

The controls on boreal peatland surface water chemistry in Northern Alberta, Canada

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Abstract:

Spatial and temporal variability in surface water chemistry, organic soil chemistry and hydrologic indicators were investigated at three poor-fen complexes in two boreal catchments in Northern Alberta to provide insight into the dominant controls on surface water chemistry. Improved understanding of these controls is required to enable prediction of runoff chemistry in the region under changing atmospheric deposition conditions. Surface water chemistry exhibited considerable variability; within each fen conductivity, dissolved organic carbon (DOC), and Cl^- tended to decrease and pH tended to increase with increasing distance from the lake edge. Variations in evaporative isotopic enrichment in ^2H and ^{18}O , expressed as deuterium excess, were used to distinguish between throughflow waters and those that were more evaporatively enriched. Throughflow surface waters were more acidic primarily due to higher concentrations of DOC and NO_3^- . Exchangeable base saturation and pH of organic soils were strongly related to surface water chemistry at two of the fen complexes, demonstrating the capacity for cation exchange to influence surface water chemistry. Fen surface water concentrations of most elements and DOC increased during the summer period (between June and August), while pH of water decreased. Evaporative concentration of the surface waters was a dominant driver, with surface water temperature increasing at both catchments. Localized groundwater discharge was an important contributor of base cations to the fens, while the organic soils are sinks for atmospherically deposited SO_4^{2-} , N and Cl^- . Copyright © 2010 John Wiley & Sons, Ltd.

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INTRODUCTION

Wetlands are recognized as a vital ecosystem component owing to their ability to regulate hydrology and influence the quality of water entering rivers and lakes (Bragg, 2002) by retaining and transforming nutrients and metals (Hunt *et al.*, 1997). Organic wetlands, composed of fens and bogs, and commonly referred to as peatlands in Canada (Zoltai and Vitt, 1995), have also been recognized for their importance as wildlife habitat (Gorham *et al.*, 1984; Ferone and Devito, 2004) and for their ability to act as a major global sink of carbon (C) (Moore *et al.*, 2004). Canada is home to one-third of the world's peatland area (Gorham *et al.*, 1984), found largely in the boreal forest of the country's north where fen-dominated peatlands form a key hydrologic link within catchments. Wetlands influence lake water chemistry in the Boreal Plains region of Northern Alberta (Prepas *et al.*, 2001), and the proportion of the catchment occupied by wetland or fen is an important determinant of runoff (Gibson *et al.*, 2002). Detailing the behaviour of these landscapes is critical to predicting their response to global stressors such as climate change and atmospheric deposition of pollutants. In recent years, increased industrial and recreational development in Canada's north (Ferone and Devito,

2004) has facilitated access and introduced regional pressures. Atmospheric emissions of sulphur (S) and nitrogen (N) have increased dramatically over the last 40 years in the Athabasca Oil Sands Region (AOSR) of Northern Alberta and are anticipated to remain elevated through the 21st century. Much of the AOSR has been classified as acid-sensitive owing to low mineral soil weathering rates and low lake alkalinity (Alk). To date, little is known about (future) catchment response to anthropogenic acid deposition in the region. The use of dynamic hydrogeochemical catchment-based models as a technique to investigate this requires an understanding of the role of peatlands for model parameterization and successful prediction of catchment response (e.g. runoff chemistry) to this stressor.

Investigation of peatland water chemistry has often compared peatland types across a gradient from bog to rich fen (e.g. Blancher and McNicol, 1987; Vitt and Chee, 1990; Reeve *et al.*, 1996) or compared the same type of peatland (e.g. Urban *et al.*, 1987; Proctor, 1994) at different sites across a region. Other studies have focussed on describing the hydrology (Reeve *et al.*, 1996), vegetation (Vitt and Chee, 1990), chemistry (Vitt *et al.*, 1995), and N and S sequestration (Moore *et al.*, 2004) of peatlands in Canada. Northern peatlands generally lack well-defined streams (Waddington and Roulet, 1997), and fen systems are dynamic, receiving non-channelized flow from groundwater and/or surrounding areas that include other

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peatlands and mineral soil deposits. Studies investigating spatial chemical variability across entire complexes have shown that waters on these landscapes are not chemically homogeneous (Nicholson, 1989); pronounced differences in some chemical parameters including dissolved organic carbon (DOC), pH, conductivity (Cond) (Marin *et al.*, 1990) and base cation concentrations (Tahvanainen *et al.*, 2002) may occur spatially within a single peatland. Investigations that consider both spatial and temporal variability are less common.

By necessity, catchment-based models (e.g. MAGIC: Cosby *et al.*, 1985; INCA-C: Futter *et al.*, 2007) typically require that landscape components (e.g. wetlands, uplands, lakes) are represented with a lumped-average compartment; each compartment representing the dominant processes occurring within the landscape type. Important processes within peatlands may include S and N reduction, elemental uptake, evapotranspiration, cation exchange, groundwater intrusions and weathering, all of which influence lake chemistry. Peatlands can exhibit considerable spatial heterogeneity and processes are unlikely to operate uniformly across their full extent or between peatlands; thus, it is a challenge to represent this variability within a model compartment without detailed study to provide insight into the dominant controls on water chemistry in the AOSR.

This study investigated the spatial and temporal variability in surface water chemistry, including stable isotopes of hydrogen and oxygen, and dissolved CO₂ concentrations, as well as organic soil chemistry of poor-fen complexes in two boreal catchments. The objectives of this work were to assess chemical variability within fens, chemical differences among fens, and to relate the dominant processes occurring within the fens to surface water chemistry. In addition, fen surface water chemistry was used in concert with lake and deposition chemistry to identify elemental sources and sinks for each lake catchment. The sampling regime involved detailed spatial sample collection across whole peatlands; it is comprehensive and includes a large number of parameters detailing physical properties, surface water chemistry, peat chemistry and hydrology. Ultimately, this information is required to predict the response of lake chemistry to elevated atmospheric S and N deposition.

METHODS

Study area and climate

Dystrophic lakes are common in the Boreal Plains ecozone of Northern Alberta, and wetland cover is high, with peatlands comprising up to 50% of the landscape in the AOSR (D.H. Vitt, pers. comm.). These northern peatlands are characterized by *Sphagnum* moss, sedges, and sparse growth of scrubby trees (Gorham *et al.*, 1984), with black spruce (*Picea mariana*) dominant in bogs and tamarack (*Larix laricina*) common in fens. Classification of these peatlands ranges from poor to rich depending on their mineral status and floristic assemblage (Vitt and Chee,

1990). The climate of the region is continental boreal, with average daily temperature ranging from -18.8°C (January) to 16.8°C (July) (Environment Canada, 2009), and annual average precipitation of approximately 0.53 m (Mesinger *et al.*, 2006).

Study sites

This study was carried out at two lake catchments, SM08 and NE07, located south (in the Stony Mountains) and northeast of Fort McMurray, respectively (Figure 1), and chosen for study owing to their contrasting hydrologic behaviour. Each lake is shallow and well mixed with low Gran Alk (SM08: -0.1 mg l^{-1} , NE07: 2.6 mg l^{-1}) and high DOC concentrations (SM08: 18 mg l^{-1} , NE07: 31 mg l^{-1}). Both catchments contain extensive fen-dominated peatland complexes that border their lakes, with one complex at NE07 and two at SM08 included in this analysis. The supply of water to the study lakes originates largely through lateral movement across these peatlands, but a small contribution of groundwater directly to the lakes also occurs (J.J. Gibson, unpublished data). The peatland complexes are considered to be typical of poor fens in the region.

SM08 demonstrates an evaporative character (Bennett *et al.*, 2008), where a large proportion of the precipitation leaves the catchment through evaporation rather than runoff. SM08 is the larger (881 ha) of the two catchments with fen complexes occupying approximately 67% of the catchment. The fen complexes are located on the east (SME) and west (SMW) borders of the lake (Figure 2) and are largely open, with short (1–2 m) black spruce and tamarack stands being sparse or absent, and only infrequent stands of denser and taller black spruce. SME is the longer and narrower fen complex, extending nearly 2 km from the lake edge. The NE07 watershed is small

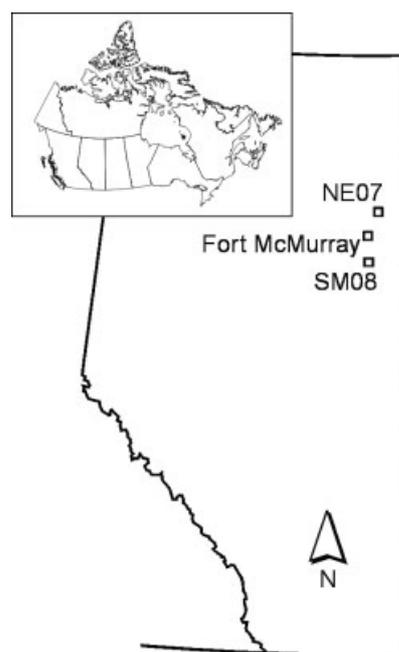


Figure 1. Location of the study catchments and the town of Fort McMurray in the Athabasca Oil Sands Region of Northern Alberta

(507 ha) with the majority (77%) of the catchment consisting of fen and bog; it is characteristic of a through-flow watershed-lake system (Bennett *et al.*, 2008) where a larger precipitation amount exits via the lake outflow. The fen complex (NEF) at NE07 extends approximately 1 km south from the shore of the lake (Figure 3).

Sample collection

Surface water and peat samples were collected at 100 m intervals along two transects within each peatland

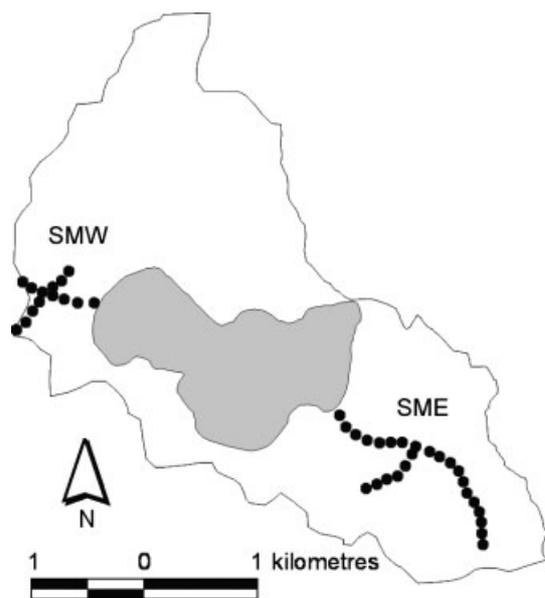


Figure 2. Overview of the SM08 catchment, with the sampling points (filled circles) in each fen complex

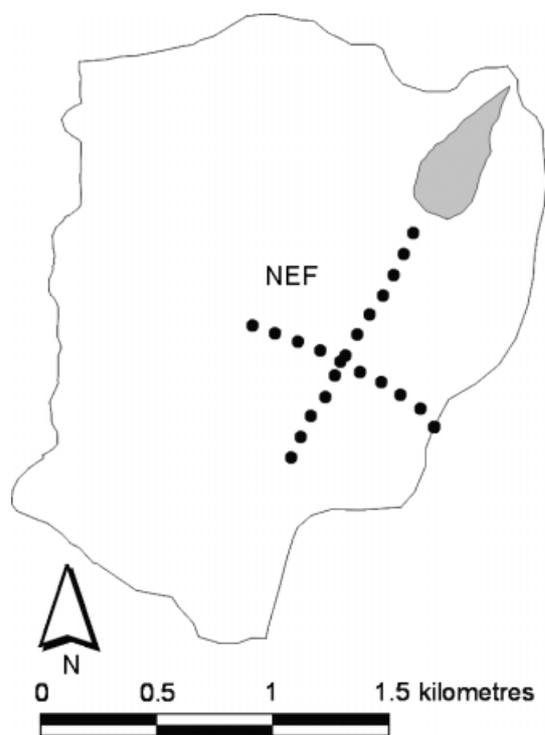


Figure 3. Overview of the NE07 catchment, with the sampling locations (filled circles) spanning the fen complex

complex. The primary transect was situated along the length of the fen, oriented approximately parallel to the long axis of the lake. At SME, the complex contained a narrower fen than the other two sites; this transect was slightly curvilinear following the fen to its apex. The second transect at each site was oriented perpendicular to the first transect and spanned the widest area of the complex. A Whitfield 2000 sampling probe, consisting of a capped and perforated PVC tube, and a siphon pump were used to isolate and collect surface water from the upper 15 cm of surficial pools. Sample water was filtered through 70- μm Nitex[®] mesh and stored in HDPE bottles. Water samples for isotopic analysis were collected in overfilled 30 ml HDPE bottles and sealed tightly to ensure no evaporation. Measurements of pH, Cond and water temperature were recorded in the field using a portable pH/conductivity meter (ExStik[®] EC500). Water samples were stored on ice within hours of collection for transport to the laboratory, where they were stored at 4 °C until analysis, usually within one week of collection. *In situ* measurement of the partial pressure of carbon dioxide ($p\text{CO}_2$) by headspace analysis technique (Raymond *et al.*, 1997) was performed on bulk water samples collected from surficial pools in overfilled 125 ml glass bottles. The concentration of CO_2 in the headspace was measured using an infrared CO_2 gas analyzer (PP Systems EGM-4). Dissolved CO_2 was corrected to 'true' values according to Hope *et al.* (1995) using Henry's Law (e.g. Raymond *et al.*, 1997) and the CO_2 fugacity–pressure relationship (Weiss, 1974). Fibric peat samples were collected from the top of the water table at each location and stored field-moist in plastic bags. For two of the peatlands, SMW and NEF, sampling was repeated in June and August 2006 at each location on the transects, while at SME full-length transects were sampled only in August. Lake surface water was sampled at a depth of 10 cm during both sampling periods following the collection procedure outlined for fen water.

Laboratory analysis

Water samples were analysed for Gran Alk using a PC-Titration Plus[®] system. Samples for DOC, anions and cations, and total Kjeldahl nitrogen (tKN) were filtered (<0.45 μm) prior to analysis. Nitrate (NO_3^-), ammonium (NH_4^+) and tKN were determined by colourimetric measurement using a Pulse Autoanalyzer System consisting of a reaction cell, spectrometer and data analyser. DOC was determined using a Shimadzu[®] TOC-V_{CPH} organic carbon analyzer. Sulphate (SO_4^{2-}) and chloride (Cl^-) concentrations were analysed using a Dionex[®] DX-600 ion chromatograph, while potassium (K^+), sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations were determined using a Varian[®] 240 FS direct aspiration flame atomic absorption spectrometer. Standard analysis of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ by isotope ratio mass spectrometry was performed on water samples at the University of Waterloo. Analytical precision for individual isotopic tracers is estimated at $\pm 0.5\%$ for $\delta^2\text{H}$ and 0.1% for $\delta^{18}\text{O}$,

and approximately $\pm 0.6\%$ for the combined deuterium excess (d-excess) factor (Dansgaard, 1964).¹ Peat was air dried and ground using a Wiley mill to obtain a particle size suitable for chemical analysis. The pH was measured in deionized water at a ratio of 1 g peat to 30 ml water using a glass electrode pH meter. Details describing measurement of exchangeable base cations (eBC) (the fraction of the total cation exchange sites occupied by the base cations: K^+ , Na^+ , Ca^{2+} , Mg^{2+}) and cation exchange capacity are given by Whitfield *et al.* (2006), with the only alteration to the method being that a smaller mass of peat (0.5 g) was used, owing to its high absorptive capacity.

Statistical analysis

Data quality was evaluated using charge balance; prior to including an estimate of anionic charge from organic sources following Oliver *et al.* (1983), the charge balance was systematically unbalanced in favour of the cations. While this was largely mitigated by including an estimate of organic charge, the waters were dilute and dominated by organic charge owing to high DOC levels. As a verifiable measure of organic charge was not available, the charge balance (including Oliver estimate of organic charge) criterion used for acceptance was $\pm 25\%$. The majority of samples (95%) passed this criterion. It is unlikely that omission of other cations contributed to the observed discrepancy, as analysis of metal concentrations of surface water at NEF and other peatlands in the region revealed concentrations several orders of magnitude lower than the cations included in the balance estimates (C.J. Whitfield, unpublished data).

The data were tested for normality using the Shapiro–Wilk test, and for outliers using the Mahalanobis distance, with outliers excluded from further analysis. Parametric correlations or nonparametric Spearman's Rho, according to the distribution of the data, were used to test for

correlation between distance from lake edge (distance) and d-excess and water chemistry (pH, temperature, Cond, DOC, Alk, NH_4^+ , NO_3^- , Cl^- , SO_4^{2-} , K^+ , Na^+ , Ca^{2+} , Mg^{2+}) at the three fen complexes (August only). Soil pH and eBC were also assessed for correlations against water chemistry variables and distance. For the SMW and NEF complexes, temporal comparisons between June and August measurements of the above water chemistry parameters, as well as d-excess, tKN, pCO_2 and soil pH were conducted using the Wilcoxon signed-rank test. An alpha value of 0.05 was used as the minimum level of significance for both the correlations and signed-rank tests.

Deuterium excess

Herein, d-excess is used as an indicator of offset below the global meteoric water line of Craig (1961) that arises in the region from heavy isotope enrichment in residual water produced during open-water evaporation (Gibson *et al.*, 2005). While open-water evaporation losses produce isotopic build-up in residual waters, transpiration losses typically do not; isotopic enrichment occurs locally within the plant and is not normally returned to the residual source waters (Gat, 1996). As a result, d-excess variations are related to evaporation from standing water pools or depressions rather than to plant-mediated vapour losses, which occur widely across the wetlands and treed zones. Systematic differences in d-excess signals in various water sources/types within local watersheds (Table I) generally reflect the significance of evaporation loss in the water balance of hydrologic compartments, ranging from upland groundwater that is highly connected to local recharge sources and has minimal exposure to evaporation, to lakes which are variably connected to runoff sources but have a high proportion of water loss by evaporation. As such, d-excess is a useful relative tracer of connectivity and sluggishness of flow.

Retention indicators

Potential elemental retention and release in the catchments (whole catchment or peatland) was identified using a concentration factor (CF). The CF was calculated as the

¹ Deuterium excess (d-excess) is $d(\text{‰}) = \delta^2H(\text{‰}) - 8\delta^{18}O(\text{‰})$ where δ^2H and $\delta^{18}O$ are ratios of $^2H/^1H$ and $^{18}O/^{16}O$ reported as deviations in per mil (‰) from Vienna Standard Mean Ocean Water (VSMOW) and reported on a standard normalized scale (Coplen, 1996). Uncertainty in d-excess is estimated as root mean square of uncertainty in individual tracers.

Table I. Deuterium excess characteristics (reported as ‰) by location type near Fort McMurray, northeastern Alberta

Water type	<i>n</i>	Mean	Max	Min	1 std
Edmonton (P)	53	6.9	19	-10	6.6
Fort Smith (P)	50	4.6	31.1	-24.2	11.1
Deep groundwater (G)*	22	6.3	12.2	3.8	2.1
Shallow (<10 m) upland groundwater (G)	17	5.4	7.4	3.7	1.1
NE07 (F)	43	5.3	8.4	-3	2.3
SM08 (F)	60	1.9	7.6	-7.9	3.2
NE07 (L)	5	-3.1	-0.5	-5.1	2.1
SM08 (L)	5	-20.1	-17.5	-21.4	1.6
Regional Aquatic Monitoring Program (L)	247	-16.1	-0.5	-34	7.7

Letters in parentheses denote precipitation (P), groundwater (G), fen complexes (F) and lakes (L).

* Deep groundwater includes local quaternary aquifers, buried channels and bedrock aquifers including Lower Grand Rapids Formation and Clearwater Formation sampled at depths ranging from 30 to 150 m.

Table II. Average pH, d-excess, water temperature (Temp), Cond, pCO₂, and average concentrations for DOC, Gran Alk, tKN and major ions for the three fen complexes (NEF, SME, SMW)

Parameter	Units	SME (32)	SMW (28)	NEF (43)
pH		3.9 (0.2)	3.9 (0.1)	4.2 (0.7)
d-excess	‰	1.0 (3.7)	2.7 (2.5)	5.3 (2.3)
Temp	°C	14 (1.9)	15 (3.4)	10 (3.8)
Cond	µs cm ⁻¹	61 (23)	69 (10)	46 (14)
pCO ₂	µatm	9.8 × 10 ³ (5.9 × 10 ³)	9.6 × 10 ³ (3.9 × 10 ³)	11 × 10 ³ (5.4 × 10 ³)
DOC	mg l ⁻¹	42 (8.5)	46 (6.3)	41 (6.8)
Alk	mg l ⁻¹	-8.9	-8.6	-3.2
tKN	mg l ⁻¹	1.3 (1.0)	1.6 (1.4)	1.0 (0.4)
NH ₄ ⁺	mg l ⁻¹	0.018 (0.027)	0.045 (0.074)	0.26 (0.24)
NO ₃ ⁻	mg l ⁻¹	0.035 (0.020)	0.035 (0.027)	0.027 (0.021)
Cl ⁻	mg l ⁻¹	0.64 (0.32)	0.63 (0.52)	0.71 (0.53)
SO ₄ ²⁻	mg l ⁻¹	0.71 (0.33)	0.52 (0.31)	0.76 (0.61)
K ⁺	mg l ⁻¹	0.52 (0.51)	0.27 (0.13)	0.46 (0.27)
Na ⁺	mg l ⁻¹	0.29 (0.14)	0.16 (0.08)	0.48 (0.22)
Ca ²⁺	mg l ⁻¹	0.74 (0.44)	0.65 (0.26)	2.1 (1.8)
Mg ²⁺	mg l ⁻¹	0.30 (0.17)	0.21 (0.06)	0.77 (0.58)

Standard deviations are in parentheses, and the number of samples is included beside each complex name.

ratio of the concentration of an element in the surface water of the lake or fen to its concentration in precipitation. This approach does not separate out the influence of ground and surface waters, but rather seeks to identify which elements have sources and which are retained, and to identify where this occurs, within the peatland or across the wider catchment. Elemental concentrations in precipitation were estimated using total deposition, and average annual precipitation amount (Mesinger *et al.*, 2006). Bulk deposition of N, S, Ca²⁺ and Mg²⁺ was measured at the study sites during the period 2005–2008 using ion exchange resin (IER) columns (R.K. Wieder, unpublished data). Total deposition was calculated using observed bulk to wet factors to adjust IER bulk data to represent wet and modelled wet to dry deposition ratios for the region (Vet and Shaw, 2004) to estimate total deposition (from wet). Total deposition of Na⁺, K⁺ and Cl⁻ was taken from mapped annual deposition for the period 1994–1998 (Vet and Shaw, 2004), assuming no change in deposition between the periods.

The study area is arid and, in the absence of any other processes, elemental concentrations will increase due to evaporative processes as water moves through the catchment. Thus, elemental CFs cannot be interpreted directly, but must instead be evaluated against a reference CF (CF_R) that represents the expected concentration due to loss of water. The CF_R was calculated as the ratio of precipitation to discharge (lake) or precipitation to water yield from the terrestrial catchment (fen). Discharge and water yield were determined at each catchment using stable isotope mass balance techniques (NE07 discharge: 0.16 m; NE07 water yield 0.18 m; SM08 discharge: 0.13 m; SM08 water yield: 0.14 m). In this regard, elemental CFs can be used to indicate the importance of other processes acting on these elements in the catchments. Concentration factors higher than the CF_R calculated from the water balance suggest a source of dissolved constituents, and those that are lower indicate

a sink. Concentration factors were calculated for the lake using long-term (2002–2006) average chemistry and hydrology. A rough estimate of retention and release in the fen complexes was also calculated using fen surface water chemistry (June and August average) and hydrology data from 2006. It was not possible to quantify the uncertainty around the estimates of deposition and hydrologic balance used in this assessment; accordingly only in cases where the CF is substantially (>20%) different from the CF_R has a net source or sink been attributed to the element in question.

RESULTS

Chemical variability

Surface water chemistry exhibited considerable variability across the three fen complexes. The general character of the surface water at each complex was acidic and dilute (Table II); for example mean (averaged over two sampling periods) pH ranged from 3.9 to 4.2, Cond from 46 to 69 µs cm⁻¹, and Alk from -8.9 to -3.2 mg l⁻¹. NEF exhibited a few characteristic differences from the two fens at SM08, having somewhat less acidic surface waters (higher average pH and Alk), higher base cation concentrations (notably Ca²⁺ and Mg²⁺) and lower temperature (Table II). In addition, some chemical parameters (e.g. pH, Alk, NH₄⁺, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺) were more variable at NEF, suggesting that the influence of controlling processes is spatially variable within this complex. Deuterium excess in peatland waters ranged from high values typical of precipitation and local groundwater (NEF) to lower values intermediate between groundwater and lakes (SME, SMW) (Table II), suggesting a predominant groundwater connection and/or lower evaporation loss at NEF as well as more rapid movement of water through this system.

Table III. Correlation coefficients between surface water parameters and distance from lake edge and d-excess at the three study fen complexes (August data)

	SME (<i>n</i> = 24)		SMW (<i>n</i> = 14)		NEF (<i>n</i> = 21)	
	Distance	d-excess	Distance	d-excess	Distance	d-excess
pH	0.59**	-0.62	0.22	-0.75**	0.29	-0.22
Temp	0.27	-0.73***	0.20	-0.21	-0.54***	-0.27
Cond	-0.52*	0.57	-0.28	0.75**	-0.30	0.07
DOC	-0.12	0.73***	-0.59*	0.55*	-0.18	0.46*
Gran Alk	0.18	-0.54**	-0.13	-0.22	0.23	0.25
NH ₄ ⁺	0.22	-0.46*	-0.46	0.23	0.07	-0.04
NO ₃ ⁻	0.05	0.41*	0.23	0.26	0.22	0.57**
Cl ⁻	-0.42*	0.15	-0.30	-0.32	-0.43*	0.24
SO ₄ ²⁻	0.42*	0.43*	0.11	0.09	0.06	0.27
K ⁺	-0.09	0.68***	0.08	0.23	-0.10	0.16
Na ⁺	0.29	0.03	0.05	0.25	-0.01	0.30
Ca ²⁺	0.68***	0.06	-0.48	-0.51	0.32	-0.18
Mg ²⁺	0.60**	0.14	-0.05	-0.58*	0.25	-0.19
d-excess	-0.45	1	-0.14	1	-0.14	1

Significant correlations denoted (0.05*, 0.01**, 0.001***).

Spatial patterns

Variability in surface water chemistry within each fen was considerable, but most parameters included in this analysis showed no clear spatial pattern. The distance (to lake edge) variable is a linear measurement used as a proxy to indicate spatial influences and does not directly indicate the functional closeness of a sample point to the lake, as flowpaths are nonlinear and samples situated at greater distance may contribute water to the lake more efficiently if they are situated along a more direct and/or stronger flowpath. A few variables demonstrated consistent relationships with distance from lake edge across the three fen complexes, but often these correlations were low. Cond, DOC, Cl⁻ and d-excess were all negatively correlated with distance at these peatlands, while pH increased with distance from the lake (Table III); however, these trends were rarely significant at more than one peatland complex. NEF was the only complex to have a significant spatial pattern for temperature, with higher temperature in closer proximity to the lake (Table III).

There is little evidence that the isotopic enrichment signature is related to distance. Instead, standing water and groundwater influences may be demonstrated by relationships between d-excess and water chemistry; these relationships were largely consistent across all three peatland complexes. Cond, DOC, NO₃⁻, SO₄²⁻, K⁺ and Na⁺ were all positively related to d-excess, while negative relationships were observed with pH, temperature and Ca²⁺ concentrations (Table III). High d-excess values indicate more throughflow and lower values are associated with more evaporative conditions. Therefore the negative relationship with temperature may be related to throughflow conditions; areas with more input of colder groundwater having higher d-excess and/or radiative heating of areas exposed to evaporation increasing water temperature. Deuterium excess relationships with DOC (Figure 4) and NO₃⁻ were strong and

significant (three and two of the complexes, respectively), and correlations with pH were also strong. These patterns suggest that waters of a more throughflow nature are under greater influence of organic acidity (high DOC and low pH in higher d-excess water). Lower NO₃⁻ where d-excess is lower suggests removal processes in more evaporatively enriched waters. Negative correlations between d-excess and Alk at two of the fens (Table III) provide additional evidence that throughflow waters are more acidic.

Soil chemistry

Investigation of the relationships between solution and solid phase chemistry revealed strong relationships for some parameters at two of the fen complexes. Soil pH and eBC were positively related to surface water pH, Alk and concentrations of base cations at NEF and SME (Table IV), while Cond, DOC and NO₃⁻ exhibited negative correlations at these complexes (Table IV). At SMW, relationships between soil pH and eBC and surface water were notably absent. Correlations between soil pH and eBC at NEF and SME were not unexpected owing to exchange between H⁺ and base cations on the soil complex. It is apparent that a strong interrelation between soil and surface water chemistry can exist, but it does not necessarily occur in all fens.

Temporal changes

There was a significant increase in water temperature (SMW: 2.5 °C; NEF: 3.8 °C) between June and August at both SMW and NEF and concentrations of most parameters also increased during this period. Only Alk, tKN and K⁺ did not show a significant change in one of the two fen complexes, while Cond, DOC, NO₃⁻, Cl⁻, SO₄²⁻, Ca²⁺ and Mg²⁺ all increased in both (Table V). Increases in August concentrations were generally less than two-fold, but were much higher for SO₄²⁻ (SMW). Deuterium excess (SMW only), pCO₂ (NEF only) and surface water

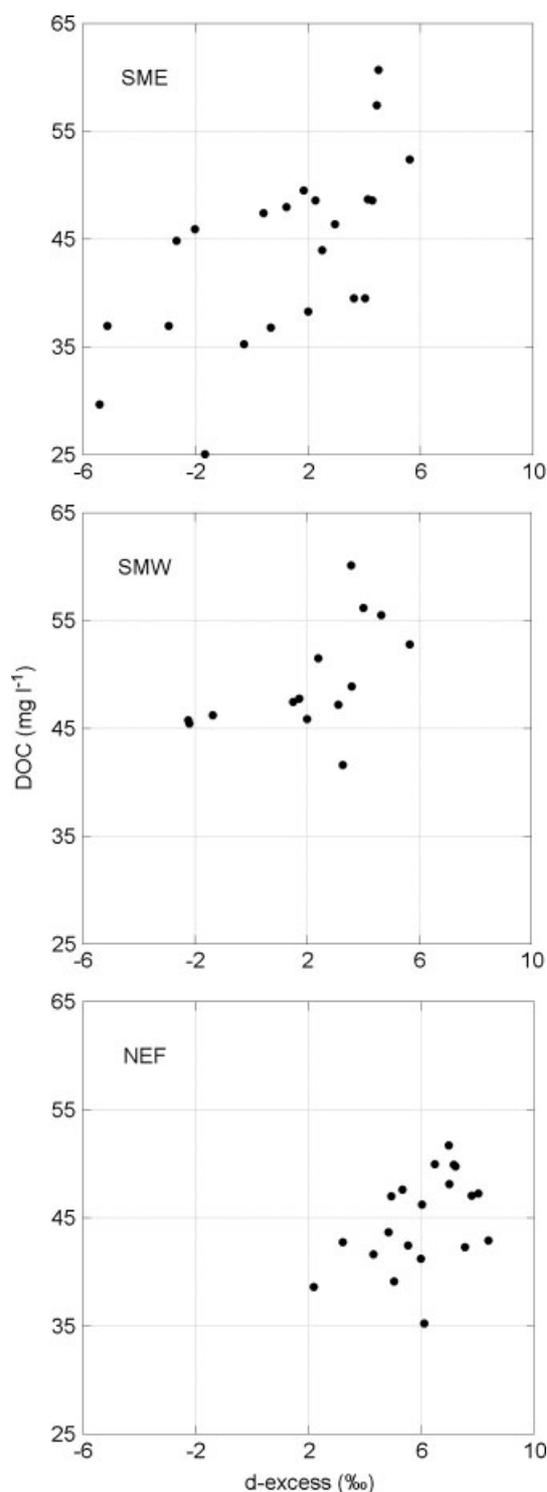


Figure 4. Relationships between DOC and d-excess at the three fen complexes. See Table III for corresponding correlation coefficients and significance levels

pH (both) decreased between June and August. Average increase in soil pH was similar (0.1 pH units) at both catchments, albeit this was only significant at NEF.

Elemental retention

The patterns of retention and release of the major elements (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , S, N) were largely consistent between catchments. Based on lake chemistry,

the catchments demonstrated a large net retention of anions, with Cl^- and SO_4^{2-} concentrations in the lakes lower than would be expected due to evaporative enrichment (Table VI). Sodium, K^+ , Ca^{2+} and Mg^{2+} CFs were higher than their respective CF_R at NE07, suggesting a source, while N is retained. At SM08, Cl^- , SO_4^{2-} , N and Ca^{2+} were retained and sources of Na^+ , K^+ and Mg^{2+} were apparent. For most elements, retention and release in the fen complexes indicated by their CF was consistent with the patterns observed for the lake catchments. Sulphate CFs for SMW and SME were much lower than for the SM08 catchment as a whole, indicating that the fen complexes are an important sink for atmospherically deposited S. While these catchments appear to be a net N sink for atmospheric deposition, the distribution of N forms is not consistent; the vast majority of export from the catchments was in organic form, while deposition occurred primarily as NH_4^+ and NO_3^- .

DISCUSSION

The use of catchment-based models to predict lake chemistry is complicated by the structure and composition of catchments in the study area. In these peatland-dominated catchments, it is necessary to have a fundamental understanding of changes in water chemistry as surface waters route across these landscapes prior to entering lakes. Given the variability (both spatial and temporal) exhibited herein, describing a lumped parameter peatland compartment in a model is difficult.

Chemical variability

Surface waters in all three peatlands exhibited low pH (~ 4), characteristic of poor fens (Sjors and Gunnarsson, 2002) and bogs (Vitt *et al.*, 1995). Poor fens elsewhere in the region have equally low pH and have low mineral concentrations and low Cond (Nicholson, 1989). Peatland pH is strongly negatively correlated to anion deficit (Tahvanainen *et al.*, 2002), and the high DOC levels and dilute waters across the three study sites highlight the importance of organic acids on overall acidity (e.g. Siegel *et al.*, 2006). At NEF, higher surface water pH in localized areas can be attributed to zones of mineral-rich groundwater inflow, with Ca^{2+} and Mg^{2+} concentrations being higher and more variable across this complex. The groundwater inputs are largely damped as surface waters move through more dilute and acidic areas of the complex; detailed spatial sampling was necessary to identify this difference between NEF and SME and SMW, where water chemistry was more uniform. Acidity, base cation concentrations and Alk have been identified as key parameters for characterizing peatlands (Vitt *et al.*, 1995; Tahvanainen *et al.*, 2003); considerable variation in these parameters at NEF indicates that small areas of moderate-rich fen are imbedded within a large poor fen.

Most N present in these catchments was organic as NH_4^+ and NO_3^- were low. Nitrification rates are expected to be low in bog and poor fens due to

Table IV. Correlation coefficients between soil pH and eBC and distance and water chemistry parameters at the three peatlands

Parameter	SME (<i>n</i> = 24)		SMW (<i>n</i> = 14)		NEF (<i>n</i> = 21)	
	Soil pH	eBC	Soil pH	eBC	Soil pH	eBC
Distance	0.30	0.30	0.16	-0.16	0.17	0.36
pH	0.58***	0.53**	0.07	-0.42	0.84***	0.56***
Temp	0.23	0.25	-0.21	-0.65*	0.24	-0.16
Cond	-0.60**	-0.40*	-0.23	0.51	-0.68***	-0.75***
DOC	-0.37*	-0.18	-0.39	0.53	-0.49	-0.03
Gran Alk	0.51*	0.08**	-0.10	-0.08	0.72**	0.55*
NH ₄ ⁺	0.39	0.02	0.14	0.46	0.22	0.29
NO ₃ ⁻	-0.30**	-0.01*	-0.24	0.10	-0.49*	-0.09
Cl ⁻	-0.26	-0.18	0.30	-0.53	0.12	-0.33
SO ₄ ²⁻	0.29	0.33	-0.28	-0.30	-0.03	0.16
K ⁺	-0.16	-0.17	0.09	0.33	-0.16	-0.05
Na ⁺	0.68**	0.48**	-0.11	0.27	0.41**	0.51**
Ca ²⁺	0.54**	0.54**	-0.22	-0.16	0.86***	0.75***
Mg ²⁺	0.40*	0.39*	-0.20	-0.22	0.89***	0.73***
Soil pH	1	0.71***	1	-0.10	1	0.61**

Significance indicated by * (0.05), ** (0.01) and *** (0.001).

Table V. Comparison of June and August measurements of surface water parameters and soil pH at SMW and NEF using a Wilcoxon signed-rank test

Parameter	SMW (<i>n</i> = 14)			NEF (<i>n</i> = 21)		
	June	August	Significance	June	August	Significance
pH	4.0	3.8	0.01	4.2	4.1	0.001
d-excess (‰)	3.6	2.1	0.01	5.5	5.9	NS
Temperature (°C)	13	16	0.01	8.7	12	0.001
Cond (µS cm ⁻¹)	67	73	0.05	39	53	0.001
DOC (mg l ⁻¹)	41	50	0.01	39	44	0.001
Alk (mg l ⁻¹)	-8.1	-8.8	NS	-1.3	-3.4	NS
tKN (mg l ⁻¹)	0.75	2.1	NS	1.3	0.98	NS
NH ₄ ⁺ (mg l ⁻¹)	0.036	0.038	NS	0.33	0.17	0.05
NO ₃ ⁻ (mg l ⁻¹)	0.006	0.054	0.01	0.008	0.045	0.001
Cl ⁻ (mg l ⁻¹)	0.14	0.93	0.01	0.44	0.98	0.001
SO ₄ ²⁻ (mg l ⁻¹)	0.072	0.72	0.05	0.45	1.0	0.01
K ⁺ (mg l ⁻¹)	0.34	0.24	NS	0.51	0.41	NS
Na ⁺ (mg l ⁻¹)	0.15	0.15	NS	0.54	0.42	0.05
Ca ²⁺ (mg l ⁻¹)	0.51	0.76	0.01	0.74	0.65	0.001
Mg ²⁺ (mg l ⁻¹)	0.17	0.23	0.01	0.68	0.97	0.001
pCO ₂ (µatm)	12 × 10 ³	8.9 × 10 ³	NS	13 × 10 ³	9.5 × 10 ³	0.05
Soil pH	3.7	3.8	NS	3.6	3.7	0.001

Table VI. Concentration factors reported for the study lake catchments

Lake	CF _R	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	N
NE07	3.3	5.5	4.3	21	8.0	1.8	0.3	2.0
SM08	4.4	5.6	10	6.5	3.2	2.3	0.7	2.9

The reference concentration factor (CF_R) indicates the expected concentration due to evaporative processes. Italicized and bolded values denote net sinks and sources, respectively.

inhibition by acidity through superior competitive traits of methanotrophic bacteria (Bayley *et al.*, 2005) and dissolved inorganic N is often dominated by NH₄⁺ in peatland systems (Tahvanainen *et al.*, 2002). Ammonium concentrations were higher and more variable at NEF, presumably due to local differences in ammonification,

nitrification and assimilation, but differential deposition between the two sites could also play a role, as NE07 is located downwind of major industrial emissions sources, whereas SM08 is more remote.

Spatial patterns

In general, fen complex surface water was spatially heterogeneous, and few spatial trends in chemistry were observed. Controlling factors that include hydrology, subsurface water chemistry, precipitation chemistry, bedrock/soil quality and weathering rate, cation exchange with soils, plant uptake and microbial processes (Vitt *et al.*, 1995; Tahvanainen *et al.*, 2002) can operate at various spatial scales, and thereby obscure spatial patterns. Nonetheless, relationships between distance from lake edge and Cond, Cl⁻, DOC and pH were observed at the

three study fens. Hydrological studies of pond–peatland complexes across North America reveal variable pore-water chemistry and evidence of seasonal flow reversals that generate spatial variation in water chemistry (Vermont: Mouser *et al.*, 2005; Wisconsin: Marin *et al.*, 1990; Alberta: Ferone and Devito, 2004). Marin *et al.* (1990) observed increasing concentrations of DOC and specific conductance with distance from lake edge in a poor fen. In the current study, where movement of surface water is believed to be unidirectional towards the lake, the opposite pattern was detected and increases in DOC concentration likely result from greater contributions of organic acids as surface water follows longer flow paths across organic soils. This finding coupled with low pH in surface waters close to the lake indicates that fen surface waters become more acidic as they move lakeward across the peatlands in these catchments. Higher Cl^- close to the lake may indicate some evaporative enrichment of these waters.

At NEF, lower water temperature with distance from the lake suggests that marginal areas are more susceptible to influences from shallow groundwater. Mineral soil deposits encompass much of the complex, and samples taken around the periphery of the complex were notably colder, likely due to groundwater inputs in contact with underlying discontinuous permafrost. Internal groundwater upwellings are also apparent in places that lead to more disorganized flow patterns, flow reversals and stagnant zones with higher evaporation loss due to standing water. Degrading permafrost is not anticipated to alter the isotopic signature of groundwater inputs, as the signature of permafrost is comparable to both precipitation and groundwater (J.J. Gibson, unpublished data). These locations of groundwater discharge have generally higher Alk and pH, and can increase variability and obscure spatial patterns in chemistry that might occur across the peatland due to processes such as ion exchange, biological uptake and evaporative concentration as water flows lakeward. Accordingly, a lumped parameter approach that describes the cumulative behaviour of these influences will be favoured within the context of a hydrogeochemical model.

No relationship between d-excess and distance was observed, but within each fen a range in d-excess reflects areas subject to evaporation or infiltration of groundwater. Deuterium excess was linked to temperature, Cond, DOC and some ion concentrations. Reduced d-excess where water temperature is elevated is possible due to radiative heating associated with higher rates of evaporation (likely predominant at SM08), or alternately that higher d-excess values (and lower temperatures) are indicative of inflows of groundwater and/or contact with permafrost in some areas of the fen complex (NEF). It is clear from d-excess variations that evaporation and transpiration vary in proportion across the wetland; however, this cannot be used to directly infer variations in total evapotranspiration losses. Lower d-excess is a strong evidence of shallow, more sluggish water movement and reduced groundwater throughput. These low d-excess

waters exhibited lower DOC concentrations, suggesting that zones of more sluggish water movement are subject to greater mineralization of DOC, due to photodegradation (increased light penetration) or other processes. Alternatively, high DOC in higher d-excess waters might be attributed to physical conditions whereby the movement of water through organic soils stimulates DOC production. Nitrate was also elevated in higher d-excess waters. Given that low NO_3^- concentrations are expected in low pH environments where nitrifying bacteria experience competition and are less effective in creating NO_3^- (Bayley *et al.*, 2005), the movement of water may also be important for N dynamics, and lower reductive assimilation in more rapidly moving waters may occur.

Soil chemistry

In the current study, shallow organic soil chemistry was strongly related to the chemistry of surface waters in contact with it at SME and NEF, while relationships were absent at SMW. Variability for most surface water chemical parameters was low at SMW (Table II) and detection of relationships to soil chemistry was likely made difficult as a result. Proctor (1994) discussed the importance of cation exchange with peat as a short-term buffer of ions in surface water. The exchange complex, which represents a much larger cation pool than that of the dilute surface waters (Sjors and Gunnarsson, 2002), responded to the cation concentrations of the surface waters. Soil eBC were higher where surface water concentrations were highest at NEF and SME. The exchangeable fraction of base cations in peatlands can be expected to respond to changes in base cation concentrations of precipitation. Upland mineral soils are subject to similar processes; however, the spatial variability demonstrated here for organic soils has not yet been reported for upland systems. Given the local nature of elevated surface water base cation concentrations in these peatlands, cation exchange with organic soils is particularly important for dampening mineral-rich groundwater inputs as the water disperses from the point of discharge.

Temporal variability

Changes in surface water chemistry are strongly influenced by hydrology, with most elements increasing in concentration between June and August. Two mechanisms influence seasonal variability in surface water concentrations. Surface waters are diluted during melt of the overlying snowpack (prior to sampling in June), with relatively slow runoff of this water. During the open-water season evaporative enrichment of the surface waters coincides with increased evaporation losses and presumably total evapotranspiration loss. This is consistent with Sjors and Gunnarsson (2002), who reported that dilution of surface waters by snowmelt is usually strong but temporary. Isotopic enrichment signals showed varied temporal responses. Lower d-excess at SMW in August confirms the influence of evaporative processes, while unchanging

d-excess at NEF can be attributed to groundwater flow to the fen complex. For a boreal fen in Norway, Kværner and Kløve (2008) found that d-excess did not decrease during low-flow periods, despite minimal groundwater inputs, and the absence of a change was believed due to low evaporation. Climatic influences such as ambient humidity may limit evaporative enrichment, and alternatively, peatlands with long water residence times might be less likely to demonstrate changes in d-excess at this temporal scale.

Decreases in surface water pH observed here are consistent with other studies. Bog water pH has been shown to fluctuate 0.1–0.2 pH units on an annual basis, with peak depression during summer in synchronization with SO_4^{2-} peaks (Proctor, 1994, 2006). Sulphate increases are likely to be observed upon rewetting of the organic soils due to the oxidation of sulphides during water table drawdown (Eimers *et al.*, 2003; Proctor, 2006), although some evaporative concentration of SO_4^{2-} in surface waters may also be important for these systems (e.g. Adamson *et al.*, 2001). Seasonal increases in cation concentrations have been reported for a poor-fen rich-fen gradient in Finland, with moderately rich fens showing a larger change than poor fens, possibly due to a concentration effect (Tahvanainen *et al.*, 2003). Ombrotrophic bogs in England also exhibit Ca^{2+} and Mg^{2+} maxima during mid to late summer and minima in winter (Proctor, 1994, 2006; Adamson *et al.*, 2001). Vitt *et al.* (1995) found increases in Ca^{2+} , Mg^{2+} and Na^+ over the course of the growing season at extreme-rich and moderate-rich fens. In the current study, no temporal change in d-excess at NEF suggests that evaporative enrichment plays a limited role in the observed concentration changes. The influence of groundwater is likely more important as groundwater concentrations of the major elements (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-}) in the study catchments are higher than both precipitation and surface water concentrations (K. Tattrie, unpublished data). A greater relative contribution of groundwater to the surface could be responsible for the higher observed concentrations in August. Potassium often demonstrates a sharp peak in early or late spring, followed by declines over the course of the summer due to vegetative uptake (Proctor, 1994; Vitt *et al.*, 1995; Tahvanainen *et al.*, 2003). This trend was likely not observed in the current study due to the later initial sampling; however, the strength of this pattern can exhibit considerable variability year over year (Proctor, 2006). Higher NO_3^- concentrations during August may result from elevated surface water temperatures, as higher temperatures may stimulate microbial activity, with more NO_3^- generated through nitrification. Experimental manipulation of peat cores with lower water levels demonstrated a similar result (Freeman *et al.*, 1993). At NEF, where higher pH is more likely to facilitate nitrification, decreased NH_4^+ between June and August could be a consequence of increased nitrification, or may be attributed to vegetative uptake (e.g. Urban *et al.*, 1988).

The increase in DOC and the decrease in pCO_2 observed during the summer are attributed to different

mechanisms. Waddington and Roulet (1997) suggested that DOC is diluted during wet periods. In the study area, DOC was likely diluted during snowmelt, and the increases between June and August are not unexpected given the potential for evaporative concentration in these systems, and likely contribute to the observed pH depression. Further, experimental manipulation by Tipping *et al.* (1999) showed that DOC increased with ambient air temperature, and thus a warmer environment in August at the study sites is also likely to stimulate DOC production. Higher water temperature might also be expected to increase respiration and raise pCO_2 concentrations; however, pCO_2 concentrations were lower in August. Decreases in pCO_2 between June and August are believed to result from the accumulation of dissolved CO_2 during respiration under the snowpack (snowpack is generally present between 6 and 7 months in the study region, but the respiration period is likely shortened according to the availability of oxygen) with subsequent decreases in pCO_2 over the course of the summer. This is consistent with fluxes of CO_2 from lakes to the atmosphere which can be greater in the summer than the fall, reflecting the dissolved CO_2 concentrations in the lakes (Rantakari and Kortelainen, 2005).

Soil pH increased as water pH decreased, apparently due to the fact that greater cation concentrations in surface waters can induce greater Ca^{2+} and Mg^{2+} binding to soil exchange sites and displace H^+ . Proctor (1994) posited that increased surface water cation concentrations are not due to a concentration effect, but rather equilibration of the surface water with peat, and that the decrease in surface water pH during the summer is the result of new H^+ originating during the production of new cation exchange sites on the peat. In the current study, the exchange complex does not appear to contribute cations to the surface water, but rather responds to evaporative concentration of the surface waters by binding more base cations and displacing H^+ .

Catchment retention and release

The boreal peatland catchments of this study exhibit retention of atmospherically deposited SO_4^{2-} , N, and Cl^- while for base cations catchment release is predominant. Retention of SO_4^{2-} occurs primarily through two processes: bacterial SO_4^{2-} reduction is common in peatland porewaters (e.g. Thompson and Bottrell, 1998) while biological uptake of S can also be a large sink in peatlands (Bayley *et al.*, 1986). Sulphur retention is estimated to be 91 and 82% of deposition inputs at NE07 and SM08, respectively. Nitrogen is retained at the catchments. Although small losses through denitrification could offset some N retention in these peatland systems, N deposition remains low relative to polluted regions, and given N-limited growth in terrestrial environments, net retention in fen systems is expected (Prepas *et al.*, 2001). Chloride is strongly retained in the study catchments. A number of studies have shown the limitations of treating Cl^- as inert and highlighted the complexity of

biogeochemical cycling of Cl^- (e.g. Lovett *et al.*, 2005; Oberg and Sanden, 2005). Briefly, inorganic Cl^- may be converted to organic Cl^- by soil micro-organisms, may adsorb to soils (Gebhardt and Coleman, 1974), and additionally, while it makes up a small percentage of biomass by weight, Cl^- is taken up as a counter ion to cationic nutrients (e.g. Lobert *et al.*, 1999). Given that these elements exhibit consistent and comparable retention across the study sites, appropriate sinks should be specified in hydrogeochemical models.

Chloride retention through incorporation into vegetation can be estimated for these peatlands using a simple calculation based on the annual photosynthetic sink of carbon in poor fens in Northern Alberta (90 g C m^{-2} ; Glenn *et al.*, 2006), the C fraction of peat in the study peatlands (0.43) and the median Cl^- content of peat ($0.35 \text{ mg Cl}^- \text{ g}^{-1}$; Lobert *et al.*, 1999). This approximation indicates that Cl^- retention (12 mg m^{-2}) in the peatlands can be a significant component ($\sim 25\%$) of the relatively low level of atmospheric deposition. As such, it will be necessary to parameterize these retention processes in order to describe runoff chemistry. Assimilatory retention of SO_4^{2-} can also be considerable, as these organic soils are approximately 0.17% S (by mass) and approximately 0.25 g S m^{-2} may be retained in biomass on an annual basis. Downward diffusion and bacterial reduction of SO_4^{2-} in deeper waters (Thompson and Bottrell, 1998) are likely to account for additional retention of atmospherically deposited S, and fen water SO_4^{2-} concentrations at NE07 decrease at depth (D.L. Laxton, unpublished data). Vile *et al.* (2003) estimated that the potential average SO_4^{2-} reduction rate for peatlands of central Alberta (low S deposition) was greater than deposition. Accordingly, peatland-dominated catchments in the study area exhibit the capacity to retain the majority of atmospheric SO_4^{2-} at present deposition levels.

With the exception of Ca^{2+} at SM08, catchment sources of base cations were apparent at the study catchments. Organic soils represent a large stock of base cations, but do not contribute a stable supply in the manner that weathering processes constitute a source in mineral soils. Weathering rates for the rooting zone of upland mineral soils in the study catchments are extremely low (McDonald, 2009) and the spatial extent of these areas is limited. Given the large sources for some base cations indicated by the mass balance, it is unlikely that they can be attributed solely to mineral weathering and contributions of base cations to the lakes from groundwater inflows are perceived to be important. At NE07, the presence of local groundwater discharge to the fen has been well established. While the fen complexes at SM08 exhibit limited evidence of a base cation source, the relative lake area is much larger at this catchment and groundwater is estimated to account for a measurable component of the water balance (J.J. Gibson, unpublished data) and a direct source of Na^+ and Mg^{2+} to the lake is probable. Unlike the retention demonstrated for S, N and Cl^- , sources of base cations can be expected to vary between catchments, and catchment-specific model

parameterization will be necessary to accurately predict runoff chemistry.

CONCLUSIONS

Peatland surface water chemistry in the AOSR exhibits substantial variability both within and between fen complexes, highlighting the limitation of characterizing peatland surface water chemistry by sampling at select or few locations, particularly in catchments where groundwater inputs of a contrasting chemical nature prevail. Cation exchange, vegetative uptake and microbial reduction are important controls on surface water chemistry across the three study peatlands. These processes are responsible for retaining large amounts of atmospherically deposited Cl^- , S and N in these fen-dominated systems. Hydrologic influences (e.g. base cation rich groundwater discharge and evaporation) are also critically important, but are difficult to discern owing to variable spatial influence. Detailed site investigations such as this are necessary to improve our understanding of the regulation of surface water chemistry by peatlands in the AOSR and will ultimately facilitate the use and development of hydrogeochemical models to predict the response of surface water chemistry to elevated deposition of S and N. Nonetheless, groundwater inflows may pose a challenge for generating reliable model predictions, especially for catchments with limited data.

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