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Impacts of experimental alteration of water table regime and vascular plant community composition on peat mercury profiles and methylmercury production

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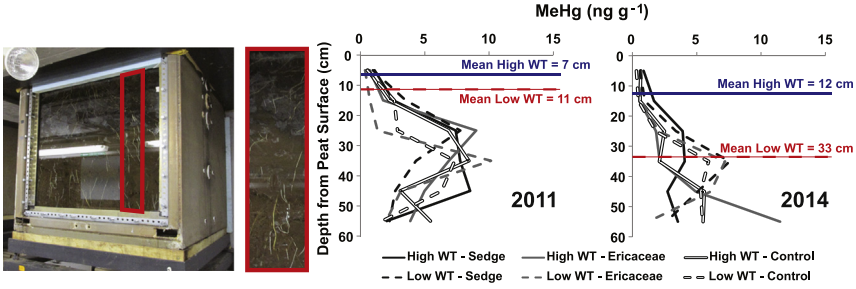
HIGHLIGHTS

- Climate change anticipated to induce shift in peatland hydrology, plant communities.
- Peat Hg(II), MeHg tracked annually over PEATcosm experiment.
- Lowered water tables, sedges increase Hg(II), MeHg in water table fluctuation zone
- High water tables promote net downward migration of Hg(II), MeHg in peat profile.
- Changes to hydrology, ecology redistribute peat Hg(II), MeHg via vertical transport

GRAPHICAL ABSTRACT



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ABSTRACT

Climate change is expected to alter the hydrology and vascular plant communities in peatland ecosystems. These changes may have as yet unexplored impacts on peat mercury (Hg) concentrations and net methylmercury (MeHg) production. In this study, peat was collected from PEATcosm, an outdoor, controlled mesocosm experiment where peatland water table regimes and vascular plant functional groups were manipulated over several years to simulate potential climate change effects. Potential Hg(II) methylation and MeHg demethylation rate constants were assessed using enriched stable isotope incubations at the end of the study in 2015, and ambient peat total Hg (THg) and MeHg concentration depth profiles were tracked annually from 2011 to 2014. Peat THg and MeHg concentrations and the proportion of THg methylated (%MeHg) increased significantly within the zone of water table fluctuation when water tables were lowered, but potential Hg(II) methylation rate constants were similar regardless of water table treatment. When sedges dominate over ericaceous shrubs, MeHg concentrations and %MeHg became significantly elevated within the sedge rooting zone. Increased desorption of Hg(II) and MeHg from the solid phase peat into pore water occurred with a lowered water table and predominant sedge cover, likely due to greater aerobic peat decomposition. Deeper, more variable water tables and a transition to sedge-dominated communities coincided with increased MeHg accumulation within the zone of water table fluctuation. Sustained high water tables promoted the net downward migration of Hg(II) and MeHg. The

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simultaneous decrease in Hg(II) and MeHg concentrations in the near-surface peat and accumulation deeper in the peat profile, combined with the trends in Hg(II) and MeHg partitioning to mobile pore waters, suggest that changes to peatland hydrology and vascular plant functional groups redistribute peat Hg(II) and MeHg via vertical hydrochemical transport mechanisms.

1. Introduction

Boreal peatland ecosystems store large amounts of atmospherically-deposited mercury (Hg) bound to organic soils (Kolka et al., 2001; Grigal, 2003), on the order of 7 to 44 μg total Hg m^{-2} y^{-1} (Kolka et al., 2011a). As a result of the strong affinity between Hg and organic matter, Hg adsorbs strongly to solid phase peat (Meilli, 1991; Schlüter, 1997; Skyllberg et al., 2000; Drexel et al., 2002). Due to the ability of peatlands to incrementally accumulate organic matter in peat deposits over long timescales, these wetland environments store atmospherically-deposited pollutants such as Hg and can be used as long-term records of atmospheric loading (Biester et al., 2007; Talbot et al., 2017).

With predominantly saturated, anoxic soils, peatlands are optimal sites for the conversion of inorganic Hg to methylmercury (MeHg) (Tjerngren et al., 2012), a process mediated by a relatively wide array of anaerobic microbes such as sulfate- and iron-reducing bacteria and fermentative archaea (Gilmour et al., 2013). These environments also facilitate the reverse process of MeHg demethylation as sulfate-reducing and methanogenic microbes are implicated in oxidative demethylation in freshwater ecosystems (Oremland et al., 1991; Marvin-DiPasquale and Oremland, 1998; Marvin-DiPasquale et al., 2000). Continuous dissolution/desorption of inorganic Hg(II) and MeHg from the solid phase soil into the aqueous phase sustains high rates of conversion in these systems (Jonsson et al., 2014; Marvin-DiPasquale et al., 2000). Overall, peat MeHg concentrations in these systems reflect the net balance between methylation and demethylation processes. As a potent neurotoxin, MeHg poses a significant threat to vulnerable wildlife and human populations as it biomagnifies to toxic concentrations at higher trophic levels (Mergler et al., 2007; Scheuhammer et al., 2007). Wetland-dominated catchments, including those comprising peatlands (Kelly et al., 1997; Heyes et al., 2000), export significantly more MeHg to downstream aquatic ecosystems (yields on the order of 26 to 79 times higher) compared to terrestrial upland-dominated environments (St. Louis et al., 1994).

Climate change, characterized by changes in temperature and precipitation patterns, is likely to impact the hydrological, biogeochemical, and microbial processes that control peatland ecosystem function and carbon storage (Ise et al., 2008). Carbon fluxes in peatland ecosystems are largely controlled by hydrology across a range of scales, from regional influences of surface and subsurface hydrology on nutrient status and the transport of dissolved organic carbon to local controls on soil oxygen availability and organic matter decomposition via water table position and flow paths (Limpens et al., 2008). Increased evaporation associated with increasing temperatures, as well as enhanced variability in precipitation patterns in the northern continental United States (Groisman et al., 2012; Janssen et al., 2014; Yu et al., 2016) will likely result in prolonged water table drawdown and considerable fluctuations in water table position, particularly during the summer months (Thomson et al., 2005; Whittington and Price, 2006). In turn, climate-induced changes in hydrology are expected to result in significant alterations in peatland Hg cycling (Yang et al., 2016).

Redox-sensitive processes such as Hg(II) methylation are likely to be affected by longer periods of peat aeration and more widely varying water table position. Some studies suggest the potential enhancement of MeHg production and export from peatlands despite increased oxygen intrusion in the peat (Coleman Wasik et al., 2015). These factors may also impact the competing process of MeHg demethylation, thereby influencing net MeHg production (Lehnherr, 2014). For example, demethylation is likely to exceed methylation under oxidative conditions in aquatic environments (Ullrich et al., 2001). Although the process of methylation has been extensively examined in peatland systems (e.g. Mitchell et al., 2008a; Mitchell et al., 2008b; Tjerngren et al., 2012; Coleman Wasik et al., 2015; Johnson et al., 2016), the hydrological controls on the balance between Hg(II) methylation and MeHg demethylation in peatlands have not been thoroughly explored.

With prolonged periods of water stress due to less frequent, but more intense precipitation events (Groisman et al., 2012; Janssen et al., 2014; Yu et al., 2016), the dominant vascular plant functional groups in oligotrophic peatlands are likely to shift (Weltzin et al., 2003; Strack et al., 2006; Breeuwer et al., 2009; Dieleman et al., 2015; Potvin et al., 2015; McPartland et al., 2019). However, there is no consensus within the literature as to the dominance of either graminoids or ericaceous shrubs. The direction of the shift will depend upon the severity of water stress and the adaptive abilities of the dominant plant functional groups (Potvin et al., 2015; McPartland et al., 2019). These shifts will likely affect Hg(II) methylation and MeHg demethylation due to the influence of different plant functional groups on oxygen availability and carbon substrate quality for microbial communities. The active shuttling of oxygen to the rooting zone by sedge aerenchyma (Crow and Wieder, 2005) may result in Hg(II) methylation being suppressed by the creation of a more oxic environment in peat. Alternatively, sedge-dominated plant communities may instead prime or shift the depth of MeHg production by regenerating terminal electron acceptors within the rooting zone (Mueller et al., 2016), and by providing labile root exudates, which stimulate sulfate and iron reduction (Windham-Myers et al., 2009, 2014). In contrast, ericaceous shrubs have non-aerenchymal roots but form a symbiotic relationship with mycorrhizal fungi, and may affect the soil microbial communities within the rooting zone (Read et al., 2004). The presence of ericaceous shrubs may decrease the redox potential of shallow peat as a result of oxygen consumption by non-aerenchymal root respiration (Romanowicz et al., 2015) and therefore may enhance peat net MeHg production in the rooting zone. The potential effects of increasing dominance of either sedges or ericaceous shrubs, with climate change-induced shifts in peatland hydrology, on peat MeHg production in peat soils have not been previously examined.

Given the large stocks of Hg in peatlands, the connection of wetlands to downstream aquatic ecosystems, and the vulnerability of these systems to a changing climate, it is important to understand how combined changes in hydrology and plant communities may affect the net production and transport of Hg(II) and MeHg in peatlands. Previous studies have examined the impacts of climate change, simulated by manipulating peatland water table positions and vascular plant functional groups, on the mobility of Hg(II) and MeHg in peat pore waters and runoff (Haynes et al., 2017a) as well as the dynamic exchange of gaseous Hg fluxes between peat and the atmosphere (Haynes et al., 2017b). Increased pore water and snowmelt runoff Hg and MeHg concentrations were observed in peat subjected to lowered, fluctuating water tables and with sedge-dominated vascular vegetation (Haynes et al., 2017a). Sedge vegetation was also observed to enhance Hg deposition to peat due to shuttling of Hg by sedge aerenchyma (Haynes et al., 2017b). However, the impacts of a changing climate on solid phase peat Hg and MeHg concentrations as well as net MeHg production have not been previously examined.

Therefore, the objective of this study was to understand the effects that altering water table position and composition of plant functional groups would have on peat Hg and MeHg concentrations, on methylation and demethylation, and on the partitioning of Hg and MeHg between peat and pore water. Our main hypotheses were: 1) Lowered water tables and the removal of Ericaceae with only sedges present will increase solid phase peat THg and MeHg accumulation within the zone of water table fluctuation and the sedge rooting zone, respectively, 2) Lowered water tables and the removal of sedges with only Ericaceae present will increase solid phase peat THg and MeHg accumulation with the zone of water table fluctuation and the Ericaceae rooting zone, respectively, and 3) Net MeHg production will be increased in the solid phase peat within the zone of fluctuation of the lowered water tables and the rooting zone of sedge vegetation with the removal of Ericaceae due to greater Hg(II) methylation potential. To test these hypotheses, peat was collected throughout the course of the PEATcosm (**P**eatland **E**xperiment **at** the Houghton Meso**cosm**) experiment, annually from 2011 through 2015. PEATcosm was an outdoor, controlled experiment that manipulated water table positions and vascular plant functional groups in peat mesocosms to simulate potential climate change impacts (cf. Potvin et al., 2015). Pore water was collected to examine the experimental influences on Hg(II) and MeHg partitioning. Enriched Hg isotope-based measurements of Hg(II) methylation and MeHg demethylation potential rate constants were completed at the conclusion of the PEATcosm study, once larger-scale destructive sampling was possible.

2. Experimental

2.1. Study site and experimental design

The PEATcosm experiment was located at the United States Forest Service 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, approximately 50% of this falling as snow. Mean temperatures in this area range from −13 °C in January to 2 4 °C in July (30 year means at Houghton County Airport; Potvin et al., 2015).

Twenty-four intact ~1-m^3 (~1 × 1 × 1 m) peat blocks were harvested from an ombrotrophic bog located in Meadowlands, MN, USA in May 2010 and transferred into individual mesocosm bins. The soils of the harvest site are listed as the Lobo-Waskish complex (0–2% slopes), which are histosols and classified as Sphagnofibrists according to the Natural Resources Conservation Service soil survey (NRCS, 2019). The Teflon-coated stainless steel mesocosm bins were open at the top, exposing the peat to the ambient climate. The mesocosms were insulated and installed in a climate-controlled tunnel, allowing belowground access to each, as well as the simulation of a natural vertical temperature gradient.

The PEATcosm study comprises a full-factorial experimental design with two water table (WT) treatments crossed with three different plant functional group (Veg) treatments, simulating an array of potential climate change outcomes. Each treatment combination was 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 USDA Forest Service Marcell Experimental Forest (MEF) in north central Minnesota, located near the harvest site of the peat blocks (Sebestyen et al., 2011). The two water table treatments simulated: 1) typical variability and average water table position (referred to as 'High WT') and 2) comparably high variability and deeper average water table position (referred to as 'Low WT'). Water table manipulations were performed only during the growing season as the 50-year record of peatland water tables at the MEF indicates increased summer droughts and increased frequency of mid-summer water table decline (Kolka et al., 2011b; Sebestyen et al., 2011). Within the record, major water table changes are restricted to the growing season, because evapotranspiration slows considerably in the fall, independent of summer conditions, and water tables generally rise back to near the surface until the following spring (Kolka et al., 2011b; Sebestyen et al., 2011). Mesocosm water table positions were allowed to stabilize throughout the winter months. The three plant functional group treatments simulating potential community composition alterations resulting from climate change (Chapin et al., 1996; Weltzin et al., 2000; Strack et al., 2006), were: 1) all Ericaceae removed (referred to as the 'sedge only' treatment), 2) all sedge removed ('Ericaceae only' treatment) and 3) both sedge and Ericaceae present ('unmanipulated control' treatment). Given that climate change may favor the dominance of either graminoids or shrubs depending upon the setting, hydrology and other contributing factors (Weltzin et al., 2000; Weltzin et al., 2003; Strack et al., 2006; Breeuwer et al., 2009; Dieleman et al., 2015; McPartland et al., 2019), the PEATcosm experimental plant functional group treatments were selected to simulate both possibilities. Ericaceae removal treatments simulate the dominance of sedge vascular vegetation and sedge removal treatments simulate the dominance of Ericaceae shrubs. Both of these removal treatments were compared to the unmanipulated treatments, which were not subjected to vegetation removal and instead had both vascular plant functional groups present. All mesocosms had *Sphagnum* species present and comprised hummock, lawn, and hollow microtopography, representative of the natural variation in the bog from which they were harvested. Vascular plant functional group and water table manipulations were initiated in June 2011 and spring 2012, respectively. Potvin et al. (2015) provide a comprehensive explanation of the peat harvest and experimental set-up. The experiment concluded in July 2015 with the destructive harvest of the mesocosms.

In 2011, mean water table positions between the beginning of June and the end of October were 7 ± 5 cm (mean ± standard deviation) and 11 ± 4 cm below the peat surface for the High WT and Low WT treatments, respectively. Mean 2012 water table positions were 11 ± 4 cm and 19 ± 8 cm below the peat surface for the High WT and Low WT treatments, respectively. In 2013, a mean differential of approximately 20 cm was imposed between the High WT (15 ± 5 cm below surface) and the Low WT treatments (35 ± 11 cm below surface). Similarly in 2014, the High WT (12 ± 5 cm below surface) and Low WT treatments (33 ± 12 cm below surface) had an approximate mean differential of 20 cm from June through to the end of October.

2.2. Peat sampling

Peat samples comprising the full peat profile were collected for ambient THg and MeHg analyses from each of the 24 mesocosms in August 2011, 2012, 2013 and 2014. Cores (2.54 cm internal diameter, typically 60 cm in length) were collected using a drill-mounted stainless steel corer from which the peat was extruded and divided into 10 cm increments. The corer was rinsed with deionized water before sampling each mesocosm. Peat samples were immediately frozen following subsectioning. In 2012, peat samples were only analyzed for Hg down to 40 cm below the peat surface as the water table treatments were not drawn down below 30 cm.

2.3. Pore water sampling

Pore water samples were collected from micro-piezometer nests, constructed of ultra-high-density polyethylene casings housing Teflon tubing, centered within a 10 cm slotted region located 20, 40 and 70 cm below the peat surface in each of the 24 mesocosms (see Romanowicz et al., 2015 for complete piezometer construction details). Both THg and MeHg analyses were performed on pore waters collected in June, August and November 2013; May, July and September 2014; and in May 2015 prior to the destructive harvest of the mesocosms at the conclusion of the experiment. Detailed description of the pore

water sampling can be found in Haynes et al. (2017a). Pore water samples for Hg analyses were not collected in 2011 and 2012.

Soil-water partition coefficients (K_D, expressed in units of L kg^{-1}) were calculated according to the equation:

$$K_D = \frac{[Hg]_S}{[Hg]_{PW}}$$

where $[Hg]_S$ is the solid phase peat Hg (either Hg(II) or MeHg) concentration (in ng kg^{-1}) and $[Hg]_{PW}$ is the pore water Hg (Hg(II) or MeHg) concentration (in ng L^{-1}). Values are expressed in log10 form. Partition coefficients were calculated for both 2013 and 2014 at 20 and 40 cm below the peat surface to coincide with the zone of greatest water table variability. Mean solid phase peat concentrations from 10 to 30 and 30–50 cm were used to correspond with the pore waters collected at 20 and 40 cm below the peat surface, respectively. Mean annual pore water Hg concentrations for each of 2013 and 2014 were used to determine the K_D coefficients since pore waters were not collected at the same time as the solid phase peat. Solid phase Hg(II) and MeHg concentrations are reflective of long-term redox conditions, whereas pore waters are more susceptible to seasonal changes and hydrological fluctuations (Haynes et al., 2017a). By incorporating pore water Hg(II) and MeHg data from samplings events throughout the growing season, the long-term mechanisms influencing the solid phase concentrations are more likely to be captured rather than associating one pore water sampling event that may only reflect short-term seasonal influences.

2.4. Potential Hg(II) methylation and MeHg demethylation rates

To determine potential Hg(II) methylation and MeHg demethylation rate constants (k_{meth} and k_{demeth}, respectively), cores collected from each mesocosm in July 2015 were injected with enriched, stable Hg (II) and MeHg isotopes (Hintelmann et al., 1995; Hintelmann and Ogrinc, 2003). Values of k_{meth} were assessed using spike additions of enriched ^{200}Hg(II) (94.3% purity), while k_{demeth} were measured using additions of enriched Me^{201}Hg (84.7% purity). Surface peat (0–20 cm) and deeper peat cores (20–60 cm) were sampled into separate clear polycarbonate corers (4.8 cm internal diameter) with silicone septa (1/16″) spaced at 1 cm intervals. Once extracted from the peat block, the core tubes were capped immediately at both ends. Capped cores remained upright and were stored at ambient peat temperatures in an incubator until the isotopic injections were completed (within 2 h of extraction). Spike solutions for the peat cores from each of the 24 mesocosms were made by diluting the ^{200}HgCl and Me^{201}HgCl stock solutions with filtered pore water collected at 40 cm below the peat surface from the corresponding mesocosm on the same day as peat collection. The solutions were allowed to equilibrate for approximately one hour prior to injection into the peat cores, with the assumption that enriched isotopes would equilibrate with the dissolved organic carbon present in the pore water. Through each of the 1 cm-spaced silicone septa from 0 to 15 cm (surface peat core) and 35–50 cm (deep peat core), 100 μL of the prepared spike solution (~2 μg mL^{-1} ^{200}Hg and ~0.07 μg mL^{-1} Me^{201}Hg) was injected into the peat using a gas-tight borosilicate glass syringe. These depths were targeted for isotopic incubation to coincide with the water table positions in the High and Low WT treatments, respectively. As the added isotopic tracers are likely more bioavailable than ambient Hg(II) and MeHg, the values of k_{meth} and k_{demeth} represent potential methylation and demethylation rate constants, respectively (Mitchell and Gilmour, 2008). Following the spike additions the cores were incubated in the dark for six hours at 18 °C (ambient peat temperature measured at approximately 5 cm below the peat surface in the mesocosms). After the incubation, the entire length of the peat in each core was extruded from the tubes and sectioned into 5 cm increments. Each peat sample was homogenized using a stainless steel hand blender that was thoroughly washed with deionized water between each sample. Samples were then immediately frozen at −20 °C to terminate the Hg(II) methylation and MeHg demethylation incubations.

2.5. Analytical methods

All frozen peat samples were freeze-dried prior to analysis. For MeHg analysis, both ambient and tracer incubated peat samples were distilled in Teflon vessels according to US EPA Method 1630 (US EPA Method 1630, 1998). Prior to distillation, a known trace amount of enriched stable Me^{199}Hg isotope was added to each sample as an internal standard (Hintelmann and Evans, 1997). Both ambient MeHg and excess Me^{20x}Hg concentrations were assessed by gas chromatography-inductively coupled plasma mass spectrometry (GC-ICP-MS) using an Agilent Technologies 7700× ICP-MS for Hg isotope detection. Concentrations were calculated as per the isotope dilution calculations of Hintelmann and Ogrinc (2003). Recovery of standard reference material (estuarine sediment ERM CC580) was 100 ± 6% (mean ± standard deviation, $n = 42$), analytical precision was 3.9 ± 3.3% (% relative standard deviation of duplicates, $n = 37$ pairs) and the MeHg detection limit was calculated ($n = 42$ matrix blanks) to be 0.05 ng g^{-1}. For THg analysis, the peat samples were digested in hot nitric acid and the diluted digests were analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) according to US EPA Method 1631 (US EPA Method 1631, 2002) using a Tekran 2600 automated Total Mercury Analyzer. For detection of the added inorganic ^{200}Hg tracer in the 2015 incubated peat samples, the Tekran 2600 analyzer exhaust was directly hyphenated to the ICP-MS inlet. Recovery of a THg spike was 101 ± 4% ($n = 38$), analytical precision was 3.4 ± 2.8% ($n = 41$) and the detection limit was 0.04 ng g^{-1} ($n = 40$ matrix blanks). Recovery of standard reference material (MESS-3) following digestion was 101 ± 5% ($n = 42$).

Potential rate constants for Hg(II) methylation (k_{meth}) were calculated using the concentration of the isotopic tracer solution that was methylated over the course of the six hour incubation period with respect to the abundance of the isotope tracer (Hintelmann et al., 1995; Hintelmann and Ogrinc, 2003). Potential MeHg demethylation rate constants (k_{demeth}) were determined assuming first-order reaction kinetics according to Lehnherr et al. (2012). The initial concentrations of excess Me^{201}Hg were equivalent to the excess total ^{201}Hg at the end of the incubation, given that the methylated Hg isotope was entirely MeHg. Detection limits for both k_{meth} and k_{demeth} potential rate constants were determined based on the error associated with isotope ratio measurements, ambient peat MeHg and Hg(II) concentrations and the tracer spike levels, as calculated by Mitchell and Gilmour (2008). The detection limit for k_{meth} ranged from 2×10^{-5} to 0.028 d^{-1} (mean 0.0028 d^{-1}). The detection limit for k_{demeth} ranged from 0.09 to 0.16 d^{-1} (mean 0.12 d^{-1}).

Analytical methods and quality control information for pore water THg and MeHg concentration determination are provided in Haynes et al. (2017a).

2.6. Statistical analyses

All statistical analyses were performed using R statistical software (R Core Team, 2017) with $\alpha = 0.05$. All data were tested for normality (Shapiro-Wilk W test) and heteroscedasticity and were successfully log-transformed to achieve normality when parametric assumptions were not met. Repeated measures analyses of variance (ANOVAs) were performed on THg and MeHg concentrations as well as the proportion of THg in methyl form (%MeHg) with water table ('WT'), plant functional group ('Veg') and depth as the main factors. This repeated measures approach facilitated the examination of the direct and interactive treatment effects from the initial sampling in 2011 following preliminary exposure to vegetation manipulation, to the initial imposed water table treatments in 2012, through to the full experimental treatment years of 2013 and 2014. In addition to concentrations of THg

and MeHg expressed in units of ng g^{-1}, solid phase stocks in units of ng cm^{-3} were also considered for this analysis to account for the changes in peat bulk density that occurred with time throughout the experiment (due to peat subsidence and enhanced aerobic decomposition in the upper peat depths with water table lowering) and that naturally occur down the peat profile.

Significant differences in soil-water partition K_D coefficients at 20 and 40 cm in both 2013 and 2014 were assessed individually with two-way ANOVAs to determine any significant direct and interactive influences of the water table and plant functional group treatments. One-way ANOVAs were subsequently applied to the K_D values to determine significant differences among the six crossed treatments.

For the k_{meth} and k_{demeth} data from the 2015 peat core incubations, two-way ANOVAs were performed for each individual isotopically-spiked 5 cm depth increment from 0 to 15 cm and 35–50 cm to assess significant influences of water table position, plant functional groups and potential interactions between these factors at each spiked depth. One-way ANOVAs were subsequently performed to determine significant differences in potential Hg(II) methylation and MeHg demethylation rate constants among the six crossed water table and vascular plant functional group treatments. The correlative relationships between k_{meth}, k_{demeth} and the ambient percentage of THg present as MeHg in the peat (compared at the same depths) were investigated using Pearson correlations.

3. Results

3.1. Treatment effects on solid phase MeHg, %MeHg and THg

The PEATcosm water table and plant functional group treatments significantly affected the ambient solid phase MeHg concentrations and %MeHg in the peat profile of the mesocosms (see Fig. 1 for annual average treatment profiles; Table 1 for statistical results; Fig. S1 for all mesocosm MeHg profiles each year). These main treatment effects, as well as peat depth within the profile, were significant for both MeHg concentrations and %MeHg (see Table 1 for *p* values). The influence of these factors is dependent upon the depth within the peat profile, with significant interactions between depth and both the water table and plant functional group treatments observed for peat MeHg concentrations and %MeHg (Table 1). Additionally for MeHg concentrations, the effect of peat depth was dependent on the sampling year (Table 1).

In the shallow, near-surface peat, MeHg concentrations were similar across the treatments in all sampling years (Fig. 1). Following one year of equilibration of the peat blocks in the mesocosm bins (2011), the MeHg concentrations and %MeHg profiles displayed no systematic trend among the assigned treatments (Fig. 1e). With the small water table treatment difference in 2012, MeHg profiles across the treatments were similar with the peak in MeHg concentrations near the position of the water table (Fig. 1f). At the end of the first full season of larger water

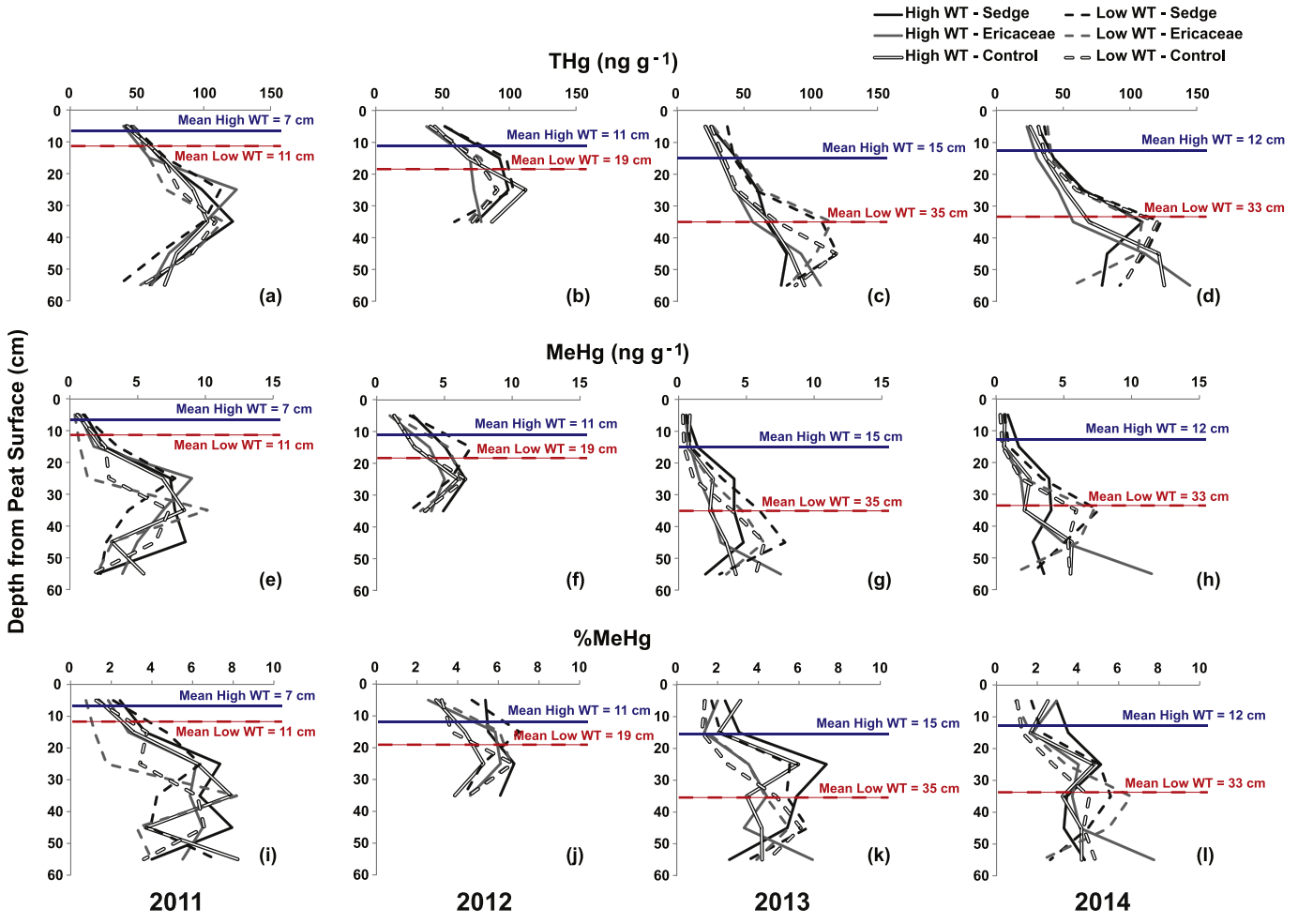

Fig. 1. Depth profiles of mean peat MeHg and THg concentration (ng g^{-1}) and %MeHg in peat for the six crossed water table and vascular plant functional group treatments throughout the PEATcosm experiment from 2011 to 2014. The associated mean June to October water table positions for the High and Low WT treatments are included as dashed horizontal lines in each pane. Peat MeHg and THg profiles for each of the 24 mesocosms in 2011 through to 2014 are presented in Figs. S1 and S2. The mean MeHg and THg stock (ng cm^{-3}) profiles for each of the four years are presented in Supplementary information Fig. S3.

Table 1
p values from repeated measures ANOVAs for ambient solid phase THg concentrations, MeHg concentrations and %MeHg. The fixed factors are the water table (WT) treatments (Low WT, High WT), the plant functional group (Veg) treatments (Sedge only, Ericaceae only, Control), and the sampling depth intervals (Depth: 0–10, 10–20, 20–30, 30–40, 40–50, 50–60 cm below the peat surface) across the four sampling years (Year: 2011, 2012, 2013, 2014).

	THg	MeHg	%MeHg
WT	0.31	**0.02**	<**0.01**
Veg	0.31	<**0.001**	<**0.001**
Depth	<**0.0001**	<**0.0001**	<**0.0001**
Year	0.28	0.30	0.39
WT * Veg	0.29	0.63	0.38
WT * Depth	<**0.0001**	**0.01**	<**0.01**
Veg * Depth	0.07	<**0.01**	**0.03**
WT * Year	<**0.01**	0.10	0.73
Veg * Year	0.76	0.50	0.20
Depth * Year	<**0.0001**	<**0.0001**	0.08
WT * Veg * Depth	0.83	0.58	0.70
WT * Veg * Year	0.89	0.70	0.46
WT * Depth * Year	0.24	0.11	0.12
Veg * Depth * Year	0.99	0.96	0.97
WT * Veg * Depth * Year	0.10	0.08	**0.02**

Bold *p* values are statistically significant ($p < 0.05$).

table differences (2013) peat MeHg concentrations in the Low WT treatments became elevated compared to the High WT treatments in the peat increments coinciding with and just below the lowered water table position (Fig. 1g). Peak MeHg concentrations occurred in the 40–50 cm sampling depth (Fig. 1g), but were not statistically greater than those of the High WT treatments ($p = 0.07$). From 20 to 50 cm below the peat surface, 2013 MeHg concentrations were elevated in the Sedge Only treatments under both water table conditions, although the effect was most pronounced with the High WT mesocosms (Fig. 1g). In 2014, significantly elevated MeHg concentrations in the Low WT treatments were measured in the 30–40 cm sampling depth, coinciding with the lowered water table position, as compared to those subjected to the High WT conditions ($p < 0.01$; Fig. 1h). The High WT treatment with Ericaceae removed (Sedge Only treatment) again resulted in elevated MeHg concentrations down to 40 cm below the peat surface in 2014 (Fig. 1h).

Total Hg concentrations significantly changed with depth ($p < 0.0001$, Table 1; see Fig. 1 for annual average treatment profiles; Fig. S2 for all mesocosm THg profiles each year). Peat profiles of THg concentrations in the first two years (2011 and 2012) were similar among the gradually-implemented treatments (Fig. 1a, b). However, the main treatment factors of water table and plant functional group did not have an overall influence on peat THg concentrations

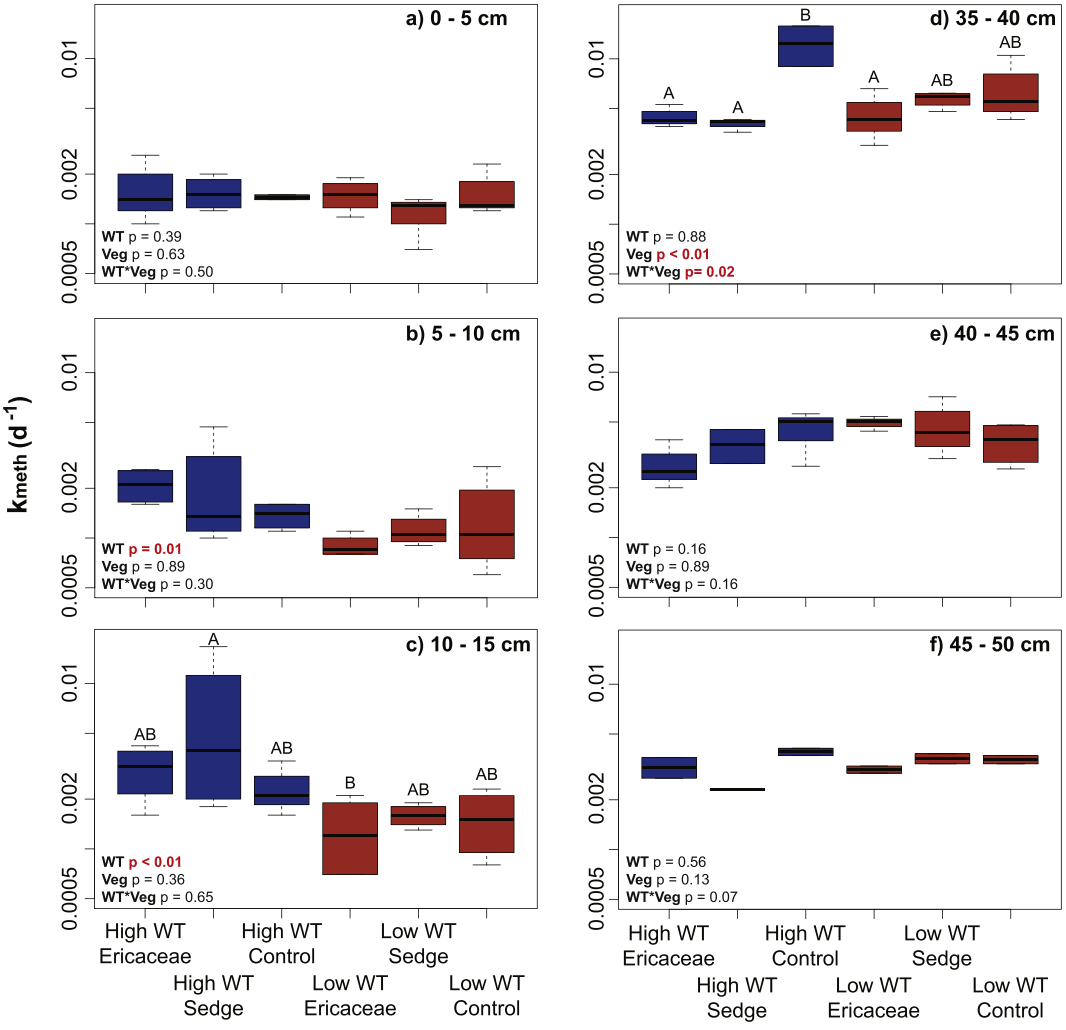

Fig. 2. Mean k_{meth} (d^{-1}) among the six experimental treatments in the upper 15 cm of the peat profile (left column) and 35–50 cm below the surface (right column). High WT treatments are presented as blue boxplots while the Low WT treatment boxplots are in red. Letters denote statistically similar groups among the six treatments in the 10–15 cm and 35–40 cm depth increments. No significant differences among treatments for any other peat depths. The bottom and top of the boxplots represent the 25th and 75th quantiles, respectively, while the whiskers represent the range of data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Table 1). Despite the lack of overall influence of the water table and plant functional group treatments, significant interactions between the water table treatment and both the sampling depth ($p < 0.0001$) and sampling year ($p < 0.01$) were observed to influence peat THg concentrations. The occurrence of significant water table effects was therefore dependent upon the peat depth within the profile and the length of exposure to drought conditions. A distinct difference between the THg profiles of the Low WT and High WT treatments became evident in 2013 after the implementation of more extreme WT treatments, near the lowered water table position of approximately 35 cm (Fig. 1c). Peat THg concentrations at both 30–40 and 40–50 cm below the peat surface in 2013 were significantly affected by the water table treatments (both $p < 0.05$), with higher peat THg concentrations in the Low WT treatments at these depths in 2013 (Fig. 1c). In 2014, water table position significantly affected THg concentrations in the peat, although only at 30–40 cm below the surface ($p < 0.01$), with greater concentrations near the mean water table positions in the Low WT treatments (Fig. 1d).

Similar trends were observed in peat THg and MeHg stocks (expressed in ng cm^{-3}) that takes into account changes in solid phase bulk density throughout the experiment (Fig. S3). As the profiles of mass concentrations of THg and MeHg (ng g^{-1}; Fig. 1) and the profiles of stocks of THg and MeHg (ng cm^{-3}; Fig. S3) are similar in each sampling year, these trends in peat Hg are not likely the result of any peat subsidence sustained during the experiment, but rather suggest the influence of hydrochemical and biological processes resulting from the imposed water table and plant functional group treatments.

3.2. Hg(II) methylation and MeHg demethylation

During the 2015 isotopic incubations, a significant, positive relationship between %MeHg and k_{meth} was observed, while the relationship between %MeHg and k_{demeth} was not significant (Fig. S4). No significant influence of either water table position or plant functional group was observed on k_{demeth} at any of the incubated depths. In terms of Hg(II) methylation, the High WT treatments had higher k_{meth} values than the Low WT treatments at depths from 5 to 15 cm (Fig. 2b, c). However, at a depth of 35 to 45 cm below the peat surface that coincides with the observed increases in ambient peat MeHg concentrations, no significant influence of water table treatment on k_{meth} was observed (Fig. 2d, e). Given that the mean water table position for the Low WT treatments was approximately 40 cm below the peat surface, this depth was predominantly oxic during the peat collection and isotopic incubation.

At 35–40 cm below the peat surface, a significant influence of the vascular plant functional group was apparent ($p < 0.01$) and this effect was dependent upon the water table treatment, with a significant interaction between water table and plant functional group ($p = 0.02$; Fig. 2d). The High WT Sedge only, High WT Ericaceae only and Low WT Ericaceae only treatments had significantly lower k_{meth} than the High WT Control treatment (Fig. 2d).

3.3. MeHg, THg masses within the peat profile

In the Low WT treatments, a decrease in the mass of THg and MeHg bound to the solid phase peat in the upper depths of the profile occurred from 2012 to 2013 (Figs. 3, S5). During this same period, an increase in THg and MeHg mass in the solid phase near the lowered water table position was observed (Figs. 3, S5). These two years were selected to directly examine the immediate impact of more severe drought conditions, as simulated by more extreme lowering of the water table position in 2013 as compared to 2012, on the mass of THg and MeHg throughout the peat profile. Water levels in the Low WT treatments were lowered to ~30–40 cm below the peat surface at the beginning of the 2013 growing season as compared to ~20 cm below the peat surface in 2012. From 2012 to 2013, the masses of both THg and MeHg in the upper 10–30 cm of the peat profile consistently decreased across all six treatments (Fig. S5a, c). At 30–40 cm below the peat surface, contrasting trends were observed depending upon the imposed water table treatment (Figs. 3, S5). In the mesocosms subjected to High WT conditions, masses of both THg and MeHg declined on average at 30–40 cm below the surface from 2012 to 2013 (Figs. 3, S5). In contrast, THg and MeHg both increased on average at a depth of 30–40 cm in the Low WT treatments (Figs. 3, S5). In the Low WT – Sedge Only treatment, all four replicate mesocosms displayed an increase in MeHg mass at 30–40 cm in the peat profile; with the mass difference between 2012 and 2013 not crossing zero (Fig. S5d).

3.4. Peat-pore water MeHg, Hg(II) partitioning

Greater dissolution/desorption of MeHg from the peat into the pore water in the upper part of the profile in the Low WT table treatments in 2013 and 2014 was reflected by significantly lower K_D values as compared to the High WT treatments (Figs. 4, S6). Similarly, relatively more Hg(II) was found to be in the pore water phase in the near-surface samples of the Low WT treatments in 2014 (Fig. 4a). Although in 2013 no significant influences of the plant functional groups were observed (Fig. S6), in 2014 these treatments significantly affected the partitioning of Hg(II) in the upper peat depths, and both Hg(II) and MeHg deeper within the peat profile in 2014 following the second full growing season of larger WT treatment differences (Fig. 4).

4. Discussion

Water table position strongly influenced THg and MeHg concentrations in the peat profiles over the course of the experimental manipulations, while altered plant functional groups significantly influenced only solid phase MeHg concentrations (Table 1). Lowering of the water table resulted in decreased THg and MeHg stocks in peat depths above the position of the water table, with a simultaneous increase in these concentrations in the peat depths at or below the experimental water table positions. The observed decrease in peat THg concentrations above the lowered water table may be the result of enhanced dissolution/desorption of inorganic Hg from the solid phase, indicated by significantly lower K_d values at 20 cm below the peat surface for Hg(II) located above the mean water table position in the Low WT treatments (Fig. 4). Surface peat is sensitive to decomposition above the lowered water table position (Ise et al., 2008). Because Hg has a strong affinity for organic matter and commonly forms complexes via thiol moieties (Graham et al., 2012), increased degradation of soil organic matter in the aerated zone releases Hg(II) from the solid phase peat and results in enhanced accumulation of Hg(II) in the pore water in association with dissolved organic carbon (Haynes et al., 2017a). Water table drawdown creates an oxic environment in the peat above the zone of saturation, which suppresses Hg(II) methylation (Ullrich et al., 2001). It is therefore plausible that the change in redox state with the imposed drawdown of the water table in the Low WT treatment could have led to the observed decrease in MeHg concentrations in the upper peat above the saturated zone. In addition to reduced Hg(II) methylation under oxic conditions, accumulation of MeHg in the pore water may further contribute to reduced solid phase MeHg concentrations in the upper peat depths above the position of the lowered water tables.

As a result of the experimental water table treatment, solid phase MeHg and THg concentrations increased near the position of the lowered water table. Despite the enhanced aeration of surface peat during periods of water table drawdown, periodic re-saturation of peat depths near the water table has been observed to promote MeHg production in peatlands (Coleman Wasik et al., 2015). Water table fluctuations experienced by the Low WT treatments simulate the likely effect of climate change (Whittington and Price, 2006; Waddington et al., 2015) and may increase MeHg production through the regeneration of the terminal electron acceptors necessary for the methylation process (Coleman Wasik et al., 2015). Periods of oxic conditions resulting from

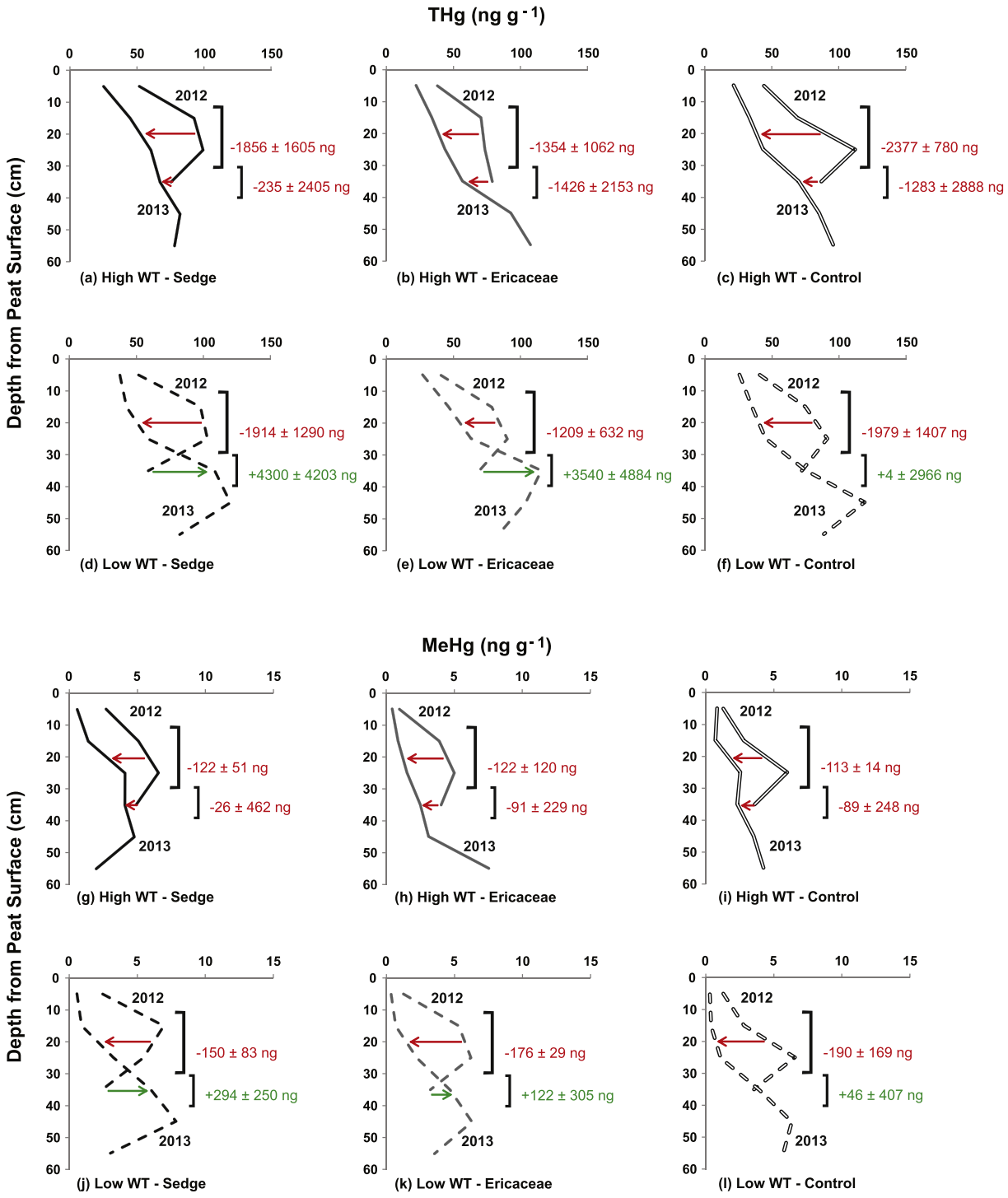

Fig. 3. Mean concentration profiles of (a–f) THg and (g–l) MeHg for the six crossed WT and plant functional group treatments. Values adjacent to the square brackets indicate the mean ± standard deviation ($n = 4$ per treatment) change of THg masses (in ng) and MeHg masses (in ng) in 1000 cm^3 of peat in the 10–30 cm and 30–40 cm increments below the peat surface in 2012 as compared to 2013 in each of the six treatment combinations. Arrows indicate direction of change in mass between 2012 with the gradually-imposed treatments and following the first full year of more extreme drought conditions in 2013. Red values and arrows represent a decrease in mass while green values and arrows represent an increase in mass. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fluctuations in the lowered water table position may therefore prime rather than suppress Hg(II) methylation as the pool of terminal electron acceptors is refreshed and available for use by methylating communities once anoxic conditions resume with subsequent episodic or seasonal water level increases (Coleman Wasik et al., 2015). The significant relationship between peat %MeHg and k_{meth} and the lack of a relationship between peat %MeHg and k_{demeth} collectively suggest that Hg(II) methylation was a stronger control on net MeHg accumulation during our measurements than the opposing process of MeHg demethylation (Mitchell and Gilmour, 2008; Lehnherr et al., 2012). However, no significant water table influence on the instantaneous methylation rate potentials measured in the peat near the lowered water table position was observed. Despite the similar Hg(II) methylation potential between the High and Low WT treatments at 35 to 45 cm below the peat surface, the elevated ambient MeHg concentrations observed at these depths in the Low WT mesocosms in 2013 and 2014 (Fig. 1) following prolonged

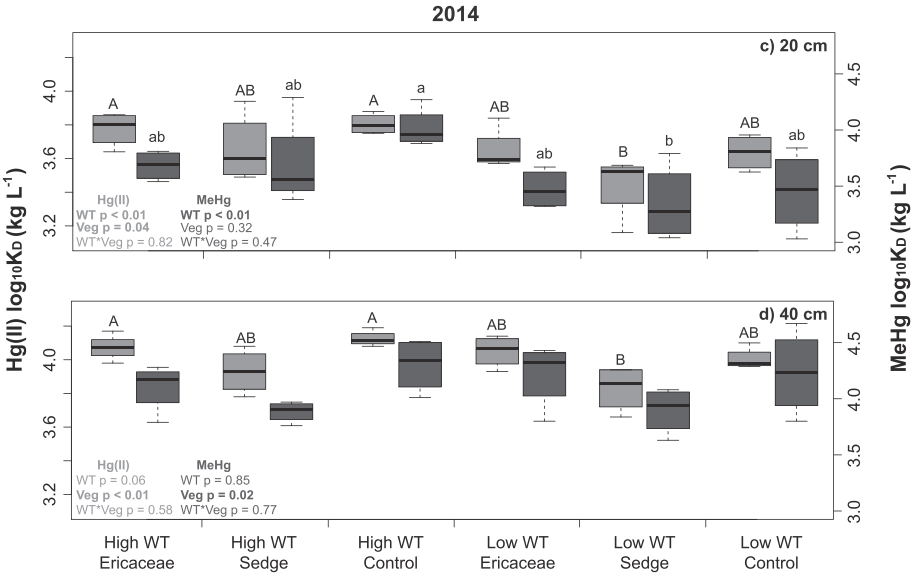

Fig. 4. Soil-water partition coefficients ($logK_D$) for Hg(II) (light gray) and MeHg (dark gray) at 20 and 40 cm below the peat surface among the six crossed water table and plant functional group treatments in 2014 ($n = 4$ per treatment). Letters denote statistically similar groups. The bottom and top of the boxplots represent the 25th and 75th quantiles, respectively, while the whiskers represent the range of data.

and increasingly severe exposure to the treatments cannot be accounted for by the k_{meth} trends. The measured k_{meth} values are instantaneous rate potentials (Mitchell and Gilmour, 2008), and may not be reflective of other time periods during which isotopic incubations were not conducted. The periodic nature of the imposed water table fluctuations may influence the stocks of MeHg in the peat depths that experience aeration and re-saturation. However, such instantaneous measurements of rate potentials cannot capture this episodic process and may not reflect previous exposure to such fluctuations in redox conditions that are evident in ambient MeHg concentration profiles. Therefore, it is likely that the increase in ambient MeHg concentrations near the lowered water table with prolonged exposure to the treatments is the result of enhanced MeHg production due to periodic refreshing of the pool of available terminal electron acceptors such as sulfate. This result aligns with the observation of elevated sulfate concentrations in pore water collected from the 40 cm depth of the treatments with lowered and variable water table positions and sedge vegetation (Haynes et al., 2017a).

Unlike ambient peat THg concentrations that were not influenced by the plant functional group treatments, peat MeHg concentrations were affected by the vascular plant community. In the rooting zone of sedge-only mesocosms, elevated MeHg concentrations were observed. Oxygen is taken up by the roots of ericaceous shrubs and the associated mycorrhizal fungi of these plants thereby limiting its availability to heterotrophs (Romanowicz et al., 2015). Sedge aerenchyma actively shuttle oxygen to their rooting zone (Crow and Wieder, 2005) and may influence MeHg production either negatively via the creation of a more oxic environment, or positively via the regeneration of terminal electron acceptors. Additionally, sedges have been observed to enhance Hg deposition to peat from the atmosphere by the sedge aerenchyma (Haynes et al., 2017b) that may contribute to elevated peat Hg(II) concentrations and provide additional Hg(II) available for methylation. The similarity in the ambient MeHg profiles for the Control and Ericaceae only treatments, particularly under saturated conditions, may suggest that oxygen leaked from sedge roots may be consumed by the ericaceous shrubs and their mycorrhizal fungi in the Control treatments. However, when Ericaceae are removed the oxygen shuttled by sedge aerenchyma to the rooting zone may function similarly to water table drawdown as a mechanism to regenerate terminal electron acceptors. Anaerobic respiration facilitated by the regeneration of the oxidized forms of nitrogen, iron, and sulfur due to root oxygen loss has been previously documented in wetland soils (e.g. Mueller et al., 2016). The influence of the removal of the ericaceous shrubs was most notable under High WT conditions, with both elevated ambient MeHg concentrations in the sedge rooting zone of the peat profile (Fig. 1g, h) and with significantly enhanced k_{meth} at 35–40 cm below the peat surface as compared to the other treatments (Fig. 2d). Therefore, the combined redox potential balanced by the anaerobic conditions of peat saturation and the contributions of oxygen by active shuttling of sedge aerenchyma may be responsible for the elevated MeHg concentrations in the sedge only treatment exposed to prolonged saturation.

4.1. Hydrochemical transport as mechanism for shifting peat Hg profile

In the Control and Ericaceae only treatments under saturated conditions, the mechanism responsible for the consistent observed decreases in ambient THg and MeHg solid phase concentrations both above and within the zone of saturation with the introduction of the treatment conditions is unclear (Figs. 3, S5). It is possible with sustained reducing conditions resulting from maintained saturation, MeHg production may become suppressed due to the accumulation of sulfide (Benoit et al., 1999), possibly enabling more dominant demethylation to result in decreased MeHg concentrations. However, the apparent accumulation of MeHg and THg near the base of the peat profile would not likely result from inhibited methylation. Another mechanism such as the diffusion of chelators from ericoid mycorrhizal fungi, which may form complexes with Hg similar to those observed with zinc (Martino et al., 2003), may facilitate the observed trends particularly under saturated conditions in the peat. Further experimental research will be required to examine the potential role of a chelator diffusion mechanism in controlling peat Hg translocation under saturated, reducing conditions.

The simultaneous decrease in the near-surface peat THg and MeHg concentrations and accumulation within the zone of active water table fluctuation in the peat profile in the Low WT treatments, combined with the trends in Hg(II) and MeHg partitioning to mobile pore waters, suggests that these observed changes in the solid phase peat with exposure to the treatments may be influenced by translocation mechanisms. Desorption of Hg from the decomposition of peat soil and subsequent re-adsorption at different depths has previously been observed to account for natural internal enrichment within the soil profile of a minerotrophic fen (Franzen et al., 2004) and in deep lake sediments resulting in the transfer and retention of Hg near the sediment-water

interface (Matty and Long, 1995). Leaching of Hg in association with dissolved organic matter from the solid phase peat in the Low WT treatments was primarily attributed to enhanced decomposition in the aerobic upper depths (Haynes et al., 2017a), which may account for the increased partitioning of both Hg(II) and MeHg from the solid phase peat to the pore water in the shallow peat depths under Low WT conditions (Fig. 4). Vertical diffusion of DOC in peat has been previously reported in sub-boreal *Sphagnum* peatlands, with the observation of relatively young DOC at a depth of 2 m below the peat surface (Wilson et al., 2016). Further to this, Tfaily et al. (2018) used detailed characterization of dissolved organic matter (DOM) composition to demonstrate the role of lateral and vertical advection of pore water. Redox oscillations with fluctuating water table depth promoted high organic matter turnover in the intermediate peat depths and downward advection transported the DOM from the surface to deeper peat layers (Tfaily et al., 2018). This advective mechanism may also facilitate the vertical translocation of Hg bound to mobile DOM. Braaten and de Wit (2016) suggest that increasing concentrations of THg with depth into the organic layers of a peatland were likely the result of downward transport of organic matter to which Hg was associated. Different plant functional types have previously been observed to affect dissolved organic matter in peat pore water, with vascular plants such as graminoids and ericaceous shrubs responsible for the destabilization of organic matter and the promotion of carbon losses (Robroek et al., 2016). In the sedge treatment, aeration of the peat in the rooting zone via oxygen leakage from the aerenchymatous tissues of the sedge vegetation (Greenup et al., 2000; Crow and Wieder, 2005; Waddington et al., 2015) and the lack of competition for available oxygen by Ericaceae (Romanowicz et al., 2015) may have contributed to peat degradation deeper within the peat profile and the release of Hg(II) and MeHg into the pore water phase. Hydrological transport with water table fluctuations may act to direct dissolved species in the pore water to accumulate in the solid phase within the fluctuation zone. Similar to mineral and other organic soils, the abundance of reduced sulfur groups may play a role in governing Hg(II) and MeHg resorption to the solid phase (Skyllberg et al., 2000; Navrátil et al., 2016). However, the mechanism responsible for Hg(II) and MeHg re-sorption to the peat deeper within the profile is not clear and requires further examination.

Susceptibility of solid phase Hg(II) concentrations to changes in water table position and plant community composition have important implications for the use of peat Hg profiles as records of historical atmospheric Hg deposition (e.g. Biester et al., 2007). Our results suggest that translocation of Hg within the peat profile could lead to erroneous interpretations of historical atmospheric contributions if the studied peatland is exposed to lowered, fluctuating water tables promoting enhanced organic matter decomposition and associated Hg partitioning to pore water. However, the overall magnitude of Hg translocation from the upper peat and resorption mechanisms deeper within the peat profile requires further investigation. Matty and Long (1995) determined that the decay of organic matter in lake sediment profiles released significant amounts of Hg into sediment pore water and resulted in the transfer and retention of Hg near the sediment-water interface. The effect of the diagenetic process of decomposition on peat records of Hg in the top 1 m of peat was determined by Biester et al. (2012) to be minimal, likely due to the high levels of industrial contributions to atmospheric deposition. For other redox-sensitive elements including iron and manganese, Biester et al. (2012) observed peat decomposition, largely controlled by climatic and hydrological conditions, to be an important factor in determining the distribution of these elements through dissolution and diffusion, particularly under anaerobic conditions. In natural peatland environments, flow through the peat may influence the relative importance of vertical Hg translocation within the peat profile as compared to lateral flushing of mobile Hg in peat pore water. The observed release of Hg from the solid phase into the mobile pore water of the PEATcosm mesocosms is indicative of the potential for redistribution of peat Hg, which would impact the reliability of peat as natural archives of atmospheric Hg deposition. Further research is required to determine the magnitude of Hg translocation within the peat profile when a natural peatland is exposed to a lowered, fluctuating water table position.

5. Conclusions

The lowering of water table position in peat, as anticipated with climate change (Whittington and Price, 2006; Waddington et al., 2015), resulted in enhanced Hg(II) and MeHg concentrations in the zone of fluctuation. With the decomposition of organic matter in peat depths exposed to oxic conditions due to water table lowering, Hg(II) and MeHg may be re-distributed within the peat profile as water tables fluctuate. This influence appears to also increase the dissolution/desorption of Hg(II) and MeHg from the solid phase peat near the lowered water table into the pore water. Vegetation dynamics overlay these patterns, with the regeneration of terminal electron acceptors and exudation of labile carbon substrates promoting enhanced MeHg concentrations within the rooting zone. These effects of sedges, combined with the influences of water table position and variability, outweigh the potential suppression of Hg(II) methylation by greater oxygen availability in the peat via aerenchymatous shuttling. Periodic flushing of the peat during more frequent high-flow events as expected with climate change (Waddington et al., 2015), will likely result in enhanced export of Hg (II) and MeHg to downstream aquatic ecosystems (Haynes et al., 2017a). If climate-induced changes favor lowered, fluctuating water tables and sedge-dominated plant communities, Hg(II) and MeHg accumulation may be enhanced in aquatic systems hydrologically connected to impacted peatland ecosystems, increasing the potential for greater uptake in food chains and exposure to wildlife and human populations.

The simultaneous decrease in Hg(II) and MeHg concentrations in the near-surface peat and accumulation in depths coinciding with the lowered water table positions, combined with the trends in Hg(II) and MeHg partitioning to mobile pore waters, suggest that vertical hydrochemical transport of Hg(II) and MeHg within the peat profile may contribute to the observed trends in ambient concentrations over time. With the decomposition of organic matter in peat depths exposed to oxic conditions due to water table lowering, Hg(II) and MeHg may be re-distributed within the peat profile as water tables fluctuate. Further examination of the mechanisms responsible for re-sorption of Hg(II) and MeHg from pore water to solid phase peat deeper with the peat profile is warranted.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.05.072.

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