https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

The role of catchment characteristics, discharge, and active layer thaw on seasonal stream chemistry across ten permafrost catchments.

Authors: Arsh Grewal[1], Erin M. Nicholls[2], Sean K. Carey[1]

[1]School of Earth, Environment, and Society, McMaster University, ON, Canada

[2]Department of Earth, Energy, and Environment, University of Calgary, AB, Canada

Corresponding Author: Arsh Grewal, akgrewal@mcmaster.ca

Corresponding Author Present Address: Department of Earth & Environmental Sciences, Michigan State University, MI, United States, grewala7@msu.edu

Keywords: Watershed Hydrology, Concentration-Discharge, Permafrost Hydrology, Water Quality, Permafrost, Solute Export,

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Abstract

High latitude catchments are rapidly warming, leading to altered precipitation regimes, widespread permafrost degradation and observed shifts in stream chemistry for major arctic rivers. At headwater scales, stream discharge and chemistry are seasonally variable, and the relative influence of catchment characteristics, climate and active layer thaw on this seasonality has been poorly addressed. To provide new insight into mechanisms driving changes in streamflow chemistry within permafrost watersheds, we measured discharge and sampled major ion and dissolved organic carbon (DOC) concentrations across ten permafrost catchments in Yukon Territory, Canada. We incorporated concentration-discharge relationships within generalized additive models to resolve the distinct influence of discharge and seasonal active layer thaw on stream chemistry and identify the role of watershed characteristics on the magnitude and seasonality of solute concentrations. After accounting for seasonal variations in discharge, results indicate both major ions and DOC were highly seasonal across all catchments, with DOC declining and major ion concentration increasing post freshet. Seasonal variability in major ion concentrations were primarily driven by active layer thaw, whereas DOC seasonality was strongly controlled by flushing of soil organic carbon during freshet. While major ion concentrations were geologically mediated, greater permafrost extent led to enhanced seasonality in major ion concentrations. Catchments with strong topographical gradients and thinner organic soils had higher specific discharge, lower DOC concentrations but greater relative seasonality. Our results highlight the important role catchment characteristics play on shaping both the seasonal variations and magnitude of solute concentrations in permafrost underlain watersheds.

1. Introduction

High latitude catchments are experiencing rapid warming due to polar amplification (Cohen et al., 2014), and are highly sensitive as thawing permafrost and altered precipitation regimes strongly affect their hydrological and biogeochemical cycles (McKenzie et al., 2021; Walvoord and Kurylyk, 2016). Frozen ground and permafrost act as impeding layers to water movement, restricting flow and separating supra, intra and sub-permafrost aquifers (McKenzie et al., 2021; Woo, 1986). Where present, permafrost enhances runoff by restricting deep percolation and encouraging flow through more hydraulically conductive near-surface pathways (Carey and Woo, 2001; Quinton and Marsh, 1999; Woo and Steer, 1983). Permafrost degradation, which includes deepening of the seasonal thawed zone (termed the

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

active layer) and wholesale loss, also influences stream chemistry (Frey and McClelland, 2009; Walvoord and Kurylyk, 2016). Dissolved solutes are expected to increase due to greater contact with mineral surfaces as flow pathways lengthen. Vast stores of frozen organic material are thawing, yet dissolved organic carbon (DOC) concentration projections are uncertain due to potential increased adsorption and in-stream processes (Frey and McClelland, 2009; Tank et al., 2023). Studies from large arctic rivers show increase exports of weathering products such as Ca, Mg and DOC (Tank et al., 2016), yet results are varied across circumpolar regions (Tank et al., 2023), and long-term studies are limited to extremely large rivers that cross multiple ecozones and permafrost extent, confounding interpretation.

Active layer dynamics along with seasonal precipitation (phase and magnitude) play a critical role in runoff and solute export processes (McNamara et al., 1998; Woo and Winter, 1993). During spring, large volumes of meltwater infiltrate the soil yet are restricted to near surface layers that are often organic, exporting large volumes of water rich with dissolved organic matter (DOM; Carey, 2003; MacLean et al., 1999; Shatilla et al., 2023; Woo and Steer, 1986). As the frost front descends, mineral layers thaw and catchment storage increases resulting in greater concentrations of weathering solutes and reduced DOM (Carey, 2003; Carey et al., 2013; Petrone et al., 2006). Concentrations of weathering derived solutes generally increase from spring to fall, whereas DOM concentrations typically decrease (Carey, 2003; Frey and Smith, 2005; MacLean et al., 1999). The position of the water table with respect to different soil horizons in the active layer has largely been used to explain seasonal patterns of dissolved solutes in the permafrost literature. Permafrost extent is also identified as a key driver of hydrological and biogeochemical processes. For example, Petrone et al. (2006) and Webster et al. (2022) attributed lower yield of NO_3^- and higher yield of fluorescent dissolved organic matter (fDOM) to greater permafrost extent in Alaska. Webster et al. (2022) found evidence of greater seasonality of NO_3^- in high permafrost catchments compared to catchments with lower permafrost extent.

Changes in hydrological connectivity across the landscape can alter streamflow chemistry and solute export (Creed et al., 2015; Li et al., 2024; Zhi et al., 2019). During wet periods, water tables are near the surface in highly conductive organic soils and areas distal to the stream can be connected. During drier conditions, flow is primarily through deeper mineral pathways and landscape connectivity declines (Stewart et al., 2022; Zhi et al., 2019). The presence and disposition of permafrost strongly affects the interaction between solute sources, water pathways and the stream network. Direct observations of

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

these interactions are rare in northern watersheds as permafrost extent is often difficult to assess and logistics are typically challenging. Concentration-Discharge (CQ) relations have increasingly been used to characterize flow-solute coupling to infer catchment processes (Godsey et al., 2009; Hall, 1970; Wymore et al., 2023). By comparing the log-log slope between the two, it is possible to characterize whether a solute displays flushing behaviour (positive slope) or dilution (negative slope). Other metrics such as CV_C:CV_Q ratios can be used to determine whether a solute is chemostatic or chemodynamic even when there is no clear directionality (Musolff et al., 2015; Thompson et al., 2011). Positive/negative slopes can indicate spatial and vertical heterogeneity within a catchment, whereas slopes close to zero can indicate homogeneity in vertical and spatial distribution of solute stores or dominance of instream biogeochemical processes (Creed et al., 2015).

Active layer thaw and streamflow are highly seasonal in permafrost catchments, making it difficult to ascertain the relative influence of each factor in driving seasonal solute dynamics. For example, major ion concentrations typically increase throughout the ice-free season. This seasonality can be driven by decreasing discharge, which can lower connectivity with the ion poor shallow organic layer. However, thawing of active layer can also lead to greater water movement through the mineral layer, increasing stream ion concentrations. The potential influence of both discharge and active layer dynamics on seasonal stream chemistry in cold regions are rarely disentangled. Shifts in CQ relationships can be used to detect changes in solute export driven by processes other than discharge, such as changes in the internal structure of the catchment (i.e. ground freeze-thaw) or in the quantity/mobility of solute stores. For example, Fork et al. (2020) examined changes in residuals of water flux versus DOC to infer changes in supply in terrestrial pools of DOC. Biagi et al. (2022) and Ross et al. (2022) utilized generalized additive models (GAMs), which are flexible models that allow for the addition of spline terms to model non-linear behaviour, to quantify changes in CQ relationships over time in agricultural environments. CQ relationships are often highly seasonal in northern catchments, particularly between snowmelt and summer periods (MacLean et al., 1999; Shatilla et al., 2023). MacLean et al. (1999) compared CQ patterns between seasons in a permafrost underlain Alaskan catchment, however the authors classified each season and thus had to assume that the transition between seasons is a discreet phenomenon. At the event scale, Shogren et al. (2021) found both seasonality and landscape drivers to be important for the relations between DOC, NO_3^- and flow. The authors determined that landscape drivers were more important to CQ relationships than seasonality for DOC and NO_3^- in Arctic catchments post freshet.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

In cold catchments, seasonal patterns of freeze-thaw, discharge, and solute stores have been identified as drivers for variability in stream chemistry (Boyer et al., 1997; Carey, 2003; MacLean et al., 1999; Petrone et al., 2006). However, the relative importance of each factor and how it is influenced by permafrost extent and other catchment characteristics remains unresolved. To address this, we characterize CQ relationships using discrete major ion and DOC data across ten permafrost influenced catchments. We utilize GAMs with an additional spline Day Of Year (sDOY) term to the traditional CQ approach to test two hypotheses:

1. As active layer thaws, concentrations will increase for major ions and decrease for DOC at all sites (irrespective of seasonal changes in discharge), due to seasonal ground thaw induced activation of deeper mineral rich flow paths.

2. Seasonal changes in concentrations for both major ions and DOC will be the largest in catchments with greater permafrost extent (irrespective of seasonality in discharge) due to greater connectivity of subpermafrost water to streams in catchments with lower permafrost extent.

Testing these hypotheses will provide new insights on the role of catchment characteristics and permafrost extent on the seasonality of major ions and DOC export. By disentangling different drivers of seasonal solute export in northern environments, we can make more informed predictions of stream biogeochemistry in a rapidly changing north.

2. Data and Methods

2.1. Study Area

Our study consists of 10 catchments with areas ranging from ~5 Km^2 to ~170 km^2, all located in Yukon Territory, Canada. Four of the catchments are part of the Wolf Creek Research Basin (WCRB; 60° 36' N, 134° 57' W; Figure 1), with WCRB outlet (WCO) being the largest. Coal Lake (CL) is a ~70 km^2 subcatchment of WCRB that has a ~ 1 Km^2 well mixed lake near the outlet. Granger Creek (GC) and Buckbrush Creek (BB) are alpine headwater subcatchments of WCRB and have areas less than 10 Km^2. WCO and CL are underlain with sporadic permafrost (Lewkowicz and Ednie, 2004). Low elevation areas of WCRB consist of primarily coniferous forests, whereas high elevation areas consist of shrub taiga and alpine tundra vegetation. High elevation subcatchments (BB, GC) are estimated to be underlain by

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

discontinuous permafrost (Lewkowicz and Ednie, 2004) and are typically colder and wetter than low elevation areas of WCRB. Near surface geology consists of mostly sedimentary rocks such as limestone, sandstone, and siltstone capped by a till mantle and glaciofluvial/glaciolacustrine deposits (Rasouli et al., 2014). WCRB is part of the traditional territories of the Ta'an Kwach'an Council, Kwanlin Dün, and Carcross/Tagish First Nations. More detailed description of WCRB can be found in (Rasouli et al., 2014, 2019). Climate normals (1991-2020) reported near WCRB at the Whitehorse airport show the average air temperature is 0.2 °C with an annual precipitation of 279.6 mm (164 mm as rain). Due to the large elevation gradient at WCRB, average temperatures in the headwater regions are several degrees lower, and precipitation volumes are larger, often exceeding 400 mm per year.

Six of our study catchments are part of the Tombstone Waters Observatory (TWO; Figure 2), which is part of the traditional territory of Tr'ondëk Hwëch'in First Nation. All TWO catchments have areas less than 35 km^2. All TWO catchments intersect the Dempster highway, a critical north-south road. All TWO catchments are named after the kilometer marker where the stream intersects the highway. The six catchments are called Km 44, Km 71, Km 99, Km 104, Km 175, and Km 185. Km 44 (64° 19' N, 138° 31' W) and Km 71 (64° 31' N, 138° 8' W) are the most mountainous catchments, with strong topographic gradients (Table 1). Km 44 primarily consists of bare earth, whereas Km 71 is largely overlain with shrub cover. Km 99 and Km 104 (64° 41' N, 138° 28' W) are treeless catchments and are overlain by a thick layer of peat except for the high elevation areas with steep slopes. Km 104 is largely flat, whereas Km 99 has mountainous uplands with more mineral soils. Km 175 (65° 12' N, 138° 26' W) and Km 185 (65° 16' N, 138° 18' W) are primarily covered by open coniferous forests and are a part of the Ogilvie Mountain range. Although there is some discrepancy between various permafrost mapping products in regard to permafrost extent, the general consensus is that the WCRB sites have less permafrost than the TWO sites (Bonnaventure et al., 2012; Obu et al., 2019; Ran et al., 2022; Surficial Geology dataset, 2024). Surficial geology maps in TWO indicate that Km 71, Km 99, Km 104, and Km 185 are underlain with continuous permafrost (>90%), whereas Km 44 is underlain with sporadic permafrost and Km 175 is underlain with discontinuous permafrost (Thomas and Rampton, 1982a, b; Surficial Geology dataset, 2024). Climate normals (1991-2020) from Dawson City, the nearest Environment Canada weather station to TWO, reports annual precipitation of 319 mm of which 208 mm is rainfall. The annual air temperature is -3.8 ℃. However, local climate can be quite variable amongst study catchments in TWO.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Bedrock geology across TWO is diverse (Colpron, 2022). Km 44 is primarily underlain by thick-bedded quartz arenite. Km 71 is primarily underlain by two geological units; the first is described as dark grey argillite, slate, and phyllite, commonly graphitic and the second is described as black graptolitic shale and black chert. Km 99 and 104 are underlain by black shale and chert, dolomitic siltstone, calcareous shale, and buff platy limestone in the low-lying areas. The uplands of the basins are underlain by interbedded maroon and apple-green slate, siltstone, and sandstone. Km 175 and 185 are primarily underlain by grey and buff-weathering dolostone, limestone, black graptolitic shale, minor chert shale, siltstone, and sandstone (Colpron, 2022).

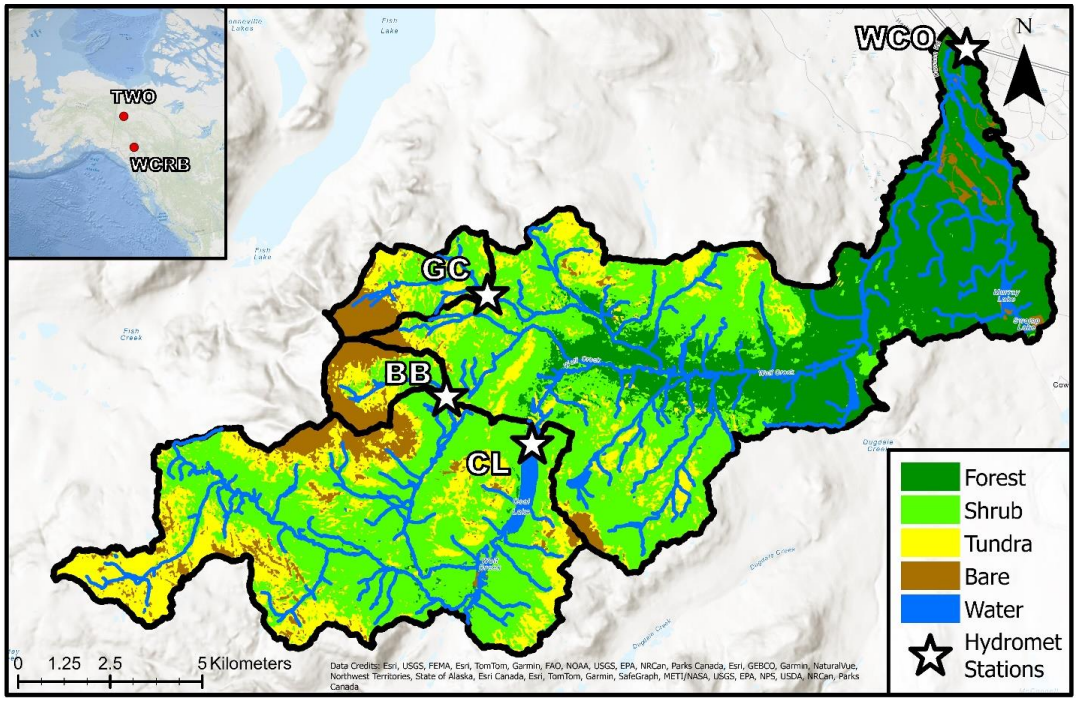
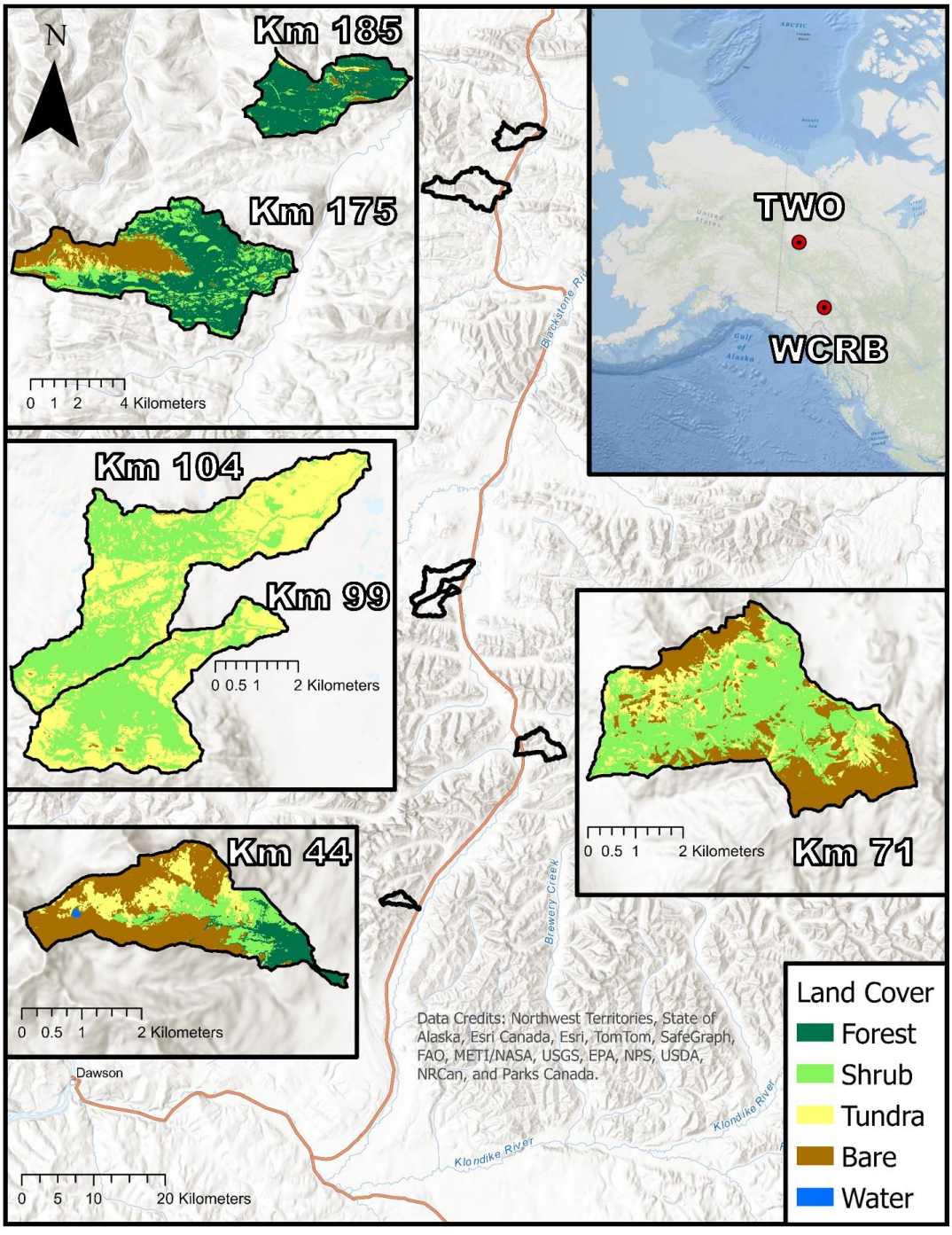


Figure 1. Study area map of Wolf Creek Research Basin (Wolf Creek Outlet, WCO) and its subcatchments (Granger Creek, GC, Buckbrush Creek, BB, and Coal Lake, CL)

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024



175

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Figure 2. Study area map of all Tombstone Waters Observatory (TWO) catchments. Insets show land cover for each catchment.

2.2. Catchment characterization

All TWO catchments were delineated using the 2 m resolution ArcticDEM product, whereas WCRB catchments were delineated using a 1-m DEM generated from a 2018 LiDAR scan. All topographic parameters including aspect, slope, and mean elevation were calculated in SAGA GIS. Land cover was determined through a supervised classification using a resampled DEM and Sentinel-2 multiband imagery via the *RStoolbox* package in R (Leutner et al., 2023). Catchment characteristics are reported in Table 1.

Table 1. Table of catchment characteristics for WCRB and TWO catchments.

Site	Area (Km^2)	Forest (%)	Shrub (%)	Tundra (%)	Bare (%)	Water (%)	Elevation (m.a.s.l)	Slope (deg)	Permafrost
Km 44	5.5	12.4	17.2	18.5	51.6	0.3	1413.9	26.7	Sporadic
Km 71	16.5	0.0	48.4	17.7	33.9	0.00	1429.5	25.1	Continuous
Km 99	11	0.0	50.7	48.3	0.9	0.1	1401.5	10.9	Continuous
Km 104	17.8	0.0	50	49.6	0.4	0	1251.2	6.8	Continuous
Km 175	35.9	48.2	25.6	3.4	22.8	0	1003.2	19.2	Discontinuous
Km 185	14.7	84.3	8.8	3.5	3.4	0	916.2	18.9	Continuous
BB	5.4	0	29.7	23	46.8	0	1678	17.5	Discontinuous
GC	7.3	0	40.5	31.5	26.6	0	1618.7	11.1	Discontinuous
CL	67.8	0.4	55.4	29.7	11.8	2.7	1464	15.4	Sporadic
WCO	169.4	25.3	46	19.3	7.5	1.9	1303.7	12.3	Sporadic

2.3. Stream chemistry

Grab samples for major ions and DOC were collected across flow states (in spring and summer) at all sites over multiple years. Grab samples were collected from 2017 to 2022 for WCO and GC. We collected samples from 2018 to 2022 for Km 99, CL, and BB. Only samples from 2021 and 2022 were collected for Km 104. Lastly, samples were collected from 2019 to 2022 for all other sites. Major ions and DOC samples were filtered through a 0.45 µm syringe filter and collected in 60 mL HDPE bottle (DOC samples stored in a brown HDPE bottle). After collection, samples were kept cool and dark in the field via

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

icepacks and immediately refrigerated at 4 °C for storage. Specific conductance (SpC) was determined in the field using a multiparameter sonde (YSI proPlus or proDSS). Only one year of samples were included for Km 104. The number of observations varied among sites and ranged from 24 (SpC at CL) to 92 (major ions at WCO). The number of samples for each solute and site can be found in Table S1.

Major ions analysis was conducted via ion chromatography (DIONEX ICS 6000, IonPac AS18 and CS12A analytical columns) at the University of Waterloo Biogeochemistry Lab. All DOC analysis was conducted on Shimadzu TOC-5000A Total Organic Carbon Analyzer by the Biogeochemical Analytical Service Laboratory in the University of Alberta. The US Environmental Protection Agency Test Method 415.1 was followed (Environmental Protection Agency (EPA), 1974). Out of all the ions measured, only Ca, Mg, and Sulphate had concentrations consistently over the detection limit, and were the only major ions considered for analysis. Continuous SpC was measured using HOBO Conductivity loggers. The loggers were calibrated in post using the YSI ProDSS handheld multiparameter sonde. If samples had concentrations below the detection limit, a value of half of the detection limit was assigned to the sample.

2.4.Runoff

All ten catchments were instrumented with Solinst leveloggers to determine continuous volumetric flow rate via stage-discharge relationships. Flow measurements were generally conducted in association with a chemistry grab sample. If samples were collected without a flow measurement, we used discharge determined from stage-discharge relationship and continuous level loggers. The majority of the catchments had very low or zero discharge over the winter. The study sites often had channel ice which made winter stage-discharge relationships highly uncertain and as such there was limited winter data available. Flow data was generally available during spring freshet with the exception BB, where spring flow data is limited due to logistical access constraints during the snowmelt period. Discharge data is available from 2017-2022 at the WCRB sites, and from 2019-2022 at the TWO sites. Km 104 was instrumented late 2021 and only had data from 2022.

2.5.Generalized Additive Models

Generalized Additive Models (GAMs) extend traditional linear models by allowing the addition of terms that are a sum of smooth functions (Hastie and Tibshirani, 1986). The additional terms can be linear or non-linear spline terms, and the flexibility of the spline terms can be set by the user to prevent

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

overfitting. In this study, we use GAMs to extend the traditional concentration-discharge models by adding day of year as a spline term to the linear CQ model.

$$log(C) = b * log(Q) + log(a) + sDOY \quad (1)$$

Where DOY is the day of year of the sample (sDOY indicates a spline fit), Q is discharge, C is the concentration of the solute, and b and a are constant coefficients. This equation can also be expressed:

$$C = e^{s(DOY)} a Q^b \quad (2)$$

GAMs provide the effective degrees of freedom (edf) for the spline term and provide p-values for both the sDOY term and the log-log slope. The standard error for the spline term can also be extracted from the model, however the standard error is not constant. In this case, standard error for the sDOY term may be higher during freshet than mid-summer due to high interannual difference in discharge. The mean standard error for sDOY can be used to determine the average uncertainty in the seasonality of a model. The range of the sDOY fit can be used to quantify the degree of seasonality in a CQ model, where a greater sDOY range means greater relative change in concentrations across seasons at a constant discharge.

We fit a GAMs model for all five reported solutes across all ten sites, where each model was fit using the restricted maximum likelihood (REML) estimation. The mgcv package in R was used for all analyses involving GAMs (Wood, 2023). GAMs provide a partial effect plot, which is the measure of the influence a particular term has on the model. We extracted the *b* term, the R^2 value, sDOY range, p-values for both the *b* term and the sDOY term, and the mean sDOY standard deviation from each model.

The presence of heterogeneity in sources within the catchment and changes in connection to these sources due to ground thaw will be indicated by statistical significance in both the log-log slope and the sDOY term. A non-significant log-log slope with significant seasonality suggests other processes (i.e. in stream biogeochemical processes) are driving seasonality. A greater sDOY range in catchments with greater permafrost extent will support the second hypothesis, suggesting a greater relative change in concentrations due to ground thaw.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

2.6. Coefficient of Variation Ratios

Ratios of the coefficient of variation of logged concentrations (CV_C) and of logged runoff (CV_Q) were used to quantify chemodynamic behaviour for solutes even when there was no directionality with runoff (Musolff et al., 2015; Thompson et al., 2011). We calculated CV_C:CV_Q for all solutes at all sites and the CV ratios were plotted against the log-log term as shown in Equation 1 and 2. CV ratios are a useful tool to broadly compare chemodynamic behaviour across catchments and solutes, particularly in situations where multiple distinct drivers influence stream chemistry.

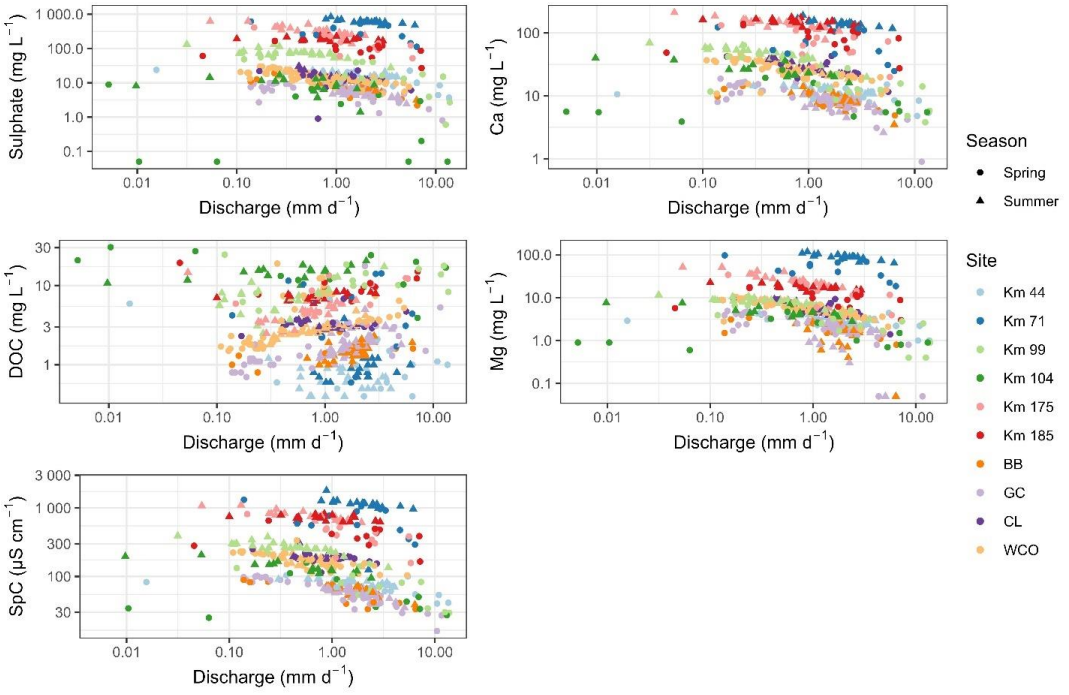
3. Results

3.1. Discharge and Concentrations Across Basins

We determined the median of specific discharge estimates of grab samples from each site as opposed to the mean to account for missed sampling at extreme low and high flows at certain sites. Median specific discharge was the greatest at Km 44 and Km 71 (2.2 mm d^{-1} and 2.03 mm d^{-1} respectively). The lowest median specific discharge occurred at Km 99, WCO, and Km 104 (0.57 mm d^{-1}, 0.64 mm d^{-1}, and 0.65 mm d^{-1} respectively). Of note, Km 44 and 71 were adjacent sites and had strongest topographical gradients (most mountainous; Table 1), whereas Km 99 and Km 104 were adjacent and had the weakest topographical gradients (least mountainous).

Solute concentrations were generally lower at all WCRB sites compared to TWO sites (Figure 3). Km 71 typically had the highest concentrations of major ions, particularly Mg (median concentration of 87.6 mg L^{-1}). Km 175 and Km 185 (underlain by discontinuous and continuous permafrost respectively) also had relatively high concentrations of major ions across both seasons (Figure 4). Km 104 and Km 99 had the highest mean concentrations of DOC, with median concentrations of 15.2 mg L^{-1} and 8 mg L^{-1} respectively. In contrast, the lowest DOC concentrations generally occurred at the WCRB sites and Km 44. Concentrations in spring were typically more variable than late season across sites, likely due to high variability in discharge (Figure 2).

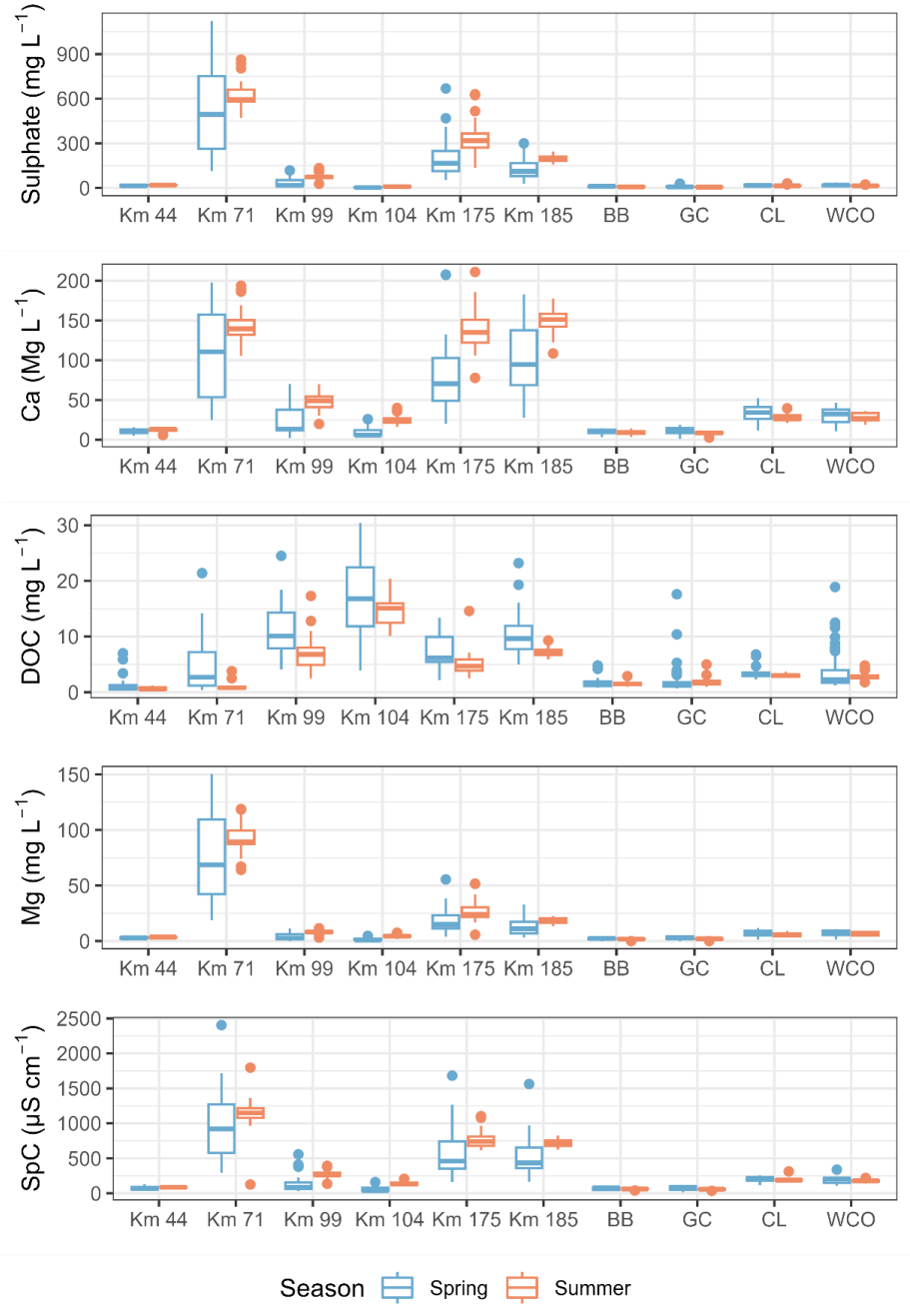
https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024



272

273 Figure 3. Solute concentrations plotted against flow for all sites. Winter samples were lumped in with
274 spring.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024



275

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Figure 4. Boxplots depicting log solute concentrations for Spring and Summer for all catchments. Winter values were grouped into spring and grab samples where flow was not available are also included in the boxplots. Samples taken on a DOY between 130 and 280 were classified as summer samples.

3.2. GAMs

3.2.1. Seasonality

Results from the GAMs indicate that not all sites showed significant seasonality for all solutes (Figure 5), which was defined by a p-value lower than 0.05 for the sDOY term. The degree of seasonality, defined as sDOY range, is reported in the SI (Table S1). Larger sDOY range indicates greater seasonal change in concentrations after accounting for discharge. In general, sDOY increased as the season progressed post freshet for major ions but decreased for DOC (Figure 5). Thus, DOC concentrations decreased over time, but major ion concentrations increased at most sites after accounting for changes in flow. The WCRB sites exhibited less seasonality (lower sDOY range) for major ions than the TWO sites, which typically have more permafrost than WCRB sites. Model performance was generally lower for DOC than other solutes, particularly for CL (a large lake dominant subcatchment of WCRB underlain with sporadic permafrost), Km 175, and Km 104, which had an R^2 less than 0.2. The models exhibited poor performance (R^2<0.25) in predicting Sulphate and SpC in CL, as well as in predicting Mg in BB (an alpine headwater subcatchment of WCRB; Figure 6). It is important to emphasize that BB had limited winter/spring samples, which may lead to lower sDOY range.

DOC had significant seasonality (sDOY p-value < 0.05) at all sites except for CL, Km 104, and Km 175 (Figure 5). Among the sites with significant seasonality, BB and Km 99 had the least pronounced seasonality for DOC, characterized by sDOY ranges of 0.52 and 0.76 respectively. Conversely, Km 44 and Km 71, the two catchments with the strongest topographical gradients, had the most pronounced seasonality, with sDOY ranges of 1.60 and 2.35 respectively. In general, the standard error for sDOY was notably higher for DOC compared to other solutes, particularly at sites exhibiting wider sDOY ranges.

Sulphate exhibited significant seasonality at across all sites. The site with the least pronounced seasonality was WCO (the largest catchment in our study underlain with sporadic permafrost), with an sDOY range of 0.42. In contrast, Km 104 (continuous permafrost) had the greatest seasonality (sDOY range: 4.1) coupled with a relatively large mean standard error (0.43) for the sDOY term. Several spring samples had Sulphate concentrations below the detection limit, potentially explaining the high

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

uncertainty at Km 104 compared with other catchments. Km 185 (continuous permafrost) had the second highest sDOY range (1.87) for sulphate with a lower mean standard error (0.1).

The GAMs seasonality results were similar for Ca, Mg, and SpC. WCO and CL, the two largest catchments, were the only sites that did not have a significant sDOY term for Ca (p-values: 0.051 and 0.16, respectively). Among the WCRB sites, Mg only exhibited significant seasonality at WCO. Among the TWO sites, Km 175 was the only site to not exhibit significant seasonality for Mg. SpC had significant seasonality for all sites except for CL (p-value: 0.37). Km 104 and Km 185 had the greatest seasonality for Ca, Mg, and SpC. For Ca, sDOY ranges were 2.14 and 1.41 for Km 104 and 185 respectively. For Mg, Km 104 and Km 185 had sDOY ranges of 2.23 and 1.73 respectively. Km 104 and Km 185 had sDOY ranges of 1.69 and 1.48 respectively for SpC.

The lowest significant seasonality for Ca, Mg, and SpC all generally occurred at WCRB sites, which have less permafrost than the TWO sites. GC and Km 44 had the weakest the weakest significant seasonality for Ca, with sDOY ranges of 0.39 and 0.4 respectively, while WCO had the lowest significant seasonality for Mg (sDOY range: 0.43). In contrast, Granger and WCO had the lowest significant seasonality for SpC with sDOY ranges of 0.32 and 0.28 respectively. Complete GAMs results are reported in the SI.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

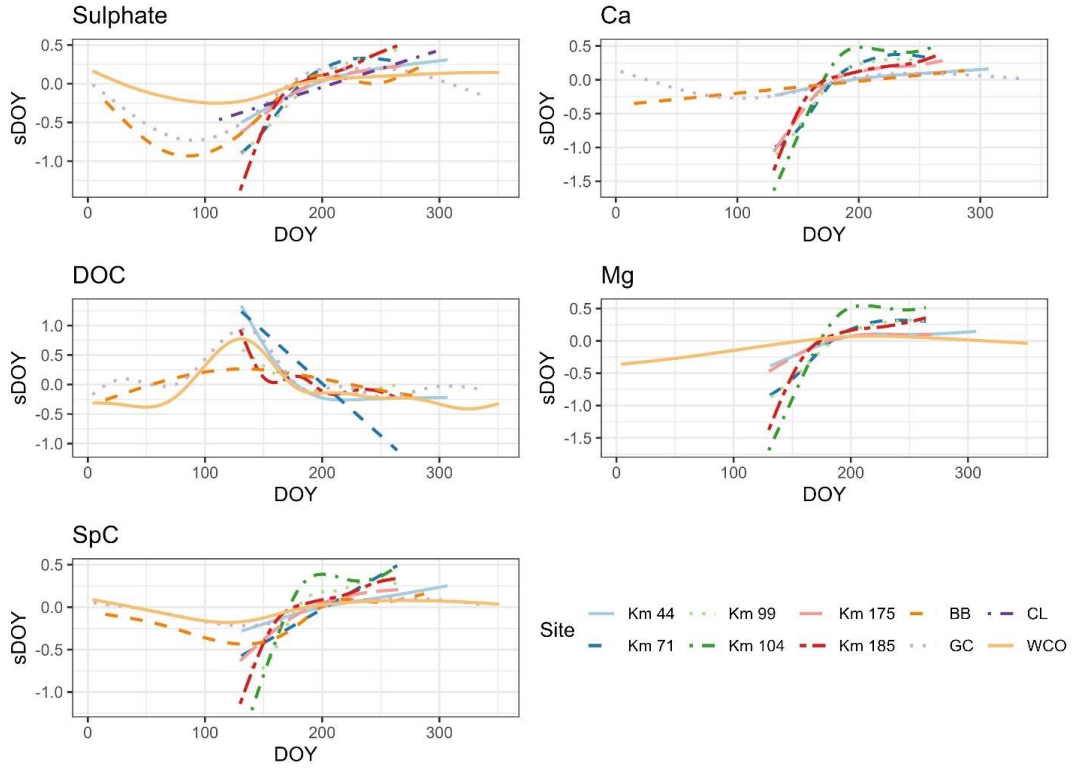


Figure 5. sDOY from GAMs for all solutes and sites where the sDOY was significant (p-value < 0.05) and mean SE was less than 0.4.

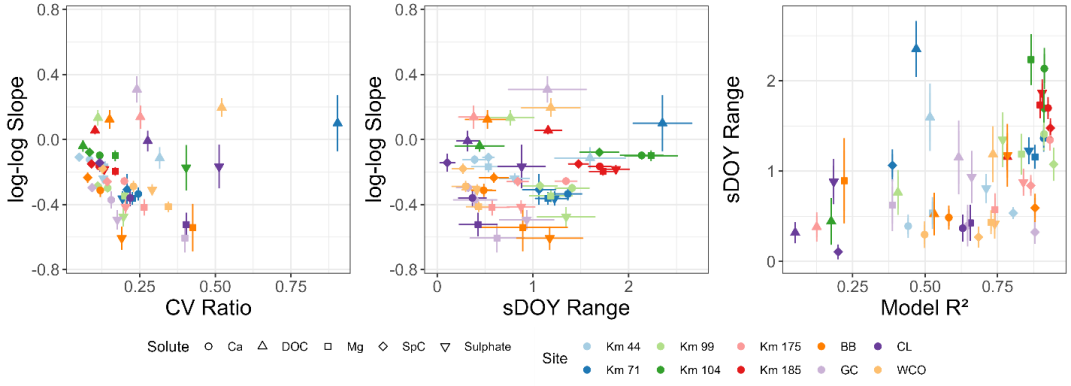
3.2.2. CV ratios and log-log slopes

Log-log slopes from the GAMs were generally negative for major ions, and positive or close to zero for DOC (Figure 6). Slopes close to zero indicate spatial and vertical homogeneity of solute source within the catchment, or dominance of in-stream/near-stream biogeochemical processes. The standard errors of the log-log slopes were typically higher for sulphate and DOC than any other solute among sites. BB and GC (alpine headwater subcatchments of WCRB) for Mg had the strongest negative slopes, approaching -0.6. For DOC, WCO (outlet of WCRB) and Granger had the strongest positive log-log slopes (0.20 and 0.31 respectively). Km 71 (strong topographical gradient), CL (lake influenced subcatchment of WCRB), and Km 104 (flat with continuous permafrost) had negative or near zero log-log slopes. All other sites had weak but positive log-log slopes for DOC close to 0.1. CV ratios for all major ions were lower than 0.7 at all sites, however the majority of sites had CV ratios of less than 0.3. Km 71 had the highest CV ratio for

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

334 DOC followed by WCO. Km 104 and CL had relatively high CV ratios for Sulphate but also had large
335 standard errors in log-log slopes. Km 104 and Km 44 (strong topographical gradient) had some of the
336 lowest CV ratios for ions along with log-log slopes close to zero, indicative of chemostatic behaviour. A
337 similar pattern can be observed for DOC for Km 104 and Km 185.

338



339

340 Figure 6. CV ratio plotted against log-log slopes from GAM models (top). Gam R^2 plotted against sDOY
341 range (bottom). Error bars indicate standard error of sDOY range (mean sDOY SE $* \sqrt{2}$) and the standard
342 error of the log-log slope from GAMs models. The sDOY range for Sulphate for Km 104 was large and was
343 not included in these plots for visualization purposes. Several samples were below the detection limit for
344 Sulphate at Km 104 potentially leading to high uncertainty in the model.

345 ## 4. Discussion

346 In permafrost influenced catchments, solute concentrations are typically highly seasonal (Carey, 2003;
347 Koch et al., 2021; MacLean et al., 1999; Shatilla and Carey, 2019; Shogren et al., 2021; Townsend-Small et
348 al., 2011). Concentrations of DOC generally decrease, and concentrations of weathering derived ions
349 generally increase over the course of the spring to fall transition. Seasonal active layer dynamics,
350 depleting solute stores, and seasonality in discharge have been used to explain these patterns previously
351 (Carey, 2003; Shatilla and Carey, 2019). However, little work has been done to resolve the relative
352 influence of these drivers of variability. Here we provide insights on the mechanisms of solute export in
353 permafrost underlain catchments by assessing changes in CQ relationships.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Results largely confirm our first hypothesis, which states that after accounting for the seasonality in discharge, concentrations for DOC would decrease and the concentrations for major ions would increase post freshet due to seasonal ground thaw. However, our results also suggest that depletion of soil organic matter during spring, not ground thaw, is the primary driver for seasonality in DOC concentrations.

Our second hypothesis states that greater permafrost extent would lead to greater seasonality for major ions and DOC. Although we found evidence to support this hypothesis for major ions, our results indicate that permafrost is less important than other catchment characteristics (i.e. topographical gradients) when considering seasonality of DOC.

4.1. Seasonal drivers for DOC and major ions

4.1.1. Spatial/vertical heterogeneity in soil chemistry is evident in most catchments

Log-log C-Q slopes were predominantly negative (dilution) for all major ions and positive (flushing) or with no significant slope for DOC. This corresponds to work of others who reported log-log slopes as typically positive for DOC (MacLean et al., 1999; Skierszkan et al., 2024) and negative for major ions (MacLean et al., 1999; Shatilla et al., 2023) in permafrost underlain catchments. The negative log-log slopes for major ions indicates the presence of greater mineral rich soils at depth. Log-log CQ slopes for major ions were closest to zero for Km 104 (a relatively flat catchment with uniform catchment characteristics), indicating high homogeneity in terms of the spatial and vertical distribution of solute sources within the catchment.

A near zero log-log slope suggests that mobile organic carbon (OC) may be homogeneous vertically/spatially, or in-stream/near-stream biogeochemical processes drive variability in DOC concentrations (Creed et al., 2015; Zhi and Li, 2020). Although many catchments had significant positive log-log slopes for DOC; CL, Km 44, Km 71, Km 104, and Km 175 all had non-significant log-log DOC slopes. Km 104 has near zero log-log slopes with a very low CV ratio. The low log-log slopes likely reflect the largely homogeneous vertical/spatial soil profile due to thick organic soils and relatively thin active layer (~40 cm), and weak topographical gradients. Additionally, the stream is slow moving and instream processes may be more important in this catchment than the other TWO catchments. CL is the second largest catchment in this study with a ~1 km^2 lake just above the sampling outlet. The non-significant log-log slope along with high CV ratio at CL indicate the dominance of in-stream/surface water processes (i.e.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

photosynthesis, respiration, photo-oxidation), as high heterogeneity of catchment characteristics in WCRB rule out homogeneity in vertical and spatial soil characteristics as a potential driver for low log-log slopes. Both Km 104 and CL had insignificant sDOY terms and near zero log-log slopes, indicating the lack of seasonality in DOC concentrations.

Despite the near zero log-log slopes, the high seasonality of Km 44 and Km 71 for DOC (Section 3.2) suggests seasonal processes other than discharge and active layer thaw are primary drivers of variability of DOC in these catchments. Km 44 and Km 71 have strong topographic gradients, a thin organic layer along with a high proportion of bare ground; particularly upslope of riparian areas. This result suggests that as the source area expands during high flows, water with low DOC concentrations from upslope rocky areas (which do not have a defined organic layer) move quickly through the organic layer near riparian areas (limiting contact time) due to the steep gradients and dilute the stream DOC signal.

4.1.2. Seasonal depletion of soil stores is important for DOC export

Our analysis suggests that flushing of organic soils during freshet is likely the primary driver for seasonal declines in DOC, yet active layer thaw may be secondary driver depending on the spatial/vertical distribution of organic matter concentrations in soil. At most sites, high seasonality for DOC (as indicated by the sDOY range) along with nonsignificant log-log slopes indicates changing flow paths due to active layer thaw is likely not the primary driver in the seasonality of DOC concentrations (Figure 6). In this scenario, seasonality in DOC concentrations would be driven primarily via flushing of organic soils during freshet. The seasonality term in GAMs accounts for changes in flow, and the presence of non-significant log-log slopes indicate a lack of vertical heterogeneity in soil OC concentrations or dominance of in/near-stream processes. Thus, seasonality in CQ relationships for DOC in catchments where log-log slopes are near zero, must be driven by processes other than changing flow paths due to active layer thaw or discharge. Previous work in snow dominated mountains has shown the flushing of organic matter in soils during freshet can reduce the soil reservoir of DOC (Boyer et al., 1997; Hornberger et al., 1994). For example, Boyer et al. (1997) attributed declines in DOC as melt progressed to source depletion in the upper soil horizons in a mountain headwater catchment in Colorado, USA. Certain sites (GC, WCO, BB, Km 99, and Km 175) did have positive log-log slopes for DOC, suggesting that depletion of DOC stores and thawing active layer may have a combined effect in controlling DOC concentrations. The strong decline of the sDOY term during freshet at several sites indicates (Figure 5) that flushing of DOM in soils during freshet rapidly deplete finite labile OC stores within catchment soils as observed elsewhere

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

(Boyer et al., 1997; Hornberger et al., 1994). Previous work at GC, attributed a strong hysteresis of DOC concentrations during freshet and summer events to both a rapid decline in organic matter and greater emphasis on deeper flow pathways (Carey, 2003; Shatilla and Carey, 2019). Townsend-Small et al. (2011) compared DOC concentrations at the same discharge level in the upper Kuparuk River in Alaska and saw a decrease in DOC concentrations over time, suggesting seasonality is at least partially driven by active layer thaw and/or depleting solute stores. Skierszkan et al. (2024) used a mixing model and found seasonality in DOC concentrations to primarily be driven by changing flow paths in the Dawson range, Yukon, Canada, which contrasts with our findings. This discrepancy is potentially a result of strong heterogeneity in spatial and vertical soil OC concentrations in the Dawson range, and greater presence of organic carbon in soils.

4.1.3. Seasonal active layer freeze-thaw is important for major ion export

Our study largely agrees with others in permafrost environments that attributed the seasonality of major ions to seasonal active layer thaw. Similar to other studies, we found CQ relationships are variable among seasons for major ions in permafrost underlain catchments (MacLean et al., 1999; Shatilla et al., 2023). Non-zero log-log slopes indicate presence of heterogeneity in soil chemistry. Significant sDOY terms indicate seasonal changes in ion concentration after accounting for variability in discharge. The negative log-log slopes and strong seasonality at multiple sites for multiple major ions suggest that activation of different flow paths from seasonal active layer thaw along with discharge influence export in these regions. Thawing of the active layer leads to greater flow from the deeper mineral rich soil horizons and bedrock and consequently higher ion concentrations. GAM results for major ions indicate seasonal increases in solute concentrations, suggesting the seasonality in CQ patterns is not primarily driven by depletion of ion stores (Figure 5). Shatilla et al. (2023) attributed ground thaw and increasing connectivity of deep groundwater to seasonal increases in solute concentrations in GC. (Lehn et al., 2017) attributed a seasonal increase of major ion concentrations in Alaskan watersheds to seasonally thawing active layer and cryoconcentration in soils during later fall and winter of the previous years. Our results are generally in agreement with these findings, although we did not have the data to assess the influence of cryconcentration in soils. Km 104 had significant but relatively low log-log slopes, with the highest seasonality. This suggests that other drivers (aside from discharge and active layer thaw) may play an important role in seasonal ion concentrations in this site. Km 104 and Km 99 were found to have highly seasonal transit time distributions, where the fraction of young water is much lower in the summer than in the spring (unpublished data). Greater transit times in the summer can lead to greater

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

contact time between water and mineral systems (Benettin et al., 2015), potentially driving seasonality in this system. However, calculating transit times requires estimates of input tracer concentrations which was difficult to do for many of our study catchments, particularly during snowmelt.

4.2. Catchment characteristics drive seasonality

4.2.1 Stronger topographical gradients lead to greater DOC seasonality

Although permafrost extent has a strong influence on DOC export (Frey and McClelland, 2009; MacLean et al., 1999; Petrone et al., 2006), greater permafrost extent did not necessarily lead to greater seasonality (sDOY range) in CQ relationships for DOC. For example, DOC was highly seasonal in WCO (sporadic permafrost) but had relatively low seasonality for Km 99 (continuous permafrost). Although DOC concentrations were generally higher in the TWO sites, they did not necessarily exhibit a greater relative change in concentrations than the sites in WCRB, which generally have a lower permafrost extent than the TWO sites. Our results are in contrast to MacLean et al. (1999) and Petrone et al. (2006) who observed stronger seasonality for DOC/DOM in catchments with greater permafrost extent. MacLean et al. (1999) reported stronger CQ relationships and greater model performance for DOC in a high permafrost catchment compared to the low permafrost catchment in central Alaska during the summer. However, CQ relationships were similar between the catchments during snowmelt. The authors attributed this to a lower variability in discharge during the summer for the low permafrost catchment. Petrone *et al.* (2006) observed larger increases of DOC export in catchments with greater permafrost extent. However, Petrone *et al.* (2006) did not assess the relative changes in DOC export or seasonality in discharge, where connectivity to DOC changes with changing catchment wetness.

In our study sites, catchment characteristics related to slope and specific discharge were more important for DOC seasonality than permafrost extent. For example, the two most mountainous sites (Km 44 and Km 71) had the highest seasonality for DOC, indicating the greatest relative seasonal changes in concentrations after accounting for discharge. Both Km 44 and Km 71 had high specific discharge, strong topographical gradients, and the lowest average concentrations for DOC, supporting the idea that organic matter stores were limited. Non-significant log-log slopes imply that nearly all the seasonality at these sites was due to the depletion of solute stores and not due to active layer thaw as conceptually outlined in Fig 7. Although other seasonal processes (water age, stream temperature, etc.) may be important, flushing of soil OC has been observed as an important mechanism in multiple mountain catchments (Boyer et al., 1997; Shatilla and Carey, 2019). The limited DOC supply and rapid flushing due

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

to high flows presumably led to a more rapid depletion in DOC stores in these catchments. Conversely, Km 99 and Km 104 had high average DOC concentrations and high permafrost extent yet exhibited lower seasonality than Km 71 and Km 44. Additionally, the CV ratio at Km 104 was also very low, indicating DOC was chemostatic. Km 99 and Km 104 had much weaker topographical gradients and specific discharge relative to other sites, potentially leading to limited flushing of soils (low specific discharge), which may have played an important role in the weak seasonality of DOC. One caveat is that Km 104 had a very low R^2 value (<0.2) for DOC and did not have significant seasonality or log-log slopes, potentially due to the lack of multi-year sampling. Km 99 is similar to Km 104, but had a significant positive log-log slope for DOC. Unlike Km 104, Km 99 is not entirely overlain with peat in the active layer as mineral soils are present in the headwaters. The significant seasonality in Km 99 may be driven by thawing of the active layer, leading to deactivation of shallow DOC rich flow paths, or due to flushing of organic layer during freshet. We cannot disentangle the influence of depletion of solute stores and thawing of the active layer on seasonality of DOC in catchments that do have significant log-log slopes. It is likely that in these catchments, both flushing of organic soils and active layer thaw drive seasonality in DOC concentrations.

The presence of a lake near the outlet of CL can lead to dampening of the terrestrial DOC signal and may be dominated by in-lake biogeochemical processes. This may explain the lack of significance in the sDOY term in CL. Low seasonality in BB relative to GC is likely a function of limited sampling during freshet at BB. Seasonality was also low in Km 175, likely due to high median Fe concentrations (1.8 mg L^{-1}) in the stream (unpublished data), which may lead to the dominance of instream processes in Km 175 as Fe interacts strongly with DOM (Gu et al., 1994; McKnight and Duren, 2004)(Gu et al., 1994; McKnight and Duren, 2004).

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

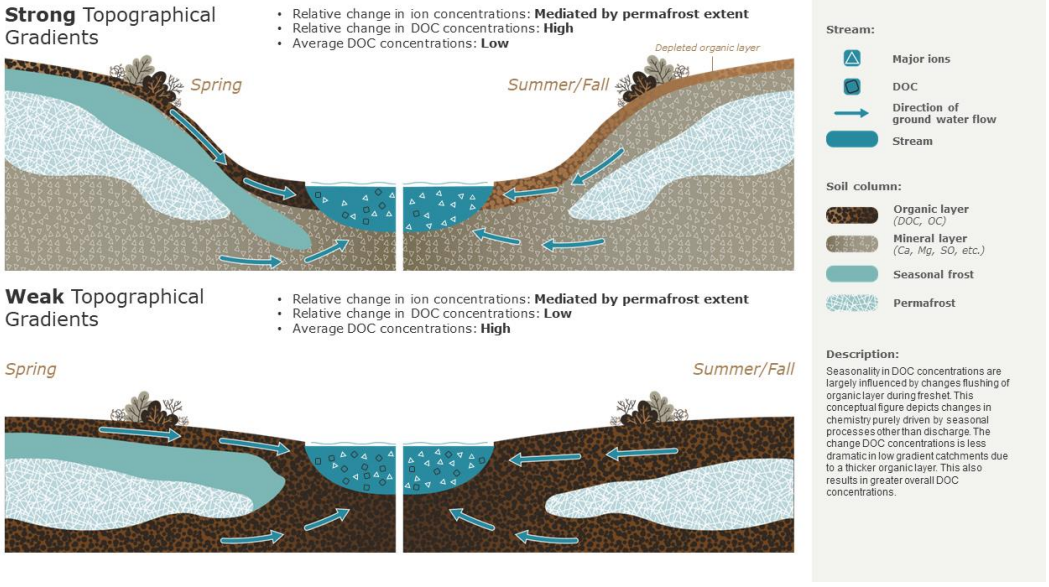


Figure 7. Conceptual diagram depicting the influence of topographical gradients on the relative seasonal change in DOC concentrations and the mean concentration of DOC after accounting for seasonal discharge.

4.2.2. Permafrost extent is important for major ion seasonality

Unlike DOC, permafrost extent and winter groundwater contributions do influence the seasonality of major ions, although the overall export is likely influenced by surficial geology. In general, catchments in WCRB had lower seasonality than TWO catchments for major ions. Km 44 and Km 175 were the only exception to this, as these sites generally had low seasonality for major ions. This may be explained by significant surface-groundwater connection throughout the ice-free season as neither of these catchments are underlain with continuous permafrost as outlined conceptually in Fig 8. Our results are similar to Webster et al. (2022) who observed seasonal increases in NO_3 in Alaska, which the authors attributed to thawing active layer in a high permafrost extent catchment but not in low permafrost catchments. The authors argued that dominance of groundwater was responsible for the lack of a seasonal trend in the low permafrost catchments. This supports our hypothesis for major ions, where the presence of deep groundwater contributions in low-permafrost catchments can dampen seasonality of CQ relationships for major ions. However, these results should be interpreted with caution as estimating permafrost extent in mountain headwater catchments is uncertain. The seasonality metrics

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

for Mg at BB have low predictive power; this is likely due to limited sampling during freshet and presence of some samples that were below the detection limit.

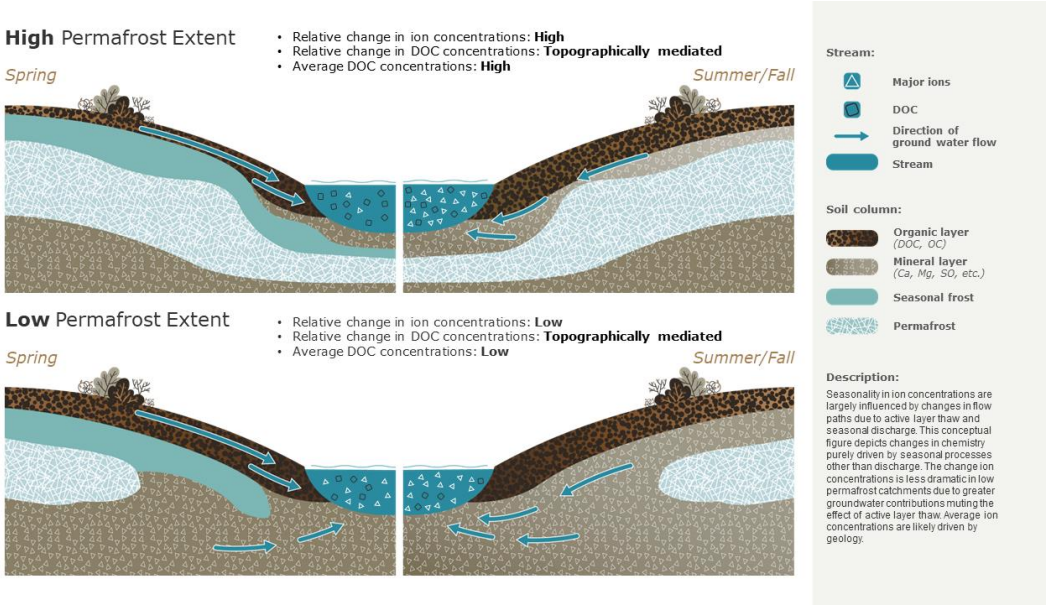


Figure 8. Conceptual diagram depicting the influence of permafrost extent on the relative seasonal change in ion concentrations and the mean concentration of DOC after accounting for seasonal discharge.

5. Conclusion and Future Directions

In this study, we assessed the role of catchment characteristics, seasonal active layer thaw, and depletion of solute stores in controlling solute export in permafrost underlain watersheds. We obtained new insights on chemical transport through hydrochemical data collected across multiple catchments and seasons, a task rarely undertaken across such a diverse range of remote, permafrost underlain environments. We utilized GAMs to assess changes in connectivity to solute sources after accounting for seasonally changing discharge. We largely confirmed our first hypothesis, where ion concentrations increased, and DOC concentrations decreased (irrespective of seasonality in discharge) after the start of freshet. However, we found evidence of differing drivers of seasonality between DOC and major ions; seasonality in DOC was primarily caused by flushing of OC from soils stores during freshet, while seasonality in major ions was driven by seasonal active layer thaw. For major ions, our second hypothesis

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

suggesting permafrost extent drove variability in chemical concentrations was found to be largely true. However, although permafrost extent was important for the average concentrations of DOC, topography was a more important driver in terms of seasonality as mountainous catchments with thin organic soils and high specific discharge lead to rapid flushing of limited soil OC stores.

GAMs can be a useful tool to assess the influence of non-linear terms. Long term trend analysis of solute concentrations is often confounded by long term trends in runoff. For example, long term increases in major ion concentrations may be driven by long term decreases in runoff. Using partial effect plots in a CQ framework within GAMs can allow for the assessment of long-term trends in chemistry after accounting for long term trends in flow. Water transit times may be an important driver of variability of stream chemistry as it can indicate contact time of water with mineral substrate. This would particularly be true in permafrost environments, where transit times of water can be highly seasonal. Future work should incorporate the influence of transit times on seasonality of stream chemistry in permafrost catchments.

Our results suggest climate change induced increases in active layer thickness and greater connectivity of subpermafrost, inter-permafrost, and suprapermafrost water will lead to elevated concentrations of weathering derived ions, reduced concentration of DOC and a decrease in seasonality of major ions in high latitude catchments. The role of permafrost extent on the seasonality of DOC concentrations remains unclear. This work highlights the need for long-term stream chemistry sampling across a biogeophysical range of high latitude watersheds. Greater sampling resolution could provide a means of quantifying the influence of secondary drivers (i.e. stream temperature) on stream chemistry in these environments. Currently, much of the literature assesses the role of catchment characteristics on solute exports, but limited work has been done on the drivers of seasonality in cold regions largely due to the lack of sampling in the shoulder seasons. This study is one of the few to assess the drivers of seasonality of stream chemistry in permafrost underlain catchments.

Data Availability Statement

The data used in this study is available in a Zenodo repository (DOI: 10.5281/zenodo.13621953; Grewal et al., 2024).

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Author Contributions

AG, SKC, and EMN conceptualized the study and reviewed/edited the manuscript. AG and EMN collected and curated the data. AG developed the methodology, conducted the analysis, made figures, and wrote the original manuscript draft. SKC was the principal investigator and acquired funding for the project.

Conflict of Interest

The authors declare that they have no conflict of interest.

Special Issue Statement

This article is part of the special issue “Northern Hydrology in Transition”. It is not associated with a conference.

Acknowledgments

We would like to thank David Barrett, Tyler de Jong, Fiona Chapman, Joseph Desmarais, Sean Leipe, Lauren Bourke, Aliana Fristensky, Anna Grunsky, Andras Szeitz, and Calvin Newbery for field assistance. We would like to thank Global Water Futures, and National Science and Engineering Council of Canada (RGPNS-2020-06722) for providing financial support for this project. We acknowledge the continued support of the Water Resources Branch, Government of Yukon, for the operation of Wolf Creek Research Basin.

References

Benettin, P., Bailey, S. W., Campbell, J. L., Green, M. B., Rinaldo, A., Likens, G. E., McGuire, K. J., and Botter, G.: Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA, Water Resour Res, 51, 9256–9272, https://doi.org/10.1002/2015WR017552, 2015.

Biagi, K. M., Ross, C. A., Oswald, C. J., Sorichetti, R. J., Thomas, J. L., and Wellen, C. C.: Novel predictors related to hysteresis and baseflow improve predictions of watershed nutrient loads: An example from Ontario’s lower Great Lakes basin, Science of the Total Environment, 826, 154023, https://doi.org/10.1016/j.scitotenv.2022.154023, 2022.

Bonnaventure, P. P., Lewkowicz, A. G., Kremer, M., and Sawada, M. C.: A Permafrost Probability Model for the Southern Yukon and Northern British Columbia, Canada, Permafr Periglac Process, 23, 52–68, https://doi.org/10.1002/ppp.1733, 2012.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

584 Boyer, E. W., Hornberger, G. M., Bencala, K. E., and McKnight, D. M.: Response characteristics of DOC
585 flushing in an alpine catchment, Hydrol Process, 11, 1635–1647, https://doi.org/10.1002/(SICI)1099-
586 1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H, 1997.

587 Carey, S. K.: Dissolved organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment,
588 Permafr Periglac Process, 14, 161–171, https://doi.org/10.1002/ppp.444, 2003.

589 Carey, S. K. and Woo, M.: Slope runoff processes and flow generation in a subarctic, subalpine
590 catchment, J Hydrol (Amst), 253, 110–129, https://doi.org/10.1016/S0022-1694(01)00478-4, 2001.

591 Carey, S. K., Boucher, J. L., and Duarte, C. M.: Inferring groundwater contributions and pathways to
592 streamflow during snowmelt over multiple years in a discontinuous permafrost subarctic environment
593 (Yukon, Canada), Hydrogeol J, 21, 67–77, https://doi.org/10.1007/s10040-012-0920-9, 2013.

594 Cohen, J., Screen, J. A., Furtado, J. C., Barlow, M., Whittleston, D., Coumou, D., Francis, J., Dethloff, K.,
595 Entekhabi, D., Overland, J., and Jones, J.: Recent Arctic amplification and extreme mid-latitude weather,
596 Nat Geosci, 7, 627–637, https://doi.org/10.1038/ngeo2234, 2014.

597 Colpron, M.: The Yukon Digital Bedrock Geology compilation, in: Yukon Exploration and Geology 2021,
598 K.E. MacFarlane (ed.), Yukon Geological Survey, 143–159, 2022.

599 Creed, I. F., McKnight, D. M., Pellerin, B. A., Green, M. B., Bergamaschi, B. A., Aiken, G. R., Burns, D. A.,
600 Findlay, S. E. G., Shanley, J. B., Striegl, R. G., Aulenbach, B. T., Clow, D. W., Laudon, H., McGlynn, B. L.,
601 McGuire, K. J., Smith, R. A., and Stackpoole, S. M.: The river as a chemostat: fresh perspectives on
602 dissolved organic matter flowing down the river continuum, Canadian Journal of Fisheries and Aquatic
603 Sciences, 72, 1272–1285, https://doi.org/10.1139/cjfas-2014-0400, 2015.

604 Environmental Protection Agency (EPA): Method 415.1: Organic Carbon, Total (Combustion Or
605 Oxidation), 1974.

606 Fork, M. L., Sponseller, R. A., and Laudon, H.: Changing Source-Transport Dynamics Drive Differential
607 Browning Trends in a Boreal Stream Network, Water Resour Res, 56,
608 https://doi.org/10.1029/2019WR026336, 2020.

609 Frey, K. E. and McClelland, J. W.: Impacts of permafrost degradation on arctic river biogeochemistry,
610 Hydrol Process, 23, 169–182, https://doi.org/10.1002/hyp.7196, 2009.

611 Frey, K. E. and Smith, L. C.: Amplified carbon release from vast West Siberian peatlands by 2100, Geophys
612 Res Lett, 32, 1–4, https://doi.org/10.1029/2004GL022025, 2005.

613 Godsey, S. E., Kirchner, J. W., and Clow, D. W.: Concentration-discharge relationships reflect chemostatic
614 characteristics of US catchments, Hydrol Process, 23, 1844–1864, https://doi.org/10.1002/hyp.7315,
615 2009.

616 Grewal, A., Nicholls, E. M., and Carey, S. K.: The role of catchment characteristics, discharge, and active
617 layer thaw on seasonal stream chemistry across ten permafrost catchments (Version 1) [Data set],
618 https://doi.org/10.5281/zenodo.13621953, 2024.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Gu, B., Schmitt, J., Chen, Z., Liang, L., and McCarthy, J. F.: Adsorption and Desorption of Natural Organic Matter on Iron Oxide: Mechanisms and Models, Environ Sci Technol, 28, 38–46, https://doi.org/10.1021/es00050a007, 1994.

Hall, F. R.: Dissolved Solids-Discharge Relationships: 1. Mixing Models, Water Resour Res, 6, 845–850, https://doi.org/10.1029/WR006i003p00845, 1970.

Hastie, T. and Tibshirani, R.: Generalized Additive Models, Statistical Science, 1, 409–435, https://doi.org/10.1214/ss/1177013604, 1986.

Hornberger, G. M., Bencala, K. E., and McKnight, D. M.: Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, Biogeochemistry, 25, 147–165, https://doi.org/10.1007/BF00024390, 1994.

Koch, J. C., Dornblaser, M. M., and Striegl, R. G.: Storm-Scale and Seasonal Dynamics of Carbon Export From a Nested Subarctic Watershed Underlain by Permafrost, J Geophys Res Biogeosci, 126, https://doi.org/10.1029/2021JG006268, 2021.

Lehn, G. O., Jacobson, A. D., Douglas, T. A., McClelland, J. W., Barker, A. J., and Khosh, M. S.: Constraining seasonal active layer dynamics and chemical weathering reactions occurring in North Slope Alaskan watersheds with major ion and isotope (δ34SSO4, δ13CDIC, 87Sr/86Sr, δ44/40Ca, and δ44/42Ca) measurements, Geochim Cosmochim Acta, 217, 399–420, https://doi.org/10.1016/j.gca.2017.07.042, 2017.

Leutner, B., Horning, N., and Schwalb-Willmann, J.: RStoolbox: Tools for Remote Sensing Data Analysis, 2023.

Lewkowicz, A. G. and Ednie, M.: Probability mapping of mountain permafrost using the BTS method, Wolf Creek, Yukon Territory, Canada, Permafr Periglac Process, 15, 67–80, https://doi.org/10.1002/ppp.480, 2004.

Li, L., Knapp, J. L. A., Lintern, A., Ng, G. H. C., Perdrial, J., Sullivan, P. L., and Zhi, W.: River water quality shaped by land–river connectivity in a changing climate, Nat Clim Chang, 14, https://doi.org/10.1038/s41558-023-01923-x, 2024.

MacLean, R., Oswood, M. W., Irons, J. G., and McDowell, W. H.: The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan (U.S.A.) taiga, Biogeochemistry, 47, 239–267, https://doi.org/10.1007/BF00992909, 1999.

McKenzie, J. M., Kurylyk, B. L., Walvoord, M. A., Bense, V. F., Fortier, D., Spence, C., and Grenier, C.: Invited perspective: What lies beneath a changing arctic?, Cryosphere, 15, 479–484, https://doi.org/10.5194/tc-15-479-2021, 2021.

McKnight, D. M. and Duren, S. M.: Biogeochemical processes controlling midday ferrous iron maxima in stream waters affected by acid rock drainage, Applied Geochemistry, 19, 1075–1084, https://doi.org/10.1016/j.apgeochem.2004.01.007, 2004.

McNamara, J. P., Kane, D. L., and Hinzman, L. D.: An analysis of streamflow hydrology in the Kuparuk River Basin, Arctic Alaska: A nested watershed approach, J Hydrol (Amst), 206, 39–57, https://doi.org/10.1016/S0022-1694(98)00083-3, 1998.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

Musolff, A., Schmidt, C., Selle, B., and Fleckenstein, J. H.: Catchment controls on solute export, Adv Water Resour, 86, 133–146, https://doi.org/10.1016/j.advwatres.2015.09.026, 2015.

Obu, J., Westermann, S., Bartsch, A., Berdnikov, N., Christiansen, H. H., Dashtseren, A., Delaloye, R., Elberling, B., Etzelmüller, B., Kholodov, A., Khomutov, A., Kääb, A., Leibman, M. O., Lewkowicz, A. G., Panda, S. K., Romanovsky, V., Way, R. G., Westergaard-Nielsen, A., Wu, T., Yamkhin, J., and Zou, D.: Northern Hemisphere permafrost map based on TTOP modelling for 2000–2016 at 1 km2 scale, Earth Sci Rev, 193, 299–316, https://doi.org/10.1016/j.earscirev.2019.04.023, 2019.

Petrone, K. C., Jones, J. B., Hinzman, L. D., and Boone, R. D.: Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost, J Geophys Res Biogeosci, 111, n/a-n/a, https://doi.org/10.1029/2005JG000055, 2006.

Quinton, W. L. and Marsh, P.: A conceptual framework for runoff generation in a permafrost environment, Hydrol Process, 13, 2563–2581, https://doi.org/10.1002/(SICI)1099-1085(199911)13:16<2563::AID-HYP942>3.0.CO;2-D, 1999.

Ran, Y., Li, X., Cheng, G., Che, J., Aalto, J., Karjalainen, O., Hjort, J., Luoto, M., Jin, H., Obu, J., Hori, M., Yu, Q., and Chang, X.: New high-resolution estimates of the permafrost thermal state and hydrothermal conditions over the Northern Hemisphere, Earth Syst Sci Data, 14, 865–884, https://doi.org/10.5194/essd-14-865-2022, 2022.

Rasouli, K., Pomeroy, J. W., Janowicz, J. R., Carey, S. K., and Williams, T. J.: Hydrological sensitivity of a northern mountain basin to climate change, Hydrol Process, 28, 4191–4208, https://doi.org/10.1002/hyp.10244, 2014.

Rasouli, K., Pomeroy, J. W., Janowicz, J. R., Williams, T. J., and Carey, S. K.: A long-term hydrometeorological dataset (1993–2014) of a northern mountain basin: Wolf Creek Research Basin, Yukon Territory, Canada, Earth Syst Sci Data, 11, 89–100, https://doi.org/10.5194/essd-11-89-2019, 2019.

Ross, C. A., Moslenko, L. L., Biagi, K. M., Oswald, C. J., Wellen, C. C., Thomas, J. L., Raby, M., and Sorichetti, R. J.: Total and dissolved phosphorus losses from agricultural headwater streams during extreme runoff events, Science of the Total Environment, 848, 157736, https://doi.org/10.1016/j.scitotenv.2022.157736, 2022.

Shatilla, N. and Carey, S.: Assessing inter-annual and seasonal patterns of DOC and DOM quality across a complex alpine watershed underlain by discontinuous permafrost in Yukon, Canada, Hydrol Earth Syst Sci, 23, 3571–3591, https://doi.org/10.5194/hess-23-3571-2019, 2019.

Shatilla, N. J., Tang, W., and Carey, S. K.: Multi-year high-frequency sampling provides new runoff and biogeochemical insights in a discontinuous permafrost watershed, Hydrol Process, 37, https://doi.org/10.1002/hyp.14898, 2023.

Shogren, A. J., Zarnetske, J. P., Abbott, B. W., Iannucci, F., Medvedeff, A., Cairns, S., Duda, M. J., and Bowden, W. B.: Arctic concentration–discharge relationships for dissolved organic carbon and nitrate vary with landscape and season, Limnol Oceanogr, 66, S197–S215, https://doi.org/10.1002/lno.11682, 2021.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

695 Skierszkan, E. K., Carey, S. K., Jackson, S. I., Fellwock, M., Fraser, C., and Lindsay, M. B. J.: Seasonal
696 controls on stream metal(loid) signatures in mountainous discontinuous permafrost, Science of the Total
697 Environment, 908, 167999, https://doi.org/10.1016/j.scitotenv.2023.167999, 2024.

698 Stewart, B., Shanley, J. B., Kirchner, J. W., Norris, D., Adler, T., Bristol, C., Harpold, A. A., Perdrial, J. N.,
699 Rizzo, D. M., Sterle, G., Underwood, K. L., Wen, H., and Li, L.: Streams as Mirrors: Reading Subsurface
700 Water Chemistry From Stream Chemistry, Water Resour Res, 58, 1–20,
701 https://doi.org/10.1029/2021WR029931, 2022.

702 Tank, S. E., Striegl, R. G., McClelland, J. W., and Kokelj, S. V.: Multi-decadal increases in dissolved organic
703 carbon and alkalinity flux from the Mackenzie drainage basin to the Arctic Ocean, Environmental
704 Research Letters, 11, 054015, https://doi.org/10.1088/1748-9326/11/5/054015, 2016.

705 Tank, S. E., McClelland, J. W., Spencer, R. G. M., Shiklomanov, A. I., Suslova, A., Moatar, F., Amon, R. M.
706 W., Cooper, L. W., Elias, G., Gordeev, V. V., Guay, C., Gurtovaya, T. Y., Kosmenko, L. S., Mutter, E. A.,
707 Peterson, B. J., Peucker-Ehrenbrink, B., Raymond, P. A., Schuster, P. F., Scott, L., Staples, R., Striegl, R. G.,
708 Tretiakov, M., Zhulidov, A. V., Zimov, N., Zimov, S., and Holmes, R. M.: Recent trends in the chemistry of
709 major northern rivers signal widespread Arctic change, Nat Geosci, 16, 789–796,
710 https://doi.org/10.1038/s41561-023-01247-7, 2023.

711 Thomas, R. D. and Rampton, V. N.: Surficial Geology and Geomorphology, Engineer Creek, Yukon
712 Territory, https://doi.org/10.4095/119068, 1982a.

713 Thomas, R. D. and Rampton, V. N.: Surficial Geology and Geomorphology, North Klondike River, Yukon
714 Territory, https://doi.org/10.4095/119397, 1982b.

715 Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., and Rao, P. S. C.: Relative dominance of
716 hydrologic versus biogeochemical factors on solute export across impact gradients, Water Resour Res,
717 47, 1–20, https://doi.org/10.1029/2010WR009605, 2011.

718 Townsend-Small, A., McClelland, J. W., Max Holmes, R., and Peterson, B. J.: Seasonal and hydrologic
719 drivers of dissolved organic matter and nutrients in the upper Kuparuk River, Alaskan Arctic,
720 Biogeochemistry, 103, 109–124, https://doi.org/10.1007/s10533-010-9451-4, 2011.

721 Walvoord, M. A. and Kurylyk, B. L.: Hydrologic Impacts of Thawing Permafrost-A Review, Vadose Zone
722 Journal, 15, vzj2016.01.0010, https://doi.org/10.2136/vzj2016.01.0010, 2016.

723 Webster, A. J., Douglas, T. A., Regier, P., Scheuerell, M. D., and Harms, T. K.: Multi-Scale Temporal Patterns
724 in Stream Biogeochemistry Indicate Linked Permafrost and Ecological Dynamics of Boreal Catchments,
725 Ecosystems, 25, 1189–1206, https://doi.org/10.1007/s10021-021-00709-6, 2022.

726 Woo, M.: Permafrost hydrology in North America, Atmosphere-Ocean, 24, 201–234,
727 https://doi.org/10.1080/07055900.1986.9649248, 1986.

728 Woo, M. and Steer, P.: Slope hydrology as influenced by thawing of the active layer, Resolute, N.W.T., Can
729 J Earth Sci, 20, 978–986, https://doi.org/10.1139/e83-087, 1983.

730 Woo, M. K. and Winter, T. C.: The role of permafrost and seasonal frost in the hydrology of northern
731 wetlands in North America, J Hydrol (Amst), 141, 5–31, https://doi.org/10.1016/0022-1694(93)90043-9,
732 1993.

https://doi.org/10.5194/egusphere-2024-2645
Preprint. Discussion started: 18 September 2024

733 Woo, M.-K. and Steer, P.: Runoff Regime of Slopes in Continuous Permafrost Areas, Canadian Water
734 Resources Journal, 11, 58–68, https://doi.org/10.4296/cwrj1101058, 1986.

735 Wood, S. N.: Mixed GAM Computation Vehicle with Automatic Smoothness Estimation, 2023.

736 Wymore, A. S., Larsen, W., Kincaid, D. W., Underwood, K. L., Fazekas, H. M., McDowell, W. H., Murray, D.
737 S., Shogren, A. J., Speir, S. L., and Webster, A. J.: Revisiting the Origins of the Power-Law Analysis for the
738 Assessment of Concentration-Discharge Relationships, Water Resour Res, 59,
739 https://doi.org/10.1029/2023WR034910, 2023.

740 Surficial Geology dataset: https://data.geology.gov.yk.ca/Compilation/33, last access: 5 January 2024.

741 Zhi, W. and Li, L.: The Shallow and Deep Hypothesis: Subsurface Vertical Chemical Contrasts Shape
742 Nitrate Export Patterns from Different Land Uses, Environ Sci Technol, 54, 11915–11928,
743 https://doi.org/10.1021/acs.est.0c01340, 2020.

744 Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., and Williams, K. H.: Distinct Source Water
745 Chemistry Shapes Contrasting Concentration-Discharge Patterns, Water Resour Res, 55, 4233–4251,
746 https://doi.org/10.1029/2018WR024257, 2019.

747