Peat porewaters have contrasting geochemical fingerprints for groundwater recharge and discharge due to matrix diffusion in a large, northern bog-fen complex

Zeno F. Levy, Department of Earth Sciences, Syracuse University, 204 Heroy Geology Laboratory, Syracuse, NY, 13244-1070, USA

Donald I. Siegel, Department of Earth Sciences, Syracuse University, 204 Heroy Geology Laboratory, Syracuse, NY, 13244-1070, USA

Paul H. Glaser, Department of Earth Sciences, University of Minnesota, Pillsbury Hall, Minneapolis, MN, 55455, USA

Scott D. Samson, Department of Earth Sciences, Syracuse University, 204 Heroy Geology Laboratory, Syracuse, NY, 13244-1070, USA

Soumitri S. Dasgupta, ARCADIS US Inc., 6041 Wallace Road Extension, Suite 300, Wexford, PA, 15090, USA

Corresponding Author: Z.F. Levy, Department of Earth Sciences, Syracuse University, 204 Heroy Geology Laboratory, Syracuse, NY, 13244-1070, USA, zflevy@syr.edu

Abstract

Although northern peatlands represent a globally significant reservoir for carbon, considerable uncertainty exists concerning solute transport systems within large ($>1000 \text{ km}^2$) peat deposits. We therefore delineated geochemical gradients linked to groundwater recharge and discharge along a 6 km transect within the 1200 km^2 Red Lake Peatland of northwestern Minnesota. We used ratios of Ca/Mg and $^{87}\text{Sr}/^{86}\text{Sr}$ to distinguish discharge of calcareous groundwater (~ 1.4 and 0.7155 , respectively) to the peatland from the mineral substratum along a topographic gradient from a bog crest downslope to an internal fen water track and bog islands. In contrast, the stable isotopes of the porewaters ($\delta^{18}\text{O}$ from -12.8 ‰ to -7.8 ‰) show that the active pore-spaces in these peat profiles has been flushed by recharge from the near-surface peat. We hypothesize that back-diffusion of groundwater-derived solutes from the peat matrix to active pore-spaces has allowed the geochemical signal from paleo-hydrogeologic discharge to persist into the current regime of dilute recharge. This effect has not been observed previously on the landform-scale and has important implications for carbon cycling in peatlands.

1.0 Introduction

Northern peatlands accumulate terrestrial carbon and develop where climatic and hydrogeological controls maintain perennially waterlogged soils (Glaser et al., 2006). The evocative spatial patterning of peat landforms and associated relationships among vegetation assemblages, surface water chemistry, and carbon dynamics have been the subject of intense scrutiny for over a century (Weber, 1902; Sjörs, 1950; Heinselman, 1963, 1970; Glaser and Janssens 1986; Chanton et al., 1995, 2008). The chemistry of porewater within the rooting zone in peatlands controls plant species composition and subsequent landform development (Glaser, 1992). Raised bogs with low surface water pH (< 4.2) maintain their saturation from meteoric water alone and develop where *Sphagnum* mosses dominate plant communities, raising the local water table above the influence of underlying mineral soils. Alternately, fens with higher surface water pH (5.0 – 6.0) derive alkalinity from mineral soil runoff or groundwater discharge, and thereby support more diverse communities of vascular plants (Siegel et al., 2006).

Peatlands store approximately one third of global soil carbon and contribute about 20% of annual atmospheric methane emissions (Gorham, 1991; Bridgham et al., 2013). Microbes generate methane in the anaerobic subsurface of peatlands by acetate fermentation or CO₂-reduction (Chasar et al., 2000; Corbett et al., 2015). Biogenic methane production is typically optimized at mid-range pH values (~6.0) (Ferry, 1993; Megonigal et al., 2003), but methanogenic bacteria in northern peatlands are also productive at lower pH ranging from 3.0 – 5.5 (Williams and Crawford, 1985; Kotsyurbenko et al., 2004; Bräuer et al., 2006). Microbial metabolism in peatlands also depends on the supply of labile carbon compounds to deeper, more recalcitrant peat. Isotopic studies show that 20 – 50 % of methane found at depth in northern

bogs and fens is metabolized from modern organic carbon transported down from the peatland surface by groundwater recharge (Chanton et al., 1995, 2008; Corbett et al., 2013).

The hydrogeological drivers in northern peatlands that control the supply of labile organic carbon to anaerobic peat strata (groundwater recharge) and the pH of the deep porewater (groundwater discharge) need to be better understood in order to forecast how subsurface methane production will be affected by climate change (McKenzie et al., 2009). Groundwater flow was long thought to be negligible beneath the zone of active water table fluctuations due to the low hydraulic conductivity (K from 10^{-4} to 10^{-7} cm s $^{-1}$) of the deeper, humified peat (Rycroft et al., 1975; Clymo, 1984). However, it is now generally accepted that peat is a heterogeneous “dual porosity” medium, where macropores and soil pipes transmit water at depth through hydrologically “active” pore-spaces within the comparatively “stagnant” peat matrix (Chason and Siegel, 1986; Hoag and Price, 1997; Holden, 2005).

Due to the complexity and heterogeneity of large peat basins at the pore-scale (mm to dm)—conceptual models of peatland hydrogeology have been developed at the landform-scale (km) to better understand the long-term ($10 - 10^3$ year) response of groundwater flow processes to changes in climate. Raised bogs develop water table mounds during wet periods that drive dilute recharge down through active pore-spaces by vertical advection (Glaser et al., 1997; Reeve et al., 2000). In contrast, fen water tracks located on the lower flanks of raised bogs are hypothesized to receive groundwater discharge from: (1) local flow systems originating beneath bog crests (Siegel, 1983), (2) convergence of local and regional flow systems (Siegel et al., 1995), or (3) transverse dispersion from lateral groundwater flow (Reeve et al., 2001a) (Figure 1).

The conceptual models above have been developed based on field hydrologic studies and numerical simulations during over 25 years of research in the Glacial Lake Agassiz Peatlands (GLAP) of northwestern Minnesota; a large expanse of patterned bogs and fens that have developed in a continental climate characterized by small annual moisture surplus and frequent droughts (Glaser et al., 2006). Since the severe regional droughts of the 1930's, precipitation rates have gradually increased in northwestern Minnesota, with decadal-scale dry/wet cycles transitioning into the wettest time period on record from 1991 to the present (<http://www.ncdc.noaa.gov/cag/>; Minnesota Climate Region 1). Vertical hydraulic gradient reversals from upwards flow during dry times to downwards flow during wet times occur in the GLAP on seasonal and multi-annual timescales across the GLAP (Romanowicz et al., 1993; Glaser et al., 1997; Reeve et al., 2013).

Geochemical analyses of peat porewater provide insights on groundwater recharge/discharge processes beyond the timescale of transient hydraulic head measurements. During the recent period of wet climate (1991 to present), Levy et al. (2014) used stable isotopes of peat porewater ($\delta^{18}\text{O}$, $\delta^2\text{H}$) to trace landscape-wide advection of shallow recharge down to the basal peat in a regional survey of *both* bogs and fens in the GLAP. Here, we present the results of a concurrent hydrogeochemical investigation of a 120 km² bog-fen complex in the Red Lake Peatland, located within the southwestern portion of the GLAP. Theoretically, the advection of shallow recharge through the peat column should lower the pH and mineral solute content of the deeper porewaters (Siegel et al., 1995, 2006); and drive the path of peatland development to become a single, large expanse of ombrogenous bog. The purpose of this study was to elucidate how the ecological diversity (controlled by pH) of a large bog-fen complex could be maintained during a period of deep recharge across the region. We therefore compared conservative tracers

for both discharge of calcareous groundwater (Ca, Mg, $^{87}\text{Sr}/^{86}\text{Sr}$) and dilute recharge ($\delta^{18}\text{O}$, $\delta^2\text{H}$) within the pore waters of the Red Lake Peatland to determine how the current period of wet climate has influenced vertical and horizontal geochemical gradients at the scale of peat landforms.

2.0 Study Area

The Glacial Lake Agassiz Peatlands (GLAP) cover 56% of Beltrami Arm of the Lake Agassiz region, a 7,600 km² area located between 48°3' and 48°35' N lat. and 95°3' and 95°40' W. long.; bordered to the south by moraines and till plains and to the north by the bedrock of the Precambrian Canadian Shield (Wright, 1972; Glaser, 1992). The mineral substrate beneath the GLAP is a complex and heterogeneous product of multiple glaciations, which deposited 30 – 40 m of calcareous glacial till over metabasalt and schist bedrock of the Quetico and Wawa sub-provinces of the Canadian Shield (Hogan et al., 2000; Glaser et al., 2006). During late Wisconsin time, the proglacial Lake Agassiz inundated the area and left a drape of lacustrine silt and clay over the landscape (characterized by K values of $\sim 10^{-5} \text{ cm s}^{-1}$), as well as discontinuous beach ridges of sand and gravel (with K values of $\sim 10^{-3} \text{ cm s}^{-1}$) in the northwestern and southern parts of the GLAP (Reeve et al., 2001b). The surface of the glacial lakebed slopes gently to the north at $\sim 1 \text{ m km}^{-1}$. Carbonates are present in the till but are highly leached beneath peat deposits up to depths of 0.75 m (Heinselman, 1963; p. 342). Groundwater flow modeling suggests that the glacial sediments beneath the GLAP transmit a regional groundwater flow system recharging at the Itasca Moraine to the south and discharging to the Rapid River to the north (Reeve et al., 2001b).

Northwestern Minnesota has a humid, continental climate that supports a winter snowpack and a warm season precipitation maximum (Glaser et al., 1997). A continuous snowpack of 0.4 – 0.8 m typically persists for over 5 months each year, with underlying soils freezing from 0.15 – 0.50 m below the land surface (Heinselman, 1970). The GLAP drains to the the Rapid River in the north, with annual precipitation roughly balancing runoff (~14%) and evapotranspiration (~86%) (Rivers et al., 1998; Reeve et al., 2001b). Average annual precipitation in northwestern Minnesota from 1885 to 2012 was 558 mm, with intermittent regional dry periods recurring on seasonal to multi-decadal timescales. Since the last major regional droughts of the 1930's, when annual precipitation fell below 457 mm, there has been a gradual shift to moister climate conditions. The years from 1991 to 2012 have been the wettest period on record; with 15 years where precipitation exceeded 660 mm (<http://www.ncdc.noaa.gov/cag/>; Minnesota Climate Region 1).

The Red Lake Peatland is a smaller subsection of the GLAP and is uninterrupted by streams or mineral uplands, making it one of the largest continuous peatlands in the conterminous United States (Glaser et al., 1981). This study focuses on the Red Lake II watershed (RLII in Glaser et al., 1981), which is dominated by an approximately 120 km² raised bog that is dissected by internally occurring fen water tracks that are hydrologically isolated from surrounding mineral uplands (Figure 2). Peat began to form at this site ~4000 years ago in the area of the presently forested bog crest (a local north-south drainage divide), following a shift in climate to cooler and moister conditions. Peat spread northward by paludification, which was followed by the establishment of a *Sphagnum* carpet over an initial sedge-meadow assemblage (Gorham and Janssens, 1992; Janssens et al., 1992). Around 2000 years ago, bog expansion stopped and a portion of the *Sphagnum* lawn in the northern part of the watershed changed into a

sedge (*Carex spp.*) dominated fen water track. The shift from bog to fen vegetation limited the accumulation of peat in that area; differentiating downgradient *Sphagnum* lawn into ovoid-shaped bog islands (Glaser et al., 1981; Glaser, 1987).

3.0 Methods

Neutralization of organic acids in peatland porewaters occurs primarily by mixing with dissolved alkalinity from upland surface runoff or groundwater discharge from the mineral substratum (Siegel et al., 2006). Our study area is hydrologically isolated from runoff draining from mineral upland soils and serves as an ideal location to examine the effects of groundwater discharge on the geochemistry of peat porewaters. We examine alkaline earth metals (Ca, Mg, Sr) as a proxy for groundwater-derived alkalinity, as these elements constitute semi-conservative tracers of carbonate mineral weathering products from the underlying glacial sediments.

We sampled profiles of peat porewater from the water table to the underlying mineral substratum at six different locations in the Red Lake II watershed. The study transect originated at the forested crest ("Bog Crest") of the Red Lake II watershed and extended downslope along the northern bog flanks in the direction of the regional water table gradient (Reeve et al., 2001b). The downslope sequence of sites along the northern bog flank includes: (1) sites on the non-forested *Sphagnum* lawn ("Upper [bog] Lawn" and "Lower [poor-fen] Lawn"), (2) a single site in a fen water track ("Fen Water Track"), which diverges around (3) ovoid-shaped bog islands containing the "Ovoid West" and "Ovoid East" sites. The approximate length of the entire transect is 5.5 km (from A to A' in Figure 2) and 6.0 km (from A to A'' in Figure 2), with an elevation difference between Bog Crest and Fen Water Track sites of about 1 m (Glaser et al.,

2004). The Red Lake Peatland slopes to the north at low relief ($\sim 0.2 \text{ m km}^{-1}$) from the Bog Crest to Troy Creek, into which the entire Red Lake II watershed drains. Individual landform elevations are transient due to the rise and fall of the peat surface (cm-scale oscillations) in response to subsurface methane accumulation and ebullition (Glaser et al., 2004; Reeve et al., 2013). At the time of sampling, the water table was approximately 0.25 m below the peat surface at the Bog Crest, nearly level with the peat surface at the lawn sites, and 0.30 m above the peat surface at the Fen Water Track. At the downslope end of the transect the water table was about 0.25 m below the surface of the ovoid island sites.

From August 10th – 12th, 2010, we collected vertical profiles of peat porewater at each of the study sites (August 10th: Upper Lawn, Lower Lawn; August 11th: Ovoid East, Ovoid West; August 12th: Bog Crest, Fen Water Track, Upper Lawn [replicate]) (Figure 2). There was negligible antecedent precipitation in August prior to our sampling dates. There was approximately 21 mm of rain in the Red Lake area (data from Waskish, MN ranger station; station identifier 218700) during the night between the August 10 and 11 sampling dates, but this rain event only affected the shallowest samples at some sites within the more porous upper layer of partially decomposed peat $\geq 0.5 \text{ m}$ depths (see Section 5.2 for further discussion). In general, variations in snowmelt and rainfall on the seasonal timescale are not expected to affect samples at $\geq 0.5 \text{ m}$ depths, where porewater flows at extremely slow rates (vertical specific discharge $\sim 10^{-7} \text{ cm s}^{-1}$; Siegel et al., 1995).

We sampled porewaters from the water table down to the underlying mineral soil at 0.5 m intervals using 1.27 cm schedule-80 PVC piezometers equipped with aluminum rod inserts for installation; following protocols described by Chason and Siegel (1986). At sites where the water table was below the land surface, we used a serrated knife to remove an approximately 0.30 by

0.30 m area section of surface peat and expose the water table. We sampled the water table directly at all sites by dipping our sampling bottles directly below the water surface while wearing rubber gloves. We waited until the water table re-equilibrated to a stable level and drove piezometers to the desired sampling depths. At each depth, the drive rod was removed and water allowed to flow into the screened interval of the piezometer. We sampled water from piezometers with a Geotech® Geopump 2™ Peristaltic Pump with silicone tubing at an approximate pumping rate of 30 ml min⁻¹. This method preferentially samples the hydrologically “active” pore-spaces of the peat profile. We measured water samples for field pH with a WTW brand, Sentix 41 model pH electrode, and then filtered the samples through 0.45 µm cellulose nitrate syringe filters. We stored the filtered samples in high-density polyethylene (HDPE) bottles at < 4° C. We preserved all samples for metals analysis with reagent grade nitric acid to lower aliquot pH to < 2.

We analyzed porewater samples for concentrations of dissolved calcium and magnesium (Ca, Mg) at SUNY-ESF using an Inductively Coupled Plasma-Optical Emission Spectrometer (Perkin Elmer Optima 3300DV model). We ran blanks and quality control (QC) standards every 10 sample runs and re-ran the previous samples if the QC deviated from the known value by > 10%. Relative standard deviations of 20 analytical replicate samples were 3% and 2% for Ca and Mg, respectively.

The University of Waterloo Environmental Isotope Laboratory (uwEILAB) personnel analyzed samples for stable isotopes of water (¹⁸O/¹⁶O, ²H/¹H) using standard techniques with IsoPrime continuous flow isotope ratio mass spectrometers. They measured oxygen-18 (¹⁸O) by CO₂ equilibration following uwEILAB protocols described in detail by Drimmie and Heemskerk (2001). They measured deuterium (²H) of hydrogen gas from water reduced on hot chromium

following uwEILAB protocols described in detail by Drimmie et al. (2001). The uwEILAB maintains quality control by running lab water standards calibrated to International Atomic Energy Agency (IAEA) reference standards (Vienna standard mean ocean water [VSMOW] and standard light Antarctic precipitation [VSLAP]) at the beginning, middle, and end of each 60 sample batch, and duplicates were run every 10 samples. Results are reported in δ -notation relative to VSMOW, where $\delta = (R/R_{\text{VSMOW}} - 1) \times 1000$ and R/R_{VSMOW} is the ratio of $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ in the sample and standard, respectively (Gat 2010). The precisions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements were ± 0.2 and ± 0.8 ‰, respectively.

In order to assess the sampling error of our porewater collection method on the landform-scale, we collected two porewater profiles in randomly selected locations (over 10 m apart from each other) at the Upper Lawn site at the beginning and end of our sampling survey. We calculated the variances of sample pairs from the two profiles taken at the same depth (not counting the water table due to the sensitivity of water isotopes to summer rain discussed above) and pooled these collective variances to calculate standard deviations of 0.2 mM, 0.1 mM, 0.1 ‰, and 0.9 ‰ for Ca, Mg, $\delta^{18}\text{O}$, and $\delta^2\text{H}$, respectively. The two replicate geochemical profiles sampled at the Upper Lawn site were remarkably similar despite the fact that they were collected on different days (before and after a rainfall event), in different locations; giving us confidence in the replicability of our porewater sampling method on the temporal and spatial scale of our survey.

We sampled Bog Crest, Upper Lawn, and Fen Water Track sites in August using the methods described above for porewater $^{87}\text{Sr}/^{86}\text{Sr}$ (Dasgupta, 2010). We extracted strontium by ion exchange using Sr Spec extraction chromatographic resin (Horwitz, 1992) and measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios using VG Sector 54 Thermal Ionization Mass Spectrometry at Syracuse

University. We loaded strontium on tungsten filament with TaF as an activator. Mass fractionation corrections were applied by normalizing the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to the $^{86}\text{Sr}/^{88}\text{Sr}$ ratios of 0.1194. Replicate analysis of standard NBS 987 yielded a mean value of $^{86}\text{Sr}/^{88}\text{Sr} = 0.710252$ ($n=120$) with a standard deviation of 0.000012.

We obtained a long-term record of atmospheric chemistry consisting of amount-weighted annual averages for Ca and Mg in precipitation from 1978 – 2010. These data were collected as part of the National Atmospheric Deposition Program (NADP) at Marcell Experimental Forest in north-central Minnesota, which is located approximately 120 km southeast of the GLAP (NADP, 2012). Details on the NADP sampling site and methods can be found in Sebestyen et al. (2011). We also sampled 10 water-supply wells finished in the local glacial till aquifer bordering the north and west shores of Upper Red Lake (at depths ranging from 15 – 88 m below the land surface) and tested for major ions by ICP as described above (Dasgupta, 2010).

4.0 Results

We report all sample depths for individual geochemical profiles relative to the position of the water table (“0” depth) at that site. The pH measurements at the water table range from 3.8 to 5.9 at the Bog Crest and Fen Water Track, respectively. Porewater pH increases with depth from the water table (mean $\pm$ standard deviation [s.d.] = 4.3 ± 0.8 , $n = 6$) to circumneutral values near the peat-mineral soil interface (mean $\pm$ s.d. = 6.3 ± 0.1 , $n = 6$). The pH-depth profile for the Fen Water Track is multimodal, with local peaks at the water table (5.9), 1.5 m depth (6.3), and the peat-mineral soil interface (6.4) (Figure 3).

The Ca and Mg concentrations in the porewaters range from 0.07 to 4.03 mmol L⁻¹ and 0.02 to 2.23 mmol L⁻¹, respectively, and show similar general depth trends to pH; except at the Fen Water Track where concentrations are fairly uniform between the shallow peat (below 1 m depths) and the mineral soil (Figure 3). The mean $\pm$ s.d. for 30 years of annual amount-weighted averages for Ca and Mg in precipitation is 5.0 ± 1.0 μ M and 1.4 ± 4.0 μ mol L⁻¹, respectively. The mean and s.d. of 10 local water-supply wells for Ca and Mg are 1.38 ± 0.62 mmol L⁻¹ and 0.96 ± 0.39 mmol L⁻¹, respectively. The Bog Crest and Fen Water Track sites have characteristic “concave” (recharge) and “convex” (discharge) concentration-depth profiles for the alkaline earth metals (e.g. Siegel et al. 1995); with inflections at depths of 3.0 and 1.0 m, respectively. The other sites along the transect have curvilinear solute-depth profiles intermediate between these extremes with inflections at 2.0 m depths, with the exception of the Ovoid East site, which has a higher solute content throughout the profile compared to the other bog sites. Dissolved Sr and ⁸⁷Sr/⁸⁶Sr ratios of the porewaters from Bog Crest, Upper Lawn, and Fen Water Track sites range from 0.01 to 2.17 μ mol L⁻¹ and 0.7116 to 0.7156, respectively (Figure 4), with Sr-depth profiles closely mimicking those of Ca and Mg.

The Bog Crest and Fen Water Track have markedly different Ca/Mg molar ratios, ranging from 2.0 – 5.6 at the former and 1.0 – 1.6 at the latter (Figure 5). The lawn and ovoid bog island sites have intermediate ratios ranging from 1.0 – 3.9, with a “+Mg-shift” to lower Ca/Mg values in the center of the peat column (1.0 – 2.5 m depths). The +Mg-shift is also most pronounced at the Ovoid East site, where Ca/Mg values overlap the range measured at the Fen Water Track in the center of the peat column. Local precipitation and groundwater sample sets have 95% confidence intervals for mean Ca/Mg values of 3.7 ± 0.1 and 1.4 ± 0.2 , respectively.

The stable isotopes of peat porewaters range from -12.8 ‰ to -7.8 ‰ and -88.8 ‰ to -59.6 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Porewater $\delta^{18}\text{O}$ was lowest at forested bog sites (Bog Crest, Ovoid East/West), intermediate at non-forested lawn sites (Upper/Lower Lawn), and highest at the Fen Water Track (Figure 3). Spatial interpolation of geochemical gradients shows that in contrast to Ca and pH, $\delta^{18}\text{O}$ has much less vertical variation within individual sites than laterally across the study transect (Figures 6 and 7).

5.0 Discussion

5.1 Sources of Alkalinity

As anticipated, pH and Ca correlated throughout the entire transect (Pearson's $r = 0.81$), indicating that groundwater-derived alkalinity (as inferred by Ca) largely controls porewater pH at the landform-scale. We compared molar ratios of Ca/Mg in peat porewaters to those from local groundwater wells and regional precipitation to identify mineral sources that control spatial variations of Ca and pH in the porewaters of the Red Lake II bog-fen complex (Figure 5). Dilute samples at the water table generally clustered around the mean ratio of Ca/Mg in precipitation. As expected, variation from this endmember occurs in some places because the Ca/Mg ratio of dilute porewaters ($\text{Ca} < 0.5 \text{ mmol L}^{-1}$) is extremely sensitive to small variations in precipitation, wind-blown dust, and near surface biogeochemical processes (e.g. biological uptake of Ca). The details of these lie beyond the scope of our study and the broad endmember value we use for our interpretation remains sufficiently robust for the purposes of our analysis.

The Ca/Mg ratios at the peat-mineral interface identify three distinctive sources of mineral solutes to the deep peat, which have similarly high Ca concentrations that show no signs of dilution by precipitation (Figure 5): a lower-Mg source (Ca/Mg = 4.8), an intermediate-Mg source (Ca/Mg range from 2.1 – 3.0), and a higher-Mg source (Ca/Mg = 1.4). The higher-Mg water we measured at the peat-mineral interface of the Fen Water Track falls within the 95% confidence interval for the mean value of water-supply wells adjacent to the peatland that tap the underlying mineral aquifer at 15 to 88 m depths. This “deep groundwater” signal propagates upwards through the entire porewater profile of the fen site even as concentrations become more dilute closer to the surface.

Spatial interpolation of Ca/Mg gradients across our study transect suggest that the higher-Mg groundwater beneath the Fen Water Track appears to extend both to the north and south beneath adjacent lawn and ovoid island sites (Figure 7), where a +Mg-shift to lower values occurs in the center of the peat profile at 1.0 – 2.5 m depths (Figure 5). The Ca/Mg ratios of dilute, near-surface bog waters are sensitive to small additions of higher-Mg groundwater, so we used a simple 2-tracer, 3-endmember mixing model to explore the amount of the higher-Mg groundwater endmember needed to cause the +Mg-shift (Appendix A). We found that porewaters from the Upper and Lower Lawn sites and the downslope Ovoid West site would require a 2 – 10% contribution from the higher-Mg endmember to induce the observed +Mg-shift, whereas porewaters at the downslope Ovoid East site would need to contain up to 27% contribution from the higher-Mg endmember.

The lateral partitioning of different Ca/Mg ratio waters within the basal peat along our study transect suggests that upward vertical transport controls solute profiles at depth. Both diffusion and transverse dispersion at the peat-mineral interface could theoretically transport

solutes into the deep peat on $10^2 - 10^3$ year timescales (Reeve et al., 2001a; McKenzie et al., 2002). However, Ca/Mg ratios show that the higher-Mg groundwater endmember has migrated both vertically through the entire fen peat column, and laterally to adjacent sites many meters distant; far beyond what could reasonably be explained by diffusion given the age of these landforms. Transverse dispersion, as heuristically modeled by Reeve et al. (2001a), would also not predict such an abrupt shift in geochemistry throughout the entire porewater profile or lateral transport through the center of the peat column. Therefore, the Fen Water Track is most likely a focal point for advective groundwater upwelling in the RLII watershed.

To explore differences among the subsurface sources of mineral solutes further, we examined the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of porewaters collected from three sites in 2007: the Bog Crest, Upper Lawn, and Fen Water Track (Figure 4). In Minnesota, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show large differences between meteoric waters (~ 0.7100) and the regional bedrock (> 0.7300), which can be used to identify the sources of solutes to peatlands (Hogan et al., 2000). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of shallow groundwater in glacial sediments beneath the GLAP ($0.7157 - 0.7209$) is lower than that of the underlying bedrock. This difference could be due to preferential weathering of lower-ratio, calcic minerals (e.g. plagioclase with a ratio of ~ 0.7200) over higher-ratio, less-reactive minerals (e.g. muscovite with a ratio of $\sim 0.8700 - 1.650$) (Hogan et al., 2000).

As expected, all the porewater profiles represent variable mixtures between recharge with lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the water table and groundwater with higher ratios at the peat-mineral interface (Figure 4). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the Bog Crest and Fen Water Track sites converge to a common mineral source at depth (with a ratio of ~ 0.7155), fingerprinting this endmember in the fen peat up to 1.5 – 2.5 m depths. However, the Upper Lawn site appears to have a slightly different solute source at the peat-mineral interface (0.7141), causing an overall shift of $^{87}\text{Sr}/^{86}\text{Sr}$

ratios within the basal peat from those found at the neighboring sites. Although $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the water table differed between the Upper Lawn and Bog Crest/Fen Water Track sites, the isotopic composition of dilute porewaters ($\text{Sr} < 0.5 \mu\text{mol L}^{-1}$) are extremely sensitive to variable meteoric Sr sources and near-surface biogeochemical processes, that are outside the scope of this study.

The greatest difference in Ca/Mg ratios occurs beneath the Bog Crest and Fen Water Track sites; although the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from these sites suggest a common source of solutes distinct from that beneath the intervening Upper Lawn. This discrepancy may be explained by local hydrogeologic setting. In glacial aquifers of northern Minnesota, groundwater typically evolves higher dissolved solids and Mg along flowpaths from points of recharge to discharge (MacLay and Winter, 1967). Siegel (1983) hypothesized that water table mounds beneath large raised bogs generate local flow cells that travel through underlying glacial sediments and discharge at adjacent fen water tracks (Figure 1, top). Buried beach ridges commonly found within the glacio-lacustrine deposits beneath the GLAP can potentially transmit such local-scale groundwater flow (Glaser et al., 1997; Reeve et al., 2000); and have contrasting mineralogy to the finer-grained sediments. Conceptually, groundwater could evolve higher-Mg water while retaining the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from the family of minerals contained along local-scale flowpaths moving through the underlying till. Intermediate-Mg and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio waters beneath the neighboring lawn and ovoid island sites could reflect a surficial mineral weathering signal disconnected from the deeper flow system that has discharged into the peat beneath the Fen Water Track.

5.2 Sources of Water

In northern Minnesota, the isotopic composition of precipitation fluctuates on a seasonal basis due to the “temperature effect” on equilibrium isotope fractionation (Dansgaard, 1964). Levy et al. (2014) presented isotopic data for 211 samples of precipitation collected at the Marcell Experimental Forest NADP site between 1989 and 2000, and found that monthly means for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ during this time followed a bell curve from January to December; with highest and lowest values for $\delta^{18}\text{O}$ in July (-8.2 ‰) and January (-21.5 ‰), respectively. Since the bulk of precipitation in northern Minnesota occurs during the warm season (May – August), the amount-weighted annual means $\pm$ 95% confidence intervals for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of precipitation (-11.1 ± 0.4 ‰ and -78.6 ± 3.1 ‰, respectively) at the Marcell Forest are closer to warm weather values. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for precipitation at the Marcell Forest define a local meteoric water line (LMWL) for northern Minnesota with a slope of 8.14 and intercept of 12.05 ‰ in δ -space (Figure 8).

Fluctuations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the shallow groundwaters of temperate climates occur seasonally due to mixing with infiltrating meteoric waters, but are progressively muted with depth until a seasonally-averaged recharge value is reached at the “critical depth.” (Clark and Fritz, 1997; p. 82). We assume that critical depth is attained at ~0.5 m in the GLAP, because porewater geochemistry at and below this depth remains extremely stable on the timescale of decades (Siegel et al., 1995). Indeed, seasonal mixing with summer rain that occurred during sampling (mean August $\delta^{18}\text{O} = -9.0$ ‰) could only be seen at the water table of the Upper Lawn and Ovoid East sites (Figure 8), and did not affect the isotopic composition of porewaters at depths ≥ 0.5 m.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of peat porewaters at depths ≥ 0.5 m cluster in three primary isotopic zones in δ -space, each of which reflect different site-specific recharge regimes (Figure 8). The first zone consists of porewaters from the forested bog sites (Bog Crest, Ovoid West, and Ovoid East), which have the isotopically lightest porewaters in our study area and follow the LMWL within with the range of δ -values for forested bogs throughout the GLAP. The second zone consists of non-forested sites (Upper/Lower Lawn), which also fall along the LMWL and have higher $\delta^{18}\text{O}$ values than the forested sites. The third zone consists of porewaters from the Fen Water Track, which plot at an acute angle from the LMWL and fall within the range of porewater δ -values for fen water tracks throughout the GLAP. Porewaters from beneath fen water tracks in the GLAP collectively integrate the effects of surface water evaporation and follow the local evaporation line (LEL) developed by Levy et al. (2014).

Surface landscape characteristics in the GLAP control the isotopic signature of recharge into the peat column (Levy et al., 2014). Porewaters from forested bog and non-forested lawn sites lie close to the amount-weighted mean for the regional precipitation in δ -space, but tend to be respectively lower and higher than the 95% confidence interval for this value. The lower δ -values of porewaters from the forested bog sites reflect their greater seasonal accumulation of isotopically light snowpack than adjacent non-forested lawns, which are exposed to greater wind ablation and removal of snow. The clustering of the isotopic data at ovoid islands with that of the bog crests in δ -space supports this hypothesis because the ovoid islands have horseshoe-shaped stands of black spruce trees (*Picea mariana*) around their margins that serve as windbreaks, allowing enhanced winter snow storage similar to the bog crests (Glaser et al., 1981). Departure of fen porewater δ -values from the LMWL is caused by isotope fractionation driven by evaporation, which occurs at the free-water surface prior to its recharge into the underlying peat

porewaters, which appear to be fairly well-mixed at depths below 1.5 m. This evaporation signature was not apparent at the other study sites where the water table is typically at or below the land surface and the dominant water loss mechanism is most likely the non-fractionating process of transpiration.

In striking contrast to solute profiles, water isotopes generally did not vary significantly with depth at any given site (Figure 3). The only exceptions are porewater profiles from the Bog Crest and Ovoid West sites in which there was a slight depletion of ^{18}O with depth resulting in a significant relationship between these two variables of at the 95% confidence level ($p \leq 0.01$). This slight isotopic depletion at these sites might reflect mixing with the Pleistocene-age groundwater endmember ($\delta^{18}\text{O} \sim -18 \text{‰}$) found in local water wells that tap glacial till (Levy et al., 2014), or long-term variations in recharge regimes. However, no other sites showed significant linear depth trends for $\delta^{18}\text{O}$ at depths greater than 0.5 m ($p > 0.05$).

Hypothetically, if the solute-rich porewaters near the base of the peat reflect that of Pleistocene-age groundwater from the deep mineral aquifer, the differing recharge values measured near the top of the peat column would converge upon this lower $\delta^{18}\text{O}$ endmember with depth. Instead, $\delta^{18}\text{O}$ -depth profiles in our study area show abrupt lateral zonation, suggesting that porewaters at each individual study site have been mixed or completely flushed with waters recharged from the shallow peat (Figure 7). The values for mineral solutes and pH discussed above do not show this flushing effect and instead can be used to identify upwards migration of groundwater from underlying glacial sediments into the Red Lake II bog-fen complex. How can this contradiction occur?

5.3 Effects of pore-scale processes on landform-scale hydrogeochemistry

The Ca/Mg and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in our porewater profiles show that underlying glacial sediments must provide dissolved alkaline earth metals (Ca, Mg, Sr) to the deeper peat porewaters, whereas the source of the solvent itself (determined from $\delta^{18}\text{O}$ and $\delta^2\text{H}$) is mostly of meteoric origin. Conservative mixing between meteoric and groundwater endmembers cannot explain this incongruity. The profound decoupling between recharge and discharge tracer suites is most pronounced at the Upper Lawn site, where Ca increases steadily at depths below 2.0 m and $\delta^{18}\text{O}$ remains virtually invariant below the water table (Figure 9). Therefore, there must be an internal reservoir for mineral solutes that buffers porewater concentrations following flushing by dilute recharge.

Hydrogeologic studies have long recognized that groundwater and associated solutes travel in active pore spaces where water moves from regions of high to low hydraulic head by advection (Freeze and Cherry, 1979). However, solutes in flowing water can also diffuse in and out of hydrologically stagnant pores by a process known as “matrix diffusion” or “dual-domain mass transfer” (DDMT) (Harvey and Nuttle, 1995; Faure, 1998; Briggs et al., 2014). This effect logically occurs in peat because partially humified plant remains have a high volume of stagnant pores within the hyaline cells of *Sphagnum* moss and the cellular matrix of vascular plant tissues (Hoag and Price, 1997; Ours et al. 1997; Rezanezhad et al. 2012). Additionally, positively charged cations such as Ca^{2+} and Mg^{2+} are preferentially exchanged for H^+ on organic functional groups in the peat, effectively titrating out matrix acidity associated with the humification process in peatlands (Clymo, 1963; Clymo and Hayward 1982; Shotyk and Steinmann, 1994). In this context, we propose as a working hypothesis that the distribution of mineral solutes and pH across our study transect, particularly the plume of higher-Mg groundwater originating below the

Fen Water Track, are relics of paleo-hydrogeologic flowpaths preserved in stagnant peat pores and now re-expressed by diffusion into actively recharging waters (Figure 10).

Groundwater discharge became active at the Fen Water Track site ~2000 years ago, when a prior bog ecosystem transitioned to fen (Gorham and Janssens, 1992; Janssens et al., 1992). The source of head driving this discharge is unknown, but could be linked to the development of a water table mound beneath the then 2000 year old Bog Crest site that exerted hydrostatic pressure on underlying glacial sediments (e.g. Siegel, 1983). At some point, perhaps linked to progressively wetter climate conditions during the past century, the entire landscape shifted to hydrogeologic regime dominated by “modern recharge,” shown by the penetration of site-specific, shallow (~0.5 m) recharge signatures throughout the peat column that show no signs of the lateral mixing suggested by spatial interpolation of Ca/Mg ratios (Figure 7).

Therefore, solutes transported into peatlands over various timescales by diffusion (thousands of years; McKenzie et al. 2002), dispersion (hundreds of years; Reeve et al. 2001a), and advection (decades; Siegel et al., 1995; Reeve et al. 2000) may persist in peat porewater profiles by diffusion between active pore spaces and the peat matrix— even as changes in regional climate (e.g. Siegel et al., 1995; Glaser et al., 1997) flush the subsurface with modern recharge. This effect has been unrecognized previously on the landform-scale. The flushing rate through the peat column by modern recharge must be *at least* 4 m per 50 years ($2.5 \times 10^{-7} \text{ cm s}^{-1}$), as evidenced by the measurement of post bomb-peak tritium in basal porewaters (up to 4 m depths) throughout the GLAP (Glaser et al., in review). This recharge rate is within an order of magnitude of previous independent estimates for vertical seepage velocity beneath raised bogs in the GLAP ($10^{-6} \text{ cm s}^{-1}$; Siegel et al., 1995).

While the mechanics of DDMT between active and stagnant zones is complex and highly depends on the geometry of the pore-network and the concentration of the stagnant reservoir, the timescale of equilibration between dilute recharge moving through active pore-spaces within the surrounding peat matrix is most likely much more rapid than advection of pore-fluids at such slow seepage rates. Field samplers that equilibrate distilled water with surrounding porewater by diffusion (“peepers”) are typically deployed for 2 – 3 weeks (Harper et al., 1997), whereas it would take 10 years to flush the active pore-spaces of a 4 m peat column with recharge by advection using the above estimate for vertical seepage velocity (Siegel et al., 1995).

The implications of this potentially ubiquitous process in peatlands are twofold. First, vegetation communities in peatlands are closely adjusted to $\text{pH} > 4.2$ and $\text{Ca} > 2$ ppm in the surface waters (e.g. fens) can persist through persistent wet periods of meteoric recharge if the acidity of the underlying peat has been neutralized by a prior regime of groundwater discharge. Second, the combination of pH buffering from the peat matrix (related to paleo-hydrogeologic conditions) and the advective downward transport of labile organic carbon produced near the surface could create methanogenic “hot spots” in the peat column (*sensu* Morris et al., 2011); where both controls are optimized with respect to each other and not limited by the cooler temperatures of the deeper peat ($\sim 5^\circ\text{C}$ below 2.0 m depths; McKenzie et al., 2007).

The buffering of pH by the peat matrix could confer additional stability to different microbial taxa that are likely adapted for optimum growth within a narrower portion of the wider wide range of pH values found in the upper ~ 2 m of peat (3.8 – 6.3; Figures 3 and 6). The center of the peat profile generally contains the highest concentrations of dissolved methane in the GLAP and is subject to frequent overpressuring by free-phase gas bubbles (Romanowicz et al. 1993; Chasar et al. 2000; Rosenberry et al., 2003; Glaser et al., 2004; Parsekian et al., 2010).

Though the effects of pH on microbial communities at these intermediate depths are unknown, the downwards advection of labile carbon from the peatland surface during periods of landscape-wide recharge clearly contributes to this phenomenon (Chanton et al. 1995, 2008; Corbett et al., 2013, 2015). Autogenic hydrogeochemical feedback mechanisms such as those described above can contribute to the resilience of peatlands systems and associated ecological functions to climate change (Waddington et al., 2015).

6.0 Conclusions

Analyses of porewater pH, Ca, Mg, Sr, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ show that the porewater chemistry within a 120 km² bog-fen complex is linked to the long-term dynamics of groundwater recharge and discharge. We used Ca/Mg and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to fingerprint groundwater discharge to the peat beneath a fen water track and the lateral seepage through a zone in the middle of the peat profile to adjacent bog sites. In contrast, stable isotopes of water indicate that the porewaters are currently being flushed by recharge from the shallow peat across this entire bog-fen complex. Therefore, the back-diffusion of solutes from the peat matrix is the most likely mechanism responsible for maintaining the geochemical signal from a former period of groundwater discharge in the current regime of dilute recharge. This effect has not been previously observed on the landform-scale and has important implications for carbon cycling in peatlands.

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Appendix A

The equation to calculate endmember mixing fractions using one conservative tracer and two endmembers is given by Faure (1998):

$$X_M = X_A f + X_B (1 - f) \quad \text{A.1}$$

Where X_A is the concentration or isotope ratio of tracer X in endmember A, X_B is the concentration or isotope ratio of tracer X in endmember B, X_M is the concentration or isotope ratio of tracer X in a mixture of endmembers A and B, and f is the decimal fraction of endmember A in mixture M.

The solutions of the simultaneous equations for mixing fractions using two conservative tracers and three endmembers given by Ogunkoya and Jenkins (1993) are adapted here as:

$$f_A = \frac{(X_M - X_C)(Y_B - Y_C) - (X_B - X_C)(Y_M - Y_C)}{(X_A - X_C)(Y_B - Y_C) - (X_B - X_C)(Y_A - Y_C)} \quad \text{A.2}$$

,

$$f_B = \frac{(X_M - X_C)}{(X_B - X_C)} - \frac{(X_A - X_C)}{(X_B - X_C)} f_A \quad \text{A.3}$$

$$f_C = 1 - f_A - f_B \quad \text{A.4}$$

Where subscript notation is the same as above for endmembers A, B, and C; and tracers X and Y.

In order to heuristically evaluate how much of the higher-Mg endmember would have to be mixed in porewaters to induce the +Mg-shift we observed at mid-range depths (1.0 – 2.5 m) beneath Upper/Lower Lawn and Ovoid East/West sites, we solved equations A.2 – A.4 for f_C . We used Ca and Mg as geochemical tracers (X and Y). We assessed mixing separately at each site, assuming the waters in the higher-Mg plume could be explained by mixing of the shallowest and deepest samples from a given site with the higher-Mg endmember we sampled at the peat-mineral interface below the Fen Water Track (Table A.1).

Table A.1. Endmembers for three component mixing model (all concentrations in mmol L⁻¹)

Endmembers	Upper Lawn	Lower Lawn	Ovoid West	Ovoid East
A (shallowest)	Ca = 0.07, Mg = 0.02	Ca = 0.13, Mg = 0.05	Ca = 0.12, Mg = 0.03	Ca = 0.10, Mg = 0.03
B (deepest)	Ca = 3.24, Mg = 1.09	Ca = 1.94, Mg = 0.74	Ca = 3.79, Mg = 1.83	Ca = 2.25, Mg = 1.07
C (Fen GW)		Ca = 3.03, Mg = 2.23		

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Figure

Bog Crest

pH < 4.2
Ca < 2 ppm

Sphagnum
Lawn

**Fen Water
Track**

pH > 4.6
Ca > 6 ppm

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Landform-scale

Pore-scale

Figure 1. Conceptual models of peatland hydrogeology that explain the occurrence of fen water tracks at the flanks of large raised bogs by: local groundwater flow systems (Siegel, 1983), converging local and regional flow systems (Siegel et al., 1995), and transverse dispersion of lateral groundwater flow (Reeve et al., 2001a).

Figure 2. Study area map showing (a) the Red Lake II bog-fen complex in northern Minnesota and (b) an enlarged image of porewater sampling sites.

Figure 3. Panel plots of geochemical-depth profiles for porewater pH, Ca, Mg, and $\delta^{18}\text{O}$.

Figure 4. Geochemical-depth profiles for porewater Sr (left) and $^{87}\text{Sr}/^{86}\text{Sr}$ from Bog Crest, Upper Lawn, and Fen Water Track sites. All profiles show mixing of precipitation ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7100$; Hogan et al., 2000) with a subsurface source of strontium. The Bog Crest and Fen derive their strontium contents from a similar subsurface source ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7155$), whereas the Upper Lawn has a different source ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7141$).

Figure 5. Ca/Mg molar ratio-depth profiles for each of the study sites. Blue and red dotted lines and shading represent the mean and 95% confidence intervals for local groundwater wells in the mineral aquifer (1.4 ± 0.2) and the long-term precipitation record (3.7 ± 0.1), respectively. Error bars represent two standard deviations of the analytical error.

Figure 6. Hydrogeochemical cross sections of porewater pH (top) and Ca (bottom) along study transect from Bog Crest to Ovoid West (left) and Ovoid East (right). The dashed line represents the peat surface and the uppermost extent of filled contours represents the water table. Grey shaded area is the approximate location of the glacial till underlying the peat. Vertical exaggeration is x1100 (left) and x1200 (right).

Figure 7. Hydrogeochemical cross sections of porewater Ca/Mg molar ratio (top) and $\delta^{18}\text{O}$ (bottom) along study transect from Bog Crest to Ovoid West (left) and Ovoid East (right). Note the nearly vertical trends in $\delta^{18}\text{O}$ and the pronounced excursion of lower Ca/Mg ratios under the Fen Water Track and neighboring bog sites. The dashed line represents the peat surface and the uppermost extent of filled contours represents the water table. Grey shaded area is the approximate location of the glacial till underlying the peat. Vertical exaggeration is x1100 (left) and x1200 (right).

Figure 8. Bivariate plot showing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for porewaters with local meteoric water (LMWL) and evaporation (LEL) lines from a regional study of bog crest and fen sites in the Glacial Lake Agassiz Peatlands (GLAP) by Levy et al. (2014) (grey symbols) compared to those measured in this study from the Red Lake II bog-fen complex (colored symbols). Peat porewaters fall into three distinct groupings based on surface landscape characteristics that control the isotopic composition of recharge: (1) forested bogs, (2) non-forested lawns, and (3) fen water tracks. Grey boxes represent 95% confidence intervals for amount-weighted annual mean precipitation and monthly mean August precipitation derived from the atmospheric record at Marcell Experimental Forest from 1989 to 2000.

Figure 9. Replicate geochemical-depth profiles for porewater Ca and $\delta^{18}\text{O}$ taken in different areas of the Upper Lawn site. Calcium increases with depth whereas $\delta^{18}\text{O}$ remains relatively constant below the water table, which is enriched due to mixing with summer rain that occurred during sampling.

Figure 10. Conceptual models of hydrogeochemical dynamics on the landform and pore-scales. Landform-scale model show bogs and fens previously connected by local-scale flowpaths through heterogenous glacial sediments are now being flushed with recharge. Pore-scale model reconciles contrasting geochemical signals from groundwater-derived mineral solutes (blue) with recharge from the shallow peat (red) by a hypothesized matrix diffusion mechanism.