



Small-scale variability in peatland pore-water biogeochemistry, Hudson Bay Lowland, Canada

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HIGHLIGHTS

- Peatlands of Hudson Bay Lowland exhibit small-scale variability in vegetation microtopography.
- High resolution sampling of surface pore-water revealed considerable geochemical variability.
- Microtopography in bogs was closely associated with differences to some geochemistry.
- Accurate geochemical estimates require a large sample size from consistent microtopographic forms.
- Variability has implications in long-term environmental monitoring and disturbance assessments.

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ABSTRACT

The Hudson Bay Lowland (HBL) of northern Ontario, Manitoba and Quebec, Canada is the second largest contiguous peatland complex in the world, currently containing more than half of Canada's soil carbon. Recent concerns about the ecohydrological impacts to these large northern peatlands resulting from climate change and resource extraction have catalyzed a resurgence in scientific research into this ecologically important region. However, the sheer size, heterogeneity and elaborate landscape arrangements of this ecosystem raise important questions concerning representative sampling of environmental media for chemical or physical characterization. To begin to quantify such variability, this study assessed the small-scale spatial (1 m) and short temporal (21 day) variability of surface pore-water biogeochemistry (pH, dissolved organic carbon, and major ions) in a *Sphagnum* spp.-dominated, ombrotrophic raised bog, and a *Carex* spp.-dominated intermediate fen in the HBL. In general, pore-water pH and concentrations of dissolved solutes were similar to previously reported literature values from this region. However, systematic sampling revealed consistent statistically significant differences in pore-water chemistries between the bog and fen peatland types, and large within-site spatiotemporal variability. We found that microtopography in the bog was associated with consistent differences in most biogeochemical variables. Temporal changes in dissolved solute chemistry, particularly base cations (Na^+ , Ca^{2+} and Mg^{2+}), were statistically significant in the intermediate fen, likely a result of a dynamic connection between surficial waters and mineral-rich deep groundwater. In both the bog and fen, concentrations of SO_4^{2-} showed considerable spatial variability, and a significant decrease in concentrations over the study period. The observed variability in peatland pore-water biogeochemistry over such small spatial and temporal scales suggests that under-sampling in northern peatland environments could lead to erroneous conclusions concerning the abundance and distribution of natural elements and pollutants alike.

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1. Introduction

Peatlands are wetland ecosystems that sequester large volumes of organic carbon and play a key role in the global carbon cycle (Gorham, 1991), modify the water quality in downstream aquatic ecosystems, and are important habitats for various species (Wieder and Vitt, 2007). Globally, peatlands cover an area of about 4×10^6 km² (~3% of the Earth's land surface), with most peatlands occurring in the boreal and subarctic regions (Gorham, 1991). In Canada, 12% of the country's

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total land area is composed of an elaborate mosaic of bogs (67%), fens (32%), and swamps/marshes (1%) (Tarnocai, 2006). Most of Canada's peatlands are located in northern Ontario and Manitoba in the Hudson Bay Lowland (HBL; Fig. 1), the second largest contiguous peatland complex in the world where approximately 147 Gt (56%) of Canada's terrestrial soil carbon is sequestered in an expanse covering 320,000 km² *ibidem* (Ibid.).

The vast majority of the HBL is covered by a layer of peat, ranging from 0 to ~3 m, and is generally underlain by low conductivity, fine-grained sediments derived of calcite and dolomite from the Paleozoic era (McDonald, 1969; Riley, 2011). Peatland formation is predominantly driven by an interplay of isostatic uplift, climate, and hydrology, beginning with a basal tidal marsh and then rapidly developing into a *Larix*-dominated swamp, *Picea*-forested bog and finally a non-forested bog (Glaser et al., 2004). Bioherms, sedimentary outcrops of karst limestone from the Tyrell Sea, are one of the only upland features in this largely flat terrain, where topographic gradients are very low (typically 0.57 m km⁻¹ towards Hudson Bay) (McDonald, 1969). Sporadically discontinuous permafrost, including palsas (elevated regions of peat with a permafrost core), can be found throughout the landscape.

Forecasted changes in temperature and precipitation in Canada's north are expected to decrease total available soil moisture in northern peatlands, affecting their hydrology and biogeochemical cycles, particularly carbon (IPCC, 2007). In addition to climate change, other natural and anthropogenic disturbances (e.g., forest fires, peat harvesting, peatland dewatering, and resource extraction) may superimpose further impacts on peatland hydrology and biogeochemistry. The collection of baseline hydrological and biogeochemical data is therefore essential for detecting environmental change and impacts to biogeochemical processes in the landscape. Moreover, unquantified spatial and temporal variability of pore-water chemistry may lead to difficulties in proper classification, or even misclassification, of peatlands, as water chemistry (e.g., pH) is often used as a classification metric (Bridgman et al., 1996).

Peatland pore-water quality is controlled by many factors, including precipitation chemistry, groundwater chemistry, plant root uptake/

release, litter inputs and decomposition, cation exchange mechanisms, and microbial decomposition and mineralization (Vitt et al., 1995). Variations in processes such as these are likely to occur at scales as small as individual peatland microtopographic features (hummocks, hollows, and lawns). Such microtopography can have a profound influence on methane production, oxidation, and emission (Mikkela et al., 1995; Waddington and Roulet, 1996). Branfireun (2004) suggested that peatland microtopography influences sulfate reduction and mercury methylation, based on observed differences in solute chemistry profiles among hummocks, lawns and hollows in surface pore-waters.

The pattern of this variability may be predictably driven by chemical reactions and transformations, however these processes vary over space and time. Areas and times of disproportionately high reaction rates relative to the surrounding environment have been described as hot spots, and hot moments, respectively (McClain et al., 2003) and are governed primarily by the convergence of hydrological flow paths and the availability of substrates and terminal electron acceptors. Such elevated biogeochemical reaction rates can lead to broad spatiotemporal variability that can impact studies where limited samples are obtained, however studies on hot spots and hot moments are quite limited in peatlands (see Mitchell and Branfireun, 2005; Mitchell et al., 2008).

Those factors which contribute to peatland pore-water variability are multiplied in large peatland complexes such as the HBL, which are highly heterogeneous at a range of nested spatial scales from the local, within-peatland microform, to intermediate/regional-scale gradients in peatland type and permafrost extent. Such enhanced heterogeneity can directly influence the chemistry of peatland surface and groundwaters, particularly shallow peat pore-waters. For example, a fluctuating water table near the peat surface can have a large influence on biogeochemical spatiotemporal variability, as it is susceptible to variations in temperature, redox conditions, infiltration and nutrient loading (e.g., Moore and Knowles, 1989; Moore and Dalva, 1993; Moore and Roulet, 1993; Silvola et al., 1996; Bellisario et al., 1999). The assessment of the spatial and temporal variability of geochemical parameters in peatland pore-waters, particularly at the local sampling scale, is important, however to the best of our knowledge no studies have been undertaken that have quantified the small-scale variability of dissolved pore-water chemistry in northern peatlands. In support of broader research initiatives on the hydrology and biogeochemistry of extensive peatland complexes, the purpose of this study is to examine the implications of sampling frequency in both space and time for sampling pore-water in two dominant peatland classes in the Hudson Bay Lowland, Ontario, Canada. The objectives of this study are to (i) quantify the small scale spatial variability of pore-water chemistry in a forested ombrotrophic bog and an open intermediate fen in the Hudson Bay Lowland, (ii) measure short-term changes to pore-water chemistry within each peatland type, and (iii) evaluate the effects of microtopography on chemistry and patterns of spatial distribution of dissolved solutes.

2. Study site

This study site is located in the HBL, approximately 90 km from the west coast of James Bay near the Attawapiskat River (52.821° N, –83.884° W; Fig. 1). The HBL is characterized as a low-subarctic region with short, warm summers and long, cold winters (National Wetlands Working Group, 1997). The mean daily temperatures are –22.3 °C and 17.2 °C in January and July, respectively. On average, the region experiences 153 days with a minimum air temperature that is greater than freezing (0 °C). The mean annual rainfall at Lansdowne House (the nearest long-term meteorological monitoring station, 250 km southwest of the study site) between 1971 and 2000 is approximately 700 mm, with about 34% falling as snow (Environment Canada, 2011). More than 75% of the rainfall falls between June and September, the peak growing season. For the duration of this study (July 22 to August 10, 2009), the site received 47 mm of total rainfall.

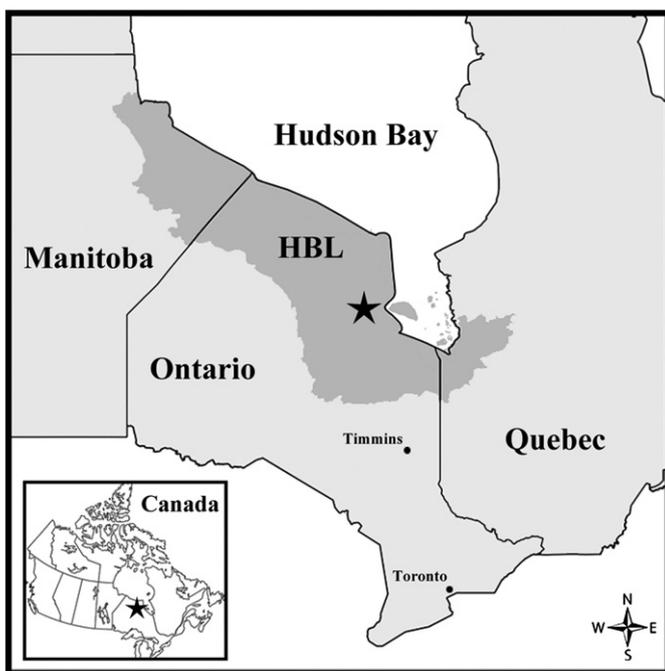


Fig. 1. Location of the study site (shown by star) within the Hudson Bay Lowland (HBL) (dark shading) in Ontario, Canada, approximately 500 km north of Timmins and 90 km west of Attawapiskat, near the Attawapiskat River.

The main wetland types in the HBL are raised bogs, fens (poor-rich), swamps, riparian channel fens, and shallow open bodies of water (National Wetlands Working Group, 1997). We chose a forested ombrotrophic bog and a sedge-dominated intermediate fen for study and comparison on the basis that they are the two dominant peatland types in the region.

The vegetation in the bog is characterized by a sparse cover of dwarf *Picea mariana* (<4 m in height) and *Larix laricina* and an understory of *Chamaedaphne calyculata*, *Rhododendron groenlandicum* (formerly *Ledum groenlandicum*), *Rubus chamaemorus*, and *Eriophorum angustifolium*. The ground layer consists of a dense layer of mosses (*Sphagnum* spp.). Typical small-scale (1–5 m wide, ± 0.5 m high) peatland microtopography (hummocks, hollows and lawns) is ubiquitous at this site. In the bog, the water table remains at or below the surface for most of the year; during the study period the water table remained approximately 3 cm below the average peat surface. The intermediate fen site is markedly wetter than the raised bog, with the water table above the peat surface for the majority of the year. During the study period, the water table was at, or slightly above, the average peat surface. Vegetation cover at the fen site comprises of sedges (*Carex* spp. and *Scirpus* spp.), brown mosses (*Tomenthypnum nitens*, *Aulacomnium palustre*, *Drepanocladus aduncus*) and plants (*Sarracenia purpurea*, *Drosera intermedia*, and *Equisetum fluviatile*). Pronounced microtopography is largely absent from the peat surface in the fen.

3. Methods

A 7 × 7 m grid (1 m grid cell spacing) was fixed at a randomly selected location in each of the bog and fen sites (n = 49 cells). Temporary wooden boardwalks were placed along the grid lines to help preserve the integrity of the peatland surface and prevent changes to microtopography during sampling. A systematic sampling scheme was chosen for this study on the basis of repeatability, simplicity, efficiency, and the prospect of obtaining a large sample size and uniform coverage within a relatively small area at a 1 m resolution. A caveat of this sampling design is that it has the potential to conceal spatial patterns if the chosen sampling interval (1 m) coincides with a periodic trait of the variable of interest. However, we do not believe this to be a concern for this study since such a regular, periodic pattern in peatland pore-water biogeochemistry has not been reported in the scientific literature.

The center of each grid cell was sampled twice within a three-week period; the first sampling session occurred during the week of July 22, 2009 when all 49 cells in each grid were sampled for pore-water. Only odd-numbered cells were sampled again during the week of August 9, 2009 (n = 28 cells). The microtopography of each sampling location was defined by the characteristics of the sampling location in the center of each grid cell.

We do not consider vertical variability throughout the peat soil profile. However connectivity to groundwater increases with depth, so variability due to groundwater mixing and diffusion is also expected with increasing proximity to the chemically different marine sediments below the peat.

Pore-water (0–5 cm below the water table) was sampled for pH and dissolved solutes using a pre-cleaned PTFE pore-water sipper, pre-cleaned PTFE tubing (3 m length, 0.64 cm i.d.), peristaltic pump, and a simple flow-through cell instrumented with an Orion® 3-Star Plus Portable pH Meter (calibrated before and after each sampling session). Pore-water samples were kept cool and syringe filtered (0.45 μm) within 24 h of collection, and then stored frozen in HDPE scintillation vials until analysis. We are aware of the potential changes to dissolved solute concentrations due to freeze preservation (e.g., Fellman et al., 2008). However, our quality assurance and quality control (QA/QC) measures on frozen and unfrozen samples indicate that freezing after filtering has had negligible effects on sample integrity.

All sample preparation and analysis were performed in our research laboratory at the University of Toronto at Mississauga following strict QA/QC protocols. Water samples were analyzed for ions of interest using suppressed ion chromatography (Dionex ICS-1600). Dissolved organic carbon (DOC) was measured using a Lachat IL-550 TOC/TN Analyzer. IBM SPSS 19.0 and Surfer 8.0 (Golden Software) were used for statistical analyses and the generation of image maps, respectively.

All of the pore-water chemistry data (pH, DOC, and major ions) are normally distributed according to the One-Sample Kolmogorov-Smirnov test, making it possible to use parametric statistical analyses. A two-tailed paired t-test ($p = 0.01$) was utilized to test whether within-site changes to a particular geochemical parameter were statistically significant between the two sampling campaigns. Differences in geochemistry between the bog and fen site were compared using a two-tailed independent t-test ($p = 0.01$).

Eq. (1) (Eckblad, 1991) was used to determine the number of samples (n) needed to obtain a representative value of the mean, within a certain confidence interval and acceptable margin of error.

$$n = \frac{(t - \text{value})^2 \times \text{sample variance}}{(\text{accuracy} \times \text{mean})^2} \quad (1)$$

4. Results

4.1. Pore-water chemistry

A summary of the arithmetic means, standard deviations, and ranges for pore-water chemistry (pH, DOC, Cl^- , SO_4^{2-} , Na^+ , Mg^{2+} , and Ca^{2+}) in both the bog and fen sites for both sampling campaigns is given in Table 1. Image maps illustrating the cell-level spatial and temporal variability for each site and sampling time are shown in Fig. 2.

4.1.1. pH

The mean *in situ* pH of the bog site within the 49 grid cells in late July was 4.32 ± 0.06 , at the upper end of that reported for bogs in this region (Sjörs, 1963; Glaser et al., 2004; Siegel et al., 2006). The pH measurements from the bog obtained in August were not significantly different from the first sampling campaign (two-tailed paired t-test, $p = 0.01$) and there was little variation spatially at either sampling time. The intermediate fen was less acidic than the bog, with an average pH of 5.77 ± 0.18 in July. The pH at the fen site significantly increased to a mean of 5.85 ± 0.19 in August ($p = 0.01$). In both July and August, within-fen pH variability was markedly greater when compared to the bog.

4.1.2. Dissolved organic carbon (DOC)

In general, DOC concentrations in surface pore-waters were similar to those reported for bogs and fens in the HBL (see Reeve et al., 1996; Glaser et al., 2004). DOC concentrations in surface pore-waters in the bog averaged $22.23 \pm 4.48 \text{ mg L}^{-1}$ in July, increasing significantly to $24.85 \pm 1.45 \text{ mg L}^{-1}$ in August ($p = 0.01$). The fen surface pore-waters had significantly lower DOC concentrations than the bog ($p = 0.01$) in both July and August ($15.05 \pm 3.69 \text{ mg L}^{-1}$ and $15.31 \pm 1.51 \text{ mg L}^{-1}$ respectively), but were not significantly different from each other. In both wetland types, variance decreased over the course of the study (Table 1). The spatial pattern of DOC is illustrated in the image maps in Fig. 2, and shows no spatial correspondence with pH or any other geochemical parameters.

4.1.3. Major ions

Only five major ions were in concentrations high enough to be consistently detected and/or quantified in the filtered pore-water samples: chloride (Cl^-), sulfate (SO_4^{2-}), sodium (Na^+), magnesium

Table 1
Summary of arithmetic means and standard deviations of pore-water in the bog and fen sites for July and August, 2009. Ranges are given in brackets, and samples with detectable (but not accurately quantifiable) concentrations are shown as being less than (<) the method detection limit.

	Bog–July 22, 2009	Bog–August 8, 2009	Fen–July 24, 2009	Fen–August 10, 2009
n	49	28	49	28
pH	4.32 ± 0.06 (4.21–4.50)	4.29 ± 0.06 (4.19–4.51)	5.77 ± 0.18 (5.20–6.27)	5.85 ± 0.19 ^a (5.50–6.34)
DOC (mg L ⁻¹)	22.23 ± 4.48 (12.31–30.44)	24.85 ^a ± 1.45 (21.87–28.69)	15.05 ± 3.69 (6.48–23.57)	15.31 ± 1.51 (11.95–18.05)
Ca ²⁺ (mg L ⁻¹)	1.81 ± 0.39 (0.41–2.50)	1.79 ± 0.22 (1.45–2.43)	5.67 ± 1.47 (2.06–9.98)	7.41 ^a ± 3.61 (4.96–15.34)
Mg ²⁺ (mg L ⁻¹)	0.21 ± 0.04 (<0.14–0.27)	0.22 ± 0.03 (0.17–0.30)	0.94 ± 0.25 (0.20–1.48)	1.32 ^a ± 0.48 (0.93–1.90)
SO ₄ ²⁻ (mg L ⁻¹)	0.29 ± 0.23 (<0.01–0.81)	0.07 ^a ± 0.05 (<0.01–0.28)	0.55 ± 0.46 (0.03–2.19)	0.03 ^a ± 0.01 (<0.01–0.06)
Cl ⁻ (mg L ⁻¹)	<0.38 (<0.38–<0.38)	<0.38 (<0.38–<0.38)	0.81 ± 0.69 (0.38–3.27)	1.25 ± 1.82 (0.39–8.08)
Na ⁺ (mg L ⁻¹)	0.48 ± 0.24 (<0.12–0.98)	0.20 ^a ± 0.10 (0.03–0.58)	2.18 ± 1.05 (0.34–6.28)	2.58 ± 1.83 (1.69–8.63)

^a Statistically significant within-site temporal changes to arithmetic means (two-tailed paired t-test, $p = 0.01$).

(Mg²⁺), and calcium (Ca²⁺). Chloride ions in the bog were detected in trace amounts (<0.38 mg L⁻¹) on both sampling campaigns, while mean concentrations in the fen were at least two-fold higher, increasing from 0.81 ± 0.69 mg L⁻¹ in July to 1.25 ± 1.82 mg L⁻¹ in August (statistically significant, $p = 0.01$). Mean concentrations of Na⁺ in the bog were 0.48 ± 0.24 mg L⁻¹ in July, decreasing to 0.20 ± 0.10 mg L⁻¹ in August (not statistically significant, $p = 0.01$). The fen site had Na⁺ concentrations that were up to ten-fold higher than in the bog, increasing significantly over the three weeks from 2.18 ± 1.05 mg L⁻¹ to 2.58 ± 1.83 mg L⁻¹ ($p = 0.01$). Overall, concentrations of Cl⁻ and Na⁺ were quite spatially variable in the fen, as compared with other dissolved solutes.

Low levels of sulfate were measured in both sites, and concentrations generally decreased over the duration of the study period. In July, mean SO₄²⁻ concentrations in the bog were 0.29 ± 0.23 mg L⁻¹, close to half of those measured in the fen (0.55 ± 0.46 mg L⁻¹). July SO₄²⁻ concentrations in both peatland types were quite spatially variable, with some fen pore-waters below our analytical limits of detection (<0.01 mg L⁻¹), and others as high as 2.19 mg L⁻¹ in samples obtained during the same sampling day. Nearly all of the samples that were taken in August from both peatland types had barely quantifiable concentrations of SO₄²⁻. These temporal decreases in SO₄²⁻ concentrations in both the bog and fen were statistically significant ($p = 0.01$).

The greatest differences in dissolved solute concentrations between the bog and fen sites were observed in Ca²⁺ and Mg²⁺ concentrations, two cations that are abundant in the underlying marine sediments, which are largely composed of calcite and dolomite. The relatively low Ca²⁺ concentrations in the bog pore-waters in both July and August (1.81 ± 0.39 mg L⁻¹ and 1.79 ± 0.22 mg L⁻¹, respectively) indicate that the surficial waters in the bog are largely disconnected from the deeper, mineral-rich groundwater. The Ca²⁺ concentrations in the fen were considerably higher than in the bog, and increased from 5.67 ± 1.47 mg L⁻¹ in July to 7.41 ± 3.61 mg L⁻¹ in August (statistically significant, $p = 0.01$). Mean concentrations for Mg²⁺ in the bog were consistently 0.21 ± 0.04 mg L⁻¹ over both sampling periods, whereas the fen had higher mean concentrations greater than 1 mg L⁻¹. As with Ca²⁺, Mg²⁺ concentrations were more variable within the fen than in the bog. A two-tailed paired t-test ($p = 0.01$) shows that Ca²⁺ and Mg²⁺ concentrations are significantly different in the fen over the three weeks.

A plot of Mg²⁺ versus Ca²⁺ concentrations in surface pore-waters (Fig. 3) shows a strong positive linear relationship for both sampling sites in July and August, suggesting simple, two-component mixing between distinct end-members: deeper, mineral-rich groundwater and dilute precipitation.

4.2. Microtopographic influence on pore-water chemistry

Pore-water geochemical data grouped on the basis of microtopographic form for the bog site are shown in Table 2. Sampling site microtopography in the bog site is dominated by hummocks in more than half of the grid cells. Frequencies of hollows and lawns in the bog's sampling grid cells were 6 and 14, respectively. The surface peat at the fen did not contain sufficient differences in microtopography for grouping and comparison based on microtopographic type.

4.2.1. pH

Differences in the arithmetic means and standard deviations of the pore-water pH among microtopographic forms are small, with a range of only 0.10 pH units.

4.2.2. Dissolved organic carbon (DOC)

Hollows had the lowest concentrations of DOC (17.08 ± 3.91 mg L⁻¹), with hummocks and lawns having increasing concentrations of 22.21 ± 4.44 and 24.35 ± 2.09 mg L⁻¹, respectively.

4.2.3. Major ions

Most major ions (Cl⁻, SO₄²⁻, Na⁺, and Mg²⁺) in the bog site were below 1 mg L⁻¹, a consequence of its ombrotrophic nature. Similar to pH, differences in means among microtopographic forms are small. Only Ca²⁺ ions were found in concentrations >1 mg L⁻¹, where hummocks and hollows exhibited nearly identical mean concentrations and standard deviations (1.76 ± 0.40 and 1.74 ± 0.32 mg L⁻¹, respectively), and lawns with a slightly higher mean of 1.91 ± 0.52 mg L⁻¹.

4.3. Representative sample size

We used Eq. (1) to calculate the number of samples that are required in order to obtain a reasonable estimate of the mean for measure of water quality in each peatland type. The resultant sample size is largely dependent on the margin of error that one is willing to accept. For example, we have selected two criteria with different levels of statistical rigor to compute the number of samples required for a reasonable estimation of the arithmetic mean for the chemical parameters discussed in this study, summarized in Table 3. If one were to choose a more strict margin of error to estimate the mean (e.g., within ±10% accuracy at a $p = 0.01$ level of significance), then a relatively large number of samples are required for the majority of geochemical parameters in order to satisfy the criteria. Disregarding pH, which only requires one measurement to achieve a representative estimate (due to its low variability in space and time), at least 33 and

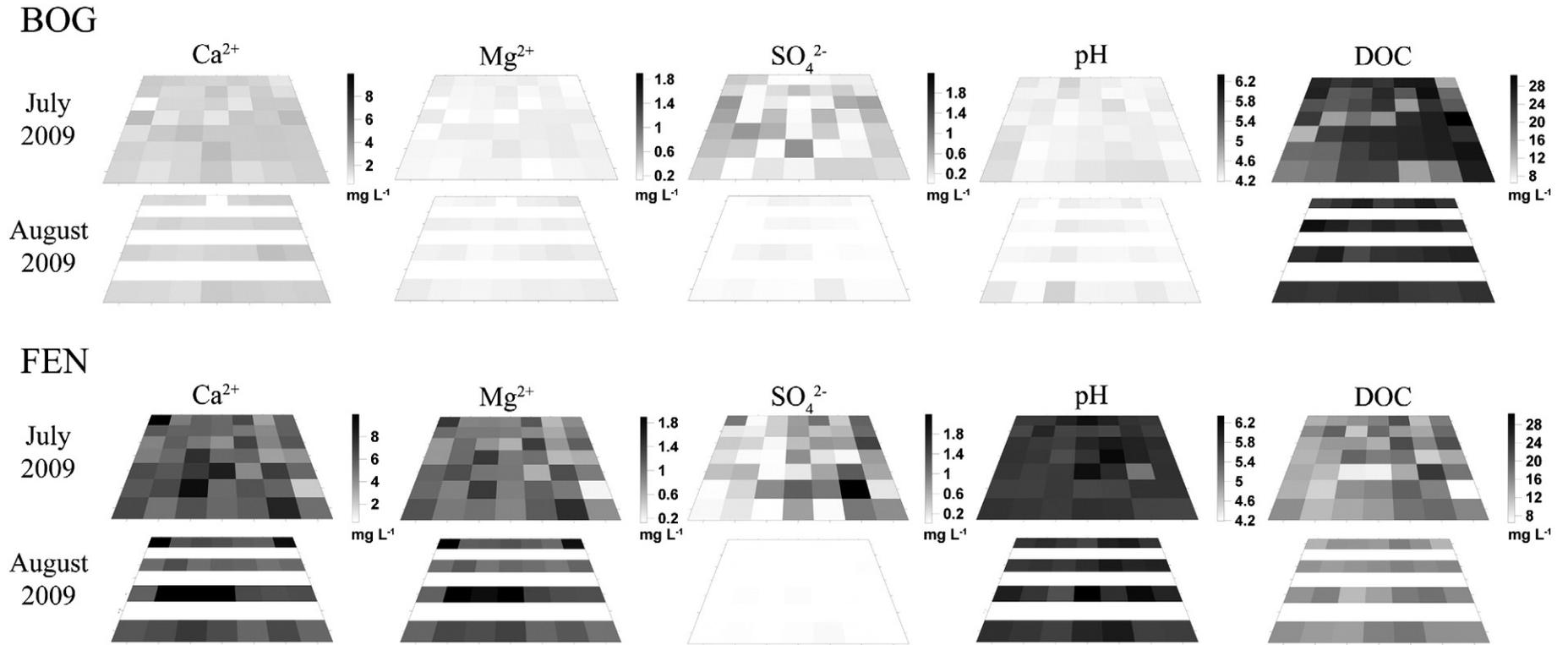


Fig. 2. Image maps for the bog and fen, displaying the spatial distribution of major ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-} mg L⁻¹), pH, and DOC (mg L⁻¹). For each 1×1 m cell unit, pore-water was sampled at a single point, but the value is represented over the entire cell unit. The white spaces in rows 2, 4, and 6 (August, 2009) represent missing values. Note the high variability in fen sulfate concentrations in July, and very low levels of sulfate in both the fen and bog sites in August, 2009.

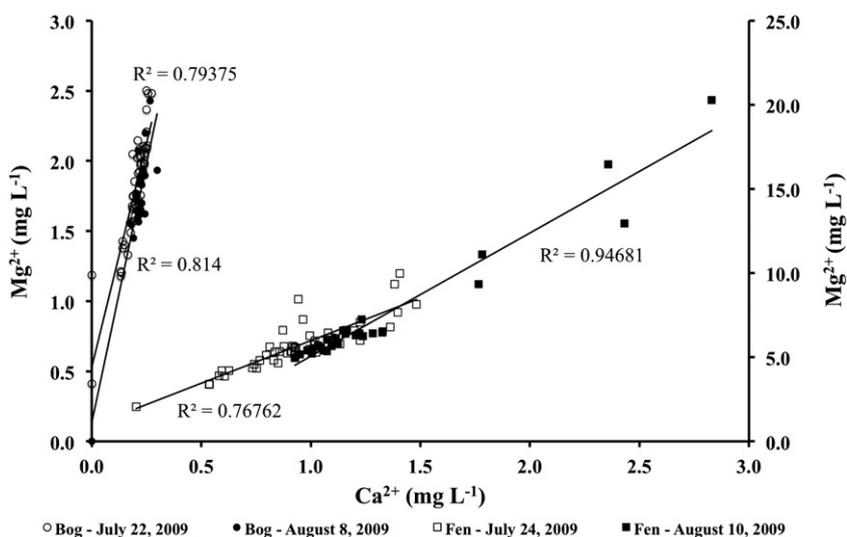


Fig. 3. Plot of Mg^{2+} versus Ca^{2+} pore-water concentrations for the bog and fen sites in July and August, 2009. A strong positive linear relationship suggests simple two-component mixing between the minerotrophic groundwater and dilute precipitation.

51 samples are needed to estimate mean concentrations of DOC, Ca^{2+} , and Mg^{2+} within $\pm 10\%$ ($p = 0.01$) for the bog and fen, respectively. For the more variable geochemical parameters, such as Cl^- , Na^+ and SO_4^{2-} , hundreds of samples are required to achieve similar results.

However, if the margins of error are relaxed so that the sample means are accurate to within $\pm 20\%$ at a $p = 0.1$ level of significance, the sample size can be reduced to a more practical number. Only ~ 3 samples are sufficient to estimate the mean for DOC, Cl^- , Ca^{2+} , and Mg^{2+} for bogs, whereas 18 and 44 samples are required for more variable ions like Na^+ and SO_4^{2-} , respectively. Similar sample sizes are required for fens: 4–5 samples are sufficient to estimate the mean for pH, DOC, Ca^{2+} , and Mg^{2+} , 16 for Na^+ and at least 49 for SO_4^{2-} and Cl^- .

5. Discussion and conclusion

There was considerable spatial and temporal variability in some dissolved solute geochemistry within and between the two sampling plots, which had some dependence to microtopographic form. Although the majority of these data fall within limits established by various wetland classification systems (see Cowardin et al., 1979; National Wetlands Working Group, 1997), some individual samples did contain elevated pH values and concentrations of dissolved solutes.

Table 2

Bog pore-water geochemical data (July, 2009) separated into microtopographic form (hollow, lawn, and hummock). Arithmetic means and standard deviations are included, and ranges are given in brackets.

	Hollow	Lawn	Hummock
n	6	14	29
pH	4.40 ± 0.06 (4.27–4.46)	4.31 ± 0.04 (4.24–4.38)	4.30 ± 0.06 (4.21–4.50)
DOC (mg L^{-1})	17.07 ± 3.91 (12.31–23.49)	24.35 ± 2.09 (20.47–26.47)	22.21 ± 4.44 (13.39–28.61)
Ca^{2+} (mg L^{-1})	1.76 ± 0.40 (1.38–2.48)	1.91 ± 0.52 (0.41–2.48)	1.74 ± 0.32 (1.18–2.36)
Mg^{2+} (mg L^{-1})	0.19 ± 0.04 (0.14–0.26)	0.23 ± 0.03 (0.18–0.27)	0.20 ± 0.03 (0.13–0.25)
SO_4^{2-} (mg L^{-1})	0.43 ± 0.15 (0.32–0.66)	0.34 ± 0.26 (0.04–0.81)	0.23 ± 0.21 (0.02–0.76)
Na^+ (mg L^{-1})	0.55 ± 0.17 (0.30–0.78)	0.40 ± 0.21 (0.13–0.77)	0.47 ± 0.25 (0.16–0.98)

Pore-water pH has long been used as a valuable indicator of peatland function and for the comparison among peatland types (Sjörs, 1963; National Wetlands Working Group, 1997; Tahvanainen, 2004). Of all the geochemical parameters measured, pH exhibited the least variability over both space and time. Such stable pH values are likely the result of low base cation concentrations, particularly in the ombrotrophic bog, which are unable to buffer the high concentrations of organic acids in the uppermost portion of the peat profile (Siegel et al., 2006). The thinner peat deposits (< 2 m) and potentially upward hydrologic gradients in the fen (Reeve et al., 2000) contribute to relatively higher base cation concentrations, and therefore higher, more spatially variable values of pH. Some variability may also be due to our measurement technique itself, given that *in situ* pH measurements are affected by the presence of colloidal and dissolved organic materials, volatile acids and oxidizable substances, and temperature of the water at the time of collection (Shotyk, 1988).

For DOC, the breakdown of larger organic substrates derived from animal and plant matter into the dissolved fraction is governed by vegetation type, redox conditions, temperature, the presence and abundance of (micro)organisms, and nutrient availability (Kalbitz et al., 2000; Siegel et al., 2006). It is therefore expected that if there is variability in any or all of these variables (which is the case in this study) there will also be considerable variability within- and between wetland types. Indeed, this was observed in the bog with DOC values ranging anywhere from 16.40 to 26.00 mg L^{-1} in July. Hollows exhibited lower levels of DOC, likely due to different decomposition rates, different vascular plant and moss assemblages, and a predominance of slower anaerobic decomposition than hummocks or lawns (Johnson and Damman, 1991).

DOC concentrations from the fen were about 35% lower than in the bog, with no significant temporal changes observed over 21 days. Although it is understood that decomposition in bogs is slower due to the pH constraints of enzymes (Williams et al., 2000) and that organic matter derived from *Carex* vegetation decomposes faster than *Sphagnum* (Moore et al., 2005), the anaerobic conditions across a relatively uniform, more permanently inundated surface may be an important limit on decomposition rates which supply DOC to pore-waters during the study period. In large peatland complexes, fens are also recognized as conduits for runoff, so DOC concentrations may also be low due to continuous flushing of surface pore-waters (Glaser et al., 2004). Moreover, a more hydrologically connected shallow subsurface environment in the fen may result in a dilution of DOC produced *in situ* through decomposition.

Table 3

Calculated minimal sample sizes required for estimating arithmetic means for each geochemical parameter, based on two different statistical criteria.

Statistical criteria	Bog—July 22, 2009		Fen—July 24, 2009	
	n = 49 t = 2.68 (p = 0.01) Accuracy = ±10%	n = 49 t = 1.68 (p = 0.1) Accuracy = ±20%	n = 49 t = 2.68 (p = 0.01) Accuracy = ±10%	n = 49 t = 1.68 (p = 0.1) Accuracy = ±20%
pH	1	1	1	1
DOC (mg L ⁻¹)	29	3	43	4
Ca ²⁺ (mg L ⁻¹)	33	3	48	5
Mg ²⁺ (mg L ⁻¹)	26	3	51	5
SO ₄ ²⁻ (mg L ⁻¹)	452	44	502	49
Cl ⁻ (mg L ⁻¹)	1	1	521	51
Na ⁺ (mg L ⁻¹)	180	18	167	16

Inputs of solutes into peatlands are generally low, and Reeve et al. (1996) suggest that interaction with deeper, minerotrophic groundwater is the primary control over peat pore-water chemistry in the HBL, and its variation is strongly influenced by dispersion rates and variability in groundwater chemistry. Our results support this, as many of the dominant ions found in pore-waters are closely associated with the calcite and dolomite-dominated marine sediments underneath the peat layer. Hydrological processes certainly govern the substantial spatial variability of Ca²⁺ and Mg²⁺ ions found in the fen where advective and/or dispersive transport processes are responsible for delivering these base cations to surface pore-waters. Similar processes may be responsible for high levels of chlorides in the fen, originating from connate seawater in the glaciomarine sediments which underlie the peat (Reeve et al., 1996). In the bog, levels of Ca²⁺ and Mg²⁺ are low, but a similar strong positive relationship suggests that groundwater exerts some influence on bog surface pore-water chemistry in this hydrologically complex landscape.

In July, sulfate concentrations in the bog were all low (<1 mg L⁻¹) and less variable than in the fen, which displayed larger ranges in concentrations and localized areas of elevated concentrations in the southeastern quadrant of the sampling grid. Fig. 2 clearly illustrates the decrease in concentrations of sulfate between July and August, likely a result of *in situ* reduction by sulfate-reducing bacteria (SRB), converting SO₄²⁻ to S⁻ or organic S species under reducing conditions. No concomitant dilution of other less reactive pore-water solutes supports the assertion that a biogeochemical process is responsible for this change. Differential SRB consumption rates could be the cause of this variability in July, and may be responsible for the disappearance of sulfate at both sites in August. This has implications in anaerobic methylation of inorganic mercury species (Zillioux et al., 1993; Branfireun et al., 1999), where rates of methylation may be greatest during the later part of the growing season.

The results of this study have clearly shown that surface pore-water chemistry in the Hudson Bay Lowland exhibits considerable spatiotemporal variability in solute concentrations in pore-waters because of the complex interactions between climate, hydrology, geology, and vegetation. This measured variability in both dominant peatland types indicates that a large number of samples are required at the sample plot scale if very accurate estimates of the central tendency of geochemistry are desired. The decrease in sulfate concentrations in both wetland types over the study period demonstrates that the *time* of sampling, in addition to location, is important in peatland biogeochemical studies.

In order to minimize variability and achieve a representative state of affairs of pore-water water quality, we suggest that if documenting change over time is the objective of the sampling program, that sampling programs focus on consistency in location, at least from similar microtopographic forms, and preferably from the same location. This does not ensure representativeness of the spatially average condition, however it will avoid the effects of substantial spatial variability. Other strategies may include intensive sampling campaigns at specific times to minimize the temporal effect on variability, and a larger sample

size. We believe that it is in the objective researcher's best interest to undertake a small, initial variability study similar to this to assess site heterogeneity, optimize a sampling strategy and to determine an appropriate representative sample size. Moreover, previously published peatland geochemical data should be considered critically with respect to representativeness, particularly where sample size is limited in both space and time.

Conflict of interest statement

The authors declare that there is no conflict of interest.

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