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Climatic Controls on the Porewater Chemistry of Mid-continental Wetlands

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General Abstract

Wetlands develop where climate and physiography conspire to maintain saturated soils at the land surface, support diverse plant and animal communities, and serve as globally important sinks for atmospheric carbon. The chemistry of wetland porewaters impacts near-surface biological communities and subsurface biogeochemical processes that influence carbon cycling in the environment. Wetland porewater chemistry is a dynamic byproduct of complex hydrogeological processes that cause meteoric waters to enter groundwater systems (recharge) or groundwater to flow to the land surface (discharge). Changes in climate can alter subsurface hydraulic gradients that determine the recharge and discharge functions of wetlands, which in turn control the hydrogeochemical evolution of wetland porewaters.

The climate of mid-continental North America is influenced by competing air masses with vastly different temperature and moisture contents originating from the Pacific Coast, the Gulf of Mexico, and the Arctic. The interactions of these air masses result in large dynamic shifts of climate regimes characterized by decadal-scale oscillations between periods of drought and heavy rain. Over the course of the 20th century, a shift occurred towards wetter climate in the mid-continental region. This dissertation examines the impact of this climate shift on the porewater chemistry of two very different wetland systems, located only 350 km apart: the Glacial Lake Agassiz Peatlands (GLAP) of northern Minnesota and the Cottonwood Lake Study Area (CLSA) of North Dakota. The former study site consists of a large (7,600 km²), circumboreal peatland that developed an extensive blanket of peat over the last ~5000 years on a relatively flat glacial lake bed within a sub-humid to semi-arid climate gradient characterized by small annual atmospheric moisture surpluses and frequent droughts. The latter study site consists of a 0.92 km² complex of small (meter-scale) “prairie pothole” wetlands located on a hummocky
glacial stagnation moraine under semi-arid climate where wetlands frequently fill and dry with surface ponds over low-permeability glacial till in response to snowmelt runoff and evapotranspiration. Both sites have been the subject of long-term hydrological study since c. 1980 and are well-established examples of the sensitivity of wetland functions to changes in climate.

The first chapter of this dissertation utilizes a semi-conservative tracer suite (pH, Ca, Mg, Sr, $^{87}$Sr/$^{86}$Sr) to fingerprint discharge of calcareous groundwater to GLAP peat along a ~6 km transect from a bog crest downslope to an internal fen water track and bog islands. However, stable isotopes of the peat porewaters ($\delta^{18}$O and $\delta^2$H) show that the subsurface throughout the entire study area is currently flushed with recharge from the near surface peat. I 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 promotes methane generation in the peatland subsurface by allowing transport of labile carbon compounds from the land surface to depth while maintaining geochemical conditions (i.e. pH) in the deep peat favorable to biogenic methane production. The results of this study show that autogenic hydrogeochemical feedback mechanisms contribute to the resilience of peatlands systems and associated ecological functions against climate change.

The second chapter of this dissertation consists of a detailed geoelectrical survey of a well-studied, closed-basin prairie wetland (P1) in the CLSA that has experienced record drought and heavy rains (i.e. deluge) during the late 20th century. Subsurface storage of sulfate (SO$_4$) salts allows many such closed-basin prairie wetlands to maintain moderate surface water salinities (TDS from 1 to 10 g L$^{-1}$) that influence communities of aquatic biota. I imaged saline lenses of sulfate-rich porewater (TDS > 10 g L$^{-1}$) in wetland sediments beneath the bathymetric
low of the wetland and within the currently ponded area along the shoreline of a prior pond stand. Analyses of long-term (1979 – 2014) groundwater and surface water levels in the wetland suggest that the saline lenses formed during paleo-droughts when the groundwater levels dropped below the wetland bed and are stable in the subsurface on at least centennial timescales. I hypothesize a “drought-induced recharge” mechanism by which wetlands maintain moderate surface water salinity by subsurface storage during droughts when the wetlands dry and intermittent runoff events flush surface salts down secondary porosity created by desiccation fractures and terrestrial plant roots. Drought-derived saline groundwater has the potential to increase wetland salinity during record wet climate conditions currently prevalent in the Prairie Pothole Region.

The third chapter of this dissertation extends the findings of the second chapter by a detailed geochemical survey of wetland porewater, pond water, and upland groundwater in the P1 basin. I use a natural geochemical tracer suite of halogens (Cl, Br, and I) to better understand the hydrogeochemical evolution of saline groundwater in the wetland subsurface during prior droughts. I found that saline porewater lenses contain SO$_4$, Cl, and Br that are ~6x more concentrated from levels measured in the surface pond, due to the effects of evapo-concentration and recharge during paleo-droughts. However, I found the highest concentrations of porewater iodine (up to ~4 µM; the highest dissolved iodine concentration ever reported for a terrestrial aquatic system) occurred in vertical profiles above the saline lenses. I hypothesize that chromatographic separation of iodine from SO$_4$, Cl, and Br occurs during droughts when sedimentary iodine oxidizes from its reduced forms (I$^-$ and organically bound I) to the less-mobile iodate compound (IO$_3^-$). Understanding the hydrogeochemical evolution and composition
of drought-derived, saline groundwater can be used to fingerprint sources of salinity to wetland ponds during the record wet climate conditions currently prevalent in the Prairie Pothole Region.

The three studies that comprise this dissertation illustrate diverse and complicated ways by which different wetland systems store and release salinity to their porewaters under dry and wet climate conditions. In the GLAP, geochemical buffering from the peat matrix stabilizes subsurface biogeochemical processing against the effects of climate change. At the CLSA, subsurface salinity storage during droughts allows closed-basin prairie wetlands to maintain moderate surface water salinities under semi-arid climate, which can be re-released back to wetland surface ponds during wetter conditions. These studies both have practical applications for forecasting the response of mid-continental wetlands to changes in climate, and highlight autogenic hydrogeochemical feedback mechanisms that help wetlands stabilize their ecological and biogeochemical functions under a changing climate.
Climatic Controls on the Porewater Chemistry of Mid-continental Wetlands

by

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Chapter 1: Peat porewaters have contrasting geochemical fingerprints for groundwater recharge and discharge due to matrix diffusion in a large, northern bog-fen complex

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Abstract

Although northern peatlands represent a globally significant reservoir for carbon, considerable uncertainty exists concerning solute transport systems within large (>1000 km²) peat deposits. We therefore delineated geochemical gradients linked to groundwater recharge and discharge along a 6 km transect within the 1200 km² Red Lake Peatland of northwestern Minnesota. We used ratios of Ca/Mg and ⁸⁷Sr/⁸⁶Sr 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 (δ¹⁸O 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.
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 ($\delta^{18}$O, $\delta^2$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 km$^2$ 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.

**Study Area**

The Glacial Lake Agassiz Peatlands (GLAP) cover 56% of Beltrami Arm of the Lake Agassiz region, a 7,600 km\(^2\) 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 \(\sim 10^{-5}\) cm s\(^{-1}\)), as well as discontinuous beach ridges of sand and gravel (with K values of \(\sim 10^{-3}\) 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 \(\sim 1\) 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).

**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 (~0.2 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 ≥ 0.5 m depths (see Sources of Water section for further
discussion). In general, variations in snowmelt and rainfall on the seasonal timescale are not
expected to affect samples at ≥ 0.5 m depths, where porewater flows at extremely slow rates
(vertical specific discharge ~10^{-7} 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 \( \delta = (R/R_{VSMOW} - 1) \times 1000 \) and \( R/R_{VSMOW} \) is the ratio of \(^{18}\text{O}/^{16}\text{O} \) or
\(^2\text{H}/\text{H} \) 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).

**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 ± standard deviation [s.d.] = 4.3 ± 0.8, n = 6) to circumneutral values near the peat-mineral soil interface (mean ± 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 (Figure 3). The mean ± s.d. for 30 years of annual amount-weighted averages for Ca and Mg in precipitation is
5.0 ± 1.0 µM and 1.4 ± 4.0 µmol 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 µmol 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 δ¹⁸O and δ²H, respectively. Porewater δ¹⁸O 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, $\delta^{18}O$ has much less vertical variation within individual sites than laterally across the study transect (Figures 6 and 7).

**Discussion**

*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 ($Ca < 0.5 \text{ mmol L}^{-1}$) 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 (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 ~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 (Sr < 0.5 μmol 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.

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 $\delta^{18}$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 ± 95% confidence intervals for $\delta^{18}$O and $\delta^2$H of precipitation (-11.1 ± 0.4 ‰ and -78.6 ± 3.1 ‰, respectively) at the Marcell Forest are closer to warm weather values. The $\delta^{18}$O and $\delta^2$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 $\delta$-space (Figure 8).

Fluctuations of $\delta^{18}$O and $\delta^2$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 $\delta^{18}$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 $\delta^{18}$O and $\delta^2$H values of peat porewaters at depths ≥ 0.5 m cluster in three primary isotopic zones in $\delta$-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 $\delta$-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 $\delta^{18}$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 ≤ 0.01). This slight isotopic depletion at these sites might reflect mixing with the Pleistocene-age groundwater endmember (δ\(^{18}\)O ~ -18 ‰) 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 δ\(^{18}\)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 δ\(^{18}\)O endmember with depth. Instead, δ\(^{18}\)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?

Effects of Pore-scale Processes on Landform-scale Hydrogeochemistry

The Ca/Mg and \(^{87}\)Sr/\(^{86}\)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 δ\(^{18}\)O and δ\(^2\)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 δ\(^{18}\)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 x 10⁻⁷ 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., 2016). 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 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 pH > 4.2 and 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 (~5 °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 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).
Conclusions

Analyses of porewater pH, Ca, Mg, Sr, $^{87}$Sr/$^{86}$Sr, $\delta^{18}$O, and $\delta^{2}$H show that the porewater chemistry within a 120 km$^2$ bog-fen complex is linked to the long-term dynamics of groundwater recharge and discharge. We used Ca/Mg and $^{87}$Sr/$^{86}$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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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 Minnestota and (b) an enlarged image of porewater sampling sites.
Figure 3. Panel plots of geochemical-depth profiles for porewater pH, Ca, Mg, and $\delta^{18}O$. 
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 δ¹⁸O (bottom) along study transect from Bog Crest to Ovoid West (left) and Ovoid East (right). Note the nearly vertical trends in δ¹⁸O 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 $\delta^{18}$O and $\delta^{2}$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 δ\(^{18}\)O taken in different areas of the Upper Lawn site. Calcium increases with depth whereas δ\(^{18}\)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.
Appendix A

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

\[ X_M = X_A f + X_B (1 - f) \]  

A1

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:

\[ f_A = \frac{(X_M - X_C)(Y_B - Y_C) - (X_B - X_C)(Y_M - Y_C)}{(X_A - X_C)(Y_B - Y_C) - (X_B - X_C)(Y_A - Y_C)} \]  

A2

\[ f_B = \frac{(X_M - X_C)}{(X_B - X_C)} - \frac{(X_A - X_C)}{(X_B - X_C)} f_A \]  

A3

\[ f_C = 1 - f_A - f_B \]  

A4

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 A2 – A4 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 A1).

Table A1. Endmembers for three component mixing model (all concentrations in mmol L\(^{-1}\)).

<table>
<thead>
<tr>
<th>Endmembers</th>
<th>Upper Lawn</th>
<th>Lower Lawn</th>
<th>Ovoid West</th>
<th>Ovoid East</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (shallowest)</td>
<td>Ca = 0.07, Mg = 0.02</td>
<td>Ca = 0.13, Mg = 0.05</td>
<td>Ca = 0.12, Mg = 0.03</td>
<td>Ca = 0.10, Mg = 0.03</td>
</tr>
<tr>
<td>B (deepest)</td>
<td>Ca = 3.24, Mg = 1.09</td>
<td>Ca = 1.94, Mg = 0.74</td>
<td>Ca = 3.79, Mg = 1.83</td>
<td>Ca = 2.25, Mg = 1.07</td>
</tr>
<tr>
<td>C (Fen GW)</td>
<td>Ca = 3.03, Mg = 2.23</td>
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Chapter 2: Drought-induced recharge promotes long-term storage of porewater salinity beneath a prairie wetland

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Abstract

Subsurface storage of sulfate salts allows closed-basin wetlands in the semi-arid Prairie Pothole Region (PPR) of North America to maintain moderate surface water salinities (TDS from 1 to 10 g L⁻¹), which influence communities of aquatic biota. However, it is unclear how the salinities of wetland ponds will respond to a recent shift in mid-continent climate to wetter conditions. To understand better the mechanisms that control surface-subsurface salinity exchanges during regional dry-wet climate cycles, we made a detailed geoelectrical study of a typical closed-basin prairie wetland (P1 in the Cottonwood Lake Study Area, North Dakota) that is currently experiencing record wet conditions. We found saline lenses of sulfate-rich porewater (TDS > 10 g L⁻¹) contained in fine-grained wetland sediments 2 – 4 m beneath the bathymetric low of the wetland and within the currently ponded area along the shoreline of a prior pond stand. During the most recent drought (1988 – 1993), the wetland switched from a discharge to a recharge function allowing salts dissolved in surface water to move into wetland sediments beneath the bathymetric low of the basin. However, groundwater levels during this time did not drawdown to the elevation of the saline lenses, suggesting these features formed during more extended paleo-droughts and are stable in the subsurface on at least centennial timescales. We hypothesize a “drought-induced recharge” mechanism that allows wetland ponds to maintain moderate surface salinity under semi-arid climate. Discharge of drought-derived saline groundwater has the potential to increase the salinity of wetland ponds during wet climate.
Introduction

Millions of prairie wetlands throughout the ~750,000 km² Prairie Pothole Region (PPR) of the glaciated North American Great Plains (Figure 1a) serve as critical habitat for amphibians and migratory waterfowl (Batt et al., 1989; Dahl, 2014). Although situated in a semi-arid climate where annual evaporation is almost double annual precipitation (Rosenberry, 2003), wetlands occupying small topographic depressions on low permeability glacial till support surface water ponds that capture snowmelt runoff in the spring and subsequently draw down during the open-water season (van der Kamp and Hayashi, 2009). The salinity of surface ponds influences habitat suitability for aquatic biota and varies widely (total dissolved solids [TDS] from < 0.5 g L⁻¹ to > 50 g L⁻¹) among proximal wetlands due to complex hydrological controls driven by landscape position and climate (Eisenlohr et al., 1972; Euliss et al., 2004; Hayashi et al., 2016).

Wetlands at higher topographic positions within hummocky glacial landscapes typically have small “seasonal” or “temporary” freshwater ponds that fill and dry annually, while those occupying lower landscape positions with greater catchment areas tend to be larger and have saltier, “semi-permanent” ponds that fill and dry in response to multi-annual trends in precipitation (Stewart and Kantrud, 1971). Pond salinity is dominated by sulfur salts generated from the oxidation of pyrite in clay-rich till. Groundwater in the till evolves from low salinity, Ca-HCO₃ facies in recharge areas to high salinity, Mg-Na-SO₄ facies in discharge areas (Goldhaber et al., 2014). Wetland ponds occupying higher landscape remain fresh by recharging surface waters and solutes into underlying fractured till (Hayashi et al., 1998a; Berthold et al., 2004; Parsons et al., 2004) and overflowing (i.e. fill-and-spill) into adjacent lower-elevation wetlands (Shaw et al., 2012). In contrast, salinity accumulates in low-lying “closed-basin” wetlands that lack surface drainage outlets and are enclosed by surroundings hummocks where
elevated groundwater levels act as a hydraulic barrier against out-migration of salinity from the basin (van der Kamp and Hayashi, 2009). While some wetlands and lakes in the PPR evolve hyper-saline surface waters (e.g. Last and Ginn, 2005), many closed-basin wetlands maintain surface ponds of moderate (i.e. brackish) salinity (TDS from 1 to 10 g L⁻¹).

Dry-wet cycles drive complex hydrological processes that control surface-subsurface exchanges of salinity in closed-basin wetlands. Seasonally, transient drawdown of the water table by transpiration of fringing phreatophytes (e.g. cattails, willows) can induce outseepage around the pond margins, forming “saline rings” of solute-rich porewater and evaporite crystals in peripheral wetland sediments (Meyboom, 1966; Hayashi et al., 1998a,b; Winter and Rosenberry, 1995; Nachshon et al., 2013). During more extended droughts when semi-permanent ponds dry, sulfate concentrates by evaporation in the shallow subsurface causing gypsum to precipitate and accumulate in wetland sediments (Eisenlohr et al., 1972; Arndt and Richardson 1989; Heagle et al., 2013; Pennock et al., 2014). During wet times, enhanced runoff from uplands, expanded pond areas, and water-table mounds in wetland margins re-mobilize salinity to surface ponds (Arndt and Richardson, 1993; Rosenberry and Winter, 1997; Nachshon et al., 2014; LaBaugh et al., 2016).

Competing air masses of vastly different temperature and moisture content originating from the Arctic, the Pacific coast, and the Gulf of Mexico control the extreme and dynamic dry-wet cycles characteristic of the mid-continental PPR (Bryson and Hare, 1974). While decadal-scale shifts between drought and deluge (sensu Winter and Rosenberry, 1998) typify the modern atmospheric record, longer and more extreme oscillations between wet and dry climate conditions were likely commonplace in the region over the past 2000 years (Fritz et al., 2000; Laird et al., 2003). Near the end of the 20th century, there was a shift throughout the PPR to a
warmer and wetter climate (Millett et al., 2009). During this time, record precipitation caused surface and groundwater levels in some parts of the PPR to rise to heights that have not occurred in the region in the past 100 – 500 years (Winter and Rosenberry, 1998). In response, lakes and wetland ponds in the PPR have expanded in volume and area (Mushet et al., 2015), and in some cases show counter-intuitive increases in salinity despite considerable additions of dilute rain and surface runoff (Nachshon et al., 2014; Goldhaber et al., 2016; LaBaugh et al., 2016).

Long-term records of prairie wetland hydrodynamics and geochemistry are essential to understand how pond salinities throughout the PPR are responding to current wet conditions, unprecedented in modern times. The Cottonwood Lake Study Area (CLSA) is a prairie wetland complex located in Stutsman County, North Dakota (ND); and has been the site of long-term groundwater and surface-water monitoring by the United States Geological Survey (USGS) since 1979 (Figure 1). We focus here on a closed-basin wetland (P1) with a semi-permanent pond of moderate salinity in the CLSA that has been the subject of numerous hydrological and biological investigations. During the period of long-term study, wetlands in this complex experienced highly variable climate conditions ranging from extreme drought to deluge (Winter, 2003). The pond in wetland P1 repeatedly dried and re-wetted each summer during a period of moderate to extreme drought from 1988 – 1993 before deluge conditions in 1993 caused the pond to expand to its current area. During the subsequent >20 years of wet climate, the mass of solutes in the P1 pond has risen steadily (LaBaugh et al., 2016).

Geoelectrical surveys can delineate the distribution of porewater salinity beneath prairie wetlands (Berthold et al., 2004; Heagle et al., 2013). However, the only other geoelectrical survey of a closed-basin wetland (i.e. Heagle et al., 2013) was during a drought when the wetland’s pond dried completely. Here, we present the first underwater geoelectrical survey of a
ponded, closed-basin prairie wetland under wet-climate conditions. The objectives of this study were to: (1) investigate the distribution of porewater salinity under a typical closed-basin prairie with a brackish, semi-permanent pond; (2) contextualize subsurface salinity patterns within the long-term hydrological record; and (3) extend current conceptual models of prairie wetland subsurface-surface salinity cycling to explain the patterns we observed during a wet climate.

**Study Area**

The CLSA is a 92 ha prairie wetland complex located on the Missouri Coteau, a glacial stagnation moraine, in Stutsman County, North Dakota (Figure 1). The Missouri Coteau (coteau from the French meaning “little hill”) rises more than 100 m above the surrounding terrain. The subsurface in the CLSA consists of poorly-sorted Pleistocene age till derived from Precambrian igneous and metamorphic rocks; early Paleozoic sandstones, limestones, and dolomites; and Cretaceous shales and siltstones deposited by repeated glacial advances and retreats over Pierre Shale of Cretaceous age. Well-sorted glaciofluvial deposits of clay, silt, sand, and gravel occur in the CLSA but are limited in extent, excepting a larger buried sand body that extends from the uplands on the east to a lowland valley on the west side of the study area (Figure 1d; Winter 2003). Regional groundwater modeling shows that the CLSA theoretically recharges intermediate flow systems discharging to Eric Lake to the west and the Pipestem Creek to the east (Winter and Carr, 1980). However, in reality groundwater flow is mostly restricted to the upper “brown zone” of oxidized till (K from $10^{-4}$ to $10^{-6}$ cm s$^{-1}$; Winter and Rosenberry, 1995) where abundant fractures have an average spacing of approximately 10 cm (Swanson, 1990). Groundwater flow is exceptionally slow through the underlying “grey” unoxidized till (K from $10^{-8}$ to $10^{-9}$ cm s$^{-1}$), which constitutes a regional aquitard at the CLSA and across the entire PPR
The brown zone of oxidized till ranges from approximately 1 – 14 m in thickness throughout the CLSA and contains abundant sulfate salts and oxidized iron compounds derived mostly from pyrite (Goldhaber et al., 2014). The brown zone is a regional phenomenon that extends throughout the PPR and is thought to have formed by exposure to atmospheric oxygen during paleo-droughts when water-table elevations were substantially lower (Hendry et al., 1986; Grasby et al., 2010).

The regional semi-arid climate has dry winters, variably wet summers, a long-term average annual temperature of 4°C, and a wide annual temperature range from -47 to 48°C. Long-term average annual precipitation and snowfall are 440 and 865 mm, respectively. Average annual maximum snow depth and lake evaporation are 300 mm and 810 mm, respectively (Rosenberry, 2003). The last regional drought in the vicinity of the CLSA lasted from 1988 to 1993 and was the second most extreme in length and intensity in the 20th century (Winter and Rosenberry, 1998). Record deluge beginning in the July of 1993 ended the drought and marked the onset of wetter climate in the region, with pre-drought (1958 – 1987) mean annual precipitation of 447 mm rising to 505 mm in the subsequent 22 years (1993 – 2014) (Mushet et al., 2015).

The CLSA, the site of long-term ecological monitoring since 1967 and long-term hydrological monitoring since 1979, contains 17 wetlands within a hummocky, glacial landscape with 33 m of local topographic relief (Figure 1b). The CLSA contains an extensive network of water table monitoring wells, piezometers, and staff gages that the United States Geological Survey (USGS) monitors regularly. Study wetlands designated by a “T” have “temporary” or “seasonal” surface water ponds. Those designated by a “P” have “semi-permanent” ponds that typically persist year round, except during droughts (Euliss et al., 2014). All of the wetland
ponds in the CLSA have dried completely at least once in response to drought during the period of long-term study (Winter, 2003). When the wetlands dry, efflorescent salt crusts (e.g. epsomite, mirabolite, gypsum) form on the exposed substrate and vegetation communities change markedly (LaBaugh et al., 1996; Swanson et al., 2003).

Wetland P1, the focus of our study, occupies a steep-sloped basin at intermediate elevation in the CLSA and typifies a closed-basin, semi-permanently ponded wetland containing oligosaline, Mg-SO₄ type pondwater with a long-term (1967 – 2002) mean specific conductance of 2.1 mS cm⁻¹ (Euliss et al., 2014). In this study we differentiate the transient wetland pond from the wetland itself, which is defined on the basis of soil type and vegetation (e.g. van der Kamp et al., 2016). What was initially identified as wetland P1 in early studies (e.g. Winter and Carr, 1980) is actually part of a contiguous wetland that was delineated by hydric soil identification to include two adjacent sub-basins (T1 and T3) (Winter, 2003). Following the onset of record wet conditions in 1993, the ponded area of P1 expanded to merge with the surface ponds in T1. The merging of the two ponds in the P1/T1 basin has persisted to present (Figure 1). Additionally, in 1995, the combined P1/T1 pond merged with the T3 pond.

The high-storage capacity and lack of surface drainage outlets within the P1 basin have allowed it to contain surface water for most of the period of record, though it has dried to expose the wetland’s substrate in 1961, 1974, 1976, 1977, 1988, 1989, 1990, 1991, and 1992 (LaBaugh et al., 1996; Swanson et al., 2003). Shallow-marsh vegetation (e.g. sprangle-top [Leptochloa fascicularis], smartweeds [Polygonum spp.], sedges [Carex spp.]) and deep-marsh vegetation (e.g. hardstem bulrush [Shoebnapectus acutus], cattails [Typha spp.]) are transient in space and time depending on pond stage and salinity (Poiani et al., 1996; Swanson et al., 2003). Recently, Zeng et al. (2011) reported that unusually high levels of reduced sulfur and dissolved organic
matter they sampled from shallow (<0.5 m depths) wetland sediments in P1 abiotically degraded recalcitrant chloroacetanilide pesticide compounds on the timescale of hours. Here, we directly address the broad hydrological processes that drive the hydrogeochemical evolution of these unique a porewaters on geological timescales.

Methods

Hydrological Measurements

To better understand how P1 responded to an extreme shift from drought to deluge, we present groundwater and pond-stage data collected from 1979 – 2014 as part of the CLSA’s long-term monitoring program (Mushet et al., 2017). Water levels in the CLSA are measured weekly during the open-water season with permanent staff gages that are re-surveyed annually and calibrated to the bathymetric low point of each wetland (Euliss and Mushet, 2011). The water level in groundwater wells is measured once every other week from April to October and once per month during the winter. Details on well installation and lithology can be found in Winter and Carr (1980), Winter and Rosenberry (1995), and Winter (2003). On August 25, 2015, we installed a temporary, steel piezometer 3.29 m beneath the sediment surface in the center of P1, developed with pond water and a drive rod, and allowed to recover for two days before head measurement on August 27, 2015.

We estimated the historic extent of the ponded area of P1 from several sources. Winter and Rosenberry (1995) present the pond area during pre-drought (1979 – 1988) conditions, delineated by plane-table survey around the date of July 26, 1983. To estimate the area of transient ponding recorded during drought conditions on July 2, 1992 we hand contoured an
isoline corresponding to the measured pond elevation from P1 basin bathymetry we measured along our geoelectrical field survey lines (Figure 1c). We used georeferenced aerial photographs from the USDA National Agriculture Imagery Program (NAIP) to estimate the area of the merged P1/T1 pond on July 20, 2014 (ESRI, 2017).

All hydrological elevation data were surveyed to a common benchmark, and have been presented in numerous studies, reviewed by Winter (2003). In 2008, light detection and ranging (LiDAR) data was collected over the entire CLSA and translated into a digital elevation model (DEM) of surface topography. In order for archival well and surface-water elevation data to be consistent with the DEM, a correction factor of 0.36 m was added to all prior elevation measurements. For example, prior studies report the bathymetric low point of P1 as 557.7 m whereas our study reports this elevation as 558.06 m. Despite this datum shift, all hydrological measurements remain internally consistent and are reported in meters above NAVD 88.

**Geoelectrical Field Surveys**

In August 2010 we collected five ~8 m length, 5 cm diameter cores at the P1 pond margin and adjacent uplands (core geochemistry data presented in Goldhaber et al., 2014) using a direct push, truck-mounted Geoprobe® tool (Figure 1). The Geoprobe® Electrical Conductivity System collected downhole electrical conductivity (EC) measurements at 0.015 m intervals using a 4-point electrode array with alternating current. Kejr, Inc. (2015) details the specifications of the Geoprobe® Electrical Conductivity System.

In August 2014 we made an underwater electrical resistivity imaging (ERI) survey beneath the ponded area of P1 to evaluate subsurface stratigraphy and wetland porewater salinity. The ERI method utilizes direct electrical current between multiple combinations of
source and potential electrode pairs located along survey lines at the land surface. Apparent resistivity values calculated from hundreds to thousands of different electrode combinations represent the weighted average of resistivity (or its inverse: conductivity) for earth materials along electric current flowpaths. Data inversion produces non-unique 2D and 3D models (herein termed “inversion models”) of gridded resistivity/conductivity values representing the subsurface that best explain surface measurements (Robinson et al., 2008).

We used a SuperSting ™ R1/IP (Advanced Geosciences, Inc.) with 28-electrode marine cables at 6 m spacing (total survey line length was 162 m) in the extended dipole-dipole array configuration included in the EarthImager 2D program (AGI, 2009). We designed our configuration with n = 6 and a = 4 electrode spacing, where “a” is the spacing between both potential and current electrode pairs and “na” is the spacing between the innermost current and potential electrodes. This array configuration has a lateral resolution of 3 m, a vertical resolution of approximately 1.5 m, and a median depth of investigation of 35 m (Loke, 2000).

At the time of our survey, the maximum depth of the wetland pond was ~2 m. We collected data along seven different survey transects traversing the ponded area of P1 (Figure 1c). Two survey lines overlapped in the center of P1 to form a 210 m transect (A to A’ in Figure 1c). We anchored one end of the marine ERI cables to the exposed wetland sediments fringing the pond shoreline and extended cables into the open-water area from a rowboat, ensuring lines were taut before lightly tamping into the underlying soft sediments by foot. We manually recorded pond depth along the survey lines at regular intervals and used a Total Station (Beijing Topcon Auto Level AT-22) to record the relative elevation of portions of our survey that ran onto land. We manually measured the conductivity of the pond water column using a WTW Multi 3400i Meter and TetraCon 325 conductivity cell.
We made inversions of our ERI survey data with EarthImager 2D, using the “smooth model inversion” setting, with smoothness and damping factors of 10. This inversion algorithm, also known as “Occam’s inversion” finds the smoothest possible model to fit the data that fits an \textit{a priori} Chi-squared statistic (AGI, 2009). We jointly inverted the two overlapping survey lines on the transect from A to A’ (Figure 1c) to create a single “merged” 2D inversion. Since underwater ERI inversions are sensitive to the specified surface-water conductivity value, we input the measured pondwater conductivity as an \textit{a priori} value in all of our inversions and also inverted our data with no specified pond conductivity (e.g. Loke and Lane, 2004). We found no substantial differences in the inversion models generated using these two inversion approaches, and present results using the measured pond conductivity (3.0 mS cm\(^{-1}\)) as an upper boundary condition in the model.

\textit{Wetland Sediment Cores}

In March 2015 we recovered 6 sediment profiles from the P1 basin (Figure 1c) ranging from 0.97 to 2.10 m depths below the sediment interface to calibrate geophysical measurements directly to the physical and chemical properties of the wetland sediments. We augured a hole through the ice at each location and collected a first drive with a Livingstone-type drive rod with a Bolivia adapter—a 7 cm diameter polycarbonate barrel in which the sample is stored until analysis (Mybro and Wright, 2008). For subsequent drives at each location we used a Livingstone corer with a 5 cm diameter stainless steel barrel, which required extrusion in the field before wrapping in plastic film and placing in PVC tubes for storage. We collected a duplicate sediment profile in the center of P1 for core rehydration experiments (Section 3.4).
We refrigerated the cores at < 4 °C and transported by van to Syracuse University for laboratory analyses. At Syracuse University, we split individual cores lengthwise and analyzed; one half for bulk EC at 10 cm intervals and the other for wet density, water content, organic matter content, and porosity at three corresponding 2 cm intervals (0 – 2 cm, 4 – 6 cm, 8 – 10 cm) using standard American Society for Testing and Material methods (ASTM, 2010, 2014). We also analyzed subsamples from the core collected in the center of P1 for grain size using a Coulter LS 230 Laser Diffraction Particle Size Analyzer (Fiorentino, 2017).

In order to measure bulk EC of the cores, we used a Scintrex Geopulse with a four-point electrode array. The Geopulse measures resistance (R) using a commutated DC square wave. We fabricated circular (0.07 m diameter) stainless-steel plates to use as current electrodes and secured one to each end of individual cores using Spectra® 360 conductive electrode gel to ensure good contact at the electrode-sediment interface. We inserted two stainless steel potential electrode leads 0.01 – 0.02 m into the sediment at the center of the core and maintained constant spacing between electrodes as we made measurements down the length of the core at 10 cm intervals. We measured R using a 5 mA current, converted R to resistivity (ρ) by multiplying R by the ratio of the core segment’s cross-sectional area to length (A/L), and calculated bulk (solid + fluid) EC as the inverse of that measurement. Since EC is also a function of temperature, we recorded internal core temperatures at the center of each 10 cm sampling interval using a thermocouple and corrected all bulk EC values to 10 °C (the average annual sediment temperature below P1 at depth) using the following equation adapted from Hayley et al. (2007):

\[
\sigma_{10} = \left[ \frac{m(T_i - 25) + 1}{m(T_{std} - 25) + 1} \right] \sigma_i
\]  
\text{Eq 1}
Where $\sigma_i$ and $\sigma_{10}$ are the initial bulk EC measurement and corresponding correction to 10 °C (in mS cm$^{-1}$), respectively; $T_i$ and $T_{\text{std}}$ are the measured temperature and the correction temperature (in this case 10 °C), respectively; and $m$ is the fractional change of bulk EC per degree Celsius. We assumed the latter as 0.0183 based on laboratory experiments for a range of glacial sediments between 0 and 25 °C (Hayley et al., 2007).

**Core Hydration Experiment**

We rehydrated relatively homogenous wetland mineral sediments with synthetic saline fluids in a controlled laboratory setting to build an empirical petrophysical relationship between bulk and fluid EC. For this experimental study, we used a duplicate core of mineral wetland sediment collected from the center of P1 at 0.90 to 1.66 depths below the sediment-water interface. We segmented this 0.76 m core interval into eleven 0.06 – 0.07 m length core segments and measured bulk EC using a SuperSting™ R1/IP (Advanced Geosciences, Inc.) with voltage divider and using the 4-point electrode array setup described above with current and potential electrode spacing of 0.06 – 0.07 m and 0.03 m, respectively. We calculated bulk EC and temperature corrected all measurements to 10 °C as described above.

We weighed and oven dried the core segments for 24 hours at 60 °C; and then weighed again, wrapped in cheesecloth, and secured with string. We used deionized (DI) water and Fischer Scientific (99+% “extra” pure) magnesium sulfate heptahydrate or “epsomite” (MgSO$_4$·7H$_2$O) to prepare 8 different fluid treatment levels: DI and 50, 150, 250, 350, 450, 550, 650 molal solutions of MgSO$_4$. We randomly placed core segments in individual plastic ziplock bags containing 200 ml of fluid at each treatment level with duplicates at the DI, 250, and 450 levels (8 levels + 3 duplicates = 11 total treatments). We then lowered the bags into 10-gallon
buckets of water until all air evacuated from the bags, and sealed them with duct tape prior to complete submersion so no water from the bucket could leak into the bags. We left the bags at the bottom of the buckets where they rehydrated for 10 days with treatment fluids under the hydrostatic pressure of the overlying water column. This approach is widely used in the ceramic industry to rehydrate desiccated pottery clay. We did an initial pilot experiment using a treatment fluid containing a dye tracer, and found the treatment fluid had homogenized within the core during the rehydration process.

After 10 days we removed core segments from treatment baths, weighed them, and measured bulk EC at three locations around the circumference of the core; temperature correcting to 10 °C as described above. We then split segments into two ~80 g subsamples and centrifuged at ~3,000 rpm for 1 hour. We measured the fluid EC (temperature corrected to 25 °C) of the resulting supernatant using an Amber Science Model 4083 EC Meter and with 535/545 Multi Purpose Cell.

Groundwater Geochemistry

We obtained archival geochemical data (Mushet et al., 2017) for select wells in the P1/T1 basin (13, 14, 15, 16, 17, 20, 23, 25, 26) for fluid EC and total dissolved solids (TDS), which were sampled between 1980 – 1991 using standard methods described in LaBaugh et al. (1987). Samples were analyzed for fluid EC, major ions (Ca, Mg, Na, K, Cl, SO4), and total alkalinity at the USGS National Laboratory in Denver or the U.S. Fish and Wildlife Service Laboratory using methods described by Fishman and Friedman (1989) or the U.S. Fish and Wildlife Service laboratory using methods described by Swanson et al. (1988). We calculated TDS as the sum of major ions and total alkalinity. In August 2013 we re-sampled select wells (13, 14, 16, 17, 20)
Results

Hydrological Record

Wetland P1 pond levels fluctuated between 1979 and 2014 in response to regional dry-wet meteorological cycles (Figure 2a,b), as shown by the Palmer Drought Severity Index (PDSI) (http://www.ncdc.noaa.gov/cag/; North Dakota Climate Region 5), an integrated metric of drought that is a function of precipitation, potential evapotranspiration, and antecedent soil moisture (Palmer, 1965). Values of the PDSI above and below +4 and -4 indicate extreme wet or drought conditions, respectively (Millett et al., 2009). During initial observations (1979 – 1988) the P1 pond was shallow (mean depth ~ 0.7 m) with annual oscillations of pond stage driven by snowmelt runoff and evapotranspiration during the open-water season (Parkhurst et al., 1998). Surrounding groundwater elevations were mostly above pond stage at this time showing that groundwater discharged into the pond except in mid-to-late summer when drawdown driven by evapotranspiration of riparian vegetation caused water-table depressions to form around the wetland that were highly variable in time and space (Figure 2; Winter and Rosenberry, 1995).

During an extended regional drought (1988 – 1993) a shallow pond (mean depth ~ 0.2 m) formed in the spring or mid-summer in response to snowmelt and rain events that occurred following the complete drying of the wetland in 1988, 1989, 1990, 1991, and 1992 (Figure 2a). Throughout the drought, water levels in wells located at the margin of the wetland (13, 15, 17, 20, 23, 25, 26) repeatedly dropped below both the pond stage and the bathymetric low of the
pond bottom surface, forming a recharge gradient into the underlying sediments (Figures 2c and 3). Discharge gradients from marginal wells into the central pond temporarily resumed following snowmelt and mid-summer rain in 1989, 1990, 1991, and 1992 (Figure 3).

Heavy rains beginning in the July of 1993 marked the onset of a period of wetter climate in east-central North Dakota that has persisted to present. During this time, the two ponded areas of P1 and T1 expanded and merged, with the maximum pond depth in the basin oscillating around 2 m, reaching a peak of nearly 3 m in 1999 (Figure 2b). Groundwater levels quickly responded to the onset of wet conditions, with water levels in surrounding upland wells rising approximately 1 – 5 m above pond stage to steepen the groundwater gradient towards the center of the basin (Figure 2c). However, drawdown of the water table beneath the elevation of the pond still occurred in response to riparian transpiration during wet conditions (Figure 2c). During this recent high stand of the P1 pond (August, 2015), we measured a vertical head gradient of 0.011 beneath the center of the wetland from a depth of 3.29 m (below the sediment-water interface) to the pond, indicating that groundwater discharged upwards beneath the center of the wetland at this time.

**Physical Properties of Wetland Sediments**

All six sediment profiles consisted of a ~0.5 m upper layer of organic-rich mud overlying fine-textured mineral sediments except for the core closest to the eastern shore of P1, which consisted of sand and gravel below the organic-rich upper layer. Since a large amount of water was lost from the latter core during extrusion, we omit quantitative analyses of its core segments from the following results. Samples from the upper 0.5 m layer of organic-rich sediments (n = 60) had higher means and standard deviations for organic matter content (18 ± 9 %), gravimetric
water content (1.91 ± 1.05) and porosity (0.60 ± 0.12) and a lower mean for wet density (1.15 ± 0.26 g cm⁻³) than the more homogenous underlying mineral sediments (7 ± 2 %, 0.41 ± 0.10, 0.46 ± 0.08, 1.60 ± 0.17 g cm⁻³, respectively; n = 127). The average texture of the mineral sediments from the core we collected in the center of P1 was 6 % sand, 63% silt, and 31 % clay. Fiorentino (2017) presents detailed results of core analyses.

**Geoelectrical Properties of Glacial Sediments**

Inversions of our ERI survey data produced six 2D cross-sectional models of the bulk electrical conductivity (bulk EC) distribution of the wetland subsurface (Figure 4). Here, we present inversion model data with water column and all model cells below 45° angles from the model edges removed. Individual 2D inversion models representing the subsurface below P1 were comprised of 673 to 704 grid cells, except for the merged line of 1393 cells (4796 cells across all 6 survey transects), with a total with inferred conductivity values ranging from approximately 0.5 – 3.5 mS cm⁻¹ and individual model root mean square (RMS) errors between 1 and 4% (Figure 4). Independent inversion results among the lines showed remarkably consistent spatial patterns, delineating a vertical transition in the subsurface beneath the ponded area of P1 from a 6 – 8 m upper layer of conductive wetland sediments (bulk EC > 1.0 mS cm⁻¹) to lower-conductivity glacial till (bulk EC from 0.5 – 1.0 mS cm⁻¹) at elevations between 550 and 552 m (Figure 4). The lower-conductivity value range is in excellent agreement with prior ERI surveys of dense glacial till containing pre-modern porewater in the PPR (0.42 – 0.66 mS cm⁻¹ in Berthold et al., 2004; ~0.75 mS cm⁻¹ in Heagle et al., 2013). Our measured depth of wetland sediments also agrees well with those from a similar wetland in the PPR (~8 m in Heagle et al.,
as well as the expected depth of fill considering regional rates of sediment accumulation in uncultivated PPR catchments over the 12 ka following glaciation (e.g. Skagen et al., 2016).

The bulk EC of the organic-rich core segments (1.92 ± 0.4 mS cm⁻¹, n = 30) was higher than the underlying mineral sediments (mean ± s.d. = 1.5 ± 0.2 mS cm⁻¹, n = 46) due to the higher porosity and water content of the former (Figure 5a). It is no surprise that our meter-scale ERI survey did not capture the thin organic surface layer due to its shallow depth (~0.5 m) and lack of geoelectrical contrast with the overlying pond (e.g. Loke and Lane, 2004). The 321 inversion grid cells positioned directly beneath the pond’s sediment-water interface at elevations between 557 and 559 m (mean ± s.d. = 1.4 ± 0.2 mS cm⁻¹) matched well with direct measurements of fine-grained wetland sediments we recovered from our sediment cores (mean ± s.d. = 1.5 ± 0.2 mS cm⁻¹, n = 46) (Figure 5b,c). The ~1 m sand and gravel core (not measured for bulk EC due to water loss) from the easternmost location of our coring transect (A to A’ in Figure 1c) agrees with the location of a lower EC zone (~1.0 mS cm⁻¹) in the upper layer of the corresponding inversion model (Figure 4). Arndt and Richardson (1993) also found a deposit of coarse-textured alluvium in the subsurface of P1, which aligns with a zone of similarly low EC in our westernmost N-S oriented inversion model next to the surface spillway from an adjacent wetland (T3) (Figure 4).

The most striking features in our inversion models were discrete and overlapping zones of bulk EC (2.5 – 3.5 mS cm⁻¹) elevated from that of the surrounding mineral sediments (1.0 – 2.0 mS cm⁻¹). The mean and median conductivity values of all model grid cells from 2.5 – 3.5 mS cm⁻¹ were ~3.0 mS cm⁻¹. Since the bulk EC of prairie wetland sediments is a direct function of porewater salinity (e.g. Heagle et al., 2013), we identify these features as “saline lenses.” Taken together, our 6 inversions consistently assigned 95% of all model grid cells with
conductivity values of 2.5 – 3.5 mS cm\(^{-1}\) to elevations between 554 and 556 m; delineating the extent of two saline lenses located 2 – 4 m under the bathymetric low of P1 and near its western margin beneath the currently ponded area (Figure 4). The saline lenses are bounded by more discontinuous transitional zones of intermediate EC (2.0 – 2.5 mS cm\(^{-1}\)) within the same elevation range.

The Geoprobe® produced ~8 m logs of “borehole EC” at high depth-resolution (0.015 m) beneath four upland sites and the western margin of P1 (Figure 6). For the most part, the range of values collected by this \textit{in situ} measurement method (<0.1 – 4.4 mS cm\(^{-1}\)) fell within the range of our model inversions (0.5 – 3.5 mS cm\(^{-1}\)). Borehole EC values that were lower and higher than the value range of our inversion models respectively corresponded to the upper ~1 m of vadose zone in upland areas, and extremely fine cm-scale saline features beneath the western margin of P1 that were far beneath the vertical resolution of our ERI survey (~1.5 m). Upland borehole EC mostly oscillated between values of 0.5 and 1.2 mS cm\(^{-1}\), matching well with the lower geoelectrical layer of our ERT survey (0.5 – 1.0 mS cm\(^{-1}\)) and further confirming that the geoelectrical contrast in our inversion models between 550 and 552 m is the boundary between glacial till extending from the uplands and more conductive, overlying wetland fill.

Borehole EC of wetland sediments along the western margin of P1 identified two zones with higher EC compared to that of surrounding shallow mineral sediments and upland tills (Figure 6). In this area, a thin (~0.10 m), less-conductive (<0.5 mS cm\(^{-1}\)) zone occurred over the more-conductive (~2.5 mS cm\(^{-1}\)) upper ~1 m of wetland sediments (559 – 560 m). Both were within where the water table fluctuated (from 558 – 561 m as inferred from co-located well 17) during the period of long-term study. A lower elevation (552 – 556 m) zone 4 – 8 m beneath the land surface had similarly high-conductivity (~2.5 mS cm\(^{-1}\)) and was overlain by a large
conductivity peak (Figure 6) occurring over a ~0.5 m depth interval with a maximum value of 4.3 mS cm\(^{-1}\) at 555.8 m. This peak is notably located within the elevation range where we estimate the offshore saline lenses to occur beneath the ponded area of P1 (554 – 556 m).

Relation of Sediment bulk EC to Porewater Salinity

The bulk EC of saturated wetland sediments is a direct function of porewater EC, though physical properties such as clay content and porosity influence this relationship (e.g. Waxman and Smits, 1968; Berthold et al., 2004). The bulk EC of sediment samples prior to treatment varied within a narrow range (mean ± s.d. = 1.5 ± 0.2, n = 11), consistent with samples from duplicate cores presented in Figure 4b. The bulk EC of samples treated with DI water remained the same (mean ± s.d. = 1.4 ± 0.1, n = 2), whereas the bulk EC of samples treated with saline fluid increased with porewater EC. Least squares regression yielded a tight linear relationship (\(R^2 = 0.94\)) between bulk and fluid EC, which we further constrained by 95% confidence bands to account for variability of physical properties among the different core samples (Figure 7a). Heagle et al. (2013) also developed a linear relationship between bulk and fluid EC for wetland sediments in the PPR, which differs from ours in slope and intercept likely due to of site-specific differences in sediment texture and lithology.

We used samples of groundwater EC and TDS collected from wells in the P1/T1 basin from 1980 – 1991 to both validate and extend experimental results. All groundwater samples were of the Mg-SO\(_4\) or Ca-SO\(_4\) types. Fluid EC has a power law relationship (\(R^2 = 0.97\)) to groundwater TDS in the P1 basin (Figure 7b). For the most part, the P1 basin contains brackish groundwater with fluid EC and TDS varying from around 1 – 5 mS cm\(^{-1}\) and 1 – 5 g L\(^{-1}\), respectively. However, two monitoring wells in the wetland (13 and 17) contained salinewaters;
with fluid EC and TDS ranging from around 10 – 16 mS cm\(^{-1}\) and 12 – 22 g L\(^{-1}\), respectively. Sulfate was the dominant component of groundwater salinity; ranging from 52 – 75% and 71 – 84% of the TDS by weight in brackish and saline groundwater, respectively. The two wells containing saline groundwater (TDS > 10 g L\(^{-1}\)) are screened within the elevation range of the offshore saline lenses we imaged by ERT, and have fluid EC within the range that we independently estimated for the saline lenses using our petrophysical model (Figure 7). The select wells we re-sampled for groundwater EC in 2013 were not substantially different from values measured from 1980 to 1991, indicating that groundwater salinity in the P1/T1 basin is extremely stable on decadal timescales, consistent with the findings of Berthold et al. (2004) for groundwater elsewhere in the PPR (Table 1).

We used the relationships defined in Figure 7 for bulk/fluid EC and fluid EC/TDS to estimate the mass of TDS contained in porefluids occupying the saline lenses. We contoured two areas beneath the ponded area of P1 where bulk sediment EC ranges between 2.5 to 3.5 mS cm\(^{-1}\), delineating a large saline lens beneath the center of the wetland basin (5850 m\(^2\)) and a smaller lens beneath the southwestern portion of the currently ponded area (223 m\(^2\)) (Figure 4). We assumed the porosity of wetland sediments to be 0.5 based on our core measurements. The pore fluid EC in the saline lenses should range from 10 to 23 mS cm\(^{-1}\) based on our re-hydration experiments, which corresponds to a TDS range from 13 to 37 g L\(^{-1}\) (Figure 7b). If we assume the bulk EC of the saline lenses can be approximated by the mean/median of their combined grid cell values (~3.0 mS cm\(^{-1}\)) they would contain a fluid of 16.6 mS cm\(^{-1}\) with TDS of 23.7 g L\(^{-1}\). Inversion model nodes with bulk EC > 2.5 mS cm\(^{-1}\) had a narrow range of elevations (554 – 556 m), with a vertical resolution of ~1.5 m. As a conservative estimate, we assumed the average thickness of saline lenses is 2 m.
Using the full range of bulk EC values (2.5 to 3.5 mS cm⁻¹), we estimate that the saline lenses we imaged in the P1 wetland sediments contain from 7.0 x 10⁴ to 2.3 x 10⁵ kg of dissolved solids, or 1.4 x 10⁵ kg assuming a uniform bulk EC value of 3.0 mS cm⁻¹. At the time of our ERI survey, the P1/T1 pond contained a TDS load of approximately 1.7 x 10⁵ kg based on measured pondwater EC (3.0 mS cm⁻¹) and stage-volume/fluid EC-TDS relationships developed by LaBaugh et al. (2016). Therefore, the saline lenses we imaged in our ERI survey could store anywhere from 50 to 130% of the current pond salinity in the subsurface, or 85% assuming a uniform bulk EC of 3.0 mS cm⁻¹.

Discussion

Influence of Surface Hydrology on Subsurface Salinity

In semi-arid regions, discrete pockets of saline groundwater can develop in recharge areas due to mobilization and evapoconcentration of surface salts by infiltrating waters (Rabemanana et al., 2005; Massuel et al., 2006; Cartwright et al., 2007a). In our study, we imaged and directly sampled saline porewater (TDS > 10 g L⁻¹) in the subsurface of P1 contrasting with brackish porewater (TDS from 1 – 10 g L⁻¹) of surrounding wetland sediments (Figure 7) and uplands (Goldhaber et al., 2014). Although P1 functioned as a groundwater discharge wetland for the majority of the period of study (1979 – 2014), evapotranspiration induces outseepage of pondwater to the shallow subsurface around the wetland margin during summer months under both wet and dry climate (Winter and Rosenberry, 1995; LaBaugh et al., 2016). Additionally, complete drying of the wetland pond and associated groundwater drawdown
during extreme drought from 1988 – 1993 effectively transformed P1 into a recharge basin (Swanson et al., 2003).

To understand the surface processes that control the subsurface distribution of salinity in P1, we compared areal patterns of bulk EC from our ERT survey to historic variations of pond extent (Figure 8). We found elevated salinity in P1 sediments was localized beneath the bathymetric low of the wetland where intermittent ponding occurred during extreme drought from 1988 – 1993 (Figure 2). We identify the reduced area of the pond during this time by the July 1992 shoreline, which corresponds to the mean pond depth during the drought (~0.2 m). Additionally, peripheral saline features around the margin of P1 align with the location of the pond shoreline in pre-drought conditions (1979 – 1988). We identify this intermediate area by the July 1983 shoreline. During this time the pond shoreline fluctuated within a large band of riparian vegetation (e.g. bulrush, cattails), which later submerged and drowned in response to pond expansion in 1993 (LaBaugh et al., 1996; Poiani et al., 1996).

Although we measured a discharge gradient beneath the bathymetric low of P1 during the recent high stand (0.011 in August, 2015), the reduced area of the central pond became a zone of depression-focused recharge (e.g. Lissey, 1971) following snowmelt and rain events during the extended drought between 1988 and 1993 (Figure 3). During this time, surface solutes in the pond concentrated within center of the basin, elevating pond EC from < 2 mS cm\(^{-1}\) in pre-drought conditions to >7 mS cm\(^{-1}\) when the ponded area contracted (LaBaugh et al., 2016). Solutes subsequently moved downward into the wetland subsurface as the wetland repeatedly dried and filled within the reduced area of ponding in response to seasonal cycles of evapotranspiration, infiltration, rainfall and surface runoff. The lattermost diluted the surface pond back to ~2 mS cm\(^{-1}\) by 1992 and allowed the salt-sensitive hybrid cattail (*Typha glauca*) to germinate in the
shallow wetland sediments (Swanson et al., 2003; LaBaugh et al., 2016). This manner of depression-focused recharge probably constitutes the ubiquitous mechanism by which surface salinity is able to concentrate beneath the bathymetric low of discharge wetlands during droughts (e.g. Eisenlohr et al., 1972; Heagle et al., 2013), which over the long-term serves to maintain the unexpectedly low surface water salinities of wetlands under semi-arid climate.

Saline rings with porewater EC > 10 mS cm⁻¹ and abundant sulfur salts occur in the riparian fringe of prairie wetlands where evapotranspiration drives lateral outseepage from ponds into the shallow subsurface (e.g. Arndt and Richardson, 1989; Rosenberry and Winter, 1997; Nachshon et al., 2013). Our imaging of a relict saline ring beneath the current ponded area corresponds well with the location of an evapotranspiration-induced groundwater trough that often formed along the margin of P1 during late summer when the pond occupied the intermediate area (Figure 8; Figure 11 in Winter and Rosenberry, 1995). This study, to our knowledge, is the first to document a relict saline ring under an inundated portion of a prairie wetland. The long-term persistence of both peripheral and centrally located saline features following pond expansion (>20 years) is a novel finding, and suggests that the location of prior pond areas may be reconstructed using geophysics where long-term hydrological records are unavailable.

Response of Groundwater Levels to Drought

The relative position of the water table adjacent to surface ponds controls the ability of surface salinity to migrate into the subsurface beneath prairie wetlands (Sloan, 1972; Jolly et al., 2008; van der Kamp and Hayashi, 2009). Multiple survey methods (ERI, borehole EC, groundwater sampling) independently corroborate a zone of elevated porewater salinity several
meters below the land surface within a narrow elevation range (554 – 556 m). Since groundwater gradients towards P1 prevail during wet times, drawdown of the water table during drought must define the lower extent to which surface salinity can mobilize into underlying wetland sediments.

To contextualize modern and paleo-responses of the water table to drought in the P1 basin, we compiled the long-term record of water-table elevations and borehole lithology for the wells occupying the P1/T1 lowland and two local drainage divides separating the basin from the downslope valley and uplands flanking its western and eastern margins, respectively (Figure 9, Table 1). Water-level maxima occurred during the recent wet period (post July 1993 deluge) when pondwater pooled in the basin lowlands and elevated water levels in surrounding hummocks drove groundwater to discharge towards the pond. In contrast, well levels reached record minima during the 1988 – 1993 drought, but did not drop into the zone of salt accumulation. Therefore, although the modern record identifies the fundamental hydrologic processes that could lead to the areal distribution of saline features we observed in the P1 basin (Figure 8), the saline lenses we imaged must have formed during a prior period of even more extended drought when the water table fell deeper below the wetland subsurface. The last regional drought of comparable intensity and duration that could have potentially affected such a drawdown was that of the 1930’s dust bowl (Winter and Rosenberry, 1998), which was not quite as severe and only slightly longer than the 1988 – 1993 drought. Thus, the saline lenses must have formed at or before that time and persist in the surface on at least centennial timescales.

The position of the brown-grey till transition provides further indirect evidence that the water table in the P1 basin maintained equilibrium levels in the deep geologic past at lower elevations than achieved during transient drawdowns between 1988 and 1993. Several geochemical studies of PPR till independently conclude that the thick (>2 m) veneer of oxidized
till throughout the PPR must have formed by exposure to atmospheric oxygen over millennial timescales (Remenda and Birks, 1999; Hendry et al., 1986; Grasby et al., 2010; Goldhaber et al., 2011). Therefore, the brown-grey till transition is broadly considered as an indicator of “paleo-water table” depths that occurred under warmer and drier climate conditions in the mid-to-late Holocene (e.g. the Altithermal period, ca 7500 – 4000 BP; Hendry et al., 1986; Grasby et al., 2010). The fact that the brown-grey till transition extends below the bathymetric low of P1 throughout its basin (Figure 9) suggests that the recharge function observed during the 1988 – 1992 drought (Figure 3) may have been the norm on millennial timescales in the geologic past when the water table was several meters lower than present.

The lithology of the CLSA suggests a physical mechanism by which the water table could be constrained at a lower elevation beneath the P1 basin during paleo-droughts. A large, sinuous buried sand body extends from the uplands to the east of P1, around its southern and western margins, and intersects with a lower elevation wetland (P8) occupying the valley to the northwest (Figure 1d). Groundwater buffering by this sand lens caused P8 to show the slowest decline in pond stage of any of the CLSA wetlands during the 1988 – 1992 drought (LaBaugh et al., 1996; Winter, 2003). Groundwater flowpaths refract towards buried sand lenses embedded in low-permeability glacial till that can act as “under-drains” (Freeze and Cherry, 1979; p. 202) to prairie wetland basins (Winter, 2003; Berthold et al., 2004). The elevation of the sand lens intersecting local drainage divides bookending the P1/T1 basin coincides with the zone of salinity accumulation (Figure 9). This groundwater drain could further reduce the elevation of the water table below P1 during extended droughts, allowing runoff that pools in the center of the basin to infiltrate to depths where we observed salinity to accumulate in the subsurface.
“Drought-induced Recharge:” A Process with Implications for Long-term Salt Cycling in Prairie Wetlands

Wet climate typically enhances groundwater recharge in semi-arid regions (Scanlon et al., 2006; Hayashi and Farrow, 2014). In the hummocky glacial landscape of the PPR, “depression-focused recharge” is an important mechanism by which runoff collecting in small depressions can overcome the warm season atmospheric moisture deficit and recharge local aquifers (Lissey, 1971; van der Kamp and Hayashi, 1998; Berthold et al., 2004). Previously, this process has only been considered to be important beneath wetlands in high landscape positions and not low lying, closed-basin wetlands where surrounding groundwater is higher than the wetland pond, creating a hydraulic barrier against outseepage from the basin (Winter, 1999; Hayashi et al., 2016). Based on the results of this study, we codify here “drought-induced recharge:” a process that occurs when an inland water body located in a groundwater discharge setting develops a recharge function during drought. This reversal of function allows intermittent runoff to mobilize surface salinity towards the bathymetric low where it can infiltrate to the water table, which draws down to some depth beneath the wetland bed in response to drought (Figure 10).

Heagle et al. (2013) proposed a similar model by which closed-basin wetlands recharge surface salinity during drought, leading to the accumulation of gypsum and saline porewaters in the shallow subsurface. They also found that the portion of porewater salinity that did not precipitate as solid salts gradually moved back to the pond after re-wetting (3 – 4 years to reach pre-drawdown salinity levels) by complex mixing processes that are not well understood but are thought to include: diffusion, bioturbation, and short-range advection/dispersion caused by fluctuations in pond stage. LaBaugh et al. (2016) observed similar increases in salinity of ponded
water following the re-wetting of P1 following deluge, and attributed this mainly to the re-
dissolution of peripheral surface salts and expansion of the pond’s groundwater-shed. Here, we 
extend prior work by showing that a portion of porewater salinity that recharges during drought 
(i.e. the saline lenses) remains extremely stable in the wetland subsurface under wet climate 
conditions and persists there on at least centennial timescales if not longer (Figure 10).

Inter-related hydrological and petrophysical factors can promote the long-term storage of 
drought-induced recharge in wetland sediments. During droughts, the vertical permeability of 
fine-grained wetland sediments is enhanced by the oxidation of organic sediments, terrestrial 
plant roots, and numerous desiccation fractures. The elevation of the water table beneath the 
wetland necessarily controls the vertical extent of this secondary porosity. Therefore, salinity can 
rapidly (timescale of minutes) be flushed down to the water table by runoff and direct rainfall. 
However, this secondary porosity does not remain when wet times resume and the wetland 
sediments are once again saturated. Desiccation cracks swell shut and flooded roots die and 
decay; reducing sediment permeability and leading to a hysteresis with respect to solute transport 
systems between wet and dry times.

We estimate that groundwater at ~3 m depths discharges to the sediment surface on 
centennial timescales based on the vertical hydraulic gradient we measured beneath the 
bathymetric low of P1 during the recent high stand (0.011 in August, 2015) and the estimated 
saturated hydraulic conductivity of fine-grained wetland sediments at similar depths (10^-6 cm s^-1; 
Heagle et al., 2013). Furthermore, groundwater discharge typically decreases from the margin to 
the center of wetlands and lakes (Phannkuch and Winter, 1984); reducing the potential for salts 
beneath the central, deepest part of the wetland basin to move back into the wetland pond. Saline 
lenses could also occupy stagnation zones in groundwater flow systems where flowpaths diverge
(e.g. Winter, 1978) when discharge gradients resume or that are beneath the zone where the shallow mixing processes discussed by Heagle et al. (2013) are active.

Additionally, contact desiccated sediments with Mg and Na in saline recharge could promote swelling of clay-rich wetland sediments and associated decreases in hydraulic conductivity (Levy et al., 1988; Shainberg et al., 1988; Jolly et al., 1994). If saline recharge hydrates hydraulically disconnected “stagnant” micropores in clays, salinity could be extremely slow to diffuse back into active porespaces and discharge to the surface when wet times resume (e.g. Cartwright et al., 2007b). Dried and fractured sediment samples consolidated and swelled when we hydrated with MgSO₄ treatment fluids under hydrostatic pressure during our laboratory experiments, raising the bulk EC of the sample. Our sediment re-hydration experiment may very well simulate saline lens formation in response to drought-induced recharge and subsequent re-wetting of the surface pond.

Subsurface storage of dissolved and solid-phase salt allows closed-basin wetlands and lakes to maintain moderate salinities in a semi-arid climate (Langbien, 1961; Heagle et al., 2013). Although we estimate saline lenses to comprise approximately 50 – 130% of the modern pond salinity, this is likely only a small fraction of the total subsurface salinity. Heagle et al. (2013) estimated that the mass of solid-phase sulphate (mostly in the form of gypsum) beneath a similar wetland was an order of magnitude greater than that dissolved in the surrounding porewaters. While a full accounting of subsurface salinity storage is outside the scope of the current study, it is clear that gypsum, carbonates, and other sulphate salts accumulate in the sediments of P1, and likely comprise a larger fraction of the total subsurface pool (Arndt and Richardson, 1989; Pennock et al., 2014). Although the saline lenses are only a fraction of the total subsurface salt storage, they merit consideration as they represent salts explicitly removed
from the wetland surface water cycle that remains in the mobile, dissolved form. In contrast, sedimentary gypsum formed during droughts is not likely to be re-mobilized back to the pond during wet times by the gypsum-saturated groundwater that discharges into P1 from surrounding uplands (e.g. Goldhaber et al., 2014). Therefore, saline lenses represent important salt sinks on time-scales intermediate to long-term storage in the solid-phase, and short-term storage in shallower porewaters that more easily re-suspend into wetland ponds after re-wetting.

The response of wetland and lake hydrochemistry to drought depends on hydrogeologic setting (Webster et al. 1996; Winter, 2000). Goldhaber et al. (2016) presented a time series of surface water chemistries for 167 prairie pothole lakes and wetland ponds in Stutsman and Kidder counties (ND) comparing pre-deluge (1966 – 1976) and post deluge (2012 – 2013) sampling periods. They found that while in most cases increased precipitation and runoff diluted surface waters, a subset of ponds and lakes showed increases of dissolved sulfate during the recent period of wet climate. Of interest to the current study, inverse mass-balance modeling showed that “saline groundwater” (a sample from well 17 at CLSA was used) had to be mixed with atmospheric endmembers to achieve measured surface-water chemistries of the ponds that gained salinity. Further, the latter occurred over fine-grained tills with thicker oxidized surface layers than those associated with cross-bedded sands (Table 5 in Goldhaber et al., 2016). These data provide additional evidence that saline groundwater is stored in zones where large water-table drawdowns occur during paleo-droughts, and has the potential to increase the surface-water salinity of prairie lakes and wetlands under wet climate.
Conclusions

We made a detailed geoelectrical study of a typical closed-basin prairie wetland (P1 in the Cottonwood Lake Study Area, North Dakota) that is currently experiencing record wet conditions. We identified saline lenses of sulfate-rich porewater (TDS > 10 g L⁻¹) contained in fine-grained wetland sediments 2 – 4 m beneath the bathymetric low of the wetland and within the currently ponded area along the shoreline of a prior pond stand. During the most recent drought (1988 – 1992), the wetland switched from a discharge to a recharge function allowing surface salinity to move into wetland sediments beneath the bathymetric low of the basin. However, groundwater levels during this time did not drawdown to the elevation of the saline lenses, suggesting these features formed during more extended or more severe paleo-droughts and are stable in the subsurface on at least centennial timescales. We hypothesize a “drought-induced recharge” mechanism that allows wetlands to maintain moderate surface salinity under semi-arid climate. Drought-derived saline groundwater has the potential to increase the salinity of prairie wetlands and lakes under the wet climate conditions.

Acknowledgements

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surface water interactions at the Cottonwood Lake Study Area and elsewhere provided data and theory that are the foundation of the current work. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.
Table 1. Hydrogeologic and geochemical characteristics of select P1/T1 basin wells at the Cottonwood Lake Study Area, Stutsman County, North Dakota.

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Landscape Position</th>
<th>Surface Elevation (m)</th>
<th>Screened interval (m)</th>
<th>mean ± s.d TDS (1980 - 1991)</th>
<th>Mean ± s.d fluid EC (mS cm⁻¹) (1980 - 1991)</th>
<th>Fluid EC (mS cm⁻¹) 2013</th>
<th>Brown-to-grey till transition (m)</th>
<th>Min h (m) [Date]</th>
<th>Max h (m) [Date]</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>NW-SE drainage divide</td>
<td>563.99</td>
<td>549.99 - 549.33</td>
<td>3.80 ± 0.71 (n = 12)</td>
<td>3.66 ± 0.31 (n = 12)</td>
<td>2.87</td>
<td>556.98</td>
<td>557.63 [23-Mar-1993]</td>
<td>562.84 [20-May-1999]</td>
</tr>
<tr>
<td>15</td>
<td>T1 lowland</td>
<td>560.09</td>
<td>552.13 - 551.53</td>
<td>3.67 (n = 1)</td>
<td>3.72 (n = 1)</td>
<td>NA</td>
<td>556.12</td>
<td>557.03 [23-Mar-1993]</td>
<td>560.95 [03-May-2011]</td>
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<td>26</td>
<td>P1 lowland</td>
<td>560.33</td>
<td>556.63 - 556.03</td>
<td>1.56 ± 0.15 (n = 2)</td>
<td>1.87 ± 0.16 (n=2)</td>
<td>NA</td>
<td>brown throughout</td>
<td>557.08 [05-Feb-1992]</td>
<td>560.79 [20-May-1999]</td>
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<td>P1 lowland</td>
<td>559.97</td>
<td>554.41 - 553.81</td>
<td>5.40 ± 0.01 (n = 2)</td>
<td>5.37 ± 0.16 (n = 2)</td>
<td>NA</td>
<td>555.09</td>
<td>555.88 [22-Apr-1992]</td>
<td>560.81 [20-May-1999]</td>
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<td>17</td>
<td>P1 lowland</td>
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<td>554.56 - 553.96</td>
<td>20.74 ± 2.19 (n = 2)</td>
<td>15.75 ± 0.64</td>
<td>16.89</td>
<td>552.82*</td>
<td>557.85 [02-Sep-1989]</td>
<td>560.64 [07-Jun-1999]</td>
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<td>P1 lowland</td>
<td>561.89</td>
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<td>5.57 (n = 1)</td>
<td>5.14 (n = 1)</td>
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<td>556.68 [12-Mar-1992]</td>
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<td>P1 lowland</td>
<td>561.05</td>
<td>556.09 - 555.49</td>
<td>17.27 ± 3.86 (n = 17)</td>
<td>12.67 ± 1.54 (n = 17)</td>
<td>13.63</td>
<td>557.54</td>
<td>557.03 [23-Mar-1993]</td>
<td>561.11 [16-Jun-2004]</td>
</tr>
<tr>
<td>14</td>
<td>NW-SE drainage divide</td>
<td>564.71</td>
<td>554.55 - 553.95</td>
<td>4.19 (n = 1)</td>
<td>4.46 (n = 1)</td>
<td>6.63</td>
<td>557.7</td>
<td>558.63 [23-Feb-1993]</td>
<td>564.12 [20-May-2009]</td>
</tr>
</tbody>
</table>

*Brown-grey till transition from co-located Geoprobe boreole (GP05)
Figure 1. (a) Location of the Cottonwood Lake Study Area (CLSA) within the Prairie Pothole Region (PPR). (b) CLSA basemap with hypsometric tint showing locations of main study wetlands (P = semi-permanent pond, T = seasonal pond), groundwater wells, and locations of Geoprobe borehole conductivity measurements. (c) Inset of satellite photograph of P1/T1 basin (July 2015) showing locations of ERI survey lines and sediment cores. An evaporation platform is visible near the center of P1. (d) Map of CLSA showing the extent of a large, buried sand body (modified from Winter, 2003). All map coordinates are in UTM (zone 14T).
Figure 2. (a) Palmer drought severity index (PDSI) for North Dakota Division 5 showing wet (PDSI > 0) and dry (PDSI < 0) meteorological cycles, highlighting a moderate to extreme drought from 1988 to 1992. (b) Wetland P1 pond elevations from 1979 through 2014, indicating three key points in time when P1 had different surface water areas. (c) Corresponding water table maps for each of the three dates indicated in panel b with a polygon representing the ponded area of P1. Pond stage is noted in the center of each polygon. Surrounding points represent groundwater wells. Point labels are the difference between pond stage and groundwater level at the well, in meters, to two significant figures. Positive, blue numbers and negative red numbers indicate well levels above and below pond stage, respectively. The origin point of water table maps corresponds to the UTM coordinate 492165 E, 5215950 N (zone 14T).
Figure 3. Comparison of P1 pond levels with surrounding lowland wells during extreme drought from 1988 to 1992 and the beginning of record wet conditions in response to deluge that occurred in 1993. The P1 pond dried out every year of the drought. Water levels in surrounding groundwater wells repeatedly fell beneath the pond stage and the bathymetric low of the basin during the drought, indicating that P1 functioned as a recharge area during these times. A recharge event that occurred in response to mid-summer rain near the end of the drought is indicated by an arrow and corresponds to the center panel in Figure 2c.
Figure 4. Fence diagram showing six inversion models of the subsurface bulk electrical conductivity (bulk EC) distribution beneath P1; labeling representative areas for: glacial till (bulk EC ~ 1 mS cm⁻¹), fine-grained wetland sediments (bulk EC ~ 1.5 mS cm⁻¹), saline lenses (bulk EC from 2.5 to 3.5 mS cm⁻¹), the location of a sandy sediment core we recovered along the transect A to A', the spillway from the adjacent T3 sub-basin, and the pond shoreline at the time of our survey. The origin point on the x-y plane corresponds to the UTM coordinate 492393 E, 5215969 N (zone 14T).
Figure 5. (a) Depth profiles of the bulk EC of sediment core segments delineating between the upper ~0.5 m of organic-rich muds and the underlying mineral sediments. (b) Frequency distribution of the bulk EC from core samples of the mineral sediments. (c) Frequency distribution of the top layer beneath the ponded area extracted all six inversion models (shown in Figure 4).
Figure 6. Borehole EC data collected using the Geoprobe downhole conductivity logging system at four upland locations and the western margin of wetland P1. The range of our ERI survey is shaded in grey and the colorbar from Figure 4 is included as reference (any colored points within the grey shaded zone correspond directly to the values measured in the ERI survey).
Figure 7. (a) Results from core hydration experiment showing linear relationship between bulk and fluid EC with 95% confidence bands. Red shading indicates the range of values for saline lenses we imaged by ERI (2.5 to 3.5 mS cm$^{-1}$). Horizontal error bars are the standard deviation of the mean for three replicate measurements of bulk EC around the core’s circumference. Vertical error bars are the standard deviation of the mean for two fluid subsamples extracted from the bulk core segments. (b) Groundwater samples from the P1/T1 basin showing power relationship between fluid EC and TDS with 95% confidence bands. Red shading indicates the range of values for saline lenses determined by ERI and the relationship shown in panel a.
Figure 8. Aerial view of ERT survey data showing areas with subsurface salinity elevated from the surrounding sediments. Historical pond shorelines from 1983, 1992, and 2014 (see Figure 2 for pond elevations corresponding to historic ponded areas) are superimposed on the data. The background image is a satellite photo from July 2015 and is credited in Figure 1c. Map coordinates are in UTM (zone 14T).
Figure 9. Compilation showing range of well water levels (h) and borehole lithology for wells occupying the P1/T1 basin lowlands and local NW-SE drainage divides bookending the basin. The P1 pond range from 1979 to 2014 and elevations of saline subsurface features detected by ERI and the Geoprobe borehole conductivity logger (see Figure 6) are shown for reference. Well fluid EC values represent the mean of measurements taken between 1980 and 1991 (Table 1). Note that the brown-grey till transition for well 17 was inferred by the co-located Geoprobe borehole since the original augured borehole for the well did not extend to the depth of the transition.
Figure 10. Conceptual model showing a characteristic wet-dry cycle whereby “drought-induced recharge” allows solutes to migrate into wetland sediments during drought. During wet times, groundwater levels in the hummocky till around the wetland are above pond stage, creating a hydraulic barrier against salt loss from the wetland basin. During droughts, the water table drops below the wetland surface and desiccation fractures and terrestrial plant roots enhance the vertical permeability of wetland sediments, allowing saline runoff to migrate into the subsurface beneath the center of the wetland. Following the re-establishment of wet conditions, a portion of the salinity is re-suspended into the wetland pond after re-wetting by complex mixing processes and diffusion (wavy arrows) and a portion remains in subsurface storage as a “saline lens.”
Chapter 3: Using halogens (Cl, Br, I) to understand the hydrogeochemical evolution of
drought-derived saline porewater beneath a prairie wetland
Abstract

Closed-basin prairie wetlands throughout the Prairie Pothole Region (PPR) of North America maintain moderate surface pond salinities (TDS from 1 to 10 g L⁻¹) under semi-arid climate by accumulation of gypsum and saline (TDS > 10 g L⁻¹) lenses of SO₄-rich porewater in wetland sediments during droughts. In order to understand the hydrogeochemical origin and composition of these saline porewaters, we made a detailed geochemical survey of Cl, SO₄, Br, and I in the porewater, pondwater, and upland groundwater of a typical closed-basin prairie wetland (P1 in the Cottonwood Lake Study Area, North Dakota). Porewater Cl ranged up to 5.9 mM in saline porewater lenses, and was strongly correlated with SO₄ and Br (Pearson’s r > 0.7, p < 0.05; concentrations ranging up to 131 mM and 39 µM, respectively) due to the conservative effects of surface water evaporation. In contrast, total dissolved iodine was not significantly correlated with Cl (Pearson’s r = 0.18, p = 0.273) and was concentrated in porewaters above the saline lenses with a peak concentration of 4.1 µM beneath the center of the wetland; the highest value for dissolved I ever measured in a terrestrial aquatic system and an order of magnitude above that of seawater. We hypothesize that chromatographic separation between more mobile anions (Cl, SO₄, Br) and I occurs during droughts when wetland ponds dry and sedimentary I oxidizes to its less-mobile form, iodate. Better understanding the origin and geochemical composition of porewater salinity that develops beneath prairie wetlands during drought can help to fingerprint sources of salinity to wetland ponds during the wet climate conditions currently prevalent in the PPR.
Introduction

Millions of prairie wetlands occupying topographic depressions on low-permeability glacial till within the ~750,000 km² Prairie Pothole Region (PPR) of the North American Great Plains (Figure 1a) provide continentally important habitat for amphibians and migratory waterfowl (Batt et al., 1989; Dahl, 2014). The PPR has a sub-humid to semi-arid climate where annual evapotranspiration rates are typically almost twice those of precipitation (Winter and Woo, 1990; Rosenberry, 2003). Despite this atmospheric moisture deficit, prairie wetlands support transient surface ponds that fill and dry primarily in response to snowmelt runoff and evapotranspiration, respectively, on seasonal and multi-annual timescales (Shjeflo, 1968; Parkhurst et al., 1998; van der Kamp and Hayashi, 2009). The salinity of wetland ponds is an important control on habitat suitability for aquatic biota, and ranges widely (total dissolved solids [TDS] from < 0.5 g L⁻¹ to > 50 g L⁻¹) due to complex hydrological controls related to landscape position and climate (Stewart and Kantrud, 1972; Euliss et al., 2004; Hayashi et al., 2016).

The primary source of salinity to prairie wetlands is sulfate generated from silt and clay-rich glacial till by the oxidation of abundant pyrite and organic sulfur contained in marine shale fragments incorporated from bedrock during glaciation (Van Stempvoort et al., 1994). Acidity generated from sulfur oxidation subsequently dissolves carbonate minerals in the till; which further react by ion exchange with clays to evolve salinity along groundwater flowpaths from dilute Ca-HCO₃ waters (representative of precipitation and runoff) in recharge areas to more saline, gypsum-saturated Mg-Na-SO₄ waters in discharge areas (Hendry et al., 1986; Keller et al., 1991; Goldhaber et al., 2014). Salinity migrates into wetland basins primarily by surface runoff and groundwater discharge, though the latter is restricted to the upper several meters of
oxidized till, which contains abundant fractures and macropores within a low-permeability matrix (van der Kamp and Hayashi, 2009).

Closed-basin wetlands lacking apparent surface and subsurface drainage outlets are commonplace in the hummocky glacial landscape of the PPR. However, many of these wetlands support surface ponds of moderate salinity (TDS from 1 – 10 g L\(^{-1}\)) instead of evolving hypersaline surface waters as predicted by basic hydrologic mass balances extrapolated over geological timescales (e.g. Heagle et al., 2013). Beginning in the early 1990’s record wet climate conditions in parts of the PPR have caused many such wetland ponds to expand greatly in surface area and volume (Mushet et al., 2015). However, pond water salinities have counterintuitively increased in some cases, despite substantial additions of dilute precipitation and surface runoff (Goldhaber et al., 2016; LaBaugh et al., 2016).

Subsurface storage of salinity in both dissolved and solid phase has been proposed as a mechanism by which some wetland ponds maintain moderate salinity in a semi-arid climate, and has been linked to frequent extended droughts characteristic of the mid-continental PPR (LaBaugh et al., 1996; Heagle et al., 2013; Levy et al., In-review). On a seasonal basis, transpiration of phreatophytic vegetation (e.g. Typha spp., Salix spp.) fringing surface ponds induces outseepage of pond water into the shallow subsurface, forming “saline rings” of solute-rich porewater and evaporite minerals around wetlands (Meyboom, 1966; Hayashi et al., 1998a,b; Arndt and Richardson, 1989; Winter and Rosenberry, 1995). During extended multi-annual droughts, wetlands dry completely and efflorescent sulfate salt crusts (e.g. epsomite, mirabilite, gypsum) form on the exposed substrate. Evapoconcentration of shallow porewater salinity following pond drawdown leads to the accumulation of gypsum and calcite in wetland sediments on geological timescales (Eisenlohr et al., 1972; Heagle et al., 2007, 2013; Pennock et
al., 2014). Heagle et al. (2013) found that sedimentary gypsum was the largest sink for salinity in a closed-basin prairie wetland.

Since $\text{SO}_4 \gg \text{Ca}$ in many closed-basin prairie wetland waters, residual fluids from pond and shallow porewater evaporation that precipitate gypsum tend to become enriched in $\text{SO}_4$ (Hardie and Eugster, 1970; Boettinger and Richardson, 2001), forming pockets of saline ($\text{TDS} > 10 \, \text{g L}^{-1}$) groundwater within fine-grained wetland sediments (Berthold et al., 2004; Heagle et al., 2013). While it has long been known that saline porewater develops in the subsurface around wetland margins (e.g. Berthold et al., 2004), recent studies using geoelectrical methods have shown that solutes also accumulate beneath the center of wetland basins when ponds contract and desiccate during extended droughts (Heagle et al., 2013; Levy et al., In-review). Levy et al. (In-review) showed that “saline lenses” of $\text{SO}_4$-rich porewater accumulate in sediments beneath the bathymetric low of a prairie wetland during drought due to the episodic flushing of surface salinity towards the basin center by rainfall and runoff before infiltration in a process of “drought-induced recharge.”

Since salinities of some wetland ponds have been increasing during recent wet climate conditions in the PPR, it is important to understand the hydrogeochemical evolution and composition of saline porewater beneath wetlands to discriminate among various sources of salinity to wetland surface waters. Halogens are often used to fingerprint sources of salinity in groundwater and surface water due to their relatively conservative transport properties in the subsurface (e.g. Panno et al., 2006). Chloride (Cl) and bromide (Br) can trace sources of salinity in groundwater (Davis et al., 1998) and the hydrogeochemical evolution of sedimentary basin brines (Carpenter, 1978). More recently, iodine (I), which is a biophilic halogen that is concentrated in organic-rich rocks and soils (e.g. Murumatsu and Wedepohl, 1998), has been
coupled with Cl and Br as a tracer of groundwater impacted by shale weathering in central New York (Lu et al., 2015). While naturally occurring Cl and introduced injections of Br have been applied previously as conservative tracers of hydrogeochemical processes and surface-subsurface salt cycling in prairie wetlands (Hayashi et al., 1998b; Berthold et al., 2004; Parsons et al., 2004; Waiser, 2006; Heagle et al., 2007, 2013), natural abundances of Br and I have not been investigated in this setting.

Here, we assess the use of halogens (Cl, Br, and I) as tracers for salinity (SO₄) generated from organic-rich shale in glacial till and modified by evaporative and biogeochemical processes within a closed prairie wetland basin. The objectives of this study are to: (1) investigate natural abundances of dissolved salinity (SO₄) and halogens (Cl, Br, I) in the pond, porewater, and surrounding upland groundwater of a closed-basin prairie wetland; (2) compare the spatial distribution of porewater salinity and halogens between the wetland margin (saline ring zone) and center; and (3) understand the hydrogeochemical evolution and composition of saline porewaters that develop in wetland sediments during droughts.

**Study Area**

The Cottonwood Lake Study Area (CLSA) is a 92 ha prairie wetland complex located in Stutsman County (east-central North Dakota) and contains 17 prairie wetlands across a topographic gradient of approximately 33 m (Figure 1a,b). Wetlands labeled with a “T” have “temporary” or “seasonal” ponds that tend to fill after snowmelt in the spring and are typically dry by the fall. Wetlands labeled with a “P” support larger “semi-permanent” ponds that persist on multi-annual timescales and dry completely only during extended regional droughts (LaBaugh et al., 1996). The CLSA is monitored by the United States Geological Survey (USGS)
and has been the subject of long-term ecological and hydrological study since 1967 and 1979, respectively (Winter, 2003). As part of the latter program, the USGS monitors and maintains groundwater wells throughout the site, and monitors the water levels of wetland ponds using staff gages.

The CLSA is located on the Missouri Coteau, a glacial stagnation moraine that is elevated approximately 100 m from the surrounding landscape. The Missouri Coteau is comprised of heterogeneous glacial drift deposited by advances and retreats of the Laurentide Ice Sheet during late Wisconsin time and consists of poorly-sorted, silt and clay rich glacial till and some fluvial deposits of well-sorted sand and gravel that are limited in extent (Winter, 2003). The mineralogy of glacial sediments includes quartz and feldspar from granite of the Canadian Shield, dolomite and calcite from southern Canadian Paleozoic carbonates, and pyrite from marine shale fragments incorporated from the underlying bedrock; the Cretaceous-age Pierre Shale. Clay minerals in the till consist of smectite, illite, and chlorite (Goldhaber et al., 2014). The depth to bedrock beneath the CLSA is approximately 133 m (Winter, 2003).

The climate of the CLSA is semi-arid; with an average annual temperature of 4°C, temperature range from -47 to 48°C, and average annual rain and snowfall of 300 and 810 mm, respectively (Rosenberry, 2003). During the period of long-term hydrological study (1979 to present) the CLSA has experienced highly variable meteorological conditions including the second most extreme drought of the 20th century (1988 – 1993) and some of the highest precipitation rates (i.e. deluge conditions) in the study region over the past 100 – 500 years (1993 to present) (Winter and Rosenberry, 1998). Mean annual precipitation prior to the 1988 – 1993 drought (1958 – 1987) was 447 mm, and rose to 505 mm in the years following the drought (1993 – 2014) (Mushet et al., 2015).
Winter and Carr (1980) used a regional groundwater flow model to show that the CLSA theoretically recharges intermediate-scale flow systems that discharge to Eric Lake to the west and the Pipestem Creek to the east. However, quantitatively important groundwater flow is likely restricted to fractures and macropores within the upper “brown zone” of oxidized till (hydraulic conductivity [K] from $10^{-4}$ to $10^{-6}$ cm s$^{-1}$) and is negligible through the underlying “grey” unoxidized till (K from $10^{-8}$ to $10^{-9}$ cm s$^{-1}$; Winter and Rosenberry, 1995). The thickness of the brown zone ranges from 1 – 14 m throughout the CLSA and generally extends below the water table. The brown zone indicates the extent of the geochemical oxidation in the till throughout the PPR and contains sulfate salts and oxidized iron compounds derived mostly from pyrite (Goldhaber et al., 2014). Exposure to atmospheric oxygen on millennial timescales may be a prerequisite for brown zone formation and it is thought to have formed throughout the PPR during a period of mid-to-late Holocene dry climate (The Altithermal; ca 7500 – 4000 BP) when regional water tables were much lower than present (Hendry et al., 1986; Grasby et al., 2010).

Wetlands with persistent groundwater gradients into and out of their central basins are typically classified as “recharge” and “discharge” wetlands, respectively (e.g. Sloan, 1972), however these functions can change in response to wet-dry climate cycles (Levy et al., In-review). Recharge wetlands typically have soils with a high degree of clay illuviation and thick, organic matter-rich A horizons that maintain freshwater ponds primarily reflective of dilute snowmelt runoff (LaBaugh et al., 1987; Arndt and Richardson, 1989). Discharge wetlands accumulate salinity in soils and surface ponds since elevated groundwater levels in surrounding hummocks act as a hydraulic barrier to salt loss by pond outseepage, except where local drawdown of the water table by phreatophytic vegetation around the wetland draws pond water and associated salinity into peripheral sediments (Hayashi et al., 2016). Discharge wetlands
accumulate gypsum and calcite in their sediments, which also contain more soluble sulfate salts
(especially following wetland drying or freezing) such as thenardite, epsomite, konyaite, and
mirabolite (Arndt and Richardson, 1989; Pennock et al., 2014). High-Mg calcite is likely the
dominant carbonate phase in prairie wetland sediments (Heagle et al., 2007; Goldhaber et al.,
2014).

In this study, we focus on wetland P1 in the CLSA, which has been the subject of
numerous hydrological and biological studies, and typifies a closed-basin prairie wetland with an
oligosaline, semi-permanent pond containing Mg-SO₄ type waters. The P1 pond has long-term
(1967 – 2002) mean concentrations for SO₄ and Cl of 10 and 0.6 mM, respectively (Euliss et al.,
2014). Although P1’s high water storage capacity and lack of surface drainage outlets have
allowed it to remain full for most of the period of record, it repeatedly dried and filled during
moderate-to-extreme drought from 1988 – 1993 (LaBaugh et al., 1996). Before the drought
(1979 – 1988) the P1 pond fluctuated within a smaller area than it occupies at present, with pond
depth of ~ 1 m in the deepest part of the basin. During this time, groundwater levels around the
wetland typically were above the pond stage except during mid-to-late summer when the
groundwater table at the wetland margin fell beneath the pond stage due to transpiration of
fringing phreatophtic vegetation (Winter and Rosenberry, 1995). When the pond repeatedly dried
and filled during the drought, an initial growth of salt-tolerant shallow marsh vegetation (e.g.
*Leptochloa fascicularis*) transitioned to less-salt tolerant hybrid cattails (*Typha glauca*) as
intermittent runoff and rain events flushed surface salts down desiccation fractures into
underlying sediments (Poiani et al., 1996; Swanson et al., 2003). During this time, groundwater
levels around the wetland margin reached their record minima, with water levels in well 17
(located in the “saline ring” zone) dropping ~2 m below the land surface (Figure 1e). In 1993,
record deluge caused the P1 pond to fill and expand to a record area, merging with ponds in the adjacent T1 sub-basin (Winter and Rosenberry, 1998). The current pond depth in P1 is ~2 m and surface connection with wetland T1 persists to present.

Shallow (<0.5 m depth) organic-rich (organic matter content ~20 %) sediments in P1 contain high levels of sulfide (~2 mM) and some of the highest levels of dissolved organic carbon (DOC) observed in palustrine sediments (~180 mg L⁻¹) (Zeng et al., 2013; Ziegelgruber et al., 2013; Levy et al., In-review). High sulfide and DOC porewaters from shallow sediments in the center of P1 have had the unexpected effect of degrading recalcitrant pesticide compounds on the timescale of hours (Zeng et al., 2011). Deeper mineral sediments (2 – 4 m depths) beneath the center of the P1 basin contain saline lenses of SO₄-rich porewater that form during droughts and are estimated to have porewater TDS concentrations ~20 g L⁻¹ (Levy et al., In-review).

Methods

We sampled wetland porewater from P1 in two areas: the wetland margin (saline ring zone) and the wetland center (Figure 1c). Porewater sampling sites at the wetland margin were established as part of a long-term study of the saline ring zone (Mills et al., 2011). Porewater sampling sites at the wetland margin extended from the upslope shallow-marsh zone, through the deep marsh zone, and into the deep zone of ponded surface water (Figure 1d). We delineated among the shallow marsh, deep marsh, and deep zone on the basis of vegetation and water depth following the Stewart and Kantrud (1971) prairie wetland classification system. Briefly, the shallow marsh zone consists of wetland grasses and forbs (e.g. Carex spp.) adapted to saturated soil conditions, the deep marsh zone consists of a swath of emergent wetland vegetation (e.g. Typha spp.) within the ponded wetland area, and the deep zone consists of open ponded water
We collected vertical porewater profiles at 13 locations at the wetland margin (Figure 1d). We made permanent installations of “vapor point” porewater samplers (gas vapor implant with 15 cm screen intervals; AMS 21010) in May and August of 2013. Samplers were equipped with a dedicated vapor point (AMS 55466) and 4.76 mm interior diameter fluoropolymer tubing, and driven to depth (between 0.61 to 1.83 m from sediment surface to middle of screen) into wetland sediments with the AMS installation kit and slide hammer. After installation, we attached a two-way luer-lock valve to the tubing and a short length of 3.8 cm diameter PVC was placed over the tubing and driven a few centimeters into the soils to protect the apparatus. We installed samplers at multiple depths in the same location within 10 cm of each other.

On August 9, 2013, we sampled porewater from vapor points after purging the previous day and allowing to recover overnight. For vapor points that produced water easily, we sampled porewater using a 60 ml syringe with luer-lock tip. For samplers with slower productions rates, we connected sampler tubing to glass filter flasks and used an automated vacuum pump to extract the porewater. On October 16, 2013 we supplemented our August sampling with a smaller subset of shallow (0.3 to 1.0 m depths) porewater samples at locations a, c, and k. For this sampling, we used a portable “Henry” pushpoint sampler (e.g. Zimmerman et al., 2005) and extracted samples using 60 ml syringes with luer-lock tips and three-way valves. Since porewater flow is extremely slow through shallow, fine-grained wetland sediments (K ~ 10^{-6} cm s^{-1}; Heagle et al., 2013) we assume that porewater composition was fairly stable over this two month sampling period and treat all samples from the wetland margin as a synoptic “snapshot” dataset. During the main August sampling the water level in well 17 (located at the wetland margin; Figure 1d) was 0.2 m lower than the P1 pond stage. The water level in an upslope well (18)
located ~70 m to the southwest (Figure 1b) was 2.3 m higher than the water level at well 17. Therefore, upslope groundwater and pondwater flowed towards the wetland margin during the time of sampling; a transient condition that develops at the P1 margin during the mid-to-late summer due to the effects of evapotranspiration (Winter and Rosenberry, 1995). This groundwater trough dissipated by our October porewater sampling survey, allowing us to collect more shallow porewater samples when the water level at well 17 rose to the approximate height of the pond stage. On August 9, 2013 we collected a vertical porewater profile in the center of P1 off of a raft using a sectional 1.27 cm diameter schedule-80 PVC piezometer equipped with an aluminum drive rod. We collected samples from the piezometer with a hand-pump at 0.30 cm intervals from 0.3 to 2.1 m below the sediment-water interface.

We collected a series of pond samples from P1 on May 17, August 9, October 18 (2013) and May 16, August 4, October 29 (2014) to assess the composition and variability of wetland surface water chemistry. The depth of the P1 pond at its center ranged from 1.8 to 2.0 m during this time period. We waded from the wetland margin towards the center to where the pond was ~1 m deep and collected a vertical profile of pond water with a water-column sampler; a tube with an internal diameter of 0.10 m and length of 0.65 m (Swanson, 1978). Since surface ponds in the PPR tend to be extremely well-mixed due shallow depths and high wind velocities (e.g. Parkhurst et al., 1998), we assume our surface water samples are representative of the geochemical condition of the entire pond at the time of sampling.

In order to quantify the geochemical composition of dilute runoff, we also collected a surface pond sample from wetland T8 (Figure 1b) on May 16, 2014, shortly after spring snowmelt. Wetland T8 is an open-basin, recharge wetland and has historically dilute surface water representative of snowmelt runoff and rain (Euliss et al., 2014). The depth of the T8 pond
was approximately 0.3 m at the time of sampling. Since the T8 pond was shallow at the time of sampling, we obtained a water sample there by dipping a 60 ml high-density polyethylene (HDPE) sample bottle directly below the pond surface while wearing latex gloves.

We obtained groundwater samples from a suite of wells occupying the uplands surrounding P1 (14, 16, 18, 22, 27, 28, 29) and at the porewater sampling site located within the wetland margin (17) (Figure 1b). Groundwater wells were installed in the late 1970’s and early-to-mid 1980’s as described in detail by Winter and Carr (1980) and Winter and Rosenberry (1995). We used a peristaltic pump to purge wells until dry or 3x the interior volume of the well casing was removed and allowed to recover overnight before sampling. We sampled wells 14, 16, 17, 18, and 22 from August 8 – 9, 2013. We obtained archival samples for wells 27, 28, and 29 that were sampled as described above in 2010 for the study of Goldhaber et al. (2014) and stored in HDPE bottles at <4 °C until analysis for Br and I in 2014.

For all water samples, we measured pH using a Sentix 41-3 probe and WTW Multi 3400i Meter and filtered through 0.45 μm syringe filters into HDPE bottles within 12 hours of collection. We preserved aliquots for analysis of dissolved metals with trace metal grade concentrated nitric acid. We kept all samples on ice or refrigerated at <4 °C until analysis. We measured split samples from all vapor point extracted porewaters and groundwater from wells 27, 28, and 29 at the USGS National Laboratory in Denver for total dissolved Ca, Mg, Na, and K using ICP-MS and ionic SO$_4^{2-}$ using IC following methods described in detail by Wolf and Adams (2015) and Taggart (2002), respectively. For these sample splits we also estimated HCO$_3^-$ by total inorganic carbon concentrations determined on an OI700 (OI Analytical) wet oxidation DOC analyzer in the Boulder NRP laboratories. We analyzed all other samples for total dissolved Ca, Mg, Na, and K at SUNY-ESF using ICP-OES (Perkin Elmer Optima 3300DV
model) and ionic SO₄²⁻ at Syracuse University using IC with a Dionex ICS-2000 with AS18 column for anions. The percent errors for the aforementioned analyses are <10 %.

We measured ionic Cl⁻ for all samples on the IC at Syracuse University. We ran quality control standards and blanks every ten samples with an overall percent error of 1%. We measured total dissolved Br and I for all samples by ICP-MS at Syracuse University using a Bruker Aurora M90. We prepared fresh iodine calibration standards before measurement using ultrapure potassium iodide powder and diluted in a tertiary amine matrix with cesium as an internal standard (Lu et al., 2015). We ran blanks every three samples and calibration standards every six samples. The percent errors for total Br and I analyses are <1%.

We assessed sampling error by obtaining field replicates for porewater samples from the wetland margin and center with sectional piezometer and Henry sampler extraction methods, respectively. There was insufficient water in vapor points to collect replicate samples. We collected duplicate samples of porewater at 1.2, 1.5, and 1.8 m depths and triplicate samples at the 2.1 m depth beneath the center of P1. We collected duplicate samples from the wetland margin at sampling site c (0.3 m depth). The relative standard deviations (RSD’s) for replicate sample analyses from the center of P1 ranged from 0.16 – 1.02 % for Cl, 0.05 – 0.51 % for SO₄, 2.04 – 4.97 % for Br, and 1.26 – 5.04 % for I. The relative standard deviations (RSD’s) for the pair of replicate samples from the margin of P1 were 8.80 % for Cl, 3.38 % for SO₄, 2.60 % for Br, and 2.90 % for I.

**Results**

Shallow (0 – 2 m depth) porewaters from the wetland margin were of the Mg-SO₄ type with TDS ranging widely from 6.4 to 13.5 g L⁻¹. Well 17, screened ~6 m beneath the sediment
surface at the wetland margin (Figure 1e), had the most saline waters we measured in this study with TDS ~20 g L\(^{-1}\); consistent with prior analyses of well 17 water in the 1980’s (Goldhaber et al., 2014). Porewaters from the center of P1 were of the Mg-SO\(_4\) type with TDS from 3.7 to 5.9 g L\(^{-1}\). In contrast, groundwater from the uplands surrounding P1 ranged from Ca-SO\(_4\) to Mg-SO\(_4\) types with TDS from 1.5 to 5.9 g L\(^{-1}\), consistent with the measurements of Goldhaber et al. (2014), and were generally less saline with greater Ca concentrations than wetland porewaters. The P1 pond water was of the Mg-SO\(_4\) type with TDS ~2 g L\(^{-1}\).

We measured major ions and trace halogens for all samples, but dissolved inorganic carbon (DIC) on only a subset of 30 samples. We expect DIC to be in the form of HCO\(_3\)\(^-\) since the pH of all water samples from the P1 basin was circum-neutral (~7). Of the 30 samples we measured for DIC, 26 had an absolute charge balance error within 10%, and the remaining four were within 15%. Least squares regression of these 30 samples showed a strong linear relationship between SO\(_4\) and TDS (TDS [g L\(^{-1}\)] = 0.14SO\(_4\) [mM] + 0.43; \(R^2 = 0.99; p < 0.001\)), which we used to estimate the TDS of the remaining 32 samples. In general, SO\(_4\) is the dominant component of salinity in natural waters of the P1 basin. In this study, we focus our results and discussion on SO\(_4\) as the primary constituent of natural salinity in the P1 basin and Cl, Br, and I as a potential, natural tracer suite for this salinity. We present complete geochemical analyses for all samples in Appendix A.

Shallow porewaters from the P1 margin had Cl, SO\(_4\), Br, and I concentrations respectively ranging from 1.1 to 5.9 mM, 47 to 131 mM, 9.1 to 39 µM, and 0.33 to 3.4 µM (Figure 2). Concentrations of Cl, SO\(_4\), and Br generally all increased with depth below the sediment surface (Figure 2) and distance from the shallow marsh to the deep zone (Figure 3). However, peak concentrations of I occurred at intermediate depths (Figures 2) within the deep
marsh and deep zones, forming a lens of high I porewater above more saline porewater beneath the currently ponded area (Figure 3). In contrast, the shallow porewaters from beneath the center of P1 were more dilute and had Cl, SO₄, Br, and I concentrations respectively ranging from 0.81 to 0.88 mM, 25 to 41 mM, 8.6 to 9.8 µM, and 1.6 to 4.1 µM (Figure 2). There was little vertical variation in Cl and Br throughout the ~2 m depth profile, with Cl concentrations virtually the same as that of the overlying pond water (~0.70 mM), and Br slightly enriched from that of the overlying pond water (~5.0 µM). Porewater SO₄ increased from close to pond water (~20 mM) in the upper 1 m of the porewater profile to stable values of ~40 mM in the lower meter. Concentrations of iodine also increased from values similar to the pond (~0.20 µM) in the upper meter of the porewater profile and reached stable values in the lower meter; reaching the highest measured concentration (4.1 µM) at a depth of 2.1 m. This is to our knowledge the highest concentration of dissolved I ever reported in a terrestrial aquatic system.

The pond water we sampled from P1 between May 2013 and October 2014 had Cl, SO₄, Br, and I concentrations respectively ranging from 0.63 to 0.75 mM, 19 to 23 mM, 4.0 to 5.5 µM, and 0.08 to 0.25 µM (Table 1). Upland groundwater we sampled around P1 in 2010 and 2013 had Cl, SO₄, Br, and I concentrations respectively ranging from 0.29 to 1.6 mM, 7.5 to 45 mM, 0.68 to 15 µM, and 0.02 to 0.35 µM (Table 2). The pond water from T8 (recharge wetland) we sampled in May 2014 (following snowmelt) is representative of dilute surface runoff and soil-water interactions within the wetland basin and had Cl, SO₄, Br, and I concentrations of 0.26 mM, 0.03 mM, 0.45 µM, 0.02 µM, respectively. The highest salinity water sample we measured was from well 17, located at the wetland margin, which had Cl, SO₄, Br, and I concentrations of 2.2 mM, 159 mM, 18 µM, 0.88 µM, respectively.
Since Cl is considered to be conservative in the subsurface of prairie wetlands (e.g. Hayashi et al., 1998b), we assessed the behavior of salinity (SO₄) and trace halogens (Br, I) with respect to Cl (Figure 4). Porewater Cl from the wetland margin had high correlations (Pearson’s r > 0.70) with SO₄ and Br, both significant at the 95% confidence level (p < 0.05) (Table 3). However, Cl had a low correlation with I (Pearson’s r = 0.18), and did not have a significant linear relationship (p = 0.273).

We assessed the contributions of pond and upland groundwater endmembers on wetland porewater chemistry by plotting theoretical “evaporation envelopes” for upland groundwater and pond water in bivariate space (Figure 4). We created evaporation envelopes by extrapolation from the lowest measured Cl value over the range of data, constrained by the maximum and minimum (SO₄, Br, I)-Cl ratios from each endmember dataset (Tables 1 and 2). Evaporation envelopes therefore represent a theoretical range of values that could be achieved by conservative evaporation or dilution of the measured endmember chemistries (pond water and upland groundwater). A horizontal trend on bivariate plots of Cl versus (SO₄, Br, I)-Cl ratios represents conservative evaporation and dilution, while non-horizontal trends represent mixing with a geochemically distinct endmember or anion flux to or from an internal sink in the wetland sediments (e.g. Panno et al., 2006).

For SO₄, most porewater values fell within evaporation envelopes for upland groundwater and pond water, and could mostly be explained by conservative evaporation of modern pond water and/or upland groundwater (Figure 4). In general, the variability of Cl and SO₄ for all samples, including those that fell outside of the evaporation envelopes, could be explained by conservative mixing between pond water, the highest Cl sample (from the deep zone: profile k, 1.83 m depth), and deeper, more saline groundwater with lower Cl content from
below the wetland margin (well 17). The other primary components of porewater salinity (Mg, Na) had similar trends to SO₄ and could generally be explained by the aforementioned mixing relationship (Appendix B). However, this was not the case with Br and I, which could not be explained by conservative evaporation/dilution or mixing of the endmembers we used to constrain salinity (Figure 4). Porewaters from the center of P1 had higher Br/Cl than those measured elsewhere in the basin. Both porewaters from the center and margin of P1 had higher I/Cl values than those measured elsewhere in the basin.

We calculated saturation indices (SI = log Q/K) for all samples using the Geochemist’s Workbench v. 10 and the associated Harvie-Møller-Weare (H-M-W) geochemical database; where Q and K are the reaction quotient and equilibrium constant for gypsum, respectively (Bethke and Yeakel, 2015). Almost all of the wetland porewaters were at or near saturation with respect to gypsum (SI ~ 0; Figure 5). Pond water was undersaturated with respect to gypsum (Figure 5, Table 1). Upland groundwater ranged from undersaturated (SI < 0) to near-saturation (Figure 5, Table 2). Some shallow porewaters with lower-range Cl values at the wetland margin and center also were undersaturated with respect to gypsum.

Discussion

Sources and Sinks for Salinity and Halogens

While the primary source of salinity in PPR groundwater and wetlands is SO₄ derived from chemical weathering of shale particles contained in silt and clay rich glacial till (e.g. Goldhaber et al., 2014), the origins of halogens (Cl, Br, I) in the northern prairie are not as well understood. Globally, the high solubility of halogen-containing minerals and their relatively high
mobility in dissolved phase cause them to concentrate in the world’s oceans with average concentrations for Cl, Br, and I of 535 mM, 813 µM, and 0.45 µM, respectively (Wong, 1991; Hem, 1992). Halogens in the ocean environment can be transported back to the continents by moving into atmospheric circulation, primarily via marine aerosols (Wincester and Duce, 1967). Atmospheric deposition of halogens is therefore highest near the coasts and decreases towards the continental interior. Ratios of Br/Cl and I/Cl increase towards the continental interior since Cl fallout from marine-derived air masses is faster than Br and I (Fuge, 1988; Davis et al., 2004). While Cl is present in comparable concentrations within both igneous and sedimentary rocks, Br and I are mostly concentrated in sedimentary rocks (particularly organic-rich marine shales) and recently deposited marine sediments (Fuge, 1998; Murumatsu and Wedepohl, 1998). Bromine and iodine are biophilic elements since they can become incorporated into organic matter, which is why they are concentrated in organic-rich soils and rocks (Fuge, 1988; Biester et al., 2006) as well as septic effluent and landfill leachate (Panno et al., 2006; Katz et al., 2011). Iodine has also been suggested to be a chalcophilic element due to associations with sedimentary sulfur in marine settings (Fuge and Johnson, 1984; Francois, 1987).

In the northern prairie, Cl and SO₄ in precipitation typically range from 0.6 – 5.6 µM and 1.7 – 15.6 µM, respectively (Hayashi et al., 1998b; Heagle et al., 2013; Goldhaber et al., 2016), with corresponding SO₄/Cl molar ratios of ~3. Mid-continental precipitation in north America typically has Br and I contents of approximately 0.13 µM and 0.02 µM, with corresponding Br/Cl and I/Cl (µM/mM) ratios of ~23 and ~3, respectively (Davis et al., 1998; Panno et al., 2006). Due to the atmospheric fallout effect, described above, Br/Cl ratios in groundwater typically increase from the coast to the mid-continental region. Groundwater in the mid-western United States typically has Br/Cl (µM/mM) ratios ranging from 5.5 – 8.9 (Davis et al., 2004),
which are within the range of values we measured for upland groundwater in this study (Table 2). Surface runoff at the CLSA is also generally dilute, with Cl and SO$_4$ on the order of 0.4 and 0.07 mM, respectively, with a SO$_4$/Cl molar ratio of 0.2 (Goldhaber et al., 2016). However, these measurements are based on limited samples, and the geochemical compositions of runoff waters likely are highly variable in space and time at the CLSA. The T8 (recharge wetland) pond was dilute following spring snowmelt, with Cl and SO$_4$ concentrations roughly on the order of surface runoff (0.03 and 0.30 mM, respectively, with a SO$_4$/Cl molar ratio of 8.7). However, the dilute pondwater had similar or slightly higher concentrations of Br and I (0.45 and 0.02 µM, respectively) and lower Br/Cl and I/Cl (µM/mM) ratios (15 and 0.7, respectively) than expected for continental precipitation, indicating a potential near-surface source for Br and I in the wetland pond and surrounding catchment. Since T8 has a large, organic-rich A horizon and is highly depleted of mineral solutes due to long-term advection of dilute recharge through the wetland subsurface (e.g. Arndt and Richardson, 1989), it is likely that Br and I in T8 pondwater are elevated with respect to meteoric values due to leaching from soil organic matter and decaying vegetation in the pond. Prairie wetland vegetation contains Br (Parsons et al., 2004), and likely I since the latter is typically incorporated into organic matter at higher concentrations than Br (Fuge, 1988).

Silt and clay-rich glacial till in the PPR containing abundant fragments of marine shale can also contribute halogens to groundwater and wetlands. Fabryka-Martin et al. (1991) found that halogen contents in the Milk River aquifer (Cretaceous-age sandstone with interbedded marine shale) in southern Alberta increased by almost two orders of magnitude on flowpaths from recharge to discharge areas. They attributed this increase to mixing with connate seawater impounded in low-permeability sediments and the diagenesis of organic matter contained in
marine shales, particularly kerogen, which altered the halogen ratios of the impounded seawater. While formations containing connate seawater are not present in the poorly sorted glacial till comprising the subsurface of the CLSA, Goldhaber et al. (2014) showed that weathering of marine shale contained in the till greatly impacts the SO$_4$ composition of groundwater, and additionally hypothesized that the weathering of kerogen contained in shales could further impact the evolution of groundwater salinity. Hayashi et al., (1998b) found variability in the Cl contents of groundwater and extracts of PPR till, and attributed this partially to Cl held in micro-pores in clay rich till. Remenda (1993) found glacial till in the PPR that was unaffected by post-glaciation water had porewater Cl contents ranging from approximately 0.5 to 1.0 mM.

Salinity and associated halogens migrate to closed-basin prairie wetlands from the aforementioned meteoric and till sources primarily via groundwater discharge, runoff, and direct precipitation (Heagle et al., 2013). In this study, we consider two primary sources of salinity and halogens to the porewaters of P1: pond water and upland groundwater (Figure 4; Tables 2 and 3). While the annual water balance of the P1 pond is dominated by runoff, direct rainfall, and ET (Parkhurst et al., 1998), long-term groundwater input is an important control on the geochemical evolution of most PPR pond waters (LaBaugh et al., 1987). Goldhaber et al. (2014) used an inverse geochemical mass balance model to show that the precipitation of high-Mg calcite, and to a lesser degree sulfur reduction and evaporation, can explain the evolution of groundwater to pond water; which is depleted in Ca compared to upland groundwater. The range of SO$_4$/Cl, Br/Cl, and I/Cl ratios for pond waters were all within the range of values measured in upland wells but not for the atmospheric endmembers discussed above, suggesting that the surrounding glacial till is the dominant source of the salinity and halogens controlling the geochemical composition of pond water in the P1 basin (Figure 4).
Porewaters from the wetland margin have Cl concentrations up to 6x more concentrated than pondwater or the post-glaciation background values for PPR till reported by Remenda (1993), demonstrating the importance of evapoconcentration on the geochemical composition of wetland porewaters (Figure 4). Transpiration of phreatophytic vegetation can concentrate wetland pondwater in the subsurface around wetland margins (e.g. Hayashi et al., 1998a,b). Additionally, during prolonged droughts when groundwater levels drop substantially below the basin surface, runoff can route surface salinity down desiccation fractures, increasing the salinity of underlying porewaters (Levy et al., *In-review*).

Drawdown of the wetland pond during drought and evapoconcentration of shallow porewaters lead to the accumulation of gypsum and carbonates in prairie wetland sediments (Heagle et al., 2013; Pennock et al., 2014). Equilibrium with gypsum exerts a strong influence on wetland porewater chemistry in the P1 basin (Figure 5), and is both an important source and sink for porewater salinity. Low Cl porewaters tended to have higher SO4/Cl ratios than the P1 pond (Figure 4) and were in some cases undersaturated with respect to gypsum (Figure 5), which could indicate mixing of comparatively dilute pondwater in the shallow subsurface and subsequent dissolution of gypsum. At the high end of the porewater Cl spectrum SO4/Cl ratios gradually decreased, which could be due to the preferential removal of SO4 by precipitation of gypsum in response to evapoconcentration during drought (Figure 4). Additionally, the lower SO4/Cl ratios of saline porewaters could have originated during paleo-droughts when ponded water in the P1 basin had a different geochemical composition than at present.

Although many porewater samples fell within pond and upland groundwater evaporation envelopes, some, particularly those from beneath the center of P1, could not be explained by the conservative evaporation and dissolution of pond or groundwater endmembers (Figure 4).
Release of SO$_4$ from dissolution of sedimentary gypsum exposed to more dilute pond water or surface runoff is the most likely explanation for the higher SO$_4$/Cl ratios beneath the center of P1. Enrichment of porewater Br and I with respect to pond and groundwater endmembers could be due to leaching from organic matter contained in P1 sediments (e.g. Gerritse and George, 1988) or differences in subsurface transport behavior during the evolution of porewater salinity (discussed further in the following section). Since we measured Br and I by ICP-MS, our measurements represent the total concentration of these species that could be present either in ionic form (i.e. halides) or the porewater DOC pool.

While dissolved Br is likely either present as a halide or a constituent of porewater DOC, the geochemical behavior of I is much more complex. Iodine speciation in natural waters is redox sensitive and can exist in both reduced and oxidized ionic forms of iodide (I$^-$) and iodate (IO$_3^-$), respectively (Fuge, 1988). Iodide is more mobile in the subsurface than iodate, but they both have been shown to adsorb strongly to sediments containing organic matter, and, to a lesser degree iron and aluminum hydroxides (Neal and Truesdale, 1976; Bird and Schwartz, 1996; Dai et al., 2009). Steinberg et al. (2008) found the majority of iodine in salt-impacted soils on the floodplain of the Virgin River, NV was organically bound. Francois (1987) showed that iodate in a marine setting could be reduced by humic substances and incorporated into sedimentary organic matter, and that sulfide and thiosulfide could displace I from the sediments back into porewater by nucleophilic substitution. In P1, iodate and organically-bound dissolved I likely are the dominant species in the well-mixed pond (e.g. Gilfedder et al., 2009), while iodide and organically-bound iodine in dissolved and solid phases likely are the most prevalent pools in reducing wetland sediments (Ashworth, 2009).
Mixing Relationships and Spatial Patterns

Hypothetically, the geochemical composition of porewater salinity can be described as a mix of P1 pond water, deeper wetland porewater from well 17, and the highest Cl porewater from the deep zone (site k, 1.8 m depths) (Figure 4, Appendix B); although it is difficult to separate the effects of mixing and conservative pond water evaporation. However, this mixing relationship falls apart when applied to Br and I, qualitatively demonstrating the incongruity between the behavior of halogens and salinity in the subsurface. While the geochemical composition of the highest Cl sample from the deep zone (~2 m below the sediment surface with TDS ~13 g L⁻¹) can be explained by conservative evaporation of modern pondwater and removal of SO₄ by precipitation of gypsum; groundwater from well 17 (~6 m below the land surface with TDS ~20 g L⁻¹) has much lower Cl, Br, and I content than can be explained by evaporation of modern pondwater.

Concentrations of porewater Cl, SO₄, and Br generally increased with depth in vertical profiles and with distance through the P1 margin towards the deep zone (Figures 2 and 3), and have high correlations (Pearson’s r > 0.70) among each other (Table 3). Concentrations of these elements in the shallow marsh zone were generally similar to that of upland groundwater, with isolated zones of elevated concentration occurring in shallow sediments within the shallow marsh and deep marsh zones due to the effects of riparian evapotranspiration. However, the lens of saline porewater at ~2 m depths below the ponded area (deep zone) must have formed during prior droughts when the pond shoreline was beyond the furthest extent of our margin transect and groundwater levels dropped substantially below the sediment surface, allowing for the penetration of surface salinity to depth via recharging waters (Figure 1e). While the general concentration trends among Cl, SO₄, and Br are consistent, porewaters are slightly enriched with
Br and SO$_4$ at intermediate (~1 m depths) with respect to modern pondwater. The increased Br/Cl ratios could be due to leaching of Br from organic matter in wetland sediments. The increased SO$_4$/Cl ratios could be due to gypsum dissolution or mixing with deeper, saline wetland water of lower Cl content (e.g. well 17) (Figure 4). Some saline porewaters at ~2 m depths beneath the deep zone had lower Br/Cl ratios than modern pondwater (Figure 3). These waters may have evolved from the evaporation of ponded surface water in the past that had a different Br/Cl ratio than that of the modern pond.

In contrast to Cl, SO$_4$, and Br, concentrations of porewater I were highest at intermediate depths (~1 m) below the currently ponded area of P1, directly above the most saline porewaters at ~2 m depths (Figures 2 and 3). Additionally, the highest I concentrations we measured in this study were from the vertical porewater profile from the center of P1 (Figures 2 and 4). While the salinity of the high I porewaters beneath the center of P1 was brackish (TDS from 3.7 to 5.9 g L$^{-1}$), a prior geophysical survey of P1 showed increased porewater salinity (TDS ~20 g L$^{-1}$) deeper in the sediment column at 2 – 4 m depths (Levy et al., In-review). Therefore, the highest I concentrations in the porewaters we sampled both at the wetland margin and center vertically overlie deeper, saline lenses of SO$_4$-rich porewater.

The non-conservative nature of I in the subsurface can be invoked to explain incongruities between the spatial occurrence of porewater I and salinity. Leaching from organic matter likely does explain some of the enrichment in porewater I/Cl ratios from groundwater and pondwater endmembers we observed in this study, as discussed with respect to Br above. However, it is unlikely this is the only process leading to I enrichment in porewaters for several reasons. First, the vertical profile of porewater Br beneath the center of P1 has near constant values where Cl is low with Br/Cl ratios elevated from those found in pond and upland
groundwater endmembers; which we attribute to leaching from organic matter. However, I increases markedly with depth in the center of P1, and seems to be controlled by a different process. Further, the upper 0.5 m of sediments beneath the ponded area of P1 have much higher organic matter contents than the underlying mineral-rich sediments (Levy et al., In-review). However, this interpretation is complicated by the fact that I may not be available in dissolved form to porewaters contained within organic-rich wetland sediments due to enhanced adsorption to humic materials. Additionally, high I concentrations were relegated to beneath the currently ponded area, and not the shallow marsh and uplands, which also contain organic-rich soils near the surface.

Perhaps the most compelling argument against organic matter leaching as the primary source of the high I concentrations is the fact that the peak values of I we measured in this study (≈4 µM) to our knowledge are considerably greater than those measured in any other terrestrial aquatic system. Globally, total dissolved I in terrestrial surface waters ranges from 0.001 to 1.08 µM (Snyder and Fehn, 2004). While there are very few published studies of iodine concentrations for wetland porewaters, the values we measured in this study greatly exceed those measured for porewaters from a peatland in Chile (0.08 – 0.16 µM; Biester et al., 2006), porewaters from a subtropical wetland in Georgia (0.07 – 0.20 µM; Zhang et al., 2014), and porewaters from a flooded rice paddy in Japan (up to 0.40 µM; Yuita et al., 2006); and are an order of magnitude above the average concentration in seawater (0.45 µM; Wong, 1991).

An alternate hypothesis for the high I values we measured in P1 porewaters is evapoconcentration of organic oxidation byproducts during drought and chromatographic separation during infiltration of saline surface waters into wetland sediments (Figure 6). During droughts when the wetland pond dries and water table drops below the wetland bed, organic
matter in shallow sediments likely oxidizes and transfers I to recharge waters associated with intermittent rainfall/runoff events that flush surface salt crusts and solutes in shallow porewaters deeper into the subsurface. During this process of drought-induced recharge (Levy et al., In-review) Cl, SO₄, and Br concentrate in infiltrating recharge and form saline lenses in the subsurface. The depths of these lenses are naturally shallower around the wetland margin than the center since surface ponding that drives recharge occurs within a smaller area above the bathymetric low of the wetland during droughts. When surface ponds dry during droughts, I that is released from decaying organic sediments is likely oxidized to IO³⁻, which adsorbs strongly to abundant iron oxides and humic materials contained in the shallow wetland sediments (Ashworth, 2009; Zeng et al., 2013), instead of moving deeper beneath the wetland with the rest of the recharge water. Therefore, a chromatographic separation between I and the other anions associated with the saline lenses may be enhanced during recharge events that occur during drought.

When wet climate resumes and the wetland ponds again, sediments become reducing and adsorbed iodate can be released back to porewaters as iodide. Nucleophilic substitution of sulfide could also further displace iodine from the solid phase, thereby increasing porewater I when wet conditions resume (Francois, 1987). Rice paddies in Japan that are alternately flooded and drained on an annual basis leach soil I into the subsurface when water ponds and reducing conditions are prevalent, and accumulate soil I in oxidized soil horizons (Yuita et al., 2005, 2006); the vertical distribution of which is largely controlled by the position of the water table (Yuita and Kihou, 2005). While this hypothesis requires further testing, it explains the vertical distribution of Cl, SO₄, Br, and I we observed in the subsurface of P1.
Conclusions

We made a detailed survey of Cl, SO$_4$, Br, and I in the surface water, porewater, and upland groundwater of a typical, closed-basin prairie wetland. We found that porewater salinity in the wetland is most likely derived from chemical weathering of the till and transport by runoff and groundwater discharge to the wetland pond. Organic matter and gypsum are major sources and sinks for biophilic halogens (Br and I) and SO$_4$, respectively, in the wetland subsurface. Wetland porewaters are strongly influenced by evapoconcentrated surface water, which accumulates in the near-surface of the margin due to evapotranspiration. However, deeper lenses of saline (TDS > 10 g L$^{-1}$) porewater ~2 m beneath the wetland likely form during more extended droughts when the water table drops substantially below the wetland surface. Porewater Cl, Br, and SO$_4$ had strong linear correlations due to the effects of evapoconcentration and were present in elevated concentrations in the saline lenses, with some minor alterations of halogen ratios likely due to interactions with organic and mineral sinks in wetland sediments. However, peak concentrations of I occurred in porewaters overlying the saline lenses. We hypothesize that chromatographic separation of I occurs during droughts due to oxidation to the less-mobile form, iodate, which adsorbs strongly to humic substances and iron hydroxides that are abundant in wetland sediments. Overall, Cl and Br appear to be effective as semi-conservative tracers for evaporative processes that modify wetland porewater salinity during droughts. However, the geochemical behavior of I in prairie wetlands is more complex and requires further research. Understanding the origin and geochemical composition of porewater salinity that develops beneath prairie wetlands during drought can help to fingerprint sources of salinity to wetland ponds during wet climate.
Acknowledgements

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Table 1. Geochemistry of P1 pondwater and water depth at center of pond from 2013 – 2014 (NM = calcium not measured).

<table>
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<tr>
<th>Sampling Date</th>
<th>Pond Depth (m)</th>
<th>Cl (mM)</th>
<th>SO4 (mM)</th>
<th>Br (uM)</th>
<th>I (uM)</th>
<th>SO4/Cl (molar ratio)</th>
<th>Br/Cl (uM/mM)</th>
<th>I/Cl (uM/mM)</th>
<th>gypsum SI (log Q/K)</th>
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<td>7.6</td>
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Table 2. Geochemistry of select upland groundwater wells surrounding wetland P1.

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<th>Cl (mM)</th>
<th>SO4 (mM)</th>
<th>Br (uM)</th>
<th>I (uM)</th>
<th>SO4/Cl (molar ratio)</th>
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Table 3. Correlation coefficients (top cell) and corresponding p-values (bottom cell) for P1 margin porewater Cl, SO4, Br, and I. Correlations and p-values significant at 95% confidence levels in bold.

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Figure 1. (a) Location of the Cottonwood Lake Study Area (CLSA) within the Prairie Pothole Region (PPR). (b) CLSA basemap with hypsometric tint showing locations of main study wetlands (P = semi-permanent pond, T = seasonal pond) and groundwater wells (wells used in this study have number labels), (c) Inset of satellite photograph of P1/T1 basin showing porewater sampling sites at the wetland margin and center. (d) Inset showing wetland margin sampling locations and wetland zones in plan view. (e) Cross-section view of porewater sampling sites along transect from A to A’ showing water table position during August 2013 sampling and water table minimum (from 1979 to 2014) for well 17 (shown in red for emphasis) during drought in 1989. The vertical exaggeration of the cross-section is x8. All map coordinates are in UTM (zone 14T).
Figure 2. Wetland porewater geochemical depth profiles (Cl, SO₄, Br, I) for the P1 margin (top panels) and center (bottom panels). Mean pondwater geochemistry from 2013 - 2014 is plotted at the “0” depth for comparison.
Figure 3. Hydrogeochemical cross sections showing porewater and pond Cl, Br, and I (left column, top to bottom) and SO$_4$, Br/Cl, and SO$_4$/Cl (right column, top to bottom) for the P1 margin transect from A to A’. The vertical exaggeration for all cross-sections is x8.
Figure 4. Bivariate plots showing wetland porewater and mean pond (2013 - 2014) Cl plotted against SO₄, Br, and I (left column, top to bottom) and corresponding SO₄/Cl, Br/Cl, and I/Cl ratios (right column, top to bottom). Dark grey and light grey polygons represent the range of values that could be achieved by conservative evaporation/dilution of pondwater and upland groundwater, respectively. A hypothetical mixing space is defined by dashed-dotted lines for the mixing of mean pond water, deep saline groundwater from well 17, and the highest Cl sample from the deep zone of the wetland margin transect (location k, 1.8 m depth).
Figure 5. Bivariate plot showing wetland porewater and pond water Cl versus the saturation index for gypsum. Values for positive and negative SI values indicate the sample was oversaturated or undersaturated with respect to gypsum, respectively, while 0 indicates equilibrium or saturation. The range of values for upland groundwater are shown for reference.
Figure 6. Conceptual model showing hypothesized chromatographic separation of porewater iodine and Cl, Br, SO$_4$ during transition from wet climate to drought. (a) During wet climate shallow porewaters concentrate by evapotranspiration at the wetland margin. (b) When the water table draws down during drought salt tolerant shallow marsh vegetation cover the land surface, desiccation fractures form in wetland sediments, sulfate salt crusts form at the land surface, organic sediments oxidize (iodine speciates to iodate [IO$_3^-$]), and shallow soil water becomes concentrated due to evaporation. (c) Recharge events that occur during drought flush surface salinity into the subsurface and towards the center of the basin. As recharge waters flush surface salinity to depth, iodate adsorbs to abundant humic compounds and iron oxides in shallow wetland sediments and becomes concentrated in porewaters overlying saline lenses enriched in more mobile anions (Cl, Br, and SO$_4^-$).
Appendix A

Table A1. Complete geochemical dataset for P1 wetland porewater, pondwater, and upland groundwater. Table cells are blank where analyses were not available.

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Appendix B

Figure A1. Bivariate plots showing wetland porewater and mean pond (2013 - 2014) Cl plotted against SO₄, Mg, and Na (left column, top to bottom) and corresponding SO₄/Cl, Mg/Cl, and Na/Cl ratios (right column, top to bottom). Dark grey and light grey polygons represent the range of values that could be achieved by conservative evaporation/dilution of pond water and upland groundwater, respectively. A hypothetical mixing space is defined by dashed-dotted lines for the mixing of mean pond water, deep saline groundwater from well 17, and the highest Cl sample from the deep zone of the wetland margin transect (location k, 1.8 m depth).
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