Hydrology drives chemical synchronicity in subarctic tundra ponds

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Abstract.

Climate change has implications for the capacity of the many small shallow ponds found at high latitudes to support organisms and store carbon, which in turn has important feedbacks for climate change. As carbon cycling in ponds is linked to nutrient supply, an improved understanding of pond biogeochemistry is needed. Due to logistical challenges, many studies rely on data
10   sets collected during a single campaign that may not be representative of the entire ice-free season. This study characterized spatial and temporal patterns in water chemistry in tundra ponds to determine: (1) if temporal variability in pond chemistry exceeded spatial variability; (2) if temporal variability existed, whether all ponds (or groups of ponds) behaved in a similar temporal pattern, linked to season or hydrology; (3) if spatiotemporal variability in pond biogeochemical signatures could be used to make inferences about processes occurring within ponds and between ponds and surrounding peatlands. Six shallow
15   ponds located in the Hudson Bay Lowlands region were monitored ~biweekly throughout the ice-free season (May 1-October 31, 2015) for concentrations of nitrogen species and major ions. Temporal variability exceeded spatial variability (variation among ponds) in pond concentrations of most major ions and dissolved organic nitrogen, which appeared to be driven by the evapoconcentration and dilution of pond water. In contrast, the dissolved inorganic nitrogen species were not directly related to pond hydrologic conditions and were instead likely mediated by biological processes within ponds. This work provides an
20   improved understanding of the relative controls of internal and external drivers of pond biogeochemical patterns, and highlights the importance of the highly variable seasonal hydrology. This work also provides insight for future field sampling campaigns.

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). These ponds maintain the capacity to store and exchange carbon (C) (Macrae et
25   al., 2004; Abnizova et al., 2012), act as habitat (Smol and Douglas, 2007), and mediate the landscape energy balance (Chapin et al., 2000), despite being historically underestimated in total areal coverage. 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 biogeochemical conditions by modifying pond hydrologic 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-driven release from shallow permafrost and increased atmospheric 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). In particular, with permafrost decay, 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 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).

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 between different hydrologic years (Morison et al., 2016, Woo and Guan, 2006). Indeed, pond storage often reflect the highly variable local climatic conditions, and can both desiccate completely (e.g. Bouchard et al., 2013; Smith et al., 2005) and spill over bankfull storage and/or coalesce (Macrae et al., 2014). The hydrology of ponds is closely tied to chemical concentrations, 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 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 hydrology 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.

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 (Table 1). 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

5   shallow ponds in remote northern catchments, despite their importance in driving key ecological functions across the circumpolar north.

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

10   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 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

15   spanning an intense rainfall-runoff event.

2 Methods

2.1 Study site and sampling design

This study was completed in the Hudson Bay Lowlands, 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

20   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 Hudson Bay Lowlands 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) due to impeded drainage and very low topographic gradients (Boudreau and Rouse, 1995), as well as the presence of permafrost at northern locations. Ponds in the Hudson Bay Lowlands

25   are well mixed due to their shallow nature (< 1 m depth), nutrient-limited (Eichel et al., 2014), restricted in surface and groundwater connection (Boudreau and Rouse, 1995, Macrae et al., 2004), and alkaline (Macrae et al., 2004, Bello and Smith, 1990; Bos and Pellatt, 2012). Most ponds have steep banks and thick, organic sediments (Macrae et al., 2004).

Pond ecology in this region is dominated by dense mats of blue-green, green and diatomaceous algae (Gray, 1987), with the dominant diatom genus being *Denticula* (Macrae et al., 2004). Symons et al. (2012) showed the most abundant phytoplankton

30   communities to be *Chlamydomonas* spp., *Sphaerocystis* spp., *Diatoma* spp. and *Crugienella* spp. However, Gray (1987) reported that benthic communities were dominant within ponds, and phytoplankton communities were regulated by non-density dependent factors. This has also been observed in other high latitude ponds (Ramlal et al., 1991). Due to their extremely

alkaline conditions (8 to 9.8 pH, Macrae et al., 2004), 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

5   the water column at a rate orders of magnitude greater than mesocosms without sediment.

The ponds and their basins 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 catchments are 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

10   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, and depth, and because they have been the subject of

15   long-term research in the area (Table 2; Macrae et al., 2004; White et al., 2014; Wolfe et al., 2011). Each pond was sampled regularly (every 14 days) throughout the snow 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 data were recorded hourly with pressure transducers (HOBO U20, Onset Ltd)

20   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-related artefacts 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) as these data have been shown to be representative of this study region (Morison et al., 2016). The perimeter and area of each pond were surveyed with a Trimble Juno SB GPS

25   unit, with a differentially corrected horizontal accuracy of ±5m

2.2 Water chemistry sampling and analysis

Samples of pond water were collected manually 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

30   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 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, (NH_4^+-N); G-103-93 (SRP-P), G-109-94 (NO_3^--N), G-189-97 (DKN)). Results for 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

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 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).

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

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

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 median value 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 $y = \beta_1 [x]^{\beta_2}$ was fit to the spatially normalized concentration (the ratio of each concentration to the mean concentration $\overline{[x]_s}$) and stage data to represent the geometry of conical bathymetry in the non-linear pond stage-volume relationship. In this case, the parameter β2 is invariant under linear translation, such as spatial-normalization, and is expected to maintain a negative value with the magnitude depending on the bathymetry of the pond. 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.

A principal component analysis (PCA) was employed to detect spatial and temporal patterns in pond chemistry variations while reducing redundancy by identifying clusters of correlated species in the data. 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). All data were logarithmically transformed prior to PCA using singular value decomposition and all variables scaled to have unit

variance before the analysis took place. All statistical analyses were conducted with R software (version 3.3.2, R Development Core Team, 2016).

3 Results

3.1 Spatial and temporal variability of pond chemistry

5 To determine if spatial variability exceeded spatial variability, the medians of the spatial and temporal deviation scores were compared (Figure 2). Spatial deviations did not significantly exceed temporal deviations for any chemical species. 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 between ponds, despite differences in magnitude, tended to be

10 strongly positively correlated which each other ($p < 0.01$) (Table 3). NO_3^- and NH_4^+ were not significantly correlated to any other species ($p > 0.01$) (Table 4) 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. Throughout 2015, the temporal trend of pond

15 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 (Figure 3). 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 260 to the end of the season (Figure 3). However, Ca^{2+} displayed a contrasting temporal trajectory to the other ions, 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 ions.

20 Generally, ponds were closest to their mean values during the mid-season (DOY 200 – 250) and pond-mean normalized concentrations differed the least between 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. In general, ponds were full

25 following snowmelt, with water levels generally declining throughout the season and eventually rising again in late summer (Figure 4). Hydrologically, all ponds were responsive to two major rain events on DOY 166 and DOY 185 (Figure 4). Following the early-season rain events, Left pond and Strange pond experienced prolonged summer drawdown while this drawdown was less pronounced in Larch and Sandwich ponds, which have larger surface inlets and outlets, suggesting greater hydrologic connectivity to peatlands (Figure 1). Frisbee pond, which also has a significant hydrologic inflow as well as some

30 thermokarst surrounding it, did not experience a drawdown over the summer season. 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 variations and pond geometry (depth, shoreline development, area, or perimeter.

Seasonal patterns in pond hydrology were compared with water chemistry to determine if pond water chemistry parameters were hydrologically driven. The hydrologic control of different nutrient species was categorized 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. As noted earlier, a linear fit is not possible due to the somewhat conical bathymetry of ponds, which causes greater drops in water levels as ponds dry and sediments are exposed. In each case, species with a consistent 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 a β_2 value inconsistent with other hydrologically driven species or poor performance (greater root mean square error; Figure 5, Table 5) were categorized as non-hydrologically driven. DON, Cl^-, Na^+, K^+ .and Mg^{2+} were classified as hydrologically driven species and Ca^{2+}, NH_4^+, NO_3^-, and SO_4^{2-} were classified as non-hydrologically driven (Table 5). Slight differences in β_2 values between ponds for hydrologically driven species are driven by the differences in bathymetry driving the stage-volume relationship.

3.4 Principal component analysis

Principle component analysis (PCA) of the data allows for a reduction in the dimensionality of the data while retaining patterns of temporal and spatial variability. This permits a reduction in the redundancy of species that are highly correlated (Table 4) and the spatial grouping of samples from a single pond in PC space. The analysis shows a clustering of groups of ions in reference to the PC axis. A collection of the hydrologically–driven chemical species (Table 5; Mg^{2+}, K^+, Na^+, Cl^-) closely follows the PC1 axis with slightly negative scores for PC2. Two other non-hydrologically driven ions have positive scores along PC1 with slightly positive (DON) and positive (Ca^{2+}) scores along PC2. Inorganic nitrogen species, (NO_3^- and NH_4^+), also non-hydrologically 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.

3.5 Event-scale variation in pond chemistry

In addition to being highly chemodynamic over the course of a snow-free season, pond chemistry varied greatly over the course of a single storm-runoff event. 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 snow 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^+; Figure 7). 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+} (Figure 7).

4 Discussion

4.1 Seasonal trends in pond chemistry

5   Ponds in this study displayed a coherent trend in several chemical concentrations over a snow-free season, despite differences in pond geometry, catchment characteristics, and absolute magnitude of chemical concentrations. This suggests that landscape-scale factors such as climate and ecotone may be driving pond nutrient cycling and hydrological processes. However, absolute magnitudes of different ionic concentrations varied between ponds, suggesting that influences such as runoff inputs, evaporconcentration, bathymetry, and internal processes (sediment-water interaction and biological cycling) may be driving

10   these differences but 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 ions are not reflective of this spatial variability and instead more reflective of landscape-level process.

The concepts of temporal/spatial coherence and synchronicity have been employed in temperate lake systems to determine the

15   role of different climatic and hydrological factors in driving lake chemical variations, where previous measures of coherence have often employed correlation of concentration values between lakes. Pace and Cole (2002) found in Northern Michigan that changes to dissolved organic carbon and colour were synchronous between lakes while total phosphorus, chlorophyll, and pH were not. 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,

20   contrasting with our results. These studies were often employed on chemistry data collected either weekly or monthly on the inter-year scale and did not incorporate event-based sampling, although the much larger total lake volumes may reduce the chemical variations associated with precipitation events.

In our study, chemical species which were classified as hydrologically driven (Table 5) were not necessarily the same species which showed that temporal variance exceeded spatial variance (Figure 5). DON and Mg^{2+} were classified as hydrologically

25   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. This indicates the potential for biogeochemical processes operating at a degree of homogeneity at the landscape scale (such as homogeneity in biological processing or release of these solutes) outside of hydrologically related landscape level factors (evaporconcentration, dilution, catchment contributions).

30   Strange, Left, and Frisbee ponds were elongated with respect to the PC1 axis, which corresponds closely with the group of ions that are hydrologically driven. Strange and Left ponds showed the greatest variation in pond stage (Table 2; Figure 3), linking the hydrological variation with the variation in concentrations of ions controlled by stage. However, Frisbee pond

showed lesser variation in stage but was elongate with the respect to the axis of the hydrologically-driven ion cluster, suggesting that variation in pond stage alone does not necessarily dictate which ions are most thermodynamic 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 ions along PC1. The redundancy in the original dataset is driven by the clustering of the hydrologically-driven ions 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 2) 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 ions (Table 5) correlated between ponds (Table 3), but they are also correlated between species (Table 4). The apparent redundancy of several of these chemical trajectories is observed in the normalized time series of concentration data, with many of the ions which align along PC1 axis showing a similar concentration trajectories at the seasonal (Figure 2) and event (Figure 6) scales.

In many of the same study ponds, similar clustering of Cl^-, Na^+, K^+, and Mg^{2+} along one PC axis and another cluster including NH_4^+ and NO_3^-. In contrast, total nitrogen was approximately orthogonal to both those clusters, instead of being aligned with the other species which were hydrologically driven. Difference may be explained by the inclusion of additional limnological measurements into the PCA, the greater number of lakes in the study (20) and the smaller number of samples taken at each lake per year (3). Sokal et al. (2012) did not report a similar clustering of ions 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 ions 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 ion clustering may not be entirely regional 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 ions and Ca^{2+} and SO_4^{2-} as was found in this study.

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 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

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.

4.2 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 and runoff volumes 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 represents a smaller proportion of the total post-event water (closer to one-quarter, Figure 5). This leads to the dampening of the storm-based concentration variability in Strange pond. Between 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., 2016), 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 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). Abnizova (2013) found that the ionic composition at the event scale of runoff water to ponds in high arctic wetlands was driven by the vegetative structure of the catchment (related to dissolved organic material) and bedrock composition.

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 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).

This mechanism is 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 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.

4.3 Implications for sampling design in future studies

Existing studies have frequently employed a great number of spatial samples without great temporal resolution. This appears to be at least partially due to difficulties in access due to logistical constraints (as reported: "A lake was sometimes added or removed from the sampling plan based on its accessibility, which varied year to year with changing water levels at the shallowest of sites" (Paterson et al., 2014), "Because of adverse weather, fewer lakes were sampled in September" (Bulbasarium et al 2015) in addition to the costs and constraints associated with extended field campaigns in remote locations. However, 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 snow-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 synchronicity in the chemical behaviour of some ions (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 ions.

Future biogeochemical research must consider the relative terms in the water balance in a pond to determine periods of greatest 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 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 six of shallow permafrost ponds in the Hudson Bay Lowlands. Generally speaking, temporal variability exceeds spatial variability in pond chemistry in this landscape. Five chemical species (Cl^-, SO_4^{2-}, Na^+, K^+ and Ca^{2+}) showed a temporal coherence in six different ponds for an entire snow-free season. However, 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 correlation matrices showed that these hydrologically driven ions are strongly correlated to each other and between 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 ions 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 ma[ ] on equal order as the variation over the course of months. This longer period variation is also not limited to the hydrologically driven ions, indicating the importance of biogeochemically active periods coinciding with periods of water movement across boundaries (catchment-pond interactions). This work has important implications for understanding the highly chemodyanmic behavior of permafrost ponds through over both short-

5   term and long-term temporal scales while remaining spatially synchronous. Further, 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. [ ]

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 S1.

Competing interests

The authors declare that they have no conflict of interest.

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. Reported sampling designs for studies focused on, or including small (< 1 km^2) lakes and ponds. When categorizing analytes of interest for each study, "nutrients" refers to the measurement of any dissolved or particulate nitrogen or phosphorus speciation, "carbon" refers to any measurements of dissolved or particulate organic or inorganic carbon, "major ions" refers to the measurement of dissolved sodium, magnesium, calcium, potassium, chloride, sulphate, and carbonate, and "metals" refers to the
20 **measurement of dissolved or suspended trace metal elements.**

Study	Analytes of interest	Region	Study year(s)	Number of ponds/lakes studied	Number of samples per year
Archer et al., 2016	Nutrients, Metals	Ross Sea, Antarctica	2009-2013	41	1
Balasubramaniam et al., 2015	Nutrients, Carbon, Major Ions	Old Crow Flats, Yukon	2007	56	3
Bos and Pellatt., 2012	Nutrients, Carbon, Metals	Hudson Bay Lowlands, Manitoba	2004	32	1
Breton et al., 2009	Nutrients, Carbon	Northern Quebec and Baffin Island	2004-2005	46	1
Hinkel et al., 2016	Nutrients, Carbon, Major Ions	North Slope of Alaska	2012-2013	28	1

Houben et al., 2016	Nutrients, Carbon, Major Ions, Metals	Northwest Territories	2009-2012	38	1
Jacques et al., 2016	Nutrients, Carbon, Major Ions	Hudson Bay Lowlands, Manitoba	2010-2012	33	1
Kokelj et al., 2009	Carbon, Major Ions	Mackenzie River Delta, Canada	2005-2006	73	1
Larsen et al., 2017	Nutrients, Carbon, Major Ions	Environmental Gradient within Alaska	2006-2013	617	1
Lim et al., 2001	Nutrients, Carbon	Bathurst Island, Arctic Canada	1994	38	1
Lyons et al., 2012	Major Ions	Taylor Valley, Antarctica	2000-2010	7	1
MacDonald et al., 2014	Nutrients, Carbon	Hudson Bay Lowlands, Manitoba	2010 - 2012	16	3
MacLeod et al., 2016	Nutrients, Carbon, Major Ions, Metals	Hudson Bay Lowlands, Ontario	2011 - 2012	98	1
Mallory et al., 2006	Nutrients, Carbon, Major Ions, Metals	Southampton Island, Nunavut	2001-2002	32	1
Manasypov et al., 2014	Carbon, Major Ions, Metals	Western Siberia	2010-2011	58	1
Michelutti et al., 2002	Nutrients, Carbon, Major Ions, Metals	Wynniatt Bay, Victoria Island, Arctic Canada	1997	34	1
Niu et al., 2011	Major Ions	Kunlun Mountain pass, Tibet	2007	10	1
Paterson et al., 2014	Nutrients, Carbon, Major Ions, Metals	Hudson Bay Lowlands, Ontario	2009-2011	17	1
Pienitz et al., 1997	Nutrients, Carbon, Major Ions, Metals	Yukon and NWT, Canada	1990	59	1
Pokrovsky et al., 2011	Carbon, Major Ions, Metals	Northewestern Siberia	2008-2010	20	1
White et al., 2014	Nutrients, Major Ions	Hudson Bay Lowlands, Manitoba	2010	20	3

Table 2. Physical characteristics and locations of study ponds near Churchill, Manitoba.

Pond	Area (m^2)	Perimeter (m)	Shoreline development* (m^1 m^{-1})	Average depth, $\mu \pm \sigma$ (cm)	Coordinates
Erin	8479	448	1.37	No data	58°43'14.3"N 93°50'20.2"W
Left	752	130	1.34	30.0 ± 6.8	58°44'44.2"N 93°49'20.6"W
Strange	6307	424	1.51	22.2 ± 10.0	58°43'36.8"N 93°50'20.6"W
Sandwich	17146	548	1.18	19.6 ± 4.8	58°43'24.2"N 93°50'34.4"W
Frisbee	4416	258	1.10	14.2 ± 2.8	58°43'35.5"N 93°50'33.9"W
Larch	4066	333	1.47	14.2 ± 4.9	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)

10 **Table 3. Correlation coefficients between 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**
SO$_4^{2-}$					
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**				
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**
Mg²⁺					
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**
Ca²⁺					
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
NH₄±					
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
NO₃⁻					
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 4. Correlation coefficients between 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 5: Values of β_2 and root mean square error (S) from the curve $[x] = \frac{[x_{st}]}{[x_s]} = \beta_1 * Stage^{\beta_2}$ for each set of normalized concentration data $[x]$

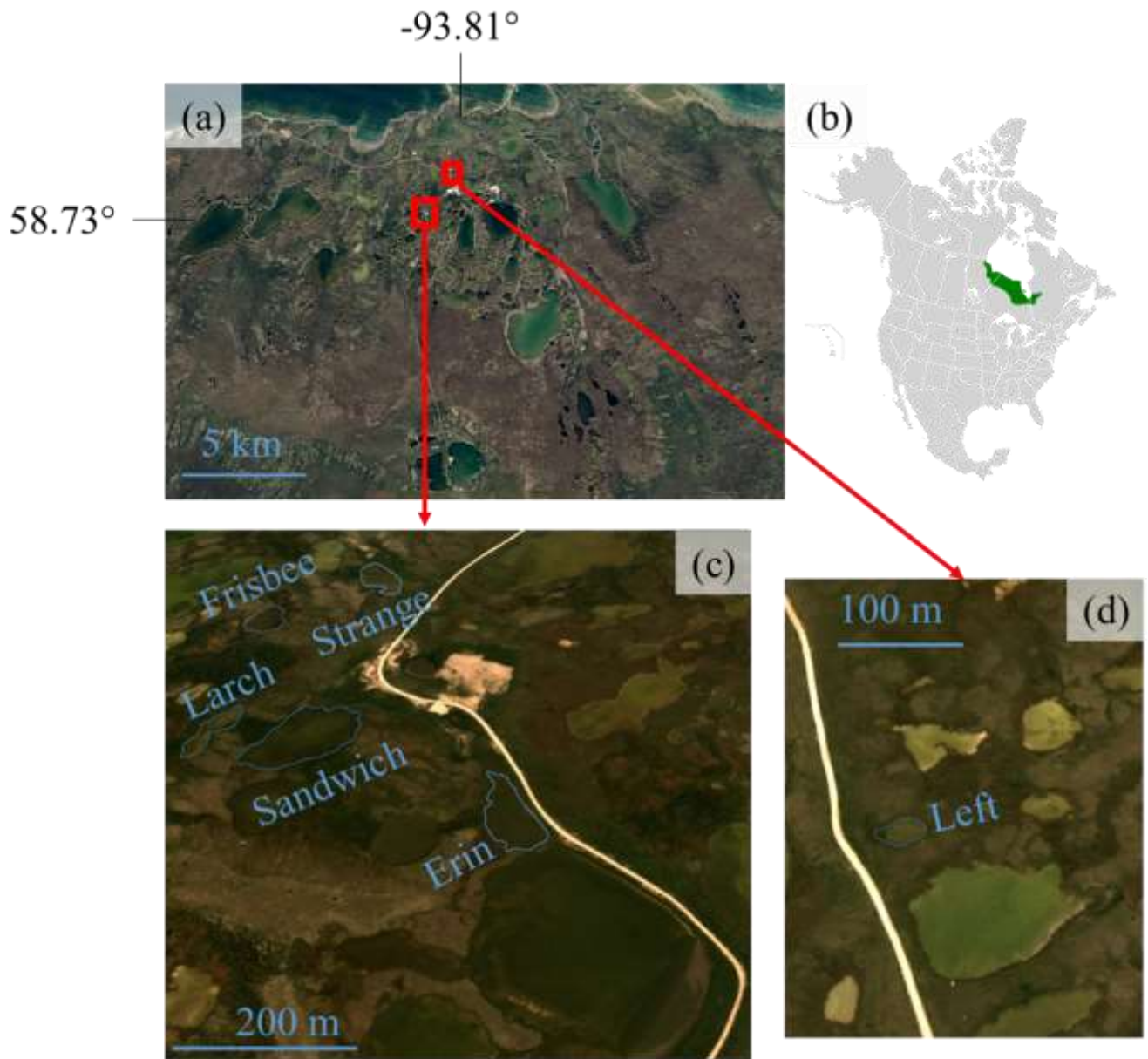
	Hydrologically Driven					Not hydrologically driven			
	DON	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	NO_3^-	SO_4^{2-}
Frisbee									
β_2	-2.61	-2.63	-2.01	-2.52	-2.15	-0.38	-0.23	0.23	-1.11
S	0.27	0.16	0.15	0.22	0.23	0.25	0.70	0.29	0.24
Larch									
β_2	-0.35	-0.28	-0.29	-0.38	-0.44	0.39	-0.73	-0.18	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 (a) the general near-coastal tundra region, (b) the Hudson Bay Lowlands highlighted in green, (c) the catchment area containing Frisbee, Larch, Strange, Sandwich, and Eric ponds, (d) the catchment containing Left pond. Map data: Google, Digital Globe, 2017.

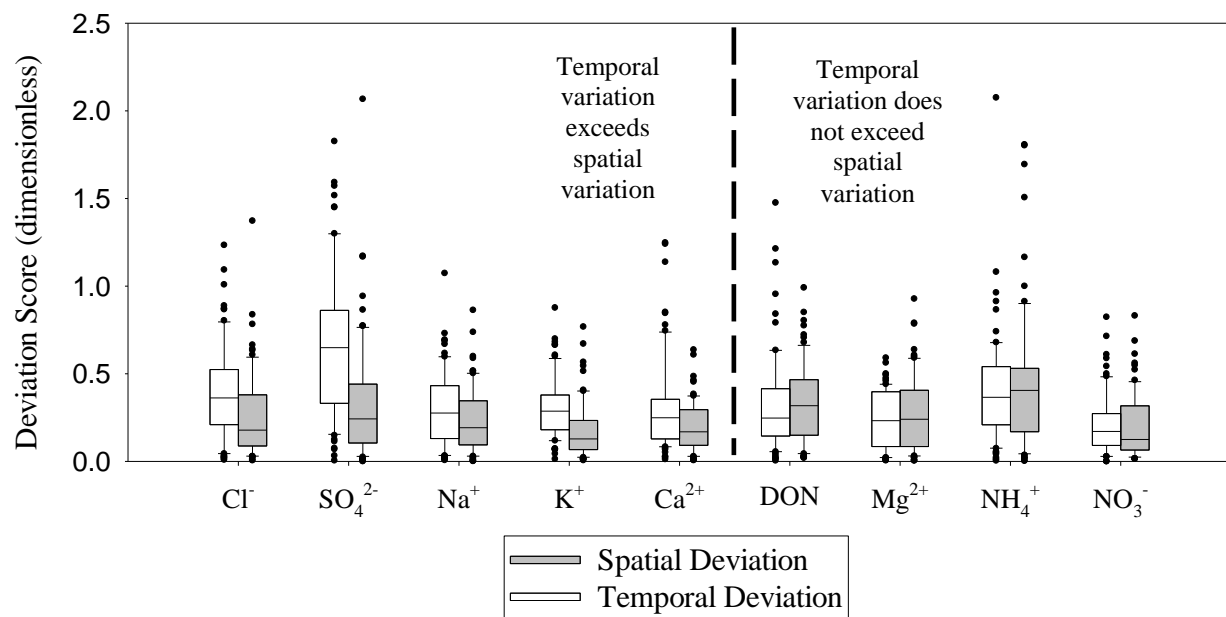



Figure 2. Boxplots of spatial and temporal proportional deviations for each chemical species. Significant differences between medians ($p < 0.01$) are present for all species on the left side of the panel (Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}), and no significant difference is present for species on the right (DON, Mg^{2+}, NH_4^+, NO_3^-).

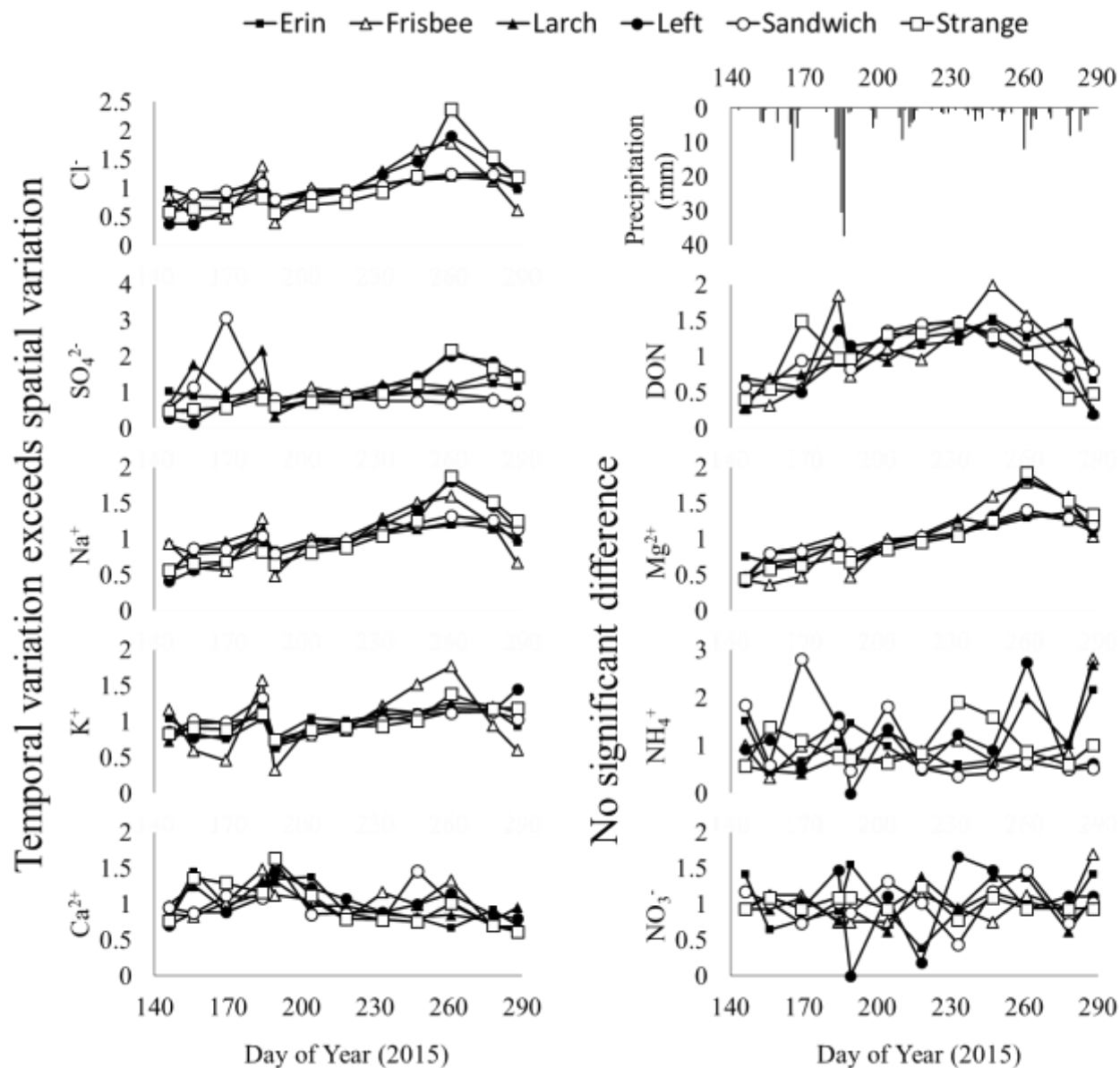



Figure 3. Pond normalized concentrations of all measured chemical species in each pond and precipitation for the 2015 snow free season.

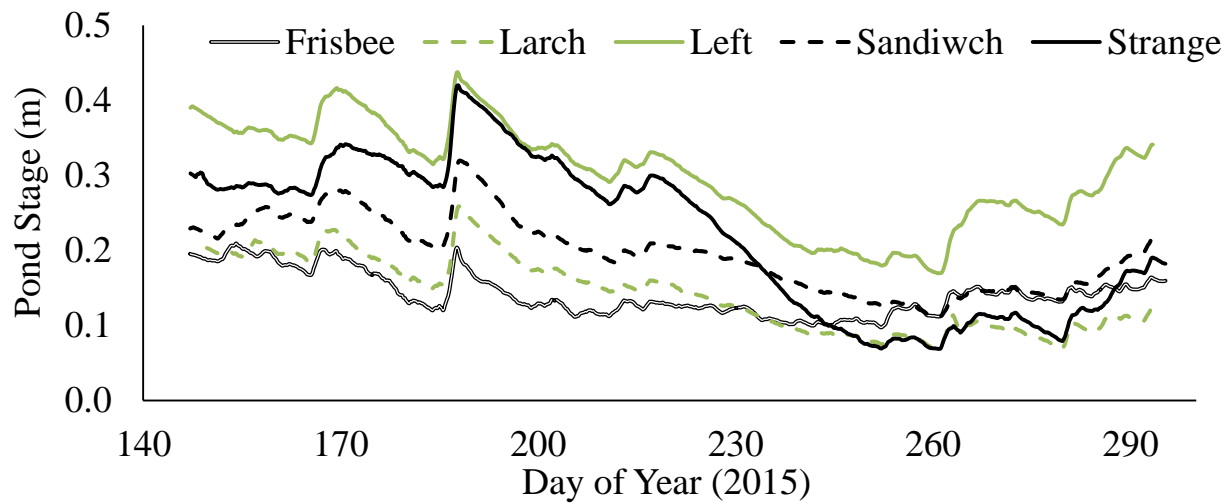
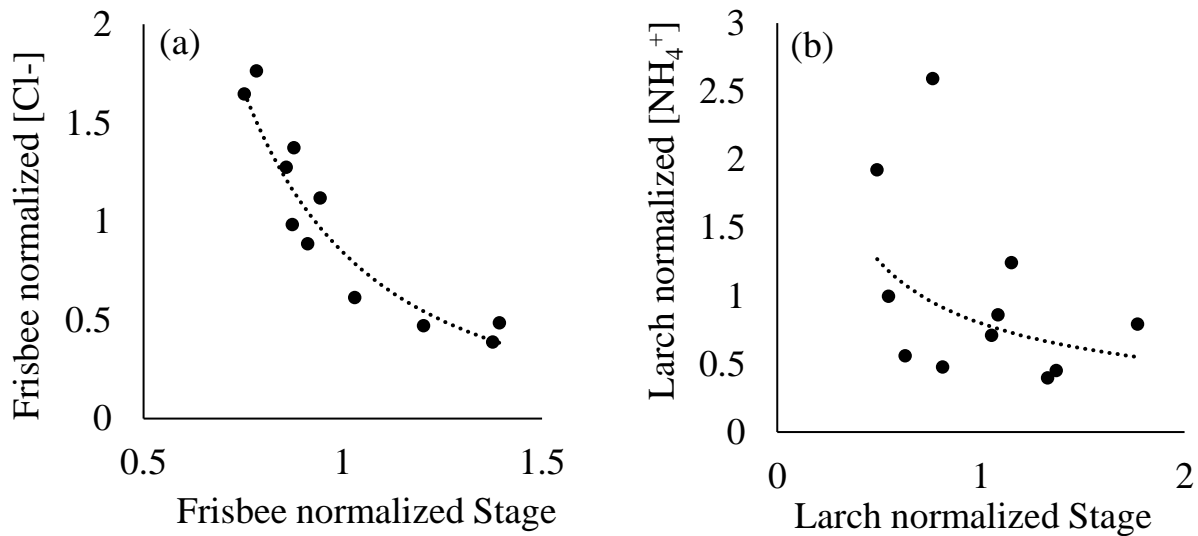



Figure 4: Pond stage in each of the instrumented study ponds over the 2015 Snow-free season.

5   **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).**

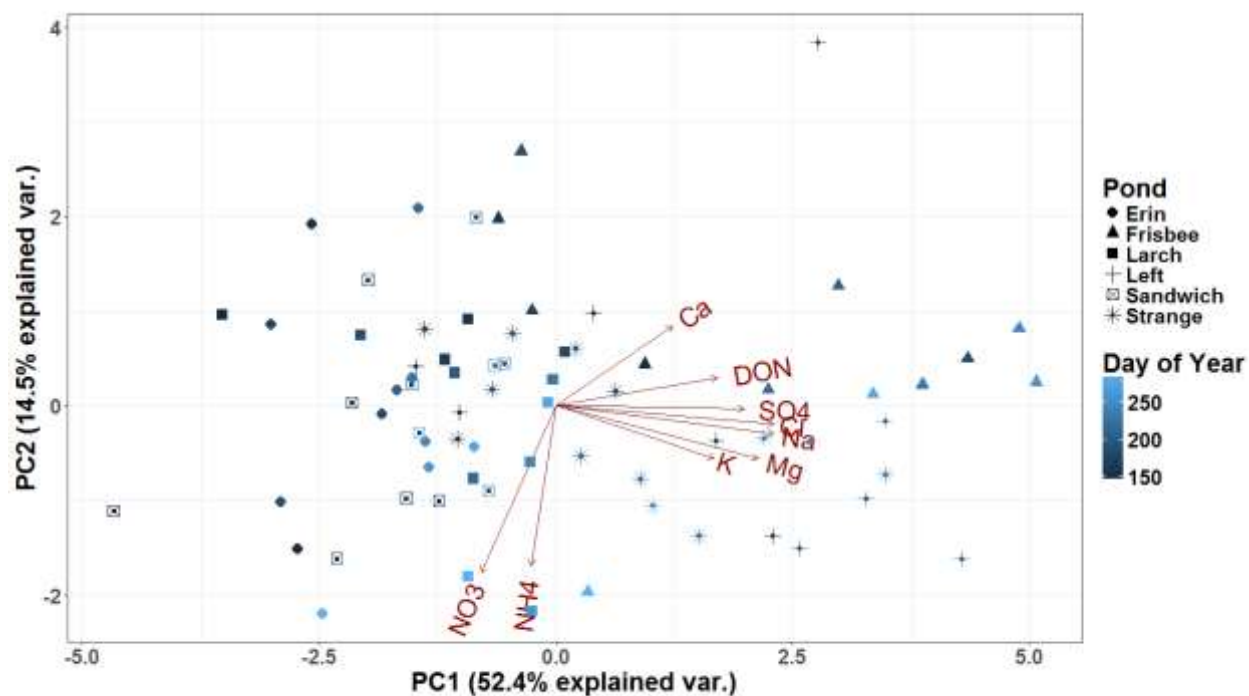



Figure 6. Principal Components Analysis of chemical concentrations in all ponds throughout the 2015 snow-free season. PC1 primarily corresponds with the hydrologically-driven chemical species (Table 3) while PC2 corresponds to inorganic nitrogen species (NO_3^-, NH_4^+).

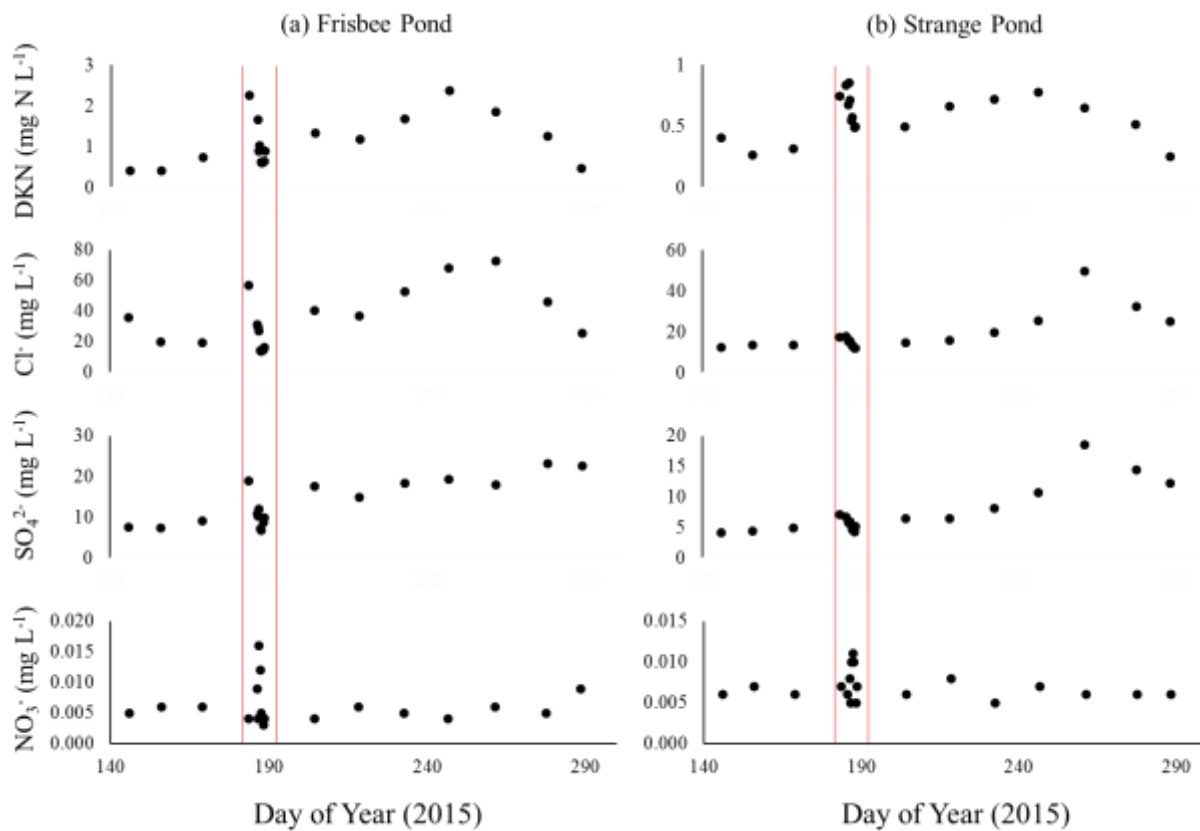



Figure 7. Short term variation in DON, Cl⁻, SO₄²⁻, and NO₃⁻ concentrations in (a) Frisbee pond and (b) Strange pond during a rain event on July 3rd to 6th, 2015 (DOY 185-188, highlighted with red bars).