Capturing temporal and spatial variability in the chemistry of shallow permafrost ponds

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Abstract.

Across the circumpolar north, the fate of small freshwater ponds and lakes (< 1 km^2) has been the subject of scientific interest due to their ubiquity in the landscape, capacity to exchange carbon and energy with the atmosphere, and their potential to
10 inform researchers about past climates through sediment records. A changing climate has implications for the capacity of ponds and lakes to support organisms and store carbon, which in turn has important feedbacks to climate change. Thus, an improved understanding of pond biogeochemistry is needed. To characterize spatial and temporal patterns in water column chemistry, a suite of tundra ponds were examined to determine (1) Does temporal variability exceed spatial variability? (2) If temporal variability exists, do all ponds (or groups of ponds) behave in a similar temporal pattern, linked to seasonal hydrologic
15 drivers or precipitation events? Six shallow ponds located in the Hudson Bay Lowlands region were monitored between May-October 2015 (inclusive, spanning the entire open-water period). The ponds span a range of biophysical conditions including pond area, perimeter, depth, and shoreline development. Water samples were collected regularly, both bimonthly over the ice free season, and intensively during and following a large summer storm event. Samples were analyzed for nitrogen speciation (NO_3^-, NH_4^+, dissolved organic nitrogen) and major ions (Cl^-, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, Na^+). Across all ponds, temporal
20 variability (across the season and within a single rain event) exceeded spatial variability (variation among ponds) in concentrations of several major species (Cl^-, SO_4^{2-}, K^+, Ca^{2+}, Na^+). Evapoconcentration and dilution of pond water with precipitation and runoff inputs were the dominant processes influencing a set of chemical species which are hydrologically driven (Cl^-, Na^+, K^+, Mg^{2+}, dissolved organic nitrogen), whereas the dissolved inorganic nitrogen species were likely mediated by processes within ponds. This work demonstrates the importance of understanding hydrologically driven chemodynamics in
25 permafrost ponds on multiple scales (seasonal and event scale).

1 Introduction

Small, shallow freshwater bodies (<1 km^2) across the circumpolar north are ubiquitous in the landscape (Muster et al., 2013; Dyke and Sladen, 2010; Macrae et al., 2014). In many regions, these features maintain the capacity to store and exchange carbon (C) (Macrae et al., 2004; Abnizova et al., 2012), act as habitat (Smol and Douglas, 2007), and mediate the landscape

energy balance (Chapin et al., 2000). These tundra ponds are highly sensitive to climate change (Schindler and Smol, 2006), which may impact their hydrology and biogeochemistry. This has implications for their ability to support organisms and store or cycle C, which in turn has important feedbacks to climate change. Thus, an improved understanding of pond biogeochemistry is needed. Climate change may impact pond hydrobiogeochemical conditions by modifying pond hydrologic

5 and thermal conditions, as well as pond-catchment connectivity. In permafrost systems, recent work has focused on the impact of climatically-induced permafrost thaw on lake and pond chemistry (Vonk et al., 2015) over a timescale of decades, generally showing increasing concentrations of ions indicative of deeper flowpaths and weathering processes (Kokelj et al., 2009). Lougheed et al. (2011) examined changes in tundra pond chemistry over 40 years in Alaska and observed substantial increases in inorganic nutrients, which were attributed to a thaw-based release from shallow permafrost and increased atmospheric

10 nitrogen (N) deposition. In addition to changing chemical contributions from thawing catchments, the water balances of ponds are sensitive to climatic changes that impact the ponds directly as well as indirectly through changing catchment hydromorphology (Walvoord and Kurylyk, 2016). Adjacent to pond edges, thermokarst expansion acts as a mechanism for lateral seepage and loss (eg, Yoshikawa and Hinzman, 2003) leading to increased connectivity, potentially modifying seasonal biogeochemical trajectories (Abbott et al., 2015). Elevated levels of nutrients and/or ions may impact the C uptake function of

15 ponds via primary productivity, which has been shown to be nutrient limited in subarctic and arctic freshwater bodies (Levine and Whalen, 2001; Bergström et al., 2005; Bergström, 2010; Bonilla et al., 2005; Symons et al., 2012). Indeed, increased nutrient loading to ponds may either bring about an increase in pond primary productivity (Levine and Whalen, 2001; O'Brien et al., 2005) or may lead to a decrease through increased turbidity and suboptimal conditions for photosynthesis (northern Sweden, Ask et al., 2009; northern Québec, Roiha et al., 2015), linking nutrient concentrations to biological markers such as

20 chlorophyll (Przytulska et al., 2016).

Although climate change may lead to long-term changes in pond permanence and hydrologic exchange, pond hydrologic storage can also vary greatly over the course of a single season or among different hydrologic years (Morison et al., 2017, Woo and Guan, 2006). Annual changes to pond storage often reflect the highly variable local climatic conditions, and ponds may either desiccate completely (e.g. Bouchard et al., 2013; Smith et al., 2005) or spill over bankfull storage and/or coalesce

25 (Macrae et al., 2014). The chemical concentrations of the water column in ponds is closely tied to hydrology, both directly through physical processes (i.e. dilution and evapoconcentration; Borghini et al., 2013) and indirectly through mediating environmental factors that control the rate of biogeochemical processes (e.g. variable pond depth controlling the diurnal water temperature amplitude; Smol and Douglas, 2007). Mazurek et al. (2012) sampled shallow ponds over several summer seasons in Svalbard and found ionic concentrations increasing in ponds over the summer months, coincident with pond drying. White

30 et al. (2014) monitored ponds at three time steps over the ice-free season and related pond seasonal biogeochemical trajectories to pond morphology and pond-peatland connectivity. Given the significant control of hydrology on pond biogeochemistry, and the highly variable hydrological conditions experienced by ponds within a single season, an improved understanding of seasonal patterns of pond hydrochemistry is needed to better understand potential pond responses to climate change.

The concepts of hydrochemical coherence (or synchrony; Baines et al., 2000) have been employed in temperate lake systems to determine the role of different climatic and hydrological factors in driving lake chemical variations, employing correlation a different chemical measures (e.g. Magnuson et al., 1990). For instance, Pace and Cole (2002) found in Northern Michigan that changes to dissolved organic carbon and colour were synchronous among lakes while total phosphorus, chlorophyll, and

5   pH were not. Other methods, such as the use of evaporative normalization factors (e.g. Borghini et al., 2013), have allowed for comparisons among difference chemical species and the degree to which they are driven by hydrological variation. Both of these methods allow for comparison of relative deviations of values which would otherwise be masked by absolute differences among lakes. Approaches of hydrochemical coherence have been less seldom employed in subarctic permafrost pond and lake settings.

10   Recent approaches to characterising shallow pond biogeochemical processes across Arctic, Antarctic, and alpine permafrost settings have used three to four water samples from each lake or pond, taken at different points of the ice-free season to represent "early-season", "mid-season", and "late-season" conditions. Other approaches have relied on a single annual sample to characterize various geochemical indicators of ponds, such as nutrient status, carbon dynamics, major ion and metal concentrations, often sampling many ponds and lakes (often 10 – 100) at that single time period (Supplementary Table S1).

15   However, given the variability in pond storage and hydrological conditions over the course of an ice-free season, it is important to frame the results of pond chemical analyses in the proper hydrologic context, and further, to be prudent in generalizing pond geochemical process from samples taken in different hydrological periods. Beyond broad spatial sampling campaigns of many periods at a coarse temporal resolution, less is known about the amplitude, drivers, and total variation in seasonal and event chemographs of shallow ponds in remote northern catchments, despite their importance in driving key ecological functions

20   across the circumpolar north. Further, as large summer storms increase in frequency and magnitude (Sauchyn and Kulshreshtha, 2008; Kaufman et al., 2009), it is important to understand how storm events control short-term water chemistry variation, which can represent a substantial proportion of the annual water balance over a period of hours to days (Macrae et al., 2014).

The objectives of this study were to characterize spatial and temporal patterns in the chemistry of a suite of tundra ponds to

25   determine if: (1) temporal variability exceeded spatial variability throughout the open water season; (2) temporal variability existed, whether all ponds (or groups of ponds) behaved in a similar temporal pattern, linked to season or hydrology; and (3) spatiotemporal variability in pond biogeochemical signatures could be used to make inferences about processes occurring within ponds and between ponds and surrounding peatlands. This information will improve our understanding of hydrobiogeochemical processes in tundra ponds, particularly in terms of seasonal patterns, and, will aid in developing

30   appropriate sampling designs in future. Further, this study provides a geochemical survey of six ponds in the Hudson Bay Lowlands region at two unprecedented temporal scales (bimonthly, spanning an ice-free season, in addition to diurnal samples spanning an intense rainfall-runoff event.

2 Methods

2.1 Study site and sampling design

This study was completed in the Hudson Bay Lowlands (HBL), approximately 20 km East of the town of Churchill, Manitoba, Canada. The regional climate is strongly influenced by the close proximity to Hudson Bay (Rouse, 1991), with average air temperatures in the region (1980-2010 normal) of -6.5 °C (annually) with a snow-free season from May-October, and maximum temperatures in July (monthly average 12.7 °C; Government of Canada, 2016).

The HBL are the largest contiguous wetland complex in North America, with thousands of lakes and ponds in the landscape (Keller et al., 2014; Dyke and Sladen, 2010) from impeded drainage due very low topographic gradients (Boudreau and Rouse, 1995) and the presence of permafrost. Ponds have been demonstrated to be stably stratified in the eastern HBL (Deshpande et al., 2015), while the very shallow (<1 m) ponds in the western HBL have been shown to be non-stratified, well mixed by wind action (Bello and Smith, 1990). Ponds in the western HBL have been shown to be nutrient-limited (Eichel et al., 2014; Symons et al., 2012), restricted in surface and groundwater connection (Boudreau and Rouse, 1995), with steep banks and thick, organic sediments with dense mats of benthic blue-green, green and diatomaceous algae (Macrae et al., 2004; Gray, 1987), with the dominant diatom genus being *Denticula* (Macrae et al., 2004). Symons et al. (2012) showed the most abundant phytoplankton communities to be *Chlamydomonas* spp., *Sphaerocystis* spp., *Diatoma* spp. and *Crugienella* spp. Due to their small size and extremely alkaline conditions (8 to 9.8 pH, Macrae et al., 2004; Bos and Pellatt, 2012), ponds are devoid of fish communities with the exception of stickleback (*Gasterosteidae*). Ponds are also devoid of aquatic macrophytes with the exception of *Carex aquatilis* found along pond perimeters in zones where water is shallow. Eichel et al. (2014) demonstrated the importance of benthic organisms to the cycling of nutrients in these ponds, showing experimentally that mesocosms with sediment removed inorganic nutrients from the water column at a rate orders of magnitude greater than mesocosms without sediment.

The ponds and their catchments are underlain by continuous permafrost, with a seasonal active layer of 40 – 100 cm thickness. In the catchments, there is a peat layer of 30 – 60 cm overlying unsorted glaciomarine till. The surface is comprised of patterned polygonal peat plateaus segregated by sedge lawn and narrow fen channel networks. Dry uplands (plateau) are dominated by lichen-heath communities, with sparse tree cover (*Larix* spp. and *Salix* spp.). Transition zones (moderate moisture, sedge lawns) are comprised of hummocks and hollows, dominated by a mixture of lichen-heath communities and *Carex mitis*. Low-lying channel fens (saturated) are dominated by *Carex aquatilis*. Dwarf shrubs (*Betula glandulosa* and *Salix arctica*) are also found in some channel fens and around pond perimeters.

Six study ponds were selected: Erin pond, Frisbee pond, Larch pond, Left pond, Strange pond, and Sandwich pond (Figure 1). These ponds were selected for their range in surface areas, perimeter, catchment area, and depth, because they have been the subject of long-term research in the area, and have been shown to be representative of a range of chemical and hydrological properties (Table 1; Macrae et al., 2004; White et al., 2014; Wolfe et al., 2011; Bos and Pellatt, 2012). Each pond was sampled regularly (every 14 days) throughout the ice-free season of 2015, from Day of Year (DOY) 140 to 300, May to October). Additionally, during an intensive storm during DOY 185 – 188, ponds were sampled twice per day during the storm and 24

hours following the event to determine the hydrochemical impacts of a storm event, including the inputs of both direct precipitation and runoff water. Pond stage (water column depth) data were recorded hourly with pressure transducers (HOBO U20, Onset Ltd) installed in PVC (50 mm inner diameter) slotted pipes located within 1m of the shore of each pond (with the exception of Erin pond) and corrected with a barometric logger housed in an identical PVC pipe to minimize temperature-

5 related artifacts in pressure differences between barometric and level loggers (McLaughlin and Cohen, 2011). Precipitation data were taken from the Environment Canada 'Churchill' station (20 km West of the study site). Runoff was determined as the residual change in pond storage exceeding the input from direct precipitation during and up to 24 h. following a rain event, after Morison et al. (2017). The perimeter and area of each pond were surveyed with a Trimble Juno SB GPS unit, with a differentially corrected horizontal accuracy of ±5m.

10 **2.2 Water chemistry sampling and analysis**

Samples of pond water were collected manually as a depth-integrated profile of the water column, approximately 3 m from the pond edge, and placed in sterile, triple-primed 50 ml polyethylene containers. Care was taken to not disturb pond sediments when samples were being collected. Samples were preserved on ice in the field and passed through a 0.45 μm cellulose acetate filter within two hours of collection. A 50 ml subsample was acidified to a final concentration of 0.2% H_2SO_4 and stored until

15 digestion. Non-acidified samples were immediately frozen. All samples were shipped to the Biogeochemistry Lab at the University of Waterloo for analysis. In the lab, acidified samples were digested (Kjeldahl digestions, Seal Analytical Hot Block Digestion System BD50, Seattle, USA) for the analysis of Dissolved Kjeldahl N (DKN). Digested samples and non-acidified subsamples were analysed for N species using colorimetric methods: (Bran-Luebbe AutoAnalyzer III, Seal Analytical: Methods G-102-93, (ammonium; NH_4^+-N); G-103-93 (SRP-P), G-109-94 (nitrate; NO_3^--N), G-189-97 (DKN)). Results for

20 NH_4^+ and NO_3^- have a detection limit of 0.001 mg N L^{-1}. Dissolved organic nitrogen (DON) concentrations were determined as the difference between DKN and NH_4^+ concentrations. Samples were analysed for other major ions: chloride (Cl^-), sulphate (SO_4^{2-}), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) using ion chromatography (DIONEX ICS 3000, IonPac AS18 and CS16 analytical columns).

2.3 Statistical techniques

25 Due to large variability (spatial and temporal) in absolute values of concentration across the data set, values were normalized as deviations from mean values to permit their comparison (Schoenfeld and Numberger, 2007; Viner, 1984). This was accomplished by examining the departure of each sampling point from the mean of either temporal or spatial groups. More specifically, for each measurement, proportional deviations from either spatial or temporal means were determined as the absolute difference from unity of either the ratio of the measured sample concentration at a particular date and pond, $[x]_{st}$, to

30 the mean concentration of the species from all ponds sampled that date, $\overline{[x]_t}$; to examine spatial deviations, Eq. (1), or the ratio

of the measured sample concentration to the mean concentration of the species from all samples taken from that pond over the entire study period, $\overline{[x]_s}$; to examine temporal deviations, Eq. (2).

$$\left| \frac{[x]_{st}}{[x]_t} - 1 \right| = \text{Spatial Deviation Score} \qquad\qquad \text{(Eq. 1)}$$

$$\left| \frac{[x]_{st}}{[x]_s} - 1 \right| = \text{Temporal Deviation Score} \qquad\qquad \text{(Eq. 2)}$$

5   Thus, each sample (n = 72; 12 samples from each of 6 ponds) is associated with both a temporal deviation score and spatial deviation score for each chemical species. Once a set of deviation scores was computed for each species, a Mann-Whitney test was used to determine if there was a significant difference between the medians of the set of spatial deviation scores and the set of temporal deviation scores for each chemical species.

To determine the relationship between pond volume and concentrations of different chemical species, a power function (Eq.
10   3) was fit to the spatially normalized concentration (the ratio of each concentration to the mean concentration $\overline{[x]_t}$) and stage data to represent the geometry of conical bathymetry (based on observations and measurements of several sediment basins) in the non-linear pond stage-volume relationship.

$$[x] = \beta_1 (\text{stage})^{\beta_2} \qquad\qquad \text{(Eq. 3)}$$

The parameter β_2 is invariant under linear translation, such as spatial-normalization, and is expected to maintain a negative
15   value with the magnitude depending on the bathymetry of the pond (with a theoretical value of 0 for a cylindrical flat-bottomed pond, and highly negative for a steep conically shaped pond basin). The fit of each power function was assessed by the root mean squared error, as the coefficient of determination R^2 is inappropriate for the nonlinear case (Spiess and Neumeyer, 2010). Since the pond mean-normalized concentrations are dimensionless and not scale-dependant, the root mean square error term is also dimensionless and can be compared across ponds and chemical species. The degree of hydrologic control on different
20   nutrient species concentrations was determined by the performance of the fitting of a power curve to each set of normalized concentration data against pond stage for each of the five instrumented ponds. In each pond, chemical species with a constant pond-specific value of β_2 (the slope of the power curve) with low root mean square error (S) were categorized as hydrologically driven, where species with either (1) a β_2 value inconsistent with other hydrologically driven species or (2) poor performance (greater root mean square error) were categorized as non-hydrologically driven.

25   A principal component analysis (PCA; Dunteman, 1989) was employed on logarithmically-transformed hydrochemistry data, using singular value decomposition scaled to have unit variance. PCA has been used before in explorations of pond chemical trajectories over a scale of months to years (White et al., 2014, Sokal et al., 2010, Wiklund et al., 2012).

Coherence was assessed by Pearson correlation following the approach of Magnuson et al. (1990), both among lakes for each chemical species as well as for each chemical species (in all lakes combined). All statistical analyses were conducted with R
30   software (version 3.3.2, R Development Core Team, 2016).

3 Results

3.1 Spatial and temporal variability of pond chemistry

Spatial deviations did not significantly exceed temporal deviations for any chemical species (Figure 2). Medians of temporal deviation scores significantly exceeded the median spatial deviation scores in several chemical species (Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}) but there was no significant difference for DON, Mg^{2+}, NH_4^+, and NO_3^-. For species that were significantly more temporally variable than spatially variable, concentrations among ponds, despite differences in magnitude, tended to be strongly positively correlated which each other ($p < 0.01$) with the notable exception of DON (Table 2). NO_3^- and NH_4^+ were not significantly correlated to any other species ($p > 0.01$) (Table 3) while all other species tended to be strongly positively correlated which each other ($p < 0.01$) although there were some exceptions.

3.2 Seasonal patterns in pond water chemistry

Pond water chemistry varied among ponds, but also throughout the season (Figure 3). Throughout 2015, the temporal trend of pond mean-normalized concentrations in the six ponds appeared to have a spatial coherency in DON, Cl^-, SO_4^{2-}, Na^+, K^+ and Mg^{2+} concentrations. There was a gradual increase in concentrations of these species from DOY 140 to 260, punctuated by small decline in concentrations following a large storm on DOY 185-188, followed by a gradual decrease from DOY 260 to the end of the season. Ca^{2+} displayed a contrasting temporal trajectory to the other chemical species, decreasing from DOY 190 to the end of the season, while NO_3^- and NH_4^+ appeared to have no coherent pattern relative to the other chemical species. Generally, ponds were closest to their mean values during the mid-season (DOY 200 – 250) and pond-mean normalized concentrations differed the least among ponds during this time, being more divergent earlier (DOY 140 – 200) and later (DOY 250 – 300) in the season.

3.3 Pond hydrology and linkages with water chemistry

As was observed for water chemistry, there was also a seasonal pattern in pond hydrologic storage (Figure 4). In general, ponds were full following snowmelt, with water levels generally declining throughout the season and eventually rising again in late summer. Catchments showed synchronous runoff responses to two major rain events on DOY 166 and DOY 185 and three smaller rain events between DOY 260 and 290, although the magnitude of response varied. Following the early-season rain events, Left pond and Strange pond experienced prolonged summer drawdown while this drawdown was less pronounced in Larch, Frisbee and Sandwich ponds. At DOY 250 all ponds began a gradual increase in stage continuing to the end of season, but did not return to post-snowmelt levels. Within these five study ponds with recorded depth, there appeared to be no clear relationship between variation in stage and pond geometry (depth, shoreline development, area, or perimeter; Table 1).

Generally, DON, Cl^-, Na^+, K^+ .and Mg^{2+} were classified as generally hydrologically driven species among ponds and Ca^{2+}, NH_4^+, NO_3^-, and SO_4^{2-} were classified as non-hydrologically driven (Table 4; Figure 5). There were few exceptions to this manual classification, most notably, DON and K^+ tended to slightly poorer fits (larger S; slightly less hydrologically driven)

in Sandwich pond, whereas SO_4^{2-} may have been hydrologically driven in Strange pond. Slight differences in β_2 values among ponds for hydrologically driven species are influenced by the differences in bathymetry which dictates the stage-volume relationship.

3.4 Principal component analysis

5   PCA allowed for a reduction in the redundancy of species that are highly correlated (Table 3) and the clustering of samples from each pond in PC space (Figure 6). The analysis also shows a clustering of chemical species along the PC axes. A collection of the hydrologically driven chemical species (Table 4; DON, Mg^{2+}, K^+, Na^+, Cl^-) closely follows the PC1 axis with slightly negative scores for PC2. Two other non-hydrologically driven chemical species have positive scores along PC1 with slightly negative (SO_4^{2-}) and positive (Ca^{2+}) scores along PC2. Inorganic nitrogen species, (NO_3^- and NH_4^+), also non-hydrologically

10 driven, have negative scores along the PC2 axis and slightly negative scores along PC1. The spread of data points for Strange Pond, Left Pond and Frisbee Pond are more elongate along the PC1 axis where the spread of data from Larch pond, Erin pond and Sandwich pond are aligned along the PC2 axis. Temporally, the data tend to move from the upper-left quadrant (positive scores for PC2, negative scores for PC1) to the lower-right quadrant (positive scores for PC1, negative scores for PC2) over the course of the season. Chemical species which were classified as hydrologically driven (Table 4) were not necessarily the

15 same species which showed that temporal variance exceeded spatial variance (Figure 2). DON and Mg^{2+} were classified as hydrologically driven but did not have the same degree of temporal coherence displayed by Cl^-, Na^+, and K^+. Conversely, Ca^{2+} and SO_4^{2-} display significantly greater temporal variability then spatial variability, but were not classified as hydrologically driven constituents. Strange, Left, and Frisbee ponds were elongated with respect to the PC1 axis, which corresponds closely with the group of chemical species that are hydrologically driven. Strange and Left ponds showed the greatest variation in

20 pond stage (Table 1; Figure 4), linking the hydrological variation with the variation in concentrations of chemical species controlled by stage. Frisbee pond showed lesser variation in stage but was elongate with the respect to the axis of the hydrologically driven species cluster, suggesting that variation in pond stage alone does not necessarily dictate which species are most chemodynamic within a pond. Larch and Sandwich ponds, which showed lesser variation in stage, were elongated with respect to PC2, orthogonal to the cluster of hydrologically driven species along PC1. The redundancy in the original

25 dataset is primarily due to the clustering of the hydrologically driven species along PC1, and the very close clustering of Na^+ and Cl^- in PC space (indicating the marine halite influence on these ponds; Bos and Pellatt, 2012). In addition, the decoupling of Mg^{2+} and Ca^{2+} trajectories (Figure 3) and in PC space (Figure 6) indicate the potential role of Ca^{2+} in either carbonate cycling associated with productivity and carbon dioxide intake (Macrae et al., 2004), precipitation, or cation substitution (Wetzel, 2001). Further, not only are the hydrologically driven species (Table 4) correlated among ponds (Table 2), but they

30 are also correlated among species (Table 3). The apparent redundancy of several of these chemical trajectories is observed in the normalized time series of concentration data, with many of the species which align along PC1 axis showing similar concentration trajectories at the seasonal (Figure 3) and event (Figure 7) scales.

3.5 Event-scale variation in pond chemistry

In addition to being highly chemodynamic over the course of a ice-free season, pond chemistry varied greatly over the course of a single storm-runoff event (Figure 7). For samples taken during, and following the storm event in Strange Pond on DOY 185-188, concentrations of some chemical species varied by the same magnitude over the course of several days as they did over the period of the entire ice-free season (DON, K^+, Ca^{2+}, NO_3^-); other species varied but not to the same extent (Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, NH_4^+; Supplementary Table S2). In Frisbee pond, chemical species tended to vary by a similar magnitude over the storm period as they did over the entire season and this was not restricted to DON, K^+, and Ca^{2+}.

4 Discussion

4.1 Seasonal and spatial variability in pond chemistry

Ponds in this study displayed a coherent trend in several chemical concentrations over a ice-free season, despite differences in pond geometry, catchment characteristics, and absolute magnitude of chemical concentrations. Landscape scale factors such as climate are controlling hydrological processes, and in turn, concentrations of chemical species (specifically, Cl^-, Na^+, K^+, Mg^{2+}, and dissolved organic nitrogen). Magnuson et al. (1990) and Baines et al. (2000) reported Ca^{2+} to be temporally coherent among groups of large lakes in Wisconsin, USA, consistent with our findings, while Magnuson et al. (1990) found K^+ or SO_4^{2-} to be less coherent, contrasting with our results. However, the magnitudes of different chemical species concentrations varied among ponds, suggesting that influences such as runoff inputs, evapoconcentration, bathymetry, and internal processes (sediment-water interaction and biological cycling) may be driving these differences while preserving seasonal trajectories relative to a pond mean value. Other authors have reported on biogeochemical properties of ponds and their extreme spatial variability, such as the conditions of nutrient limitation of primary productivity in different lakes (Hogan et al., 2014, Symons et al., 2012). This work suggests that the concentration of at least some chemical species are not reflective of this spatial variability and instead more reflective of landscape-level process.

In many of the same study ponds as this work, White et al. (2014) found similar clustering of Cl^-, Na^+, K^+, and Mg^{2+} along their first PC axis (most variance explained) and another cluster including NH_4^+ and NO_3^- along their second axes. In contrast, total nitrogen was approximately orthogonal to both those clusters, instead of being aligned with the other species which were identified as hydrologically driven in our method. Differences between the findings of White et al. (2014) and this work may be explained by the inclusion of additional limnological measurements into the PCA, the greater number of lakes in the study (20), the smaller number of samples taken at each lake per year (3), and the reporting of total N as opposed to the dissolved fraction. Sokal et al. (2012) did not report a similar clustering of chemical species in PC space, with TKN, Cl^-, Na^+, Mg^{2+}, and K+ showing great variation relative to the tight clustering found in this study in the Slave River Delta and with less separation from the non-hydrologically driven chemical species in our study (Ca, SO_4). This could be due to larger and deeper lakes studied in the region (~10^6 m^2 surface area; 1.5 m deep) in addition to additional limnological and isotopic measurements into

the PCA. However, this difference in species clustering may not be region-specific as Wiklund et al. (2012) found a clustering of Na^+, Cl^-, TKN, K^+ and Mg^{2+} in PC space from lakes in the Peace Athabasca Delta region. Wiklund et al. (2012) also report approximately equal difference between the angle for the vectors of the cluster of hydrologically driven chemical species and Ca^{2+} and SO_4^{2-} as was found in this study.

5   **4.2 Event-scale variation in pond chemistry**

Short-term variation in concentrations during a storm was pronounced in Frisbee pond during the storm of DOY 185 – 188, 2015. This is likely due to the difference in the proportion of new water entering the pond relative to the volume of old water in the pond. In Frisbee pond, the rainfall inputs represent a much greater fraction of the total pond water at the conclusion of the event (nearly one-half), compared to Strange pond, which is larger and more full of water pre-event, where event water

10   represents a smaller proportion of the total post-event water (approximately one-quarter) despite the lesser runoff amount (Figure 4). This leads to the dampening of the storm-based concentration variability in Strange pond. Among chemical species, those species that may have elevated concentrations in event water relative to lower concentrations in pond water, such as DON (Morison et al., 2017), show a heightened response in terms of pond concentrations in both Frisbee pond and Strange pond, whereas species which have event water concentrations which are similar to background pond water concentrations

15   show a lesser response. Although the volume of event water being added may not represent a great fraction of the total water in the pond, it is enriched in species that occur naturally in rainwater or through primary runoff pathways (shallow, organic subsurface material). This is consistent with the findings of Abnizova (2013) which showed that the ionic composition at the event scale of runoff water to ponds in high arctic wetlands was caused by the vegetative structure of the catchment (related to dissolved organic material) and bedrock composition.

20   **4.3 Inferring hydrological and biogeochemical process from patterns in pond chemistry**

This study does not aim to present direct measurements of any biogeochemical process, including the magnitude and direction of which physiochemical transformations are operating to which extent. Each chemical species measured in this study in subject to differing degrees of reactivity/conservativism. Future research is needed to elucidate the individual or coupled cycling processes of these elements in subarctic freshwater ecosystems. Chemical species which appear to be driven primarily

25   by non-hydrological processes (Table 4) are likely those which are most reactive. However, our results can be contextualized within the existing body of knowledge of hydrobiogeochemical processes which have been measured in similar environments previously to determine if our observations are consistent with previous findings of different species.

Biogeochemical variations large in magnitude also often occur on short time scales, which are typically associated with the movement of water across geochemical boundaries (McClain et al., 2003). Previous work in tundra and high Arctic

30   environments have shown pathways for transformations of runoff water through the catchments, including biological incorporation of nutrients (Thompson and Woo, 2009) and geochemical processes of weathering and ion exchange (Quinton and Pomeroy, 2006), which impact the quality of the runoff water arriving at the pond. Once the runoff water is delivered to

the ponds, the biological factors driving responses to the incorporation and sedimentary burial of nitrogen and phosphorus on short timescales (< 72 hours of return to pre-event levels) were demonstrated experimentally by Eichel et al. (2014). These observations are consistent with the delivery of nutrients followed by rapid uptake to pre-event levels which was observed during and following the storm event around DOY 185 (Figure 7) in this study. These mechanism of runoff contributions to

5   pond chemical variability are important for future studies that aim to use seasonal and interannual variations in pond and lake chemistries to examine changing flowpaths in thawing permafrost environments. The relative change of concentrations in ponds and lakes over events, seasons, and years will be a product of the difference in concentrations between new and old water and the degree of dilution of new water arriving at the pond. If the concentration of a constituent in old water is not significantly different from that in new water, future work which infers understand changing flow paths from changing

10   chemical concentrations over time may significantly underestimate the degree of change to the movement of water and solutes due to thawing permafrost (Lougheed et al., 2011), or conversely overestimate the change in flowpaths in solutes which are radically different in concentration from old water. In this work, no clear relationship between chemical trajectory (Figure 3) and runoff (Figure 4) was observed, nor were either related specifically to total catchment area (Table 1). However, this may be a result of the variable source area concept applying in this fill-and-spill system (Spence et al., 2010; Morison et al., 2017),

15   in which substantial portions of the catchment are not contributing runoff to the ponds for some storms.

The method of fitting curves to stage-concentration relations to determine the degree to which pond hydrology dictates chemical concentrations may not capture all of the complex dynamics related to hydrological controls. For example, pond volume controls diurnal temperature fluctuation amplitude, and indirectly the rate of biogeochemical processes. In northern tundra environments, low temperatures limit the rates at which biogeochemical processes occur (Stark, 2007). Microbial

20   decomposition remains the crucial bottleneck (rate limiting step) in nutrient cycling (Stark, 2007; Andersen et al., 2013). Temperatures are often the most important factor limiting the rate of microbial decomposition of organic matter in cold region aquatic and terrestrial ecosystems (Wallenstein et al., 2009; Vonk et al., 2015, Wickland et al., 2012). On the North shore of Alaska, Koch et al. (2014) showed that the chemical dynamics were less pronounced in ponds that maintained lower temperatures, limiting evaporation and biological uptake; larger ponds with dilute inflows were subject to greater evaporation

25   as a fraction of pond volume and greater nutrient depletion over the course of the year, linking the combined effects of hydrology both directly and indirectly impacting nutrient concentrations.

4.4 Implications for sampling design in future studies

Generally, the current standard of measurements per annum are unlikely to be sufficient to capture the variability in highly chemodynamic systems, such as shallow ponds in which storage varies by up to 80% of the mean value over the course of the

30   ice-free season. In contrast, and campaigns that may be more temporally coarse but spatially intensive are applicable for larger, less chemodynamic lakes and ponds, in which total water inputs and outputs represent a much smaller proportion of the total volume. Further, the synchrony in the chemical behaviour of some spices (Cl^-, Na^+, K^+, SO_4^{2-}, Ca^{2+}) in these ponds suggests potential redundancy in the sampling of a great deals of lakes if the research goals are related to the measurement of these

chemical species. This study may be subject to the converse problem by observing water column chemistry in only 6 lakes over the ice-free season. However, it appears these six ponds capture a representative range of chemical concentrations, spanning 1-2 orders of magnitude, (Supplementary Table S2) which are representative of much wider spatial surveys in much of the work outlined in Supplementary Table S1 (and more specifically, in line with the variance observed by other authors

5   who have studied ponds in our specific region, Bos and Pellatt, 2012; White et al., 2014; Jacques et al., 2016). The fact that these ponds are closely spatially clustered may remove effects of microclimates on the scales of 10-100 kilometers which may reduce the degree of synchrony observed in chemical concentrations, due to different precipitation, runoff, and evaporative drawdown regimes.

Future biogeochemical research must consider the relative terms in the water balance in a pond to determine periods of greatest

10   variability (such as snowmelt vs. rainwater dominated ponds, e.g. Bouchard et al., 2013). A water budget approach should be incorporated into future studies which attempt to use changing solute concentrations as a proxy for changes to ensure that appropriate hydrological weighting to changes of concentrations in surface water are properly represented. Alternately, approaches characterizing total mass depletion of different ions and nutrients (e.g. Koch et al., 2014), an evaporative normalization factor (e.g. Borghini et al., 2013), the use of the Shannon index in a hydrochemical context (Thompson and

15   Woo, 2009), hydrologic context through isotopic composition (e.g. White et al., 2014) may provide a hydrologic context to concentration measurements which is lacking otherwise.

5 Conclusions

This study reported on the degree of hydrologic control on nutrient and major ion chemistry of a set of six of shallow permafrost ponds in the Hudson Bay Lowlands. Generally speaking, temporal variability exceeds spatial variability in pond chemistry in

20   this landscape. Five chemical species (Cl^-, SO_4^{2-}, Na^+, K^+ and Ca^{2+}) showed a temporal coherence in six different ponds over the course of an ice-free season (Figure 8). No pond demonstrated a spatial coherence in concentration trajectory which was distinct from every other pond. A set of species was determined to be hydrologically controlled (DON, Cl^-, Na^+, K^+ and Mg^{2+}), either directly through processes of evapoconcentration/dilution or indirectly through pond hydrology exerting an influence on biogeochemical characteristics. Approaches of PCA and coherence/correlation showed that these hydrologically driven

25   chemical species are strongly correlated to each other and among ponds. This evidence suggests that landscape level controls on pond hydrology may reduce the spatial heterogeneity in pond chemical trajectories for the hydrologically driven chemical species, but not for those species that are not hydrologically controlled (Ca^{2+}, SO_4^{2-}, NO_3^-, NH_4^+). Further, at the event scale, variation over the course of days during, and following precipitation events may be on equal order as the variation over the course of months. This longer period variation is also not limited to the hydrologically driven species, indicating the importance

30   of biogeochemically active periods coinciding with periods of water movement across boundaries (catchment-pond interactions). This work has important implications for understanding the highly chemodynamic behavior of permafrost ponds through over both short-term and long-term temporal scales while remaining spatially synchronous. Our findings indicate the

design of future sampling regimes, which continue to rely on inference from broad spatial sampling at coarse temporal scales must consider the hydrologic context of the samples taken. In particular, the proximity of recent rain events and the trajectory of pond water balance are important considerations for interpreting pond chemical concentration data for the purpose of inferring landscape level changes to permafrost environments.

5 Data availability

Unprocessed data (not subject to temporal or spatial deviation normalization) from all chemical analyses are available as a supplement to this work, Table S2.

Competing interests

The authors declare that they have no conflict of interest.

10 Author contributions

M.Q. Morison, R.M. Petrone, M.L. Macrae and L.A. Fishback designed the sampling strategy and study objectives, L.A. Fishback supervised the field sample collection, M.Q. Morison performed the laboratory analyses, analysed the data, generated the figures, and prepared the manuscript, R.M. Petrone and M.L. Macrae provided comments on the manuscript composition and figure presentation.

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Tables

Table 1. Physical characteristics and locations of study ponds near Churchill, Manitoba.

Pond	Area (m²)	Perimeter (m)	Shoreline development* (m¹ m⁻¹)	Average depth, μ ± σ (cm)	Catchment area (m²)	Coordinates
Erin	8479	448	1.37	No data	108160	58°43'14.3"N 93°50'20.2"W
Left	752	130	1.34	30.0 ± 6.8	5737	58°44'44.2"N 93°49'20.6"W
Strange	6307	424	1.51	22.2 ± 10.0	20441	58°43'36.8"N 93°50'20.6"W
Sandwich	17146	548	1.18	19.6 ± 4.8	34638	58°43'24.2"N 93°50'34.4"W
Frisbee	4416	258	1.10	14.2 ± 2.8	31128	58°43'35.5"N 93°50'33.9"W
Larch	4066	333	1.47	14.2 ± 4.9	15228	58°43'26.9"N 93°50'41.5"W

*Shoreline development, D_L, is the ratio of measured shoreline perimeter, P, of a given pond to the shoreline perimeter of a perfectly circular pond of equal area, A, such that $D_L = \frac{P}{2\sqrt{\pi A}}$ (Aronow, 1982)

Table 2. Correlation coefficients among ponds for all species. Values are bolded when the correlation is significant at the $p < 0.01$ level.

	Erin	Frisbee	Larch	Left	Sandwich
DON					
Frisbee	**0.761**				
Larch	**0.802**	**0.687**			
Left	**0.794**	**0.912**	**0.846**		
Sandwich	**0.860**	**0.689**	**0.965**	**0.829**	
Strange	**0.763**	**0.904**	0.659	**0.900**	**0.688**
Cl⁻					
Frisbee	**0.859**				
Larch	**0.762**	**0.751**			
Left	**0.875**	**0.787**	**0.884**		
Sandwich	**0.649**	0.539	**0.941**	**0.851**	
Strange	**0.774**	**0.680**	**0.751**	**0.889**	**0.746**
SO₄²⁻					
Frisbee	**0.745**				
Larch	-0.056	-0.007			
Left	**0.740**	**0.836**	-0.271		
Sandwich	-0.415	-0.388	0.134	-0.285	
Strange	**0.731**	**0.728**	-0.133	**0.958**	-0.318
Na⁺					
Frisbee	**0.863**				
Larch	**0.667**	**0.625**			
Left	**0.875**	**0.765**	**0.818**		
Sandwich	**0.777**	**0.643**	**0.920**	**0.948**	
Strange	**0.843**	**0.682**	**0.711**	**0.963**	**0.897**
K⁺					
Frisbee	**0.847**				

	Frisbee	Larch	Left	Sandwich	Strange
Larch	0.561	0.490			
Left	0.401	0.261	**0.584**		
Sandwich	0.428	0.562	**0.794**	0.523	
Strange	**0.614**	0.563	**0.834**	0.734	0.725
Mg^{2+}					
Frisbee	**0.935**				
Larch	**0.830**	**0.881**			
Left	**0.912**	**0.944**	**0.878**		
Sandwich	**0.904**	**0.905**	**0.946**	**0.952**	
Strange	**0.929**	**0.905**	**0.831**	**0.979**	**0.939**
Ca^{2+}					
Frisbee	0.138				
Larch	**0.700**	0.330			
Left	0.278	0.571	0.102		
Sandwich	0.226	0.433	0.354	0.274	
Strange	**0.772**	0.419	**0.723**	0.340	0.566
$NH_4^{\pm}$					
Frisbee	**0.715**				
Larch	**0.605**	**0.619**			
Left	-0.135	-0.250	0.261		
Sandwich	0.000	-0.003	-0.256	-0.103	
Strange	-0.449	-0.040	-0.277	-0.024	-0.325
NO_3^-					
Frisbee	0.000				
Larch	-0.087	0.320			
Left	0.404	-0.346	-0.366		
Sandwich	0.136	-0.011	0.295	-0.289	
Strange	-0.294	-0.133	0.353	-0.504	0.292

Table 3. Correlation coefficients among species for all ponds. Values are bolded when the correlation is significant at the $p < 0.01$ level.

	DON	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
Cl^-	**0.710**							
SO_4^{2-}	**0.594**	**0.827**						
Na^+	**0.615**	**0.971**	**0.802**					
K^+	0.276	**0.504**	**0.462**	**0.595**				
Mg^{2+}	**0.563**	**0.892**	**0.787**	**0.940**	**0.585**			
Ca^{2+}	**0.605**	**0.408**	**0.531**	**0.285**	0.000	0.166		
NH_4^+	-0.097	0.034	0.039	0.000	-0.163	0.027	-0.082	
NO_3^-	-0.134	-0.201	-0.143	-0.207	-0.076	-0.158	-0.078	0.218

Table 4. Values of β2 and root mean square error (S) from the curve $[x] = \frac{[x_{st}]}{[x_s]} = \beta_1(\text{stage})^{\beta_2}$ **for each set of normalized concentration data $[x]$. Chemical species were manually classified as hydrologically driven if they shared a common (approximate)**

β_2 value within a pond with a low S relative to other species in the same pond. Notable exceptions to the general classification in the table heading are italicized.

	Hydrologically driven					Not hydrologically driven			
	DON	Cl⁻	Na⁺	K⁺	Mg²⁺	Ca²⁺	NH₄⁺	NO₃⁻	SO₄²⁻
Frisbee									
β_2	-2.61	-2.63	-2.01	-2.52	-2.15	-0.38	-0.23	0.23	-1.11
S	0.27	0.16	0.15	0.22	0.23	0.25	0.70	0.29	0.24
Larch									
β_2	-0.35	-0.28	-0.29	-0.38	-0.44	0.39	-0.73	-0.18	0.08
S	0.16	0.06	0.09	0.09	0.08	0.14	0.65	0.29	0.52
Left									
β_2	-0.70	-1.20	-1.07	-0.21	-1.05	-0.12	-1.44	-0.29	-1.30
S	0.28	0.19	0.14	0.19	0.16	0.15	0.52	0.38	0.35
Sandwich									
β_2	*-0.47*	-0.43	-0.53	*-0.28*	-0.63	0.36	0.82	-0.35	0.85
S	*0.19*	0.08	0.05	*0.15*	0.07	0.30	0.78	0.28	0.66
Strange									
β_2	-0.16	-0.75	-0.55	-0.23	-0.57	0.42	-0.08	0.07	*-0.71*
S	0.37	0.18	0.11	0.11	0.15	0.24	0.45	0.13	*0.18*

Figures
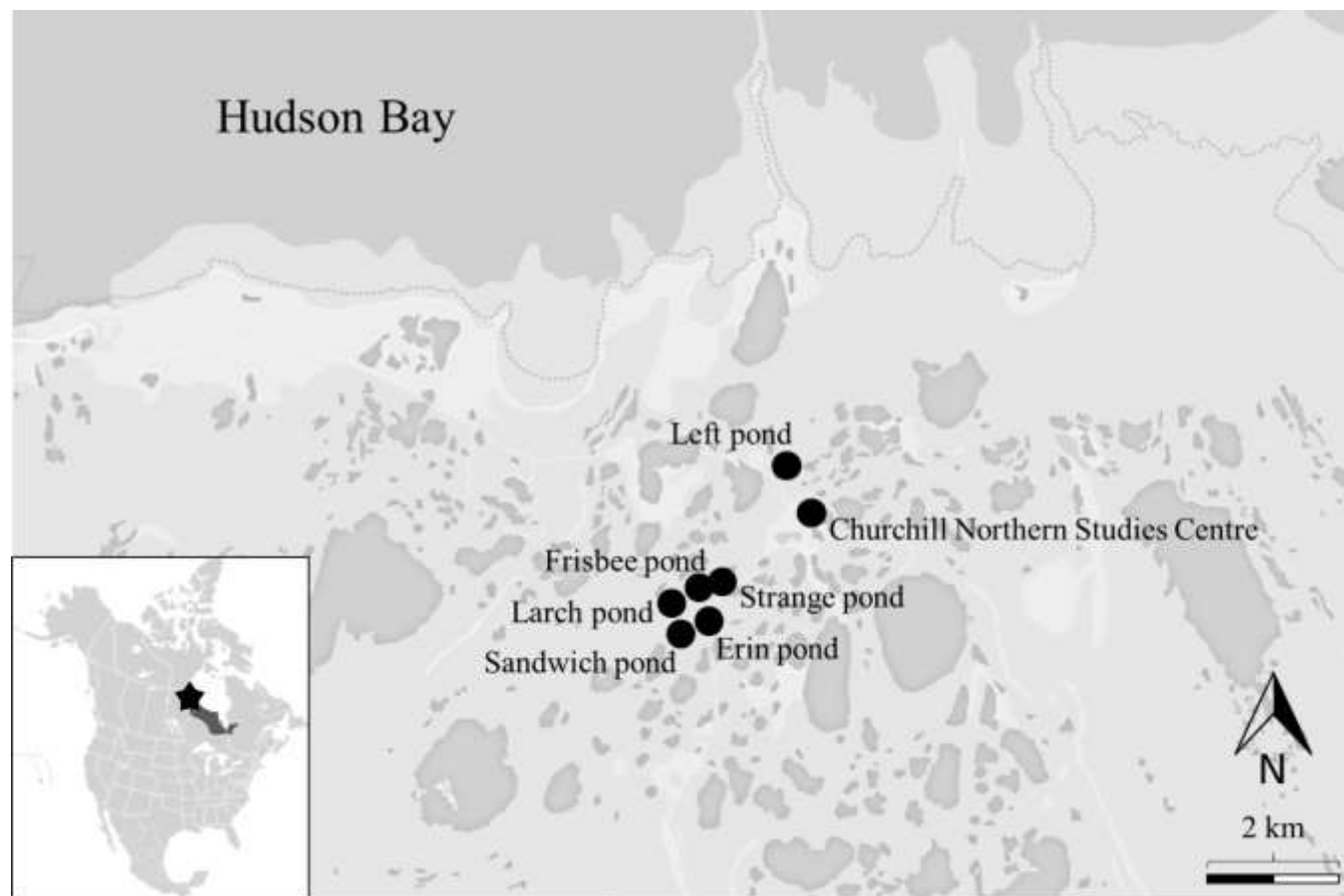
Figure 1. Site map of the general near-coastal tundra region with the catchment areas containing Frisbee, Larch, Strange, Sandwich, Left, and Erin ponds. Inset map highlights the Hudson Bay Lowlands (dark colour) and the Churchill region (star). Map data: Google, Digital Globe, 2017.
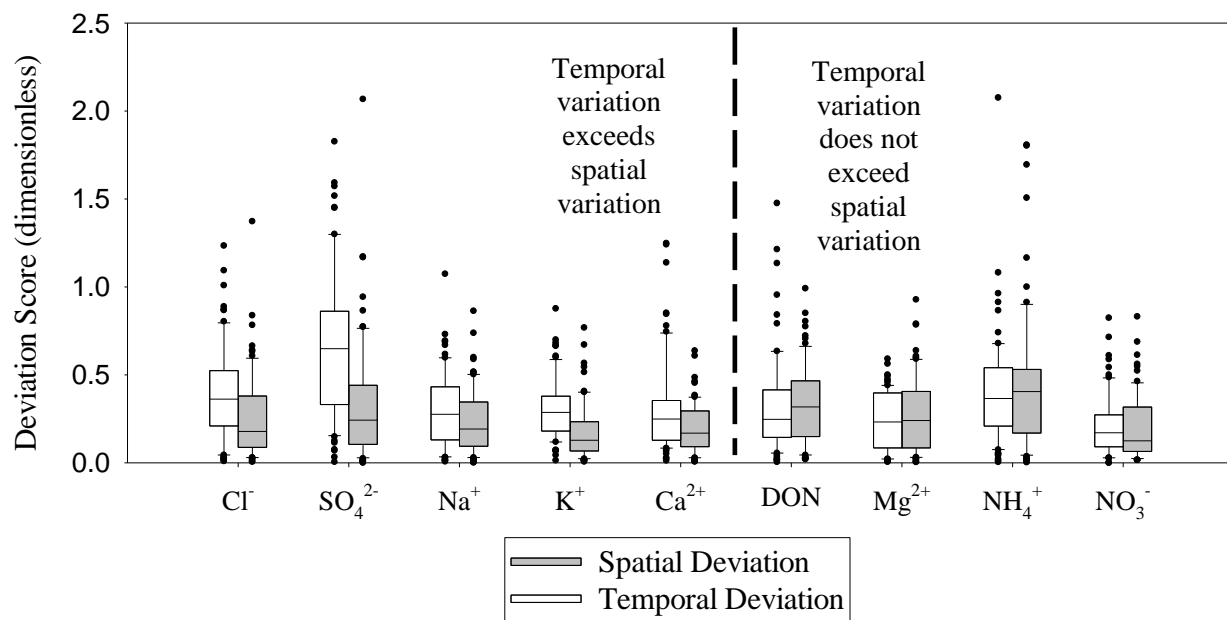
Figure 2. Boxplots of spatial and temporal proportional deviations for each chemical species. Significant differences between medians ($p < 0.01$) are present for all species on the left side of the panel (Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}), and no significant difference is present for species on the right (DON, Mg^{2+}, NH_4^+, NO_3^-).

Figure 3. Pond normalized concentrations of all measured chemical species in each pond and precipitation for the 2015 snow free season. In chemical species on left side of the panel (Cl⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺) temporal variation exceeds spatial variation, and no significant difference is present for species on the right (DON, Mg²⁺, NH₄⁺, NO₃⁻).
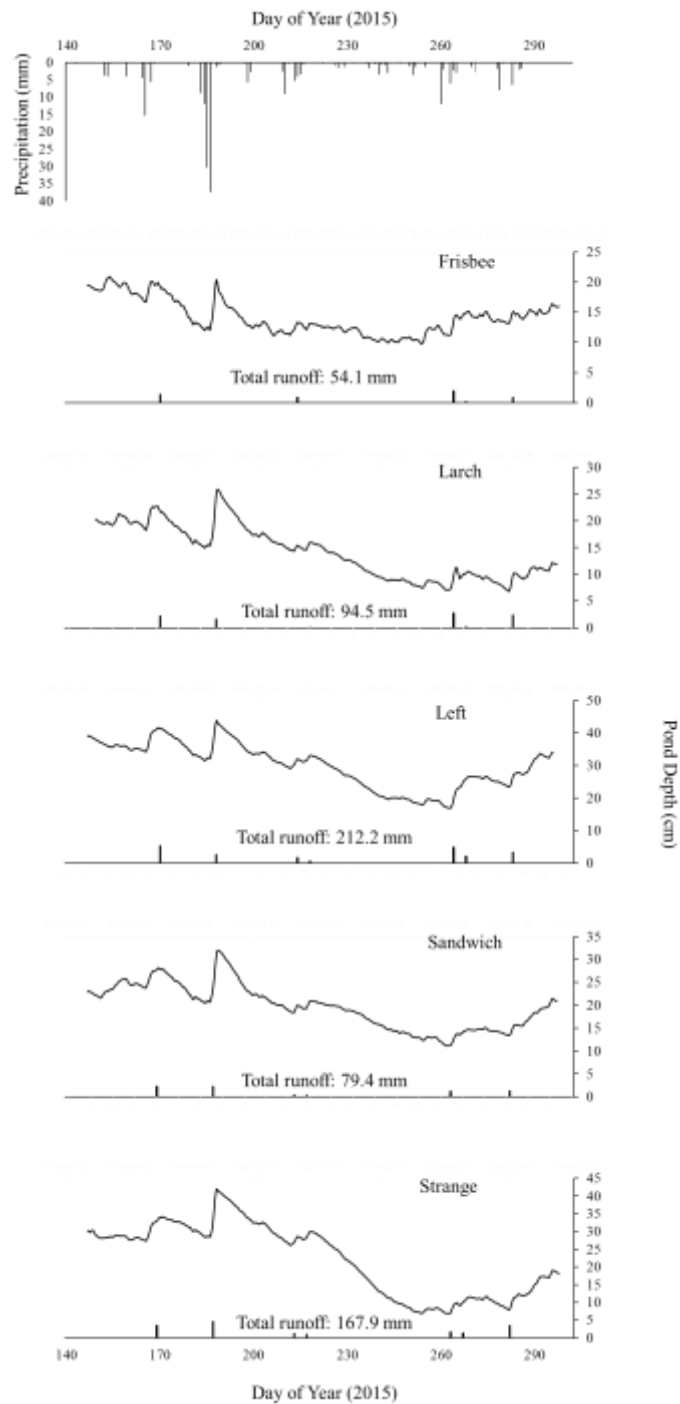
Figure 4: Precipitation (vertical bars, top panel), as well as depth of water column (continuous line) and runoff depths (vertical bars) in each of the instrumented study ponds over the 2015 ice-free season.
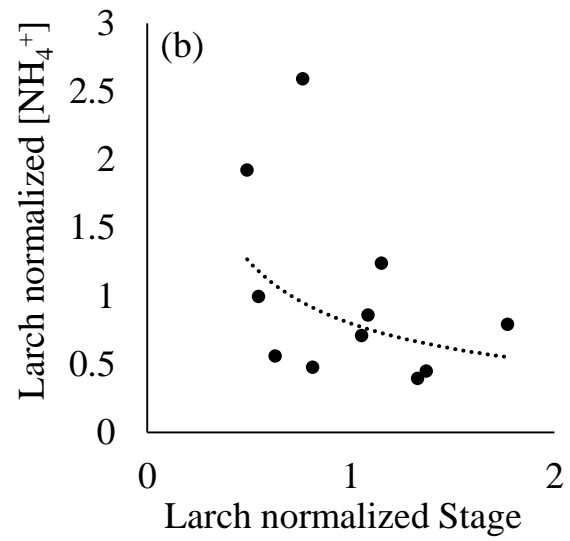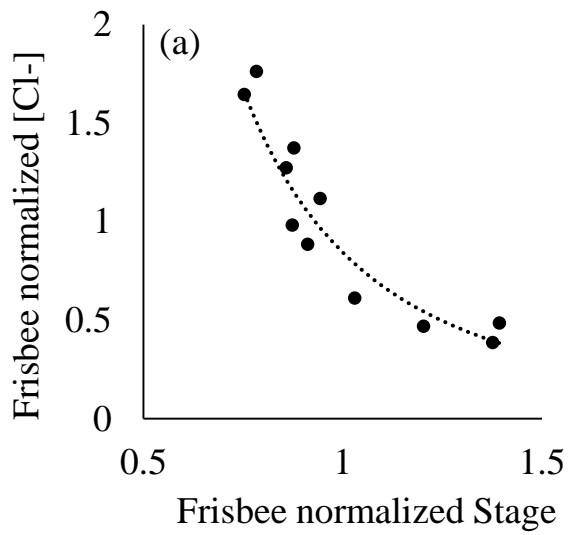
Figure 5: Comparison of the stage-concentration relationship in a (a) hydrologically driven chemical species (Cl⁻, in Frisbee pond), and (b) a non-hydrologically driven species (NH₄⁺, in Larch pond).
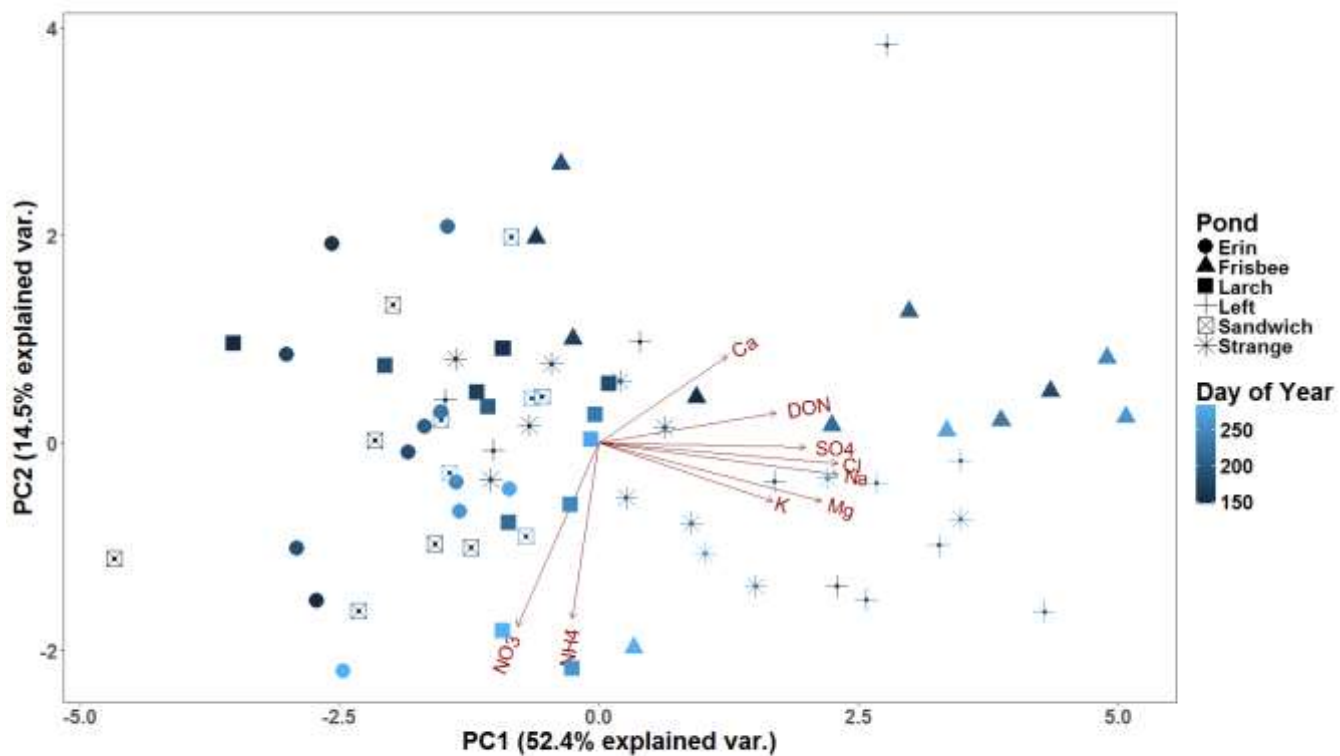
Figure 6. Principal Components Analysis of chemical concentrations in all ponds throughout the 2015 snow-free season. PC1 primarily corresponds with the hydrologically driven chemical species while PC2 corresponds to inorganic nitrogen species (NO$_3^-$, NH$_4^+$).
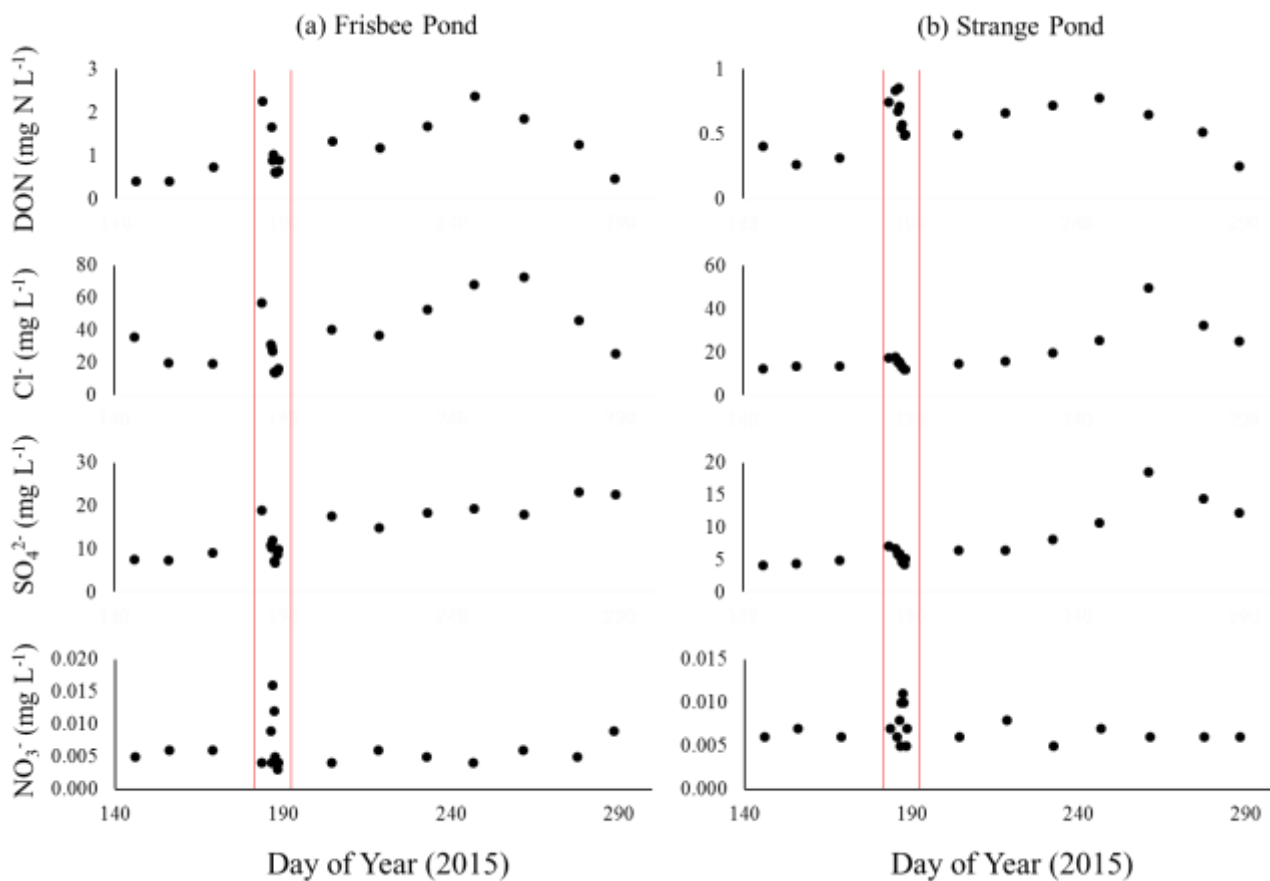
Figure 7. Short term variation in DON, Cl⁻, SO₄²⁻, and NO₃⁻ concentrations in (a) Frisbee pond and (b) Strange pond during a rain event on July 3ʳᵈ to 6ᵗʰ, 2015 (DOY 185-188, highlighted with red bars).
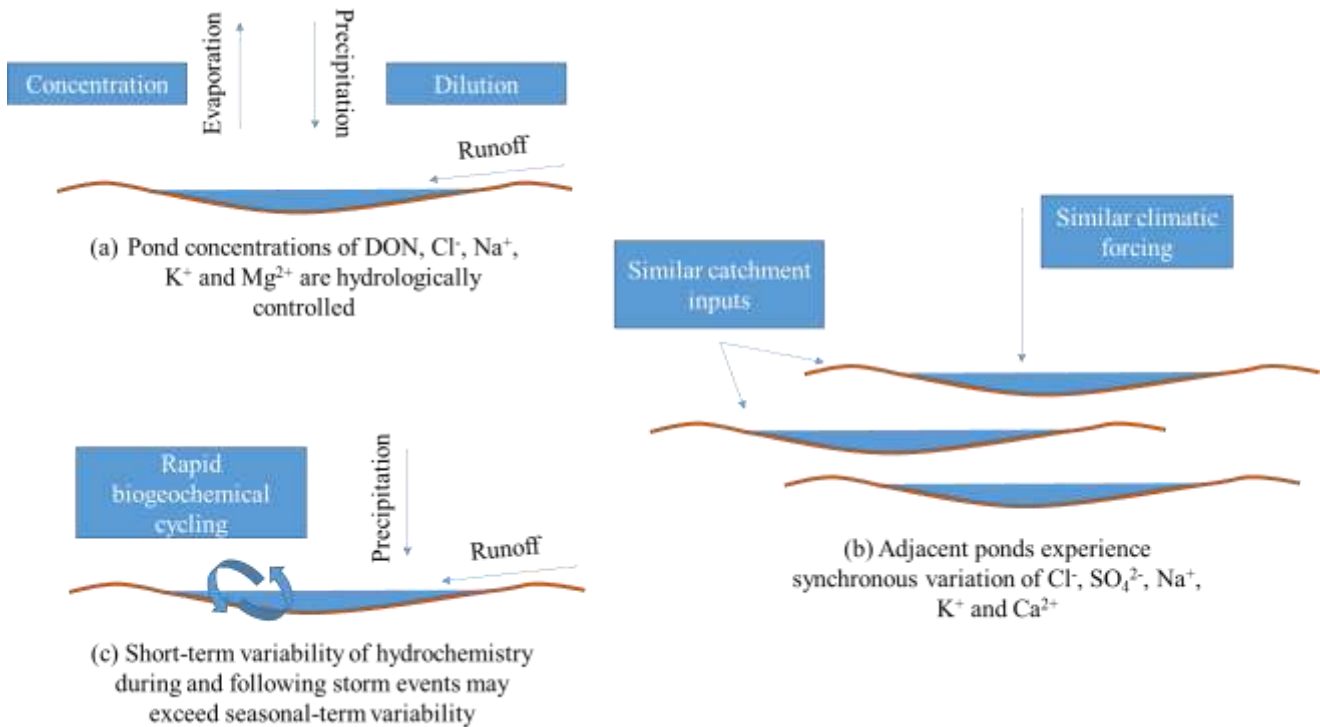
Figure 8. Graphical summation of major findings from this study; (a) factors driving hydrological control of particular chemical species in ponds, (b) hypothesised factors driving temporal coherence in chemical species in ponds, and (c) short-term variation in hydrochemistry can exceed seasonal-scale variation despite the large difference in timescales.