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Alkalinity and acidity cycling and fluxes in an intermediate fen peatland in northern Ontario

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Abstract Peatlands are important to global carbon (C) sequestration and surface water acid–base status, both of which are affected by peatland alkalinity and acidity cycling. Relationships among sulfate (SO_4^{2-}), nitrate (NO_3^-), organic acids (OA^-), base cations (i.e., Ca^{2+}, Mg^{2+}, K^+, and Na^+), proton (H^+) acidity, and bicarbonate (HCO_3^-) alkalinity were investigated in an intermediate fen peatland in northern Ontario during 2004 (an average precipitation year) and 2005 (a dry summer). Potential evapotranspiration was higher and the water table, groundwater input from the uplands, and runoff were lower during 2005. Net inputs of base cations, HCO_3^-, SO_4^{2-}, and OA^-, and to a lesser degree NO_3^-, were lower during the drier year, mainly due to lower groundwater transfer to the fen. Fen porewater HCO_3^- concentration and net output were also lower in the drier year, whereas Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentrations and net output were higher. During the climatically average year, N immobilization, carbonic acid (H_2CO_3) dissociation, and OA dissociation were equally important H^+-producing reactions. Peat cation exchange accounted for 50% of the H^+ sink, while SO_4^{2-} reduction and denitrification accounted for an additional 20 and 25% of the H^+ sink, respectively. During the dry year, S oxidation accounted for 55% of the H^+ net production, while that for H_2CO_3 dissociation was 70% lower than that during the climatically average year. Peat cation exchange consumed three times the acidity, and accounted for 92% of the H^+ consumption during the dry year compared to the climatically average year. This was consistent with a three-fold higher net base cation export from the fen during the dry year. Based on the study results, a conceptual model was developed that describes the role of acidity formation and its implications to intermediate fen acidification.

Keywords Acidification · Bicarbonate · Calcium · Sulfate · Drought

Introduction

Peatlands are important to the global carbon (C) cycle because of their role in C sequestration (Gorham 1991; Vitt et al. 2000), global warming potential (GWP) [carbon dioxide (CO_2) plus methane (CH_4) production and fluxes] (Moore and Knowles 1990; Blodau 2002; McLaughlin 2004), and surface water acidification and subsequent aquatic C export (Gorham et al. 1984; Hruska et al. 1996). Most research has focused on C sequestration and GWP potential with much less on alkalinity and acidity production and consumption. Improving the understanding of

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peatland alkalinity cycling and its role in acidification is important because it has been linked to acid recovery in a number of lakes in North America and Europe (Evans et al. 2001; Aherne et al. 2006), as well as peatland succession (Gorham et al. 1984; Vitt and Chee 1990; Siegel et al. 2006).

Peatlands are classified as bogs and fens and the general sequence of peatland succession is from aquatic ecosystems to fens and ultimately to bogs (Gorham 1953). Bogs are ombrotrophic peatlands that receive most of their water from precipitation (Glaser et al. 1981) and have low peat base saturation (Gorham et al. 1984; Urban et al. 1995; Gunnarsson et al. 2000). Bogs acidify surface water through the production and flux of hydrogen ions (H^+) dissociated from mineral acids [e.g., sulfuric acid (H_2SO_4)] and organic acids (e.g., dissolved organic C; DOC) (Hemond 1980; McKnight et al. 1985). In contrast, fens are minerotrophic peatlands that, in addition to precipitation, receive water from upslope mineral soils (Gorham et al. 1984). These water inputs have high base cation (e.g., Ca^{2+}, Mg^{2+}, K^+) concentrations and bicarbonate (HCO_3^-) alkalinity, resulting in circumneutral pH (pH = 6–8) (Siegel et al. 2006).

Fens are subdivided into rich, intermediately rich, and poor, with surface water Ca^{2+} and HCO_3^- concentrations decreasing along the gradient from rich to poor fen (Sjors 1950; Gorham 1953; Gunnarsson et al. 2000). Due to reductions in HCO_3^- alkalinity and increases in acidity production (Gorham et al. 1984; Vitt and Chee 1990; Siegel et al. 2006), intermediate fens have been identified as one of the most transient phases (e.g., 10–100 years) in peatland succession.

Climate change-induced drought may lower peatland alkalinity, increase acidity (Van Haesebroeck et al. 1997), and thus shorten the time needed to transition from intermediate to poor fen. This occurs primarily through rapid organic and inorganic S oxidation to SO_4^{2-}, which acidifies the peat through net H^+ production and HCO_3^- consumption (Urban and Bayley 1986; Cirmo et al. 2000). Similar effects are attributed to nitrification (e.g., Creed et al. 1996; Schiff et al. 2005).

Hydrogen ions produced from S oxidation and nitrification can displace base cations held on fen peat exchange sites where the bases can be transported to surface water by SO_4^{2-}, organic acids (OA^-), or nitrate (NO_3^-), contributing to base cation depletion and soil acidification (Gorham et al. 1984). This may further decrease the transition time from intermediate to poor fens. In contrast, high water tables favor anoxic situations, promoting SO_4^{2-} reduction as the primary S redox reaction (Bayley et al. 1986; Urban et al. 1989) and denitrification can become an important N redox reaction (van Hoewyk et al. 2000; Davidsson et al. 2002); both processes consume H^+, producing HCO_3^- alkalinity (van Breeman et al. 1983; Cirmo et al. 2000). Consequently, alkalinity increases and fewer protons are available at peat exchange complexes to exchange for base cations or to be transported to surface waters.

The effects of a lower water table on alkalinity and acidity cycling of intermediate fens will thus depend on the interactions among (i) precipitation and groundwater inputs and subsequent water residence time, (ii) biological processes, such as microbially-mediated S and N oxidation–reduction (redox) reactions, (iii) chemical processes such as carbonate equilibrium and cation exchange reactions, and (iv) the amount of exchangeable bases on surface peat exchange sites. However, few studies have investigated the effects of water table levels on net alkalinity or acidity balances in intermediate fens. Therefore, the objectives of this study were to (1) describe seasonal patterns in porewater chemistry during two climatically contrasting years (2004 and 2005), in which water table heights varied, (2) describe the net input:output cation and anion balance for the 2 years, (3) develop a general H^+ mass balance using net input:output fluxes to identify H^+ consumption and production reactions and how this affects base cation exchange from peat and its depletion, and (4) to develop a conceptual model of alkalinity and acidity formation in intermediate fens and how these contribute to peatland succession from intermediate to poor fens.

Materials and methods

Site description

The study area consisted of an 817 ha sub-watershed in the Lake Superior Drainage Basin in northern Ontario (48°21′N, 85°21′W). Elevation of the watershed is between 500 and 600 m. The growing season ranges from 70 to 100 days and mean January and July temperatures are −14.2 and 14.7°C, respectively, with maximum winter and summer temperatures seldom exceeding 0 and 30°C, respectively (McLaughlin 2009). Mean annual precipitation is 1,090 mm, with 40% occurring as snowfall, typically forming a snow pack of 1.0–3.0 m from December to March.

The site is located on the southern limits of OMAR (Omarolluk Formation of the Belcher Group, exposed in the Belcher Islands of eastern Hudson Bay) glacial erratics of massive dark siliceous greywacke that contain light-toned calcareous concretions (Prest et al. 2000) redistributed over mainly Archean strata during the Cochrane re-advances of the Wisconsinan ice sheet. Soils in the upland forests are bouldery, coarse, loamy sand, mixed, frigid Typic Haplorthods derived from Precambrian bedrock underlying surficial deposits of dense basal till with OMAR erratics and frequent rocky outcrops. Soil depth ranges from 0 to more than 1 m.

The intermediate fen studied is 5.3 ha and is vegetated mainly by sedges (*Eriophorum vaginatum* L. and *Carex* sp.), which cover more than 80% of the peatland, with minor components of sweet gale (*Myrica gale* L.), leatherleaf (*Chamadaphne calyculata* (L.) Moench.), and Labrador tea (*Ledum groenlandicum* Oeder) as the dominant shrubs, and brown (e.g., *Scorpidium* sp., *Rhizomnium* sp.) and *Sphagnum* mosses as the dominant bryophytes. Soils in the fen consist of 0.5–3 m of peat that overlies compacted fine sandy sediment and coarse sandy deposits.

Sampling and analyses

Hydrometric data

To record local climate, a weather station was installed and consisted of a HOBO H21-001 (Onset Computer Corp., Cape Cod, MA, USA) datalogger that recorded air temperature and an Onset Computer Corp., S-RGA-M002 sensor to record rainfall, both measured at 1 min intervals but recorded as 15 min averages. Six water table wells (5-cm diameter PVC pipe) were installed to 100 cm and pressure transducers (Solonist 3001 LT Levelogger M5) were fitted to each well to assess continuous water table depths.

Measurements of hydraulic head were made monthly from May to November in 2004 and 2005. Five transects (separated by 75 m) were established across the width of the fen in 2002 (Fig. 1). For groundwater hydraulic head and chemical sampling, each transect consisted of six piezometer (slotted 5-cm diameter PVC pipe) nests (separated by 50 m), with piezometers inserted to 0.25, 0.50, and 1.0 m, extending from the stream edge to the fen/upland interface. At each piezometer location, hydraulic conductivity was measured using the Hvorslev water recovery method (Freeze and Cherry 1979).

The mass flux of water from one part of the fen to another was calculated following the methods of Waddington and Roulet (1997). The fen was divided into four zones based on position and topography (Fig. 1). The mass flux from one zone to another was computed assuming the boundaries between zones extended perpendicularly from the fen's surface to its base. Discharge was converted into a unit area depth of subsurface runoff by dividing by the area of the zone from which the groundwater was received. Potential evapotranspiration (PET) was calculated using the Hamon equation (Hamon 1961):

$$\mathrm{PET}_{\mathrm{Hamon}} = 13.97\, dD^2 W_{\mathrm{t}} \qquad (1)$$

where $\mathrm{PET}_{\mathrm{Hamon}}$ is Hamon potential evapotranspiration in mm per month, d is the number of days in a month, D is the mean monthly hours of daylight in units of 12 h, and W_{t} is a saturated water vapor density term calculated by:

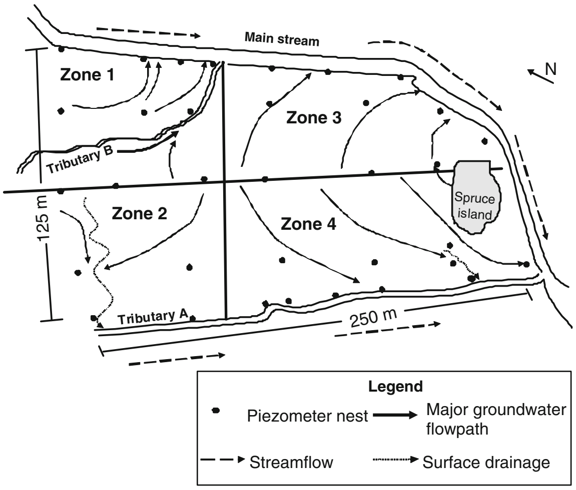

Fig. 1 Hydrologic monitoring setup in an intermediate fen in northern Ontario

$$W_t = \left(4.95^{0.062T}\right)/100 \tag{2}$$

where T is the average daily air temperature in °C obtained from the weather station.

Precipitation atmospheric deposition

Wet atmospheric deposition data were obtained from the closest Environment Canada atmospheric deposition monitoring site located near Sault Ste. Marie, Ontario (Turkey Lakes Watershed), ~200 km from the study site. Precipitation chemistry may differ somewhat between the Turkey Lakes Watershed and the study site but both locations are relatively remote and it was assumed that the precipitation chemistry was similar enough to estimate atmospheric contributions to chemical inputs for the study.

Soil chemistry

Peat samples were collected to the peat/mineral sediment interface using a Russian peat corer (Aquatic Research Instruments, Hope, Idaho, USA) at five randomly selected locations within the peatland. Samples were taken at 20 cm depth intervals, returned to the laboratory, and stored at 4°C until dried. Samples were dried at 60°C until constant mass, passed through a 2 mm sieve, and analyzed for total Kjeldahl nitrogen (TKN), total S, and exchangeable bases [Ca, magnesium (Mg), and potassium (K)] using 1 M Na-acetate (pH 7). The cations were measured using a Varian Liberty Series II ICP. Total C was measured using a LECO CR-12 carbon analyzer and TKN measured as liberated NH_4^+ ions using a flow injection system (TRAACS 800, Braun and Lubbe) auto analyzer. Total carbonates were measured using the sequential LOI method described by Heiri et al. (2001).

Porewater chemistry

After hydraulic head was measured, the water in piezometers was pumped out until the piezometer was dry or three times the piezometer volume removed. The next day, water pH was measured using an Oakton 10 Series pH/conductivity/temperature meter after which water for other chemical analyses was collected using a low-speed peristaltic pump. These samples were placed on ice and transported to the laboratory. Samples were filtered through Gelman 0.45 μm filters and analyzed for: DIC using a Shimadzu TOC 5000 carbon analyzer; SO_4^{2-}, NO_3^-, and Cl^- by ion chromatography using a Dionex Ion Chromatography ICS 2000 anion system; NH_4^+ using a flow injection system (TRAACS 800, Braun and Lubbe) auto analyzer; and Ca^{2+}, Mg^{2+}, K^+, and Na^+ using a Varian Liberty Series II ICP. Soil solution pH and DIC concentrations were used to calculate the fractional carbonate equilibrium of the DIC assuming an open system (Boudreau and Canfield 1993). Organic acid (OA^-) concentration was estimated by the charge balance approach where:

$$OA^-_{\mu eq/l} = \text{cations}_{\mu eq/l} - \text{anions}_{\mu eq/l} \tag{3}$$

$$\text{Cations} = 2\left[Ca^{2+}\right] + 2\left[Mg^{2+}\right] + [Na^+] + [K^+] + [NH_4{}^+] + [H^+] \tag{4}$$

$$\text{Anions} = 2\left[SO_4{}^{2-}\right] + [NO_3{}^-] + [Cl^-] + [HCO_3{}^-] + 2\left[CO_3{}^{2-}\right] + [OH^-] \tag{5}$$

where inorganic cation and anion concentrations are in μM.

Porewater samples collected in September 2005 were analyzed for δ^{13}C-DIC at the Environmental Isotope Laboratory of the University of Waterloo using either a VG Micromass 903 or a VG Prism mass spectrometer following the methods of Schiff et al. (1997).

Mass balances

Mass balance calculations were based on inputs to, and outputs from, the fen focusing on the 0–25 cm depth because this region is the most susceptible to drying and rewetting during periods of drought (Sigel 1983; Vitt and Chee 1990; Clark et al. 2005). Atmospheric precipitation chemistry from Turkey Lakes was combined with groundwater inputs calculated from piezometer nests at the upland/fen interface to estimate total inputs for each constituent. The piezometers located at the bottom of the major drainage areas were used to calculate runoff.

The net flux of each constituent was used to construct an H^+ mass balance by assuming that net output of each constituent was associated with either net production or net consumption of H^+ (e.g., Steinmann and Shotyk 1997; Cirmo et al. 2000).

Specifically, carbonic acid and OA dissociations, S and N redox reactions, calcite and carbonate equilibrium reactions, and cation exchange (Table 1) were used to construct the mass balance. Although, H_2CO_3 dissociation produces both H^+ and HCO_3^-, the fate of those ions can differ relative to soil moisture. For example, when conditions are oxic, HCO_3^- can be used as a substrate for S oxidation and nitrification, both acid producing reactions (Steinmann and Shotyk 1997; Cirmo et al. 2000). However, under anoxic conditions, HCO_3^- contributes to porewater alkalinity.

Bicarbonate in fen porewater is the product of both organic matter decomposition and carbonate mineral dissolution (Komor 1994). Therefore, both processes need to be assessed because they contribute differently to H^+ production and consumption. The contribution of organic matter decomposition and carbonate mineral dissolution to H^+ mass balance were estimated by calculating the proportion of HCO_3^- from the δ^{13}C-DIC values, where δ^{13}C-DIC values of -24 and 0‰ represented 100% contribution from organic matter decomposition and carbonate dissolution, respectively (Nascimento et al. 1997). Similarly, the contributions of cation exchange and carbonate weathering for Ca^{2+} and Mg^{2+} were estimated from the δ^{13}C-DIC using stoichiometries of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) dissolution reactions.

Silicone oxide was not used in the calculations because of the difficulty in estimating the contributions of biogenic and mineral processes to SiO_2 in soil water and porewater (Conley 2002). In addition, some studies indicate that SiO_2 in fen peatlands arises predominately from quartz hydrolysis (Bennett et al. 1991). Therefore, mineral contribution to HCO_3^- was assumed to be carbonate minerals and because neither iron (Fe) nor aluminum (Al) were measured, they were not considered in the calculations.

Statistical analyses

All statistical analyses were conducted using SAS (SAS Institute 1992). Analysis of variance on the ranks of the data was used to test the hypothesis of no porewater chemical differences between years, among

Table 1 Hydrogen ion producing and consuming reactions used in H^+ mass balance calculations for the upper 25 cm of peat in an intermediate fen peatland in northern Ontario

Reaction type	Equation	Net H^+ (mol)
Hydrogen-releasing reactions		
Sulfur oxidation	$H_2S + 2O_2 = SO_4^{2-} + 2H^+$	+2
Nitrification	$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$	+2
Nitrogen immobilization	$NH_4^+ + R^a\text{–COH} = R\text{–}C_2H_2O_2NH_2 + H^+$	+1
Peat cation exchange	$Ca^{2+} + H_2X^b = CaX + 2H^+$	+2
	$Mg^{2+} + H_2X = MgX + 2H^+$	+2
	$K^+ + HX = KX + H^+$	+2
Calcite precipitation	$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$	+1
Organic acid dissociation[c]	$R\text{–COOH} = R\text{–COO}^- + H^+$	+1
Carbonic acid dissolution	$H_2CO_3 = HCO_3^- + H^+$	+1
Hydrogen consuming reactions		
Sulfate reduction	$SO_4^{2-} + 2CH_2O + 2H^+ = H_2S + 2CO_2 + H_2O$	−2
Denitrification	$NO_3^- + 1.25CH_2O + H^+ = 1.25CO_2 + 0.5N_2 + 1.75H_2O$	−1
Peat cation exchange	$CaX + 2H^+ = Ca^{2+} + H_2X$	−2
	$MgX + H^+ = Mg^{2+} + H_2X$	−2
	$KX + H^+ = K^+ + HX$	−1
Calcite dissolution	$CaCO_3 + CO_2 + H_2O = Ca^{2+} + CO_3^{2-}$; $CO_3^{2-} + H^+ = HCO_3^-$	−1

[a] R denotes rest of organic compound

[b] X denotes peat cation exchange site

[c] Assuming monoprotic acid

months, and among depths, as well as their interactions for each chemical constituent independently.

Results

Hydrometric data

Total June thorough October precipitation input was relatively similar for both years, but the distribution differed between years (Table 2; Fig. 2). Groundwater input during 2005 was only one-half that of 2004 (Table 2) and PET was 66 mm higher during 2005 than 2004 (Table 2; Fig. 2). Runoff showed a similar pattern to groundwater inputs, where runoff in 2005 was only one-half of that in 2004 (Table 2).

Mean fen peatland water table level was higher ($P \leq 0.05$) in 2004 (7.7 cm below the peat surface) than 2005 (21.5 cm below the peat surface). The water table was always below the surface of the peat during 2005 and was more than 50 cm below it from mid-July to late September (Fig. 2b). This coincided with higher PET during the 2005 summer (Fig. 3).

During 2004, water table depth responded rapidly to precipitation events, and maximum water table level occurred 3 days after a precipitation event (Fig. 2). In 2005, water table level was not responsive to precipitation events from mid-July to late September; again associated with the higher summer 2005 PET compared to the same period in 2004 (Fig. 3). However, from late September through October when PET decreased, although the water table remained below the surface of the peat it responded to precipitation.

Table 2 Water balance during the 2004 and 2005 growing seasons for an intermediate fen peatland in northern Ontario

Year/month	Hydrologic component				
	Precipitation input	Groundwater input	PET	Runoff	ΔS
2004	(mm)				
June	31	25	63	20	−27
July	49	25	85	10	−21
August	146	10	71	50	35
September	94	5	64	40	−5
October	165	40	34	85	86
Total	485	105	317	205	68
2005					
June	70	20	82	20	−12
July	21	5	100	5	−79
August	38	0	96	0	−58
September	105	2	68	8	31
October	223	25	37	75	136
Total	457	52	383	108	18

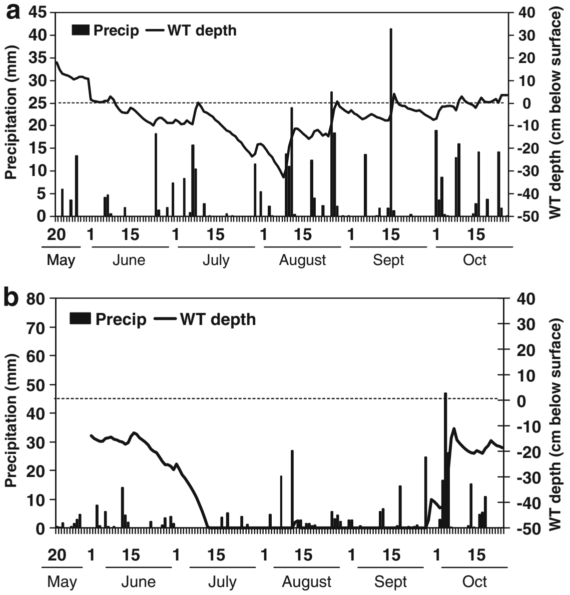

Fig. 2 Precipitation and water table depth for an intermediate fen peatland in northern Ontario in **a** 2004 and **b** 2005

Soil and porewater chemistry

Soil C, N, S, and base cation profiles in the peat were relatively consistent (Table 3). However, the exchangeable base content peaked at 40–60 cm below the peat surface. Furthermore, the percentage of the total C composed of carbonates increased from 5% in the upper 40 cm of peat to 22% between 40 and 80 cm and 40% between 80 and 100 cm.

Porewater HCO_3^- concentration was higher ($P \leq 0.05$) in 2004 than 2005 but Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentrations were higher ($P \leq 0.05$) in 2005. Porewater Ca^{2+}, Mg^{2+}, and HCO_3^- concentrations and pH were highest ($P \leq 0.05$) while SO_4^{2-} concentration was lowest ($P \leq 0.05$) at 100 cm depth (Table 4). Calcium was the dominant cation during 2004 and 2005, accounting for 61–71% of the total cation charge across depths and years (Fig. 4a, b).

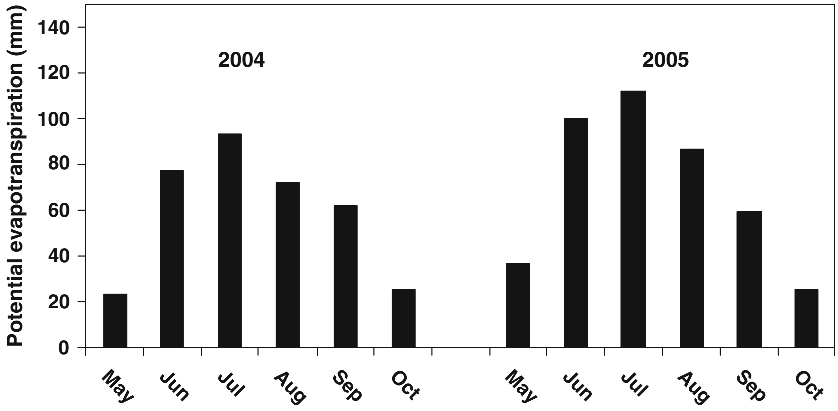

Fig. 3 Monthly potential evapotranspiration during June through October 2004 and 2005 for an intermediate fen peatland in northern Ontario

Table 3 Mean (and standard deviation) peat chemistry for intermediate fen peatland in northern Ontario sampled in 2004–2005

Depth interval (cm)	Constituent					
	Organic C (kmol ha^{-1})	Total N (kmol ha^{-1})	Total S (kmol ha^{-1})	Exchangeable Ca^{2+} (keq ha^{-1})	Exchangeable Mg^{2+} (keq ha^{-1})	Exchangeable K^{+} (keq ha^{-1})
0–20	5,910 (2,420)	1,430 (1,100)	620 (100)	26.6 (8.2)	4.8 (1.2)	0.7 (0.2)
20–40	4,860 (1,510)	1,210 (920)	530 (240)	29.6 (5.3)	3.1 (0.9)	0.3 (0.1)
40–60	3,630 (1,860)	1,430 (1,320)	420 (310)	43.1 (6.3)	14.0 (3.2)	0.8 (0.2)
60–80	5,350 (2,310)	1,360 (1,150)	410 (650)	32.8 (5.2)	6.6 (1.0)	0.3 (0.1)
80–100	5,400 (2,420)	1,320 (1,400)	350 (400)	31.9 (5.4)	6.4 (1.0)	0.2 (0.1)
Total	25,150	6,750	2,330	164	34.9	2.3

Bicarbonate was the dominant anion at 25 and 50 cm depths during 2004, accounting for 82–95% of the anion charge, but SO_4^{2-} accounted for 60% of the anion charge at 25 cm during 2005 and the contribution of SO_4^{2-} to the anion charge increased from 4% in 2004 to 36% in 2005 at 50 cm (Table 4; Fig. 4c, d). Bicarbonate accounted for more than 98% of the inorganic anion charge at 100 cm during both years.

Monthly patterns in Ca^{2+} and Mg^{2+} concentrations at 25 and 50 cm were not apparent in 2004. However, Ca^{2+} and Mg^{2+} concentrations were two to five times higher in fall 2005 than fall 2004 (Fig. 4a, b). Elevated Ca^{2+} concentrations at both 25 and 50 cm corresponded with increased SO_4^{2-} rather than HCO_3^- concentrations in 2005 (Fig. 4c, d).

The relationship between δ^{13}C-DIC and DIC concentrations was similar to that between Ca^{2+} and DIC concentrations, where increases in DIC were associated with increases in both δ^{13}C-DIC and Ca^{2+} concentrations across depths (Fig. 5a, b). The variability in both DIC and Ca^{2+} and δ^{13}C-DIC and DIC was greater at intermediate DIC concentrations (1.4–2.0 mmol). These concentrations occurred primarily in the groundwater at 50 cm, indicating higher variability in organic matter and calcite contribution to DIC at that depth, consistent with the peak in peat exchangeable Ca and Mg content (Table 3). At DIC concentrations less than 1.0 mmol, DIC was primarily a function of organic matter decomposition that occurred at 25 cm. However, at DIC concentrations greater than 2.0 mmol, both organic matter decomposition and calcite dissolution contributed to DIC, which was frequently within the range of δ^{13}C-DIC values accepted as background levels in carbonate-based groundwater (e.g., −10–0‰; Nascimento et al. 1997). Dissolved inorganic C concentrations greater than 2.0 mmol commonly occurred at 100 cm depth.

Mass balances

The fen was a net exporter of base cations, HCO_3^-, and OA^- during both years (Table 5). Net base cation losses were approximately three times higher in the dry compared to the climatically average year. Based on the stoichiometric relationships from the δ^{13}C-DIC values, only about 10% of the base cation loss was attributable to carbonate mineral dissociation, and the remaining 90% to cation exchange processes. Although, a net export of HCO_3^- occurred during both years, it was about 70% lower during the drought year, which was consistent with the lower HCO_3^- concentrations in the peat porewater (Fig. 4d). In contrast, the fen consumed SO_4^{2-} during the climatically average year, but exported it during the dry year (Table 5). Inorganic N and H^+ were consumed during both years, with NH_4^+ and H^+ consumed at similar rates. However, the fen consumed 92% of the NO_3^- input during the climatically average year compared to only 58% during the dry year (Table 5).

Using the stoichiometric balances for H^+ production and consumption (Table 1), N immobilization, H_2CO_3 dissociation, and OA dissociation were relatively equally important in H^+ production in 2004. Base cation exchange, SO_4^{2-} reduction, and denitrification were important H^+ consuming processes during 2004 (Table 6). In contrast, S oxidation dominated the H^+ production during 2005 (Table 6), with N immobilization, OA dissociation, and H_2CO_3 dissociation also contributing to H^+ production.

Table 4 Mean (and standard error) porewater chemistry in an intermediate fen peatland in northern Ontario sampled from 2004–2005

Constituent (μeq l^{-1})	Depth (cm below surface)		
	25	50	100
Ca^{2+}	292^{c}* (18)	586^{b} (36)	$1{,}817^{a}$ (86)
Mg^{2+}	96^{b} (6)	165^{b} (12)	572^{a} (34)
Na^+	52 (24)	55 (27)	59 (16)
K^+	6 (6)	4 (4)	4 (2)
NH_4^+	4 (28)	5 (16)	7 (22)
HCO_3^-	181^{c} (11)	555^{b} (36)	$2{,}178^{a}$ (107)
SO_4^{2-}	156^{a} (23)	144^{a} (25)	27^{b} (6)
NO_3^-	12 (43)	11 (43)	3 (5)
Cl^-	10 (12)	9 (9)	9 (16)
Organic acid (μeq l^{-1})	112^{b} (18)	130^{b} (24)	231^{a} (51)
SiO_2 (μmol l^{-1})	48^{c} (4)	103^{b} (8)	191^{a} (10)
pH	6.38^{c} (0.19)	6.71^{b} (0.23)	7.27^{a} (0.03)

* Numbers in rows within the soil solution followed by different *small case letters* differ between depths at $P \leq 0.05$

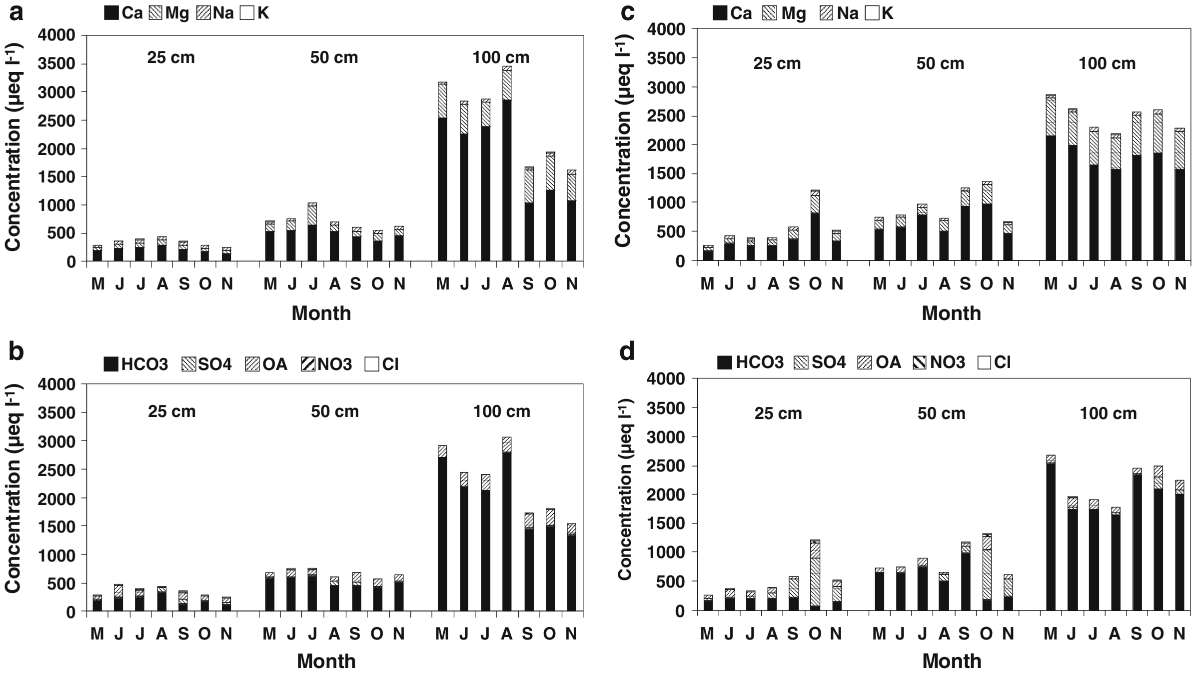

Fig. 4 Monthly mean porewater chemistry at 25, 50, and 100 cm depths for an intermediate fen peatland in northern Ontario: inorganic cations and anions in 2004 (**a**) and 2005 (**b**)

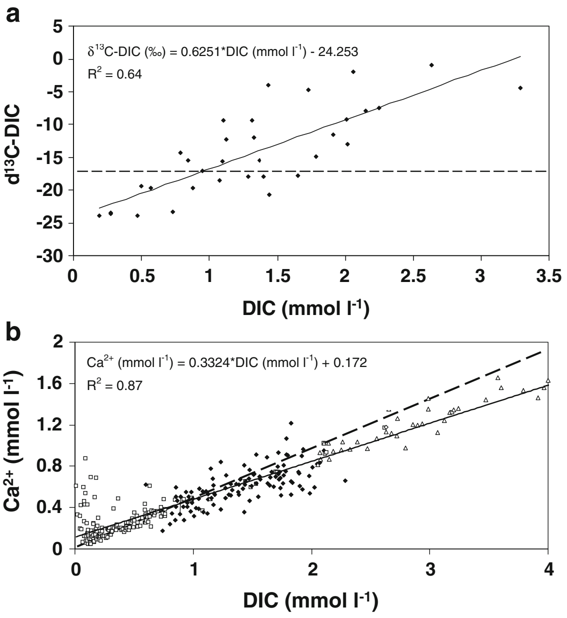

Fig. 5 Correlations between fen groundwater dissolved inorganic carbon (DIC) concentrations and **a** δ^{13}C-DIC and **b** Ca^{2+} for an intermediate fen peatland in northern Ontario (*open squares* = 25 cm, *closed diamonds* = 50 cm, and *open triangles* = 100 cm depth). In **a** δ^{13}C-DIC values above horizontal *dashed line* represent DIC concentrations predominately from $CaCO_3$ dissolution and values below *dashed line* represent DIC predominately from organic matter decomposition; in **b** *dashed line* represents the DIC and Ca^{2+} relationship of $CaCO_3$ dissolution (1 mm l^{-1} Ca^{2+} and 2 mm l^{-1} DIC). *Solid line* represents regression line

However, the majority of this acidity was consumed by peat cation exchange processes. The H^+ mass balance generally followed the porewater cation/anion balance and base cation and SO_4^{2-} export during the 2 years (Table 5; Fig. 4).

Table 5 June–October chemical inputs, outputs, and net change for an intermediate fen peatland in northern Ontario

Year/constituent	Input (precipitation + groundwater) (eq ha^{-1})	Output (eq ha^{-1})	Net (input–output) (eq ha^{-1})
2004			
H^+	112	1	111
Ca^{2+}	272	452	−180
Mg^{2+}	87	146	−59
Na^+	57	108	−51
K^+	10	17	−7
NH_4^+	133	3	130
HCO_3^-	228	448	−220
SO_4^{2-}	237	93	144
NO_3^-	130	11	119
Cl^-	12	13	−1
OA^-	91	212	−121
$\sum$cations	671	726	−56
$\sum$anions	660	777	−75
2005			
H^+	62	1	61
Ca^{2+}	100	723	−623
Mg^{2+}	31	256	−225
Na^+	10	52	−42
K^+	3	16	−13
NH_4^+	165	4	161
HCO_3^-	56	125	−69
SO_4^{2-}	180	724	−544
NO_3^-	119	50	69
Cl^-	8	8	0
OA^-	15	150	−138
$\sum$cations	371	1052	−681
$\sum$anions	378	1057	−682

Discussion

Conceptual model of intermediate fen acidification and alkalinization

A conceptual model of fen acidification and alkalinization is presented in Fig. 6, which proposes that lowering the water table increases the thickness of the acrotelm (aerobic portion of peat) and speeds soil respiration reactions, intensifying net H^+ production and HCO_3^- consumption. During droughts, water table level decreases primarily due to increased PET (e.g., Moore et al. 1998) and water export is smaller and its residence time in the fen is longer (e.g., Devito et al. 1996; Waddington and Roulet 1997). Higher PET during dry months may also contribute to groundwater flow reversals in fens (e.g., Devito et al. 1996; Fraser et al. 2001), which can transport base cations and HCO_3^- from deep to shallow peat (Siegel and Galser 1987; Glaser et al. 1997; Almendinger and Leete 1998), thereby conserving base cations in surface peat. However, it would expected that DIC (and thus HCO_3^-, Ca^{2+}, and Mg^{2+}) of the shallow peat would have a δ^{13}C signal of carbonate mineral

Table 6 Hydrogen ion net production and consumption mass balance for an intermediate fen in northern Ontario

Year/process	Net H^+ production (eq ha^{-1})
2004	
Input	+112
Nitrogen immobilization	+130
Carbonic acid dissociation	+198
Organic acid dissociation	+121
Sulfur oxidation	0
Base cation exchange	−297
Sulfate reduction	−144
Denitrification	−119
Calcite dissolution	−22
Balance	−29
2005	
Input	+62
Nitrogen immobilization	+161
Carbonic acid dissociation	+69
Organic acid dissociation	+138
Sulfur oxidation	+544
Base cation exchange	−903
Sulfate reduction	0
Denitrification	−69
Calcite dissolution	−7
Balance	−5

Positive numbers indicate net H^+ production and negative numbers indicate net H^+ consumption (see Table 1 for specific reactions)

dissolution (δ^{13}C-DIC = −10–0‰; Nascimento et al. 1997) if transport through groundwater flow reversals was significant. Because the δ^{13}C-DIC was measured on samples collected when the water table was low and had a signature representative of predominately organic matter decomposition (δ^{13}C-DIC = −25 to −15‰; Nascimento et al. 1997), the base cations in the peat porewater were from cation exchange with H^+ rather than from carbonate mineral weathering.

Other work in northern peatlands has shown that acidity production and alkalinity consumption increases at lower water tables (e.g., Gorham et al. 1984). This primarily occurs due to S oxidation, producing both H^+ and SO_4^{2-} while consuming HCO_3^- (Cirmo et al. 2000; Clark et al. 2005). In addition, higher CO_2 efflux to the atmosphere at low water table levels reduces the amount of CO_2 dissolved in porewater, also lowering porewater HCO_3^- concentrations (e.g., van Haesebroeck et al. 1997). The H^+ produced through S oxidation exchanges with the base cations on peat exchange sites, which are then flushed from the peat by rainfall following drought (e.g., Siegel et al. 1995), with SO_4^{2-} as the major counter ion for base cation export. This differs from climatically average years when HCO_3^- is the dominant counter ion.

Equally important is a larger net acidification of the peat at low water table levels due to H^+ exchange for base cations. Should droughts become more frequent in summer, and if winter recharge of soil water deficits decrease, base cation depletion and H^+ enrichment of intermediate fen peat may occur, thereby shortening this peatland successional transition phase. For example, in the upper 25 cm of peat, a net loss of 0.8% of the exchangeable bases occurred during the climatically average year, whereas a net loss of 3% occurred during the dry year (Table 3). Based on these data, we estimate that given an average climate about 125 years are required to completely strip the base cations from cation exchange sites. However, under increased drought this period may decrease to about 30 years. These calculated years are consistent with the 10–100 year timeframes reported for the longevity of intermediate fens (Gorham et al. 1984; Vitt and Chee 1990).

Hydrology and porewater chemistry

Runoff from the fen ceased during the summer drought in 2005. This has been shown to occur in various peatlands, increasing water residence time and SO_4^{2-} concentrations (e.g., Devito et al. 1996; Schiff et al. 2005) and lowering HCO_3^- concentrations (e.g., Van Haesebroeck et al. 1997).

The fen porewater HCO_3^- and SO_4^{2-} concentrations in the shallow peat were highly responsive to water table fluctuations, i.e., HCO_3^- decreased and SO_4^{2-} increased when the water table was low, while the opposite occurred when the water table was high. Sulfate was the dominant inorganic anion to balance base cations at SO_4^{2-} concentrations higher than 200 μeq l^{-1}, but HCO_3^- was the dominant inorganic anion at SO_4^{2-} concentrations <50 μeq l^{-1}. Between 50 and 200 μeq l^{-1} of SO_4^{2-}, HCO_3^- and SO_4^{2-} were both important to the charge balance, with

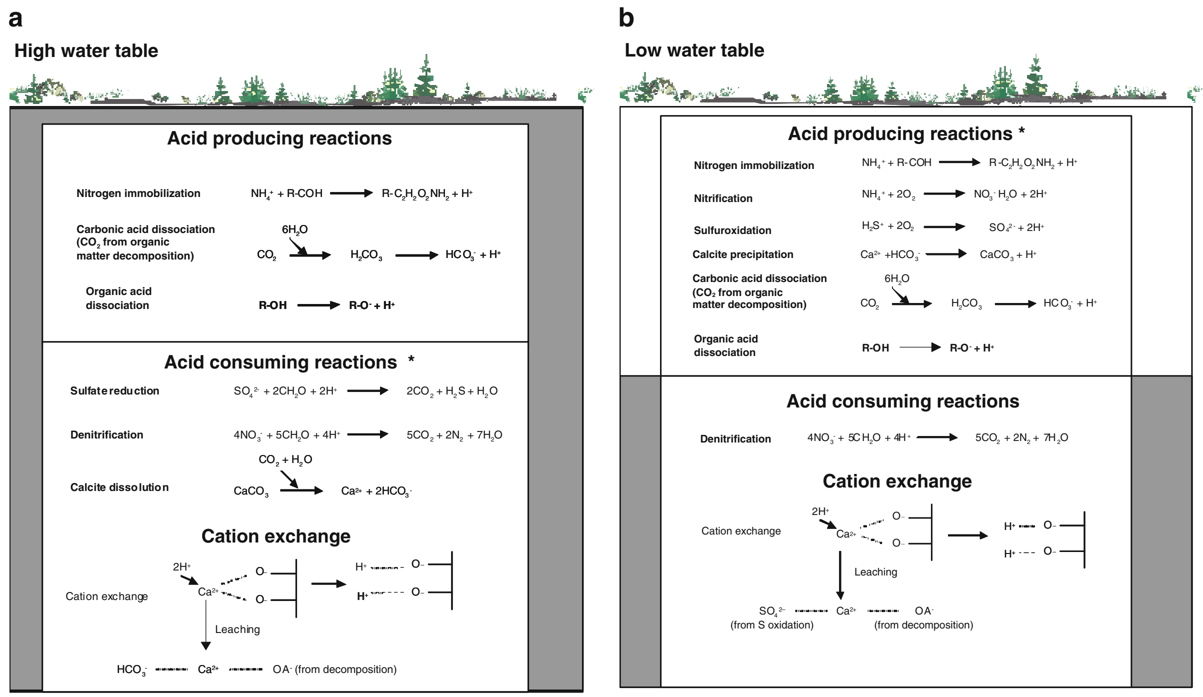

Fig. 6 Conceptual model for H^+ production and consumption for an intermediate fen peatland in northern Ontario. **a** High water table (dominated by H^+ consuming reactions) and **b** low water table (dominated by H^+ producing reactions). * Indicates dominant reaction types

HCO_3^- contribution highest at lower SO_4^{2-} levels and lowest at higher SO_4^{2-} levels. These patterns were consistent with other studies in Europe and North America. For example, HCO_3^- consumption and SO_4^{2-} production occurred when water table levels were low in fen peatlands in The Netherlands (Kemmers et al. 2003), higher downstream export of SO_4^{2-} and base cations occurred from a minerotrophic conifer swamp following summer droughts in Ontario (Lazerte 1993), aeration of a poor-fen peat to 40 cm during a dry summer resulted in a net SO_4^{2-} mobilization of 10–70 mg SO_4^{2-} m^{-2} d^{-1} in Ontario (Devito and Hill 1999), and S stable isotope studies have shown that both organic S mineralization and sulfide oxidation (Marnette et al. 1992; Schiff et al. 2005) increase peatland porewater SO_4^{2-} concentrations when water table levels are low.

Porewater HCO_3^- in the current study was the product of both organic matter decomposition and calcite or dolomite dissolution as evidenced by δ^{13}C-DIC values ranging between −23 and −12‰ in the shallow porewater and a high variability in the Ca^{2+}:HCO_3^- ratio. Our calculations point to only about 10% of the HCO_3^- in shallow porewater attributable to carbonate minerals, with the remainder produced through organic matter decomposition and carbonate equilibrium reactions. However, additional data are needed to quantify the amount of HCO_3^- that is converted to CO_2 and degassed from the fen soil versus that lost through calcite and dolomite precipitation in the surface peat. The latter process can further acidify peat, but may be a mechanism that conserves Ca^{2+}, Mg^{2+}, and HCO_3^- in the shallow peat (e.g., Komor 1994; Almendinger and Leete 1998).

Mass balances

The larger cation and anion net export in 2005 were associated with a shift from net SO_4^{2-} consumption in 2004 to net production in 2005, with a concomitant reduction in HCO_3^- net export; other studies have shown similar results (Devito and Hill 1999; Van Haesebroeck et al. 1997). A modeling study at this site using Wetland-DNDC (Webster and McLaughlin unpublished data, 2009) indicates higher CO_2 efflux from the fen soil during 2005 than 2004. Therefore, the lower HCO_3^- concentration in porewater during

2005 is likely due to interactions between increased HCO_3^- consumption by S oxidation and CO_2 degassing to the atmosphere. Additional research is needed to identify these interactions.

The dominance of cation exchange processes in H^+ consumption was consistent with higher porewater Ca^{2+} and Mg^{2+} concentrations in 2005, providing further evidence that a shift from SO_4^{2-} reduction to S oxidation can increase fen peat acidification and base cation depletion. This has also been reported in other circumneutral peatlands (e.g., van Haesebroeck et al. 1997). The 3% of the exchangeable Ca^{2+} and Mg^{2+} that were lost from the peat following the summer drought could potentially increase due to cumulative droughts followed by intense fall rains. Therefore, the role of S redox reactions in peat acidification and base cation depletion warrant further research to characterize their contributions to intermediate to poor fen succession and subsequent implications to C sequestration and surface water acidification. Combinations of in situ water table manipulation experiments and chronosequence studies substituting space for time should provide more in-depth understanding of climate controls on peatland acidity and its implications to peatland succession, C sequestration, and aquatic acidification.

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