of climate change-induced increases in soil and air temperatures combined with altered water table regimes and shifts in plant functional groups on TGM fluxes, further integrated investigation into how these factors may, in combination, affect the exchange of gaseous Hg between the atmosphere and peatland systems is warranted.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.01.049.

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