

Dear Helge Niemann,

Thank you for your handling of the manuscript and compiling the referee reports. We appreciate the opportunity to have substantially revised the manuscript for resubmission and feel that the work has been greatly improved by the helpful suggestions of the referees. In particular, we have now included additional hydrological data, including catchment area and runoff amounts for each pond. As well, we have clarified our terminology (synchrony vs synchronicity vs coherence) in the main text as well have altered our title to reflect this. Further, we address the issues of stratification and mixing, as well as representativeness of the ponds, through references in literature in the methods and discussion section, respectively. Specific details are available in our below point-by-point response to the referees. Some of the issues with the figure formatting appear to persist due to the way that this submission is processed as a single .pdf file which resulted in images being resized. The final submitted versions of these figures will have a consistent font size when submitted as individual files.

Included below is a point-by-point response to the referees as per our author comments made during the discussion period for the paper, in which we mark referee comments with an (R) and author responses with an (A). At the conclusion of this document there is a complete marked-up manuscript with every change highlighted.

Referee #1

(R): This paper summarizes a study evaluating aquatic chemistry dynamics in the Hudson Bay Lowlands in northern Canada. The objectives were to determine if temporal or spatial variability in pond chemistry is more prevalent and any variability could be used to infer processes occurring in ponds and their catchments. The paper is certainly within the scope of Biogeosciences. The authors' point is well taken that many synoptic scale studies of aquatic chemistry use very few samples, yet make broad statements about the processes at play to produce these signals. In that respect, the dataset presented for this region is quite good. However, the paper could be improved to substantively deliver on its objectives, specifically the one on relating processes to patterns. The title could be "Hydrology drives chemical synchronicity in subarctic tundra ponds sometimes".

(A): We have changed the title to reflect the fact that indeed, hydrology does not dictate the synchronous behaviour of each chemical species in this study. The new proposed title for this study is "Capturing temporal and spatial variability in the chemistry of shallow permafrost ponds". This is an important distinction and the original title may have been an overstatement on our behalf. We more specifically address the comment regarding delivering on our stated objectives later in this response.

(R): Two major issues with the paper that should be addressed. The first is that while the data suggests there are some constituents in some ponds that are clearly influenced by hydrological processes (e.g., evaporation), there are no data presented on pond hydrological fluxes or states besides pond stage. There is a diversity of responses that are interpreted through the lens of this drawdown, and the authors make some, what I think are unsubstantiated classifications of their data. For instance, what defines "consistent" in the relationship between pond stage and concentration? Another interpretation of the data in Table 5 could be that each pond has hydrologically driven chemical species, but these species may not be hydrologically driven in all

ponds; "hydrologically driven if necessary, but not necessarily hydrologically driven" so to speak. There needs to be data provided on basin area, pond:catchment ratio, etc., because these may allude to runoff fluxes into and through the ponds, that may help explain these differences. This would help address a feeling the reader gets that the authors use the literature too much to help interpret their results. The paper does show how hydrology does and does not drive chemistry in these ponds, but it needs more hydrological data, and this could elevate the paper.

(A): We agree that providing catchment characteristics would better allude to some of the processes which we speculate on in the paper. Thus we have now included some additional hydrometric data in the paper which we had collected in the field but initially had not included in this paper (runoff measured into each pond over the course of the study period as well as catchment area) although to further reduce speculation we present this data as a depth of water over the pond surface as opposed to the catchment surface. We present this as a depth over the pond surface as we recognize that the variable contributing area concept applies here due to the very flat topography (regional gradient of < 1 m/km, Dyke and Sladen, 2010) and the confining role of ground frost in prohibiting or redirecting subsurface flow at different periods over the course of the season (Wright et al., 2009) and not all of the catchment may be contributing during a given event (and hence why we give runoff over the pond surface, which is also more relevant to the dilution effect). Additionally, we have clarified in the caption to Table 4, as well as increased detail in the methods section, what drove the classification schema to determine if a species was hydrologically driven, as well as noting specific instances in which a species was hydrologically driven in some ponds but not all (as the referee notes, "hydrologically driven if necessary, but not necessarily hydrologically driven")

(R): The second issue is related, and it relates to the difference between "synchronicity" and temporal coherence". First, synchronicity is not a word, but that is an argument for another day. Because the hydrological process discussed in the paper is really just a drawdown process, it is likely correlated with time, so are some of the terms really hydrologically driven, or are they just exhibiting temporal coherence? This is why discussing other hydrological processes is necessary. Also, I agree with the authors that there are landscape scale factors at play, but this relationship between time and hydrology needs to be better thought through and expressed in the paper. Doing so, and gleaning why some species seem to be hydrologically driven, in some ponds sometimes, but not all, could bring it all together quite nicely. This could also allow the authors to better deliver on objective #3.

(A): This paper does not present data reflecting specific biogeochemical process, and certainly more research is needed to understand individual components of the cycling of these elements in these aquatic ecosystems. To reflect this we have modified our discussion to be wary of overstating the degree to which we understand exactly which processes are driving elemental concentrations. However we do believe that our results indicate a temporal coherence which appears to be very strongly tied to variations in pond water level, which we interpret as a result of close relationship with conservation of chemical mass associated with conical bathymetry. We have modified the discussion to reflect on the seasonal variation in biogeochemical characteristics (such as primary productivity) which are closely tied to hydrological variation. However, we believe we have reasonable confidence to associate the general temporal coherence in some chemical concentrations with hydrological variations given the relative degree of homogeneity in

hydrological forcing to these ponds (given their proximity to each other to receive similar precipitation inputs and exposure to similar atmospheric conditions driving evapotranspiration).

(R): Some minor issues include a lot of misreferenced tables and figures. The authors use "between" when they should use "among". Also, while great data for context, I'm not sure the higher frequency data adds that much to the manuscript. I've attached a marked up pdf version of the manuscript.

(A): We appreciate the close attention to detail by the referee and outline the comprehensive comments made in the supplement to the referee comment, and our responses below. In addition, we have carefully reviewed each figure and table reference to ensure each table and figure is correctly referenced.

(R): P.1 Line 19: "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" Is this then different than what is suggested by the title?

(A): As noted earlier in this response, we altered the title to reflect the fact that hydrology only regulates the synchrony of some, but not all, chemical species.

(R): P.2 Line 21: "The hydrology of ponds is closely tied to chemical concentrations" - Or is it the other way around?

(A): Correct, it is the other way around. This sentence has been inverted to reflect this.

(R): P.4 Line 21: "artefacts" spelling

(A): We had spelled initially with the British/Canadian spelling, now changed here to "artifacts".

(R): P.4 Line 25: "The perimeter and area of each pond were surveyed with a Trimble Juno SB GPS unit, with a differentially corrected horizontal accuracy of $\pm 5\text{m}$ ". This is terribly large. Is this the correct value?

(A): This is the error of the accuracy as listed by the differential correction software. This was a handheld GPS unit and these values are typical for these units: <http://www.trimble.com/mappingGIS/junoS.aspx>. We believe the precision is likely much better than the accuracy (C. Storie, personal communication), but we do not have a measure of that. The perimeter and area of the ponds as determined by GPS were checked against manual pond polygon tracing over satellite imagery (Google Earth) and were both within 5% of the values calculated with GPS measurements.

(R): P.5 Line 4: "Dissolved organic nitrogen (DON) concentrations were determined as the difference between DKN and NH_4 ". First use of this acronym.

(A): We have included a definition of DKN as Dissolved Kjeldahl Nitrogen in the methods section previous to this, and now consistently refer to solely to DON in the remainder of the document.

(R): P.5 Line 22: "To determine the relationship between pond volume and concentrations of different chemical species, a power function $y = \beta_1[x]^{\beta_2}$ was fit". Maybe present this as an equation. Make it more visible, because it is an important part of your interpretation. Right now, it is buried in the text. It is also unclear of the form; what is x and what is y, because the form of this equation in this text is backwards to that in the caption for Table 5.

(A): The previous form was backwards (with x and y in the opposite positions based on their definitions) and we have corrected this. We have now presented this as its own equation, while replacing y with “stage” to clarify the relationship between the concentration and hydrology.

(R): P.5 Line 22: “(the ratio of each concentration to the mean concentration [x])” isn't spatial concentrations normalized by xt?

(A): This was a typo in our text, we have corrected it to read x subscript t.

(R): P.6 Line 5: “To determine if spatial variability exceeded spatial variability,” temporal variability?

(A): This was a typo in our text, we have corrected it to read “spatial variability exceeded temporal variability”.

(R): P.6 Line 9: “concentrations between ponds”, maybe this should be "among"

(A): We have changed this language here (and elsewhere, where appropriate) to “among”.

(R): P.6 Line 10: “tended to be strongly positively correlated which each other ($p < 0.01$)”. Except for DON, maybe say so explicitly.

(A): We have included an explicit list of those chemical species which tended to be significantly correlated between ponds (DON, chloride, sodium, magnesium) and were not (sulphate, calcium, ammonium, nitrate).

(R): P.6 Line 17: “from 260 to”. DOY.

(A): This was a typo in our text, we have corrected it to “DOY 260”.

(R): P.6 Line 26: “As was observed for water chemistry, there was also a seasonal pattern in pond hydrologic storage. In general, ponds were full following snowmelt, with water levels generally declining throughout the season and eventually rising again in late summer (Figure 4).” Since you talk about "full", maybe put the outlet stage for each on Figure 4. You'll have to do it in such a way that it won't be too crowded. Maybe a panel for each pond; maybe a notch on the y-axis instead of a horizontal line across the whole graph.

(A): We appreciate the helpful comment to improve Figure 4 and have separated each pond runoff and continuous stage by panels as suggested.

(R): P.6 Line 26 “all ponds were responsive to two major rain events on DOY 166 and DOY 185 (Figure 4).” Would it be hard to add rainfall to Figure 4?

(A): We have added rainfall (as well as runoff amounts, as discussed previously in these author responses) to Figure 4.

(R): P. 6 Line 28 “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).” How would the morphology of the inlets and outlets relate to higher connectivity? There may be a quantum leap in logic here. Why not just examine catchment size? Also, what does "greater" connectivity mean? Does it mean a higher volume of water flows into it? Or a larger transfer of water from the peatlands to the pond? Basin area may be a better index than outlet/inlet morphology.

(A): As discussed earlier in this response, we have now included some of this data, in particular, runoff volumes and catchment areas for each pond.

(R): P. 7 Line 2 “between variation in stage variations” Delete.

(A): This was a typo in our text, we have deleted the repeated word.

(R): P. 7 Line 3 “pond geometry (depth, shoreline development, area, or perimeter).” Where are the data to show this?

(A): We have presented this data in a table and added a reference to this table for this sentence.

(R): P. 7 Line 8 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” Could you explain why you chose to use pond specific terms? If it were really hydrologically driven would it not be common across all ponds, because you have normalized for time; (divide by xs)? It seems that the data point to instances where some terms of hydrologically driven in some ponds but not others. Some are consistent (Mg), some are not (K). A more rigorous explanation is needed about what was considered “consistent”, because for instance, why was sulphate not considered hydrologically driven in Strange pond?

(A): As mentioned earlier in this response, we have clarified in the caption to Table 4 what drove the classification schema to determine if a species was hydrologically driven, as well as noting specific instances in which a species was hydrologically driven in some ponds but not all (as the referee notes, “hydrologically driven if necessary, but not necessarily hydrologically driven”).

(R): P. 7 Line 13 “differences in β_2 values between ponds for hydrologically driven species” again, “among”

(A): We have changed this language here (and elsewhere, where appropriate) to “among”.

(R): P. 7 Line 13 “hydrologically driven species are driven by the differences in bathymetry” “influenced”? You use “drive” three times in this sentence.

(A): We have replaced driven” with “influenced”. Thank you for the suggestion to improve the writing.

(R): P. 7 Line 14 “bathymetry driving the stage-volume relationship.” But you just said at the end of the previous paragraph that bathymetry (depth-area) didn't influence stage. So why would B_2 vary?

(A): To clarify, the specific shape of the pond bottom (typically a rough single-deepest-point-basin cone) differs slightly between ponds and thus dictates the value of B_2 based on the slope from the deepest point of the pond to the edges, although generally being extremely gradual with similarly very low slopes of $<0.1\%$ in the terrestrial landscape (Dyke and Sladen, 2010). We chose the power function to capture this and allowed the exponent in the function to vary. Theoretically, for a height-volume relationship (and under the assumption of some ions being conservative, we extend this to height-concentration relationship) the value of this coefficient should be between 0, for a perfectly cylindrical pond basin with a flat bottom, to highly negative, for a very steep cylindrical pond basin. We have clarified this in-text in the methods section.

(R): P. 7 Line 15 “3.4 Principal component analysis” There is no reference to Figure 6 in this section. Also there is some inconsistency between what is defined as “hydrologically driven” in Table 5 and the caption to Figure 6. The latter separates nitrogen species from the rest, but the former does not.”

(A): We have added a reference to Figure 6 in this section, and added additional clarification to the captions of Figure 6 and Table 5 regarding specific instances in which a species was hydrologically driven in some ponds but not all (“hydrologically driven if necessary, but not necessarily hydrologically driven”).

(R): P. 7 Line 21 “Two other non-hydrologically driven ions have positive scores along PC1 with slightly positive (DON) and positive (Ca²⁺)...” This is hydrologically driven in Table 5.

(A): This was a typo in our text, and was meant to be a reference to sulfate which did not show a clear relationship with stage in any pond. The sentence has been corrected to “Two other non-hydrologically driven ions have positive scores along PC1 with slightly negative (SO₄²⁻) and positive (Ca²⁺)...”

(R): P. 7 Line 31 “same magnitude over the course of several days as they did over the period of the entire snow free season (DON, K⁺, Ca²⁺, NO₃⁻);” You seem to substitute DON and DKN sometimes.

(A): We have now defined DKN as Dissolved Kjeldahl Nitrogen and [DON] = [DKN] – [NH₄] in the methods section previous to this, and now consistently refer to only DON in the remainder of the document.

(R): P. 8 Line 7 “This suggests that landscapescale factors such as climate and ecotone may be driving pond nutrient cycling and hydrological processes” nitrogen did not follow this behaviour (Figure 3).

(A): We have modified this sentence to reflect that primarily major ions follow this behavior but not nitrogen species.

(R): P. 8 Line 14 “The concepts of temporal/spatial coherence and synchronicity have been employed in temperate lake systems” Even though growing in popularity, I do not think this is a word. Synchrony is.

(A): This is duly noted, and we have removed mention of the word synchronicity and replaced with synchrony following the referee’s suggestion.

(R): P. 8 Line 18 “Magnuson et al. (1990) and Baines et al. (2000) reported Ca²⁺ to be temporally coherent among groups of large lakes in Wisconsin, USA, consistent with our findings” OK. What is the difference between temporal coherence and synchronicity?

(A): In this document we did not explicitly define these terms separately, but instead had used them synonymously. We have removed reference to the word synchronicity and replaced it with synchrony. We have made the interchangeable use of these terms to be explicit in the introduction, as both have been employed previously to define the behaviour of chemical concentrations in pond or lakes behaving similarly through time (e.g. Magnuson et al., 1990; Baines et al., 2000).

(R): P. 8 Line 24 “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).” Figure 3?

(A): This was a typo in our text, we have changed the reference to read Figure 3.

(R): P. 8 Line 26 “Conversely, Ca^{2+} and SO_4^{2-} display significantly greater temporal variability than spatial variability, but were not classified as hydrologically driven constituents.” You may be combining things here. Since your hydrologically driven is really just a drawdown process, it is likely correlated with time, so should Ca and sulphate be “hydrologically driven”? More thought needs to go into how these species are classified. Furthermore, this discussion about processes is speculation without some measurements that can inform understanding about process.

(A): Indeed we feel that there are other processes at play, including both reactive (biogeochemical) and also transport-driven (different amounts of runoff). We do not have measurements of these reactive process(es) to support any claims of the magnitude and rate of which processes are operating to which extent. However, the data do at least suggest some sort of homogeneity in process between these ponds which are spatially clustered (and thus subject to similar landscape-level controls such as precipitation, runoff, and general catchment characteristics). We have ensured that the language of the discussion reflects the degree of uncertainty we have regarding the magnitude and rates of specific biogeochemical processes given that we do not have any direct measurements.

(R): P. 8 Line 31 “Strange and Left ponds showed the greatest variation in pond stage (Table 2; Figure 3),” Table 3 does not show this, and it is Figure 4 that shows stage

(A): This was a typo in our text, we have changed the reference to the correct Figure and Table.

(R): P. 9 Line 2 “suggesting that variation in pond stage alone does not necessarily dictate which ions are most chemodynamic within a pond” Would adding data about stream order, basin size, flow, help?

(A): We have added catchment area data to the paper. Regarding stream order and flow, there are few persistent overland flowpaths. Due to very high hydraulic conductivity in upper parts of peat profile (Quinton et al., 2008) most of the flow is shallow subsurface flow in the upper part of the peat profile (Holden and Burt, 2003) as opposed to stream networks appearing in these small closed-basin systems.

(R): P. 9 Lines 11-12 similar concentration trajectories at the seasonal (Figure 2) and event (Figure 6) scales. Figure 3? Figure 7? I think I know what might have happened in this section with the Figure numbering.

(A): This was a typo in our text, we have changed the reference to the correct Figures (3 and 7).

(R): P. 9 Line 15 “Differences may be explained by the inclusion of additional limnological measurements into the PCA” What differences are we talking about?

(A): This was a typo in our text. A reference has been added to differentiate between our work and a study by White et al (2014) who did a study of the chemical properties of some of these same ponds in 2014 at three points of the course of the year and found difference alignment of PC axis for some of the same chemical species.

(R): P. 9 Line 33 “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.” It would improve this paper if data on such processes were collected and discussed.

(A): We do appreciate the need for coupling our understanding of the hydrological processes operating in northern regions with any temporal or spatial assessment of their chemical variability. In a previous study in the same catchments as this work, we completed an assessment of how different flow paths (driven by the seasonal evolution of the frost table) access different layers of the peat profile, which directly impact hydrochemical export (Morison et al., 2017). In order to strengthen this paper we have added runoff data, however, we do not have the same sampling frequency of measurements of inflow chemistry, which we presented in the aforementioned study. Future work could attempt to address both spatial and temporal variability in pond chemistry as both a function of physical hydrology (dilution and evapoconcentration) and also hydrochemistry (changing inflow concentrations as a result of differing catchment characteristics, for example).

(R): P. 10 Line 7 “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),” This is another reason it would be good to have outlet stage in Figure 4

(A): We have split Figure 4 by panels as suggested above.

(R): P. 10 Line 8 “where event water represents a smaller proportion of the total post-event water (closer to one-quarter, Figure 5).” Figures 4 and 7

(A): This was a typo in our text, we have changed the reference to the correct Figures 4 and 7.

(R): P. 11 Line 2 “Existing studies have frequently employed a great number of spatial samples without great temporal resolution” This section has plenty of good ideas, but it does not quite relate to the objectives outlined at the end of the introduction. It may be a better approach to finish the discussion with sections on each of these objectives; not just some.

(A): We have restructured this section to more directly address each objective, renaming and reorganizing the discussion to align with the stated objectives.

(R): P. 11 Line 23 “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.” of six.

(A): This was a typo in our text, we have added the word “of”

(R): P. 12 Line 1 “and following precipitation events may be on equal order as the variation over the course of months” While a fair point, I'm not sure the higher frequency data adds much to the discussion with the format of the manuscript as it is now.

(A): We believe, given the projected increase in frequency and magnitude of large precipitation events over the ice-free season (Sauchyn and Kulshreshtha, 2008; Kaufman et al., 2009; Macrae et al., 2014), it is important to include this to deliver on our objective of discussion both of temporal variability and also sampling designs. We have included more motivation with references to this literature for this need for understanding chemical responses to large summer storm events in the introduction section.

(R): P. 12 Line 9 Objective 3 is not addressed at the end of the paper.

(A): We have added runoff data to the paper and speculated on biogeochemical processes which are likely to be occurring (using references to the literature from this region and similar subarctic landscapes) to guide our interpretation of the temporal trajectories of chemical concentrations of these ponds, and included a paragraph-by-paragraph breakdown of our conclusions as relating to each research objective in this season.

References:

Baines, S. B., Webster, K. E., Kratz, T. K., Carpenter, S. R., and Magnuson, J. J.: Synchronous Behavior of Temperature, Calcium, and Chlorophyll in Lakes of Northern Wisconsin, *Ecology*, 81(3), 815-815, 2000.

Dyke, L. D., and Sladen, W. E.: Permafrost and peatland evolution in the northern Hudson Bay Lowland, Manitoba. *Arctic*, 429-441, 2010.

Holden, J., and Burt, T. P.: Runoff production in blanket peat covered catchments. *Water Res. Res.*, 39(7), 2003.

Kaufman, D.S., Schneider, D.P., McKay, N.P., Ammann, C.M., Bradley, R.S., Briffa, K.R., and Lakes, A.: Recent warming reverses long-term Arctic cooling. *Science*, 325, 1236-1239, 2009.

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Magnuson, J. J., Benson, B. J., and Kratz, T. K.: Temporal coherence in the limnology of a suite of lakes in Wisconsin, U.S.A. *Freshwater. Biol.*, 23, 145-159, 1990.

Quinton, W. L., Hayashi, M., and Carey, S. K.: Peat hydraulic conductivity in cold regions and its relation to pore size and geometry. *Hydrol. Proces.*, 22(15), 2829-2837, 2008.

Sauchyn, D., and Kulshreshtha S.: Prairies. In *From Impacts to Adaptation: Canada in a Changing Climate 2007*. Government of Canada: Ottawa, 2008.

Wright, N., Hayashi, M., and Quinton, W. L.: Spatial and temporal variations in active layer thawing and their implication on runoff generation in peat-covered permafrost terrain. *Water Res. Res.*, 45(5), 2009.

Referee #2

(R): The study by Morison et al. presents some interesting data on the variability of water chemistry in shallow subarctic ponds. Authors make a point that most studies in high latitude lakes are based on few water samples taken during the summer and do not account for temporal changes

driven by, for example, hydrological events. This is a strong and valid statement, and the dataset presented in this manuscript is certainly unique by showing how variable water chemistry in thermokarst ponds can be during the ice-free season. Authors attempt to relate this variability to local hydrology by calculating index of hydrological dependence that is somehow arbitrary. Perhaps, in the general approach, it would be better to calculate a simplified mass balance for some ions of interests; knowing the catchment area for each pond (run-off) and temporal changes in concentrations through the water column?

(A): We agree that providing catchment characteristics would better allude to some of the processes on which we speculate on in the paper. Thus we have now included some additional hydrometric data in the paper which we had collected in the field but initially had not included in this paper (runoff measured into each pond over the course of the study period as well as catchment area) although to further reduce speculation we present this data as a depth of water over the pond surface as opposed to the catchment surface. We present this as a depth over the pond surface as we recognize that the variable contributing area concept applies here due to the very flat topography (regional gradient of < 1 m/km, Dyke and Sladen, 2010) and the confining role of ground frost in prohibiting or redirecting subsurface flow at different periods over the course of the season (Wright et al., 2009) and not all of the catchment may be contributing during a given event (and hence why we give runoff over the pond surface, which is also more relevant to the dilution effect).

(R): The manuscript lacks context data that would allow better understanding of the processes driving water chemistry. For example, many shallow thermokarst ponds show strong thermal and oxygen stratification; were the 6 studied ponds stratified or mixed? What was the approximate rate of water exchange both vertically and horizontally? Water samples were taken from the shore or from the middle of each pond? How representative were studied ponds in terms of nutrient concentration and biological production for other ponds and lakes in the area. Authors discuss biological processes that may be responsible for rapid uptake of nutrients but do not include any indices of the trophic status or plankton biomass in studied ponds. Indeed part of the variability in chemistry between ponds can be probably explained by different patterns of uptake. All these information are required to better appreciate presented data and would much improve the manuscript.

(A): We appreciate the referee's comments and overview of information we could provide to better contextualize our results within the greater literature on permafrost pond chemistry. In particular we have included in the methods section that these ponds have been found to be well-mixed (Bello and Smith, 1990), and that water samples were taken approximately 3 meters from each pond edge. The ponds are representative of a greater set of study ponds in the region in terms of chemical variability between 10s to 100s of ponds generally spanning 1-2 orders of magnitude of major ion and nutrient concentrations (White et al., 2014; Bos and Pellatt, 2012; Jacques et al., 2016; Supplementary Table S1). In-situ mesocosm experiments in ponds of this region have shown ponds to be nutrient-limited (Symons et al 2012) with uptake of nutrient additions occurring within a matter of hours to day (Eichel et al., 2014) motivating our discussion of rapid nutrient uptake. A key motivation for future work is more intensive measurements which can capture individual biogeochemical processes in the cycling of each of the elements in these ponds, particularly of

those which are most reactive, such as inorganic nitrogen species. We have adapted the language to be clearer and more explicitly speculative regarding the lack of data on individual biogeochemical process and that inferences we make on process are guided by our measurement of patterns of chemical concentrations.

(R): Authors attempt to compare temporal and spatial variability; Is 6 (5?) ponds enough to encompass spatial variability, particularly if temporal variability is assessed with 12 time points? This would probably bias the entire analysis toward higher temporal variability. Finally, in the Discussion authors provide an outline on how to better plan field campaigns for sampling of high latitude lakes. Such guidelines are much needed and some unification of methods would help greatly to determine effects of recent environmental changes in Arctic freshwaters. However, I think that this can be done with instructive diagram that would be readily accessible for broad scientific community rather than by quoting and refuting methods used by others. Focus on the positives and how much your own research can add to future improvements.

(A): We address this concern more specifically below in the response to the referee comments on the methods section, with reference to our data being representative of spatial variability in the region. In short, we believe from comparing our data to many other studies of permafrost ponds that additional sample points may strengthen the statistical power of our analysis, however there is adequate variation in the spatial survey of six ponds for the purposes of comparing the two degrees of variation among the chemical constituents we measured in this study. As well, we appreciate the comment suggesting an instructive diagram and a constructive approach in building on method development in writing the text as opposed to a refuting tone. We have developed an instructive summary diagram to inform future sampling designs (including direction on research questions regarding different specific chemical constituents).

(R): Abstract - This part can be much improved; mainly by streamlining and including some key point data. For example first sentence is confusing and introduces biology; biogeochemistry and climate change with mentioning feedbacks. This is probably not a right place for such a broad and somewhat conclusive statement. Focus on importance on variability in pond biogeochemistry and controlling processes. Please do not use very general descriptions such as “most ions; either mention % or which species.

(A): We have rewritten the first sentence of the abstract to be more specific without introducing such a broad range of topics simultaneously. We have removed any vague phrasings, including “most ions”, and replaced with a specific list of ions which meet the criterion.

(R): Introduction Again already in the first paragraph there is a need for editing. Two sentences start with similar phrase: “these ponds”. Also first sentence from the abstract is repeated almost word-by-word.

(A): We have edited the first introductory paragraph to have less repetition, both within the wording (ie, not repeating the phrasing “these ponds”), as well as expanding on the first sentence in the introduction instead of merely repeating the first sentence of the abstract.

(R): Page 2; Recently Przytulska et al (2016, Biogeosciences) described inter-annual variability in thermokarst pond chemistry.

(A): Thank you for drawing our attention to this reference. We have included this in our literature review of varying length of study periods of permafrost pond chemistry, which includes valuable data on nutrient speciation.

(R): Page 3 First paragraph; this is all true and most of the studies in the Arctic are based on the few samples taken within short time frame. However please consider also recent research showing that some shallow high latitude ponds are remarkably stable in terms of oxygen and temperature stratification during the open water period (Deshpande et al 2015).

(A): Again, thank you for drawing our attention to this reference. The stability in stratification observed in this work is remarkable, considering their relatively shallow depths. We have included this reference in our text to note the stability observed in some regions, although prior work in this area (northern Manitoba) of the Hudson Bay Lowlands has found study ponds to be well-mixed, as they are considerably shallower than the pond depths recorded in Nunavik in this study. However, the issue of stratification impacting chemical variability is an important point to address in the study region background, particularly if the objective regarding informing sampling design is to be properly answered (as this study addresses chemical variability in nonstratified ponds), and we thank the referee for raising this concern.

(R): Page 4 Water for chemical analyses was taken in profiles? Why these profiles are not shown?

(A): Water samples were taken as a depth-integrated sample of the water column, due to the lack of stratification noted earlier. We have made this more explicit in the method section.

(R): Statistical techniques. I question the design of the variability analysis. If I understand correctly for the spatial deviation score Authors used mean from all ponds sampled on the same date ($n=6$?) and for the temporal variability authors used mean from each single pond over the entire study period ($n=12$); this would probably introduce some bias. Anyway it should be clearly stated how many samples have been used for this calculations.

(A): We have included a more explicit description of the sample sizes which resulted from each normalization treatment in the methods/statistical analyses section. To clarify, for each chemical measurement, both a temporal deviation and spatial deviation score is computed, so the Mann-Whitney test was applied to equal sample sizes. For computation of the deviation scores themselves, we believe the concern is valid regarding the normalization procedures varying in terms of how many points were included to determine a mean value to normalize by in each instance (6 vs. 12). However, we also believe that we have captured a sufficient degree of spatial variation within our 6 ponds for this work despite the great deal of spatial sampling which is

typically captured (as outlined more explicitly in Table 1) to compare with our 12 temporal points at each pond. We suggest this is the case we observed approximately 1-2 orders of magnitude difference in absolute chemical concentrations of most chemical species among the six ponds in our dataset (see Supplementary Table 1) which is in line with the degree of spatial variance in much of the work outlined in Table 1 (and more specifically, in line with the variance observed by other authors who have studied ponds in our specific region, Bos and Pellatt, 2012; White et al., 2014; Jacques et al., 2016).

(R): "and stage data to represent the geometry of conical bathymetry in the non-linear pond stage volume relationship. In this case, the parameter β_2 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." This is unclear to me. Data on bathymetry were available or modelled? Even if for one pond Authors do not record the average depth? How was this accomplished?

(A): To clarify, bathymetry data were not presented in this study (although some sparse measurements were collected in the field). Based on our observations of very gently sloping conical bathymetry, we chose the power function to capture this and allowed the exponent in the function to vary. Theoretically, for a height-volume relationship (and under the assumption of some ions being conservative, we extend this to height-concentration relationship) the value of this coefficient should be between 0, for a perfectly cylindrical pond basin with a flat bottom, to highly negative, for a very steep cylindrical pond basin. We have clarified this in-text in the methods section and in the caption to Table 4.

(R): In this paragraph Authors introduced pond-stage; this should be clearly explained as pond stage is later used in analyses and discussion. Stage means volume, depth? and how was it classified based on the dataset from pressure transducers?

(A): By stage we are referring to the water level (height) in the pond. This was logged hourly by a pressure transducer in a standpipe in the pond which was barometrically corrected. We have clarified this in-text in the methods section.

(R): Definition of the PCA is not needed, citation would suffice.

(A): We have removed the broad background on PCA and replaced with a citation to standard methods.

(R): PCA can be also used to elucidate relationships between control variables (hydrology) and controlled variables (chemistry). For this you would need to use PCA on your meteorology/hydrology dataset, extract components and relate these to concentrations of different ions using stepwise forward lineal regression. Perhaps this would be a clearer method for this

analysis. Alternatively citations for the method used to differentiate between hydrologically driven and nohydrologically driven ions is needed.

(A): To our knowledge our specific method of categorizing hydrologically driven ions is novel, although it is not dissimilar to the approach of an evaporative normalization factor, although extended to dilution (Borghini et al., 2013). Unfortunately, we may lack sufficient hydrological measurements to employ a separate PCA on those data. Based on comparability of our PCA to existing work employing the same technique, we decided to maintain the current inputs to the analysis being strictly hydrochemical. As noted above, additional background and clarification of the manual sorting of hydrologically driven chemical species has been added.

(R): Results - Any data on changes in temperature and oxygen stratification?

(A): We do not present data on stratification. In these ponds, the water column which has been shown to be well-mixed by wind action given the very shallow depth (< 1 m) of these ponds in the region (Bello and Smith, 1990) – we have added a note of this in the description of the study region. As a quality measure to ensure well-mixing we occasionally took simultaneous duplicate samples at multiple points in the lake, which produced nearly identical chemical results (data not presented in this paper).

(R): Does this paragraph belong in the results? "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"

(A): We have modified this paragraph and transferred appropriate sections to the methods section to better differentiate between on reporting actual reports as opposed to methodological approaches in this section.

(R): Discussion - In general well written; needs some trimming i.e., first and second paragraph are superfluous.

(A): We have reduced the redundancy at the beginning of the discussion section by combining the key messages of the first two paragraphs into a single paragraph.

(R): Some paragraphs rewind the results e.g. detailed PCA description

(A): The discussion around the PCA has been shortened in order to reduce repetition with the results and focus instead primarily on contextualizing our results in literature from other permafrost regions, and the implications of the alignment of data from certain ponds along the two PC axes.

(R): I question utility of Table 1 and Table 3; I Authors need to provide an outline of similar studies

(A): We have included an outline of similar approaches (using correlation coefficients between ponds for various chemical species as a measure of coherence) in the introduction section.

(R): Table 1 can be included as Supplementary Material

(A): We have now included Table 1 as supplementary material (now Table S1) instead of being contained within the main text.

(R): Results from Table 2; showing coherence between different ponds can be outlined in the text.

(A): We have outlined in the text the link between our coherence results and the hydrologic/geometric characteristics of the study ponds listed in Table 2 (now Table 1).

(R): Table 5 need to be revised, less spacing between numbers, less vertical lines

(A): Table 5 (now Table 4) has been visually modified to read more clearly as per the referee's suggestion.

(R): Figure 1 needs improvement, maybe provide a high quality map go the province

(A): Figure 1 has been re-done.

(R): Figure 3 Description of axes not symmetrical, should be "temporal variation does not exceed spatial variation"

(A): Axes have been aligned and the prior text "No significant difference" has been clarified as per the referee's suggestion.

(R): Figure 4 Caption unclear, what is pond stage? Ice-free rather than snow-free season.

(A): Pond stage has been clarified throughout the document as pond height, and the text “snow-free” has been replaced with “ice-free” here and elsewhere throughout the text where appropriate.

(R): Figure 6 Normalize fonts style and size with other figures, perhaps enlarge the symbols and remove thin horizontal lines

(A): We have normalized the font size between this figure and others, as well as enlarged the symbols and removed the background grid. The issue regarding figure formatting appear to persist due to the way that this submission is processed as a single .pdf file which resulted in images being resized (along with fonts). The final submitted versions of these figures will have a consistent font size when submitted as individual files.

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

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Climate change across the circumpolar north, the fate of small freshwater ponds and lakes ($< 1 \text{ km}^2$) 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 inform researchers about past climates through sediment records. A changing climate has implications for the capacity of the many small shallow ponds found at high latitudes ponds and lakes 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, thus, an improved understanding of pond biogeochemistry is needed. Due to logistical challenges, many studies rely on data sets collected during a single campaign that may not be representative of the entire ice-free season. This study characterized to characterize spatial and temporal patterns in water column chemistry in a suite of tundra ponds were examined to determine: (1) if temporal variability in pond chemistry exceeded spatial variability? (2) if temporal variability existed, whether exists, do all ponds (or groups of ponds) behaved behave in a similar temporal pattern, linked to season seasonal hydrologic drivers 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: precipitation events? Six shallow ponds located in the Hudson Bay Lowlands region were monitored biweekly throughout the ice-free season (May–October 31, 2015) for concentrations of 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 species-speciation (NO_3^- , NH_4^+ , dissolved organic nitrogen) and major ions. Temporal variability (Cl^- , SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} , Na^+). Across all ponds, temporal variability (across the season and within a single rain event) exceeded spatial variability (variation among ponds) in pond concentrations of most several major ions and dissolved organic nitrogen, which appeared to be driven by the evapoconcentration species (Cl^- , SO_4^{2-} , K^+ , Ca^{2+} , Na^+). Evapoconcentration and dilution of pond water. In contrast, 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 not directly related to pond hydrologic conditions and were instead likely mediated by biological processes within ponds. This work provides an improved understanding of the relative controls of internal and external drivers of pond biogeochemical patterns, and highlights demonstrates the importance of the highly variable seasonal

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hydrology. This work also provides insight for future field sampling campaigns understanding hydrologically driven chemodynamics in permafrost ponds on multiple scales (seasonal and event scale).

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1 Introduction

Small, shallow freshwater bodies (<1 km²) across the circumpolar north are ubiquitous in the landscape (Muster et al., 2013; Dyke and Sladen, 2010; Macrae et al., 2014). These ponds, 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), 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 hydrobiogeochemical 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 based 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 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 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 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 between among different hydrologic years (Morison et al., 2016, 2017; Woo and Guan, 2006). Indeed, Annual changes to pond storage often reflect the highly variable local climatic conditions, and can both ponds may either desiccate completely (e.g. Bouchard et al., 2013; Smith et al., 2005) and/or spill over bankfull storage and/or coalesce (Macrae et al., 2014). The hydrology chemical concentrations of the water column in ponds is closely tied to chemical concentrations 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 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~~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 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.

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 1). ~~Given~~S1. 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 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 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

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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 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 Hudson Bay Lowlands 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) due to from impeded drainage and due very low topographic gradients (Boudreau and Rouse, 1995), as well as and the presence of permafrost at northern locations. Ponds have been demonstrated to be stably stratified in the Hudson Bay Lowlands are well-mixed due to their eastern HBL (Deshpande et al., 2015), while the very shallow nature (<1 m depth) 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; 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 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. 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 (Ramalal et al., 1991). 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 basins/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 catchments are 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, ~~and~~ 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 [21](#); 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 ~~snow-ice~~ 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 ([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-related ~~artefacts~~ 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) ~~as these data have been shown to be representative of this study region (Morison et al., 2016);~~. ~~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 ± 5 m.

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 μ m cellulose acetate filter within two hours of collection. A 50 ml subsample was acidified to a final concentration of 0.2% H₂SO₄ 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~~ 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~~; NH₄⁺-N); G-103-93 (SRP-P), G-109-94 (~~nitrate~~; NO₃⁻-N), G-189-97 (DKN)). Results for NH₄⁺ and NO₃⁻ have a detection limit of 0.001 mg N L⁻¹. Dissolved organic nitrogen (DON) concentrations were determined as the difference between DKN and NH₄⁺ concentrations. Samples were analysed for other major ions: chloride (Cl⁻), sulphate (SO₄²⁻), sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), and calcium (Ca²⁺) 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, $[\bar{x}]_t$; 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, $[\bar{x}]_s$; to examine temporal deviations, Eq. (2).

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

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

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 median-value 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 $y = \beta_1 [x]^{\beta_2}$ (Eq. 3) was fit to the spatially normalized concentration (the ratio of each concentration to the mean concentration $[\bar{x}]_s [x]_t$) 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. In this case, the

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

The parameter β_2 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. (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 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.

A principal component analysis (PCA; Duntzman, 1989) was employed to detect spatial and temporal patterns in pond chemistry variations while reducing redundancy by identifying clusters of correlated species in the on logarithmically-transformed hydrochemistry data, using singular value decomposition scaled to have unit variance. PCA has been

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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.~~

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 software (version 3.3.2, R Development Core Team, 2016).

3 Results

3.1 Spatial and temporal variability of pond chemistry

~~To determine if spatial variability exceeded temporal 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. (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 ~~between~~among ponds, despite differences in magnitude, tended to be strongly positively correlated with each other ($p < 0.01$) with the notable exception of DON (Table 32). NO_3^- and NH_4^+ were not significantly correlated to any other species ($p > 0.01$) (Table 43) while all other species tended to be strongly positively correlated with 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. ~~(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 DOY 260 to the end of the season. ~~(Figure 3).~~ However, Ca^{2+} displayed a contrasting temporal trajectory to the other ~~ions~~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 ~~ions~~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 ~~between~~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. ~~(Figure 4).~~ Hydrologically, all ponds were responsive. Catchments showed synchronous runoff responses to two major rain events on DOY 166 and DOY 185 ~~(Figure 4).~~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 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 thermokarst surrounding it, did not experience a drawdown over the summer season. 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 variations and pond geometry (depth, shoreline development, area, or perimeter; Table 1).

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. Generally, DON, Cl⁻, Na⁺, K⁺ and Mg²⁺ were classified as generally hydrologically driven species among ponds and Ca²⁺, NH₄⁺, NO₃⁻, and SO₄²⁻ were classified as non-hydrologically driven (Table 5; 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 SO₄²⁻ may have been hydrologically driven in Strange pond. Slight differences in β_2 values between among ponds for hydrologically driven species are driven/influenced by the differences in bathymetry driving which dictates the stage-volume relationship.

3.4 Principal component analysis

Principle component analysis (PCA) of the data allows allowed 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 clustering of samples from a single each pond in PC space. (Figure 6). The analysis also shows a clustering of groups of ions in reference to chemical species along the PC axis axes. A collection of the hydrologically driven chemical species (Table 5; Figure 4; DON, Mg²⁺, K⁺, Na⁺, Cl⁻) closely follows the PC1 axis with slightly negative scores for PC2. Two other non-hydrologically driven ions chemical species have positive scores along PC1 with slightly positive (DON) negative (SO₄²⁻) and positive (Ca²⁺) scores along PC2. Inorganic nitrogen species, (NO₃⁻ and NH₄⁺), 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. Chemical species which were classified as hydrologically driven (Table 4) were not necessarily the 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 than 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 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 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 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 ~~snow~~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 ~~snow~~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^+ ; Figure 7; 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+} -(Figure 7)-.

4 Discussion

4.1 Seasonal trends and spatial variability in pond chemistry

Ponds in this study displayed a coherent trend in several chemical concentrations over a ~~snow~~ice-free season, despite differences in pond geometry, catchment characteristics, and absolute magnitude of chemical concentrations. This suggests that landscape-Landscape scale factors such as climate and ecotone may be driving pond nutrient cycling and 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, absolute magnitudes of different ionic chemical species concentrations varied between 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 but 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 ionic chemical species 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 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. 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.~~ 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. ~~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 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 than 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 (evapoconcentration, dilution, catchment contributions).~~

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 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 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 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 and), the smaller number of samples taken at each lake per year (3 and), and the reporting of total N as opposed to the dissolved fraction. Sokal et al. (2012) did not report a similar clustering of ions/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 ions/chemical species in our study (Ca , SO_4). This could be due to larger and deeper lakes studied in the region ($\sim 10^6 \text{ m}^2$ surface area; 1.5 m deep) in addition to additional limnological and isotopic measurements into the PCA. However, this difference in ion/species clustering may not be entirely regional/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 ions/chemical species and Ca^{2+} and SO_4^{2-} as was found in this study.

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 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 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.

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/conservatism. 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 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 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 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 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), 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 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 understanding 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-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 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 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 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 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 of six 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 over the course of an entire snow-free season. However, no (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 matrices showed that these hydrologically driven ions/chemical species are strongly correlated to each other and between/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 ions/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 ions/species, 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 chemodynamic behavior of permafrost ponds through over both short-term and long-term temporal scales while remaining spatially synchronous. Further, 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.

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 S4S2.

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 km²) 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 measurement of dissolved or suspended trace metal elements.

Study	Analytes of interest	Region	Study year(s)	Number of ponds/lake s 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

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Michelutti et al., 2002	Nutrients, Carbon, Major Ions, Metals	Wynniatt Bay, Victoria Island, Arctic Canada	1997	34	4
Niu et al., 2011	Major Ions	Kunlun Mountain pass, Tibet	2007	10	4
Paterson et al., 2014	Nutrients, Carbon, Major Ions, Metals	Hudson Bay Lowlands, Ontario	2009–2011	17	4
Pienitz et al., 1997	Nutrients, Carbon, Major Ions, Metals	Yukon and NWT, Canada	1990	59	4
Pokrovsky et al., 2011	Carbon, Major Ions, Metals	Northwestern Siberia	2008–2010	20	4
White et al., 2014	Nutrients, Major Ions	Hudson Bay Lowlands, Manitoba	2010	20	3

Table 2-
Table 1. Physical characteristics and locations of study ponds near Churchill, Manitoba.

Pond	Area (m ²)	Perimeter (m)	Shoreline development* (m ¹ m ⁻¹)	Average depth, μ ± σ (cm)	Catchment area (m ²)	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 32. Correlation coefficients between among ponds for all species. Values are bolded when the correlation is significant at the *p* < 0.01 level.

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	Erin	Frisbee	Larch	Left	Sandwich
<u>DON</u>					
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
<u>Cl⁻</u>					
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
<u>SO₄²⁻</u>					
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
<u>Na⁺</u>					
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
<u>K⁺</u>					
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
<u>Mg²⁺</u>					
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
<u>Ca²⁺</u>					
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
<u>NH₄⁺</u>					
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
<u>NO₃⁻</u>					
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 4.3. Correlation coefficients between 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 5.4. Values of β_2 and root mean square error (S) from the curve $[x] = \frac{[x_{st}]}{[x_s]} = \beta_2 * Stage^{\beta_2} \beta_1 (stage)^{\beta_2}$ 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 <i>driven</i>					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	<i>-0.47</i>	-0.43	-0.53	<i>-0.28</i>	-0.63	0.36	0.82	-0.35	0.85
S	<i>0.19</i>	0.08	0.05	<i>0.15</i>	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	<i>-0.71</i>
S	0.37	0.18	0.11	0.11	0.15	0.24	0.45	0.13	<i>0.18</i>

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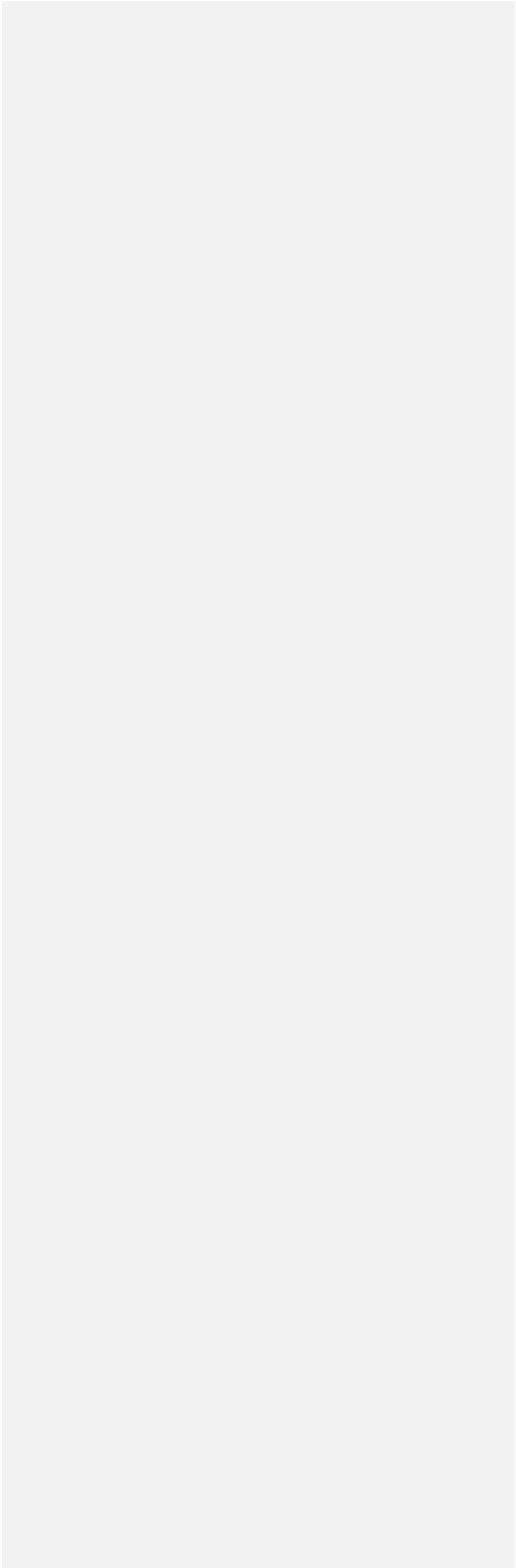
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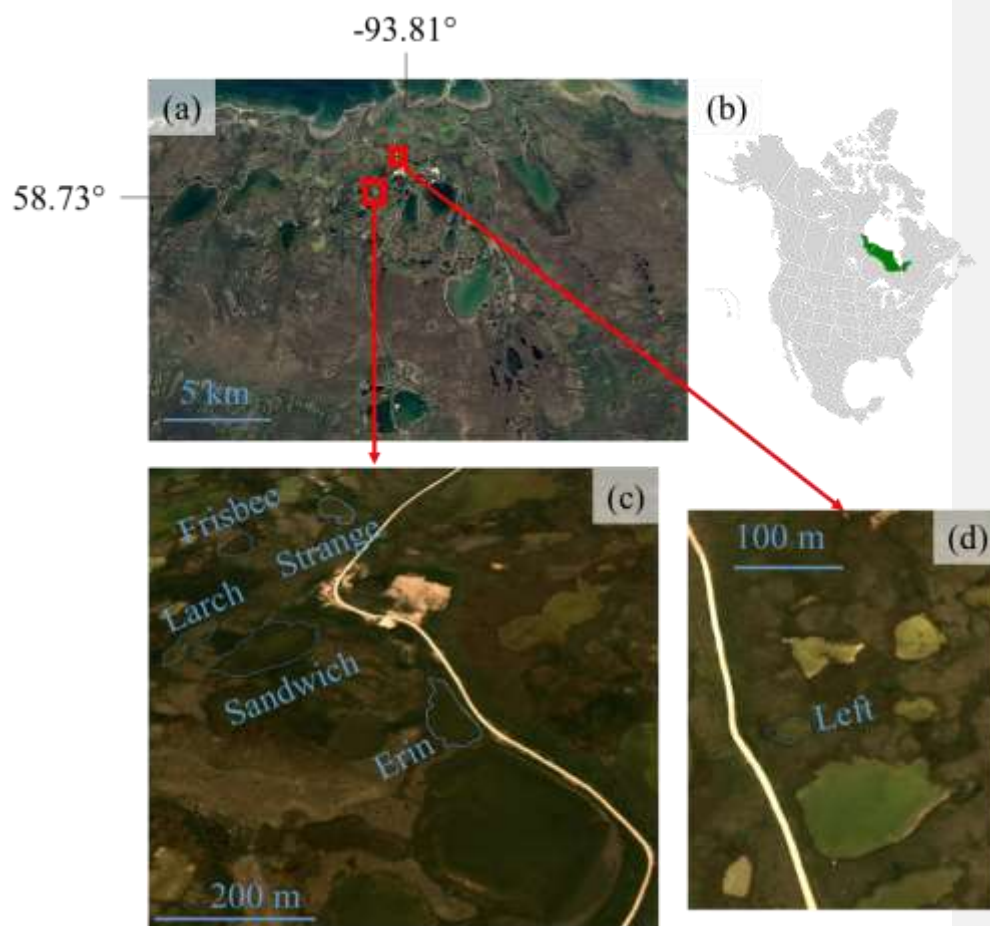
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Figures

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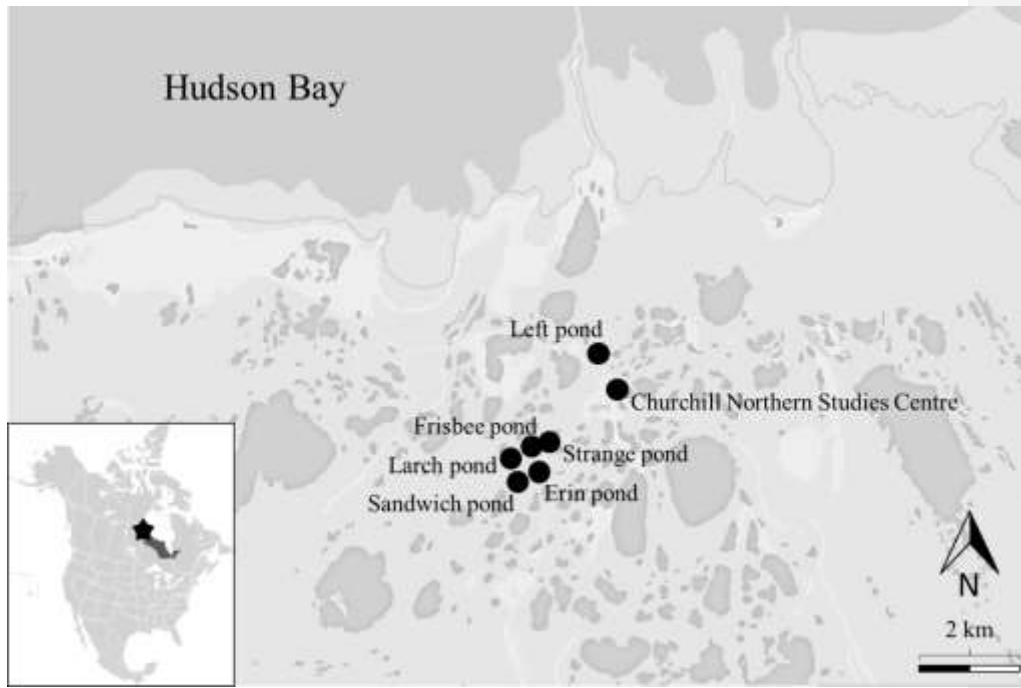


Figure 1. Site Map of (a) the general near-coastal tundra region, (b) the Hudson Bay Lowlands highlighted in green, (c) with the catchment areas containing Frisbee, Larch, Strange, Sandwich, Left, and Erin ponds, (d). Inset map highlights the Hudson Bay Lowlands (dark colour) and the catchment containing Left pond-Churchill region (star). Map data: Google, Digital Globe, 2017.

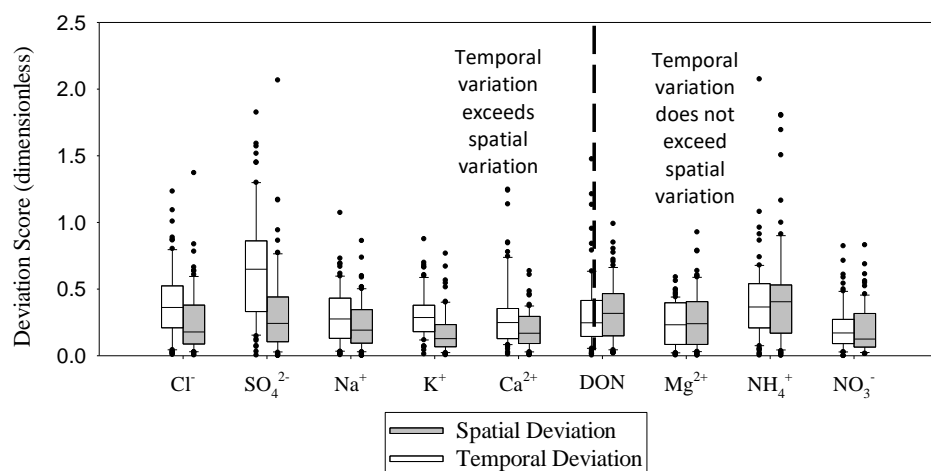
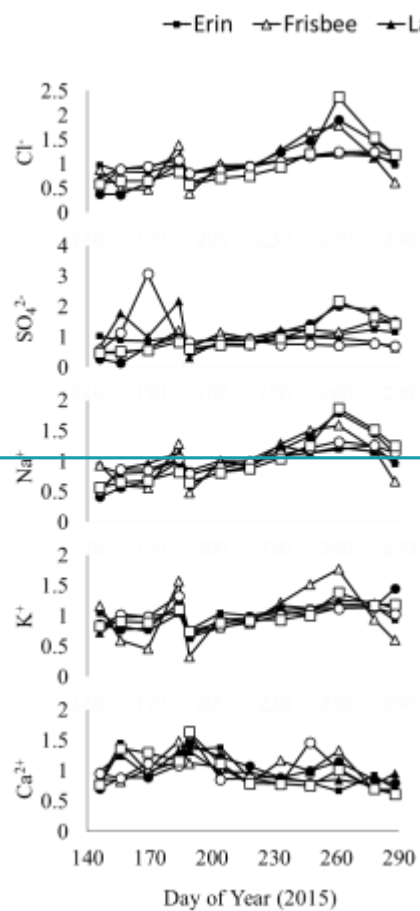
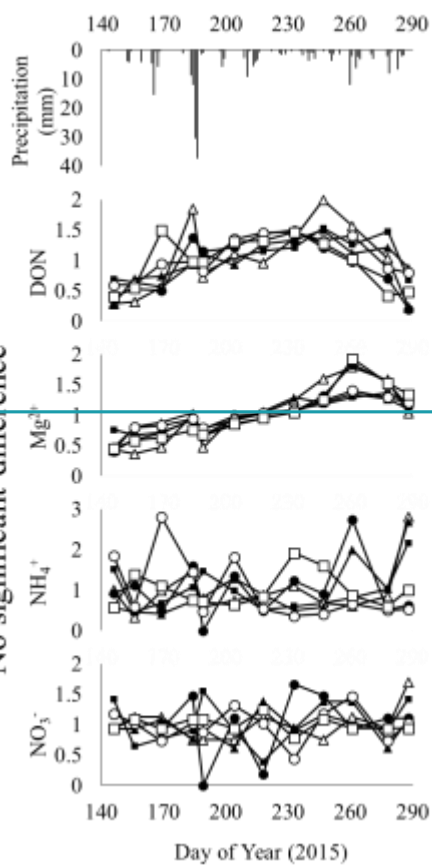


Figure 2. Boxplots of spatial and temporal proportional deviations for each chemical species. Significant differences between medians ($p < 0.01$) are present for all species on the left side of the panel (Cl^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+}), and no significant difference is present for species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

Temporal variation exceeds spatial variation



No significant difference



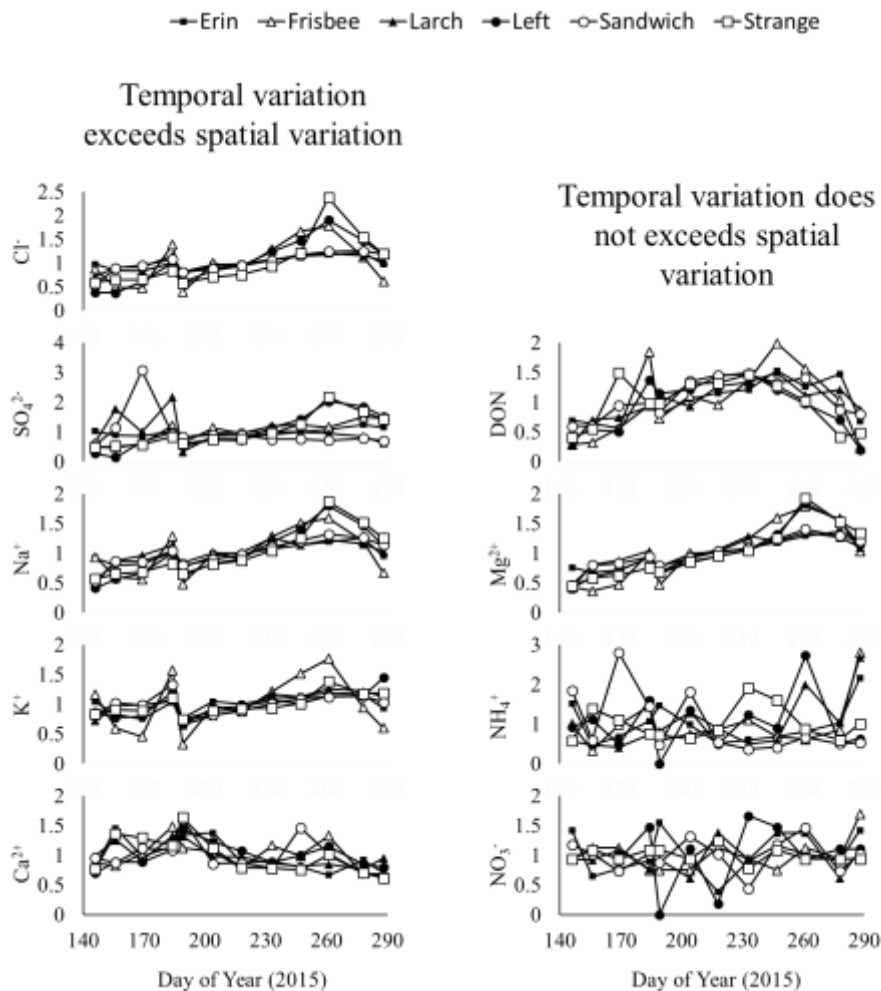
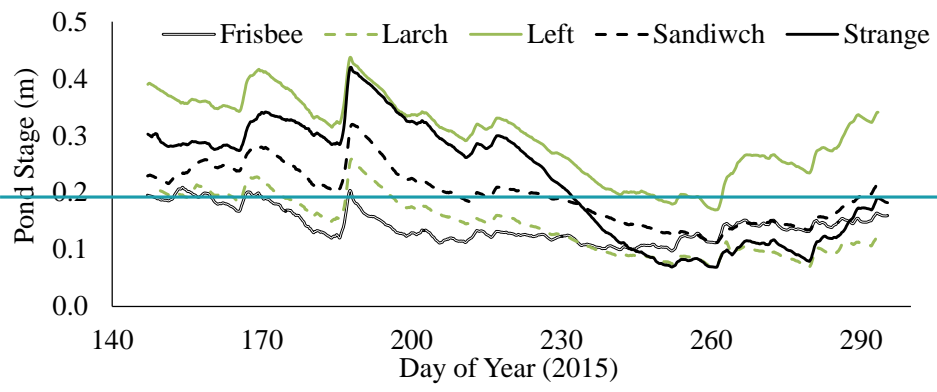


Figure 3. Pond normalized concentrations of all measured chemical species in each pond and precipitation for the 2015 snow free season. **In chemical species on left side of the panel (Cl⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺) temporal variation exceeds spatial variation, and no significant difference is present for species on the right (DON, Mg²⁺, NH₄⁺, NO₃⁻).**

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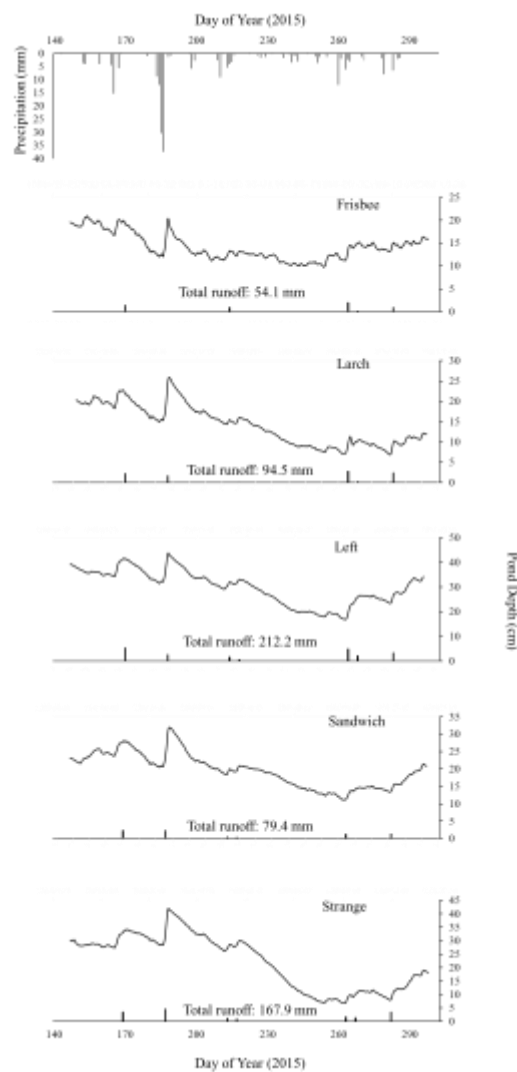


Figure 4: Pond-stage Precipitation (vertical bars, top panel), as well as depth of water column (continuous line) and runoff depths (vertical bars) in each of the instrumented study ponds over the 2015 ~~Snow~~ ice-free season.

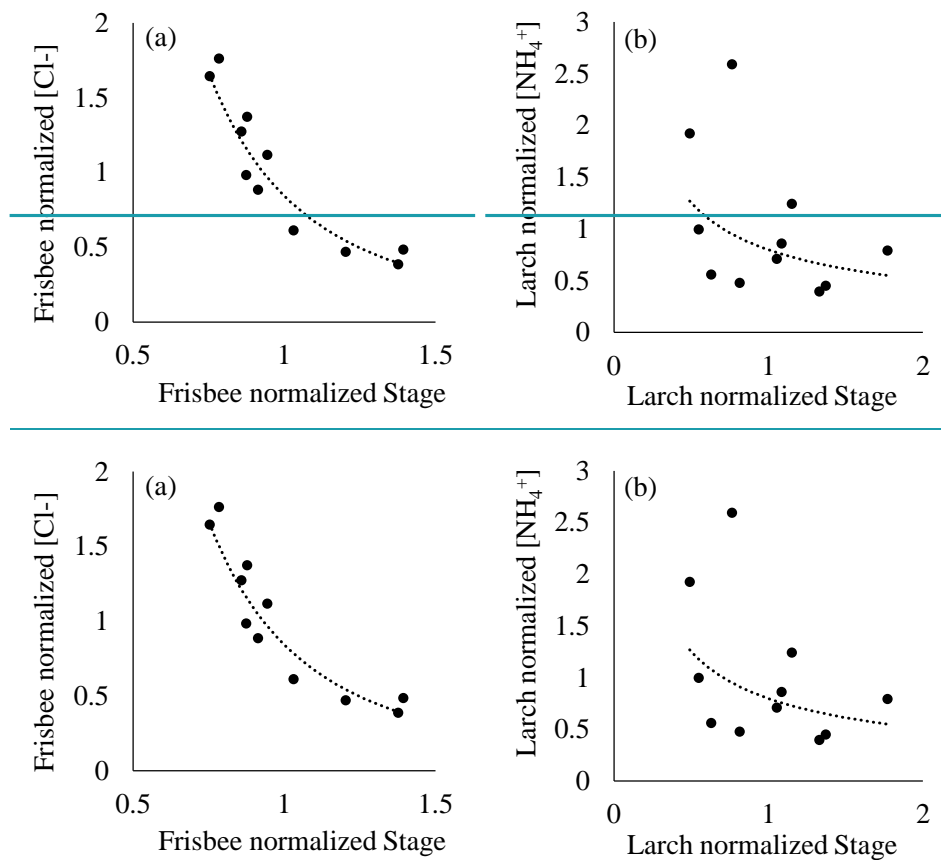
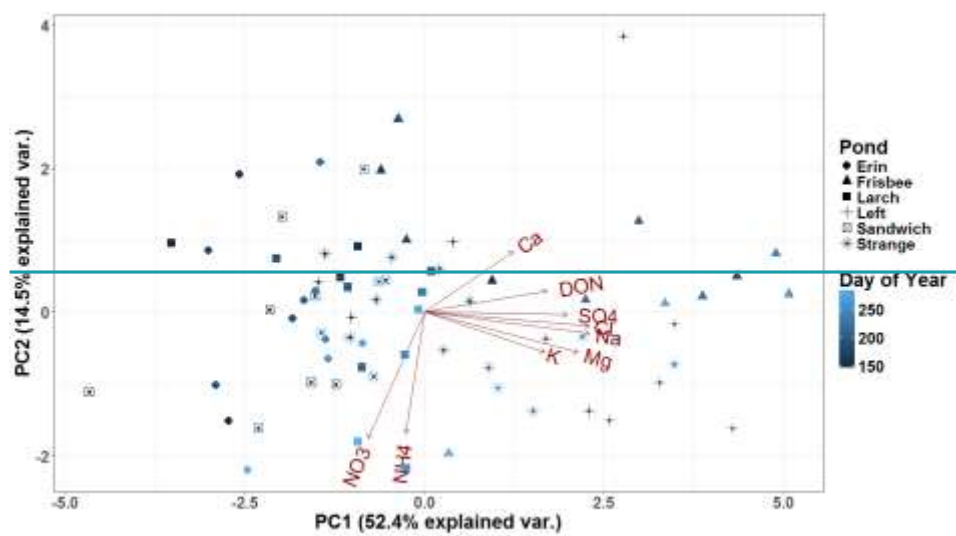


Figure 5: Comparison of the stage-concentration relationship in a (a) hydrologically driven chemical species (Cl^- , in Frisbee pond), and (b) a non-hydrologically driven species (NH_4^+ , in Larch pond).



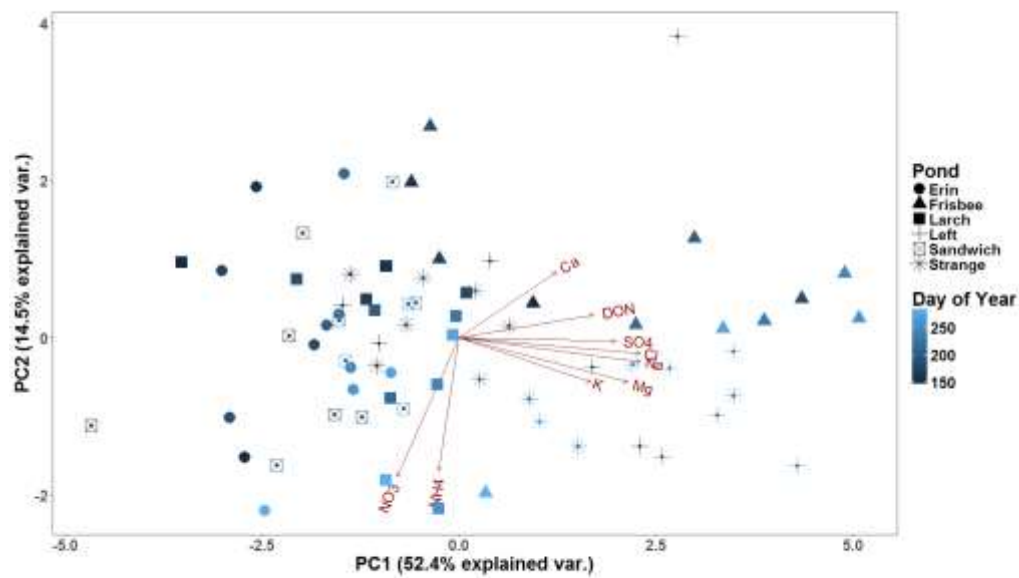
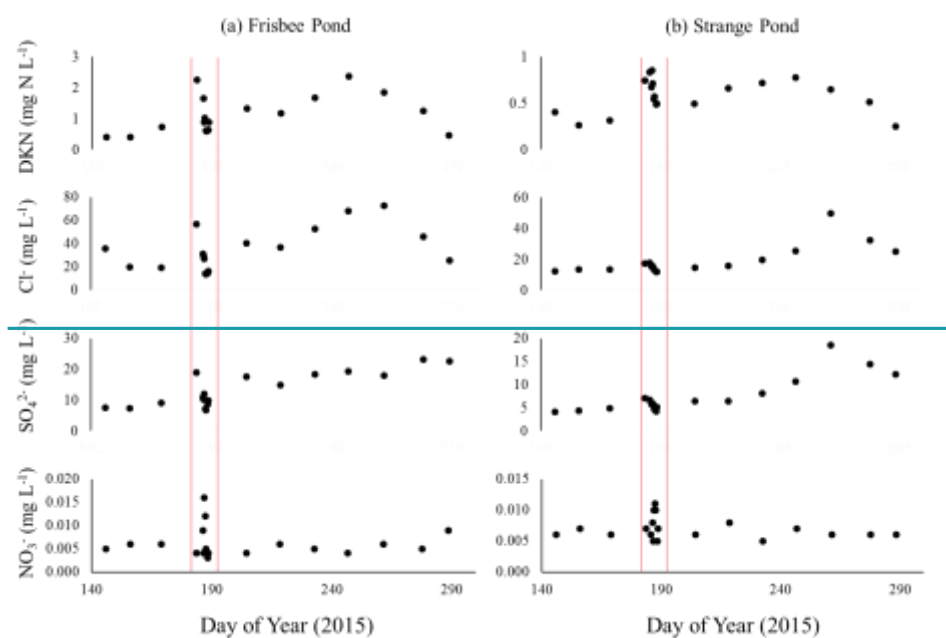


Figure 6. Principal Components Analysis of chemical concentrations in all ponds throughout the 2015 snow-free season. PC1 primarily corresponds with the hydrologically-driven chemical species (Table 3) while PC2 corresponds to inorganic nitrogen species (NO_3^- , NH_4^+).



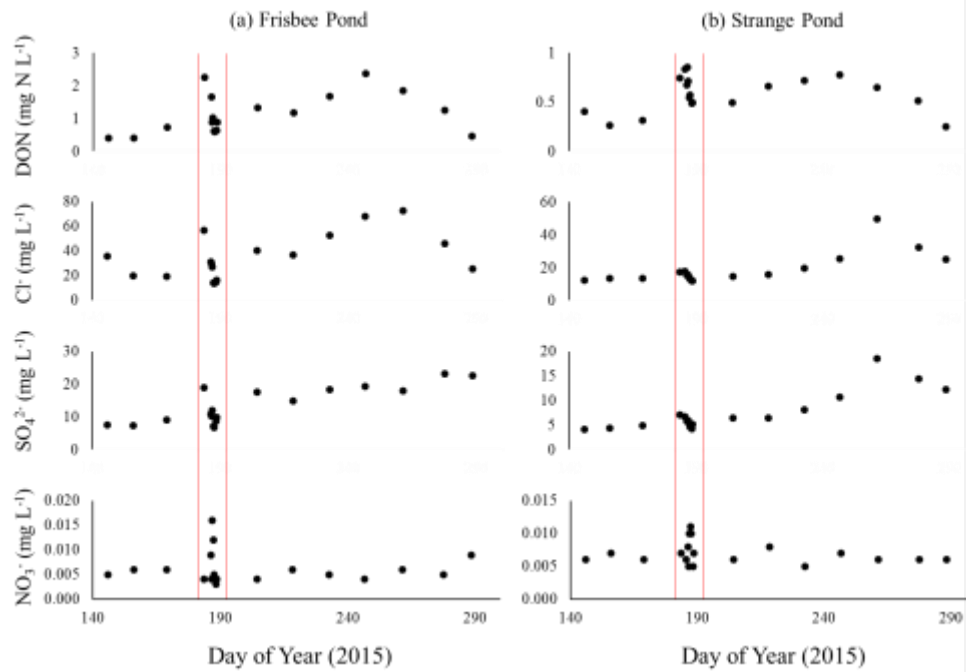


Figure 7. Short term variation in DON, Cl⁻, SO₄²⁻, and NO₃⁻ concentrations in (a) Frisbee pond and (b) Strange pond during a rain event on July 3rd to 6th, 2015 (DOY 185-188, highlighted with red bars).

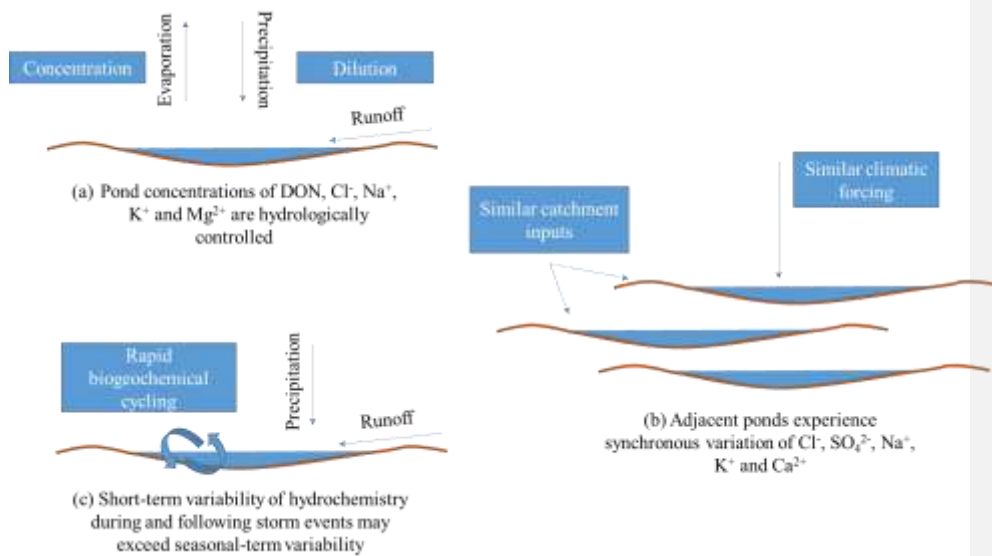


Figure 8. Graphical summation of major findings from this study: (a) factors driving hydrological control of particular chemical species in ponds, (b) hypothesised factors driving temporal coherence in chemical species in ponds, and (c) short-term variation in hydrochemistry can exceed seasonal-scale variation despite the large difference in timescales.

