

Dynamic Vertical Profiles of Peat Porewater Chemistry in a Northern Peatland

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Abstract We measured pH, cations, nutrients, and total organic carbon (TOC) over 3 years to examine weekly to monthly variability in porewater chemistry depth profiles (0–3.0 m) in an ombrotrophic bog in Minnesota, USA. We also compared temporal variation at one location to spatial variation in depth profiles at 16 locations across the bog. Most solutes exhibited large gradients with depth. pH increased by two units and calcium concentrations increased over 20 fold with depth, and may reflect peatland development from minerotrophic to ombrotrophic conditions. Ammonium concentrations increased almost 20 fold and TOC concentrations decreased by half with depth, and these patterns likely reflect mineralization of peat or decomposition of TOC. There was also considerable temporal variation in the porewater

chemistry depth profiles. Ammonium, soluble reactive phosphorus, and potassium showed greater temporal variation in near-surface porewater, while pH, calcium, and TOC varied more at depth. This variation demonstrates that deep peat porewater chemistry is not static. Lastly, temporal variation in solute chemistry depth profiles was greater than spatial variation in several instances, especially in shallow porewaters. Characterizing both temporal and spatial variability is necessary to ensure representative sampling in peatlands, especially when calculating solute pools and fluxes and parameterizing process-based models.

Keywords Black spruce-*Sphagnum* ombrotrophic bog · Solute chemistry · Spatial and temporal variability · Depth profiles · Groundwater

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Introduction

Peatlands are carbon-rich ecosystems, comprising ~30 % of the terrestrial carbon supply while covering only 3 % of the world's land surface (Gorham 1991; Yu et al. 2010). The majority of this carbon (>98 %) is stored belowground in peat, and these soils are hotspots for biogeochemical cycling on the landscape. Hydrology is a dominant driver of biogeochemical cycling in peatlands. Peatlands that are rain-fed (ombrotrophic bogs) are characterized by low cation concentrations and pH (Ca < 1 mg/L, pH < 4), while peatlands that are groundwater-fed (minerotrophic fens) have higher cation concentrations and pH (Ca 20–45 mg/L, pH > 7 for rich fens) (Verry 1975; Glaser et al. 1990). These differences between bogs and fens are widely accepted as principle (e.g., Verry 1975; Pakarinen and Tolonen 1977; Waughman 1980; Bourbonniere 2009) and have been used to classify, assess, and model peatlands. In contrast, temporal and spatial variation in porewater chemistry

within a peatland has been less well characterized, especially for resource assessment and ecosystem modeling. These points are especially salient as peatlands and their carbon stocks are more vulnerable to environmental disturbance from climate change than most other ecosystem types (Collins et al. 2013). Consequently, characterization of spatial and temporal variability in porewater chemistry is needed to ensure representative sampling in peatlands (Ulanowski and Branfieriun 2013), calculate solute pools and yields, and scale up results from point sampling, which is vital to the parameterization of physical and biogeochemical processes in Earth System Models.

While spatial variability in porewater chemistry has been reported, research on temporal variability over seasons and years is less common. Within a peatland, porewater biogeochemistry varies at small spatial scales due to changes in microtopography (Ulanowski and Branfieriun 2013). Gradients also exist at larger scales (i.e., from the edge to center of a peatland) due to changes in mineral inputs and vegetation composition (Bragazza and Gerdol 2002). In addition to lateral variability, there can also be substantial vertical gradients in porewater chemistry. Porewater pH and cation concentrations often increase with depth (Siegel et al. 1994; Vitt et al. 1995). Nutrient (N, P) and dissolved organic carbon (DOC) concentrations also vary with depth in bogs (e.g., Vitt et al. 1995; Clymo and Bryant 2008; Tfaily et al. 2014), but are reported less often than pH and cations. When temporal variation has been studied, the focus has usually been on surface water and near-surface porewater chemistry (e.g., Proctor 1994; Glaser et al. 1997; Bragazza et al. 1998; Proctor 2006; Tahvanainen et al. 2003; Koehler et al. 2009; Seifert-Monson et al. 2014). One study that examined temporal variability in depth profiles found that pH, alkalinity, and ammonium concentrations were more variable at shallower depths, while nitrate concentrations were similarly variable along the depth profile (Vitt et al. 1995). Few studies have examined variation over time and across multiple depth profiles.

The primary objective of our study was to examine temporal variation in porewater chemistry depth profiles (0–3.0 m). We measured pH, nutrients, total organic carbon (TOC), and cations weekly (2011) or monthly (2012 and 2013) in an ombrotrophic peatland in Minnesota, USA, to examine depth profiles and temporal variation in these profiles. We also compared temporal variation from one frequently sampled profile to spatial variation in 16 depth profiles located across the bog. We expected greater temporal variation in surface (0–0.5 m) than deeper (1.0–3.0 m) peat porewater chemistry due to the proximity to incoming rainfall and snowmelt, uptake by shallowly rooted vegetation, and feedbacks from fluctuating water levels on elemental cycling. In contrast, we hypothesized that porewater chemistry in deeper, permanently saturated peat would be less variable and influenced by decomposition dynamics (i.e., reflecting centuries of mineralization) and

potential interactions with groundwater. Lastly, we predicted that depth profiles would vary more temporally than spatially at shallow depths because of the multiple factors potentially affecting near surface porewaters.

Methods

Study Site

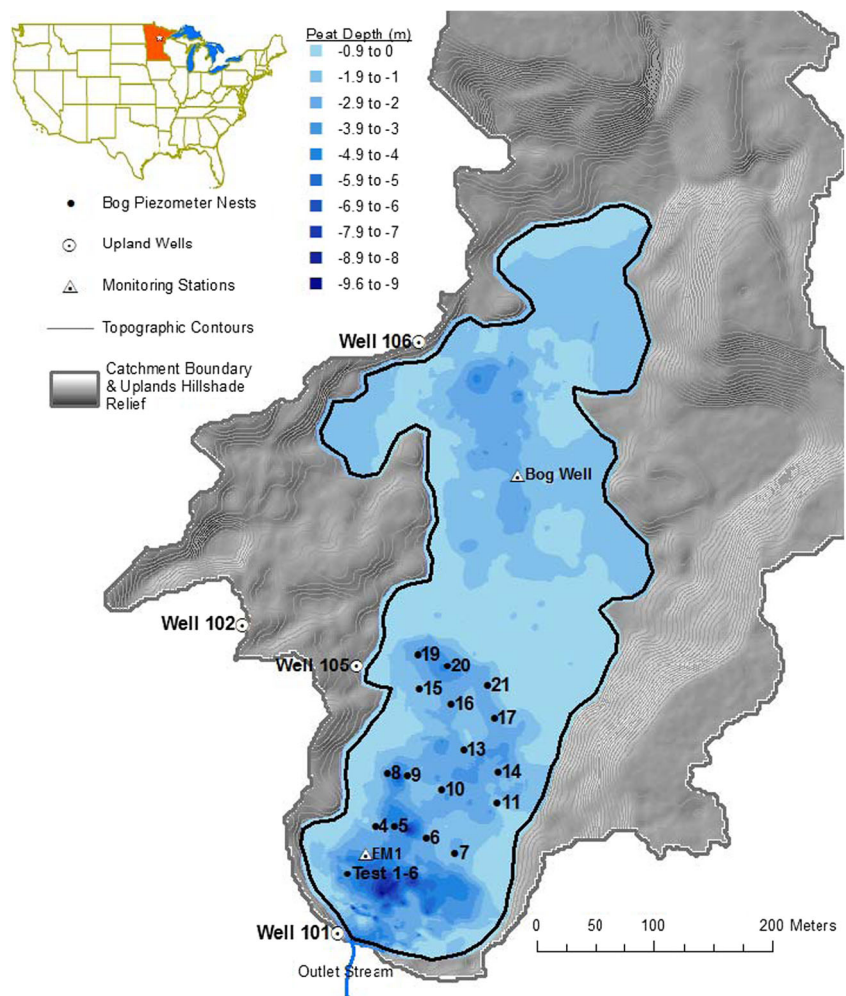
The S1 bog is located in the Marcell Experimental Forest (MEF) in north-central Minnesota (Fig. 1). From 1961 to 2009, mean annual air temperature and precipitation at the MEF was 3.4 °C and 780 mm, respectively (Sebestyen et al. 2011). Snow typically falls from November through April, and is about one-third of annual precipitation. The landscape of the MEF is covered by forested uplands, peatlands, and lakes. The peatlands began to develop roughly 12,000 years ago as post-glacial lakes and ice-block depressions infilled with organic soils (Verry and Janssens 2011).

The 8.1-ha S1 bog (47°30.476'N; 93°27.162'W) is vegetated with black spruce (*Picea mariana*) and tamarack (*Larix laricina*) trees, Ericaceous shrubs (mainly *Rhododendron* (*Ledum*) *groenlandicum* and *Chamaedaphne calyculata*), graminoids and forbs, and *Sphagnum* mosses (*S. angustifolium*, *S. fallax*, and *S. magellanicum*). The bog surface has a hummock-hollow microtopography, with approximate elevations of 10–30 cm from the tops of the hummocks to the hollows. A stream, which develops at the southern margin, drains the bog and uplands (Fig. 1). Bog water table measurements began in 1961, and the water table typically fluctuates within the top 30 cm (Sebestyen et al. 2011). Average peat depth measured using ground-penetrating radar was 2.38 m, with deeper peat located in the southern end of the bog at a maximum depth of 8.6 m (Parsekian et al. 2012; Fig. 1). Chemistry and environmental monitoring data from this study are available online (Griffiths and Sebestyen 2016a, b; Hanson et al. 2015). Some data used in this study were collected as part of the long-term research program at the MEF, which is administered by the USDA Forest Service (Kolka et al. 2011).

Field Sampling

To examine temporal variation in porewater chemistry depth profiles, porewater was collected for 3 years from a nest of 6 piezometers (Test 1–6) that were installed in a hollow in the south end of the S1 bog (Fig. 1). We also compared temporal variation to spatial variation in porewater chemistry by collecting porewater for one year from 16 separate piezometer nests (Plots 4–21) located in hollows across the southern half of the S1 bog (Fig. 1). Each piezometer was 5.1 cm in diameter and had a 10-cm long screened section (machined 0.25-

Fig. 1 Map of the S1 bog located in north-central Minnesota, USA. The piezometer nest sampled for temporal variability was located in the southern end of the bog (Test 1–6), and the 16 piezometer nests for spatial variability were located across the southern half of the bog (Plots 4–21). The S1 outlet stream is at the south end of the bog, and the 4 groundwater wells were located throughout the S1 watershed. The Environmental Monitoring 1 (EM1) station was located near Test 1–6. Peat depths were from Parsekian et al. (2012)



mm slots) to collect porewater at 0, 0.3, 0.5, 1.0, 2.0, and 3.0 m. The piezometers were installed with the top of the 10-cm screened section at the reported depth. The top of the screened section of the 0 m piezometer was at the hollow surface. The piezometers were anchored in underlying sediment or deep peats to minimize vertical movement.

For temporal variation analysis, porewater was sampled beginning in July 2011. Water samples were collected approximately weekly in 2011, and monthly in 2012 and 2013 whenever water in the piezometers was not frozen. Porewater sampling from the 16 locations across the bog occurred from August to November 2013.

The piezometers were purged the day before (for the slower-filling 2.0 and 3.0 m piezometers) or several hours before (0–1.0 m piezometers) sampling. An unfiltered water sample was pumped from each piezometer into a clean 250-mL HDPE bottle. The 0, 0.5, and 1.0 m piezometers on occasion did not yield enough water for chemical analysis. Samples were not filtered as the collected water had few particulates. All samples were immediately placed on ice and then refrigerated until laboratory analysis.

The S1 outlet stream was sampled weekly in 2011 (biweekly until July and then weekly), 2012, and 2013 for chemistry, providing better temporal resolution to examine how surface water chemistry of the S1 bog varied seasonally.

Groundwater was sampled from 4 fully screened wells (3.3 to 8.2 m deep, 0.03-m diameter galvanized steel pipe) in the uplands of the S1 watershed weekly from August to November 2013 (Fig. 1). Upland well and deep peat (3.0 m) porewater chemistries were compared to assess whether groundwater was a potential source of solutes to deep peat porewater.

Environmental Measurements

Precipitation was measured with an all-weather precipitation gauge (NOAH IV, ETI Instrument Systems, Inc) at the Environmental Monitoring (EM1) station in the south end of the S1 bog (Fig. 1). The bog water level was recorded every 30 min using a TruTrack WT-VO Water Height Probe at the EM1 station. Due to winter freezing, winter water levels were not reported from the EM1 station. Instead, water level data

from a heated bog well, located in the middle of the S1 bog, were reported in winter. Water level was recorded using a float-driven stripchart recorder, which was housed inside a heated enclosure (Sebestyen et al. 2011). Peat soil temperature was measured every 30 min at the hollow surface (0 m), and at 0.05, 0.2, 0.4, 0.8, 1.6, and 2.0 m depth at the EM1 station using Type-T Thermocouples.

Laboratory Analysis

Water samples were analyzed for pH and cation (calcium, potassium), nutrient (nitrate, ammonium, soluble reactive phosphorus [SRP], total nitrogen [TN]), and TOC concentrations. pH was measured on a Mettler Toledo DL53 Auto Titrator. Nitrate was measured using the cadmium reduction method, ammonium was measured using the alkaline phenol method, TN was measured using the persulfate-UV digestion method, and SRP was measured using the antimony-molybdate method (APHA 2005) on a Lachat QuikChem 8000 Autoanalyzer. TOC was measured via high-temperature combustion on a Shimadzu TOC-VCP. Cations were measured using an Inductively Coupled Plasma spectrophotometer (Thermo Elemental Iris Intrepid ICP-OES). The detection limits were as follows: calcium (0.05 mg/L), potassium (0.5 mg/L), nitrate (0.02 mg N/L), ammonium (0.02 mg N/L), TN (0.05 mg N/L), SRP (0.001 mg P/L), and TOC (0.5 mg C/L).

There were some issues with the ammonium analyses in 2011 and 2013. The deep porewater samples (2.0 and 3.0 m) collected in 2011 had much higher ammonium concentrations (>1 mg N/L) than TN concentrations measured on the same samples. In 2013, four of the six 3.0 m samples had low (or undetectable) ammonium concentrations and high nitrate concentrations (~2–3 mg N/L), which was not consistent with 2.0 m samples that all had high ammonium and low or undetectable nitrate concentrations. Ammonium may have been nitrified while these samples awaited analysis. Because of these uncertainties, we excluded all ammonium data from 2011 and ammonium and nitrate data from the four 3.0-m samples in 2013 from analyses.

Statistical Analyses

Kruskal-Wallis tests were used to examine whether solute chemistry varied with depth. To examine temporal variability in porewater chemistry across the depth profile, a coefficient of variation (CV) was calculated for each solute at each depth across all years. To examine spatial variability in porewater chemistry, CV was calculated for each solute at each depth across all 16 plots. Paired t-tests were used to compare near surface (0 m) porewater chemistry with S1 stream chemistry, and Pearson's correlations were used to examine whether the seasonal patterns in near surface porewater chemistry and S1

stream chemistry were similar. One-way ANOVAs were used to compare the chemistry of groundwater to the chemistry of deep (3.0 m) porewater. Because solute chemistry from 4 groundwater wells was compared to chemistry from one 3.0-m piezometer, a paired t-test approach was not used. Instead, the mean value from each of the 4 groundwater wells in 2013 and the 6 samples collected from the 3.0 m piezometer in 2013 were used as the replicates in the ANOVA. Statistical significance was $p \leq \alpha = 0.05$. All statistics were carried out in SYSTAT v.13.

Results

Physical Characteristics of the S1 Bog

The bog water level varied both seasonally and annually (Fig. 2a). The water level increased with snowmelt each spring, and then decreased throughout the growing season. When water level was highest, there was over 0.1 m of standing water in the hollows. In 2012, summer precipitation was low, and the lowest water level was 0.20 m below the hollow surface (Fig. 2a). Water level was higher during the growing seasons in 2011 and 2013 and only reached maximum depths

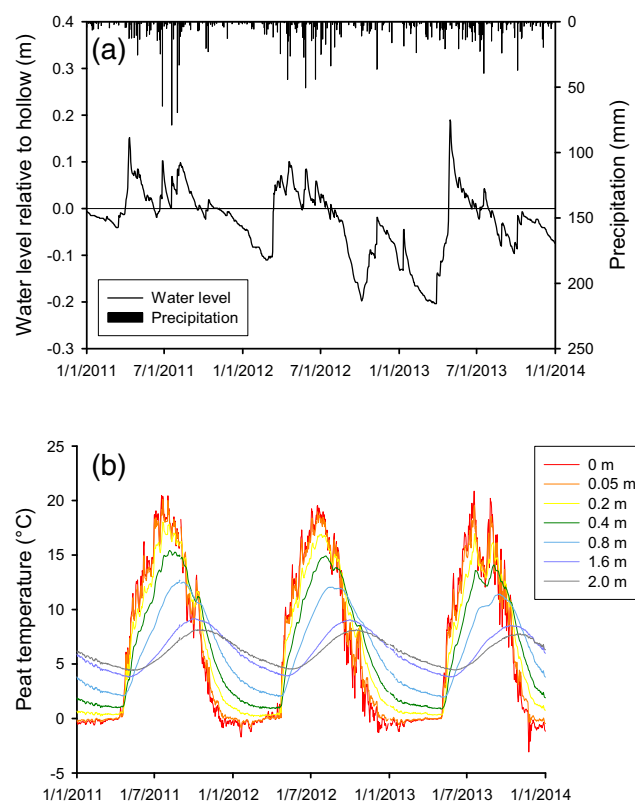


Fig. 2 **a** Bog water level relative to the hollow surface (0 m) and total daily precipitation at the EM1 station. **b** Mean daily peat temperature from the hollow surface (0 m) to 2.0 m into the peat at the EM1 station

of 0.02 m and 0.10 m below the hollow surface, respectively (Fig. 2a).

Peat temperatures varied with depth and patterns were fairly consistent across years (Fig. 2b). At the hollow surface, temperature ranged from slightly below 0 °C to ~20 °C over each year, while temperature at 2.0 m depth ranged from ~4.5 to 8 °C (Fig. 2b).

Vertical Profiles of Peat Porewater Chemistry

Most porewater chemistry profiles revealed large gradients with depth (Figs. 3–5). Porewater pH increased significantly with depth (Kruskal-Wallis test, $p < 0.0001$); porewater was over 100 times more acidic at 0 m than at 3.0 m (Fig. 3). Calcium concentrations increased over 20 fold with depth (Kruskal-Wallis test, $p < 0.0001$; Fig. 4a). Calcium concentrations were low above 0.5 m, and then increased fairly linearly from 1.0 to 3.0 m. Porewater potassium concentrations also varied by depth (Kruskal-Wallis test, $p < 0.0001$), with potassium concentrations highest at 0 m and lowest at 0.5 m (Fig. 4b).

Ammonium and TN concentrations both increased greatly with depth (Kruskal-Wallis tests, $p < 0.0001$; Fig. 5a). The majority of TN was comprised of ammonium, especially at depth. On average, ammonium was 90 % of TN at 2.0 and 3.0 m, 83 % at 1.0 m, and 35 % at 0 m. The depth profile of porewater ammonium was similar to that of TN. Ammonium

concentrations were typically low from 0 to 0.5 m depth, and then increased by 1.0 m. Porewater nitrate concentrations were mostly below detection (<0.02 mg N/L). Out of 146 total samples, there were only 6 dates when porewater nitrate concentrations were higher than the detection limit (values ranged from 0.02–0.18 mg N/L). Porewater SRP concentrations also varied significantly with depth (Kruskal-Wallis test, $p < 0.0001$), with the lowest concentrations at 0.5 m and the highest at 3 m (Fig. 5b). Porewater TOC concentrations decreased by half with depth (Kruskal-Wallis test, $p < 0.0001$; Fig. 5c).

Temporal and Spatial Variability in Peat Porewater Chemistry Depth Profiles

There was considerable temporal variation in the 3-year record of porewater chemistry depth profiles (Fig. 3, Online Resources 1, 2). pH, and calcium and TOC concentrations were more variable in deeper porewater than in shallower porewater (Table 1); however, there were some depths at which there was very little variation in porewater chemistry (i.e., CV of calcium concentration at 3 m; Table 1). In contrast, potassium, ammonium, TN, and SRP concentrations were generally more variable in shallower than deeper porewater (Table 1).

The temporal variation in porewater chemistry at one location was often greater than spatial variability (i.e., across 16

Fig. 3 Depth profiles (0–3.0 m) of porewater pH in (a) 2011 (weekly sampling), (b) 2012 (monthly sampling), (c) 2013 (monthly sampling), and (d) in 16 locations across the S1 bog (mean pH at each location in 2013)

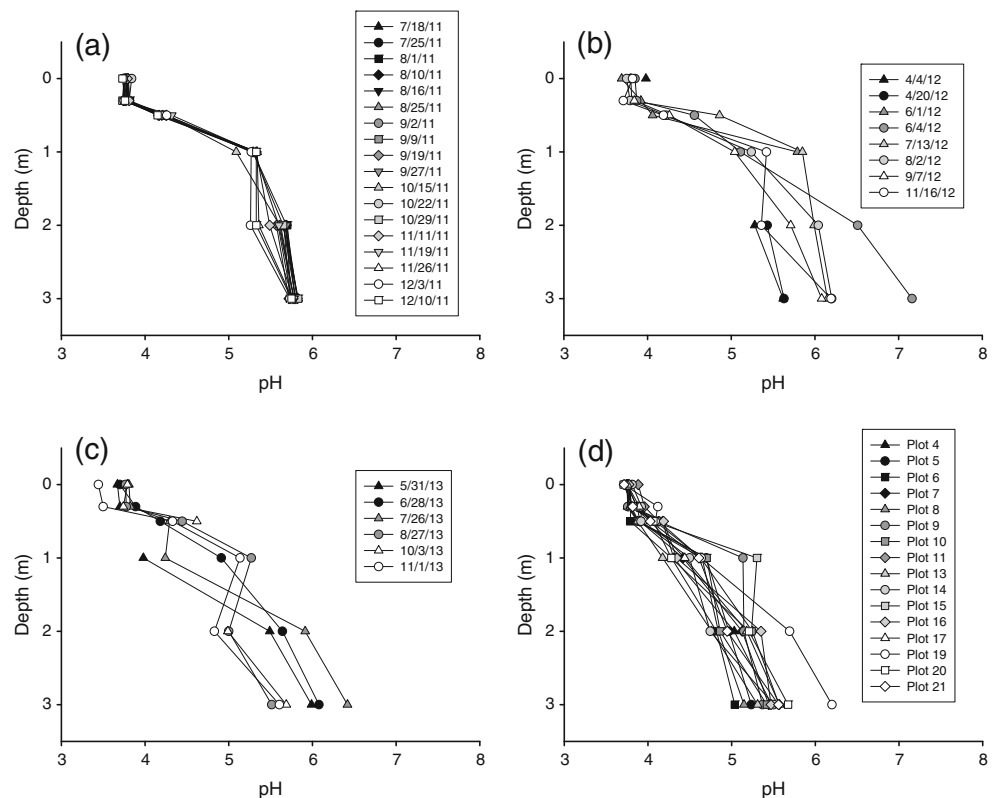
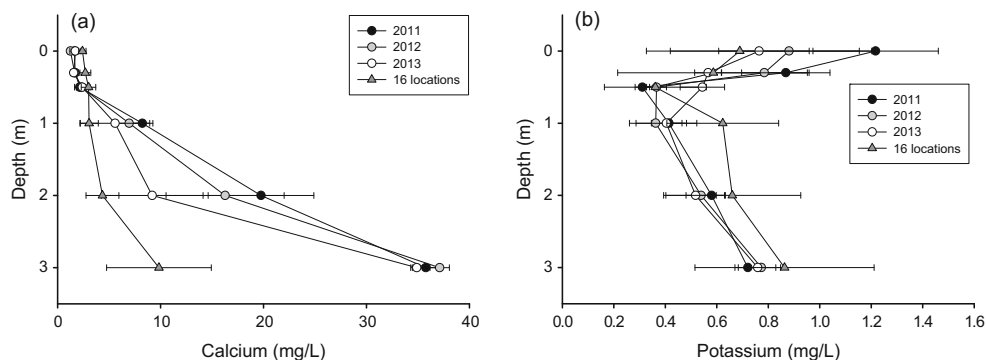


Fig. 4 Depth profiles (0–3.0 m) of mean porewater ($\pm$ SD) (a) calcium and (b) potassium concentrations in 2011, 2012, and 2013, and in 16 locations across the S1 bog



locations in the S1 bog) (Table 1, Online Resource 2). For all solutes except potassium and SRP, temporal CV was greater than spatial CV at 3 to 4 of the 6 sampled depths (Table 1). There was a general trend of larger temporal CVs than spatial CVs in near surface porewaters (0 m), and larger spatial CVs than temporal CVs at depth (3 m) (Table 1).

Seasonal Variation in Stream Water Chemistry

We examined seasonal patterns in solute chemistry at the S1 stream where samples were collected at a higher frequency (weekly) and over a longer duration each year. Stream chemistry was similar to chemistry of near surface (0 m) porewater, with subtle differences. For example, pH and Ca concentrations were significantly higher in the S1 stream than in 0 m porewater (paired t-tests, $p < 0.0001$); however, the differences were small relative to the pH and high cation concentrations in deep peat porewater (Online Resource 1). Overall, S1 stream chemistry was broadly representative of near surface (0 m) porewater chemistry as the temporal patterns in calcium ($r = 0.66$, $p = 0.0001$), potassium ($r = 0.66$, $p = 0.0001$), and TOC concentrations ($r = 0.79$, $p < 0.0001$) at these two locations were similar.

The temporal patterns in S1 stream chemistry varied by solute (Fig. 6). pH decreased from summer to autumn each year (data not shown). Calcium increased from spring to summer (in 2012 and 2013), and concentrations were lower when the water level was low (Fig. 6a). Potassium concentrations

were highest in spring (in 2012 and 2013), and tended to be lower when the water level was low (Fig. 6b).

There were also temporal patterns in ammonium and TOC concentrations in S1 stream water, but there were no clear patterns in SRP and TN concentrations. Ammonium concentrations were highest when the water level dropped in late summer/early autumn (Fig. 6c). TOC concentration showed a clear seasonal pattern; concentrations increased until early September, and then decreased through autumn (Fig. 7). This seasonal pattern was similar among years (Fig. 7) except during early autumn in 2012 when the water table dropped to its lowest level in the 3-year, ice-free measurement period. The decrease in water level was paralleled by a decrease in TOC concentration, and the lower TOC concentrations persisted for a few weeks (Fig. 6d).

Comparison of Deep Peat Porewater and Groundwater Chemistry

The pH of deep (3.0 m) peat porewater was similar to that measured in 4 groundwater wells within the uplands of the S1 watershed (ANOVA, $p = 0.10$). Calcium concentrations in deep peat porewater were also similar to calcium concentrations in the upland groundwater wells (ANOVA, $p = 0.07$), but there was very large well-to-well variation in calcium concentrations (Online Resource 1). In contrast, there were substantial differences in groundwater vs. deep peat porewater nutrient and TOC chemistry. Ammonium, TN, and SRP

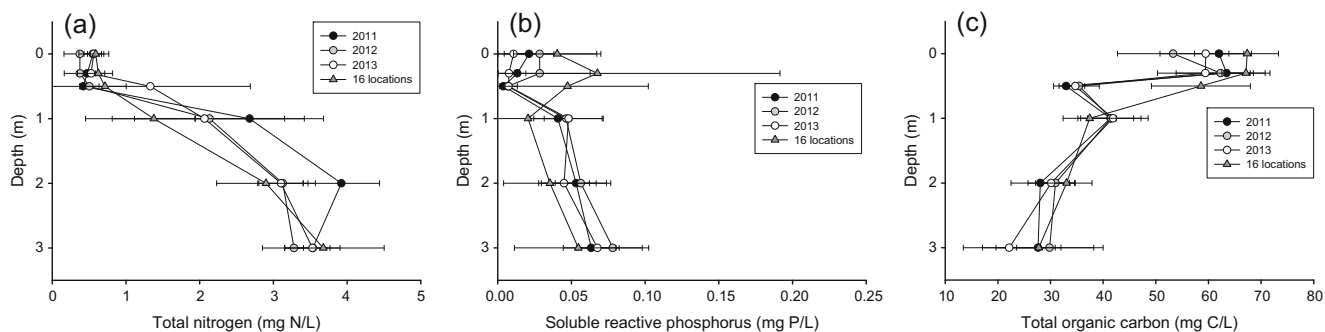


Fig. 5 Depth profiles (0–3.0 m) of mean porewater ($\pm$ SD) (a) total nitrogen, (b) soluble reactive phosphorus, and (c) total organic carbon concentrations in 2011, 2012, and 2013, and in 16 locations across the S1 bog

Table 1 Coefficients of variation (CV) for pH, and calcium, ammonium, total nitrogen, soluble reactive phosphorus, and total organic carbon concentrations in porewater. To characterize temporal variability, CV was calculated from the 3-year-long record of porewater chemistry at each depth. To characterize spatial variability, CV was calculated across the 16 sampling locations for each depth

Depth (m)	pH	Calcium		Potassium		Ammonium		Total nitrogen		Soluble reactive phosphorus		Total organic carbon	
		Temporal CV	Spatial CV	Temporal CV	Spatial CV	Temporal CV	Spatial CV	Temporal CV	Spatial CV	Temporal CV	Spatial CV	Temporal CV	Spatial CV
0	0.02	0.01	0.15	0.33	0.39	1.19	0.30	0.34	0.19	1.09	0.73	0.13	0.09
0.3	0.02	0.02	0.20	0.24	0.63	0.83	1.09	0.28	0.31	1.11	1.83	0.10	0.07
0.5	0.04	0.03	0.23	0.28	0.55	1.38	1.18	1.08	0.41	0.59	1.16	0.08	0.16
1.0	0.08	0.07	0.29	0.23	0.38	0.66	0.65	0.45	0.41	0.40	1.07	0.12	0.14
2.0	0.06	0.05	0.36	0.13	0.40	0.18	0.29	0.17	0.23	0.40	0.89	0.17	0.15
3.0	0.05	0.05	0.52	0.08	0.40	0.05	0.26	0.08	0.22	0.29	0.79	0.38	0.15

concentrations in upland groundwater wells were lower than in deep peat porewater (ANOVAs, $p \leq 0.0001$), while potassium concentrations in groundwater were higher than in deep peat porewater (ANOVA, $p = 0.02$). Nitrate concentrations were similar in groundwater and deep peat porewater (ANOVA, $p = 0.38$); however, nitrate data from only 2 deep porewater samples in 2013 were available for analysis. TOC concentrations were an order of magnitude lower in groundwater in 3 of the 4 upland wells (mean concentrations ranged from 3.3–5.5 mg C/L) than in deep peat porewater (Online Resource 1); however, concentrations were not significantly different (ANOVA, $p = 0.08$) because one well that was located closest to the S1 stream had a high TOC concentration (25.9 mg C/L).

Discussion

Vertical Profiles of Peat Porewater Chemistry

Porewater chemistry profiles showed large gradients with depth, and these patterns differed by solute. pH increased by two units and calcium increased over 20 fold with depth. The higher pH and calcium concentrations at 3.0 m depth (range = 33.5–38.4 mg/L) were within the ranges reported for moderately rich (0.8–179 mg/L) and rich (1.4–428 mg/L) fens (summarized in Bourbonniere 2009), and may reflect a previous minerotrophic stage during bog development (Shotyk and Steinmann 1994; Vitt et al. 1995; Gorham and Janssens 2005). A previous paleobotanical (*Sphagnum* and other mosses) analysis of a peat core from the nearby S2 bog at the MEF showed a transition between forested bog and open poor-fen around 0.75 m depth, and transitional fen characteristics appeared at approximately 3.25 m depth (Verry and Janssens 2011). The S2 bog record is generally representative of black spruce bog development in the vicinity, including the S1 bog. Despite similar geochronologies and topographic settings, peat in the S2 bog is shallower, the land elevation is higher, the hydraulic head gradient is higher by ~6 m, and surficial peats are dryer than in S1 (Sebestyen et al. 2011). Although likely similar in sequence, the transition depths and layer thicknesses may be different in the S1 bog.

The higher pH and calcium concentrations at depth may also reflect exchange of porewater with the surrounding groundwater. However, while the exchange of solutes in the groundwater aquifer with S1 porewater is possible (Nichols and Verry 2001), the low hydraulic conductivity of deep peat (Verry et al. 2011) and the hydraulic gradient from the bog water level to the surrounding groundwater table (~1 m) may preclude or reduce the inflow of water from the surrounding groundwater aquifer into the peat, especially on relatively fast time scales (i.e., weeks/months/years). Over the long term (i.e., years/decades), limited and slow exchange and geochemical equilibration is plausible.

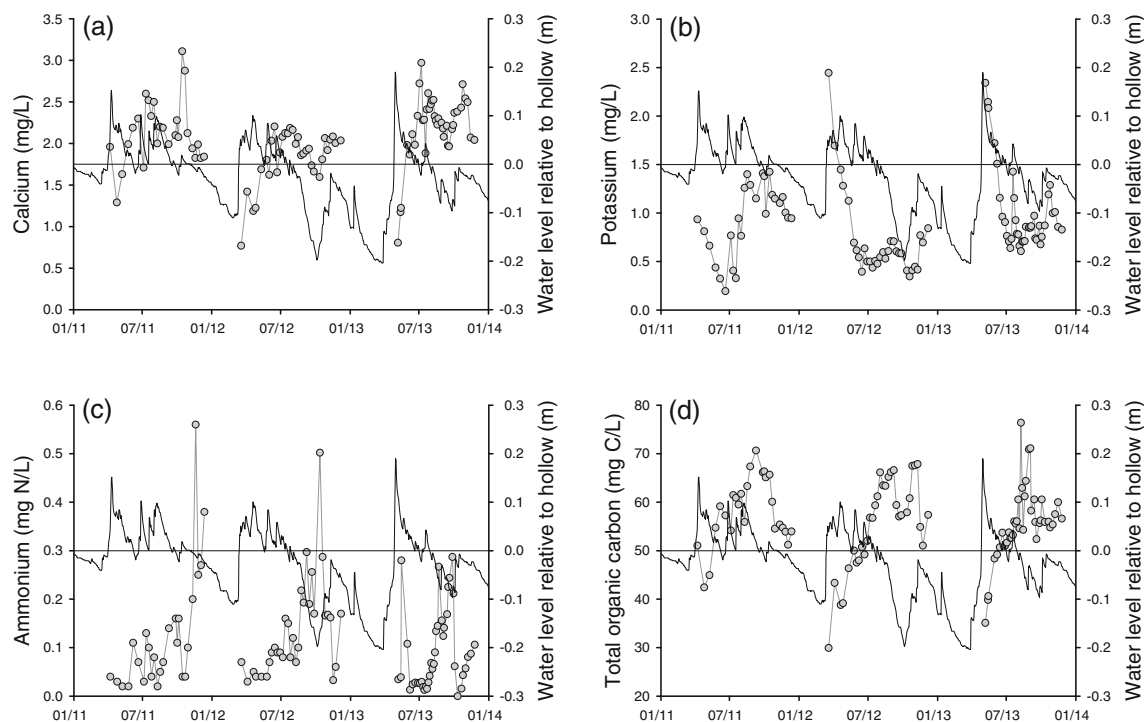


Fig. 6 Bog water level relative to the hollow surface (0 m) and (a) calcium, (b) potassium, (c) ammonium, and (d) total organic carbon concentrations in S1 stream water in 2011, 2012, and 2013 (weekly sampling)

There were also large changes in porewater ammonium and TOC concentrations with depth, and these patterns likely reflected N and C cycling at various temporal scales. Ammonium concentrations at 3.0 m depth were high (mean = 3.04 mg N/L) and an order of magnitude greater than ranges reported in surface and groundwater in human-impacted systems (Dubrovsky et al. 2010). These high concentrations suggest that there is a large ammonium pool in the S1 bog. Based on the 8.1-ha peatland area, an average peat depth of 2.38 m (Parsekian et al. 2012), a 75 % water-filled porosity of peat in the top 0.3 m, and 25 % water-filled

porosity from 0.3–2.38 m depth (Verry et al. 2011), we estimated a total mass of 6 kg of porewater ammonium-N in the top 1.0 m of peat, 35 kg in the next 1.0 m of peat (1–2 m), and 21 kg in the last 0.38 m of peat (2–2.38 m depth), for a total of 62 kg of porewater ammonium-N in 2.38 m of saturated peat (across the estimated 192,780 m³ of peat in the S1 bog) (Table 2). High porewater ammonium concentrations (~1 mg/L at 1.5 m depth) have also been reported in a bog in Alberta (Vitt et al. 1995), though these large ammonium pools may not be common to all bogs.

The high ammonium concentrations at depth may reflect accumulation from centuries of peat mineralization with minimal uptake or transformation, which would also support our hypothesis on the limited exchange of water between peat porewater and the surrounding groundwater aquifer. Mineralization of organic matter at depth is consistent with the measured decrease in porewater TOC concentrations along the vertical profile. Research at the S1 bog has shown that the DO^{14}C at 2.0 m depth is modern (Tfaily et al. 2014) suggesting some vertical connectivity of porewater and associated solutes. Therefore, modern DOC may be moving along a vertical flowpath and decomposing at depth, resulting in the accumulation of ammonium. It is not known whether ammonium is being taken up by microorganisms at depth, but it is likely not being nitrified, as this process is negligible in peatlands (Urban and Eisenreich 1988). Consequently, nitrate concentrations were almost always below detection (<0.02 mg N/L) throughout the depth profile. The lower

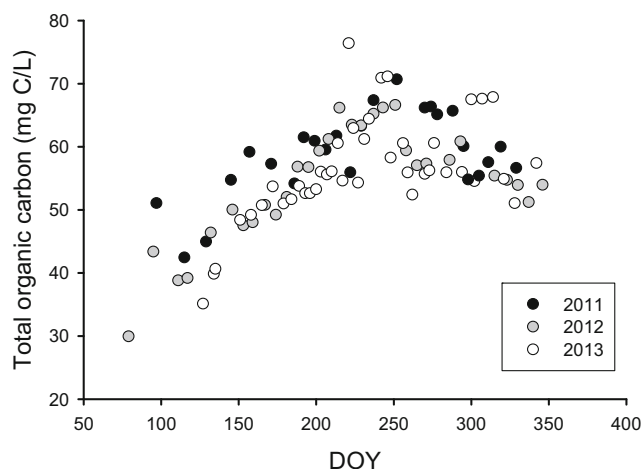


Fig. 7 Total organic carbon concentrations in S1 stream water over time (DOY = day of the year) in 2011, 2012, and 2013

Table 2 Pools of ammonium, total nitrogen, soluble reactive phosphorus, total organic carbon, calcium, and potassium in S1 bog porewater (across 192,780 m³ of peat) estimated from the temporal and spatial variation depth profiles. To examine how temporal variation affected the calculation of solute pools, the mean pool was calculated

Solute	S1 solute pool in porewater (kg) based on temporal variability			S1 solute pool in porewater (kg) based on spatial variability		
	<i>Min</i>	<i>Mean</i>	<i>Max</i>	<i>Min</i>	<i>Mean</i>	<i>Max</i>
Ammonium-N	20	62	117	20	49	111
Total nitrogen-N	39	91	169	42	71	127
Soluble reactive phosphorus-P	0.4	1.8	5.1	0.6	2.2	10.0
Total organic carbon-C	1981	2716	3412	2412	3105	3758
Calcium	124	314	474	128	181	291
Potassium	18	37	56	13	36	68

concentrations of ammonium and TN in the surrounding groundwater than in 3.0 m porewater also provides evidence that groundwater inflow was not a source of high ammonium concentrations in deep porewater.

Temporal Variation in Vertical Profiles of Peat Porewater Chemistry

While there were distinct vertical gradients in porewater chemistry, there was also considerable temporal variation in the vertical profiles across sampling dates and years. Variability in both pH and calcium concentrations generally increased with depth while biologically important solutes (ammonium, SRP, potassium) showed greater temporal variation in the near surface porewater. However, concentrations of these actively cycled solutes were still variable at deeper depths, and TOC concentrations were more variable in deeper than shallower depths over time. Vitt et al. (1995) sampled porewater depth profiles (0–1.5 m) weekly or bi-weekly for 2 years across a bog to fen gradient. In the bog, porewater chemistry was less or similarly variable with depth into the peat; variation in ammonium concentration decreased with depth, while variation in nitrate was similar across depths (Vitt et al. 1995). The smaller variation in ammonium concentrations with depth is similar to our findings, but we could not determine temporal variation in nitrate depth profiles as the majority of these samples were below detection.

The rate of vertical and horizontal water and solute movement at different peat depths is not known, so whether these patterns represent mixing of water and solutes from shallow porewaters into a more stagnant and slowly exchanged deep pool cannot be determined. Variation in the hydraulic head due to inputs of rain and melting snow could drive mixing dynamics of shallow and deeper porewater at different temporal scales. The permanent saturation and smaller fluctuations in temperature at depth suggest that variation in these physical

from the mean concentration of each solute at each depth across all 3 years, and the minimum and maximum pools were calculated from the minimum and maximum concentrations measured at each depth over the 3-year study. For spatial variation, the same calculations were carried out for each solute at each depth across all 16 sampling locations

factors likely did not contribute to solute variability. Overall, there was considerable variation in chemical constituents along vertical profiles, and capturing this variation may be important when parameterizing Earth Systems Models to include northern peatlands as a fundamental model feature (e.g., Shi et al. 2015) or when characterizing ecosystem-scale pools and fluxes. For example, if the minimum and maximum ammonium concentrations measured over the 3-year study were used to calculate the ammonium pool in the S1 bog, the estimates would vary over 5-fold from 20 to 117 kg of ammonium-N in peat porewater (Table 2). Similarly large ranges were calculated for other solute pools (Table 2).

Seasonal Patterns in Surface Water Chemistry

S1 stream water chemistry was dynamic and reflected sources and cycling of various solutes. TOC concentrations increased from spring to summer and then decreased in late autumn, likely reflecting release of recently fixed photosynthate throughout the summer, and then reduced vegetative production into late autumn (Hughes et al. 1997; Strack et al. 2008; Whitfield et al. 2010). The increase in TOC concentrations in summer could also be due to evaporative concentration as the bog water level recesses. However, TOC concentrations were high in summer 2011 when the water table was high relative to the other two years, and in summer 2012, TOC concentrations decreased with water table recession, suggesting evaporative concentration was not an important mechanism controlling TOC concentrations. The lower TOC concentrations in summer 2012 may reflect greater oxidation of dissolved organic matter (DOM) as shallow peats were aerated (Freeman et al. 1993; Hughes et al. 1997; Strack et al. 2008). Ammonium concentrations were also higher when the water level was lower further suggesting that DOM mineralization (and associated ammonification) increased under these conditions.

Calcium concentrations also increased from spring to summer, as is consistent with other findings in surface water (Proctor 1994; Vitt et al. 1995; Bragazza et al. 1998), and may reflect large inputs of dilute snowmelt waters in spring (Urban et al. 2011) and release of calcium from mineralization of organic matter when peat decomposes during summer (Bragazza and Gerdol 1999). Calcium concentrations were higher during summer when the water table was near the surface suggesting a surficial source of calcium. When the water table dropped, that calcium source may have been less hydrologically connected to the stream. pH decreased from summer to autumn when the water table decreased potentially due to oxidation of organic sulfur within the peat (Shotyk 1988; Hughes et al. 1997).

Potassium concentrations were initially high each spring and markedly decreased after snowmelt until the beginning of summer. During 2012 and 2013, potassium concentrations remained relatively low throughout the summer, possibly due to vegetative uptake (Proctor 1994; Vitt et al. 1995; Bragazza et al. 1998). Litterfall in autumn and leaching during the subsequent snowmelt events may explain the initially high potassium concentrations each spring.

Ammonium, nitrate, and SRP concentrations in S1 stream water were low (or below detection limits), reflecting the nutrient-limited status of the bog. Nutrients (N, P) often limit production and decomposition in peatlands. For example, 60–86 % of inorganic nitrogen inputs were retained within the nearby S2 bog when denitrification was considered to be negligible (Verry and Timmons 1982; Urban and Eisenreich 1988). However, when denitrification rates were measured, outputs exceeded inputs (Hill et al. 2016). Regardless of the exact input-output balances, these studies illustrate the biological demand for N. Nitrate and ammonium concentrations can be elevated during snowmelt when uptake is low (Urban and Eisenreich 1988). However, we did not measure an early spring pulse of dissolved inorganic nitrogen in any year. It is not known whether the nitrogen pulse did not occur or whether weekly sampling was too coarse to detect flushing pulses of these nutrients (Sebestyen et al. 2009). The magnitude of nitrate and ammonium inputs in precipitation to the MEF has been similar (Sebestyen et al. 2011); however ammonium concentrations in near surface porewater were higher than nitrate concentrations, suggesting preferential uptake of nitrate by vegetation including *Sphagnum* (Woodin et al. 1985; Urban and Eisenreich 1988) or removal via denitrification (Hill et al. 2016).

Comparison of Temporal and Spatial Variation in Porewater Chemistry

Temporal variation in porewater chemistry in the S1 bog was substantial, as there were several solute and depth combinations that varied more over time than across the southern half of the

bog. For almost all solutes, temporal variation was greater than spatial variation in near surface porewater. This greater variation in near surface porewater likely reflects seasonal dynamics in solute sources and cycling, as described above.

The range in calculated solute pools was similar when accounting for either spatial or temporal variation. For instance, the minimum and maximum ammonium pool estimated in the S1 bog was similar when calculated from the minimum and maximum concentrations measured over the 3-year study (20 to 117 kg) and when calculated from the minimum and maximum concentrations measured across the S1 bog (20 to 111 kg) (Table 2). Overall, these results suggest that it is necessary to characterize both temporal and spatial variability to ensure representative sampling in peatlands. Future work characterizing both the spatial (across the bog) and temporal (seasonal and inter-annual) variation in vertical porewater profiles is necessary to determine how representative the findings from our work and others (e.g., Vitt et al. 1995) are for northern peatlands.

Accounting for Variability in Porewater Chemistry when Assessing Climate Change Effects

High-latitude ecosystems are projected to experience significant warming under climate change (Collins et al. 2013). While the predicted effects of climate change on peatland ecosystems tend to focus on carbon, the fate of other biogeochemical cycles should also be considered. The S1 bog will be the site of a planned 10-year-long climate change experiment, and the data presented here provide a baseline characterization of porewater chemistry prior to any manipulations. The vertical nutrient profiles in the S1 bog suggest that there is a large pool of ammonium in deep peat. Peatland water levels are projected to decrease with warming (Roulet et al. 1992; Moore et al. 1998), which may allow roots and microbes to access this deep ammonium pool, with potential cascading effects to aboveground productivity and community structure. Capturing temporal and spatial variability in porewater chemistry under current conditions establishes a baseline for considering how concentrations, pools, and fluxes may change under future climate scenarios.

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References

- APHA (2005) Standard methods for the examination of water and wastewater, 21st edn. American Public Health Association, Washington DC.
- Bourbonniere RA (2009) Review of water chemistry research in natural and disturbed peatlands. *Canadian Water Resources Journal* 34: 393–414
- Bragazza L, Gerdol R (1999) Hydrology, groundwater chemistry and peat chemistry in relation to habitat conditions in a mire on the south-eastern alps of Italy. *Plant Ecology* 144:243–256
- Bragazza L, Gerdol R (2002) Are nutrient availability and acidity-alkalinity gradients related in *Sphagnum*-dominated peatlands? *Journal of Vegetation Science* 13:473–482
- Bragazza L, Alber R, Gerdol R (1998) Seasonal chemistry of pore water in hummocks and hollows in a poor mire in the southern alps (Italy). *Wetlands* 18:320–328
- Clymo RS, Bryant CL (2008) Diffusion and mass flow of dissolved carbon dioxide, methane, and dissolved organic carbon in a 7-m deep raised peat bog. *Geochimica et Cosmochimica Acta* 72: 2048–2066
- Collins, M, Knutti, R, Arblaster, J, Dufresne, J-L, Fichetef, T, Friedlingstein, P, Gao, X, Gutowski, WJ, Johns, T, Krinner, G, Shongwe, M, Tebaldi, C, Weaver, AJ, Wehner, M (2013) Long-term climate change: projections, commitments and irreversibility. In: Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM (eds) *Climate Change 2013: The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp 1029–1136
- Dubrovsky NM, Burrow KR, Clark GM, Gronberg JM, Hamilton PA, Hitt KJ, Mueller DK, Munn MD, Nolan BT, Puckett LJ, Rupert MG, Short TM, Spahr NE, Sprague LA, Wilber WG (2010) The quality of our Nation's waters: nutrients in the Nation's streams and groundwater, 1992–2004. US geological survey Circular 1350, USGS, Reston, VA <http://water.usgs.gov/nawqa/nutrients/pubs/circ1350>
- Freeman C, Lock MA, Reynolds B (1993) Fluxes of CO₂, CH₄, and N₂O from a Welsh peatland following simulation of water table draw-down: potential feedback to climatic change. *Biogeochemistry* 19:51–60
- Glaser PH, Janssens JA, Siegel DI (1990) The response of vegetation to chemical and hydrological gradients in the lost river peatland, northern Minnesota. *Journal of Ecology* 78:1021–1048
- Glaser PH, Siegel DI, Romanowicz EA, Ping Shen Y (1997) Regional linkages between raised bogs and the climate, groundwater, and landscape of North-Western Minnesota. *Journal of Ecology* 85:3–16
- Gorham E (1991) Northern peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecological Applications* 1:182–195
- Gorham E, Janssens JA (2005) The distribution and accumulation of chemical elements in 5 peat cores from the mid-continent to the eastern coast of North America. *Wetlands* 25:259–278
- Griffiths NA, Sebestyen SD (2016a) SPRUCE S1 bog porewater, groundwater, and stream chemistry data: 2011–2013. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN. doi:10.3334/CDIAC/spruce.018
- Griffiths NA, Sebestyen SD (2016b) SPRUCE porewater chemistry data for SPRUCE experimental plots: 2013–2015. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN. doi:10.3334/CDIAC/spruce.028
- Hanson PJ, Riggs JS, Dorrance C, Nettles WR, Hook LA (2015) SPRUCE environmental monitoring data: 2010–2014. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN. doi:10.3334/CDIAC/spruce.001
- Hill BH, Jicha TM, Lehto LLP, Elonen CM, Sebestyen SD, Kolka RK (2016) Comparisons of soil nitrogen mass balances for an ombrotrophic bog and a minerotrophic fen in northern Minnesota. *Science of the Total Environment* 550:880–892
- Hughes S, Reynolds B, Hudson JA, Freeman C (1997) Effects of summer drought on peat soil solution chemistry in an acid gully mire. *Hydrology and Earth System Sciences* 1:661–669
- Koehler A-K, Murphy K, Kiely G, Sottocornola M (2009) Spatial variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in south western Ireland. *Biogeochemistry* 95:231–242
- Kolka RK, Sebestyen SD, Bradford JH (2011) An evolving research agenda of the Marcell Experimental Forest. In: Kolka RK, Sebestyen SD, Verry ES, Brooks KN (eds) *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest*. CRC Press, Boca Raton, FL, pp 73–91
- Moore TR, Roulet NT, Waddington JM (1998) Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands. *Climatic Change* 40:229–245
- Nichols DS, Verry ES (2001) Stream flow and ground water recharge from small forested watersheds in north Central Minnesota. *Journal of Hydrology* 245:89–103
- Pakarinen P, Tolonen K (1977) Nutrient contents of *Sphagnum* mosses in relation to bog water chemistry in northern Finland. *Lindbergia* 4: 27–33
- Parsekian AD, Slater L, Ntarlagiannis D, Nolan J, Sebestyen SD, Kolka RK, Hanson PJ (2012) Uncertainty in peat volume and soil carbon estimated using ground-penetrating radar and probing. *Soil Science Society of America Journal* 76:1911–1918
- Proctor MCF (1994) Seasonal and shorter-term changes in surface-water chemistry on four English ombrogenous bogs. *Journal of Ecology* 82:597–610
- Proctor MCF (2006) Temporal variation in the surface-water chemistry of a blanket bog on Dartmoor, Southwest England: analysis of 5 years' data. *European Journal of Soil Science* 57:167–178
- Roulet N, Moore T, Bubier J, Lafleur P (1992) Northern fens: methane flux and climatic change. *Tellus* 44B:100–105
- Sebestyen SD, Shanley JB, Boyer EW (2009) Using high-frequency sampling to detect effects of atmospheric pollutants on stream chemistry. In: Webb RMT, Semmens DJ (eds) *Proceedings of the Third Interagency Conference on Research in the Watersheds: Planning for an Uncertain Future: Monitoring, Integration, and Adaptation*. United States Geological Survey, Washington, DC, pp 171–176
- Sebestyen SD, Dorrance C, Olson DM, Verry ES, Kolka RK, Elling AE, Kyllander R (2011) Long-term monitoring sites and trends at the Marcell Experimental Forest. In: Kolka RK, Sebestyen SD, Verry ES, Brooks KN (eds) *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest*. CRC Press, Boca Raton, FL, pp 15–72
- Seifert-Monson LR, Hill BH, Kolka RK, Jicha TM, Lehto LL, Elonen CM (2014) Effects of sulfate deposition on pore water dissolved organic carbon, nutrients, and microbial enzyme activities in a northern peatland. *Soil Biology and Biochemistry* 79:91–99
- Shi X, Thomson PE, Ricciuto DM, Hanson PJ, Mao J, Sebestyen SD, Griffiths NA, Bisht G (2015) Representing northern peatland microtopography and hydrology within the community land model. *Biogeosciences* 12:6463–6477
- Shotyk W (1988) Review of the inorganic geochemistry of peats and peatland waters. *Earth-Science Reviews* 25:95–176
- Shotyk W, Steinmann P (1994) Pore-water indicators of rainwater-dominated versus groundwater-dominated peat bog profiles (Jura Mountains, Switzerland). *Chemical Geology* 116:137–146
- Siegel DI, Reeve AS, Glaser PH, Romanowicz EA (1994) Climate-driven flushing of pore water in peatlands. *Nature* 374:531–533
- Strack M, Waddington JM, Bourbonniere RA, Buckton EL, Shaw K, Whittington P, Price JS (2008) Effect of water table drawdown on

- peatland dissolved organic carbon export and dynamics. *Hydrological Processes* 22:3373–3385
- Tahvanainen T, Sallantausta T, Heikkilä R (2003) Seasonal variation of water chemical gradients in three boreal fens. *Annales Botanici Fennici* 40:345–355
- Tfaily MM, Cooper WT, Kostka JE, Chanton PR, Schadt CW, Hanson PJ, Iversen CM, Chanton JP (2014) Organic matter transformation in the peat column at Marcell Experimental Forest: humification and vertical stratification. *Journal of Geophysical Research-Biogeosciences* 119:661–675
- Ulanowski TA, Branfieri BA (2013) Small-scale variability in peatland pore-water biogeochemistry, Hudson Bay lowland, Canada. *Science of the Total Environment* 454–455:211–218
- Urban NR, Eisenreich SJ (1988) Nitrogen cycling in a forested Minnesota bog. *Canadian Journal of Botany* 66:435–449
- Urban NR, Verry ES, Eisenreich SJ, Grigal DF, Sebestyen SD (2011) Nutrient cycling in upland/peatland watersheds. In: Kolka RK, Sebestyen SD, Verry ES, Brooks KN (eds) *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest*. CRC Press, Boca Raton, FL, pp 213–241
- Verry ES (1975) Streamflow chemistry and nutrient yields from upland-peatland watersheds in Minnesota. *Ecology* 56:1149–1157
- Verry ES, Janssens J (2011) Geology, vegetation, and hydrology of the S2 bog at the MEF: 12,000 years in northern Minnesota. In: Kolka RK, Sebestyen SD, Verry ES, Brooks KN (eds) *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest*. CRC Press, Boca Raton, FL, pp 93–134
- Verry ES, Timmons DR (1982) Waterborne nutrient flow through an upland-peatland watershed in Minnesota. *Ecology* 63:1456–1467
- Verry ES, Boelter DH, Päivänen J, Nichols DS, Malterer TJ, Gafni A (2011) Physical properties of organic soils. In: Kolka RK, Sebestyen SD, Verry ES, Brooks KN (eds) *Peatland biogeochemistry and watershed hydrology at the Marcell Experimental Forest*. CRC Press, Boca Raton, FL, pp 135–176
- Vitt DH, Bayley SE, Jin T (1995) Seasonal variation in water chemistry over a bog-rich fen gradient in continental western Canada. *Canadian Journal of Fisheries and Aquatic Sciences* 52:587–606
- Waughman GJ (1980) Chemical aspects of the ecology of some south German peatlands. *Journal of Ecology* 68:1025–1046
- Whitfield CJ, Aherne J, Gibson JJ, Seabert TA, Watmough SA (2010) The controls on boreal peatland surface water chemistry in northern Alberta, Canada. *Hydrological Processes* 24:2143–2155
- Woodin S, Press MC, Lee JA (1985) Nitrate reductase activity in *Sphagnum fuscum* in relation to wet deposition of nitrate from the atmosphere. *New Phytologist* 99:381–388
- Yu Z, Loisel J, Brosseau DP, Beilman DW, Hunt SJ (2010) Global peatland dynamics since the last glacial maximum. *Geophysical Research Letters* 37:L13402