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Storage and release of road-salt contamination from a calcareous lake-basin fen, western Massachusetts, USA



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Field study investigates dissolved salt movement in a fen during hydrologic events.
- We characterize adsorption and desorption reactions for sodium on peat.
- Calculations of selectivity coefficients show that sodium exchanges with magnesium.
- We measured geochemical flux of Na and Cl exiting the fen during snowmelt.
- Non-winter rain events more effectively export salt because snowmelt introduces contamination.

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ABSTRACT

Road salt (NaCl) applications to highways have increased stream sodium and chloride concentrations due to retention within watersheds. The mechanisms for retention and export of Na⁺ and Cl⁻ from different environments are not fully understood. This field study examines the hydrologic and cation exchange processes that store and release Na⁺ and Cl⁻ from a calcareous fen adjacent to a highway. Despite high concentrations of Ca²⁺ and Mg²⁺, elevated salt concentrations enable Na⁺ to occupy up to 15% of the cation exchange capacity of shallow peat. Calculations of selectivity coefficients show that Na⁺ preferentially exchanges with Mg²⁺, and Na⁺ can be desorbed under more dilute conditions caused by precipitation and snowmelt.

Detailed sampling of surface and ground waters during three snowmelt events illustrate early releases of Na⁺ and Cl⁻ at the onset of melting, with maximum fluxes coinciding with peak discharge. From 7 March through 4 April 2005, the flux of dissolved salt exiting the wetland amounts to 13% (Na) and 17% (Cl) of annual rock salt applied to the highway. For all of 2005, the total salt mass leaving the wetland via Kampoosa Brook is similar to the amount of road salt applied; 50% of the annual salt efflux occurred during the snowmelt season of March through May. In general, exported Na⁺ and Cl⁻ correlate with the number of lane miles of highway crossing the watershed. Large rain events outside of winter months are more effective than snowmelt with reducing dissolved salts because snowmelt also introduces contamination. For this and other wetlands having alkaline geochemistry and high flushing rates, management strategies that reduce rock salt amounts to roadways will assist with reducing salt contamination to levels less toxic to vegetation and aquatic organisms.

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Abbreviations: [X], activity of ion X; CEC_e, cation exchange capacity, equivalents per mass (cmol_c kg⁻¹); CEC_m, cation exchange capacity, moles per mass (cmol kg⁻¹); $E_{X(CECe)}$, charge fraction of exchangeable ion X of total CEC_e; $M_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $M_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $M_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $M_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, $K_{X(CECe)}$, mole fraction of exchangeable ion X of total CEC_e; $K_{X(CECe)}$, K_{X

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1. Introduction

Large quantities of road salt (NaCl) are commonly applied to highways and other impervious surfaces to improve driving conditions in snowbelt regions. Yet, pollution from road salt and other deicing agents has lowered surface water and groundwater quality (Scott, 1980; Rhodes et al., 2001; Godwin et al., 2003; Thunqvist, 2004; Kaushal et al., 2005; Ramakrishna and Viraraghavan, 2005; Kelly et al., 2008; Daley et al., 2009; Mullaney et al., 2009; Likens and Buso, 2010; Trowbridge et al., 2010; Novotny and Stefan, 2012; Corsi et al., 2015) and stressed ecosystems (Wilcox, 1986a; Richburg et al., 2001; Green et al., 2008; Corsi et al., 2010; Findlay and Kelly, 2011). Usage of road salt in the United States has increased steadily since the 1940s due to increased urban (Novotny et al., 2009; Corsi et al., 2010) and suburban (Likens and Buso, 2010) development. In Massachusetts, applications of road salt to state and interstate highways average ~500,000 tons (453,590 metric tons) per year with annual amounts varying by ~200,000 tons (181,440 metric tons) based on the severity of the winter season (MassDOT, 2012).

Observed increases in salinity of streams over decadal timeframes have been attributed to long-term retention and accumulation of dissolved salts within watersheds (Godwin et al., 2003; Kaushal et al., 2005; Kelly et al., 2008; Daley et al., 2009; Novotny et al., 2009; Trowbridge et al., 2010). For example in the rural watershed of the Mohawk River, New York, chloride concentrations increased from 7.7 mg/L in the 1950s to 20.4 mg/L in the 1990s, whereas other dissolved constituents decreased or remained the same (Godwin et al., 2003). In New Hampshire (Daley et al., 2009; Trowbridge et al., 2010), high road-salt application rates due to harsh winter climates and increased urbanization have caused chloride concentrations in streams to exceed chronic toxicity levels of 230 mg/L (USEPA, 1988) in both winter and summer months. Retention of dissolved salts in soils, surface water, and groundwater from past road-salt applications result in high concentrations in streams year round, not just when road salt is applied (Rhodes et al., 2001; Kelly et al., 2008; Daley et al., 2009; Novotny et al., 2009; Trowbridge et al., 2010). As an example of high retention, large metropolitan watersheds in Minneapolis/St. Paul, Minnesota have an average chloride retention rate of 72% of road salt applied (Novotny et al., 2009). Shallow groundwater retains significant amounts of dissolved salts, with concentrations as high as 2000 mg L^{-1} , and these urban watersheds have not reached equilibrium conditions where inflow = outflow even after decades of road salt use (Novotny et al., 2009).

Wetlands, which are often crosscut by interstate and state highways (e.g. Forman and Deblinger, 2000), can contribute to retention of road salt within watersheds. The retained salts subsequently can have adverse effects on wetland vegetation, including alteration of plant community attributes and spread by invasive species (Isabelle et al., 1987; Panno et al., 1999; Richburg et al., 2001). As an example, vegetation in peatlands-whose ecology is largely defined by their chemistry-can be particularly sensitive to geochemical alterations (Wilcox, 1986a; Schot and Wassen, 1993; Panno et al., 1999; Richburg et al., 2001). Bogs, acidic peatlands isolated from regional groundwater flow, retain dissolved salts in peat pore spaces (Wilcox, 1986b; Panno et al., 1999), and sodium readily exchanges with H⁺ on peat surfaces in these acidic environments (Pugh et al., 1996). The extent of sodium retention in more alkaline peatlands, such as fens, is less understood, however. The high concentration of divalent cations (Ca^{2+} and Mg^{2+}) in fens may inhibit cation exchange with Na⁺, as has been shown for organic material in calcareous soils (Green and Cresser, 2008). Additionally, unlike bogs, groundwater and surface water flow through fens provides a potential mechanism for release of road-salt pollution during hydrologic events, such as snowmelt.

This investigation characterizes the conditions under which sodium and chloride are mobilized and retained in a large (70 ha) calcareous, graminoid, lake-basin fen that receives road-salt runoff from an interstate highway. In particular, we measure the geochemical response of the fen to significant snowmelt and rain, and we determine the flux of sodium and chloride exported from the fen during snowmelt. Measurement of exchangeable cations on peat is used to interpret the chemical reactions with groundwater that affect sodium retention on peat surfaces. Ultimately, understanding the storage and release of road-salt pollution by fens will help inform conservation and management decisions for other salt-sensitive wetland environments.

2. Background

The study site is Kampoosa Bog (42.293N, 73.305W, elev. = 300 m, 70 ha), located in the Paleozoic marble region of the Berkshire Mountains of western Massachusetts and in the towns of Stockbridge and Lee. Misnamed a bog, Kampoosa Bog is the largest and most biologically diverse calcareous lake-basin fen remaining in Massachusetts. It is a member of the Massachusetts Areas of Critical Environmental Concern (ACEC) based on the ecological significance of its habitat and stewardship by local landowners, regional planning commissions, and state conservation agencies (Mass EEA, 2015). Approximately 19 statelisted rare plant and animal species occur in Kampoosa Bog; descriptions of plant assemblages are found in Richburg (1999). The diversity of wetland plants has been diminished by road-salt contamination from the Massachusetts Turnpike, an adjacent interstate highway (Richburg et al., 2001). In their study of plant diversity and shallow groundwater chemistry, Richburg et al. (2001) showed an association between lower plant species richness, cover, and abundance in areas of the fen having high concentrations of sodium (>112 mg/L) and chloride (>54 mg/L). In some localities within the fen, the road-salt contamination may have facilitated spread of the invasive plant *Phragmites* australis australis (Richburg et al., 2001), a salt-tolerant, giant reed that can colonize rapidly in wetlands located alongside transportation corridors (Brisson et al., 2010).

Fens are peatlands that have a strong connection to alkaline, minerotrophic groundwater rich in calcium, magnesium and bicarbonate. Some water movement—albeit slow—is required in fens to provide nutrients to plant root zones and to remove organic acids (Schot and Wassen, 1993; Almendinger and Leete, 1998; Bedford and Godwin, 2003; Duval and Waddington, 2012). Otherwise, the dissolved minerals are removed by vegetation and not replaced, resulting in acidic, nutrient-poor environments more characteristic of bogs. However the slow movement of water in fens lowers the rate of plant decomposition, which enables the buildup of peat (Bedford and Godwin, 2003). Even though water chemistry and hydrology strongly control the ecological structure within Kampoosa Bog, little is known about the major flow paths of water that supply nutrients and dissolved minerals to vegetation, in addition to those that mobilize salt contamination.

2.1. Site description

Kampoosa Bog lies within a 4.7 km² watershed with 160 m of relief (Fig. 1). The Bog is a circumneutral wetland complex that consists of a central open pond (1.3 ha) surrounded by an open, graminoid fen (9.2 ha), a shrub fen (4.4 ha), and a red maple, calcareous seepage swamp (55.8 ha, Richburg et al., 2001). The four-lane Massachusetts Turnpike crosses the northern edge of the wetland, and a two-lane state highway (Rt. 7) crosses the southern margin. The primary inlet stream to the wetland is Marsh Brook, which is renamed Kampoosa Brook after it flows beneath the Massachusetts Turnpike and enters the wetland complex. Kampoosa Brook (KB) flows south through the fen, the open pond, and eventually beneath Rt. 7. A second, unnamed inlet stream enters the wetland through the red maple swamp in the southeastern region of the complex and flows southwest, parallel to Rt. 7, before joining Kampoosa Brook. In addition to receiving runoff



Fig. 1. Maps of Kampoosa Bog, subcatchments, and sample site locations. Top panel shows classification of wetland vegetation communities within the wetland complex, adapted from Sadighi (unpublished, for The Nature Conservancy). Bottom panel shows watershed and subcatchments. Contour interval = 3 m. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

from Rt. 7, this unnamed inlet also receives road-salt runoff from the Massachusetts Turnpike. Both of these tributaries have low hydrologic gradients (~0.0005 for KB to KB-100 and 0.003 for KB-150), and stream discharge of Kampoosa Brook at the watershed outlet commonly is less than 0.3 m³ sec⁻¹ (<1 ft³ sec⁻¹) under baseflow conditions. The graminoid fen is located too far upgradient to receive road salt from Rt. 7.

Total annual precipitation in the region averages 1208 mm, as determined from climate data measured at Lenox Dale, MA (Arguez et al., 2010), located 7.3 km northeast of Kampoosa Bog and at similar elevation, 306 m. Monthly total precipitation ranges from 83–119 mm and is greatest in the months of June, July and October, whereas the months of January and February have the least total rainfall. Mean monthly air temperature ranges from -6 °C (January) to 20.5 °C (July) in the region (Supplementary Fig. 1).

2.2. Geology and geochemistry

The calcareous geochemistry of the fen at Kampoosa Bog is due to the composition of regional bedrock and contributions of minerotrophic groundwater to the wetland. The watershed surrounding Kampoosa Bog is underlain by Cambrian and Ordovician metamorphic rocks of the Walloomsac, Stockbridge, and Dalton Formations (Ratcliffe, 1974, See Supplementary Fig. 2 for bedrock geology map). The Stockbridge Formation, which underlies the western and eastern sides of the watershed and margins of the wetland, consists of calcitic and dolomitic marbles. The younger Walloomsac Formation, which directly underlies the Kampoosa Bog wetland basin, consists of impure, calcitic marble and biotite-quartzite schist that contains disseminated potassium and plagioclase feldspar and is locally rich in pyrite. The Walloomsac formation weathers orange-tan to rusty brown depending on the amount of pyrite present. The Dalton Formation, which is largely composed of quartzite, is more resistant to weathering and makes up Rattlesnake Mountain within the highest elevation region of the watershed (Ratcliffe, 1974). Much of the bedrock is covered with a thin layer of glacial till deposited during the last glaciation.

The stratigraphy within the wetland is characterized by an 8-m core collected from the open fen (Kehoe, 2003; Newton et al., 2005). Peat occurs to a depth of 2.5 m, below which is organic-rich mud that contains an interval of gastropod shells between 4.5-5.3 m. The organic content of the mud decreases below 6 m, and varved lake mud occurs below 7.5 m, evidence of lake deposits that formed in the basin prior to formation of the Kampoosa wetland. A radiocarbon date of 13,110 years before present obtained near the bottom of the core indicates continuous sedimentation since the retreat of continental ice (Newton et al., 2005). The hydraulic conductivity of the peat and sediment in the fen was determined by a series of rising-head slug tests performed in shallow and deep wells at five locations within the fen and analyzed according to the Hvorslev method (Hvorslev, 1951). The upper meter of peat is highly permeable, (mean hydraulic conductivity = $13.0 \pm 1.4 \text{ m day}^{-1}$, n = 25 for depths of 1–2 m at Sites A–E), with higher permeability in the upper 1 m, and within range of hydraulic conductivity for fens measured elsewhere (Chason and Siegel, 1986; Siegel and Glaser, 1987; Reeve et al., 2000). Hydraulic conductivity is an order of magnitude lower when measured in the deepest wells that sample organic mud (mean hydraulic conductivity = $2.4 \times 10^{-5} \pm$ 9.5×10^{-7} m sec⁻¹, n = 7, depths 2.9–3.8 m).

The minerals calcite and dolomite from bedrock readily weather and account for the high alkalinity and concentrations of calcium and magnesium in surface and groundwater at Kampoosa Bog. The average airequilibrated pH of groundwater in the floating peat mat of the open fen is 8.26 ± 0.58 , and calcium and magnesium concentrations average 81 ± 28.3 mg/L and 14.1 ± 3.6 mg/L (n = 169). The chemistry is further altered by road salt from the Massachusetts Turnpike.

2.3. Salt application

The Massachusetts Turnpike is a four-lane, divided highway that crosses the Kampoosa Bog watershed for 2.74 km. The drainage system along the Massachusetts Turnpike where it crosses the Kampoosa watershed was designed in the 1950s, and it discharges directly into the wetland (McCullough, 2007). During the study, the Massachusetts Turnpike Authority (now Massachusetts Department of Transportation) used 100% rock salt (NaCl) as its primary deicing agent; occasionally it also applied a 2:1 rock salt to sand mix (McCullough, 2007). Other deicing agents, such as calcium chloride, were not used on the Turnpike during the time frame of this study (McCullough, 2007). Our chemical analysis of rock salt crystals collected adjacent to the Turnpike showed that the NaCl also contained trace amounts of calcium (0.4%) balanced by sulfate (0.4%) and lesser amounts of potassium (0.1%).

The Mass. Turnpike Authority (MTA) trucks were calibrated to apply ~100 kg of rock salt per lane mile with the number of applications varying with storm event. Between November 2003–March 2007, the MTA applied a total of 1630.1 metric tons of rock salt to the stretch of highway that crosses Kampoosa Bog. Between 263.7–633.5 metric tons were applied each winter season (Table 1, McCullough, 2007). The amount of road salt applied during a winter storm season correlates directly with the overall winter severity (MassDOT, 2012).

3. Methods

3.1. Watershed classifications

The 470 ha watershed, which drains to Kampoosa Brook just before it crosses Rt. 7 at a point given the name KB-100, is outlined in Fig. 1. We divide the watershed into three catchments (Table 2). The Marsh Brook catchment (defined by point MB-100) represents a relatively

Table 1

Rock salt applied to the Massachusetts Turnpike within the Kampoosa Bog watershed between mile markers 6.4 to 8.3, corresponding to a road length of 3.1 km (McCullough, 2007).

Winter storm season	Rock salt applied (metric tons)	Number of storms
12 Nov 2003–21 Mar 2004	416.1	33
12 Nov 2004–28 Mar 2005	633.5	37
25 Oct 2005–4 Apr 2006	316.8	31
5 Dec 2006-19 Mar 2007	263.7	26
Total	1630.1	127
Mean	407.5 (±163.4)	31.8 (± 4.6)

undisturbed, upstream area unaffected by the application of salt to the Massachusetts Turnpike, and, therefore, serves as a reference catchment for background chemistry. It represents 17% (82 ha) of the total watershed area. The KB-150 catchment (166 ha, 35% area) defines the eastern portion of the watershed that does not drain through the open fen of Kampoosa Bog. It receives runoff from both the Turnpike and Rt. 7 that drains to an unnamed tributary, which joins Kampoosa Brook just upstream of KB-100. The third catchment, "Southwest Region," refers to the portion of watershed that drains to KB-100 but is not contained in either the MB-100 or KB-150 catchments. It encompasses 222 ha (47%) of the total watershed area (Table 2). This portion of the KB-100 watershed includes the open pond and fen, and it also receives runoff from the Massachusetts Turnpike. The locations of KB-100 and KB-150 were chosen based on the presence of culverts beneath Rt. 7 that channelized streamflow and facilitated discharge measurements and event sampling.

3.2. Geochemistry sampling

Surface and groundwater samples were collected from 9 sites from 2004-2007 (Fig. 1). Marsh Brook was sampled upstream of the Massachusetts Turnpike at a relatively undisturbed location (MB-100), which served as the reference site for background chemistry. The locations of groundwater sampling sites within the open fen (Sites A-E) were selected to monitor geochemistry along a southern transect extending down gradient from the Turnpike. Sites A-E were co-located with several well site locations from the Richburg (1999) investigation. At each site in the open fen, groundwaters were sampled from nested wells at approximately 1 m, 2 m and 4.5 m depths. Wells were constructed from 2-inch PVC pipe with a one-foot screen at the base of the well, and groundwater was sampled using a 1 m-long bailer after purging the well and rinsing the collection bottles three times with the sample. Water on the surface of the floating peat mat was sampled at each well location in the open fen. Kampoosa Brook was sampled at the culvert where it exits the wetland and flows beneath Rt. 7 (site KB-100) and periodically where it flowed through the pond in the open fen (site P). The unnamed tributary was sampled at the culvert where it flows beneath Rt. 7 (site KB-150). All samples were collected in 500 ml acid-washed polyethylene bottles after rinsing the bottle three times with the sample water. Snow and precipitation samples were also collected periodically at different locations around the study area for geochemical analysis during the study period. To capture fluctuations in stream water chemistry during hydrologic events, ISCO autosamplers were programmed to collect 1 L volumes of water at either 1 or 2 hour intervals for three

Table 2Areas of the Kampoosa Bog watershed and subcatchments.

Watershed	Area (ha)	Area (% of total)
MB-100	82	17.4
KB-150	166	35.4
Southwest region	222	47.2
KB-100	470	100.0

snowmelt events and one large rain storm. All water samples were transported in a cooler to Smith College and stored in refrigerators until ready for analysis for major ion chemistry.

3.3. Field and laboratory measurements

Specific conductance, dissolved oxygen, and water temperature of surface and groundwaters were measured in the field at each site using Yellow Springs Instrument field meters (YSI 95 and YSI 30). Collected samples were analyzed at the Center for Aqueous Biogeochemical Research at Smith College for air-equilibrated pH, specific conductance, acid neutralizing capacity (ANC), major cation (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anion concentrations (Cl⁻, NO_3^- , SO_4^{2-}), dissolved organic carbon (DOC), and dissolved silica. ANC, pH, specific conductance and dissolved silica were measured on unfiltered samples. ANC was determined by the inflection point method by burette titration with 0.02 N HCl; after January 2007, ANC was measured by a Man-Tech autotitrator with Titra-Flow pH electrode. Dissolved silica concentrations were determined by colorimetry using a Bauch and Lomb Spectronic 21 spectrometer. All other analyses were performed on samples vacuum filtered through a 0.45 µm Millipore membrane. DOC was measured using a Shimadzu 5000A Total Carbon Analyzer after acidifying samples with 100 μ L of 2 M HCl and purging CO_{2(g)} from the sample. Cation concentrations of acidified splits and anion concentrations of unacidified splits were determined by ion chromatography using a Dionex 500DX ion chromatograph. Instruments were standardized to solutions of known concentrations. Samples having high concentration $(>\!25~mg/L)$ of $Ca^{2+},$ Na^+ and Cl^- were reanalyzed after a 10:1 dilution. For each sample, charge imbalances were calculated in equivalents as $(\Sigma cations - \Sigma anions) / (\Sigma cations + \Sigma anions) * 100\%$. Samples having imbalances greater than \pm 5% were reanalyzed and assessed for cause of imbalance. For ground and surface waters samples, the average charge imbalance is -1.4% ($\pm 4.2\%$); 30% of all analyses have charge imbalances $>\pm$ 5%; 9% of analyses have charge imbalances $>\pm$ 7%. In most cases, charge imbalances were due to presence of organic acids, identified through DOC measurements, that are not included in the charge imbalance calculations. In total, 707 samples were collected and analyzed.

3.4. Gage stations and hydrology

Water level (stage, staff), specific conductance, water temperature, and precipitation were recorded at 10 min intervals by gage stations outfitted with Campbell Scientific data loggers (Model CR10X-2M) at three locations: the inlet stream to the fen (MB-100), the outlet stream (KB-100), and also within the fen (Site A). Discharge at MB-100, KB-100 and at KB-150 was determined by measuring the geometry of the channel and water velocity at many points across the stream. For the 2005 snowmelt event, discharge results were correlated with stage readings to produce a continuous hydrograph; however changes in stream morphology accompanied by periodic flooding within Kampoosa Bog make this stage-discharge relationship invalid for other events.

3.5. Cation exchange capacity

On 14 November 2004, shallow peat samples from the open fen were collected from the upper 20 cm near sites A–D, and at five additional sites within the surrounding calcareous seepage swamp (Fig. 1), to identify (1) spatial variability in the cation exchange capacity of peat within the plant root zone, and (2) whether the cation exchange capacity varied with groundwater chemistry. At the time of peat sampling, shallow groundwater (1 m depth) was collected from a screened, PVC well at each peat sample site location. All peat and soil samples were air-dried, weighed, and then soaked and shook overnight in a 1 N NH₄Cl solution. Filtered extracts were analyzed for exchangeable base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) by atomic adsorption spectrometry, and lanthanum chloride was added to samples analyzed for Ca^{2+} and Mg²⁺ to eliminate matrix effects. Concentrations of exchangeable acid cations (H⁺ and Al³⁺) were not measured because preliminary acidic cation exchange analyses from Kampoosa Bog showed consistently 100% base saturation. Therefore, the total cation exchange capacity (CEC_e) for Kampoosa Bog is defined as the sum of base cations. Exchangeable base cation concentrations are normalized by the dry sample weight and reported in units of moles of charge per mass of peat (cmol_c kg⁻¹_{peat}). When calculating the selectivity coefficient for different cation exchange reactions (Section 4.1), cation exchange capacity is reported in molar units (CEC_m = cmol kg⁻¹_{peat}).

4. Theory

4.1. Determining selectivity coefficients for cation exchange reactions from field data at Kampoosa Bog

Adsorption of sodium onto cation exchange sites of peat at Kampoosa Bog will reduce the concentration of sodium in water, and the abundance of Ca^{2+} and Mg^{2+} in groundwater suggests potential exchange between Na^+ and these divalent cations. The equation below (Eq. (1)) illustrates a heterovalent, binary reaction following the Vanselow convention (Vanselow, 1932; Stoessell, 1998), where Na^+ competes with Mg^{2+} for exchange sites on the peat.

$$2Na^{+} + Ex_2Mg \leftrightarrow Mg^{2+} + Ex_2Na_2 \tag{1}$$

For this reaction, Ex_2 denotes a divalent negative surface site on the solid exchanger phase (e.g. peat), although exchange sites on solids are likely to be monovalent (Langmuir, 1997); Na⁺ and Mg²⁺ represent species in solution.

Assuming ideal solution behavior, the Vanselow exchange selectivity coefficient (K_v) describes the equilibrium behavior of Eq. (1) with the following mass law equation:

$$K_{v} = \frac{\left[Mg^{2+}\right](M_{Na})}{\left[Na^{+}\right]^{2}(M_{Mg})} \tag{2}$$

where [] represent the activities of Na^+ and Mg^{2+} in solution and M_{Na} and M_{Mg} in parentheses represent the mole fractions of Na^+ and Mg^{2+} on the exchanger phase.

A number of researchers have determined values for K_v for heterovalent binary exchange reactions by conducting controlled laboratory experiments (e.g. Ogwada and Sparks, 1986; Evangelou and Marsi, 2003; Kopittke et al., 2006). For our field data, however, multiple cations potentially compete for exchange sites, and groundwater samples may only approximate the actual pore water chemistry in contact with peat surfaces. Therefore, we apply the Langmuir-power exchange function (Eq. (3)) based on the Vanselow convention to calculate the selectivity coefficient based on our field observations.

$$K_{Na \to Mg} = \frac{\left[Mg^{2+}\right]}{\left[Na^{+}\right]^{2}} \left(\frac{(M_{Na})}{(M_{Mg})}\right)^{n}$$
(3)

 M_{Na} and M_{Mg} are mole fractions of exchangeable Na⁺ and Mg²⁺ normalized by the total cation exchange capacity (CEC_m) of the sample, as shown by Eqs. (4)–(6).

$$M_{Na} = \frac{ExNa}{CEC_m}$$
(4)

$$M_{Ca} = \frac{Ex_2 Mg}{CEC_m}$$
(5)

$$CEC_m = Ex_2Ca + Ex_2Mg + ExNa + ExK$$
(6)

ExNa and Ex₂Mg represent the moles of exchangeable Na⁺ and Mg²⁺, and CEC_m represents the molar sum of all exchangeable cations, measured per mass of peat (units = cmol kg⁻¹ of peat). The exchangeable cations comprising Eq. (6) are the dominant cations present in the alkaline environment at Kampoosa Bog.

In the Langmuir-power exchange function, the exponent (n) is determined from empirical data and accounts for non-ideal behavior $(n \neq 1)$ due to electrostatic imbalances possibly caused by exchange of other cations not represented by the binary reaction (Langmuir, 1997) and/or by empty exchange sites on the solid (Stoessell, 1998).

Taking the logs of the power exchange function (Eq. (3)) and transposing gives

$$\log\left(\frac{\left\lfloor Mg^{2+}\right\rfloor}{\left\lfloor Na^{+}\right\rfloor^{2}}\right) = \log K_{Na \to Mg} + n \log\left(\frac{M_{Mg}}{M_{Na}}\right)$$
(7)

Based on Eq. (7), a linear regression of the logs of solution activity and mole fractions of exchangeable cations on the solid will have a slope of *n*. The intercept will determine log $K_{Na \rightarrow Mg}$.

5. Results and discussion

5.1. Spatial variability of water chemistry

The geochemistry results for surface and groundwater show that road-salt runoff has greatly altered the geochemistry of Kampoosa Bog, particularly compared to the upstream reference site on Marsh Brook (Table 3). In Marsh Brook (MB-100), calcium is the dominant cation, followed by magnesium, sodium, and potassium $(Ca^{2+}>> Mg^{2+} > Na^{+} > K^{+})$. In Marsh Brook, the anions that contribute to acid neutralizing capacity (HCO₃⁻ and CO₃²⁻) are greatest, followed by sulfate, chloride, and nitrate (ANC \gg SO₄²⁻ > Cl⁻ > NO₃⁻). These results are consistent with mineral weathering, particularly by carbonate minerals, being the dominant reactions that control water chemistry. Runoff from an abutting dirt road adds a minor amount of Na⁺ and Cl⁻ (means = 5.3 and 9.7 mg L⁻¹, respectively).

Downstream of the Massachusetts Turnpike, however, the relative abundance of major ions changes, where $Na^+ > Ca^{2+} > Mg^{2+} \gg K^+$ and $Cl^- > ANC \gg SO_4^{2-} > NO_3^-$. In the shallow groundwater of the open fen (~ 1 m depth), the sum of major ions is approximately $\sim 5-7$ times more concentrated than at MB-100 due to increases of dissolved salts. Mean Na⁺ and Cl⁻ concentrations in shallow fen groundwater range from 35.5–141.1 mg L^{-1} (Na⁺) and 66.3–252.7 mg L^{-1} (Cl⁻), and concentrations of these ions overall are higher closer to the Turnpike and decrease with increasing distance from the Turnpike. Fig. 2 illustrates this spatial difference for Cl⁻ over ~5.5 years of the study. These observations are consistent with the sodium-chloride dispersion pattern previously mapped for Kampoosa Bog (Richburg et al., 2001), which showed elevated concentrations of Na⁺ and Cl⁻ more than 600 m from the Turnpike. Mean concentrations of Na⁺ and Cl⁻ of Kampoosa Brook in the pond (Na⁺ = 36.5, Cl^- = 66.6 mg L^{-1}) and at KB-100 (Na⁺ = 59.0, Cl⁻ = 114.6 mg L⁻¹) are lower than fen groundwater, and they are ~3 times greater at KB-100 than at MB-100. Average Na^+ and Cl^- concentrations are also high at KB-150 $(Na^+ = 118.2; Cl^- = 216 \text{ mg } L^{-1})$, showing that the unnamed stream also receives substantial road-salt contamination. A Piper plot of mean concentration values from each location shows how the relative proportions of major ions vary spatially and contrast with the reference site, MB-100 (Fig. 3). Supplementary Tables 1 and 2 show mean concentration values for all sample sites.

Groundwater samples from the nested wells in the open fen show that sodium and chloride concentrations decrease with depth, whereas calcium increases with depth and magnesium remains relatively constant (Fig. 4). Differences in concentration with depth are most pronounced between the shallowest and deepest wells. These results

Mean geochemistry of upstream to dow	results for streams and surveyed and surveyed surveyed and surveyed surveyed surveyed stream. Units are mg L	challow fen gro -1, except for	oundwater (1 m) . Nur - pH, ANC (µeq L ⁻¹) a	nber of samples is 1 nd SC (μ S cm ⁻¹). S	listed in () adja See Supplement	cent to site name, tary Tables 1 and	and standard c 2 for mean che	leviations are liste mistry results for	d in () adjacer all sample site	nt to mean value 35.	s. Stream and fe	n groundwater sar	ples listed in order
Site (n)	Dates	ЬН	ANC	Ca ²⁺	Mg^{2+}	Na^+	K^+	Cl ⁻	SO_4^2 -	NO_3^-	$SiO_{2(aq)}$	DOC	SC
MB-100 (46)	7/17/02-8/2/07	8.3 (0.3)	2307.6 (351.1)	34.2 (6.7)	8.9 (1.5)	5.3(1.5)	1.3 (0.5)	9.7 (2.9)	5.9 (2.6)	0.2(0.1)	5.8 (2.5)	5.0 (3.6)	253.6 (71.7)
Pond (11)	7/12/04-6/27/06	8.5(0.1)	3200.9(425.6)	47.5 (5.7)	13.8 (2.6)	36.5 (3.7)	1.3 (0.5)	66.6(10.5)	4.2 (2.9)	1.0(3.1)	6.9(1.7)	7.7 (3.0)	500.8(132.0)
KB-150 (40)	11/14/04-8/2/07	8.2(0.4)	3311.1 (743.0)	64.5(12.1)	15.9(4.3)	118.1 (33.3)	3.6 (0.9)	216.2 (72.3)	9.1 (3.5)	1.5(1.1)	6.3 (3.4)	5.0(1.6)	891.0 (342.2)
KB-100 (356)	2/15/02-8/2/07	8.4(0.2)	2890.0(648)	44.3(10.9)	13.6 (3.4)	59.0(16.9)	2.3 (0.6)	114.6 (36.6)	6.7 (2.3)	0.8(1.8)	5.3 (1.7)	6.0(2.5)	630.0(165.7)
E Well 1 (5)	7/19/06-4/8/07	7.9 (0.8)	5525.3(62.4)	113.7 (2.3)	21.3 (0.7)	141.1 (7.4)	3.8 (1.1)	252.7 (9.5)	5.1(1.4)	8.0 (17.9)	8.3 (1.4)	15.7 (n = 1)	1020.5(197.5)
B Well 1 ^a (29)	9/21/02-4/8/07	8.2 (0.7)	4745.2 (984.7)	88.7 (20.3)	17.7 (4.7)	144.1 (27.5)	6.5 (2.0)	272.7 (61.1)	7.2 (4.4)	0.4(0.8)	10.0(3.7)	12.0(3.3)	1241.1(319.5)
A Well 1 (30)	6/4/02-4/8/07	8.2 (0.6)	3407.9 (322.4)	65.4(10.1)	13.8 (3.2)	93.8 (17.5)	3.0 (0.7)	184.2(41.1)	5.4 (3.3)	0.2 (0.3)	7.0 (2.2)	8.7 (1.9)	851.8 (209.7)
C Well 1 (20)	6/4/02-7/31/07	8.2 (0.6)	3064.5 (325.9)	58.4 (7.2)	11.9 (1.8)	79.6 (9.8)	2.8 (0.6)	160.9(29.9)	5.2 (2.9)	0.1 (0.1)	6.9(3.0)	9.0(1.5)	773.8 (167.4)
D Well 1 (10)	7/24/04-7/31/07	8.3 (0.5)	3070.0 (313.3)	48.5 (7.6)	11.4 (2.1)	35.5 (4.7)	1.6(0.3)	66.3 (13.7)	2.2 (1.2)	0.1 (0.1)	7.9 (4.1)	9.3 (1.6)	452.1 (83.8)

Mean values for Site B Well 1 exclude 16 event samples collected between 22–24 March 2007 that were not collected contemporaneously at other well locations

Table 3 Mean ge



Fig. 2. Chloride concentrations of shallow groundwater (~1 m) in the open fen (Sites A–D) over time. Legend shows the linear distance between the groundwater sample sites and the Turnpike. Overall, dissolved salt concentrations are less with greater distance from the Turnpike.

suggest that road-salt contamination is greatest within the upper 2 m of the peat profile and that groundwater contamination is largely a nearsurface phenomenon. Concentrations of calcium and magnesium, which are expected to be elevated in groundwater based on the regional bedrock composition, likely are less concentrated closer to the surface because of dilution by precipitation. Even so, samples collected from the surface of the open fen showed high concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- , particularly compared to MB-100. These results show that water on the peat surface is hydrologically connected to shallow groundwater in the fen. The mean concentrations for surface water are less than the mean shallow groundwater samples, however, consistent with dilution by precipitation.

5.2. The sodium-chloride imbalance and cation exchange reactions

As expected for a rock salt source of chloride, Na⁺ is strongly correlated with Cl⁻ (p < 0.0001; R² = 0.96). More surprisingly, Mg²⁺ also is significantly correlated with Cl⁻ (p = 0.002; R² = 0.46), and no significant correlation occurs with Ca²⁺ (Fig. 5 top). The composition of rock salt (NaCl) applied to the Massachusetts Turnpike predicts a 1:1 molar ratio between sodium and chloride in aqueous samples. However, all samples located downstream of the turnpike show a strong molar imbalance, where Cl⁻ concentrations exceed Na⁺ concentrations (Fig. 5 top). The imbalance is ~20% at the outlet (at KB-100). The range of the imbalance is greater (between 15–55%) for fen groundwater samples, with Na–Cl imbalances increasing with depth (Fig. 5 bottom). Even though both sodium and chloride concentrations decrease with depth, sodium decreases more, creating a larger imbalance.

Observations of Na:Cl molar imbalances suggest that sodium is being adsorbed onto negatively charged exchange sites in peat and other organic-rich sediments of the fen (Sun et al., 2012). The molar ratio deviates more strongly from 1 as the salt pollution moves down through the peat profile and additional sodium is adsorbed onto the peat. The strong correlation between Mg^{2+} and Cl^- , and an absence of $MgCl_2$ in



Fig. 3. Piper diagram of mean concentrations for shallow groundwater (~1 m) samples collected from the open fen (Sites A–E) and stream sample sites (MB-100, KB-150, and KB-100). Legend shows linear distance between groundwater sample sites and the Turnpike. Na⁺ and Cl⁻ concentrations constitute a high percentage (>40%) of the overall chemistry of fen groundwater, with proportionally more Ca²⁺, Mg²⁺, and HCO₃⁻ + CO₃⁻ at the location (Site D) most distant from the Turnpike. MB-100, upstream of the Turnpike and fen, illustrates regional water chemistry consistent with weathering of regional bedrock; an abutting dirt road adds a relatively minor amount of NaCl. KB-150 samples a stream south of the fen that receives road-salt runoff from the Turnpike and Rt. 7. KB-100 receives input from MB-100, the fen, and KB-150.



Fig. 4. Variations in major ion chemistry in fen groundwater at Kampoosa Bog. In general, concentrations of sodium and chloride decrease with depth, whereas calcium increases with depth. The 2 m-depth at Site B was only sampled during fall and summer periods; dilute conditions during snowmelt are not represented by its mean concentration, creating a relatively higher mean value.

the rock salt (Fig. 5 top), suggests that Na^+ exchanges with Mg^{2+} and that this reaction is favored at higher dissolved salt concentrations, which is explored through cation exchange capacity (CEC_e) measurements on peat.

At Kampoosa Bog, CEC_e values range from 49.8 to 76.0 cmol_c kg⁻¹_{peat} (mean = 63.2 ± 9.8 cmol_c kg⁻¹_{peat}; n = 9). Ca²⁺ is the dominant exchangeable cation (mean = 74% of CEC_e) followed by Mg²⁺ (19%), Na⁺ (6%) and K⁺ (1%; Table 4). Exchangeable Na⁺, normalized by CEC_e (E_{Na(CECe)}), shows a positive correlation with the activity of sodium [Na⁺] in groundwater (R² = 0.74, p-value = 0.003; Fig. 6). Exchangeable Mg²⁺ (E_{Mg(CECe)}) is negatively correlated with the activity of sodium [Na⁺] in groundwater, but the linear regression is not as strong (R² = 0.45; p-value = 0.047). Exchangeable calcium and potassium do not show any correlation with sodium in groundwater. These results suggest that Na⁺ is adsorbed onto peat surfaces at the expense of Mg²⁺, and the amount of sodium on exchange sites is dependent on the activity of sodium in solution. The weaker regression between [Na⁺] and $E_{Mg(CECe)}$ may be due to multiple cation exchange reactions occurring simultaneously. An evaluation of selectivity coefficients provides insight to the important cation exchange reactions happening at Kampoosa Bog.

5.3. Calculation of selectivity coefficients

Using Eq. (7), we determined selectivity coefficients (K) by linear regression using our cation exchange and groundwater data (Tables 4–5) for four cation exchange reactions: $Na \rightarrow Mg$, $Na \rightarrow Ca$, $Ca \rightarrow Mg$ and $Na \rightarrow K$ (Table 6). Activity of each ion was calculated using the extended Debye–Hückel Equation (c.f. Langmuir, 1997), with measured concentrations of ions and the ionic strength of the solutions. Activity was calculated at 9 °C (the average temperature of groundwater at time of sampling), and the ionic strength was determined from a full geochemical analysis of the groundwater. The linear regressions for all four reactions are significant (p < 0.05).

Fig. 5. Top: Plot of Cl vs. Ca, Mg, Na for mean concentrations of fen surface and groundwater (Sites A–D) and streams. Cl is most strongly correlated with Na; its slope is less than one, indicating a loss of Na to cation exchange sites. A significant positive correlation between Cl and Mg (p = 0.002) and no significant correlation with Ca (p = 0.12) suggests Na exchanges with Mg and that this reaction is favored at higher dissolved salt concentrations. Bottom: The Na:Cl imbalance in fen groundwater increases with depth within the peat profile, illustrating greater adsorption of Na⁺ to deeper peat and organic sediments.

The calculated exchange coefficient values (K) show that Na⁺ will preferentially exchange with Mg²⁺ over Ca²⁺ (Na \rightarrow Mg, K = 51.4 whereas Na \rightarrow Ca, K = 4.6). Likewise, the calculated selectivity coefficients show the exchange sites favor Ca²⁺ over Mg²⁺ (Ca \rightarrow Mg, K = 2.2). These results are consistent with the CEC_e data: Ca²⁺ is the dominant exchangeable calcium on peat does not vary with [Na⁺] in groundwater, whereas exchangeable magnesium is negatively correlated with [Na⁺]. The high selectivity coefficient value for the exchange reaction between sodium and magnesium reaction shows that Na⁺ is more likely to exchange with Mg²⁺ than with any of the other base cations.

Table 4

Concentrations and charge fractions of exchangeable cations on peat at Kampoosa Bog.

Exchai	ngeable	cation, o	cmol _c k	g ⁻¹ pe	eat	Charge fra	actions of e	xchangeabl	e cations
Site	Ca^{2+}	${\rm Mg}^{2+}$	Na^+	\mathbf{K}^+	CEC _e	E _{Ca(CECe)}	$E_{Mg(CECe)}$	$E_{Na(CECe)}$	E _{K(CECe)}
A	48.0	9.2	4.4	0.7	62.2	0.772	0.147	0.070	0.011
B	47.4	8.7	10.3	2.2	68.6	0.691	0.127	0.150	0.032
C	40.7	7.0	2.7	0.8	51.2	0.795	0.137	0.052	0.016
D	56.3	16.0	2.1	1.5	76.0	0.742	0.211	0.028	0.019
F	61.4	11.0	2.1	0.3	74.7	0.821	0.147	0.028	0.004
G	56.0	9.6	3.9	0.3	69.8	0.802	0.138	0.055	0.005
H	42.8	14.8	3.9	0.2	61.7	0.693	0.239	0.064	0.004
R	37.1	15.0	2.5	0.4	54.9	0.675	0.273	0.045	0.006
U	33.6	15.3	0.5	0.4	49.8	0.674	0.306	0.010	0.009
Mean	47.0	11.8	3.6	0.8	63.2	0.741	0.192	0.056	0.012
Stdev	9.4	3.4	2.8	0.7	9.8	0.059	0.068	0.040	0.009

For all the cation exchange models involving the divalent cations (Table 6), the slope of the regressions is greater than one (n = 1.2-2.3). Langmuir (1981, 1997) showed that if n = 1, then the value of the selectivity coefficient (K) does not depend on the ratio of exchangeable cations, and K represents an equilibrium constant. For the Kampoosa Bog data, the deviation of n from unity suggests disequilibrium conditions. In the case of the reaction Na \rightarrow Mg, the result n > 1 shows that the preference for Na⁺ on exchange sites increases when the ratio $E_{Mg(CEC)}$: $E_{Na(CEC)}$ is greater, which occurs when less Na⁺ occupies the total CEC. Therefore, localities that have less exchangeable sodium favor increased adsorption of sodium to peat. This may contribute, in part, to the higher Na:Cl imbalance measured in deeper groundwater wells within the wetland where dissolved salt concentrations are generally lower.

The Kampoosa Bog data show that Na⁺ adsorption is possible in alkaline environments when road-salt pollution is significant. Typically for uncontaminated calcareous soils, sodium is least likely to adsorb onto cation exchange sites because of its monovalent charge and large

Fig. 6. Variation in exchangeable cation charge fraction ($E_{cation(CECe)}$) with activity of dissolved sodium in shallow groundwater. $E_{Na(CECe)}$ is positively correlated with [Na⁺] (p = 0.003), and $E_{Mg(CECe)}$ is negatively correlated (p = 0.047). There is no correlation between [Na⁺] and $E_{Ca(CECe)}$ and $E_{K(CECe)}$.

Table 5

Measured concentrations and calculated ionic strengths and activities of ions ir	n shallow groundwater s	sampled proxima	l to peat samples
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		Concentra	tion, μ mol L $^{-1}$				Activity coe	fficient (γ) at 9 °C	C	
Site	рН	Ca ²⁺	Mg^{2+}	Na ⁺	K ⁺	lonic strength ^a	Ca ²⁺	Mg^{2+}	Na ⁺	K ⁺
А	8.55	1504	202	4982	58	0.0097	0.6858	0.6991	0.9051	0.9025
В	8.66	2738	851	6315	158	0.0175	0.6185	0.6378	0.8790	0.8747
С	8.47	1542	462	2976	59	0.0090	0.6935	0.7062	0.9080	0.9055
D	8.53	1395	606	1397	43	0.0072	0.7165	0.7274	0.9162	0.9142
F	8.46	2158	905	2179	64	0.0121	0.6611	0.6765	0.8959	0.8927
G	8.56	2090	818	4125	92	0.0135	0.6484	0.6649	0.8910	0.8875
Н	8.53	2123	1786	4666	77	0.0171	0.6211	0.6402	0.8801	0.8759
R	8.25	1392	1131	1533	28	0.0089	0.6947	0.7073	0.9084	0.9059
U	8.54	1249	990	217	13	0.0067	0.7233	0.7338	0.9186	0.9167

^a Ionic strength calculated from full chemical analysis of water sample.

hydrated radius (Green and Cresser, 2008). The divalent cations (Ca²⁺ and Mg^{2+}) are energetically favored on exchange sites over Na⁺. Even at Alton Bog, where the base saturation of peat averaged 35%, Ca^{2+} dominated the exchangeable base cations, and Na⁺ occupied only 2% of the CEC (Pugh et al., 1996). Therefore, we might predict the retention capacity of sodium at Kampoosa Bog to be similarly low because of its calcareous geochemistry and 100% base saturation. In fact Na⁺ occupies on average 6% of the CEC at Kampoosa Bog and percent Na⁺ is as high as 15% in the most contaminated areas (Table 4); these values are classified as sodic to strongly sodic for agricultural soils (as reported by Kopittke et al., 2006). This degree of exchange results from the high concentrations of sodium from road-salt pollution that drive sodium onto peat exchange sites. The selectivity coefficients at Kampoosa Bog show a relative adsorption strength of $Na^+ > Ca^{2+} > Mg^{2+}$, and $K^+ > Na^+$. In the calcareous setting of Kampoosa Bog, neither K^+ nor H^+ are abundant in groundwater. Na⁺ preferentially exchanges with Mg²⁺, creating the observed molar imbalance with Cl⁻.

These CEC results contrast with interpretations in other watersheds that attribute Na:Cl imbalances in stream water to exchange between Na^+ and Ca^{2+} , in addition to Mg^{2+} . For example, Ostendorf et al. (2009) showed that groundwater contaminated by Na⁺ derived from a road-salt storage facility stripped divalent cations from minerals in underlying glacial till prior to discharge to a nearby stream. Shanley (1994) interpreted Na⁺ exchange with Ca²⁺ and Mg²⁺ based on ion mass balance calculations applied to geochemistry data from a watershed receiving highway runoff; he attributed cation exchange with Na⁺ as causing a 44% increase in Ca²⁺ and Mg²⁺ concentration downstream of salting activities. Perhaps concentrated soil pore waters drove Na⁺ exchange with both Ca²⁺ and Mg²⁺ in that setting. High concentrations of Na⁺ (~7900 mg/L; 344 mM) in soil pore water have been measured in a road-salt contaminated organic horizon of an acidic podzol (Green et al., 2008), and in this case, Na⁺ occupied 85% of the soil CEC due to exchange with H⁺. Saturated soils in peatlands, however, will have much lower sodium concentrations in pore water than vadose zone soils contaminated by road salt, thereby reducing the potential for Na-adsorption when Ca²⁺ is present. Although several investigations have focused on Na⁺ exchange with Ca²⁺ and Mg²⁺ on clay mineral surfaces to understand salinization mechanisms within irrigated, agricultural soils (Amrhein and Suarez, 1991; Kopittke et al., 2006), further soil science research is needed to comprehend the thresholds by which Na⁺ will exchange with Ca^{2+} and Mg^{2+} on organic material from a variety of settings so that the conditions by which saltcontaminated watersheds will retain and release Na^{+\} is better understood. Determining selectivity coefficient values for competing cation exchange reactions with sodium will help calibrate groundwater transport models of salt-contaminated systems and quantify the fate of individual cations over time (Ostendorf et al., 2009).

5.4. Geochemical response to hydrologic events

At Kampoosa Bog, road-salt pollution in groundwater has the potential to move quickly through the wetland during hydrologic events. Although hydraulic head variations were not measured, we expect that groundwater flows laterally through peat from northeast to southwest and discharges to the open pond and Kampoosa Brook. Reeve et al. (2000) showed that groundwater flow through large peatlands is predominantly horizontal when the hydraulic conductivity of peat is several orders of magnitude greater than the underlying mineral soil. Field hydraulic head data collected by Duval and Waddington (2012) also showed predominate horizontal groundwater flow in calcareous fens in southern Ontario. Localized areas of vertical flow caused by recharge and discharge can exist within fens and can reverse flow direction due to small fluctuations in hydraulic head (Drexler et al., 1999) caused by weather variations (Duval and Waddington, 2012), although permeability of vertical flow paths is typically 1-2 orders of magnitude lower than permeability in the horizontal flow direction (Chason and Siegel, 1986).

At Kampoosa Bog, variations in topography within the wetland complex, such as relatively elevated regions of forested areas within the calcareous swamp on the fen's northern margin, could promote localized upward flow of groundwater to the peat, analogous to what has been modeled for bog hummocks by Reeve et al. (2000). Overall, the high hydraulic conductivity within the upper 2 m of the fen suggests that Kampoosa Bog should respond quickly to hydrologic events. Snowmelt and large rain events should be times of significant salt transport through the wetland complex.

To characterize salt export from the wetland during hydrologic events, we conducted detailed sampling of Kampoosa Brook at the outlet point (KB-100) during snowmelt 2004 and snowmelt 2005 (Figs. 7–8). We also sampled the outlet in detail during a smaller, late winter snowmelt event in 2007 (Fig. 8), which was coordinated with collection of water from the unnamed, eastern tributary (KB-150) and fen groundwater (Site B). Additionally, we sampled a 6.1 cm rain event in September 2004 (Fig. 9). Sampling occurred for many days over the duration of

Table 6

Selectivity coefficients at 9 °C for possible cation exchange reactions. Slope, R² values and p-values describe the linear regressions used to determine K (Eq. (7)).

Reaction	Selectivity coefficient (K)	Slope (n)	R ²	p-Value	Comment
$2Na^+ + Ex_2Mg \leftrightarrow Mg^{2+} + Ex_2Na_2$	51.40	2.2	0.87	0.0002	K > 1; Reaction favors Na on peat.
$2Na^+ + Ex_2Ca \leftrightarrow Ca^{2+} + Ex_2Na_2$	4.57	2.3	0.78	0.002	K > 1; Reaction favors Na on peat.
$Ca^+ + Ex_2Mg \leftrightarrow Mg^{2+} + Ex_2Ca$	2.24	1.2	0.61	0.01	K > 1; Reaction favors Ca on peat.
$Na^+ + ExK \leftrightarrow K^+ + ExNa$	0.04	0.4	0.61	0.01	K < 1; Reaction favors K on peat.

Fig. 7. Hydrologic and geochemical responses of Kampoosa Bog to Snowmelt in 2004 (left column) and 2005 (right column). Top row shows changes in water level at KB-100 (outlet) and in the fen due to melt (indicated by rising temperature) and precipitation. Middle and bottom rows show effects on geochemistry, including first flush pulse of a Na⁺ and Cl⁻ prior to water level rise that is asynchronous with changes in Ca²⁺, Mg²⁺, and ANC. Na⁺ and Cl⁻ show a strong molar imbalance. Following peak stage, Na⁺, Cl⁻, Ca²⁺, Mg²⁺, and ANC increase, which signals a rise in the contribution of salt-contaminated baseflow to stream discharge. See text for discussion of SO²₄ - and NO⁻₃ data.

Fig. 8. Temperature and geochemical response during a late-season snowmelt event in 2007 for fen groundwater, KB-150, and KB-100. Top panel shows periods of groundwater upwelling and mixing with snowmelt water, as illustrated by pulses of warmer water temperatures (groundwater) superimposed over an overall decline in groundwater temperature caused by snow water (measured at Site A, 1 m depth). Samples of fen groundwater at Site B (1 m) captured a reversed molar imbalance where Na⁺ > Cl⁻. This change in Na:Cl imbalance is attributed to release of Na⁺ from cation exchange sites during more dilute conditions of the wetland prior to melting. As the melt proceeded, upward vertical flow mixes with deeper groundwater, as indicated by the groundwater pulses, rise in Ca²⁺ and ANC, and equalization of the Na:Cl ratio. The first-flush response of first-flush response at KB-100. KB-100 shows the integrated geochemical response of the wetland and KB-150 stream.

Fig. 9. Changes in water level, specific conductance, and ion chemistry during three tropical storm events in September 2004 (events numbered in top and middle panels). All three events show immediate dilution of specific conductance and lack a first-flush response. Lower panel: Detailed sampling during event 3 shows synchronous dilution for Na⁺, Cl⁻, and Ca²⁺, although Ca²⁺ is diluted less. Mg²⁺ concentrations remain constant over the event.

these events at either one or two hour intervals. The differences in chemistry between shallow and deep groundwater in the fen, where Na⁺ and Cl⁻ concentrations are more concentrated closer to the surface and Ca²⁺, Mg²⁺ and ANC are more concentrated at depth, provide insights on the timing of export of dissolved salts from fen groundwater to KB-100.

5.4.1. Observations of salt pulses during snowmelt and rain events

Event sampling at the wetland outlet stream (KB-100) during the 2004 and 2005 snowmelts revealed similar geochemical responses (Fig. 7). Both of these events captured the bulk of the snowpack that accumulated over the prior winter months. Based on snow depth measurements recorded in Lenox Dale, MA, located 7.3 km northeast of Kampoosa Bog (42.34N, 73.25W, elevation 306 m, Station ID Coop 194131), the snowpack was ~2.5 times greater in 2005 than in 2004 (2004 snow depth = 12.7 cm and 2005 snow depth = 30.5 cm atLenox Dale, NRCC, 2015). In 2007, we sampled melting of a spring snowstorm (snow depth = 38.1 cm at Lenox Dale, NRCC, 2015) that occurred after almost complete melting of a prior snowpack (where snow depth \approx 25.4 cm). Therefore, our sampling of the 2007 snowmelt captured a shorter melt period under more dilute conditions due to prior snowpack melting. Event sampling during the last of three, successive tropical storms during September 2004, where rainfall totaled 20.2 cm, shows the geochemical response to significant rainfall outside of the season when road salt is applied to roads. Details regarding pulses

of Na⁺ and Cl⁻ concentrations, signaling input of dissolved salts to the watershed during all three of these snowmelt events, are described below.

5.4.1.1. Geochemical response to snowmelt 2004. In 2004, five successive days of daytime air temperatures exceeding 0 °C (days 57-61) coincided with an overall rising trend in Na⁺ and Cl⁻ concentrations while stream stage and fen groundwater levels also began to rise. On day 61.5, stream and fen stage began to rise more sharply and Na⁺ and Cl⁻ concentrations peaked on day 62.5, directly after which Na⁺ and Cl⁻ concentrations became rapidly diluted. Prior to dilution between days 57.5-62.5, Na⁺ and Cl⁻ concentrations increased by ~700 and 1000 $\mu mol \ L^{-1}$, respectively. Air temperature remained above 0 $^\circ C$ through day 64, during which time stream stage continued to rise and a second pulse of elevated Na⁺ and Cl⁻ concentrations (an increase of ~250 μ mol L⁻¹) occurred a few hours in advance of a peak stage on day 64. In contrast, Ca²⁺ and Mg²⁺ remained at constant levels until day 62.5 before becoming diluted through day 64; unlike Na⁺ and Cl⁻, Ca²⁺ and Mg²⁺ did not show a concentration pulse during this timeframe. The behavior of ANC contrasted further during these initial stages of snowmelt. As Na⁺ and Cl⁻ concentrations began to rise, ANC decreased by approx. 1000 μ eq L⁻¹ on day 59.5 and dropped again by another 500–1000 μ eg L⁻¹ on day 62.5 when Na⁺, Cl⁻, Ca²⁺, and Mg²⁺ were simultaneously diluted through day 64. The declines in ANC mark inputs of acidic meltwater that mixed with alkaline baseflow.

Between days 64–66 of 2004, stream and fen stage declined while Na⁺, Cl⁻, Ca²⁺, Mg²⁺, and ANC levels rose simultaneously, signaling an increasing proportion of salt-contaminated baseflow as the stream water level dropped. Between days 66–67, above-freezing temperatures coincided with 1.7 cm of rain, during which time Na⁺, Cl⁻, Ca²⁺, and Mg²⁺ were simultaneously diluted while stream and fen water levels reached a second, higher peak stage on day 67.5. After day 68, the snowpack had fully melted.

5.4.1.2. Geochemical response to snowmelt 2005. In 2005, we documented early, episodic melting of the snowpack over a 21-day period (days 66–87), during which time day and night air temperatures fluctuated above and below 0 °C (Fig. 7). The bulk and remainder of the snowpack melted during a 4.95 cm rain event that coincided with above-freezing temperatures between days 87–96. Specific conductance (SC) recorded at the outlet by the data logger was most sensitive to Cl[–], and continuous monitoring of SC enabled inference of dissolved salt concentrations when water samples were not collected.

During the period of episodic snowmelt between days 66-78, concentrations of Na⁺ and Cl⁻ increased by ~1100 and 2800 μ mol L⁻¹, respectively, whereas Ca²⁺ and Mg²⁺ concentrations remained relatively uniform. Beginning on day 74, daytime air temperatures consistently exceeded 0 °C. At this time, stream and fen stage began to rise slightly, coinciding with an increase in Na⁺, Cl⁻, and SC that peaked on day 78. Following day 78, concentrations of Na⁺, Cl⁻, Ca²⁺, Mg²⁺, and SC declined as snow continued to melt. Between days 84-87, daytime and nighttime air temperatures cycled between above and below freezing temperatures, producing a cyclical rise and fall in stream stage due to cyclical input of snowmelt. Concentrations of Na⁺, Cl⁻, Ca^{2+} , Mg^{2+} , and SC all increased at this time due to higher relative input of baseflow during nighttime, below-freezing conditions that approached -8 °C. Following day 87, combined melting of the snowpack and heavy rain contributed more predominately to streamflow and diluted ion concentrations. Peak streamflow represented a combination of melt and rain water with an equivalent depth of 13.2 cm (4.95 cm was from rain). A disruption in water sampling occurred prior to peak streamflow, due to an unfortunate flooding of the autosampler; however the SC signal recorded by the data logger on day 87 showed a brief rise by ~100 μ S cm⁻¹, suggesting a release of dissolved salts prior to melting of the bulk snowpack, similar in timing to the Na⁺ and Cl⁻ pulse observed during snowmelt 2004. Similar to snowmelt 2004, concentrations of Na⁺, Cl⁻, Ca²⁺, and Mg²⁺ increase following peak stage as the stream returns to baseflow conditions.

5.4.1.3. Geochemical response of watershed to snowmelt 2007. With the goal of capturing the relative timing of initial salt pulses within different regions of the Kampoosa Bog watershed, we measured the geochemistry of the eastern tributary (KB-150), of fen groundwater (Site B at 1 m depth), and at the watershed outlet (KB-100) during a late-season snowmelt event in 2007. Sampling of the 2007 snowmelt occurred after a spring snowstorm that fell during the previous week and after almost complete melting of a prior snow pack that accumulated over the winter months. At all three sites, concentrations of Na⁺ and Cl⁻ began to increase at the same time, which coincided with the onset of the rise in stream stage. However, the behavior of the salt pulses differed at each site. The eastern tributary showed the fastest response with highest concentrations (max $Cl^- = 7900 \ \mu mol \ L^{-1}$ and max $Na^+ = 7000 \mu mol L^{-1}$; and the peak in Na^+ and Cl^- concentration at KB-150 occurred ~9.5 h prior to the peak at KB-100 (Fig. 8). In contrast, the groundwater response in the fen initially showed a slow rise followed by a sharp peak in Na⁺ and Cl⁻ concentrations that occurred ~4 h after the peak at KB-100. The range in Na⁺ and Cl⁻ concentrations in fen groundwater was about one half the magnitude of what was observed at KB-150.

Kampoosa Brook at KB-100 shows an integrated geochemical response of the entire watershed. Its salt pulse is broad, having the longest duration of the three sites, and concentrations of Na⁺ and Cl⁻ are similar to fen groundwater. For both KB-100 and fen groundwater, concentrations of Na⁺ and Cl⁻ at the end of the pulse were greater than at the onset of snowmelt, whereas Na⁺ and Cl⁻ concentrations at KB-150 were less after the pulse than before the event. These differences illustrate the slower flow and greater retention of dissolved salts by the wetland relative to the faster flow and mobilization of Na⁺ and Cl⁻ in the eastern tributary. The short distance (600 m) between KB-150 and KB-100 and an estimated average stream velocity (~0.15- 0.3 m sec^{-1}) of the eastern tributary at KB-150 during the rising limb of the hydrograph predicts a 0.5-1 hour travel time between the two sites. Therefore, the high concentrations of Na⁺ and Cl⁻ measured in the eastern tributary are largely diluted by discharge from the fen, and the behavior of the salt pulses observed at KB-100 better reflects the geochemical response of the wetland. Different regions within the fen, such as the areas adjacent to the open pond and channel, may thaw and mobilize salt more quickly than what was observed at Site B, explaining the earlier arrival and broader salt pulse at KB-100 than at Site B. The higher concentrations of both Na⁺ and Cl⁻ measured at the end of the sampling interval in fen groundwater may also result from the addition of road-salt pollution to the wetland during snowmelt.

5.4.1.4. Geochemical response to tropical storms, September 2004. Unlike the snowmelt events, three tropical storm events in September 2004, which totaled 20.2 cm and occurred over a 20-day period, showed dilution in specific conductance at the onset of a rise in stage (Fig. 9). As illustrated by detailed sampling during the third event (precipitation = 6.1 cm; highlighted in the bottom graph of Fig. 9), an early pulse of dissolved salts did not occur at the onset of precipitation (day 272.0); Na⁺ and Cl⁻ concentrations are diluted synchronously with Ca²⁺ and Mg²⁺. However, an increase in Na^+ and Cl^- concentrations by 400 and 600 μ mol L⁻¹ between day 272.7–273.0 (about 17 h into the rain event) suggest flushing of dissolved salts by precipitation as stream stage continued to rise. Ca²⁺ also increased slightly during this period, although the magnitude of change for calcium is much lower, suggesting that the dissolved salts were derived from fen groundwater. Mg^{2+} showed very little change in concentration as stream stage rose. Flooding downstream of KB-100 caused stage to remain elevated for 16 days following the event, obscuring the timing of peak flow. Notably,

specific conductance at KB-100 following these three rain events remained suppressed after day 290 until road salt application resumed during the subsequent winter, indicating that these successive tropical storm events flushed significant dissolved salts from the watershed.

5.4.2. Interpretations of salt export during hydrologic events

These observations (Figs. 7–8) suggest that the onset of snowmelt events creates a first flush of dissolved salts derived from both the snowpack and shallow groundwater. The imbalance between Na⁺ and Cl⁻ suggests that these initial salt pulses are not derived from surface runoff carrying excess rock salt from roads proximal to the sampling site. In that case, the molar ratio between Na⁺ and Cl⁻ would be closer to unity. Rather, the Na–Cl molar imbalance results from Na⁺ adsorption by cation exchange (Sun et al., 2012), which shows that these salt pulses include salt-contaminated water that flowed through peat and soils. However, the lack of similar behavior by Ca²⁺, Mg²⁺, and ANC indicates that the flow path of water during this initial stage of salt export is shallow, perhaps derived from the base of the snowpack, and it does not include significant contributions from deep ground water or base flow. Indeed, the observation of the initial pulse prior the dramatic rise in stage occurs when streamflow is still low.

Through mass balance calculations of geochemistry data of a roadside snowpack, Buttle and Labadia (1999) showed that the snowpack releases sodium and chloride to its adjacent environment throughout the salt application season, not just during spring snowmelt. Snow infused with salt will melt episodically prior to the bulk of the pack due to the ability of salt to depress melting temperature of ice. This not only can create the observed first flushes of Na⁺ and Cl⁻ at the onset of spring melt (Buttle and Labadia, 1999), but it can add Na⁺ and Cl⁻ to unfrozen soil earlier in the season, enabling Na⁺ adsorption to organic material that is reflected by the sodium-chloride molar imbalances. In fact, the Na-Cl imbalance increases as Na⁺ and Cl⁻ concentrations rise (the difference Cl-Na changes from ~750 to 1000 µmol/L in 2004 and from ~1000 to 1500 µmol/L in 2005), which suggests that cation exchange reactions slow the mobilization of Na⁺ relative to Cl⁻. For all events, Mg^{2+} is not diluted as much as Ca²⁺, which is consistent with Mg^{2+} being added to groundwater from cation exchange sites.

Rain from the 2004 September event mobilized dissolved salts from groundwater, as illustrated by the synchronous pulse of Ca^{2+} (and also ANC, not shown) with Na⁺ and Cl⁻. A first flush of sodium and chloride was not captured due to absence of a snowpack, but sustained rain released dissolved salts from groundwater 17 h into the event. Similarly, Ostendorf (2013) documented the strongest first flushes of Na⁺ and Cl⁻ during winter but minimal first-flush responses from summer storms.

The second pulse of Na⁺ and Cl⁻ observed at peak stage at KB-100 on day 64 during snowmelt 2004 may be derived, in part, from dissolved salts washed in by the melting snowpack. Not only does the rapid rise in stage signal the timing of significant input of snowmelt water, but NO_3^- concentrations show an inverse response to Ca^{2+} , ANC, and SO_4^{2-} – ions characteristic of baseflow. For both snowmelt 2004 and 2005, NO₃⁻ concentrations increased from ~50 μ mol L⁻¹ to ~100 μ mol L⁻¹ during the rising limb of the hydrograph. NO₃⁻ is expected in snow, particularly in the northeastern U.S. where air pollution from fossil fuel combustion is significant. Sulfate should be present in snow too, but its snowmelt signal is masked by the relatively high concentration of SO_4^{2-} in baseflow in Kampoosa Bog. Its presence in groundwater is likely derived from mineral weathering of pyrite present in bedrock. Mean SO_4^{2-} concentrations in shallow groundwater range from 5-9 mg/L, and the response of sulfate during snowmelt mirrors other ions present in groundwater. In contrast, NO₃⁻ occurs in low concentrations in fen groundwater (mean = 0.8 mg L^{-1} or 12.9 μ mol L⁻¹), so NO₃⁻ derived from snowmelt dominates the signal. During snowmelt 2004, the second pulse of Na⁺ and Cl⁻ on day 64 coincides with the rise in NO_3^- . Therefore, salt in surface melt water may be added to KB-100 at peak flow; a decrease in the Na–Cl imbalance at this time supports this conclusion.

5.4.3. Cation exchange reaction reverses direction

Cation exchange is a reversible reaction (Sun et al., 2012), and the 2007 snowmelt sampling captured an episode when sodium was released from cation exchange sites. Surprisingly, the shallow groundwater chemistry of the fen at Site B (Fig. 8) showed concentrations of Na⁺ that were *higher* than Cl⁻ *before* the snowmelt event began. This imbalance is opposite to what has been observed during almost all other measurements of ground and stream water; we measured another exception during the 2004 September rain event when concentrations of Na⁺ also exceeded Cl⁻ at KB-100, but only for approximately 6 h (Fig. 9).

Additionally, the SC of shallow groundwater, monitored at Site A, showed fen geochemistry to have less dissolved salt after a 21.2 cm rain event occurred in October 2005, as demonstrated by a drop in SC by ~750 μ S cm⁻¹ due to the rain. SC values increased after the rain event but remained suppressed relative to pre-event measurements for over 400 days (See Section 5.7 and R5 noted in Fig. 13). Overall, groundwater conditions in the fen in spring 2007 were more dilute than other sample periods of this study (Table 7). Therefore, lower sodium concentrations in the upper part of the peat profile enabled a reversal of the cation exchange reaction between Na^+ and Mg^{2+} (Eq. (1)), causing Na⁺ to be released from peat back to groundwater and shifting the balance to excess Na⁺. As the groundwater level in the fen rose and sodium and chloride concentrations increased, the Na-Cl imbalance diminished and the Na:Cl ratio approached one. Additionally, concentrations of calcium and ANC in the fen at Site B increased, rather than becoming diluted. These observations suggest that the snowmelt caused deeper groundwater – which has higher concentrations of Ca^{2+} , higher ANC, and proportionally less Na^+ than Cl^- – to rise toward the surface and mix with shallow groundwater. Mixing of the two waters increased the concentrations of Ca²⁺ and ANC and lowered the Na:Cl ratio from 1.2 at the beginning of the event to 1.04 at the end. A similar Na:Cl ratio (1.05) in shallow groundwater was observed at Site B fifteen days after the snowmelt event, and it is unknown how long it may have persisted. These results suggest the mixing of near-surface water with upwelling groundwater that had acquired desorbed Na⁺ from the peat. These geochemical observations are also consistent with fen groundwater temperature data that show pulses of warmer groundwater from depth superimposed on an overall decline in temperature caused by infiltration of snow water (Fig. 8).

The dilute conditions during the 2007 snowmelt favor release of Na⁺ from peat across the shallow regions of the fen, although the observation of higher Na⁺ than Cl⁻ in shallow groundwater of the fen appears localized to Site B (Table 7). Shallow groundwater sampled at Sites A and E, two other locations where salt contamination is high, did not show excess Na⁺ relative to Cl⁻. Additionally, Cl⁻ consistently exceeded Na⁺ at KB-100 during the 2007 snowmelt, suggesting that desorption of Na⁺ is not a robust signal on a watershed scale, although variations in the Na:Cl molar ratio at KB-100 over time indicate that adsorption and desorption affect the amount of Na⁺ released from the fen. In fact, shallow groundwater at Sites A and E did show relatively high Na:Cl ratios (0.87-0.91 and 0.82-0.88, respectively) during the 2007 snowmelt, particularly compared Na:Cl ratios in shallow groundwater at Sites A and B averaged over the study period (0.79 and 0.83, respectively) and compared to deeper ground water at Sites A, B and E (Na:Cl ranges from 0.63-0.8 in deeper wells). Furthermore, Ca:Mg ratios in shallow groundwater at Site B are higher than average in 2007, likely due to adsorption of Mg^{2+} to peat when Na^+ is released (Table 7).

Fluctuations in shallow groundwater chemistry could have important effects on vegetation, particularly if they occur during the growing season. For example, McLaughlin and Webster (2010) showed that dry summer conditions in an intermediate fen located in northern Ontario generated acidity (H⁺) due to sulfur oxidation, and that peat cation

Table 7

Na:Cl molar ratios, Ca:Mg molar ratios, ion concentrations, and acid neutralizing capacity for fen groundwater during Snowmelt 2007, as follows: 3/21/07 = pre-event, 3/24/07 = event end; 4/8/07 = post event. Average values for the study (2004–2007) at Sites A and B are shown for comparison (n = sample size) to illustrate the dilute conditions in the shallow wells prior to the 2007 snowmelt. Mean values at Site E are not shown because of the lower sampling frequency at this location (n = 5) and results are weighted toward the 2007 snowmelt values. Well depths (in meters) are listed in parentheses below the well name. Ion concentrations and ANC are reported in μ mol L⁻¹ and μ eq L⁻¹, respectively.

	Date	2007 event timing	Site A		Site B		Site E	
			Well 1 (1.0 m)	Well 3 (3.9 m)	Well 1 (1.0 m)	Well 3 (3.8 m)	Well 1 (1.2 m)	Well 2 (2.9 m)
Na:Cl	3/21/2007	Pre	0.87	0.77	1.20	0.78	0.86	0.63
	3/24/2007	End	0.88	0.78	1.04	0.80	0.88	0.67
	4/8/2007	Post	0.91	0.76	1.05	0.79	0.82	0.69
Average N	a:Cl 2004-2007 ((n)	0.79 (26)	0.74 (18)	0.83 (27)	0.71 (16)		
Ca:Mg	3/21/2007	Pre	3.5	3.8	4.3	4.7	3.2	4.4
	3/24/2007	End	3.5	3.9	3.9	4.6	3.2	3.6
	4/8/2007	Post	3.4	3.8	3.7	4.7	3.2	4.0
Average C	a:Mg 2004–2007		2.9	3.4	3.1	4.5		
Na ⁺	3/21/2007	Pre	3442.8	3147.4	3477.2	3587.6	5914.3	2629.4
	3/24/2007	End	3415.4	3112.2	4006.9	3544.1	6129.2	2853.8
	4/8/2007	Post	3469.8	3040.4	4012.2	3494.6	5736.4	3159.6
Average N	a ⁺ 2004–2007		4035.1	3016.0	6381.0	3386.1		
Cl ⁻	3/21/2007	Pre	3969.3	4078.7	2886.1	4593.6	6849.4	4183.4
	3/24/2007	End	3871.4	3990.7	3835.6	4434.7	6971.3	4250.0
	4/8/2007	Post	3804.6	4014.7	3833.9	4431.1	6992.7	4588.5
Average C	l ⁻ 2004–2007		5092.9	4064.9	7731.4	4751.3		
Ca ²⁺	3/21/2007	Pre	1727.5	2615.5	928.6	3792.4	2897.2	3378.7
	3/24/2007	End	1630.2	2656.2	1220.3	3693.4	2845.1	2845.1
	4/8/2007	Post	1622.3	2545.4	1203.8	3506.5	2881.5	3181.4
Average C	a2 ⁺ 2004–2007		1590.7	2177.0	2206.8	3277.6		
Mg ²⁺	3/21/2007	Pre	488.7	683.3	217.2	812.4	896.7	775.4
	3/24/2007	End	470.2	689.0	316.3	803.0	898.8	790.6
	4/8/2007	Post	476.8	666.4	321.7	753.2	893.5	792.3
Average N	1g2 ⁺ 2004–2007		552.8	636.9	718.2	734.7		
ANC	3/21/2007	Pre	3409.8	4867.6	2035.7	7246.0	5423.8	6054.6
	3/24/2007	End	3228.9	4912.8	2449.1	7210.9	5574.9	5958.0
	V4/8/2007	Post	3284.6	4934.6	2540.4	6934.4	5577.9	5776.8
Average A	NC 2004-2007		3392.1	4685.8	4678.6	6445.1		

exchange adsorbed the H⁺ by releasing base cations, which were later removed from the ecosystem by storm runoff. They postulated that continued dry conditions could sustain the increased acidity of the peat and promote vegetation succession from an intermediate to poor fen. Just as the strong supply of alkaline ground water at Kampoosa Bog strengthens the resilience of this ecosystem to potential acidification caused by climate and weather fluctuations (Duval and Waddington, 2012), the high alkalinity should limit the extent of sodification of the peat provided that sustained wet conditions induce Na⁺ desorption and net export.

To summarize the observations of geochemical responses of the Kampoosa Bog watershed to different hydrologic events, snowmelt causes an early mobilization of salt from shallow groundwater as stream stage begins to rise. Additionally, dilution of dissolved salts can be sustained following large precipitation events, such as was observed by the suppressed SC measurements following the three successive tropical storms during September 2004. The high permeability of the shallow regions of the fen permits changing chemical conditions through dilution, upwelling, and introduction of nonpoint source pollution. Adsorption and desorption of sodium to and from peat is dynamic, particularly for this rich calcareous fen where sustained input of alkaline groundwater potentially can reduce levels of peat sodification.

5.5. Flux of dissolved salts during snowmelt 2005

To understand if snowmelt is an important period of salt export, we calculated and characterized the flux of Na⁺ and Cl⁻ during the 2005 snowmelt event relative to the seasonal application of road salt to the Massachusetts Turnpike. We quantified the mass of salt exiting the fen during Snowmelt 2005 between 7 March–4 April 2005. Simultaneous measurements of water chemistry and discharge at the three tributaries within the watershed–Marsh Brook (at MB-100), Kampoosa Brook (at KB-100), and the eastern tributary (at KB-150)–determined the percent contribution that each subcatchment contributed to the flux of

ions exiting the wetland. We compared the flux values of Na⁺ and Cl⁻ against the flux of Ca²⁺ and Mg²⁺ to provide context with the dominant cations in groundwater derived from mineral weathering.

Flux values for each ion were calculated by multiplying the concentration in each sample by stream discharge (Eq. (8)):

$$F_i = C_i * Q \tag{8}$$

where $F_i =$ flux of the ion (mmol sec⁻¹), $C_i =$ concentration of the ion (mmol L⁻¹), and Q = stream discharge (L sec⁻¹).

The flux at KB-100 captures the total export of ions from the watershed, presuming a negligible loss to deep groundwater. MB-100 quantifies the ion flux upstream of the Massachusetts Turnpike, and KB-150 measures the ion flux from the eastern region of the watershed that is outside of the fen complex. The net ion flux from the southwest region, which includes the open fen, is determined by difference where,

$$F_{\text{Southwest}} = F_{\text{KB}-100} - F_{\text{KB}-150} - F_{\text{MB}-100}.$$
 (9)

Additionally, total mass of Na⁺, Cl⁻, Ca²⁺ and Mg²⁺ exported from the watershed during the entire snowmelt event was calculated by integrating flux values calculated at 10-minute intervals from 7 March–4 April 2005. We determined ion concentration values at 10 minute intervals by linearly interpolating between the hourly concentration measurements. These interpolated values were then multiplied by the 10 min discharge record and integrated to calculate the total ion flux.

The ion fluxes are largely controlled by stream discharge, and they are greatest at peak discharge (Fig. 10) despite dilution of ion concentrations (Fig. 7). The flux of calcium and magnesium ions derived from mineral weathering correlate well with the area of each subcatchment (Fig. 11). For example, 51% of the Ca and Mg flux is derived from the southwest region of the watershed, 40% is from KB-150, and 9% is from MB-100, and these values are consistent with the percent discharge that these regions contribute to KB-100. In contrast, the Na⁺

Fig. 10. Fluxes of chloride and calcium during Snowmelt 2005 at Sites MB-100, KB-150, and KB-100, shown relative to discharge at KB-100. Timing of peak ion fluxes from Kampoosa Bog are highly correlated with discharge. Approximately 42% and 54% of the Cl⁻ and Ca²⁺ flux, respectively, measured at KB-100 is derived from the southwest region of the Kampoosa watershed, which includes the fen.

and Cl⁻ fluxes measured for each subcatchment (MB-100 = 1%; Southwest Catchment = 41%; KB-150 = 58%) correlate not with basin area but with the total number of lane miles of the Massachusetts Turnpike and Rt. 7 that drain within each catchment. Thus, salt export scales with the salt application (as measured by lane miles) for each subcatchment (Fig. 11). A larger percentage of Na⁺ and Cl⁻ at KB-100 is derived from the KB-150 tributary because both the Massachusetts Turnpike and Rt. 7 pass through its drainage area.

Based on the integrated calculations, the total flux of Na⁺ and Cl⁻ leaving the watershed at KB-100 during the 2005 Snowmelt event are 35.4 and 70.8 metric tons, respectively. This corresponds to 13% of

Fig. 11. Comparison of ion fluxes during Snowmelt 2005 with area of catchments, stream discharge, and lane miles crossing each subcatchment. Discharge, Ca^{2+} , and Mg^{2+} correlate well with catchment area. In contrast, Na^+ and Cl^- are better correlated with the contributing number of lane miles in each subcatchment. The "Wetland" bar on the graph corresponds with the "Southwest Region" of the Kampoosa Bog watershed (Fig. 1).

Na⁺ and 17% of Cl⁻ from the 633.5 metric tons of rock salt (NaCl) applied to the Massachusetts Turnpike within the watershed during the 2004–2005 winter season (Table 8). The analyses for 2005 indicate that the period around snowmelt is a time of significant salt transport through Kampoosa Bog. Yet, it accounts for less than a fifth of the total amount of salt applied in 2004–2005. Additional hydrologic events are required to release Na⁺ and Cl⁻ in amounts equivalent to what is added over a winter season.

5.6. Estimate of annual flux of sodium and chloride

The flux calculations determined for the 2005 Snowmelt are made possible by the fine temporal resolution of the discharge and geochemical data for this period. While such high-resolution data do not exist for an entire year, estimates of annual geochemical fluxes through the watershed can be obtained through some extrapolations of measurements and historical data.

Data from the USGS gage station for a small (2.12 mi²) catchment approximately 6 km north of Kampoosa Bog (USGS gage 01197300, 42.350 N 73.2999 W, Lenox Dale, MA) and at a similar elevation (302 m) provide monthly values of streamflow, normalized by watershed area for the period 1963–1974. Taking these values to be representative of streamflow for the KB-100 watershed during the time of this study, one can determine estimates of monthly discharges at KB-100 by scaling by watershed area. These discharge values can be combined with geochemical data from samples collected throughout the year to estimate monthly fluxes of major ions at KB-100. Multiple samples within a given month are averaged to provide a characteristic concentration for the month in question (Table 8 and Fig. 12).

While this method allows the extension of field measurements, it has three limitations that should be considered when interpreting the results. First, it relies on a proxy watershed to estimate monthly stream discharge. Given the similarity of basin size, location, and outlet elevation of the two basins, however, one would expect the streamflow per watershed area to be similar. Second, some of the months are represented by very few geochemical samples (Table 8), and the mean concentrations have a high degree of uncertainty. Third, and most significantly, the method combines an average geochemical concentration determined from a few samples with a long-term monthly average discharge to determine an average monthly ion flux. Effectively, this is using the product of two averages (mean discharge and mean concentration) to estimate the average of a product (average flux), and this is only appropriate when the two data sets are independent. In the case of

Table 8

Total flux of major ions during snowmelt, 7 March 2005 through 4 April 2005. N/A = Not applicable.

Ion	Total flux (moles)	Total flux (metric tons)	Total flux (% applied to Turnpike)
Na ⁺	$\begin{array}{c} 1.5 \times 10^{6} \\ 1.7 \times 10^{6} \\ 5.2 \times 10^{5} \\ 2.9 \times 10^{5} \end{array}$	35.4	13
Cl ⁻		70.8	17
Ca ²⁺		24.5	N/A
Mg ²⁺		8.2	N/A

streamflow and concentration, however, we know that the two are negatively correlated — concentrations are diluted when discharge is high and vice versa. Thus, the results from the method described above are likely to overestimate the monthly ion flux.

Table 9 presents estimates of monthly discharge and sodium and chloride chemistry and fluxes for KB-100. From these results, it is clear that the months of March, April, and May are the primary months for salt export from the area, accounting for more than half of the annual salt flux. The significance of these months is due primarily to the high rates of discharge because the chemistry is relatively constant throughout the year. These data show that the estimated annual salt export (370 metric tons of chloride, equivalent to 610 metric tons of rock salt) is similar in magnitude to the annual salt application to the Massachusetts Turnpike in 2004–2005 (633.5 metric tons), and it is about 1.5 times greater than the average annual salt application from 2003–2007 (mean = 407.5 \pm 163.4 metric tons).

For additional insight, the monthly estimates of salt fluxes for March can also be compared to the more detailed analyses carried out for 2005 (Section 5.5). Detailed data from 7 March through 4 April 2005 indicate streamflow of 14.73 cm and salt fluxes of 35.4 metric tons for sodium and 70.8 metric tons for chloride. Combining the characteristic concentrations of 64.1 mg L⁻¹ for sodium and 126.4 mg L⁻¹ for chloride (Table 9) with the discharge of 14.73 cm gives a sodium flux of 44.5 metric tons and a chloride flux of 87.1 metric tons. These values are 25% and 23% greater than the fluxes determined from the detailed analysis. Despite the limitations of the method, the results from the monthly analysis indicate a substantial annual flux of salt through the system – an amount on par with or slightly greater than the annual application.

5.7. Longer-term dissolved salt trends at Kampoosa Bog

The annual mass balance calculations for 2005 suggest that outflow of dissolved salts equals or exceeds the annual application. Longer-term trends of dissolved salt at Kampoosa Bog show an overall decline in dissolved salts that occurs between 2002–2007, consistent with a net export (Fig. 13). At Site A, specific conductance (SC) of shallow ground water of the fen recorded by the data logger was monitored from 2002–2007 as a proxy for dissolved salt concentrations. Over this timeframe, SC trends downward from ~1200 to 750 μ S cm⁻¹. As a quality control check against the data logger, SC was measured periodically for grab samples; these results are consistent with the data logger readings, but they show a greater decline in SC, from 1200 to 500 μ S cm⁻¹. Agreement between SC measurements by the data logger and of grab samples diverges in 2006, due to a loss of sensitivity of the specific conductance probe connected to the data logger; the trend is similar, however.

As expected for a road salt proxy, the observed decline in SC correlates most strongly with a decline in Na⁺ and Cl⁻, and Ca²⁺ and Mg²⁺ concentrations also decline during this timeframe (Fig. 13). Uncertain is whether the downward trend is caused by a greater annual release of Na⁺ and Cl⁻ from the wetland, which should occur in years with higher than usual annual rainfall, whether the downward trend may represent less road salt added to the Massachusetts Turnpike during the time of monitoring relative to previous decades, or a combination of these effects. The role of large rain events is evaluated here.

Seasons of heavy rainfall and high stream flow are important in mobilizing salt-contaminated ground water from watersheds (Daley et al., 2009), and this is illustrated at Kampoosa Bog by the high monthly flux estimates for Na⁺ and Cl⁻ from March–May (Fig. 12). Although the 2005 analysis showed significant export of Na⁺ and Cl⁻ during snowmelt, large precipitation events that occur outside of winter months may be even more important in mobilizing salt-contaminated ground water from the fen. For example, declines in SC are greater following several large rain events than after the snowmelt events (Fig. 13). One noteworthy example occurred when 21.2 cm of rain fell between 7–9 October 2005. An ~800 μ S cm⁻¹ drop in specific conductance coincides with a rise in groundwater levels in the fen of more than 0.6 m.

Fig. 12. Estimate of monthly and annual salt flux from KB-100 calculated for Na⁺ and Cl⁻. The difference between the Na⁺ and Cl⁻ results estimates the amount of Na⁺ retained by the wetland. Streamflow data are from 1963–1974 for USGS gage 01197300, approximately 6 km north of Kampoosa Bog. Sodium and chloride fluxes recalculated by combining the streamflow estimates with characteristic monthly ion concentrations, determined from samples collected from 2002–2007 (Table 9).

Table 9

Estimates of characteristic monthly discharge, geochemistry, and ion fluxes for KB-100 based on average monthly discharge measured at Lenox Dale, MA and concentrations measured at KB-100 from 2004–2007.

Month	Q(cm)	Average Q	Number of Geo-chemical	Sodium, Na ⁺			Chloride, Cl ⁻		
		$(m^3 \text{ sec}^{-1})$	Samples	Mean concentration $(mg L^{-1})$	CV	Flux (metric tons)	Mean concentration $(mg L^{-1})$	CV	Flux (metric tons)
January	5.08	0.0906	0	50.8 ¹	-	12	96.7 ^a	-	24
February	5.08	0.0963	21	76.1	13%	18	148.7	5%	35
March	13.46	0.2351	195	64.1	28%	40	126.5	32%	80
April	16.00	0.2917	46	41.1	7%	31	82.5	5%	62
May	10.67	0.1869	2	66.1	0%	33	126.2	1%	63
June	5.33	0.0935	7	63.1	20%	15	115.4	28%	28
July	3.05	0.0538	4	50.1	15%	7	91.6	26%	13
August	2.08	0.0368	3	51.4	26%	5	85.9	15%	8
September	1.47	0.0255	65	53.7	12%	4	99.1	11%	7
October	1.50	0.0312	11	46.7	12%	4	85.1	14%	7
November	5.08	0.0935	1	57.2	-	14	137.9	-	35
December	7.11	0.1274	1	18.1	-	6	32.6	-	11
Annual	75.95	0.1133				189			373

^a The concentrations for January are estimated as the average of the monthly concentrations during the other non-snowmelt months (May-December).

Following this event, specific conductance values rise, presumably as the fraction of water added by precipitation exits the wetland and is replaced by salt-contaminated groundwater and as road salt is applied to the Turnpike during the 2005–2006 winter. However, SC values do not recover to pre-event values during the remainder of the monitoring period. These observations illustrate that large and high intensity precipitation events are effective with removing Na⁺ and Cl⁻ from the fen, and they upset what may have been prior equilibrium conditions between the fen and its dissolved salt concentrations that were established under more typical weather patterns.

In contrast, road salt is both added and exported from the fen during snowmelt events, resulting in a smaller drop in SC and presumably a lower net export of Na⁺ and Cl⁻ (Fig. 13). Even though the 2005 snowmelt exported from the fen ~13% of Na⁺ and Cl⁻ that was applied during the winter season (Section 5.5), the *net* export of Na⁺ and Cl⁻ from the fen is not equivalent because salt contamination also is added during the event. Rain events during non-winter months, on the other hand, are more important with contributing to a net decline of salt contamination in the wetland than snowmelt events. Even so, how the application of road salt to major highways is managed will still have significant control over the annual budget of dissolved salts entering and exiting the fen.

5.8. Management of road-salt application

The flux analysis of the Mar–Apr 2005 snowmelt shows that the amount of Na⁺ and Cl⁻ released at the outlet relates to the number of lane miles crossing the watershed (Fig. 11). This illustrates a direct relationship between the road-salt application amounts and dissolved salt concentrations in the fen. Other researchers investigating road salt impacts on streams (Rhodes et al., 2001; Kaushal et al.,

2005; Kelly et al., 2008; Daley et al., 2009) have shown significant correlations between chloride concentrations and percent impervious surfaces and lengths of roadways. Of these studies, Daley et al. (2009) measured the highest concentrations of Cl⁻ proportional to the area of roadways draining to New Hampshire streams because more severe winters in this region result in greater road salt usage. Roads that are over-salted exacerbate the problem. In their study of salinization of Mirror Lake at Hubbard Brook, NH, Likens and Buso (2010) showed surprisingly greater contributions of road salt from a residential road than from an interstate highway despite less traffic and fewer lanes. Altering salt management practices can create opportunities for reducing the impact of road salt runoff to wetlands and other environmentally sensitive regions is a first-order preventative measure.

In Massachusetts, economic pressures combined with attentiveness to protect potable water supplies and critical habitats has motivated the Department of Transportation (MassDOT) to monitor more closely its road-salt usage. To ensure transportation safety, the amount of road salt applied is directly related to the severity of winters, with more salt applied during harsher winters (MassDOT, 2012). Improvement in equipment technology, such as satellite tracking of plows coupled with road weather information sensors, has increased efficiency with which MassDOT applies road salt, resulting in less overall road-salt use. In recent years, MassDOT has supplemented NaCl with applications of liquid CaCl₂ and rock salt pre-wetted with CaCl₂, which lowers the freezing temperature of water and lessens the need for NaCl; use of CaCl₂ is limited to highways crossing potable water supplies (MassDOT, 2012). Additions of CaCl₂ via road runoff should alter the geochemistry of a calcareous fen, such as Kampoosa Bog, less than would NaCl additions. However, chloride from CaCl₂ will significantly

Table 10

Description of major hydrologic events identified by changes in specific conductance of shallow groundwater in the fen at Site A (1 m depth). Event labels refer to Fig. 13. Periods of rain coincided with all snowmelt events. * Indicates detailed sampling of event, this study.

Rain event	Date	Precipitation ^a (cm)	Snowmelt event	Date	Precipitation ^a (cm)	Snow depth ^b (cm)
R1	1-5 Aug 2003	6.6	S1	16-30 Mar 2003	5.6	33.0
R2	9 Sept 2003	3.6	S2*	1-11 Mar 2004	1.7	12.7
R3	26 May 2004,	4.8	S3*	7 Mar-7 Apr 2005	5.7	30.5
	1–2 Jun 2004					
R4*	9–30 Sept 2004	20.2	S4	8-14 Mar 2006	1.5	5.1
R5	7-9 Oct 2005	21.2	S5*	20 Mar-3 Apr 2007	3.2	38.1
R6	29 Sept 2006	2.1				

^a Sum of precipitation depths for date duration recorded at the Pittsfield Municipal Airport (42.43°N, 73.29°W, elevation 394 m, Station ID Coop 196414), which is located 19 km north of Kampoosa Bog.

^b Snow depth prior to melt event recorded at Lenox Dale, MA (42.34°N, 73.25°W, elevation 306 m, Station ID Coop 194131), which is located 7.3 km northeast of Kampoosa Bog (NRCC, 2015).

Fig. 13. Changes in air temperature (A), specific conductance (B), water level (C), and ion concentration (D) in shallow groundwater of fen at Site A (1 m depth) from 2002–2007. Periods of sizeable snowmelt (S) and rain (R) are shown in graph B and detailed in Table 10; a "*" denotes if event was sampled in detail. Graph B also shows cumulative road salt application rates to Massachusetts Turnpike from 2004–2007. Specific conductance (SC) shows larger declines during rain events than snowmelt events, illustrating that large rain events, such as R4 and R5, are important times of export of dissolved salts. Concentrations of major ions decrease significantly over time from 2002–2007 (p-values for regressions: Cl < 0.0001; Na < 0.001; Ca < 0.05; Mg < 0.001). Gaps in SC, staff, and temperature show periods when sensors malfunctioned.

change the geochemistry of wetlands such as ombrotrophic bogs and poor-intermediate fens that support vegetation adapted to lower nutrient conditions. As illustrated through the cation exchange results of this and other studies (Pugh et al., 1996; Green and Cresser, 2008; Green et al., 2008), the strong affinity of peat and organic soils to adsorb Ca^{2+} will displace limiting nutrients (NH_4^+, K^+) and raise soil pH. Unlike at Kampoosa Bog where alkaline conditions promote desorption of sodium from peat when the concentration of Na^+ in groundwater is reduced, desorption of anthropogenic Ca^{2+} from acidic organic soils is less favored and soil geochemistry may be more permanently altered by $CaCl_2$, which could alter plant community assemblages.

6. Conclusion

Even though road salt is applied to highways only during winter seasons, elevated concentrations of sodium and chloride in watersheds persist year-round. Wetlands contribute to long-term increases of dissolved salt concentrations in watersheds because they are areas of accumulation and retention of road salt contamination due to low hydraulic gradients and high cation exchange capacity of saturated soils. At Kampoosa Bog, retention and accumulation of road salt contamination from the Massachusetts Turnpike contributes to Cl⁻ concentrations in shallow groundwater of the open fen that approach and exceed levels of chronic toxicity (>230 mg L⁻¹) for aquatic organisms (USEPA, 1988). However, high hydraulic conductivity of peat within the upper 2 m of this calcareous fen enables lateral flow when water levels rise in response to hydrologic events. Overall, net export is greater for large rain events than for snowmelt events because road salt is also added to the wetland from melting snow.

The observed Na:Cl molar imbalances in water geochemistry result from adsorption of Na⁺ to cation exchange sites on peat. Calculated selectivity coefficients for different possible exchange reactions show that Na⁺ preferentially exchanges with Mg²⁺ when sodium adsorbs on peat. Although Na⁺ concentrations in shallow groundwater are high enough to drive Na⁺ onto exchange sites (mean = 6% of CEC and ranging from 1–15% depending on [Na⁺] in groundwater), the more dilute conditions during the last year of the study upset prior equilibrium conditions with groundwater concentrations, and they caused measureable desorption of Na⁺ in regions of the fen that contributed to export of sodium from the wetland complex. Ultimately, the export of Na⁺ and Cl⁻ within subcatchments of the watershed correlates with the length of crosscutting road lanes, showing that the flux of dissolved salts is directly related to the amount applied to roads. Release of Na⁺ and Cl⁻ is facilitated by the high flushing rates of the wetland complex during hydrologic events. Therefore, management strategies by highway departments that reduce road-salt usage will assist with reducing Na⁺ and Cl⁻ contamination to levels that may be less toxic to vegetation and aquatic organisms at Kampoosa Bog and for other alkaline wetlands elsewhere.

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.scitotenv.2015.12.060.

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