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# Mercury and methylmercury biogeochemistry in a thawing permafrost wetland complex, Northwest Territories, Canada

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## Abstract:

In arctic and sub-arctic environments, mercury (Hg), more specifically toxic methylmercury (MeHg), is of growing concern to local communities because of its accumulation in fish. In these regions, there is particular interest in the potential mobilization of atmospherically deposited Hg sequestered in permafrost that is thawing at unprecedented rates. Permafrost thaw and the resulting ground surface subsidence transforms forested peat plateaus into treeless and permafrost-free thermokarst wetlands where inorganic Hg released from the thawed permafrost and draining from the surrounding peat plateaus may be transformed to MeHg. This study begins to characterize the spatial distribution of MeHg in a peat plateau–thermokarst wetland complex, a feature that prevails throughout the wetland-dominated southern margin of thawing discontinuous permafrost in Canada's Northwest Territories. We measured pore water total Hg, MeHg, dissolved organic matter characteristics and general water chemistry parameters to evaluate the role of permafrost thaw on the pattern of water chemistry. A gradient in vegetation composition, water chemistry and dissolved organic matter characteristics followed a toposequence from the ombrotrophic bogs near the crest of the complex to poor fens at its downslope margins. We found that pore waters in poor fens contained elevated levels of MeHg, and the water draining from these features had dissolved MeHg concentrations 4.5 to 14.5 times higher than the water draining from the bogs. It was determined through analysis of historical aerial images that the poor fens in the toposequence had formed relatively recently (early 1970s) as a result of permafrost thaw. Differences between the fens and bogs are likely to be a result of their differences in groundwater function, and this suggests that permafrost thaw in this landscape can result in hotspots for Hg methylation that are hydrologically connected to downstream ecosystems. Copyright © 2016 John Wiley & Sons, Ltd.

KEY WORDS mercury; methylmercury; discontinuous Permafrost; permafrost thaw; wetlands; poor fens; dissolved organic matter (DOM); dissolved organic carbon (DOC)

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## INTRODUCTION

The Taiga Plains ecoregion in north-western Canada has been one of the most rapidly warming regions on Earth in recent decades (Jorgenson *et al*., 2010). For example, average temperatures in the Mackenzie Valley have increased at least 1.7 °C in the last century (Environment Canada, 1995). There is mounting evidence that this warming is affecting the water cycle throughout the Taiga Plains. For example, the frequency of mid-winter melt events has increased (Semmens *et al*., 2013), end-of-winter snow melt occurs earlier (Francis and Vavrus, 2012), and key variables such as snowpack depth (Cohen *et al*., 2012), snow cover extent (Derksen and Brown, 2012), surface water storage (Kurylyk *et al*., 2014a, b), groundwater flows (Bense *et al*., 2012) and seasonal precipitation patterns (Climate Change, 2013) have deviated from long-term means. These changes have resulted in significant changes in the environmental chemistry and particularly how the landscape cycles nutrients and metals. Being a critical factor in the piscavorious diets of northern communities, the impact of these warming-induced changes to the water cycle on mercury cycling is not well understood.

Permafrost thaw is one of the most important and dramatic manifestations of warming (Rowland *et al*., 2010) in the Taiga Plains. The southern Taiga Plains lies within the discontinuous permafrost zone (Kwong and Gan, 1994), where permafrost is largely confined to treed peat plateaus that occur as islands within wetland complexes along with treeless non-permafrost collapse scar bogs, fens and channel fens (Robinson and Moore, 2000).

As permafrost in peat plateaus thaws, the ground surface subsides, which allows for the expansion of

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surrounding wetlands (Jorgenson and Osterkamp, 2005), thus permafrost thaw transforms forested peatland plateaus into treeless, permafrost-free (thermokarst) wetlands. Between 30 and 65% of the permafrost in the southern fringe of the discontinuous permafrost zone has degraded or disappeared over the last 100 to 150 years (Beilman and Robinson, 2003). This change brought about concomitant increases in thermokarst wetland coverage (Quinton *et al*., 2011a, b, c) and peat plateau-to-permafrost free wetland conversion rates that have increased in recent decades (Patankar *et al*., 2014; Baltzer *et al*., 2014). Rapid climate warming is projected to accelerate permafrost thaw (Schaefer *et al*., 2011; Schuster *et al*., 2011; Lawrence *et al*., 2012), leading to the disappearance of permafrost throughout much of the southern discontinuous permafrost zone over the next half century (Delisle, 2007).

Each ecosystem within the peat plateau wetland complexes has specific hydrological and biogeochemical roles. Peat plateaus have a limited capacity to store water and a relatively large snowmelt water supply. Much of this excess water is directed into adjacent thermokarst wetlands (Wright *et al*., 2009). As such, peat plateaus function primarily as runoff generators, with runoff occurring predominately through the seasonally thawed, saturated layer between the water table and the impermeable frost table below (Hayashi *et al*., 2004). Isolated bogs are entirely surrounded by the raised peat plateaus and are therefore unable to exchange surface or near-surface water with the basin drainage network of channel fens and open-stream channels, although being permafrost-free, they can interact with groundwater. Connected bogs and fens produce runoff, specifically through hydrologically connected cascade sequences which sequentially connect these wetlands to channel fens (Connon *et al*., 2014). Some connected wetlands are suitably topographically situated to receive groundwater inputs and are more properly described as poor fens. During periods of high moisture supply and/or limited ground thaw, such connected sequences cascade water through the series and into a channel fen. Finally, channel fens collect water from adjacent plateau–wetland complexes and convey it downstream along their broad (~50–100 m), hydraulically rough channels to streams and rivers.

### *Implications of permafrost thaw on mercury cycling*

Methylmercury (MeHg) is a potent neurotoxin of growing environmental concern in communities throughout the Taiga Plains and much of northwestern Canada where bioaccumulation and biomagnification in food webs (Fitzgerald and Lamborg, 2003) have led to advisories against the consumption of high trophic level piscivorous fish species that are an important part of traditional diets. In the study region of the southern Taiga Plains (refer to Figure 1), several lakes have had consumption advisories placed on certain fish species as a result of mercury levels. In its inorganic forms, mercury (Hg) is readily eliminated by bodily systems; however, as MeHg bioaccumulates in aquatic foodwebs, MeHg concentrations in fish tissues can reach over one million-fold greater than the water, in which the fish live (Driscoll *et al*., 2007), so even though mercury and methylmercury concentrations are low in the surface

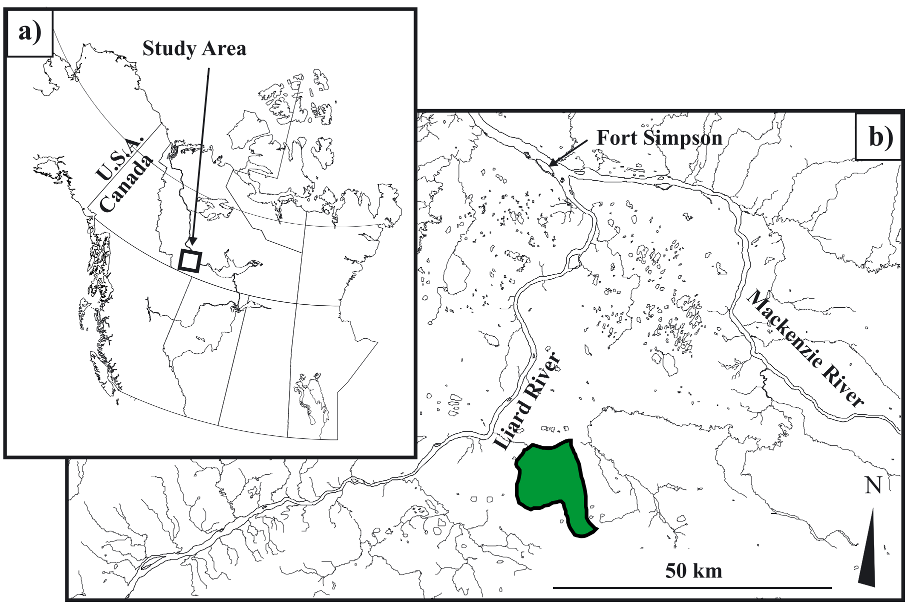


Figure 1. (A) Locations of Taiga Plains study area in Northwest Territories, Canada. (B) The Scotty Creek drainage basin is highlighted. Nearby Jean-Marie and Blackstone systems have mercury (Hg) advisories regarding fish consumption

 

waters in this remote environment, higher trophic level fish such as walleye and pike can exceed human consumption guidelines.

Mercury methylation is principally a biotic process facilitated by the metabolic actions of anaerobic organisms, dominantly sulphate-reducing bacteria (Gilmour *et al*., 2013) which thrive in anoxic environments such as those common in peatlands. Temperate and low boreal peatlands are known sources of MeHg to downstream ecosystems (St. Louis *et al*., 1996; Branfireun and Roulet, 2002; Mitchell *et al*., 2008a, b, c); however, there is a comparative lack of knowledge on Hg cycling in thawing peatland environments. Increased Hg loadings have been documented in rivers draining permafrost landscapes. Leitch *et al*. (2007) observed higher Hg concentrations in the Mackenzie River during periods of high water and implicated the inundation of land and increased bank erosion during high flows. Schuster *et al*. 2011 compared the Total Hg (THg) export from the Yukon River basin to the export from other major northern hemisphere river basins and found it to be between 3 and 32 times higher. The authors specifically implicated widespread permafrost thaw throughout the drainage basin for these increased loadings. Mechanistically, it was shown in northern Sweden that thawing raised peat palsas subsiding into mires released ~40–95% of their stored Hg once submerged (Klaminder *et al*., 2008), suggesting that collapsing peatlands in boreal regions can release significant stores of Hg which can be subsequently methylated.

Studies in the southern Taiga Plains have identified possible mechanisms that support the observations of increasing Hg loadings in northern rivers, specifically that permafrost collapse has the potential to transform the landscape from a net sink of Hg to a net source. Analysis of historical imagery (Quinton *et al*., 2011a, b, c) shows that permafrost thaw causes thermokarst wetlands to expand laterally and coalesce with neighbouring wetlands which transforms bogs from being internally drained to being hydrologically connected to the basin drainage network (Connon *et al*. 2014). Exported Hg resulting from the expanded runoff producing area includes Hg on and within the thawed active layer of peat plateaus, Hg stored in once hydraulically isolated bogs and older Hg released from thawing permafrost.

Because permafrost thaw in the southern Taiga Plains results in ground surface subsidence and inundation, it stands to reason that the saturated and anoxic conditions that favour MeHg production are becoming more prevalent. This suggests that in the drainage basins of the southern Taiga Plains with thawing permafrost-wetland complexes, there is an increase in both the pool of mobilized inorganic Hg (owing to its release from thawing organic permafrost) and in the portion of the landscape that is saturated, resulting in anoxic and potentially methylating conditions. MeHg concentrations also heavily depend on the productivity of methylating bacteria, which requires that sufficient concentrations of sulphate and labile dissolved organic matter (DOM) be available to facilitate their metabolic processes (Branfireun and Roulet, 2002). It has been shown that microbes associated with thawing permafrost in Alaska have among the strongest expression of the gene cluster that is now known to be responsible for Hg methylation (Gilmour *et al*., 2013). The net effect of thaw-induced increases in saturated area, changes to the pool of bioavailable Hg and changing water quality in drainage basins of the southern Taiga Plains leaves little certainty about the potential magnitude of changes in methylmercury production in this region.

### *Objectives*

Given the knowledge gap described in the preceding texts, this study seeks to characterize patterns of MeHg concentrations and related controls within a representative permafrost-wetland complex. Specifically, we examined the THg, MeHg concentrations and DOM characteristics along a peat plateau-hosted thermokarst wetland sequence that includes bogs of ombrotrophic nature at higher elevations and poor fens at lower elevations near the edge of the peat plateau. Along the cascade, each wetland is distinctive in terms of catchment area, water chemistry and vegetation. As such, each wetland provides a unique condition for methylation and mobilization of Hg. Such cascade sequences are common on the landscape, and we hypothesized that MeHg concentrations and the fraction of THg as MeHg (%MeHg) are higher in poor fens than ombrotrophic bogs. Our hypothesis is based on field observations in low boreal, permafrost-free landscapes of northern Ontario. In these regions, poor fens with higher pH than in ombrotrophic bogs exhibit elevated MeHg production partly as a result of some degree of groundwater connectivity and delivery of sulphate and labile organic carbon (Branfireun *et al*. 1996; 2002, 1996; Mitchell *et al*., 2008a, b, c). Assessing the ability of different wetland types produced on thawing landscapes to enhance Hg methylation, and mobility is the first step in understanding the mechanisms responsible for elevated Hg loadings in the Taiga Plains and other wetland-dominated regions with degrading permafrost.

## METHODS

### *Study site*

This study was conducted within the Scotty Creek catchment, a drainage basin located approximately 50 km South of Fort Simpson, Northwest Territories, Canada (refer to Figure 1). Scotty Creek drains 152 $km^2$ of discontinuous permafrost terrain dominated by permafrost peat plateau – thermokarst wetland complexes, separated by channel fens (Quinton *et al*., 2009). Peat has accumulated to depths of between 3.0 and 4.5 m and is underlain by low permeability silt and clay and patterned sands (likely eskers) of glaciofluvial origin. Electrical resistivity imaging across the width of plateaus at Scotty Creek indicated that permafrost is on the order of 10 m thick with edges that are vertical or nearly so, making the transition from permafrost to non-permafrost terrain abrupt (McClymont *et al*., 2013). The upland peat plateau (i.e. permafrost) portion of the wetland complexes occupies approximately 43% of the Scotty Creek basin. However, historical aerial photograph analysis indicates that this value was as high as 70% in 1947 (Quinton *et al*., 2011a, b, c) – a 27% loss in permafrost area in less than 70 years. This study focusses on a ~80 ha plateau–wetland complex bounded upstream and to the south by Goose Lake and by two channel fens which converge at the northern apex of the complex (refer to Figure 2A). The complex contains approximately 50 collapse scar bogs and fens ranging in an area from 0.05 to 5 ha. Most of these wetlands are hydrologically isolated from the basin drainage network with respect to surface and near-surface flows as they are entirely surrounded by peat plateau which occupies a higher elevation than the wetlands. Differentiation between bogs and fens is typically based on vegetation community composition, where the fens have vegetation that includes grasses and sedges indicative of higher nutrient availability. The fens are also typically located in lower topographic positions, and therefore, downstream of the bogs.

*Description of sampled bog and fen landscape sequence*

The representative area selected for study contained six bogs and fens (refer to Figure 2B). The three bogs at higher elevation (B1 to B3) are ombrotrophic in nature, with vegetation dominated by *Sphagnum* spp. and pore water characterized by low pH (<4.6) values (refer to Table I). The lower three wetlands in the series (PF1 to PF3) receive some groundwater inputs and are poor fens with a nearly continuous cover of vascular plants and higher pH (>5) values [National Wetland Working Group (NWWG), 1988]. The bog at the uppermost end of the cascade (B1) receives drainage only from the surrounding plateau, but wetlands downstream of it also receive water from upstream wetland(s) through ephemeral channels which are incised into the permafrost. The hydrological cascade has two terminal connections, each draining into separate arms of a channel fen. The first (denoted 'terminal ombrotrophic discharge') discharges from the north side of the ombrotrophic bog B3, while the second (denoted ' terminal poor fen discharge') discharges from the lowest wetland on the cascade (PF3) (refer to Figure 2 B). Aerial imagery is available for the study site for 1947, 1970, 1977, 2000 and 2010. The upper three wetlands were present in 1947, but each was smaller in area. The three poor fens (PF1, PF2 and PF3) do not appear in the image archive until 1970, indicating that the permafrost thaw and ground surface subsidence that formed these features are relatively recent.

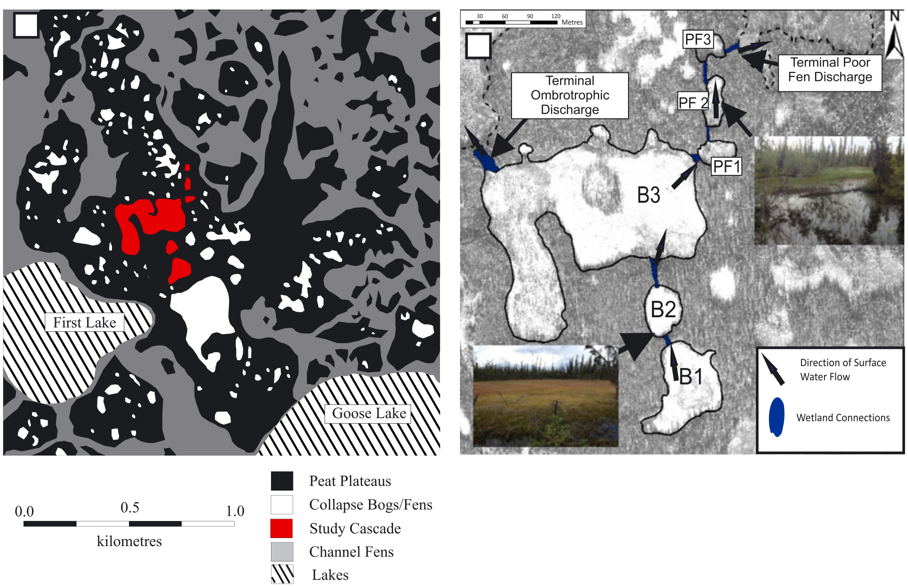


Figure 2. (A) Study wetland/plateau complex with subject cascade highlighted. The plateau is bounded by lakes and channel fens. (B) Outlay of cascade, bogs (B1, B3, B3), poor fens (PF 1, PF2, PF3) and terminal discharge channels labelled. Pictures of B2 and PF 2 inset

 

Table I. Average (mean) recorded characteristic for pore water samples in each wetland.

| | Mercury | | | Dissolved organic carbon (DOC) | | | General chemistry | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Hg [] ng $L^{-1}$** | **MeHg [] ng $L^{-1}$** | **%MeHg** | **DOC (mg/L)** | **SUVA (L/mg/m)** | **HIX** | **Temp (Celsius)** | **pH** | **ORP (mv)** |
| **B1** | 4.46 | 0.04 | 0.69 | 32.22 | 2.48 | 0.91 | 11.74 | 4.01 | 258.1 |
| **B2** | 4.54 | 0.1 | 2.13 | 36.35 | 2.62 | 0.921 | 12.82 | 4.47 | 2.09 |
| **B3** | 5.65 | 0.1 | 1.46 | 47.35 | 2.91 | 0.937 | 14.6 | 4.51 | 186.88 |
| **PF1** | 5.95 | 0.42 | 6.07 | 41.97 | 3.17 | 0.941 | 15.69 | 5.15 | 137.4 |
| **PF2** | 4.82 | 0.43 | 10.67 | 49.06 | 3.42 | 0.954 | 11.78 | 5.46 | 139.71 |
| **PF3** | 6.75 | 0.41 | 5.08 | 42.26 | 3.3 | 0.95 | 13.51 | 5.33 | 17.28 |

*Water sampling*

Pore water samples were taken from each of the bogs and poor fens and from the active (thawed layer) on the adjacent plateau. Sampling was conducted 29 May and 4 June 2013, starting after the main freshet was over to minimize the diluting effects of snowmelt. Samples were taken from a slotted, 0.4 m long, 3/8 inch diameter low-density polyethylene tubing, inserted to a depth of 0.25 m below the wetland ground surface. Pore water was withdrawn with a designated disposable syringe that was used only once. After discarding the first 200 ml, the sampled water was field filtered through 0.45 μm filter and preserved with ultra-trace HCl (1% by volume). Surface water samples were taken from the ephemeral channels draining each of B1, B2 B3, PF1, PF2 and PF3, including the terminal connections (i.e. ephemeral connections draining into the fen). The samples were taken mid-way between the upstream and downstream wetlands after the bottle was rinsed twice with stream water. The samples were then processed through a 0.45 μm filter. Pore water sampling points within the wetlands were arranged along a transect perpendicular to the wetland/plateau interface extending towards the centre of the wetland. Sampling points were established at the wetland–plateau interface, and 1, 3, 7 and 12 m into the wetland. Further sampling points were included in the substrate of each connection. Transects were positioned in an area of the wetland which appeared best represented its overall biophysical and chemical character. The pH, temperature and oxygen reduction potential (ORP) of pore water and surface water samples were measured using a YSI 600XLM multi-parameter probe. Filtered sample splits were taken, including dissolved organic carbon (DOC) and DOM quality analysis.

Additionally, samples for mercury, MeHg and DOC quality from the terminal bog connection (i.e. the channel draining B3) and the terminal poor fen connection (i.e. the channel draining PF3) were sampled nearly daily over the freshet period in order to establish if the poor fens were contributing comparatively more MeHg to the regional flow system than the bogs. In each wetland connection, the water stage was measured and recorded every 30 min using a Solinst Levellogger® installed inside a slotted 10 cm diameter polyvinyl chloride pipe bridging the water table. Levels were calibrated against regular manual discharge measurements and used to establish a rating curve and estimate a full discharge time-series.

*Chemical analyses*

*Mercury.* Ultratrace mercury analysis was performed in the trace metal analytical facility at the Biotron Institute for Experimental Climate Change Research (CALA ISO 17025 accredited). Total mercury was analysed on a Tekran 2600 mercury analyzer in accordance with EPA Method 1631 (Method Limit of Detection (LOD) = 0.02 ng $L^{-1}$). Methylmercury analysis was performed on a Tekran 2700 analyzer according to EPA Method 1630 (Method LOD = 0.02 ng $L^{-1}$). All reported analytical data meet strict ISO Quality Assurance and Quality Control standards, with all blank samples having unquantifiable levels of THg and MeHg and variation among replicates of <20%. Pore water samples with MeHg levels <LOD were assumed to have a concentration of one half the detection limit (0.01 ng $L^{-1}$). Although this assumption would be inappropriate for estimating mass fluxes or landscape yields, it is made here so that non-detected samples are not assigned a value of zero and can be included in the graphical presentation of the data.

*Dissolved organic matter.* Dissolved organic carbon concentration was determined using a Shimadzu TOC-V analyser. The samples were acidified prior to analysis to remove inorganic carbon. Analysis included 10 and 100 mg C $L^{-1}$ standard solutions and Milli-Q water to assure that there was no drift during analysis. Ultraviolet–visible absorption was measured between 200 and 600 nm using a Varian Cary 100 spectrophotometer in a 10 mm quartz cuvette with a Milli-Q water used as a blank. Absorbance at the 254 nm frequency divided by DOC concentration yields the specific UV absorbance ($SUVA_{254}$) value, which is positively and linearly related to the aromacity of the DOC (Weishaar *et al.*, 2003). Fluorescence was measured on a Varian Cary Eclipse spectrofuorometer, and all data were multiplied by the instrument-specific excitation and emission-correction factors as well as corrected for primary and secondary inner filter effects using corresponding absorbance spectra (Ohno, 2002). Analytical drift of the instrument was checked daily by locating and calculating the area of the Raman peak at 350 nm excitation with 0.25 nm steps. Finally, fluorescence scans were used to calculate the Humification Index (HIX), a value between 0 and 1 which is associated with how degraded the DOM is. HIX is calculated from the sum of fluorescence intensities at excitation wavelengths between 435 and 480 nm divided by the sum of intensities between 300–345 and 435–480 using a 254 nm excitation (Ohno, 2002).

## RESULTS

### *Water flux and storage*

The freshet began on 9 May 2013 with flows peaking around May 11. By the beginning of June, flows were low and had generally stagnated in connections 1 and 2 (i.e. those linking B1 with B2 and B2 with B3). Low flows continued in the poor fen connections throughout the thaw season. Water levels in the connections reflected those in the wetland delivering the water. Two trends in levels were observed, which were distinct to the wetland's topographic position on the cascade. Water levels in connections 1 and 2 lowered continually throughout the season. This was also found for the water level in the 'terminal ombrotrophic discharge' linking B3 to the channel fen (refer to Figure 3). The water level in the connections linking the poor fens, however, generally stabilized after the freshet flush. It was observed also that water in the poor fen connections continued to flow throughout the year, while the upgradient connections in the ombrotrophic bogs stagnated by the beginning of July. During the peak of the freshet, both terminal connections were discharging approximately 150 to 180 $m^3 day^{-1}$, dropping to between 2 and 10 $m^3 day^{-1}$ by the end of May (refer to Figure 4A).

### *Surface water*

*DOM*. Strong trends in DOM specific ultraviolet absorbance (SUVA) characteristics were observed during the freshet in both terminal outlets B3 and PF3. SUVA values were similar in the bog and fen outlets but showed similar trends of increasing values on the declining limb of freshet (refer to Figure 4B). DOC concentrations also showed weak increasing concentrations trends in each discharge channel as the freshet progressed.

*Total Hg and MeHg*. Total Hg levels in surface water samples taken from the terminal outlets of the cascade were similar in both connections and ranged between 2.32 and 5.46 $ng L^{-1}$ over the freshet period. Total Hg concentrations were generally higher in water discharged from the terminal ombrotrophic discharge than in the terminal poor fen discharge (refer to Figure 4C). The waters showed marked differences in MeHg concentration. Throughout the freshet, surface water samples taken from the terminal poor fen discharge had dissolved MeHg levels between 4 and 17 times higher than the samples from the ombrotrophic terminal discharge taken on the same day (refer to Figure 4D). The %MeHg in waters discharged from PF3 varied between 5 and 19%, while

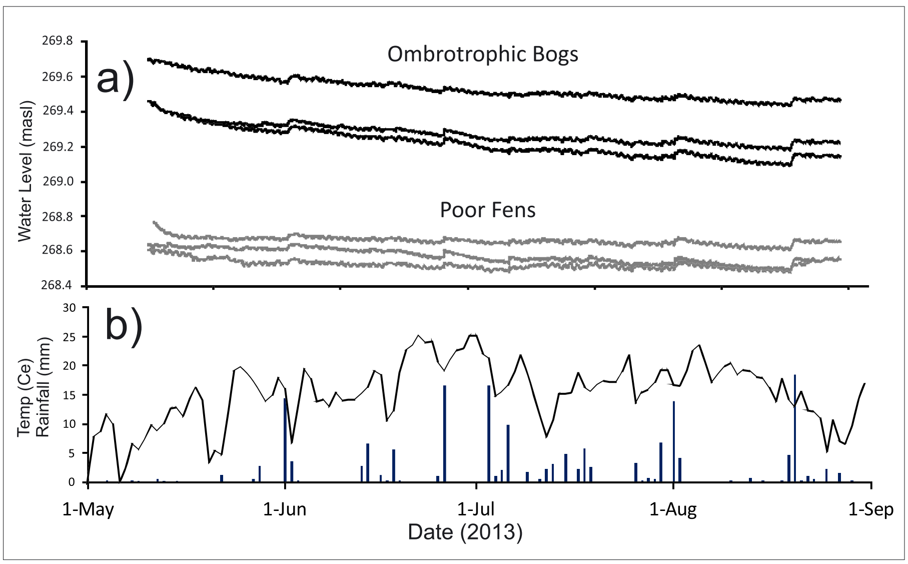


Figure 3. (A) Water levels in each connection in order of elevation: B1/B2, B2/B3, terminal ombrotrophic discharge, PF1/PF2, PF2/PF3 and terminal poor fen discharge. (B) Average daily temperature and rainfall over study period

 

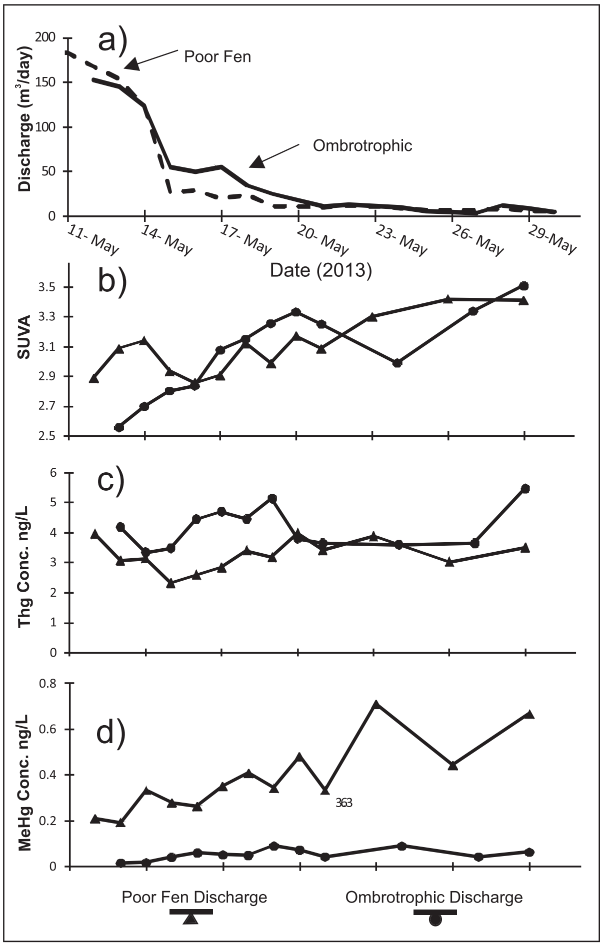


Figure 4. (A) Discharge volumes from each outlet. (B) Specific ultraviolet absorbance (SUVA) values in surface waters from each. (C) Total Hg concentrations in freshet samples. (D) Methylmercury (MeHg) concentrations in freshet samples

those from B3 were between 0.5 and 2.6%. MeHg concentrations in surface waters increased over the freshet period in the poor fen discharge. A similar but less pronounced trend was observed in the ombrotrophic discharge. By extending measured concentrations against flows between measuring events, the terminal ombrotrophic and poor fen discharges were assessed to have exported ~3.0 and 3.6 mg of THg respectively. Similarly, the terminal ombrotrophic discharge exported approximately 0.025 mg of MeHg and poor fen discharge 0.25 mg of MeHg.

### *Pore water*

*General chemistry*. Bog pore waters were more acidic and displayed higher ORP values than the poor fens (Table I). The mean pH for pore waters in each wetland increased from 4.01 to 5.33 between the upper ombrotrophic bog (B1) and the lowest poor fen (PF3). The mean ORP in each wetland was highest in B1 at 258.1 mV and lowest in PF2 at 139.7 mV. No marked differences were observed in electrical conductivity or dissolved oxygen content between bog and fen.

*Total mercury and methylmercury*. Total mercury concentrations from pore water taken from the active (i.e. seasonally thawed) layer of the peat plateaus were on average higher than the pore water samples taken in the bogs and poor fens with THg concentrations between 8.43 and 17.0 $\mathrm{ng\,L^{-1}}$. No clear differences in THg concentrations were observed between the bog and poor fens (refer to Figure 5A).

Methylmercury concentrations on the peat plateaus ranged from 0.01 to 0.11 $\mathrm{ng\,L^{-1}}$ and were generally much lower than the pore water concentrations found in the bogs and fens. Within the bogs and fens, MeHg concentrations in pore water were on average lower in upper, ombrotrophic bogs (B1, B2 and B3) (Figure 5B). In order of toposequence, the mean MeHg concentrations were 0.04 (B1), 0.10 (B2), 0.10 (B3), 0.42 (PF1), 0.43 (PF2) and 0.41 $\mathrm{ng\,L^{-1}}$ (PF3). PF1 and PF3 each had a sample with particularly high levels of MeHg at 2.43 and 2.16 $\mathrm{ng\,L^{-1}}$ respectively. In general, concentrations were higher proximal to the plateau edge in all wetlands.

The percentage of Hg that is methylated is as an indication of the methylating potential of the local environment (Mitchell *et al*., 2009). There was a clear difference between bog and fen pore water %MeHg, with higher mean/median %MeHg in fens (Figure 5C). The mean %MeHg in each wetland can be found in Table I.

Pore water sampled from substrate within the connections ranged from 0.055 to 0.301 $\mathrm{ng\,L^{-1}}$, with 1 to 8% of THg as MeHg. In general, higher MeHg concentrations were observed within connections 3 and 4 (PF1/PF2 and PF2/PF3). The highest concentrations were observed in the connections linking the poor fens, consistent with the overall trend of higher MeHg concentrations in those wetlands.

*Dissolved organic matter*. While there was no clear trend in DOC concentrations between bogs and fens along the cascade (refer to Figure 5D), clear shifts in DOM characteristics were observed. Higher pore water SUVA values indicate that the nature of the bulk DOC is more aromatic in the poor fens and becomes increasingly so with flow distance down the cascade (refer to Figure 5E). Likewise, the HIX values demonstrate that the bulk DOM is increasingly humic in character in the poor fens, indicating that it is relatively more degraded and recalcitrant (refer to Figure 5F). The samples taken from the peat plateau adjacent to the bogs and fens generally exhibited higher SUVA, HIX and DOC concentrations.

*Chemistry and methylmercury relationships*. The median values for pore water MeHg concentration in each wetland were plotted against the respective median values

 

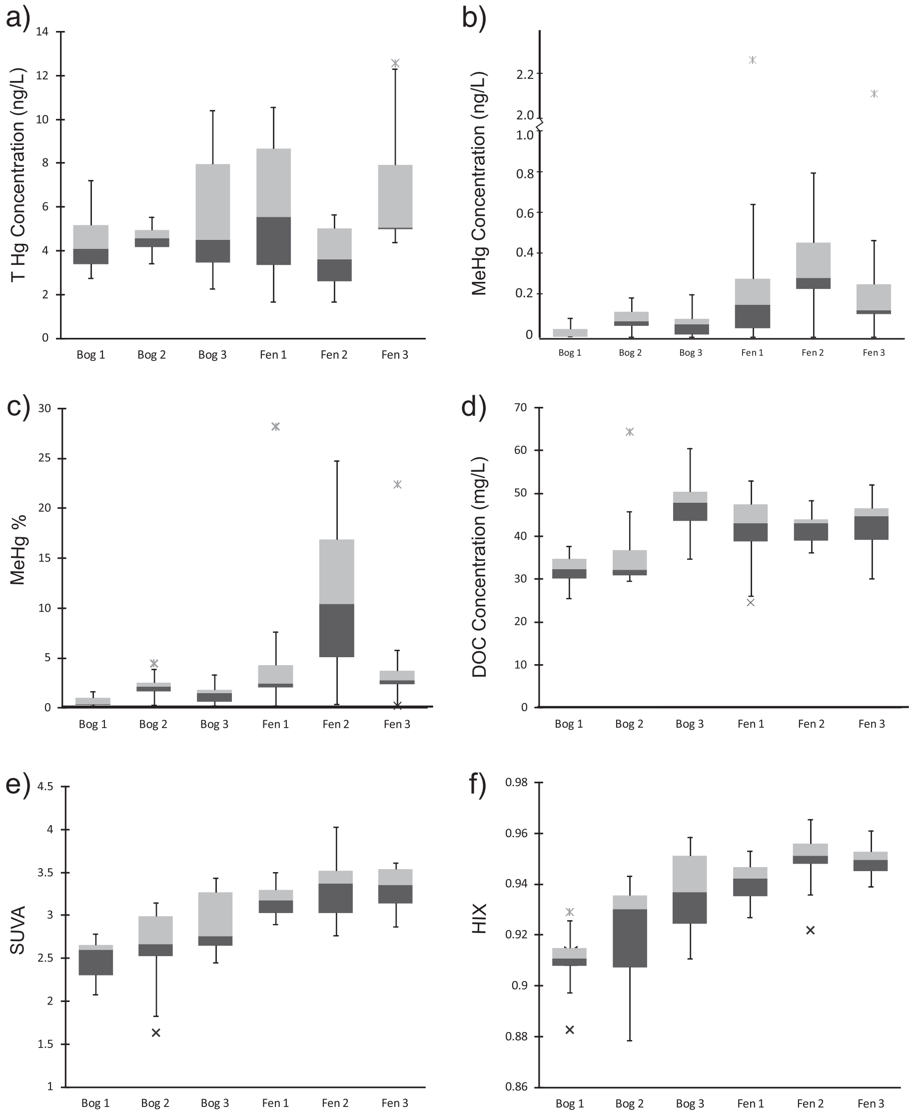


Figure 5. Box plot displaying median and quartile ranges for select properties of each wetland. Whiskers represent 1.5 inter-quartile range. Outliers are displayed. (A) Total mercury concentrations, (B) MeHg concentrations, (C) %MeHg, (D) dissolved organic carbon concentrations, (E) SUVA and (F) Humification Index

for SUVA, pH and ORP in the pore water samples (refer to Figure 6A–C) and a linear regression applied. The median values were used because of the non-normal distribution of the data set. The *p*-values of $<0.05$ were calculated for SUVA and pH, indicating some causal relationship to the comparatively higher MeHg concentrations in the poor fens. A *p*-value $>0.05$ was found for MeHg *versus* ORP, although it was still positively correlated with reducing conditions.

## DISCUSSION

This study found increasing MeHg pore water concentrations along a cascade of collapse scar wetlands within a peat plateau complex, with lower concentrations measured within the ombrotrophic bogs than in the poor fens. Similar trends among ombrotrophic to minerotrophic wetlands have been observed in boreal peatland regions south of the permafrost limit (e.g. Branfireun and Roulet, 2002; Mitchell *et al.*, 2008a, b, c). Southern boreal studies have suggested that poor fens produce and export more MeHg than ombrotrophic bogs as a likely result of increased sulphate availability from groundwater upwelling (Heyes *et al.*, 2000; Branfireun and Roulet, 2002). Our results indicate that the similar mechanisms control the spatial variability of MeHg within peatland complexes on the Taiga Plains, which has important implications for future climate change and permafrost thaw.

 

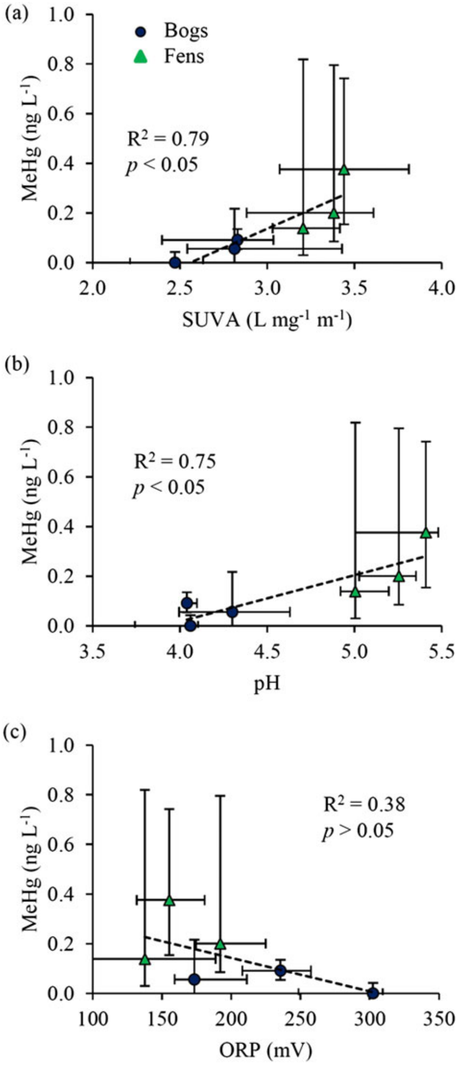


Figure 6. Median values of MeHg ($ng\,L^{-1}$) *versus* median values of SUVA, pH and oxygen reduction potential in pore water samples. Applied linear regression shown (dashed line). The error bars indicate first and third quartiles

Peatland complexes on the Taiga plains have been indicated to be increasingly significant sources of Hg (Leitch *et al*., 2007; Schuster *et al*., 2011). Connon *et al*. (2014) provided a hydrological mechanism for increased Hg export by documenting increasing hydrological connectivity caused by permafrost thaw, whereby previously isolated bogs expand until they become connected to the basin drainage network. This study further demonstrates that hydrological pathways that develop because of thaw, may create areas of high methylation potential at critical points (poor fens) before water is discharged to the wider drainage system. Thus, continued permafrost thaw may increase the production and mobility of MeHg in peatland complexes on the Taiga plains by increasing peatland hydrological connectivity and by enhanced methylation in the type of wetlands that form because of thaw (Connon *et al*. 2014).

Between the upstream B1 bog and the downstream PF3 poor fen within the cascade, we observed consistent trends for not only MeHg concentrations but also for vegetation communities, water chemistry (ORP, pH) and DOM characteristics. The poor fens at lower elevations had the highest pore water MeHg levels, which could both be the result of higher *in situ* net MeHg production or a result of transport from upstream sources. The absence of elevated MeHg concentrations in the upgradient landscape units (peat plateaus and bogs) suggests that increased MeHg production is the most parsimonious explanation. Linear regression analysis between MeHg levels and pH/SUVA would also suggest that the conditions within the wetlands themselves are more conducive with methylation. In agreement with the pore water results, water discharged from the terminal poor fen outlet contained significantly higher concentrations of MeHg than the terminal outlet from the ombrotrophic bog. The general rise in the SUVA values in these outlet samples over the freshet is indicative of a higher percentage of the waters originating from deeper in the peat profile as the water level in the wetlands drop (Olefeldt *et al*., 2013a, b). The SUVA values tend to increase with depth as peat in these deeper layers is more biologically degraded and aromatic.

Characteristics of DOM can affect both the production and mobility of Hg, as labile DOM has been found to increase rates of Hg methylation (Mitchell *et al*., 2008a, b, c), and DOM with high aromaticity have been preferentially associated with the produced MeHg (Graham *et al*., 2013). The change in DOM characteristics (SUVA, HIX) along the cascade suggests that less degraded and more biologically labile DOM is more prevalent in the near-surface water of the bogs than in the poor fens. *Sphagnum* mosses are known to produce not only highly recalcitrant litter but also highly labile DOM (Olefeldt *et al*., 2013a, b). The bogs contain near-continuous *Sphagnum* coverage, while the more recently formed fens are dominated by graminoid vegetation. Further, the fens are smaller, and thus, receive proportionally more DOM inputs from the surrounding peat plateaus, which were shown to have DOM with high SUVA and HIX. Lastly, higher SUVA in fens could indicate greater rates of microbial DOM turnover, as microbial degradation both produce and selectively enrich highly aromatic DOM compounds (Kalbitz *et al*., 2003). Hence, the difference in DOM characteristics between bogs and fens could be a result of both differences in internally produced and degraded DOM as well as differences in the relative mixing of internal and external DOM sources. The poor fens are also likely to have a groundwater discharge function, as high SUVA groundwater upwells through more degraded peat at depth.

 

Concurrent with the rise in DOM aromaticity along the bog to fen cascade, we observed a more than fivefold increase in average wetland MeHg concentration and % MeHg. We also observed increasing DOM aromaticity and MeHg concentrations at the bog and fen outlets during the declining limb of freshet. Our results are thus in agreement with studies that have shown how DOM compounds with higher aromaticity have a higher capacity to bind methylated Hg (e.g. Dittman *et al.*, 2010). However, high DOM aromaticity is not causally linked to high rates of MeHg production. For example, we found high SUVA and HIX but much lower MeHg concentrations and %MeHg in the saturated active zone of peat plateaus than in the wetlands of the cascade. While production of MeHg requires microbially labile DOM, there are also several other rate-limiting reactants and environmental conditions (Ravichandaran, 2004). The fact that the measured pore water DOM aromaticity was higher in the fens than in the bogs and was concurrent with higher MeHg concentrations, suggests that microbially labile DOM is not rate limiting in these environments. This observation may be explained by the rapid consumption of labile DOM in fen pore water making in challenging to measure or a dependency on other environmental variables (e.g. sulphate, pH).

Clearly then, the formation of these cascades results in wetlands of disparate nature in terms of chemical composition, methylation potential and their hydrological function. We suggest that the topographic position of a wetland within a peat plateau-collapsed scar wetland complex determines its chemical makeup and possibly its ability to produce and mobilize MeHg. Permafrost acts as an aquiclude with a potentiometric head beneath it; the head is controlled by upgradient lakes along the channel fen drainage system. When permafrost thaw leads to the formation of a collapsed scar wetland within the peat plateau complex, the new wetland, being free of permafrost can interact with groundwater systems in two ways. First is when the collapse scar wetland is formed above the potentiometric surface, and thus, receives water only from precipitation and from slope runoff draining from the active layer of the surrounding peat plateaus. As such, the new wetland develops as an ombrotrophic bog which can recharge the groundwater system (e.g. B1, B2, B3). Alternatively, the new wetland is at (or below) the potentiometric surface, and thus, receives groundwater discharge. Groundwater input into the wetland is maintained as the head is dissipated by evapotranspiration and/or drainage from the wetland through the flow connection to the next wetland downslope along the cascade. In this case, the new wetland develops into a poor fen (e.g. PF1, PF2, PF3).Weak upward vertical gradients have been consistently observed in poor fens and channel fens at the study site (Christensen, 2014), and the continued overland flow observed in this study in the channels draining the poor fens and their relatively consistent water levels suggest some groundwater discharge into them throughout the summer season. These inputs in turn affect the wetland chemistry, which promotes the chemical conditions (pH, sulphate, etc.) conducive with elevated net methylation rates.

This points to the need for further research in several key areas, including the need for improved understanding of the rates and patterns of groundwater flow between individual wetlands and how this varies over the thaw season (including winter flows) and the link between developing thaw features and areas of preferential methylation on the landscape. Improved understanding is also needed on the possible feedbacks and linkages among hydrological, geochemical and ecological processes operating within these systems that may either enhance or diminish permafrost thaw-induced changes to Hg cycling. Perhaps most importantly, it needs to be investigated if surface flow systems transport the released Hg to critically positioned wetland types where methylation potential is potentially relatively high before being transported to the basin outlet.

## CONCLUSION

This study investigated the surface runoff pathways of a wetland cascade (Connon *et al.*, 2014a, b), local groundwater flows (Christensen, 2014) and spatial patterns of Hg methylation processes for wetland systems all within the context of a wetland cascade on a thawing permafrost–wetland complex. Thermokarst wetlands of permafrost–wetland complexes were shown to have a wide range of chemical and physical characteristics. We attribute this variability to groundwater reactivation, as thaw features develop and evolve into collapsed scar wetlands. Our results suggest that these poor fens, which form as the landscape thaws at critical points in drainage flowpaths, may be areas of preferential methylation

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