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Variation in peatland porewater chemistry over time and space along a bog to fen gradient☆

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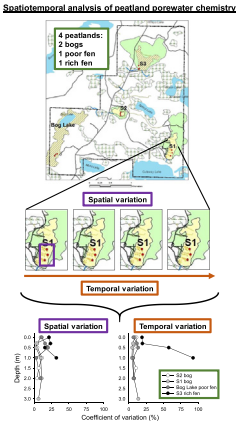
HIGHLIGHTS

- Studied spatiotemporal variation in porewater chemistry along a bog to fen gradient
- Some solutes (calcium, organic C) varied from bog to fen; nutrients did not.
- Spatial and temporal variation in porewater chemistry similar in fens and bogs
- Important to capture variation by collecting water samples in multiples over time
- Quantifying spatiotemporal variation important for understanding solute export

GRAPHICAL ABSTRACT



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ABSTRACT

Porewater chemistry is an integrative measure of the physical, chemical, and biological processes occurring within peatland ecosystems, and therefore some chemistry measures (e.g., pH, calcium concentrations) have been used to classify bog vs fen peatlands. However, porewater sampling is often limited in spatial and temporal resolution, highlighting the need for a more comprehensive analysis of spatiotemporal variation in porewater chemistry. We examined depth profiles of porewater chemistry in four nearby peatlands that fall along a bog to rich fen gradient in northcentral Minnesota, USA. Porewater was sampled ~monthly during one ice-free season from three replicate piezometer nests per peatland to quantify temporal and spatial variability of those depth profiles. Porewater depth profiles of pH, calcium and total organic carbon concentrations, and $\delta^{18}O\text{-}H_2O$ varied along the bog to fen gradient, but total nitrogen and total phosphorus concentrations did not. Porewater chemistry was similar in the bogs and poor fen which were all quite different from the rich fen. In contrast, temporal and spatial variation in porewater chemistry, quantified using coefficients of variation, did not differ between bogs and fens despite the hypothesis that variation in porewater chemistry would be lower in fens than bogs

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Nutrients
Coefficient of variation

due to the perennial throughput of large volumes of discharging groundwater in the rich fen. Spatial and temporal variability in porewater chemistry across all peatland types highlights the importance of collecting porewater samples in multiples over time in both near-surface and deeper peats. This variation can be important when scaling findings to the peatland scale, assessing the representativeness of peatlands within a larger landscape, and understanding variability in solute export to downstream ecosystems.

1. Introduction

A large fraction of the global terrestrial carbon pool, nearly 30%, is stored in organic-rich peat soils (Gorham, 1991; Yu, 2012). In order to accurately represent these critical peatland ecosystems in Earth System Models (Wania et al., 2009; Melton et al., 2013; Shi et al., 2015; Xu et al., 2016), it is important to characterize the diversity of peatland types at multiple spatial and temporal scales. The characteristics of peatland ecosystems are wide ranging and expressed in terms of hydrologic, topographic, biogeochemical, and plant community properties (Moore and Bellamy, 1974; Glaser, 1987; Bridgham et al., 1996; Wheeler and Proctor, 2000; Sjörs and Gunnarsson, 2002). A variety of terms are used to describe peatlands; however, as stated by Bridgham et al. (1996), peatlands are broadly defined as bogs or fens based on acidity and plant community composition. Bogs are acidic with a plant community primarily consisting of *Sphagnum* mosses, ericaceous shrubs, and conifers, while fens are less acidic and have a more diverse plant community, including graminoids, brown mosses, and coniferous and deciduous trees (Bridgham et al., 1996). Fens may be further classified as poor or rich fens based on acidity, alkalinity, and cation concentrations (Sjörs, 1950).

Peatland water chemistry reflects local hydrology, topography, biogeochemistry, and floristic composition, and therefore multiple chemical parameters are often used to characterize the bog to fen gradient (Gorham et al., 1985; Bourbonniere, 2009). Both pH and calcium concentrations in surface and near-surface porewater are usually higher in fens than bogs, largely due to the exchange of mineral-rich groundwater with fens (Bay, 1967; Glaser et al., 1990). Surface water in bog and fen landforms can also have distinctive water stable isotope signatures as evaporation from standing water in some fens can lead to differences due to kinetic isotope fractionation (Levy et al., 2014). Some studies have investigated whether nutrient concentrations (i.e., nitrogen [N], phosphorus [P]) vary between bogs and fens but in general there are no clear differences among peatland types (Vitt et al., 1995) or within peatlands (Bragazza and Gerdol, 2002) likely because N and P are often limiting in these ecosystems (Urban and Eisenreich, 1988; Verhoeven et al., 1996; Bedford et al., 1999; Hill et al., 2014).

The chemistry of peatland surface water and porewater varies with multiple factors, including the balance between precipitation and groundwater inputs (chemistry and volume), microbial and plant uptake, mineralization, cation exchange, and peatland water level (a driver of chemical transport and redox conditions) (Verhoeven, 1986; Vitt et al., 1995; Bragazza et al., 1998; Tahvanainen et al., 2002; Proctor, 2006; Whitfield et al., 2010; Ulanowski and Branfireun, 2013). These many factors can operate and interact at different spatial (i.e., micro- to kilometer) and temporal (i.e., second to interannual) scales. Therefore, it is important to characterize spatiotemporal variation in peatland surface water and porewater chemistry (Whitfield et al., 2010). Many studies have investigated spatial (horizontal) or temporal variation in near-surface water chemistry among or within peatlands, sometimes along depth profiles (e.g., Gerdol, 1990; Glaser et al., 1990; Malmer et al., 1992; Bragazza and Gerdol, 2002; Tahvanainen et al., 2002; Bendell-Young, 2003; Crushell et al., 2009). In addition, some studies investigate both spatial and temporal dimensions of porewater chemistry (e.g., Moore, 1987; Proctor, 1994; Vitt et al., 1995; Waddington and Roulet, 1997; Bragazza et al., 1998; Tahvanainen et al., 2003; Whitfield et al., 2010; Ulanowski and Branfireun, 2013; Avagyan et al., 2014; Griffiths and Sebestyen, 2016a), though these measurements are less common. For example, studies may include several solutes, peatlands, or depths, with replicates over time or within a peatland, but rarely all of these aspects together. A more complete quantification and analysis of spatiotemporal variation in porewater chemistry, inclusive of the aforementioned aspects, may provide foundational knowledge, inform future measurement efforts, and allow for a better representation of the diversity of peatlands and peatland processes in biogeochemical, land surface, and global change models.

The objective of this study was to quantify depth-specific profiles of porewater chemistry. We examined how similar or different those profiles were over time, with spatial replication, and among different types of peatlands. We studied a bog to rich-fen gradient including two bogs, one poor fen, and one rich fen, all within a local area in northcentral Minnesota to minimize geographic and climatic variation. We included a broader suite of solutes (pH, concentrations of cation, nutrient, and total organic carbon (TOC), and natural-abundance water stable isotopes), more sites, and more depths than most studies. We hypothesized that pH, calcium and TOC concentrations, and water stable isotopes would differ between bogs and fens, while nutrient concentrations would not. We also hypothesized that temporal and spatial variation in porewater chemistry, quantified using coefficients of variation, would decrease along the bog to rich-fen gradient as fens have perennial exchange with groundwater.

2. Materials and methods

2.1. Study sites

The S1, S2, S3, and Bog Lake peatlands are located in the South Unit of the Marcell Experimental Forest (MEF) in northcentral Minnesota, USA (Fig. 1) and are all within ~4 km of each other. The four study peatlands encompass a gradient from bogs to a poor fen and a rich fen in the post-glacial landscape of northern Minnesota (Verry and Janssens, 2011). These peatlands have been defined as bog, poor fen, or rich fen based on multiple characterizations, including soil and water chemistry, hydrology, and plant communities (Sebestyen et al., 2011a). The fens formed in landscape depressions where water-saturated organic matter accumulated. Bogs in this area formed as ice-block depressions that filled with organic soils following the Wisconsinan glaciation or as secondary features when a bog formed on a fen as the peatland surface rose with the slow accumulation of peat. The groundwater aquifer is sandy outwash. Till covers two-thirds of the 1100 ha MEF, with outwash exposed on the remaining one-third of the landscape (Sebestyen et al., 2011a). Fens exchange water with the aquifer. A bog is above the level of groundwater inflow, though groundwater may exchange with peat underlying a bog. For example, the S2 bog, with up to 7 m of peat, is perched with nearly 7 m of hydraulic head above the aquifer (Verry and Janssens, 2011). In contrast, the S1 bog surface, with peat up to 11-m deep (Parsekian et al., 2012), is about 1 m above the aquifer. Bogs are precipitation fed (ombrotrophic). Water level in fens is less variable than in the small, isolated bogs because of the exchange with a large groundwater body (Sebestyen et al., 2011a). S2 has a Loxley series peat (Dysic, frigid

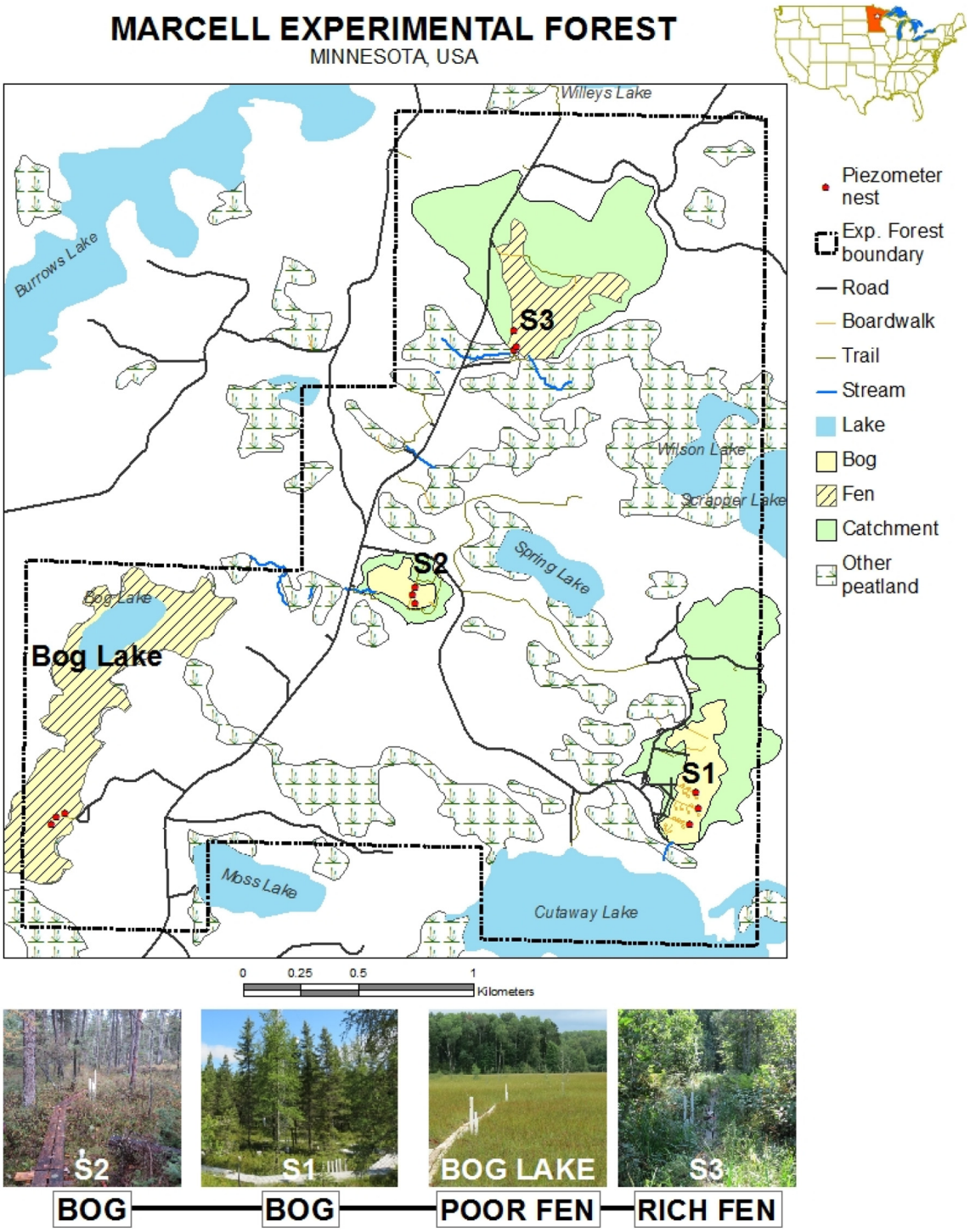

Fig. 1. Map of the four study peatlands located in the Marcell Experimental Forest in northcentral Minnesota, USA. The four peatlands fall along a bog (S2, S1), poor fen (Bog Lake fen), and rich fen (S3) gradient.

Typic Haplosaprists), S1 and Bog Lake have Greenwood series peat (Dysic, frigid Typic Haplohemists), and S3 has a Mooselake mucky peat (Euic, frigid Typic Haplohemists) (Nyberg, 1987).

The bog to fen gradient is as follows: S2 bog, S1 bog, Bog Lake poor fen (BLF), and S3 rich fen. The S2 bog is 3.2 ha in size and is surrounded by a 6.5-ha upland watershed. The S2 bog is considered a reference, with no major disturbance to the bog or the surrounding uplands for nearly a century (Sebestyen et al., 2011a). The S1 bog is 8.1 ha in size and is surrounded by a 25.1-ha upland watershed. Both S1 and S2 have similar vegetation, including a primarily black spruce (*Picea mariana*) overstory with some tamarack (*Larix laricina*), ericaceous shrubs, and *Sphagnum* moss carpets. However, the overstory of the S1 bog is younger natural secondary regrowth following harvest. The S1 bog trees were harvested in strip cuts in 1969 and 1974 to examine the effects of forest harvest on watershed hydrology (Sebestyen et al., 2011b; Sebestyen and Verry, 2011). The S1 bog is also the site of a long-term experiment (beginning in 2014) evaluating the effects of elevated temperature and CO_2 concentrations on peatland ecosystem

processes (Wilson et al., 2016; Hanson et al., 2017; Richardson et al., 2018); however, the porewater data presented here were not affected by the warming and CO_2 treatments as these water samples were collected outside of the experimental enclosures (i.e., within ambient plots 7, 14, and 21). BLF is a poor fen that is 20 ha in size, with a small area of open water fringed by black spruce. The poor fen has a primarily open canopy, with some free-standing, stunted tamarack trees, and an understory of *Sphagnum*, sedges, and pitcher plants. There were no tamarack trees where we sampled. No experimental large-scale manipulations have occurred at BLF, though adjacent upland areas were commercially clearcut and thinned over the last century (Perala and Verry, 2011). The S3 peatland is a rich fen that is 18.6 ha in size and surrounded by a 53.4-ha upland. The fen was clear cut in 1972–1973 and most logging slash was burned onsite before replanting with black spruce and white cedar (*Thuja occidentalis*) (Sebestyen et al., 2011b; Sebestyen and Verry, 2011). In either the bog (S1) or fen (S3), forest harvesting had no effect on water table fluctuations or stream water yields, and effects on downstream chemistry were limited in scope and short lived (Sebestyen et al., 2011b, Sebestyen and Verry, 2011). Vegetation in the S3 rich fen is mostly tamarack with some black spruce, alder, willow, ericaceous shrubs, *Sphagnum*, ferns, sedges, rushes, and herbs. All peatlands have hummock/hollow microtopographies, with more pronounced expanses of lawns in addition to hummock/hollow microtopography at BLF. Most vegetation types are present in hummocks and lawns, while *Sphagnum*, graminoids, and forbs are primarily present in hollows.

2.2. Field sampling and measurements

Piezometers were used to collect porewater for chemical analyses. Three piezometer nests were installed in each peatland, separated by as little as 15 m and as much as 145 m (Fig. 1). The locations were chosen to include different areas, though choice was not random, and it was not possible to cover the entire expanse of any particular peatland. Locations were related to access points from roads and boardwalks, which were needed to maintain integrity of the peatland surfaces from foot traffic disturbance. While some new, short lengths of boardwalks were built in BLF, existing boardwalks were used in S1, S2, and S3. These three piezometer nests were considered replicates in this analysis and were included to capture spatial variation in porewater chemistry within a peatland.

Each piezometer nest consisted of 4–6 piezometers that were screened to collect water at different depths. Piezometers were 5.1-cm in diameter, and each piezometer collected water from a 10-cm screened section (0.25 mm slots). Piezometer depths were referenced relative to the surface of the peat in hollows, so that the screened section of the 0 m piezometer collected porewater from 0 to 0.1 m. Because peat depth varied within and among the four peatlands, porewater from the same depth (especially the deeper depths) could not be sampled in all peatlands. Further, the deepest replicate piezometers were sometimes not installed to a consistent depth (1.75 or 2 m in S2 and 1.85 or 2 m in BLF) due to difficulties in inserting deep piezometers and a variable peat depth. S2 bog piezometers were screened at 0, 0.3, 0.5, 1, 1.5, and 1.75 or 2 m depths. Peat was deeper than 2 m, but the tightly packed peat precluded deeper insertion and resulted in inconsistent depths of the deepest replicate piezometers. S1 bog piezometers were screened at 0, 0.3, 0.5, 1, 2, and 3 m depths, spanning the entire peat profile. BLF piezometers were screened at 0, 0.3, 0.5, 1.0, and 1.85 or 2 m depths, spanning the entire peat profile with deepest piezometers installed to inconsistent depths based on peat depth (i.e., installed to 1.85 or 2 m depth). S3 rich fen piezometers were screened at 0, 0.3, 0.5, 1 m depths. S3 had fewer depths due to the shallow peat in this peatland, and only two of the three nests in S3 had a 1-m piezometer. For the purposes of the depth-specific interpretation and analyses, the deepest piezometers in S2 and BLF were considered to be at 2 m.

During the active season (i.e., non-frozen period; Richardson et al., 2018) of 2014, porewater was sampled approximately monthly from all piezometers in the four peatlands. Porewater was sampled from June through November 2014, except for porewater from the S3 rich fen, which was sampled from June to August 2014. Piezometers were purged immediately before sampling except for some deeper piezometers that took longer than 10 min to refill. The deep and slow-to-refill piezometers were purged the day before sampling and allowed to refill overnight with fresh porewater. Water samples were collected with a peristaltic pump and dispensed into clean, 250-mL high-density polyethylene bottles for chemistry (rinsed three times with porewater before filling) and 16-mL clear glass vials with Poly-Seal lined caps for water isotope analysis. The water isotope vials were completely filled with water and inspected to ensure that no air bubbles were visible in the samples. Water samples were then placed on ice and refrigerated in the laboratory at 4 °C until analysis. Samples were not filtered as the porewater contained few particulates. Water isotope samples were stored at room temperature.

Measurements of water table elevation and soil temperature were used to examine relationships with porewater chemistry. Both water table elevation and soil temperature were measured from January through December 2014 (except for soil temperature measurements in the S1 bog, which began on February 25, 2014). Water table was measured daily in a well in each peatland using a strip chart recorder (Belfort model FW-1) with a float and pulley system (Verry et al., 2018). Soil temperature was measured ~weekly by hand at multiple peat depths (5, 10, 20, 30, 40, 50, 100, 200 cm) using Type-T thermocouples (twisted constantan-copper wire pairs) and read with an Omega meter (HH-25TC Thermometer, Omega Engineering Inc., Norwalk, CT) in S2, S3, and BLF. Soil temperature was logged every half hour at the same depths in plot 7 in the S1 bog using a multipoint thermistor probe (Hanson et al., 2015). For S1, we subsampled one weekly value to correspond to the same general time of day as the weekly soil temperature measurements in S2, S3, and BLF.

2.3. Chemical analyses

In the laboratory, the pH of water samples was measured on a Mettler Toledo DL53 Auto Titrator (Columbus, OH) using Standard Method 4500-H^+ B (APHA, 2005). pH was analyzed on all samples collected from S1, S2, and BLF, but only on about one of five samples collected from S3. Other than pH, every sample collected from S3 was analyzed for every other chemistry described in this paper. Before pH was measured, the titrator was calibrated following the manufacturer's instructions. Cations (including calcium and potassium) were measured on an Inductively Coupled Plasma spectrophotometer (Thermo Elemental, Iris Intrepid ICP-OES, Waltham, MA) using Standard Method 3120 B (APHA, 2005). Total nitrogen (TN) and total phosphorus (TP) were measured using the persulfate-UV digestion method (Lachat QuikChem 10-107-04-1-P and Lachat QuikChem 10-115-01-3-A, respectively) on a Lachat QuikChem 8000 Autoanalyzer (Milwaukee, WI). Total organic carbon (TOC) was measured on a Shimadzu TOC-VCP (Columbia, MD) using the high-temperature combustion method (Standard Method 5310 B; APHA, 2005). Stable isotopes of water ($\delta^{18}O$-H_2O and δD-H_2O) were measured using a Los Gatos liquid water isotope analyzer (T-LWIA-45-EP) (San Jose, CA). For all chemical analyses, certified calibration standards were used to develop calibration curves and certified and internal check standards were used to assess measurement accuracy. Duplicate samples were run on every 10th sample for all chemical analyses to check reproducibility.

2.4. Calculations and statistics

To examine the effects of peatland type and peat depth on porewater chemistry, we used analysis of covariance (ANCOVA), with peatland as the factor, depth into the peat as the covariate, and the chemical

parameter as the dependent variable. Mean chemistry values across piezometer nests and sampling dates were used in these ANCOVAs.

To examine similarities and differences in porewater chemistry among the four study peatlands, we used Principal Components Analysis (PCA). Because of strong gradients in porewater chemistry with depth into the peat, separate PCA's were carried out at each depth (0 m, 1 m, 2 m). The 2 m depth PCA included data only from S1, S2, and BLF, as the peat was too shallow in S3 to install piezometers below 1 m. The same porewater chemistry variables were included in each PCA: calcium, potassium, TN, TP, and TOC concentrations and $\delta^{18}O\text{-}H_2O$ values. $\delta D\text{-}H_2O$ values were not included due to covariance with $\delta^{18}O\text{-}H_2O$ values. pH was not included due to the low number of measurements from the S3 rich fen.

ANCOVAs were also used to examine the seasonal drivers (i.e., soil temperature, water table elevation) of porewater chemistry. Mean chemistry values across the three replicate piezometer nests per peatland on each sampling date were used in these ANCOVAs. To examine whether soil temperature affected porewater chemistry, we used ANCOVA, with peatland as the factor, peat depth and temperature as covariates, and the chemical parameter as the dependent variable. Soil temperature was measured at all depths in which porewater chemistry samples were collected, except soil temperature was not measured at 1.5 m in the S2 bog. Soil temperature at 1.5 m was thus estimated as the mean of temperatures measured at 1 m and 2 m. We used the same ANCOVA model structure to examine the effect of water table on porewater chemistry, with peatland as the factor, peat depth and water table as covariates, and the chemical parameter as the dependent variable. When there was a significant effect of temperature or water table elevation (either alone or as an interaction with peatland, depth, or both) on porewater chemistry, we used linear regression to investigate specific responses. Data were normalized using natural log or square root transformations when necessary. Statistical significance was designated as $P \le \alpha = 0.05$. All statistical analyses were carried out in SYSTAT v.13.

To examine how spatial and temporal variation in porewater chemistry varied among peatlands, we used coefficients of variation (CV; standard deviation / mean × 100) similar to Griffiths and Sebestyen (2016a) and Griffiths et al. (2017). For spatial variation, the mean value for each chemistry metric (e.g., calcium concentration) was calculated from the multiple samples collected over time (i.e., 3–7 sampling dates, depending on the peatland) from an individual piezometer (e.g., one of the three 0 m piezometers in a peatland). Then, the mean and standard deviation were derived from the 3 values (e.g., three 0 m piezometers) and used to calculate the CV. 'Spatial variation' here reflects variation among different sampling locations within a peatland at a given depth, and therefore represents variation on the scale of 10^1 to 10^2 m within a peatland. A similar approach was used to calculate CVs describing temporal variation in each peatland. However, in this case, the mean value for each chemistry metric was first calculated from the multiple samples collected across the peatland (e.g., three 0 m piezometers) on each sampling date. Then, the overall mean and standard deviation were calculated from those multiple means, and the CV was computed. 'Temporal variation' here reflects seasonal variation (during the ice-free season) at a given depth. CVs can only be calculated from ratio data (i.e., not interval-scale data such as pH), and therefore were not computed for pH.

Data analyzed in this paper are available from Hanson et al. (2015), Griffiths and Sebestyen (2016b), and Verry et al. (2018).

3. Results

3.1. Among-peatland variation in porewater chemistry depth profiles

There were distinct differences in some chemistry depth profiles among peatlands (Table 1). For instance, pH and calcium concentrations varied across peatlands (ANCOVAs: $F_{3,13} = 343.8$, $P < 0.0001$ for pH; $F_{3,13} = 41.2$, $P < 0.0001$ for calcium) and with depth ($F_{1,13} = 110.2$, $P < 0.0001$ for pH; $F_{1,13} = 158.4$, $P < 0.0001$ for calcium), with significant depth × peatland interaction terms ($F_{3,13} = 26.5$, $P < 0.0001$ for pH; $F_{3,13} = 58.6$, $P < 0.0001$ for calcium) (Table 1). The depth profiles of pH revealed more acidic conditions in the S1 bog, S2 bog, and BLF compared to the S3 rich fen (Fig. 2A). In the near-surface peat (0.5 m depth or less), BLF porewater had a higher pH by ~0.5 units compared to S1 and S2 bogs. Depth profiles of calcium concentrations were also distinct in the S3 rich fen compared to the other three peatlands, with much higher calcium concentrations in S3 (Fig. 2B).

There were no significant differences in potassium concentrations across peatlands (ANCOVA: $F_{3,13} = 0.1$, $P = 0.94$) or with depth ($F_{1,13} = 2.3$, $P = 0.15$) (Table 1, Fig. 2C).

There was considerable variation in the depth profiles of porewater TN and TP concentrations among peatlands (Fig. 2D, E). Both TN and TP concentrations varied with depth into the peat (ANCOVAs: $F_{3,13} = 54.5$, $P < 0.0001$ for TN; $F_{3,13} = 8.2$, $P = .01$ for TP); however, there were significant interactions between peatland and depth ($F_{3,13} = 6.6$, $P = 0.006$ for TN; $F_{3,13} = 5.7$, $P = 0.01$ for TP) (Table 1). In surface peat porewater, TN concentrations were similarly low across peatlands (Fig. 2D). However, in deeper peat porewater (>1 m), differences in TN concentrations among peatlands became more evident, with lower concentrations in BLF, moderate concentrations in the S1 bog, and higher concentrations in the S3 rich fen and S2 bog (Fig. 2D). In general, TN concentrations increased with depth in S1, S2, and S3, while concentrations were more uniform throughout the peat profile in BLF. Similar to TN, there was considerable variation in TP depth profiles among peatlands. Total P concentrations were generally low and similar in surface peat porewater across all peatlands (Fig. 2E). In contrast, differences in TP concentrations among peatlands were more distinct at deeper depths (Fig. 2E). Total P concentrations increased with depth in the S2 bog and S3 rich fen, and TP concentrations were higher in S2 and S3 than the S1 bog and BLF at these deeper depths (>1 m) (Fig. 2E).

Total organic carbon concentrations varied among peatlands (ANCOVA: $F_{3,13} = 14.3$, $P = 0.0002$) and with depth ($F_{1,13} = 11.6$, $P = 0.005$) (Table 1), with highest concentrations generally in the S2 bog, followed by the S1 bog, BLF, and S3 rich fen (Fig. 2F). All depth profiles of TOC in porewater were similar in shape, with TOC concentrations higher in surface peats and lower in deeper peats (Fig. 2F).

Both $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ varied across peatlands (ANCOVAs: $F_{3,13} = 48.2$, $P < 0.0001$ for $\delta^{18}O\text{-}H_2O$; $F_{3,13} = 7.9$, $P = .003$ for $\delta D\text{-}H_2O$) but not with depth ($F_{1,13} = 0.4$, $P = .54$ for $\delta^{18}O\text{-}H_2O$; $F_{1,13} = 0.8$, $P = .39$ for $\delta D\text{-}H_2O$) (Table 1). The depth profile of $\delta^{18}O\text{-}H_2O$ in S3 rich fen porewater was distinct compared to the other three peatlands, with lower $\delta^{18}O\text{-}H_2O$ values across the depth profile in S3 (Fig. 2G). In contrast, the $\delta^{18}O\text{-}H_2O$ values in S1, S2, and BLF were similar (Fig. 2G).

Table 1
Analysis of covariance (ANCOVA) results examining the effect of peatland type and depth on porewater chemistry (pH, and calcium, potassium, total nitrogen [TN], total phosphorus [TP], total organic carbon [TOC] concentrations, and $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ values). Statistical significance, designated as $P \le \alpha = 0.05$, is shown in italics.

Factor	pH		Calcium		Potassium		TN		TP		TOC		$\delta^{18}O\text{-}H_2O$		$\delta D\text{-}H_2O$	
	F	*P*	*F*	*P*	*F*	*P*	*F*	*P*	*F*	*P*	*F*	*P*	*F*	*P*	*F*	*P*
Peatland type	343.8	*<0.0001*	41.2	*<0.0001*	0.1	0.94	1.2	0.34	2.4	0.12	14.3	*0.0002*	48.2	*<0.0001*	7.9	*0.003*
Depth	110.2	*<0.0001*	158.4	*<0.0001*	2.3	0.15	54.5	*<0.0001*	8.2	*0.01*	11.6	*0.005*	0.4	0.54	0.8	0.39
Peatland * depth	26.5	*<0.0001*	58.6	*<0.0001*	1.6	0.25	6.6	*0.006*	5.7	*0.01*	2.0	0.17	2.3	0.13	1.5	0.27

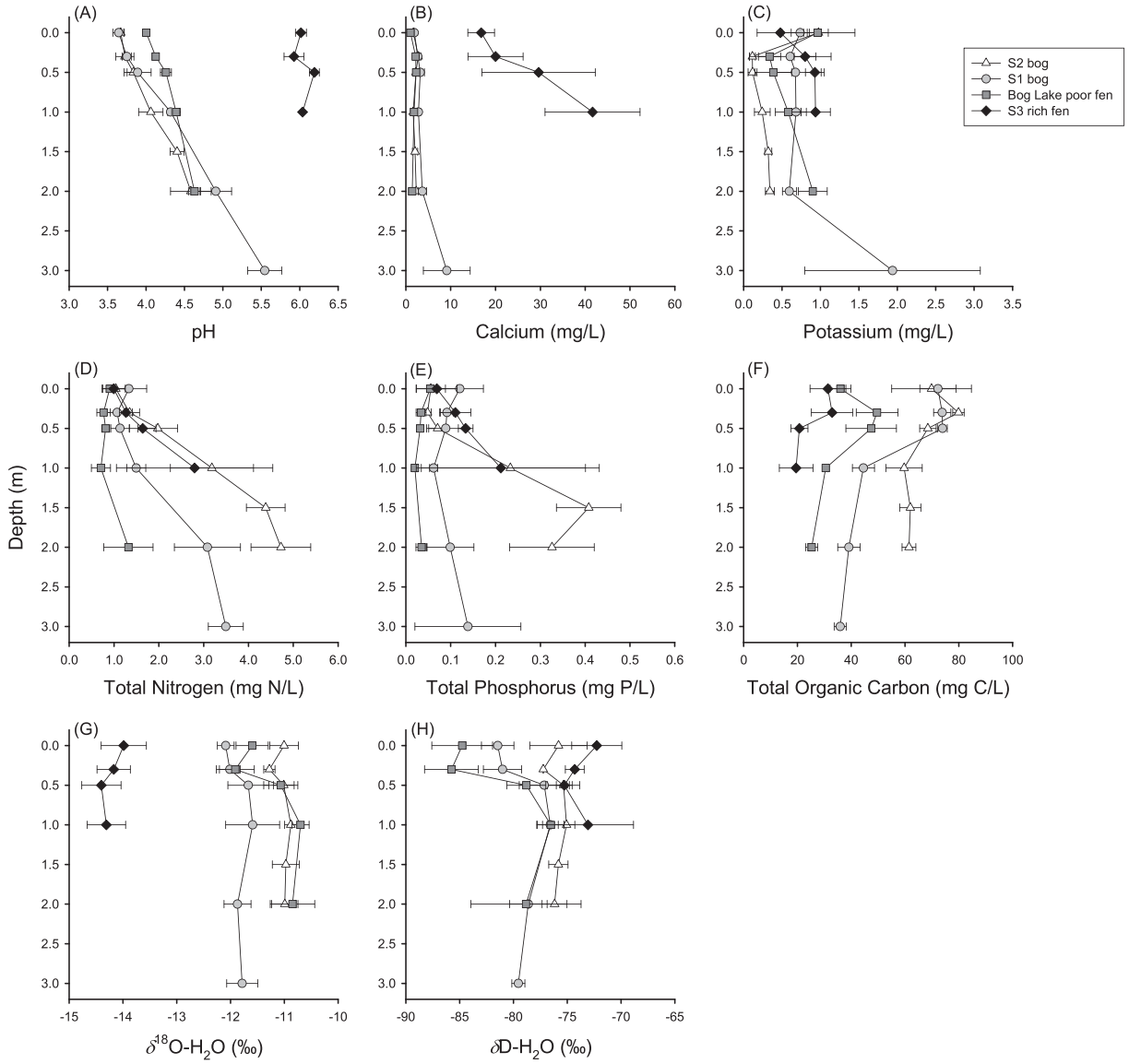

Fig. 2. Depth profiles of (A) pH and (B) calcium, (C) potassium, (D) total nitrogen, (E) total phosphorus, and (F) total organic carbon concentrations, and (G) $\delta^{18}O$-H_2O and (H) δD-H_2O values in the S2 bog (white triangles), S1 bog (light grey circles), Bog Lake poor fen (dark grey squares), and S3 rich fen (black diamonds). Data represent mean concentrations over the measurement season and across the 3 replicate sampling sites, and error bars represent standard deviation across the sampling sites.

There were generally lower δD-H_2O values in shallow peat porewater from BLF and S1 bog, and higher values in S2 bog and S3 rich fen. However, at depths >0.5 m, these differences were no longer evident (Fig. 2H).

When all water chemistry data were analyzed together, Principal Components Analysis (PCA) revealed distinct chemical signatures in each peatland across depths (Fig. 3). In near-surface porewater (0 m), water chemistry in the S3 rich fen was distinct from the other three

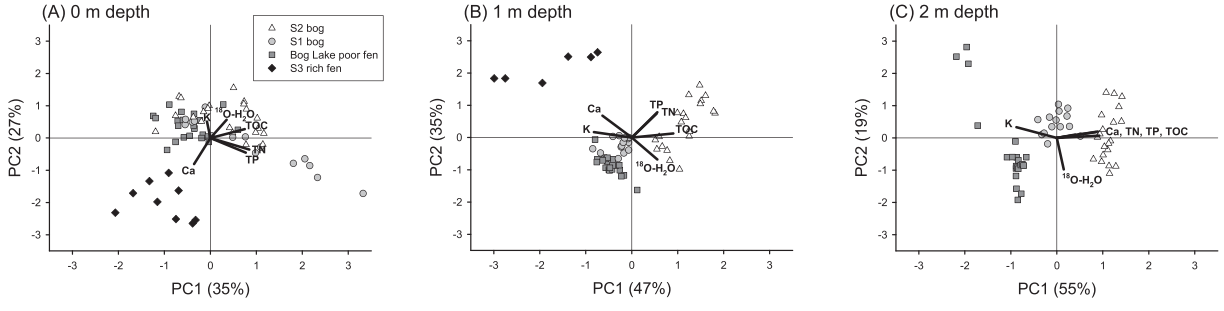

Fig. 3. Principal Components Analysis of porewater chemistry variables at (A) 0 m, (B) 1 m, and (C) 2 m in the S2 bog (white triangles), S1 bog (light grey circles), Bog Lake poor fen (dark grey squares), and S3 rich fen (black diamonds) (porewater only sampled to 1 m depth in S3). The porewater chemistry variables are component loadings, with longer lines indicative of stronger correlations with the nearest axis. The dots indicate factor scores for each measurement (multiple values per peatland represent data from the three replicate piezometers and the multiple sampling dates in 2014).

peatlands, and there was less separation in the chemistry among S1, S2, and BLF (Fig. 3A). Differences between S3 and the other peatlands occurred along both Principal Component Axis 1 (PC1), which explained 35% of the variation, and PC2, which explained 27% of the variation, primarily reflecting differences in calcium, potassium, and TOC concentrations, and δ^{18}O-H_2O values (Fig. 3A, Table 2). Differences in near-surface porewater chemistry among S1, S2, and BLF were primarily evident along PC1, and partially reflected differences in nutrient (TN, TP) concentrations (Fig. 3A, Table 2). At 1 m depth, there was a more distinct separation in porewater chemistry among all four peatlands, and similar solutes and isotopes were driving these patterns as at 0 m depth (Fig. 3B, Table 2). However, there was clearer separation in S2 than S1 and BLF at 1 m (Fig. 3B). At 2 m depth, there were also clear differences in porewater chemistry among S1, S2, and BLF peatlands (S3 not included as there were no piezometers installed to 2 m in S3). Differences in porewater chemistry among the three peatlands at 2 m were primarily observed along PC1, which explained 55% of the variation, and reflected differences in calcium, potassium, TN, and TP concentrations (Fig. 3C, Table 2).

3.2. Water table elevation and soil temperature: seasonal variation and drivers of porewater chemistry

Water table elevation varied least over the year in the S3 rich fen and varied most in the S1 bog (Fig. 4). Specifically, water table varied by 0.52 m over the year in S1, 0.43 m in S2, 0.36 m in BLF, and 0.16 m in S3. The soil temperature depth profiles in each peatland had larger seasonal variation and warmer summer temperatures in near surface peats, and smaller seasonal variation and cooler summer temperatures in deeper peats (Fig. 5). However, the mean temperature and range in temperature measured across the active season varied among peatlands. Mean active season soil temperature was highest in the S3 rich fen at the shallowest depth (5 cm), but at deeper depths, a consistent pattern emerged of highest mean active season soil temperature in BLF, followed by S1, S2, and S3. In S3, soil temperatures exhibited a larger range over the active season in near-surface peats (5, 10 cm depths) than in the other peatlands. The range in soil temperature over the active season was 26.3 °C at 5 cm depth in S3, compared to 20.8 °C in BLF, 17.4 °C in S1, and 14.6 °C in S2. Temperature values and dynamics are impacted by water table and vegetation at each site. For example, the closed canopy forest at S2 may be responsible for the reduced mid-summer surface warming at that site while groundwater inputs to S3 may be driving the cooler temperatures at depth in that fen.

Both soil temperature and water table elevation were significant drivers of porewater chemistry; however, the effects of soil temperature and water table elevation were not consistent across peatlands, depths, and chemical parameters. There was no effect of soil temperature on pH, and TN and TP concentrations (ANCOVAs: $F_{1,102} = 2.6$, $P = 0.11$ for pH; $F_{1,103} = 2.4$, $P = .12$ for TN; $F_{1,103} = 1.7$, $P = 0.19$ for TP). In contrast, there was an interactive effect of temperature and depth on potassium concentrations ($F_{1,103} = 8.7$, $P = 0.004$) and significant interactions between temperature, depth, and peatland for calcium and TOC concentrations, and δ^{18}O-H_2O and δD-H_2O values ($F_{3,103} = 8.4$, $P < .0001$ for calcium; $F_{3,103} = 3.4$, $P = .02$ for TOC; $F_{3,103} = 4.4$, $P = .006$ for δ^{18}O-H_2O; $F_{3,103} = 12.9$, $P < 0.0001$ for δD-H_2O). Calcium concentrations were negatively related to soil temperature at some depths in S1, S2, and BLF (Fig. 6), although there was a significant positive relationship at 2 m depth in BLF (Fig. 6C). There were no significant relationships between calcium concentration and temperature in S3 (Fig. 6D). For the remaining analytes (TOC, δ^{18}O-H_2O, and δD-H_2O), the responses to temperature by peatland and depth were variable and mostly non-significant. For example, there was a significant, positive relationship between temperature and TOC concentration at 2 m in BLF ($r^2 = 0.80$, $P = .007$), and a significant, negative relationship between temperature and TOC concentration at 2 m in S2 ($r^2 = 0.63$, $P = 0.03$); relationships in all other peatland-depth combinations for TOC were not significant ($P > .05$).

There were no significant relationships between water table elevation and pH, and calcium, potassium, and TN concentrations (ANCOVAs: $F_{1,102} = 0.1$, $P = .71$ for pH; $F_{1,103} = 1.2$, $P = 0.28$ for calcium; $F_{1,103} < 0.1$, $P = .94$ for potassium; $F_{1,103} = 2.2$, $P = .14$ for TN). There was a significant effect of water table elevation for δD-H_2O ($F_{1,103} = 7.9$, $P = 0.006$), significant peatland by water table elevation interactions for TP concentration ($F_{3,103} = 2.9$, $P = .04$) and δ^{18}O-H_2O ($F_{3,103} = 2.9$, $P = 0.04$), and a significant water table by depth interaction for TOC ($F_{1,103} = 6.4$, $P = 0.01$). Similar to the effects of temperature, the effects of water table elevation on porewater chemistry varied by peatland and depth and were mostly non-significant. For example, there was a significant negative relationship between water table elevation and TP concentration in S1 at 0 m ($r^2 = 0.83$, $P = 0.03$) and a significant positive relationship in S2 at 1.5 m ($r^2 = 0.70$, $P = 0.02$), while all other peatland-depth combinations for TP were not significant.

3.3. Spatial vs temporal variability in porewater chemistry depth profiles

There was no consistent decrease in temporal and spatial variation (based on CVs) in porewater chemistry along the bog to rich-fen gradient (Fig. 7), counter to our hypothesis. While temporal variation in calcium, potassium, TN, and TP concentrations and δ^{18}O-H_2O values was lower in the S3 rich fen than in the other peatlands (Fig. 7A, B, C, D, F), there was greater variation (both spatial and temporal) in TOC concentrations in S3 (Fig. 7E), and no clear pattern in spatial variation across the bog to rich-fen gradient for the other analytes (Fig. 7A–D, F–G). Further, there were no clear patterns in spatial and temporal variation with depth, except that temporal variation in water stable isotopes was highest in near-surface porewater (0 m) in all peatlands (Fig. 7F, G) and some chemistries at 3 m depth in S1 (potassium, nitrate, and TP concentrations) had high CVs compared to the rest of the depth profile.

When all data were analyzed together, porewater chemistry (across all depths and solutes/isotopes) was generally more temporally than spatially variable (i.e., temporal CV > spatial CV for a given measurement) in all peatlands except S3 (Table 3). In S2, S1, and BLF, porewater chemistry was slightly more temporally than spatially variable (52%, 55%, and 54% of chemistry measurements in these three peatlands were more temporally than spatially variable, respectively) (Fig. 8). In S3, 39% of measurements were more temporally than spatially variable (Fig. 8).

The importance of temporal variation in porewater chemistry was more evident in near-surface (0, 0.3 m depths) peats (Table 3). In S2, S1, and BLF, 64%, 86%, and 64% of porewater chemistry measurements in these peatlands were more temporally than spatially variable, respectively. In contrast, near-surface porewater chemistry was more spatially (57% of measurements) than temporally (43% of measurements) variable in S3, consistent with the pattern observed throughout the entire depth profile.

Table 2
Component loadings from Principal Components Analysis (PCA) of porewater chemistry variables at (A) 0 m, (B) 1 m, and (C) 2 m in the S2 bog, S1 bog, Bog Lake poor fen, and S3 rich fen (porewater only sampled to 1 m depth in S3, so S3 was not included in the 1 m depth PCA).

Water chemistry	0 m depth		1 m depth		2 m depth	
	PC1	PC2	PC1	PC2	PC1	PC2
Calcium	−0.35	−0.81	−0.63	0.67	0.40	0.10
Potassium	−0.07	0.51	−0.82	0.17	−0.88	0.33
Total nitrogen	0.85	−0.36	0.56	0.78	0.89	0.20
Total phosphorus	0.77	−0.45	0.54	0.74	0.85	0.18
Total organic carbon	0.75	0.27	0.91	0.13	0.92	0.07
δ^{18}O-H_2O	0.35	0.56	0.56	−0.68	0.15	−0.98

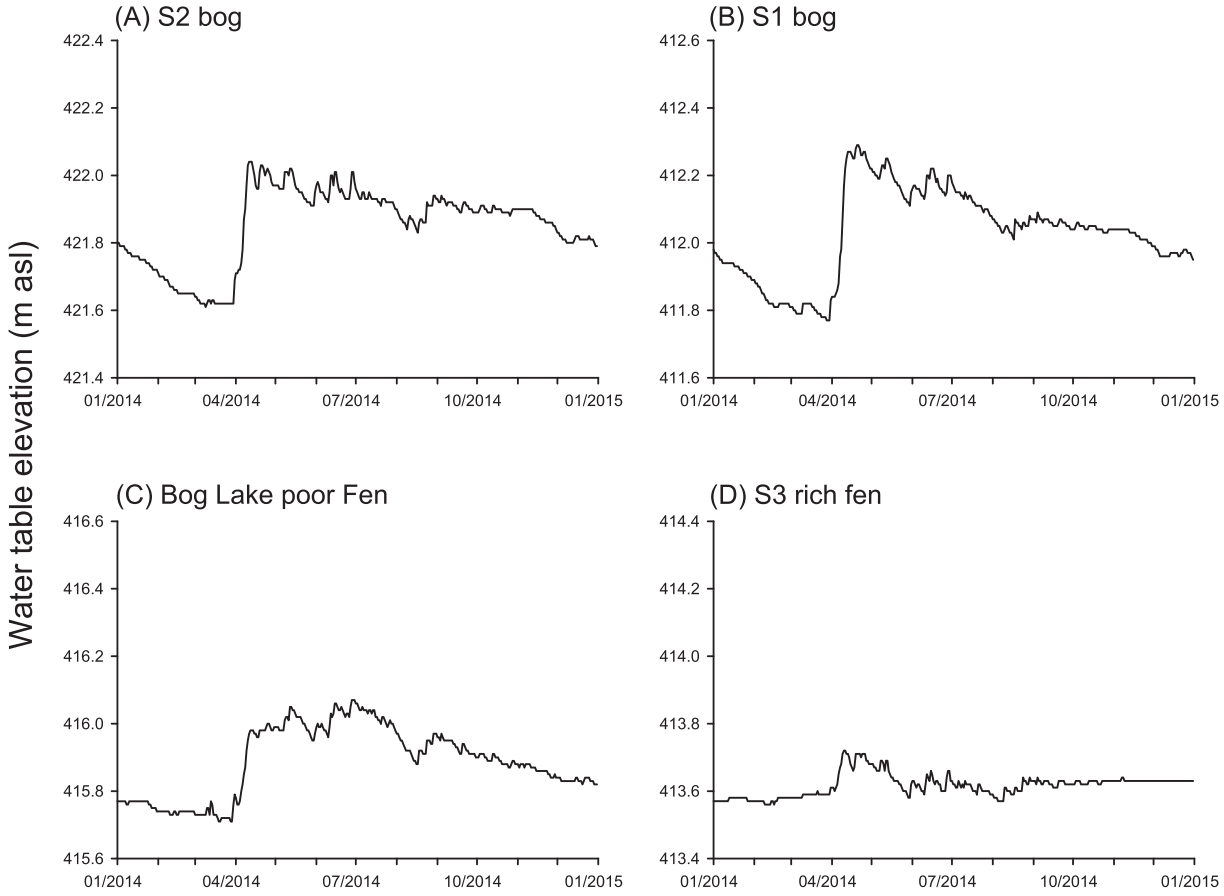

Fig. 4. Daily water table elevations (as meters above sea level) in the (A) S2 bog, (B) S1 bog, (C) Bog Lake poor fen, and (D) S3 rich fen in 2014. While the absolute values differ, the y-axis range on each of the four panels is the same so that the variability in water table elevations can be compared across peatlands.

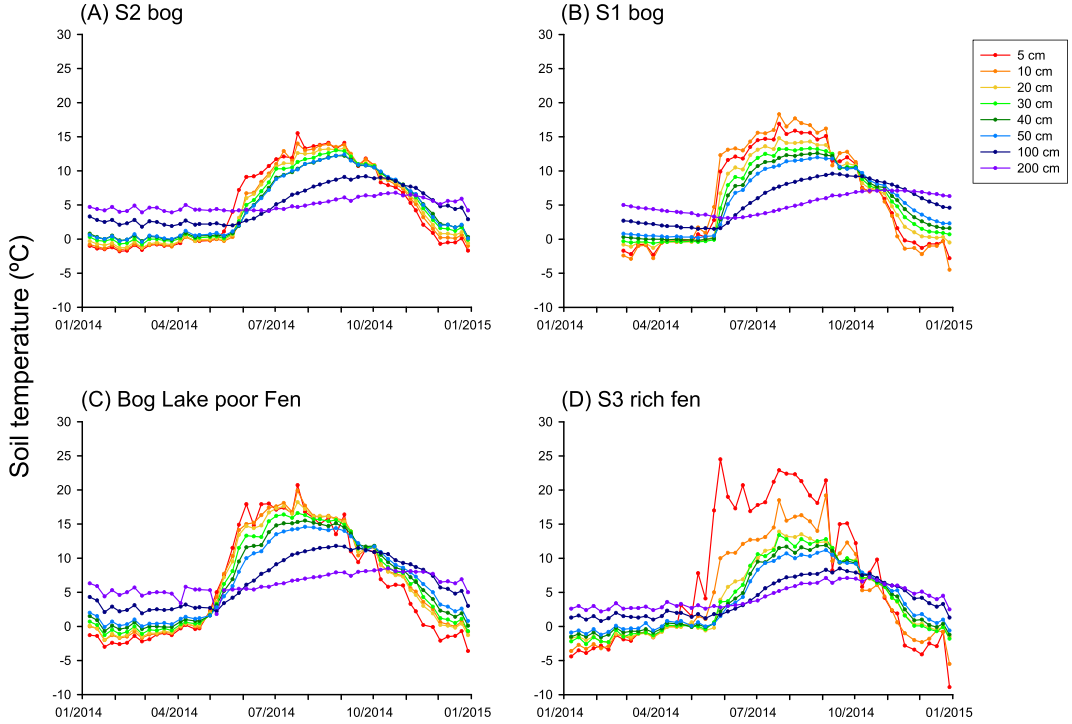

Fig. 5. Soil temperature at 5, 10, 20, 30, 40, 50, 100, and 200 cm depths measured ~weekly in the (A) S2 bog, (B) S1 bog, (C) Bog Lake poor fen, and (D) S3 rich fen in 2014. Soil temperature measurements in the S1 bog began on February 25, 2014.

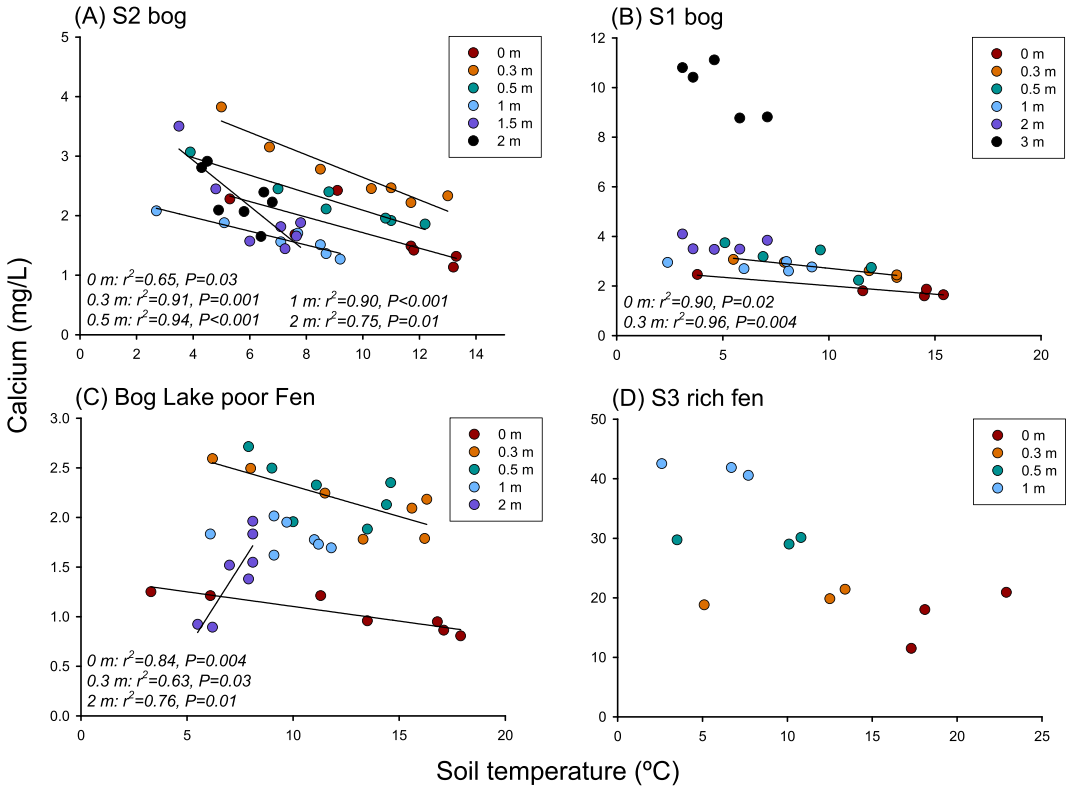

Fig. 6. Depth-specific relationships between soil temperature and porewater calcium concentration in the (A) S2 bog, (B) S1 bog, (C) Bog Lake poor fen, and (D) S3 rich fen. Each datapoint represents the mean concentration across the 3 replicate sampling sites measured during a sampling event. Significant regressions between soil temperature and calcium concentration are shown as linear relationships, along with the corresponding statistical results.

4. Discussion

4.1. Among-peatland variation in porewater chemistry depth profiles

Porewater chemistry generally followed the patterns expected along the bog to fen gradient; however, there were some differences. As hypothesized, and supported by many other studies (Sjörs, 1950; Glaser et al., 1990; Sjörs and Gunnarsson, 2002; Bourbonniere, 2009), the S3 rich fen had the highest pH and calcium concentrations compared to the Bog Lake poor fen (BLF), and the S1 and S2 bogs. However, pH and calcium concentrations were fairly similar between the poor fen and the two bogs.

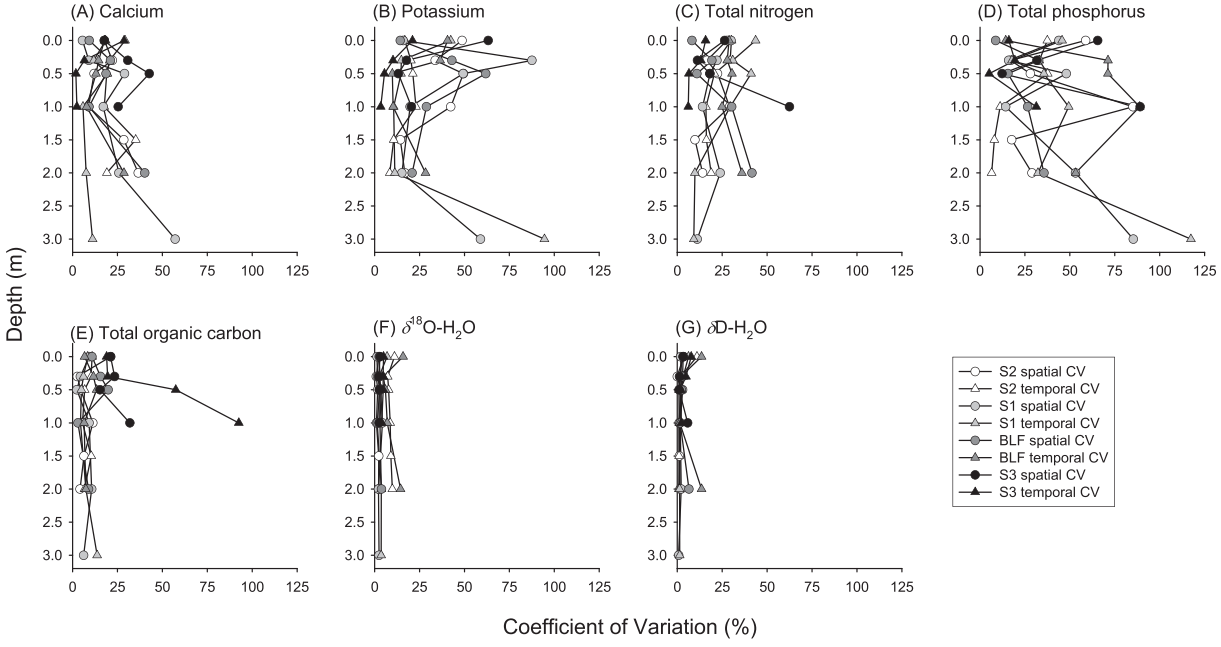

Fig. 7. Depth profiles of the spatial (circles) and temporal (triangles) coefficients of variation (in percentage; CV) for (A) calcium, (B) potassium, (C) total nitrogen, (D) total phosphorus, and (E) total organic carbon concentrations, and (F) $\delta^{18}O$-H_2O and (G) δD-H_2O values in the S2 bog (white symbols), S1 bog (light grey symbols), Bog Lake poor fen (BLF; dark grey symbols), and S3 rich fen (black symbols).

Table 3
The percentage of measurements where the temporal coefficient of variation (CV) was greater than the spatial CV across all depths (0, 0.3, 0.5, 1, 1.5, 2, 3 m depending on the peatland) and only within the near-surface porewater (0, 0.3 m depths) in the S2 bog, S1 bog, Bog Lake poor fen, and S3 rich fen.

Peatland	% of measurements with temporal CV > spatial CV	
	All porewater depths	Shallow subsurface porewater depths
S2 bog	52%	64%
S1 bog	55%	86%
Bog Lake poor fen	54%	64%
S3 rich fen	39%	43%

In addition to variation among peatlands, spatial variation in porewater chemistry was also evident with depth for pH and calcium concentrations. pH increased with depth in the poor fen and the two bogs, while the largest increase in calcium concentrations with depth was measured in the rich fen. The higher pH and calcium concentrations at depth in these peatlands may be due to exchange with surrounding groundwater in the fens and S1 bog (at depth) or reflect a previous minerotrophic state in the bogs and poor fen (Vitt et al., 1995; Gorham and Janssens, 2005; Griffiths and Sebestyen, 2016a). Overall, the patterns in pH and calcium concentrations with depth were not consistent across the four study peatlands, suggesting that the sources and drivers of these chemistries along the depth profiles were also not consistent across peatlands.

It was also expected that water stable isotopes would vary between bog and fen peatlands (e.g., Levy et al., 2014) if the predominant groundwater source for fens and the atmospheric water source for bogs had distinctive isotopic signatures. Similar to the patterns for pH and calcium concentrations, $\delta^{18}O\text{-}H_2O$ was more depleted in the S3 rich fen compared to the other peatlands suggesting a different predominant source of water, which is consistent with past findings of a groundwater discharge through the S3 fen (Bay, 1967; Sander, 1976). In contrast, the different $\delta^{18}O\text{-}H_2O$ values at S2 and S1 compared to S3 are consistent with different water sourcing in the bogs vs the rich fen (i.e., meteoric-only inputs of water to bogs). The greater similarity between the $\delta^{18}O\text{-}H_2O$ values at S2, S1, and BLF relative to S3 suggest recharge from precipitation, with some groundwater flow through BLF.

Total organic carbon concentrations also varied along the bog to fen gradient, with higher TOC concentrations in the bogs (S2 and S1), moderate concentrations in Bog Lake poor fen, and lower concentrations in S3 rich fen. A pattern of higher TOC concentrations in near-surface porewater and lower concentrations in deeper porewater was also consistent across all four peatlands, and may reflect vertical advection and mineralization of TOC along the depth profile (Chasar et al., 2000; Corbett et al., 2013; Tfaily et al., 2014; Griffiths and Sebestyen, 2016a; Wilson et al., 2016; Tfaily et al., 2018) as well as exchange with groundwater in S1 (at depth), BLF, and S3. The observed gradient in TOC concentrations from fens to bogs was clearer than our expectations from previous studies that have found lower, equal, or higher dissolved organic C (DOC) or TOC concentrations in bogs than in fens (Glaser et al., 1981; Urban et al., 1989; Reeve et al., 1996; Moore, 2003; Pastor et al., 2003; Lin et al., 2012; Ulanowski and Branfireun, 2013; Avagyan et al., 2014). Several processes contribute to the formation and loss of DOC from peatlands, and these processes are in turn governed by multiple drivers (Freeman et al., 1993, 2001; Moore and Dalva, 2001; Moore, 2003; Pastor et al., 2003; Fenner et al., 2007; Mitchell et al., 2008; Strack et al., 2008; Trinder et al., 2008; Armstrong et al., 2012). The dominant processes and drivers regulating DOC concentrations may vary from peatland to peatland, leading to the inconsistent patterns in DOC concentrations between bogs and fens observed across multiple studies (Ulanowski and Branfireun, 2013). In this study, the lower concentration of TOC in fens vs bogs likely reflects dilution due to groundwater inputs to the poor and rich fens. It is also possible that a higher and less variable water table in the fens vs the bogs may have resulted in slower litter and soil decomposition rates and therefore less TOC released into porewater (Ulanowski and Branfireun, 2013).

In contrast to the chemistry patterns described above, we found that nutrient (TN, TP, potassium) concentrations in near-surface and deeper porewater did not differ along the bog to fen gradient. The lack of differences in near-surface porewater nutrient concentrations across

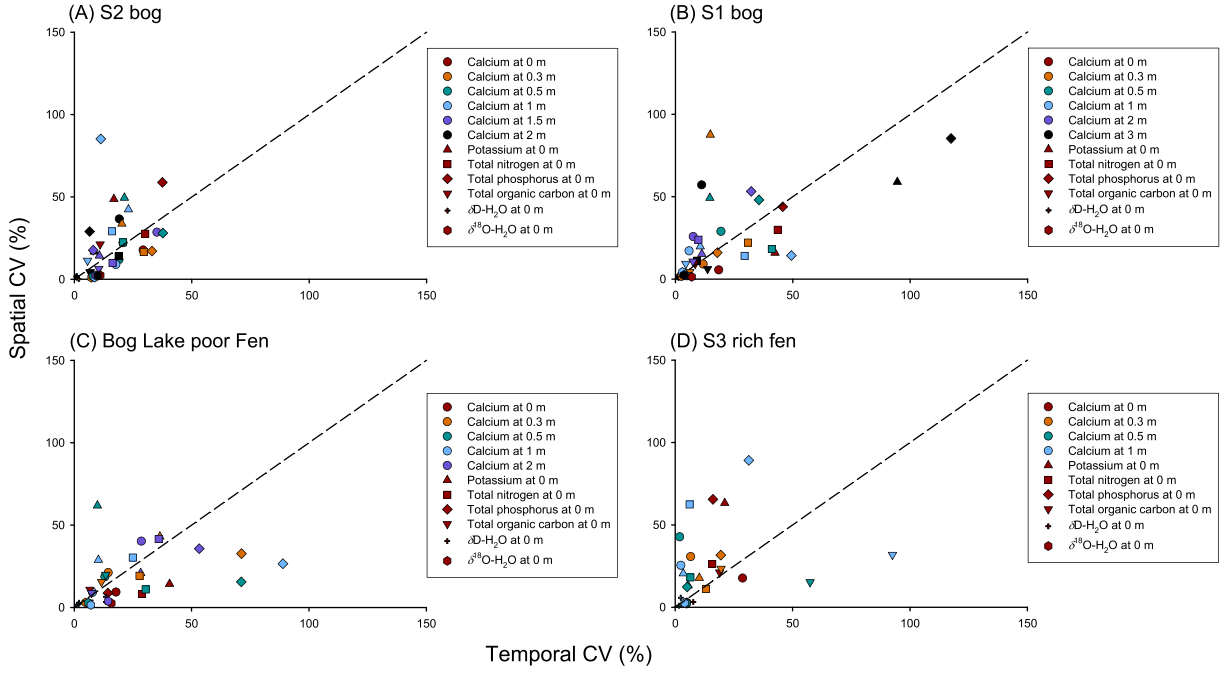

Fig. 8. Temporal vs spatial variation (as coefficients of variation in percentage; CV) in porewater calcium, potassium, total nitrogen, total phosphorus, and total organic carbon concentrations and stable isotopes of water ($\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$) depth profiles in the (A) S2 bog, (B) S1 bog, (C) Bog Lake poor fen, and (D) S3 rich fen. The dotted line is the 1:1 line. Different symbols represent the different chemistries, and different colors represent the different depths (shown for calcium in the legend, as an example).

peatlands suggests that drivers other than those that typically dictate bog vs fen characteristics (e.g., hydrology, plant community composition) are affecting nutrient dynamics in these ecosystems. Peatlands are often nutrient limited (e.g., primarily N-, P-, or co-limited for N and P) (Bridgham et al., 1996; Boeye et al., 1997; Williams and Silcock, 1997; Bedford et al., 1999; Kellogg and Bridgham, 2003; Gotelli et al., 2008; Hill et al., 2014; Seifert-Monson et al., 2014). While nutrient availability is expected to increase along a bog to fen gradient (e.g., Bridgham et al., 2001), nutrient concentrations in porewater may not always reflect this gradient (Vitt et al., 1995; Bragazza and Gerdol, 2002) if porewater nutrient measurements represent what remains in water after biotic uptake in these nutrient-limited systems. Overall, if a nutrient availability gradient from bogs to fens exists in these study peatlands, it was not measurable using total nutrient concentration data from porewater. Instead, a combination of dissolved (nitrate, ammonium, phosphate) and total nutrient concentration measurements, process-based evaluations (e.g., nutrient limitation and enzyme activity assays), and ecosystem nutrient budgets would provide a more thorough analysis of nutrient dynamic differences in bogs and fens. As an example, despite similar TN and TP concentrations in the S2 bog and S3 rich fen found this study, ecoenzyme and microbial activity analysis in these same peatlands showed that S2 tended toward greater N and P limitation than S3 (Hill et al., 2014).

In summary, pH, $\delta^{18}O\text{-}H_2O$, and calcium and TOC concentrations tended to follow the bog to fen gradient, while there was no clear pattern in TN and TP concentrations in near-surface porewater across peatlands. However, an analysis of all porewater chemistry parameters together (i.e., via Principal Components Analysis) highlighted that differences in peatland chemistry were partially explained by TN and TP concentrations. In near-surface porewater, PCA analysis revealed that the S3 rich fen chemistry was most different, with less variation among S1 bog, S2 bog, and BLF near-surface chemistry. Porewater chemistry at S1, S2, and BLF was more distinct in deeper peats, showing that the sources, transport, and cycling of solutes are more divergent at depth.

Multiple factors are used to characterize peatlands, including hydrology, chemistry, and vegetation (Moore and Bellamy, 1974; Glaser, 1987; Bridgham et al., 1996; Wheeler and Proctor, 2000; Bragazza and Gerdol, 2002; Sjörs and Gunnarsson, 2002). We used porewater chemistry to assess among-peatland variation and found that measuring multiple solutes at different spatial scales (among peatlands, with depth) identified both similarities and differences in water chemistry among peatland types. Characterizing among-peatland variability can be useful when representing the extent of peatland properties in ecosystem models and can be helpful in evaluating the representativeness of peatlands within a given region. For example, the S1 bog is the site of SPRUCE, a decade-long, ecosystem-scale experiment examining how warming and elevated atmospheric CO_2 concentrations affect peatland ecosystem processes (Wilson et al., 2016; Hanson et al., 2017; Richardson et al., 2018). To understand how the responses of porewater to climate change may be applicable to peatlands beyond the S1 bog, it is important to assess similarities and differences in peatland properties, such as porewater chemistry. These results suggest that near-surface porewater chemistry is similar in bog and poor fen peatlands (e.g., S1, S2, BLF) and dissimilar in rich fen peatlands (S3) in the Marcell Experimental Forest in Minnesota. A more complete characterization of solute dynamics (e.g., solute pools, process rates, and drivers of those processes) is needed to fully compare these peatlands and assess representativeness, especially those that have similar porewater chemistries.

4.2. Spatial vs temporal variability in porewater chemistry depth profiles

In this study, the porewater chemistry of Marcell Experimental Forest peatlands was shown to vary both among peatlands and with depth into the peat. However, additional scales of variability should be considered when assessing porewater chemistry dynamics, including variability within peatlands and over time. Of these two, more studies have examined temporal variation in porewater chemistry (e.g., Gerdol, 1990; Bragazza, 1993; Vitt et al., 1995; Bragazza et al., 1998; Proctor, 2003, 2006; Griffiths and Sebestyen, 2016a) than spatial variation within a peatland (e.g., Moore, 1987; McNamara et al., 1992; Bragazza and Gerdol, 2002; Whitfield et al., 2010; Griffiths and Sebestyen, 2016a), and those that examined the latter primarily assessed changes in chemistry along spatial gradients (e.g., from an ombrotrophic bog center to a minerotrophic margin; Glaser et al., 1990, Bragazza and Gerdol, 1999, 2002, Tahvanainen et al., 2002, Crushell et al., 2009, Levy et al., 2014). By measuring porewater chemistry depth profiles monthly during one ice-free (active) season at three replicate locations per peatland, we found that porewater chemistry was both temporally and spatially variable; highlighting the importance of collecting porewater chemistry samples at multiple locations within a peatland over time.

We expected that porewater chemistry would be less variable in fens than bogs because of the persistent groundwater exchange in fens as evidenced by the smaller water table fluctuations over the year. However, temporal and spatial variation did not consistently decrease along the bog to fen gradient, suggesting that factors other than water sources (i.e., predominantly groundwater in fens vs predominantly atmospheric in bogs) may be influencing variation in porewater chemistry.

Near-surface porewater chemistry was more temporally than spatially variable in the two bogs and the poor fen and was more spatially than temporally variable in the rich fen. Greater temporal variability in near-surface porewater chemistry may reflect the effect of multiple physical and biological drivers (e.g., biotic uptake and transformation, changing water table, intermittent precipitation inputs, daily and seasonal deviations in temperature) that are known to vary over time and affect peatland processes. In fact, we found that both soil temperature and water table elevation were important drivers of temporal variation in porewater chemistry, but effects were inconsistent across peatlands, depths, and chemical parameters, and we could not determine whether other covarying factors may have been driving these relationships. It is not clear why near-surface porewater chemistry in the S3 rich fen was found to be more spatially than temporally variable, but the temporal assessment in this peatland may be limited because samples were only collected over 3 months, while in all other peatlands, sampling took place over a 6-month period. Overall, while near-surface porewater chemistry was generally more variable from month to month than within a peatland, except in S3 rich fen, there was still considerable spatial variation in porewater chemistry in all peatlands, highlighting the need to incorporate both forms of variation into peatland studies.

Temporal and spatial variation in porewater chemistry also did not consistently change with peat depth, and there was still considerable spatial and temporal variability in deeper porewater chemistry in all peatlands. Further, soil temperature and water table elevation were sometimes significant drivers of deeper peat porewater chemistry, although the mechanisms behind these relationships were not clear. Porewater chemistry may be less variable in deeper peats in part due to lower hydraulic conductivities that diminish the rate of transport at depth (McKenzie et al., 2009; Verry et al., 2011a). However, water and solutes in peatlands are transported vertically (upwards and downwards) and laterally via advection and dispersion (Siegel et al., 1995; Reeve et al., 2001; McKenzie et al., 2009). Flow can switch from predominantly vertical to predominantly lateral, or vice versa, on both seasonal and decadal time scales (Siegel and Glaser, 1987; Siegel et al., 1995; Fraser et al., 2001). Further, rapid changes in near-surface water table elevations and solute concentrations suggest turnover from month to month (or faster; e.g., Griffiths and Sebestyen, 2016a). While groundwater exchange may drive the high spatial

variation in deeper peat porewater chemistry observed in this study, we do not have peat physical property and hydraulic data to explore these hypotheses. Spatial variation in deep porewater chemistry in our study may also in part be attributable to slight variation in depths of the deepest piezometers. In general, however, deeper porewater chemistry has been shown to be spatially and temporally variable in the Marcell Experimental Forest and in other peatlands worldwide (Siegel et al., 1995; Vitt et al., 1995; Waddington and Roulet, 1997; Fraser et al., 2001; Moore, 2003; Avagyan et al., 2014; Griffiths and Sebestyen, 2016a), highlighting the need for studies that couple porewater chemistry with intensive hydrological and biotic measurements in order to better elucidate spatial and temporal patterns in peatland porewater chemistry.

5. Concluding remarks

Porewater chemistry was sometimes more spatially than temporally variable, but not uniformly so among peatlands, or in consistent ways to be applicable to all bogs and fens at the Marcell Experimental Forest. Our findings help to reinforce that some measures of porewater chemistry are generalizable by peatland type, with acidic conditions, lower calcium concentrations, and higher TOC (or DOC) concentrations expected in bogs and less acidic to circumneutral conditions, higher calcium concentrations, and lower TOC (or DOC) concentrations in fens. These expectations of pH and calcium concentration are consistent with past conceptualizations of peatland classification. $\delta^{18}O\text{-}H_2O$ was also distinct in near-surface porewater of the rich fen than the other three peatlands, suggesting that natural abundance stable isotopes of water may be a useful tool for differentiating bogs vs fens. In contrast, our findings identify that site-specific information may be needed for TN, TP, and potassium concentrations rather than a broadly applicable concept of differences from bogs to fens, which may be particularly relevant to modeling of peatland nutrient cycles.

Beyond extending our baseline of understanding for peatlands, patterns and concentrations in porewater solutes are relevant to the role of peatlands as terrestrial-aquatic interfaces. Peatlands are sources of solutes to downstream water bodies and most of that water moves laterally along near-surface flow paths in bogs (Verry et al., 2011a, 2011b). Additionally, downstream water yields are exponentially higher from fens that discharge groundwater than bogs that drain near-surface runoff of precipitation (Verry, 1975; Urban et al., 2011). Therefore, quantifying temporal and spatial variation in porewater chemistry depth profiles between bogs and fens can help advance our understanding of biological productivity and biogeochemical processes within and downstream of peatlands.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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