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

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11 Keywords: ~~Watershed Hydrology~~Stream Chemistry Seasonality, Concentration-Discharge, Permafrost
12 Hydrology, ~~Water Quality~~Active layer thaw, Permafrost, Solute Export,

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17 Abstract

18 High latitude catchments are rapidly warming, leading to altered precipitation regimes, widespread
19 permafrost degradation, and ~~observed~~ shifts in stream chemistry ~~for~~ across major arctic rivers. ~~At~~ For
20 headwater ~~scales, stream catchments, seasonal deepening of flow paths due to active layer thaw and~~
21 ~~declining~~ discharge ~~and post snowmelt drive variability in stream~~ chemistry ~~are seasonally variable, and~~
22 ~~during the open water period. In North American permafrost regions, activation of deeper mineral layers~~
23 ~~as the season progresses typically increases major ion concentrations while decreasing dissolved organic~~
24 ~~carbon (DOC) concentrations. Despite decades of research on seasonality in stream chemistry within~~
25 ~~permafrost regions,~~ the relative influence of ~~catchment characteristics, climate~~ active layer thaw and
26 discharge remains unresolved. Additionally, the role of permafrost extent and active layer thaw on
27 ~~this~~ topography in driving seasonality ~~has been~~ of these solutes is poorly ~~addressed~~ constrained. To
28 ~~provide new insight into mechanisms driving changes in streamflow chemistry within permafrost~~
29 ~~watersheds~~ address these knowledge gaps, we measured discharge and sampled major ion and dissolved
30 organic carbon (DOC) concentrations across ten permafrost catchments in Yukon Territory, Canada. We
31 ~~incorporated~~ analyzed concentration-discharge relationships ~~within~~ using generalized additive models to
32 resolve the distinct influence of discharge and seasonal active layer thaw on stream chemistry, and to
33 identify the role of watershed characteristics on the magnitude and seasonality of solute concentrations.
34 After accounting for seasonal variations in discharge, ~~results indicate~~ we found both major ions and DOC
35 were highly seasonal across all catchments, with DOC declining and major ion ~~concentration~~
36 ~~concentrations~~ increasing post-freshet. Seasonal variability in major ion concentrations ~~were~~ was
37 primarily driven by active layer thaw, whereas DOC seasonality was strongly ~~controlled~~ influenced by
38 flushing of soil organic carbon during freshet. While average major ion concentrations were geologically
39 mediated, greater permafrost extent led to enhanced seasonality in ~~major ion~~ concentrations.
40 Catchments with strong topographical gradients and thinner organic soils had higher specific discharge,
41 and lower DOC concentrations but greater relative seasonality. Our results highlight the important role
42 catchment characteristics play ~~on~~ in shaping ~~both~~ the seasonal variations and magnitude of solute
43 concentrations in permafrost-~~underlain~~ watersheds.

44 1. Introduction

45 High latitude catchments are ~~experiencing~~undergoing rapid warming due to polar amplification (Cohen
46 ~~et al., 2014)~~, ~~and~~which is leading to marked shifts in hydrological and biogeochemical cycling that are
47 ~~highly sensitive as~~primarily attributed to thawing permafrost and altered precipitation regimes ~~strongly~~
48 ~~affect their hydrological and biogeochemical cycles~~ (McKenzie et al., 2021; Walvoord and Kurylyk, 2016).
49 ~~Frozen ground and permafrost act as~~Permafrost acts as an impeding ~~layers~~layer to water movement,
50 restricting flow and separating supra, intra, and sub-permafrost aquifers (McKenzie et al., 2021; Woo,
51 1986), ~~1980~~. ~~Where present, permafrost enhances runoff by restricting deep percolation and~~
52 ~~encouraging flow through more hydraulically conductive near surface pathways (Carey and Woo, 2001;~~
53 ~~Quinton and Marsh, 1999; Woo and Steer, 1983)~~. Permafrost degradation, which includes deepening of
54 the seasonal thawed zone (termed the active layer) and wholesale loss, ~~also~~influences stream chemistry
55 by lengthening and deepening flow pathways; facilitating greater contact with mineral surfaces (Frey and
56 McClelland, 2009; Walvoord and Kurylyk, 2016). ~~Dissolved solutes are~~This increased contact is expected
57 to increase ~~due to greater contact with mineral surfaces as flow pathways lengthen. Vast stores of frozen~~
58 ~~organic material are thawing, yet~~weathering-associated solute export, although changes in dissolved
59 organic carbon (DOC) ~~concentration projections are~~export remains uncertain due to potential
60 ~~increased~~increases adsorption and in-stream ~~processes~~processing (Frey and McClelland, 2009; Tank et
61 al., 2023). Studies ~~from~~of large arctic rivers ~~show increase~~report increased exports of ~~weathering~~
62 ~~products such as Ca, Mg and DOC~~organic carbon (Tank et al., 2016), yet results ~~are varied~~vary across
63 circumpolar regions (Tank et al., 2023), and long-term studies are limited to extremely large rivers that
64 cross multiple ecozones and permafrost extent, confounding interpretation.

65
66 ~~Active~~Seasonal active layer dynamics ~~along with seasonal precipitation (phase and magnitude) play a~~
67 ~~critical role in~~catchment wetness strongly influence runoff and solute export in permafrost regions
68 (Carey, 2003; Carey and Woo, 2001; MacLean et al., 1999; processes (McNamara et al., 1998; Woo and
69 Winter, 1993). During spring, large volumes of meltwater infiltrate ~~the soil yet are restricted to near~~
70 ~~surface layers that are often~~organic, exporting large volumes of water-rich soils and activate near
71 surface and preferential flow pathways that are rich with dissolved organic matter (DOM); (Carey, 2003;
72 MacLean et al., 1999; Shatilla et al., 2023; Woo and Steer, 1986). ~~As the frost front descends, mineral~~
73 ~~layers thaw and catchment storage increases resulting in greater concentrations of weathering solutes~~

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74 and reduced DOM (Carey, 2003; Carey et al., 2013; Petrone et al., 2006). Concentrations of weathering
75 derived solutes generally increase from spring to fall, whereas DOM concentrations typically decrease
76 (Carey, 2003; Frey and Smith, 2005; MacLean et al., 1999). The position of the water table with respect
77 to different soil horizons in the active layer has largely been used to explain seasonal patterns of
78 dissolved solutes in the permafrost literature. Permafrost extent is also identified as a key driver of
79 hydrological and biogeochemical processes. For example, Petrone et al. (2006) and Webster et al. (2022)
80 attributed lower yield of NO_3^- and higher yield of fluorescent dissolved organic matter (fDOM) to greater
81 permafrost extent in Alaska. Webster et al. (2022) found evidence of greater seasonality of NO_3^- in high
82 permafrost catchments compared to catchments with lower permafrost extent.

83 . At this time Changes in hydrological connectivity across the landscape can alter streamflow chemistry
84 and solute export (Creed et al., 2015; Li et al., 2024; Zhi et al., 2019). During wet periods, water tables
85 are near the surface in highly conductive organic soils and areas and distal areas are connected to the
86 stream can be connected. During drier conditions, flow is primarily through deeper mineral pathways
87 and landscape connectivity, mobilizing solutes from shallow soil layers across large areas when flows are
88 typically their greatest. As the active layer thaws and water in storage declines (Stewart et al., 2022; Zhi
89 et al., 2019). The presence and disposition of permafrost strongly affects the interaction between solute
90 sources, water following snowmelt, flow pathways and descend into the underlying mineral soils and
91 distal areas become disconnected from the stream network resulting in greater concentrations of
92 weathering solutes and reductions in DOM concentrations, reflecting longer and deeper flow pathways
93 prior to freezeback (Carey, 2003; MacLean et al., 1999). Flow pathways continue to shift in response to
94 additional summer precipitation, resulting in short term variability in stream chemistry (Koch et al.,
95 2021; Shatilla. Direct observations of these interactions are rare in northern watersheds as permafrost
96 extent is often difficult to assess and logistics are typically challenging. Concentration-Discharge (CQ)
97 relations have increasingly been used to characterize flow-solute coupling to infer catchment processes
98 (Godsey et al., 2009; Hall, 1970; Wymore et al., 2023); Stewart et al., 2022; Zhi and Li, 2020). By
99 comparing the log-log slope between the two, it is possible to characterize whether a solute displays
100 flushing behaviour (positive slope) or dilution (negative slope). Other metrics such as $\text{CV}_c:\text{CV}_q$ ratios can
101 be used to determine whether a solute is chemostatic or chemodynamic even when there is no clear
102 directionality (Musolff et al., 2015; Thompson et al., 2011). Positive/negative slopes can indicate spatial
103 and vertical heterogeneity within a catchment, whereas slopes close to zero can indicate homogeneity in

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104 ~~vertical and spatial distribution of solute stores or dominance of instream biogeochemical processes~~
105 ~~(Creed et al., 2015).~~

106 ~~The degree of seasonality in stream chemistry is mediated by catchment characteristics such as~~
107 ~~permafrost extent and topography, where greater permafrost extent leads to higher yield of DOM and~~
108 ~~lower export of weathering associated ions (Petroni et al., 2006; Webster et al., 2022). Topographic~~
109 ~~gradients can also play an important role in driving DOC concentrations and export, as higher slopes~~
110 ~~result in thinner organic layer and faster travel times (Jantze et al., 2015; Lee et al., 2019). In cold~~
111 ~~mountain catchments, flushing of thin organic layers during snowmelt has shown to lead to high DOC~~
112 ~~concentrations, followed by a rapid decrease in concentrations post freshet (Boyer et al., 1997; Carey,~~
113 ~~2003).~~

114 ~~Active layer thaw and streamflowcatchment wetness~~ are highly seasonal in permafrost catchments,
115 making it difficult to ascertain the relative influence of each factor in driving seasonal solute dynamics.

116 ~~For example, major ion concentrations typically increase throughout the ice-free season. This seasonality~~
117 ~~can be driven by decreasing discharge, which can lower connectivity with the ion-poor shallow organic~~
118 ~~layer. However, thawing of active layer can also lead to greater water movement through the mineral~~
119 ~~layer, increasing stream ion concentrations. The potential influence of both discharge~~
120 ~~influence of both discharge (as a proxy for catchment wetness) and active layer dynamics on seasonal~~
121 ~~stream chemistry in cold regions are rarely disentangled. Shifts in Concentration-Discharge (CQ)~~
122 ~~relationships can be used to detect changes in solute-exportstream chemistry driven by processes other~~
123 ~~than discharge, such as changes in the internal structure of the catchment (i.e. ground freeze-thaw) or in~~
124 ~~the quantity/mobility of solute stores. For example, Fork et al. (2020) examined changes in residuals of~~
125 ~~water flux versus DOC to infer changes in supply in terrestrial pools of DOC. Biagi et al. (2022) and Ross~~
126 ~~et al. (2022) utilized generalized additive models (GAMs), which are flexible models that allow for the~~
127 ~~addition of spline terms to model non-linear behaviour, to quantify changes in CQ relationships over~~
128 ~~time in agricultural environments. CQ relationships are often highly seasonal in northern catchments,~~
129 ~~particularly between snowmelt and summer periods (MacLean et al., 1999; Shatilla et al., 2023).~~
130 ~~MacLean et al. (1999) compared CQ patterns between seasons in a permafrost underlain Alaskan~~
131 ~~catchment, however the authors classified each season and thus had to assume that the transition~~
132 ~~between seasons is a discrete phenomenon. At the event scale, Shogren et al. (2021) found both~~
133 ~~seasonality and landscape drivers to be important for the relations between DOC, NO₃⁻ and flow. The~~
134 ~~authors determined that landscape drivers were more important to CQ relationships than seasonality for~~

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135 ~~DOC and NO₃⁻ in Arctic catchments post freshet~~ Similar techniques have yet to be applied in permafrost
136 ~~environments to quantify the influence of seasonal drivers on CQ relationships.~~

137 In cold catchments, seasonal patterns of ground freeze-thaw, discharge, and solute stores have been
138 identified as drivers for variability in stream chemistry (Boyer et al., 1997; Carey, 2003; MacLean et al.,
139 1999; Petrone et al., 2006). However, the relative importance of each factor and how it is influenced by
140 permafrost extent and other catchment characteristics remains unresolved. To address this, we
141 characterize CQ relationships using discrete major ion and DOC data across ten permafrost influenced
142 catchments: in Yukon, Canada. We utilize GAMs with an additional spline Day Of Year (sDOY) term to the
143 traditional CQ approach ~~to test two~~ along with standard statistical tests to resolve three hypotheses:

144 1. As Seasonal active layer ~~thaws, thaw~~ activates deeper mineral-rich flowpaths, increasing major
145 ion concentrations ~~will increase for major ions~~ and ~~decrease for~~ decreasing DOC at all sites ~~(,~~
146 ~~irrespective of seasonal changes in discharge), due to~~ ,

147 1. ~~Permafrost extent is the dominant driver for the magnitude of seasonal ground thaw induced~~
148 ~~activation of deeper mineral rich flow paths.~~

149 2. Seasonal changes in concentrations for both major ions and DOC ~~will be the largest in~~
150 catchments, where seasonality is higher in catchments with greater permafrost extent
151 (irrespective of seasonality in discharge), ~~due to~~ greater ~~reduced stream~~ connectivity ~~of~~ with
152 ~~subpermafrost water to streams in catchments with~~ ,

153 2-3. Catchments with greater permafrost extent exhibit higher average DOC concentrations and
154 ~~lower permafrost extent~~ major ion concentrations.

155 Testing these hypotheses ~~will provide~~ provides new insights on the role of ~~catchment characteristics and~~
156 permafrost extent and topography on the seasonality of major ions and DOC export. ~~By disentangling~~
157 ~~different drivers of seasonal solute export in northern environments, we can make more informed~~
158 ~~predictions of stream biogeochemistry in a rapidly changing north.~~ As circumpolar regions warm at
159 unprecedented rates, these insights will contribute to a broader understanding of how climate driven
160 changes in precipitation and permafrost degradation will impact carbon cycling and other geochemical
161 processes.

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162 2. Data and Methods

163 2.1. Study Area

164 Our study consists of 10 catchments with areas ranging from ~5 Km² to ~170 km², all located in Yukon
165 Territory, Canada. Four of the catchments are part of the Wolf Creek Research Basin (WCRB; 60° 36' N,
166 134° 57' W; Figure 1), with ~~the largest being the~~ WCRB outlet (WCO) ~~being the largest.~~ Coal Lake (CL) is
167 a ~70 km² subcatchment of WCRB that ~~has contains~~ a ~ 1 Km² well mixed lake near ~~theits~~ outlet. Granger
168 Creek (GC) and Buckbrush Creek (BB) are alpine headwater subcatchments of WCRB ~~and have areas less,~~
169 ~~each smaller~~ than 10 Km². WCO and CL are underlain ~~withby~~ sporadic permafrost (Lewkowitz and Ednie,
170 2004) ~~-, while high-elevation subcatchments (BB and GC) are underlain by discontinuous permafrost~~
171 ~~(Lewkowitz and Ednie, 2004).~~

172 Low elevation areas of WCRB consist ~~of~~ primarily ~~of~~ coniferous forests, whereas high ~~elevation areas~~
173 ~~consist of elevations have~~ shrub taiga and alpine tundra vegetation. ~~High elevation subcatchments (BB,~~
174 ~~GC) are estimated to be underlain by discontinuous permafrost (Lewkowitz and Ednie, 2004) (Lewkowitz~~
175 ~~and Ednie, 2004) are typically colder and wetter than low elevation areas of WCRB.~~ Near surface geology
176 consists of mostly sedimentary rocks such as limestone, sandstone, and siltstone capped by a till mantle
177 and glaciofluvial/glaciolacustrine deposits (Rasouli et al., 2014). WCRB is part of the traditional territories
178 of the Ta'an Kwach'an Council, Kwanlin Dün, and Carcross/Tagish First Nations. More detailed description
179 of WCRB can be found in (Rasouli et al., 2014, 2019).

180 Climate normals (1991-2020) reported near WCRB at the Whitehorse airport ~~show indicate~~ the average
181 air temperature is 0.2 °C with an annual precipitation of 279.6 mm (164 mm as rain). Due to the large
182 elevation gradient at WCRB, average temperatures in the headwater regions are several degrees lower,
183 and precipitation volumes are larger, often exceeding 400 mm per year.

184
185 ~~Six of our study~~The other six catchments are part of the Tombstone Waters Observatory (TWO; Figure 2),
186 which is part of the traditional territory of Tr'ondëk Hwëch'in First Nation. ~~All~~Unlike WCRB, all TWO
187 catchments have areas less than 35 km². ~~All TWO catchments and~~ intersect the Dempster highway, a
188 critical north-south road. ~~All TWO catchments are named~~Named after the kilometer marker where the

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189 stream intersects the highway. ~~The six, these~~ catchments are ~~called~~ Km 44, Km 71, Km 99, Km 104, Km
190 175, and Km 185.

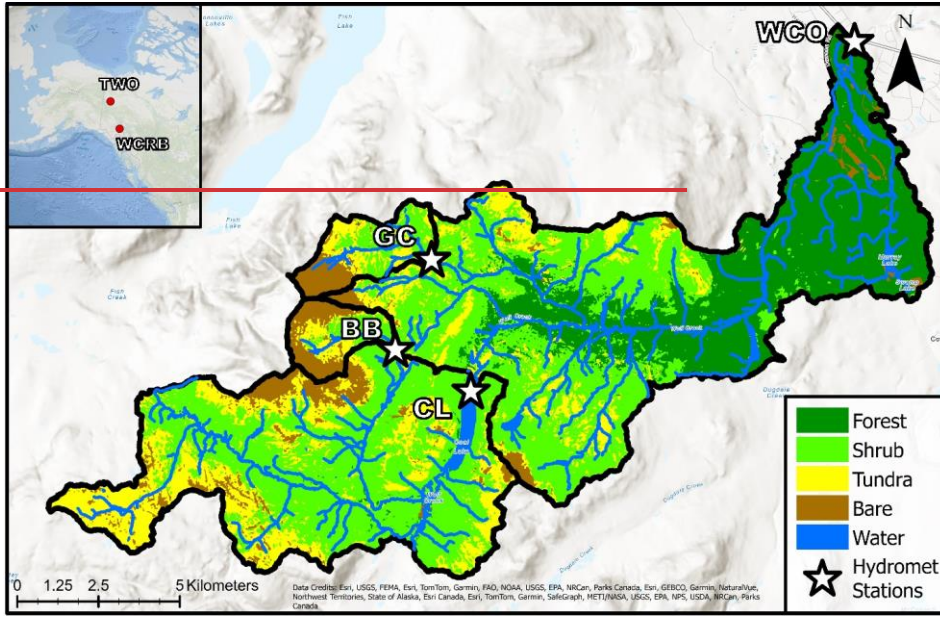
191 Km 44 (64° 19' N, 138° 31' W) and Km 71 (64° 31' N, 138° 8' W) are the most mountainous catchments,
192 with strong topographic gradients (Table 1). Km 44 primarily consists of bare earth, whereas Km 71 is
193 largely overlain with shrub cover. Km 99 and Km 104 (64° 41' N, 138° 28' W) are treeless catchments ~~and~~
194 ~~are~~ overlain by a thick layer of peat except for the high elevation areas with steep slopes. Km 104 is
195 largely flat, whereas Km 99 has mountainous uplands with more mineral soils. Km 175 (65° 12' N, 138°
196 26' W) and Km 185 (65° 16' N, 138° 18' W) are primarily covered by open coniferous forests and are a
197 part of the Ogilvie Mountain range.

198 Although there is some discrepancy between various permafrost mapping products ~~in regard to~~ ~~regarding~~
199 permafrost extent, the ~~general~~ consensus is that the WCRB sites have less permafrost than the TWO
200 sites (Bonnaventure et al., 2012; Obu et al., 2019; Ran et al., 2022; Surficial Geology dataset, 2024).
201 Surficial geology maps in TWO indicate that Km 71, Km 99, Km 104, and Km 185 are underlain with
202 continuous permafrost (>90%), whereas Km 44 is underlain with sporadic permafrost and Km 175 is
203 underlain with discontinuous permafrost (Thomas and Rampton, 1982a, b; Surficial Geology dataset,
204 2024). Climate normals (1991-2020) from Dawson City, the nearest Environment Canada weather station
205 to TWO, reports annual precipitation of 319 mm of which 208 mm is rainfall. The annual air temperature
206 is -3.8 °C. However, local climate can be quite variable amongst study catchments in TWO.

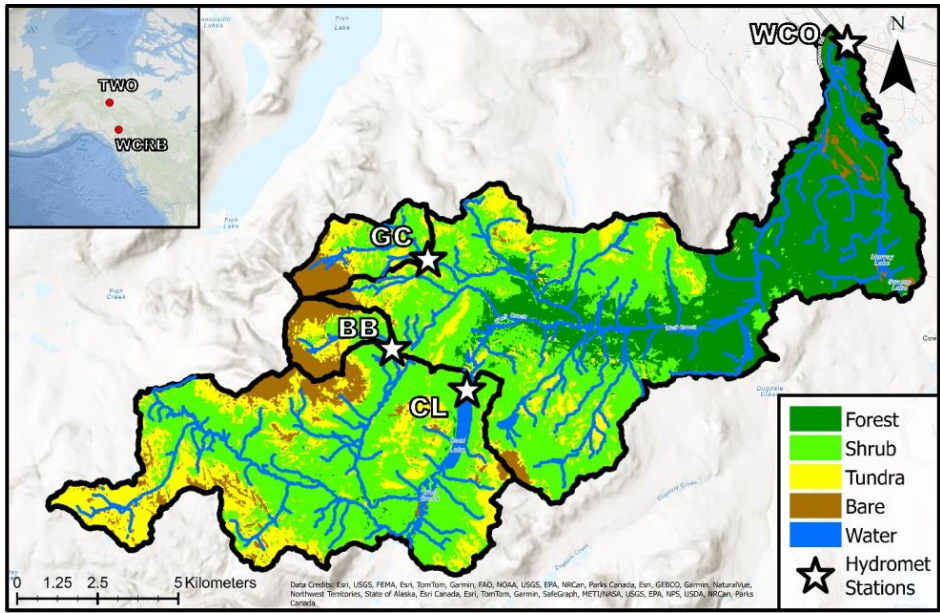
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208 Bedrock geology across TWO is highly diverse (Colpron, 2022). Km 44 is primarily underlain by thick-
209 bedded quartz arenite-, while Km 71 ~~is primarily underlain by two geological units; the first is described~~
210 ~~as features~~ dark ~~greygray~~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

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216 (Colpron, 2022).



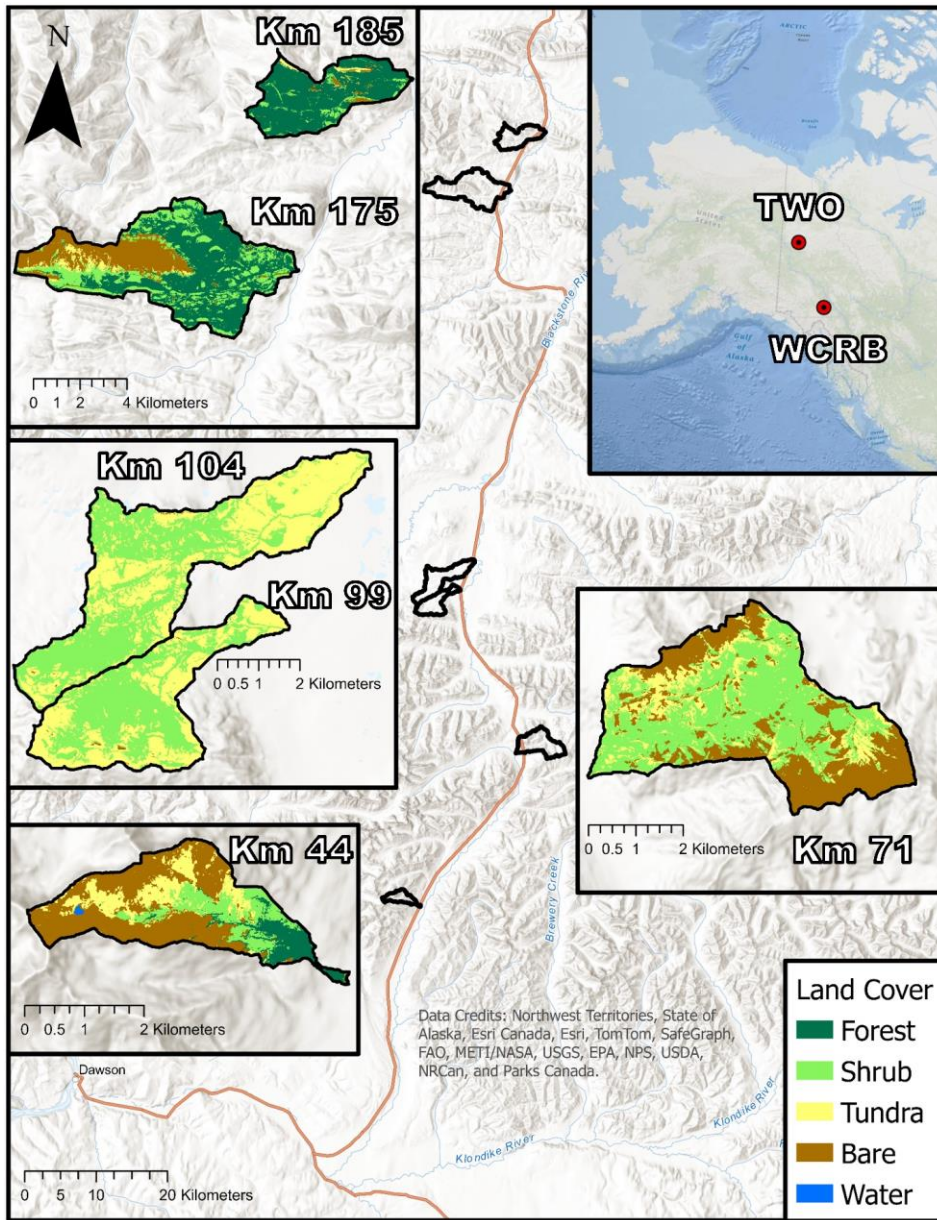
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219 Figure 1. ~~Study area map~~Map of ~~the~~ Wolf Creek Research Basin (~~Wolf Creek Outlet,~~ WCO)
220 ~~and~~highlighting its subcatchments ~~(~~Granger Creek, ~~_~~(GC, ~~)~~, Buckbrush Creek, ~~_~~(BB, ~~)~~, and Coal Lake, ~~_~~(CL, ~~)~~.



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

224 **2.2. Catchment characterization**

225 All TWO catchments were delineated using the high-resolution digital elevation models
 226 (DEMs): a 2-m resolution ArcticDEM product, whereas WCRB for TWO catchments were delineated
 227 using a 1-m DEM generated from a 2018 LiDAR scan. All for WCRB catchments. We calculated
 228 topographic parameters, including aspect, slope, and mean elevation were calculated using SAGA GIS.
 229 Land cover was determined through a supervised classification approach using a
 230 resampled DEM and Sentinel-2 multiband imagery with the RStoolbox package in R (Leutner et al.,
 231 2023). A summary of catchment characteristics is provided in Table 1.

232 Table 1. Table of catchment characteristics for WCRB and TWO catchments. Permafrost extent
 233 classification determined based on surficial geology dataset (Surficial Geology dataset, 2024).
 234 Topographical gradient classified using mean catchment slope.

Site	Area (km ²)	Forest (%)	Shrub (%)	Tundra (%)	Bare (%)	Water (%)	Elevation (m.a.s.l)	Slope (deg)	Median Specific Discharge (mm d ⁻¹)	Permafrost	Topographical Gradient
Km 44	5.5	12.4	17.2	18.5	51.6	0.3	1413.9	26.7	2.2	Sporadic	Strong
Km 71	16.5	0	48.4	17.7	33.9	0.00	1429.5	25.1	2.03	Continuous	Strong
Km 99	11	0	50.7	48.3	0.9	0.1	1401.5	10.9	0.57	Continuous	Medium
Km 104	17.8	0	50	49.6	0.4	0	1251.2	6.8	0.65	Continuous	Weak
Km 175	35.9	48.2	25.6	3.4	22.8	0	1003.2	19.2	0.81	Discontinuous	Medium
Km 185	14.7	84.3	8.8	3.5	3.4	0	916.2	18.9	0.92	Continuous	Medium
BB	5.4	0	29.7	23	46.8	0	1678	17.5	1.91	Discontinuous	Medium
GC	7.3	0	40.5	31.5	26.6	0	1618.7	11.1	1.51	Discontinuous	Medium
CL	67.8	0.4	55.4	29.7	11.8	2.7	1464	15.4	1.07	Sporadic	Medium
WCO	169.4	25.3	46	19.3	7.5	1.9	1303.7	12.3	0.64	Sporadic	Medium

237 **2.3.2.2. Stream chemistry**

238 ~~Grab~~We collected ~~grab~~ samples for major ions and ~~dissolved organic carbon (DOC were collected)~~ across
239 flow states ~~(in spring and summer) open water seasons~~ at all sites over multiple years. ~~Grab samples~~
240 ~~were collected~~ Sampling timelines varied by site: from 2017 to 2022 for WCO and GC. ~~We collected~~
241 ~~samples;~~ from 2018 to 2022 for Km 99, CL, and BB. ~~Only samples;~~ from 2021 ~~and to 2022 were collected~~
242 ~~for Km 104. Lastly, samples were collected;~~ and from 2019 to 2022 for all other sites. ~~Major ions~~
243 ~~summary of sample numbers for each solute~~ and ~~DOC~~ site is provided in Table S1.

244 ~~Grab~~ samples were filtered through a 0.45 µm syringe ~~filter filters~~ and ~~collected in 60 mL HDPE bottle~~
245 ~~(DOC samples stored in a 60 mL high-density polyethylene (HDPE) bottles (brown HDPE bottle). After~~
246 ~~collection, bottles for DOC samples). Samples~~ were kept cool and dark in the field ~~via ice packs using ice~~
247 ~~packs and were~~ immediately refrigerated at 4 °C ~~for storage upon return from the field~~. Specific
248 conductance (SpC) was ~~determined~~ ~~measured~~ in the field using a multiparameter sonde (YSI
249 ~~proPlus ProPlus~~ or ~~proDSS~~). ~~Only one year of samples were included for Km 104. The number of~~
250 ~~observations varied among sites and ranged from 24 (SpC at CL) to 92 (major ions at WCO). The number~~
251 ~~of samples for each solute and site can be found in Table S1. ProDSS).~~

252 ~~Major ions analysis was conducted via~~ Major ion concentrations were analyzed at the University of
253 ~~Waterloo Biogeochemistry Lab using~~ ion chromatography (DIONEX ICS 6000, IonPac AS18 and CS12A
254 analytical columns). ~~DOC concentrations were determined~~ at the University of ~~Waterloo~~
255 ~~Biogeochemistry Lab. All DOC analysis was conducted on~~ Alberta Biogeochemical Analytical Service
256 ~~Laboratory using a Shimadzu TOC-5000A Total Organic Carbon Analyzer by the Biogeochemical Analytical~~
257 ~~Service Laboratory in the University of Alberta. The following the~~ US Environmental Protection Agency
258 Test Method 415.1 ~~(EPA was followed (Environmental Protection Agency (EPA), 1974)).~~

259 ~~Out of all the ions measured, only calcium (Ca²⁺), magnesium (Mg²⁺), and Sulphate had~~
260 ~~concentrations sulfate (SO₄²⁻) consistently over the exceeded~~ detection limit, ~~limits~~ and were ~~included in the~~
261 ~~only major ions considered for analysis. Continuous SpC was measured using HOBO Conductivity loggers.~~
262 ~~The loggers were calibrated in post using the YSI ProDSS handheld multiparameter sonde. If~~ For samples
263 ~~had with~~ concentrations below ~~the~~ detection limit, ~~limits~~, we ~~assigned~~ a value of half of the detection
264 limit ~~was assigned to the sample~~. The number of observations varied across sites, ranging from 24
265 ~~samples for SpC at CL to 92 samples for major ions at WCO.~~

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2.4. Runoff

2.3. All Specific discharge

We instrumented all ten catchments ~~were instrumented~~ with Solinst levelloggers to determine continuous volumetric flow rate via stage-discharge relationships. ~~Flow measurements were generally conducted in association with a chemistry Whenever grab sample. If samples for stream chemistry were collected without a concurrent flow measurement measurements, we used estimated discharge determined from using the stage-discharge relationship relationships and continuous level loggers. The majority of the logger data. We then used to catchment area to determine specific discharge (mm d⁻¹) for easier comparison among catchments had very. Most catchments experienced low or zero discharge over the during winter. The study sites often had, and the presence of channel ice which made often introduced significant uncertainty in winter stage-discharge relationships highly uncertain and as such there. Consequently, winter flow data 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 We collected flow data is available from 2017- to 2022 at the WCRB sites, and from 2019- to 2022 at the TWO sites. Km 104 was instrumented in late 2021 and only had data available from 2022.~~

2.4. Coefficient of Variation ratios

We used ratios of the coefficient of variation of logged concentrations (CV_c) and of logged discharge (CV_Q) to quantify chemodynamic behaviour for solutes at all sites. CV ratios are a valuable tool to broadly compare chemodynamic behaviour across catchments and solutes, particularly in situations where discharge is not the primary driver of stream chemistry (Musolff et al., 2015; Thompson et al., 2011).

2.5. Concentration-Discharge relationships via Generalized Additive Models

The log-log slope of discharge and solute concentrations can be used to characterize whether a solute displays flushing behaviour (positive slope) or dilution (negative slope; Godsey et al., 2009; Hall, 1970). Positive/negative slopes can also indicate the presence of spatial and vertical heterogeneity of solute sources within a catchment (Stewart et al., 2022; Zhi and Li, 2020), whereas slopes close to zero can reflect homogeneity of solute sources, or dominance of instream biogeochemical processes (Creed et al., 2015).

294 Generalized Additive Models (GAMs) extend traditional linear models by ~~allowing the addition of terms~~
295 ~~that are a sum of incorporating~~ smooth functions ~~that capture non-linear relationships~~ (Hastie and
296 Tibshirani, 1986)~~(Hastie and Tibshirani, 1986)~~. ~~The additional terms can be linear or non-linear spline~~
297 ~~terms, and the flexibility of the spline terms can be set by the user to prevent overfitting.~~ In this study,
298 we ~~used~~ GAMs to ~~extend the enhance~~ traditional ~~concentration-discharge-CQ~~ models by adding day
299 of year (DOY) as a spline term ~~to the linear CQ model,~~ allowing seasonal variability to be explicitly
300 ~~modeled. The modified CQ equation is expressed as:~~

301
$$\log(C) = b * \log(Q) + \log(a) + sDOY \quad (1)$$

302 Where DOY is the day of year of the sample (sDOY indicates a spline fit), ~~sDOY~~ smooth term that accounts for
303 ~~seasonal variation,~~ Q is discharge, C is the concentration of the solute, and ~~b~~ and ~~a~~ are constant
304 coefficients. ~~The effect of the sDOY term on the model can be visualized via partial effect plots.~~ This
305 equation ~~can also be expressed in exponential form becomes:~~

306
$$C = e^{s(DOY)} 10^{sDOY} aQ^b \quad (2)$$

307 ~~The flexibility of the sDOY is user defined to prevent overfitting.~~ GAMs provide the effective degrees of
308 freedom (edf) for the spline term and ~~provide provides~~ p-values for both the sDOY term and the log-log
309 slope ~~(b).~~ The standard error ~~for the spline term can also be extracted from the model, however the~~
310 ~~standard error is not constant. In this case, standard error for the sDOY term may be higher of sDOY~~
311 ~~varies with day of year, often increasing~~ during freshet ~~than mid-summer~~ due to ~~high~~ interannual
312 ~~difference in discharge. The variability in its timing and magnitude. We calculated the mean standard~~
313 ~~error for sDOY can be used to determine the to estimate~~ average uncertainty in ~~the seasonal effects. To~~
314 ~~quantify~~ seasonality ~~of a model. The , we used the range of the sDOY fit can be used to quantify the~~
315 ~~degree of seasonality in a CQ model. This range is logarithmic, where a greater sDOY range means~~
316 ~~greater relative value of 1 represents a tenfold~~ change in ~~concentrations across seasons at a~~
317 ~~constant concentration after accounting for discharge variability.~~

318 We fit a GAMs model for all five reported solutes across all ten sites, ~~where each model was fit~~ using the
319 restricted maximum likelihood (REML) estimation. ~~The We used the~~ mgcv package in R ~~was used~~ for all
320 analyses involving GAMs (Wood, 2023). ~~GAMs provide a partial effect plot, which is the measure of the~~
321 ~~influence a particular term has on the model. We extracted the b term, the We reported the b term, R²~~

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322 value, sDOY range, p-values for both the b term and the sDOY-term, and the mean standard error of
323 sDOY standard deviation from for each model.

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

330 **2.6. Coefficient of Variation Ratios**

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

337 **2.6. Influence of topography and permafrost extent on stream chemistry**

338 Accurately measuring permafrost extent remains challenging, so we categorized it as a nominal variable
339 for statistical analyses: continuous, discontinuous, and sporadic permafrost. To evaluate the influence of
340 permafrost extent on solute seasonality (sDOY range), we performed ANOVA and Tukey tests. Given the
341 limited number of sites within each permafrost category, we combined the sDOY ranges for weathering-
342 associated solutes (Mg, Ca, SpC, and SO_4) to assess significant differences.

343 We did not group DOC with the other ions for ANOVA testing, as it exhibits flushing behavior. To increase
344 the sample size for statistical testing, we grouped sites with discontinuous and sporadic permafrost into
345 a single category. We then performed t-tests comparing sDOY ranges of DOC between continuous and
346 discontinuous/sporadic permafrost categories. Similarly, we used t-tests to examine the relationship
347 between permafrost extent and median concentrations for all solutes, applying the same grouping
348 strategy.

349 We conducted Pearson's correlation tests to evaluate the relationship between mean catchment slope
350 and both sDOY range and median solute concentrations for all five solutes.

351 3. Results

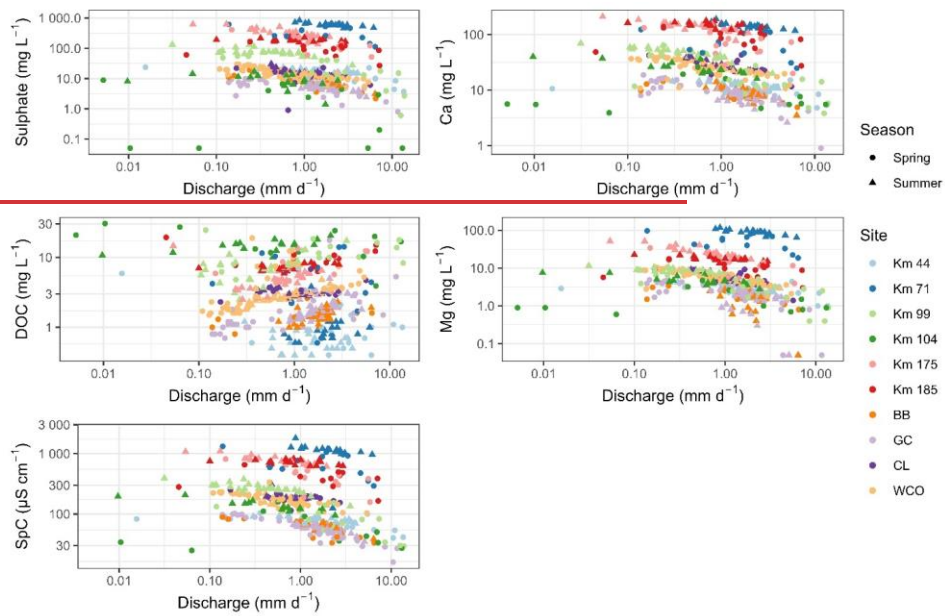
352 3.1. Discharge and ~~Concentrations Across Basins~~concentrations across catchments

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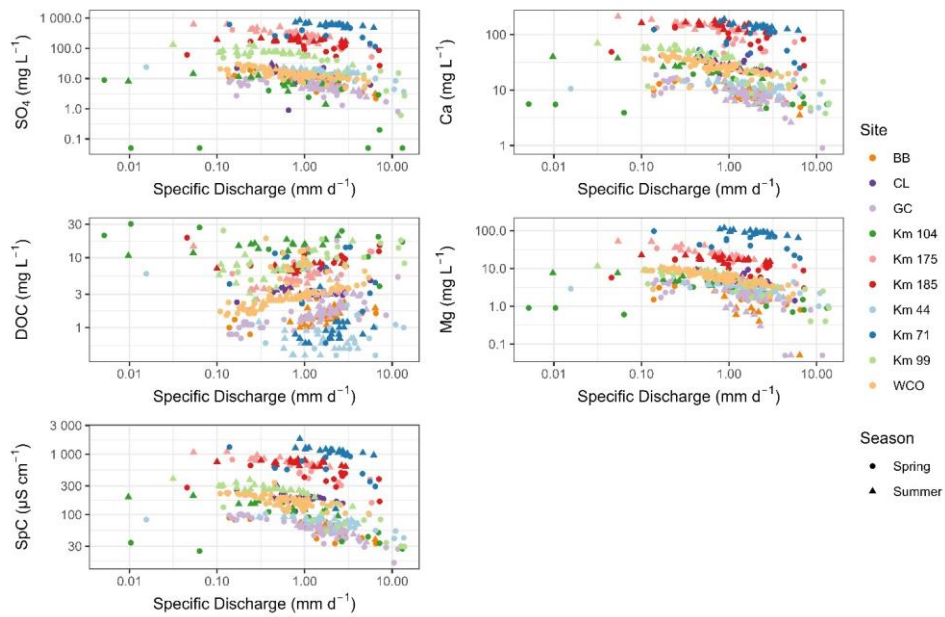
353 ~~We determined~~To account for sampling gaps at extreme low and high flows, we used the median of
354 specific discharge ~~estimates~~ of grab samples ~~from each site as opposed to the mean to account for~~
355 ~~missed sampling at extreme low and high flows at certain sites.~~ Median comparisons. The highest median
356 specific discharge was ~~the greatest~~observed at Km 44 and Km 71 (2.2 mm d⁻¹ and 2.03 mm d⁻¹
357 respectively). ~~The~~, while the lowest median specific discharge occurred at Km 99, WCO, and Km 104
358 (0.57 mm d⁻¹, 0.64 mm d⁻¹, and 0.65 mm d⁻¹, respectively). ~~Of note~~Notably, Km 44 and Km 71 were
359 ~~adjacent sites and had strongest~~characterized by steep topographical gradients ~~(most mountainous;~~
360 ~~Table 1),~~ whereas Km 99 and Km 104 ~~were adjacent and~~ had the ~~weakest~~lowest topographical gradients
361 ~~(least mountainous).~~

362 Solute concentrations were generally lower at all WCRB sites compared to TWO sites (Figure 3). Km 71
363 typically had the highest concentrations of major ions, particularly Mg (median concentration of 87.6 mg
364 L⁻¹). Km 175 and Km 185 (underlain by discontinuous and continuous permafrost respectively) also had
365 relatively high concentrations of major ions ~~aeross both~~for all seasons (Figure 4). Km 104 and Km 99 had
366 the highest ~~mean concentrations of DOC, with~~ median concentrations of DOC, 15.2 mg L⁻¹ and 8 mg L⁻¹
367 respectively. In contrast, the lowest DOC concentrations generally occurred at the WCRB sites and Km
368 44. Concentrations in spring were typically more variable than late season across sites, likely due to high
369 variability in discharge (Figure 2-4). Detailed time series information on when samples were collected
370 are represented in Figure S1.

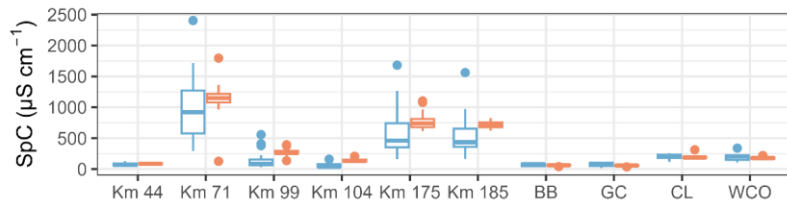
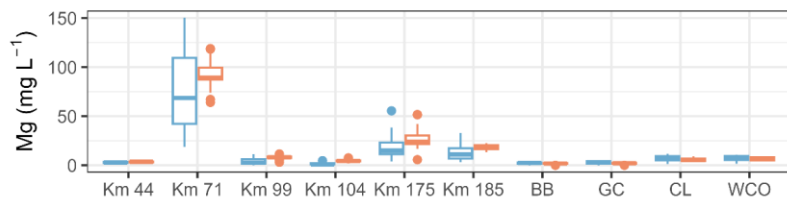
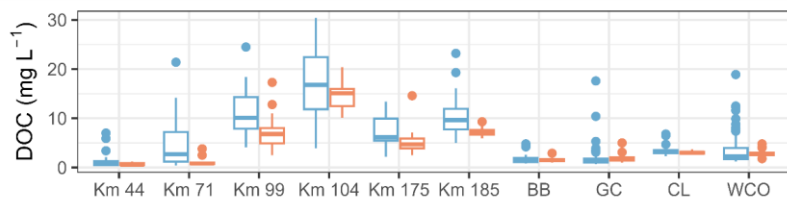
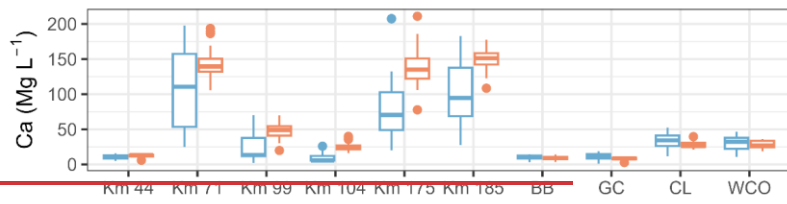
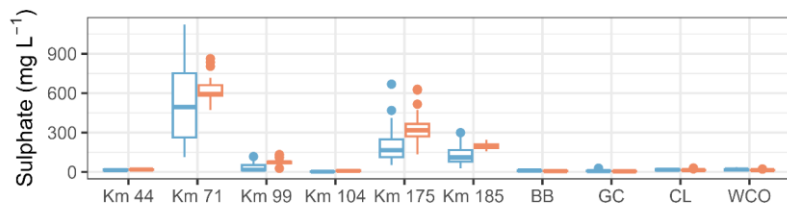
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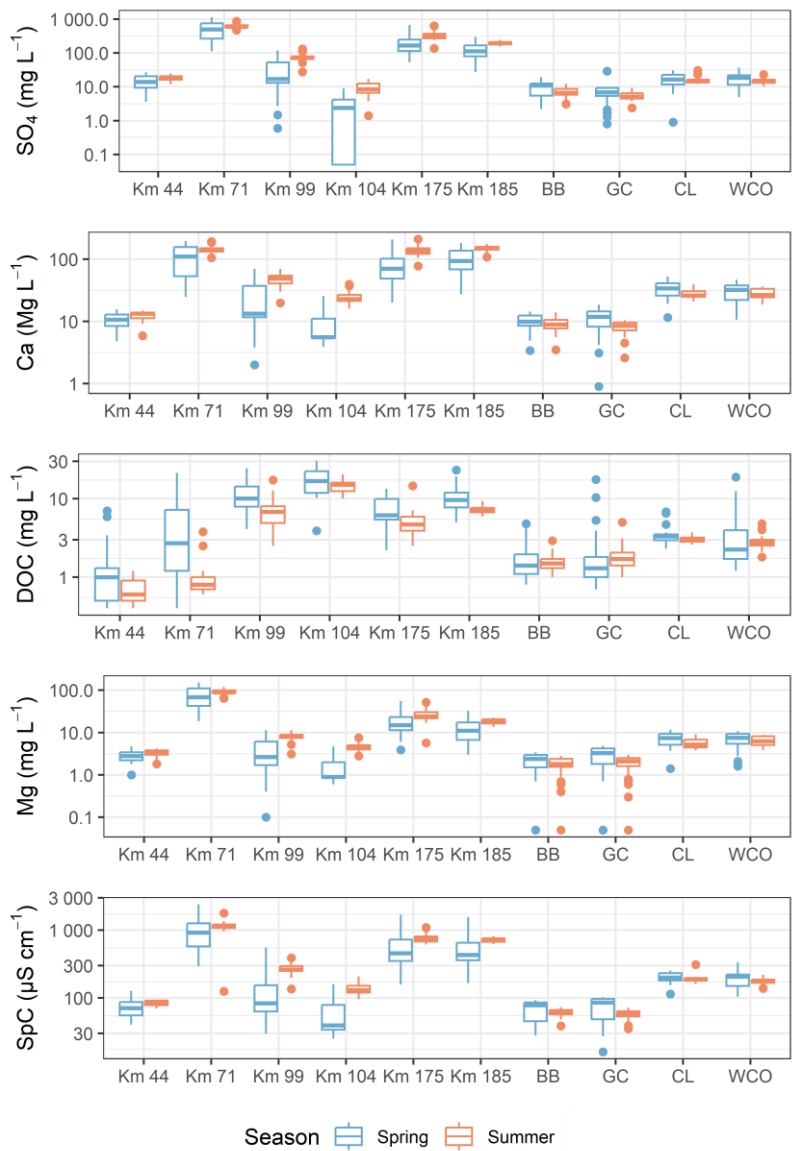
372



373 Figure 3. Solute concentrations plotted against flow for all sites. Winter samples were lumped in with
374 spring. Analogous figures where samples are color coded by permafrost extent and topographical
375 gradients instead of site names are available in the SI (Figure S2; Figure S3).



Season  Spring  Summer



377

378 Figure 4. Boxplots depicting showing log solute concentrations for Spring and Summer for all catchments.
 379 Winter values were grouped into with spring and grab samples where flow was not available are also

380 included in the boxplots. Samples taken on a DOY between 130 and 280 were classified as summer
381 samples.

382 ~~3.2.~~ 3.2. GAMs

383 3.2.1. Seasonality

384 ~~Results from the GAMs indicate~~GAM results revealed that ~~not all sites showed significant~~seasonality for
385 ~~all, defined by the sDOY term (p < 0.05), varied across sites and among~~ solutes (Figure 5), ~~which was~~
386 ~~defined by a p-value lower than 0.05 for the sDOY term-). The degree of seasonality, defined as sDOY~~
387 ~~range, is reported in the SI (Table S1). Larger sDOY range indicates greater~~ indicating the magnitude of
388 relative changes in seasonal ~~change in~~ concentrations changes after accounting for discharge. ~~In general,~~
389 is detailed in Table S1.

390 For major ions, sDOY generally increased post-freshet, reflecting rising concentrations as the season
391 progressed ~~post freshet for major ions but decreased for~~. In contrast, DOC (Figure 5). Thus, DOC
392 concentrations decreased over time, but major ion exhibited decreasing concentrations increased at
393 most sites after accounting for changes in flow. The WCRB sites exhibited less over time. Sites within
394 WCRB, characterized by less permafrost, showed weaker seasonality (lower sDOY range) for major ions
395 than the TWO sites, which typically have compared to the more permafrost than WCRB rich TWO sites.

396 Model performance was generally lower for DOC than other solutes, particularly for CL (a large lake
397 dominant subcatchment of WCRB with an outlet lake underlain with sporadic permafrost), Km 175, and
398 Km 104, which all had an R^2 less than 0.2. The models exhibited poor performance ($R^2 < 0.25$) in
399 predicting Sulphate SO_4 and SpC in CL, as well as in predicting Mg in BB (an alpine headwater
400 subcatchment of WCRB; Figure 6). It is important to emphasize that BB had limited winter/spring
401 samples, which may lead to lower sDOY range.

402 DOC ~~had seasonality was~~ significant seasonality (sDOY p-value < 0.05) at all most sites except ~~for~~ CL, Km
403 104, and Km 175 ~~(Figure 5)~~. Among ~~the~~ sites with significant seasonality, BB and Km 99 ~~had the least~~
404 pronounced seasonality for DOC, characterized by exhibited the lowest sDOY ranges of 0.5223 and
405 0.7633, respectively. Conversely, Km 44 and Km 71, the two catchments with which have steep
406 topography, had the strongest topographical gradients, had the most pronounced seasonality with
407 (sDOY ranges of 1.60; 0.69 and 2.35 1.02, respectively. In general, the). The standard error for sDOY was

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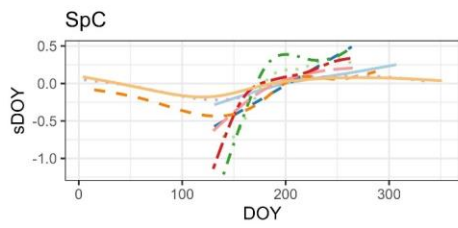
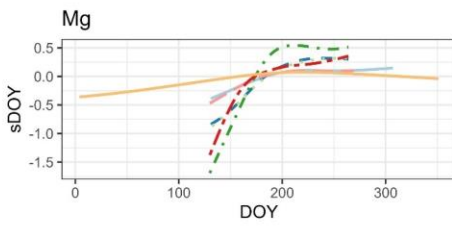
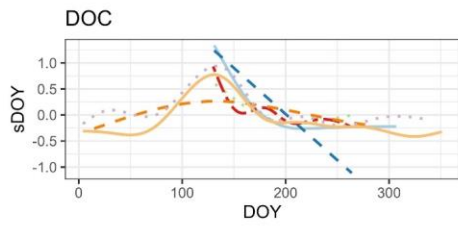
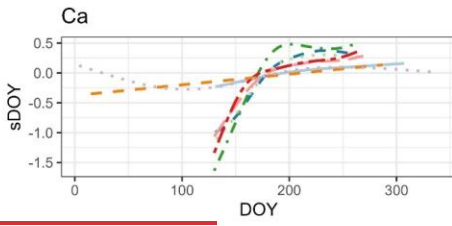
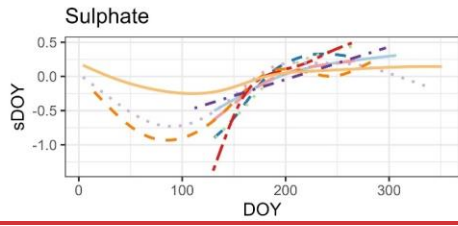
408 notably ~~generally~~ higher for DOC compared to other solutes, ~~particularly at sites exhibiting wider sDOY~~
409 ~~ranges.~~

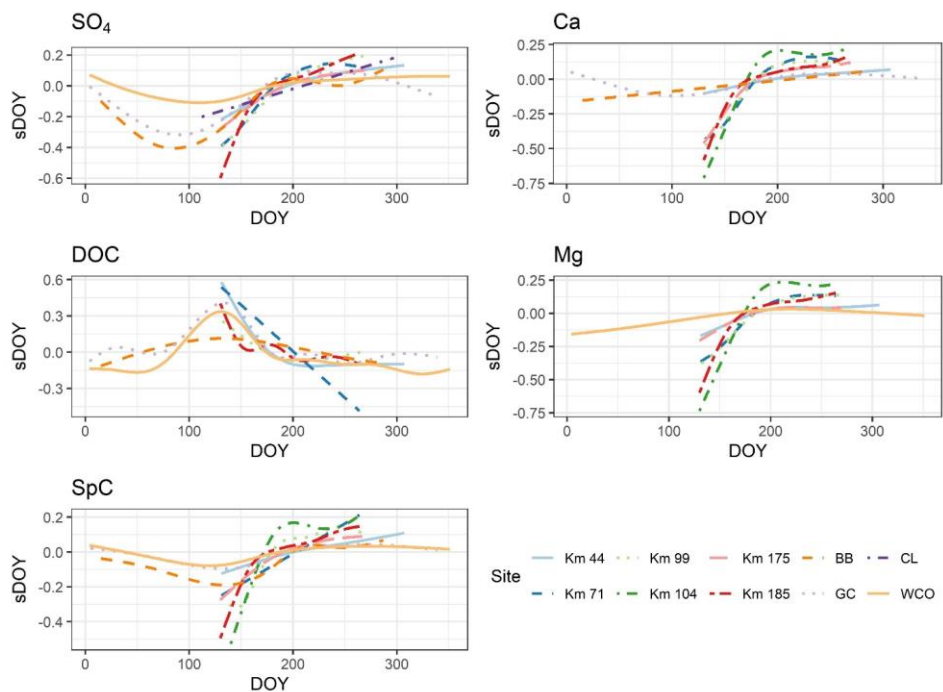
410 Sulphate SO_4 exhibited significant seasonality at ~~across all sites. The site with the least pronounced~~
411 ~~seasonality was WCO (the largest catchment in our study underlain with sporadic permafrost), with an~~
412 ~~had the weakest seasonality (sDOY range of: 0.42. In contrast, 18), whereas~~ Km 104 (continuous
413 permafrost) ~~had displayed~~ the ~~greatest seasonality~~ ~~strongest~~ (sDOY range: ~~4.1~~ ~~coupled~~ ~~7.8~~) with a
414 ~~relatively large high uncertainty (mean standard error of: 0.43) for the sDOY term. Several spring samples~~
415 ~~had Sulphate concentrations 19). Limited data along with some values being below the detection limit,~~
416 ~~potentially explaining the limits may explain this high uncertainty at Km 104 compared with other~~
417 ~~catchments.~~ Km 185 ~~(also underlain by continuous permafrost),~~ had the second ~~highest~~ sDOY range
418 ~~(1.87) for sulphate 0.81) with a lower mean standard error (0.1) 0.05).~~

419 The ~~GAMs~~ seasonality ~~results were similar~~ ~~patterns~~ for Ca, Mg, and SpC. ~~were similar.~~ WCO and CL, the
420 ~~two largest catchments, were the only sites that did not have a without significant sDOY term seasonality~~
421 ~~for Ca (p-values: 0.051 and 0.16, respectively). Among the WCRB sites, Mg only exhibited Mg seasonality~~
422 ~~was significant seasonality only at WCO. Among the among WCRB sites and at most TWO sites, Km 175~~
423 ~~was the only site to not exhibit significant seasonality for Mg. SpC had significant seasonality for all sites~~
424 ~~except for Km 175. SpC seasonality was significant at all sites except CL (p-value: 0.37).~~

425 Km 104 and Km 185 ~~had showed~~ the ~~greatest~~ ~~strongest~~ seasonality for Ca, Mg, and SpC. ~~For Ca,~~ (sDOY
426 ~~ranges were 2.14: 0.93 and 0.74), Mg (0.97 and 1.41 for Km 104 and 185 respectively. For Mg, Km~~
427 ~~104 0.75), and SpC (0.74 and Km 185 had sDOY ranges of 2.23 and 1.73 respectively. Km 104 and Km 185~~
428 ~~had sDOY ranges of 1.69 and 1.48 respectively for SpC.~~

429 ~~The lowest significant 0.64). In contrast, weaker seasonality for Ca, Mg, and SpC all generally occurred at~~
430 ~~WCRB sites, which have less permafrost than the TWO sites. For CL, GC and Km 44 had the weakest the~~
431 ~~weakest significant seasonality for Ca, with sDOY ranges of 0.39 and 0.4 respectively, while WCO had the~~
432 ~~lowest significant seasonality for Mg (sDOY range: 0.43). In contrast, sDOY ranges (0.17), while WCO~~
433 ~~exhibited the weakest Mg seasonality (0.19). SpC seasonality was weakest at Granger and WCO had the~~
434 ~~lowest significant seasonality for SpC with sDOY ranges of (0.32 14 and 0.28 12, respectively).~~ Complete
435 GAMs results are reported in the SI.





437

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

440 **3.2.2. CV ratios and log-log slopes**

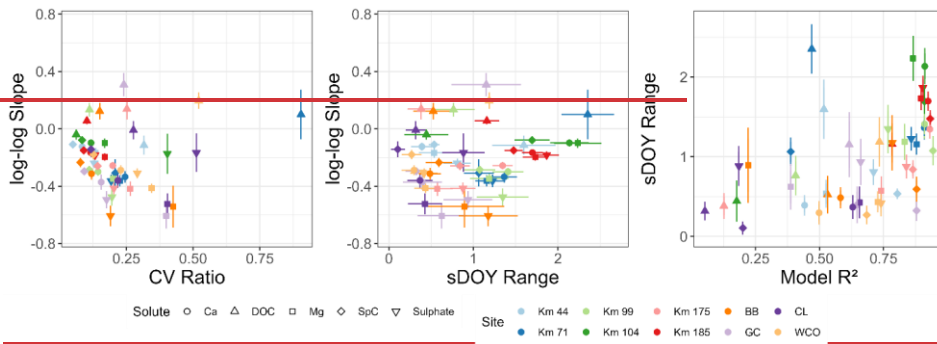
441 Log-log slopes from the GAMs were generally negative for major ions, and positive or close to zero for
 442 DOC (Figure 6). Slopes close to zero indicate spatial and vertical homogeneity of¹⁵. The plots represent
 443 how the value of the sDOY term in equation 1 and 2 changes depending on the day of year a sample was
 444 taken. Larger sDOY shift over time represents greater relative change in solute source within the
 445 catchment, or dominance of in-stream/near-stream biogeochemical concentrations driven by processes
 446 other than seasonal discharge. The standard errors of the log-log slopes were typically higher for
 447 sulphate and DOC than any other sDOY value is logged, thus a shift of 1 (i.e. Mg for Km 104) would result
 448 in a 10x increase or decrease of solute among sites concentrations if discharge is constant.

449 **3.2.2. Log-log slopes, sDOY ranges, and CV ratios.**

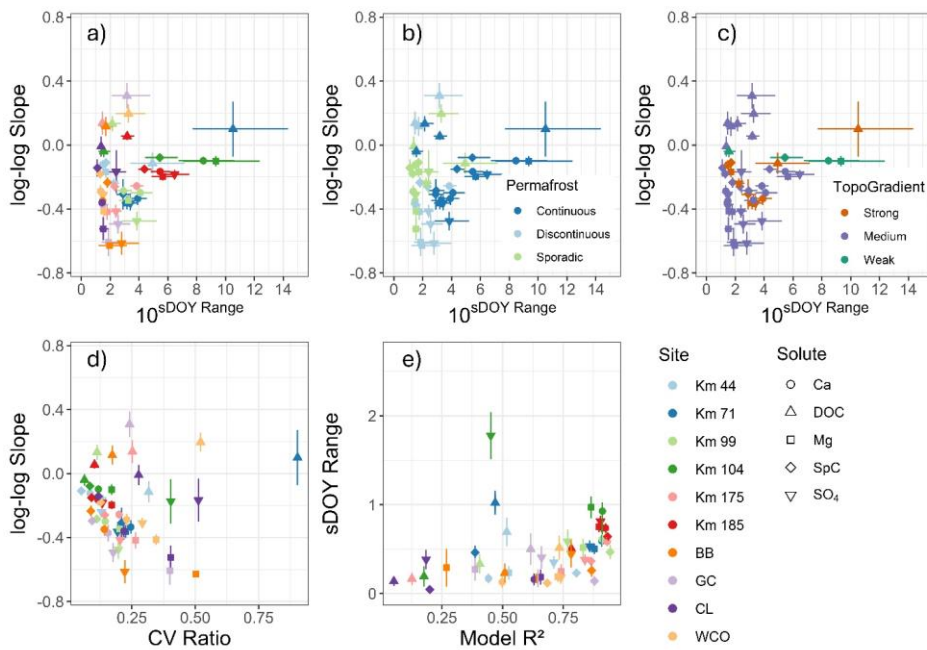
450 ~~For major ions, BB and GC (alpine headwater subcatchments of WCRB) for Mg had exhibited the~~
451 ~~strongest steepest~~ negative slopes, ~~particularly for Mg, with values approaching -0.6. For DOC, (Figure 6).~~
452 ~~Km 104, showed low CV ratios and log-log slopes near zero, indicating chemostatic behavior for major~~
453 ~~ions. This is likely due the presence of a thick organic layer in Km 104, which largely extends to the~~
454 ~~permafrost table. CV ratios for major ions were generally below 0.7 across all sites, with most sites~~
455 ~~showing values below 0.3. Km 104 and CL had relatively high CV ratios for SO₄. However, these sites also~~
456 ~~showed large standard errors in their log-log slopes, reflecting greater uncertainty in their estimates.~~

457
458 ~~For DOC, log-log slopes were either positive or close to zero at most sites. The strongest positive slopes~~
459 ~~were observed at WCO (outlet of WCRB0.20) and Granger had the strongest positive log-log slopes (0.20~~
460 ~~and (0.31 respectively), indicating high heterogeneity in the soil profile. Conversely, Km 71 (strong~~
461 ~~topographical gradient), CL (lake-influenced subcatchment of WCRB), and Km 104 (flat with continuous~~
462 ~~permafrost) had showed negative or near zero log-log slopes. All other sites had weak but positive log-log~~
463 ~~slopes for DOC close to 0.1. CV ratios for all major ions were lower than 0.7 at all sites, however the~~
464 ~~majority of sites had CV ratios of less than 0.3. Km 71 had the highest zero slopes (insignificant b term).~~
465 ~~Km 104 had relatively low CV ratio for DOC followed by WCO, whereas Km 10471 and CL had relatively~~
466 ~~high higher CV ratios for Sulphate but also had large standard errors in. This indicates that the near zero~~
467 ~~log-log slopes. Km 104 and Km 44 (strong topographical gradient) had some of the lowest CV ratios for~~
468 ~~ions along with log-log slopes close to zero, indicative of chemostatic for DOC reflect chemodynamic~~
469 ~~behaviour. A similar pattern can be observed for driven by processes other than discharge at Km 71 and~~
470 ~~CL. In contrast, DOC for Km 104 and Km 185 is chemostatic in Km 104, likely due to the largely~~
471 ~~homogenous soil profile in the catchment.~~

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473



474

475 Figure 6. CV ratio plotted against log-log slopes from GAM models (top). Gam R² plotted against sDOY
 476 range (bottom). Error bars indicate standard error of sDOY range (mean sDOY SE $\times \sqrt{2}$) and the standard
 477 error of the logLog-log slope from GAMs models. The sDOY range for Sulphate plotted against 10^{sDOY Range}
 478 from the GAMs models (a-c). Points are colour coded by site (a), permafrost extent (b), and
 479 topographical gradients (c). 10^{sDOY Range} can be interpreted as the magnitude of change in solute

480 concentrations if discharge remains unchanged. For example, a $10^{\text{sDOY Range}}$ value of 10 (or sDOY Range of
481 1) indicates a 10x increase in concentrations of weathering associated solutes (decrease for DOC
482 concentrations), if discharge is constant. The sDOY range for SO_4 for Km 104 was large and was not
483 included in these plots for visualization purposes. CV ratio plotted against log-log slopes from GAM
484 models (d). Gam R^2 plotted was plotted against sDOY range (e). Error bars for sDOY range represent the
485 mean standard error of sDOY Range (mean sDOY SE $\cdot \sqrt{2}$). Several samples were below the detection
486 limit for Sulphate SO_4 at Km 104 potentially leading to high uncertainty in the model.

487 3.3. Influence of topography and permafrost extent on seasonality

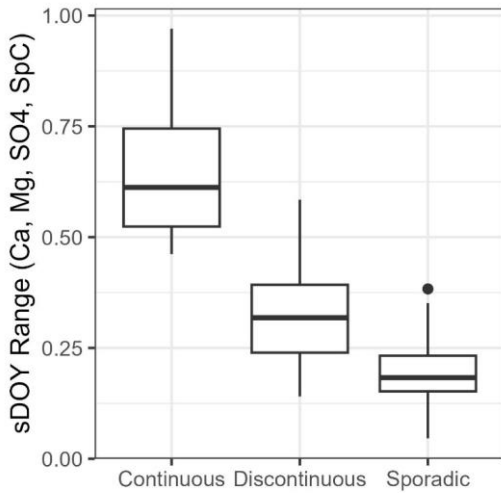
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489 ANOVA revealed significant differences in sDOY ranges for weathering-associated solutes based on
490 permafrost extent (Figure 7). Tukey tests showed that sites underlain by continuous permafrost exhibited
491 significantly greater sDOY ranges compared to those with discontinuous or sporadic permafrost
492 (adjusted $p < 0.01$). The difference between discontinuous and sporadic permafrost was significant
493 (adjusted $p = 0.061$). In contrast to major ions, no significant differences in sDOY ranges for DOC were
494 found between continuous and discontinuous/sporadic permafrost sites (t-test, $p > 0.1$).

495 Median solute concentrations did not differ significantly between continuous and discontinuous
496 permafrost sites for any solutes. However, DOC concentrations showed a marginally lower p-value ($p =$
497 0.156). Notably, three of the four sites with the highest median DOC concentrations were classified as
498 continuous permafrost, with Km 71 being the only continuous permafrost site exhibiting low DOC
499 concentrations.

500 Pearson's correlation analysis revealed that sDOY ranges for DOC were positively correlated with mean
501 catchment slope ($r = 0.59$, $p = 0.07$), while all other solutes showed negative but insignificant
502 correlations between sDOY ranges and catchment slope ($p > 0.1$). Median DOC concentrations were
503 negatively correlated with mean catchment slope ($r = -0.62$, $p = 0.057$). For SO_4 , a marginally significant
504 positive correlation ($r = 0.55$, $p = 0.097$) was observed with catchment slope, but no other solutes
505 exhibited significant relationships between median concentrations and slope.

506 Sites such as Km 71, characterized by both continuous permafrost and strong topographical gradients,
507 can limit statistical significance. As high permafrost extent has shown to lead to higher DOC
508 concentrations, but strong topographical gradients are associated with lower median DOC
509 concentrations.



510

511 [Figure 7. Boxplots of sDOY ranges for weathering-associated solutes grouped by permafrost extent.](#)

512 4. Discussion

513 In permafrost influenced catchments, solute concentrations are typically highly seasonal (Carey, 2003;
 514 Koch et al., 2021; MacLean et al., 1999; Shatilla and Carey, 2019; Shogren et al., 2021; Townsend-Small et
 515 al., 2011). Concentrations of DOC generally decrease, and concentrations of weathering derived ions
 516 generally increase over the course of the spring to fall transition. Seasonal active layer dynamics,
 517 depleting solute stores, and seasonality in discharge have been used to explain these patterns previously
 518 (Carey, 2003; Shatilla and Carey, 2019). However, little work has been done to resolve the relative
 519 influence of these drivers of variability. Here we provide insights on the mechanisms of solute export in
 520 permafrost underlain catchments by assessing [changes in the influence of seasonality on](#) CQ relationships
 521 [using GAMs.](#)

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

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

531 Our third hypothesis states that greater permafrost extent would lead to higher median DOC and lower
532 median concentrations of weathering associated ions. We found some evidence for higher DOC
533 concentrations in catchments with continuous permafrost. However, we found stronger evidence for
534 high topographical gradients leading to lower median DOC concentrations. We found no evidence of
535 permafrost extent influencing median concentrations of weathering derived ions.

536 4.1. Seasonal drivers for DOC and major ions

537 4.1.1. Spatial/vertical heterogeneity in soil chemistry is evident in most catchments

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538 Log-log C-Q slopes were predominantly negative (dilution) for all major ions, and positive (flushing) or
539 ~~with no significant slope~~ not significantly different than zero for DOC. This corresponds to work of others
540 in permafrost underlain catchments who reported log-log slopes as typically positive for DOC (MacLean
541 et al., 1999; Skierszkan et al., 2024) and negative for major ions (MacLean et al., 1999; Shatilla et al.,
542 2023). ~~Negative in permafrost underlain catchments. The negative~~ log-log slopes for major ions indicates
543 the presence of greater ~~more~~ mineral rich soils at depth. Log-log CQ slopes for major ions were closest to
544 zero for Km 104 (a relatively flat catchment with uniform catchment characteristics), indicating high
545 homogeneity in terms of the spatial and vertical distribution of solute sources within the catchment.

546 A near zero log-log slope suggests that mobile organic carbon (OC) may be homogeneous
547 vertically/spatially, or in-stream/near-stream biogeochemical processes drive variability in DOC
548 concentrations (Creed et al., 2015; Zhi and Li, 2020). Although many catchments had significant positive
549 log-log slopes for DOC; CL, Km 44, Km 71, Km 104, and Km 175 all had non-significant log-log DOC slopes.
550 Km 104 has near zero log-log slopes with a very low CV ratio. The low log-log slopes likely reflect the
551 largely homogeneous vertical/spatial soil profile due to thick organic soils and relatively thin active layer
552 (~40 cm), and weak topographical gradients. Additionally, the stream is slow moving and instream
553 processes may be more important in this catchment than the other TWO catchments. CL is the second
554 largest catchment in this study with a ~1 km² lake just above the sampling outlet. The non-significant log-
555 log slope along with high CV ratio at CL indicate the dominance of in-stream/surface water processes (i.e.

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

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

567 **4.1.2. Seasonal depletion of soil stores is important for DOC export**

568 Our analysis suggests that flushing of organic soils during freshet is likely the primary driver for seasonal
569 declines in DOC, yet active layer thaw may be a secondary driver depending on the spatial/vertical
570 distribution of organic matter concentrations in the soil. At most sites, high seasonality for DOC (as
571 indicated by the sDOY range) along with nonsignificant log-log slopes indicates changing flow paths due
572 to active layer thaw is likely not the primary driver in the seasonality of DOC concentrations (Figure 6). ~~↔~~
573 ~~this scenario, seasonality in DOC concentrations would be driven primarily via flushing of organic soils~~
574 ~~during freshet. The seasonality term in GAMs accounts for changes in flow, and the~~The presence of non-
575 significant log-log slopes indicate a lack of vertical heterogeneity in soil OC concentrations or dominance
576 of in/near-stream processes. Thus, seasonality in CQ relationships for DOC in catchments where log-log
577 slopes are near zero, must be primarily driven by processes other than changing flow paths due to active
578 layer thaw or discharge. Previous work in snow dominated mountains has shown the flushing of organic
579 matter in soils during freshet can reduce the soil reservoir of DOC (Boyer et al., 1997; Hornberger et al.,
580 1994). For example, Boyer et al. (1997) attributed declines in DOC as melt progressed to source
581 depletion in the upper soil horizons in a mountain headwater catchment in Colorado, USA. Certain sites
582 (GC, WCO, BB, Km 99, and Km 175) did have positive log-log slopes for DOC, suggesting that depletion of
583 DOC stores and thawing active layer may have a combined effect in controlling DOC concentrations. The
584 strong decline of the sDOY term during freshet at several sites ~~indicates~~ (Figure 5) ~~indicates~~ that flushing
585 of DOM in soils during freshet rapidly deplete finite labile OC stores within catchment soils as observed

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586 elsewhere (Boyer et al., 1997; Hornberger et al., 1994). Previous work at GC₇ attributed a strong
587 hysteresis of DOC concentrations during freshet and summer events to both a rapid decline in organic
588 matter_r and greater emphasis on deeper flow pathways (Carey, 2003; Shatilla and Carey, 2019).
589 Townsend-Small et al. (2011) compared DOC concentrations at the same discharge level in the upper
590 Kuparuk River in Alaska and saw a decrease in DOC concentrations over time, suggesting seasonality is at
591 least partially driven by active layer thaw and/or depleting solute stores. Skierszkan et al. (2024) used a
592 mixing model and found seasonality in DOC concentrations to primarily be driven by changing flow paths
593 in the Dawson range, Yukon, Canada, which contrasts with our findings. This discrepancy is potentially a
594 result of strong heterogeneity in spatial and vertical soil OC concentrations in the Dawson range, and
595 greater presence of organic carbon in soils.

596 4.1.3. Seasonal active layer freeze-thaw is important for major ion export

597 Our study largely agrees with others in permafrost environments that attributed the seasonality of major
598 ions to seasonal active layer thaw. Similar to other studies, we found CQ relationships are variable
599 among seasons for major ions in permafrost underlain catchments (MacLean et al., 1999; Shatilla et al.,
600 2023). Non-zero log-log slopes can indicate presence of heterogeneity in soil chemistry. ~~Significant,~~
601 whereas significant sDOY terms indicate seasonal changes in ion concentration after accounting for
602 variability in discharge. The negative log-log slopes and strong seasonality at multiple sites for multiple
603 major ions suggest that activation of different flow paths ~~from~~ due to seasonal active layer thaw along
604 with variability in discharge ~~influence export~~ drives concentrations of weathering associated solutes in
605 these regions. ~~Thawing of the active layer leads to greater flow from the deeper mineral rich soil~~
606 ~~horizons and bedrock and consequently higher ion concentrations. GAM results for major ions indicate~~
607 ~~seasonal~~ Seasonal increases in solute ions concentrations, ~~suggesting~~ suggests the seasonality in CQ
608 patterns is not primarily driven by depletion of ion stores (Figure 5). Shatilla et al. (2023) attributed
609 ground thaw and increasing connectivity of deep groundwater to seasonal increases in solute ion
610 concentrations in GC. ~~Lehn et al., (2017)~~ attributed a seasonal increase of major ion concentrations in
611 Alaskan watersheds to seasonally thawing active layer and cryoconcentration in soils during later fall and
612 winter of the previous years. Our results are generally in agreement with these findings, although we did
613 not have the data to assess the influence of cryoconcentration in soils.

614 Km 104 had significant but relatively low log-log slopes, with the highest seasonality for major ions. This
615 suggests that other drivers (aside from discharge and active layer thaw) may play an important role in

616 seasonal ion concentrations in this site. Km 104 and Km 99 were found to have highly seasonal transit
617 time distributions, where the fraction of young water is much lower in the summer than in the spring
618 (unpublished data). Greater transit times in the summer can lead to greater contact time between water
619 and mineral ~~systems~~soils (Benettin et al., 2015), potentially driving seasonality in this system. However,
620 calculating transit times requires estimates of input tracer concentrations, which was difficult to do for
621 many of our study catchments, particularly during snowmelt.

622 4.2. Catchment characteristics drive magnitude of seasonality

623 4.2.1 Stronger topographical gradients lead to greater DOC seasonality

624 ~~Although permafrost extent has~~We found median DOC concentrations to be generally higher in sites
625 ~~with a strong influence on DOC export~~greater permafrost extent, which supports findings from other
626 ~~permafrost catchments~~ (Frey and McClelland, 2009; MacLean et al., 1999; Petrone et al., 2006).
627 ~~However, we did not find evidence of~~ greater permafrost extent ~~did not necessarily lead~~leading to a
628 greater ~~seasonality (sDOY range)~~relative change in ~~CQ relationships for~~concentrations of DOC. For
629 example, DOC was highly seasonal in WCO (sporadic permafrost) ~~but~~and had relatively low seasonality
630 for Km 99 (continuous permafrost). ~~Although DOC concentrations were generally higher in the TWO~~
631 ~~sites, they did not necessarily exhibit a greater relative change in concentrations than the sites in WCRB,~~
632 ~~which generally have a lower permafrost extent than the TWO sites.~~Our results are in contrast ~~to~~with
633 MacLean et al. (1999) and Petrone et al. (2006) who observed stronger seasonality for DOC/DOM in
634 catchments with greater permafrost extent. MacLean et al. (1999) reported stronger CQ relationships
635 and greater model performance for DOC in a high permafrost catchment compared to the low
636 permafrost catchment in central Alaska during the summer. However, ~~the authors found the~~ CQ
637 relationships ~~were to be~~ similar between the catchments during snowmelt. The authors attributed this to
638 a lower variability in discharge during the summer for the low permafrost catchment. ~~Petrone et al.~~
639 ~~(2006) observed larger increases of DOC export in catchments with greater permafrost extent. However,~~
640 ~~Petrone et al. (2006) did not assess the relative~~ changes in DOC export or seasonality in ~~influence of~~
641 ~~seasonal discharge, where connectivity to DOC changes with changing catchment wetness.~~

642 In our study sites, ~~catchment characteristics related to slope and specific discharge~~catchments with
643 ~~steeper topographic gradients~~ were more important for DOC seasonality than permafrost extent.
644 ~~Correlation analysis revealed catchments with stronger topographical gradients, which are often~~
645 ~~associated with thin organic soils, had higher seasonality in DOC.~~ For example, the two most

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646 mountainous sites (Km 44 and Km 71) had the highest seasonality for DOC, indicating the greatest
647 relative seasonal changes in concentrations after accounting for discharge. Both Km 44 and Km 71 had
648 high specific discharge, strong topographical gradients, and the lowest average concentrations for DOC,
649 supporting the idea that organic matter stores were limited- in these catchments. Non-significant log-log
650 slopes imply that nearly all the seasonality at these sites was due to the depletion of solute DOC stores
651 and not due to active layer thaw as conceptually outlined in Fig 7 Figure 8. Although other seasonal
652 processes (water age, stream temperature, etc.) may be important, flushing of soil OC has been
653 observed as an important mechanism in multiple mountain catchments (Boyer et al., 1997; Shatilla and
654 Carey, 2019). The limited DOC supply and rapid flushing due to high flows presumably led to a more
655 rapid depletion in DOC stores in these catchments.

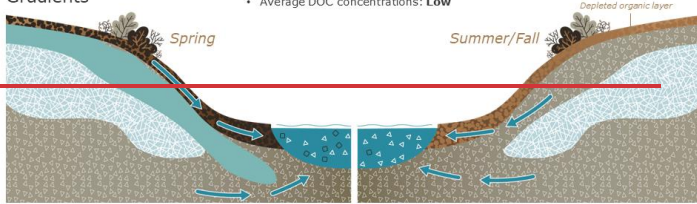
656 Conversely, Km 99 and Km 104 had high average DOC concentrations and high permafrost extent yet
657 exhibited lower seasonality than Km 71 and Km 44 which are underlain by sporadic and continuous
658 permafrost but have stronger topographical gradients. Additionally, the CV ratio at Km 104 was also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

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

676 interacts strongly with DOM (Gu et al., 1994; McKnight and Duren, 2004)(Gu et al., 1994; McKnight and
 677 Duren, 2004).

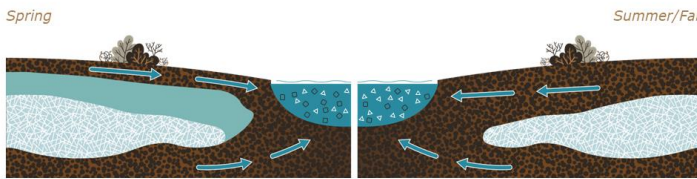
Strong Topographical Gradients

- Relative change in ion concentrations: **Mediated by permafrost extent**
- Relative change in DOC concentrations: **High**
- Average DOC concentrations: **Low**



Weak Topographical Gradients

- Relative change in ion concentrations: **Mediated by permafrost extent**
- Relative change in DOC concentrations: **Low**
- Average DOC concentrations: **High**



Stream:

- ▲ Major ions
- DOC
- Direction of ground water flow
- Stream

Soil column:

- Organic layer (DOC, OC)
- Mineral layer (Ca, Mg, SO₄, etc.)
- Seasonal frost
- Permafrost

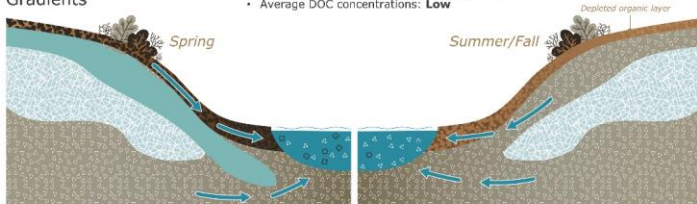
Description:

Seasonality in DOC concentrations are largely influenced by changes flushing of organic layer during freshet. This conceptual figure depicts changes in chemistry purely driven by seasonal processes other than discharge. The change DOC concentrations is less dramatic in low gradient catchments due to a thicker organic layer. This also results in greater overall DOC concentrations.

678

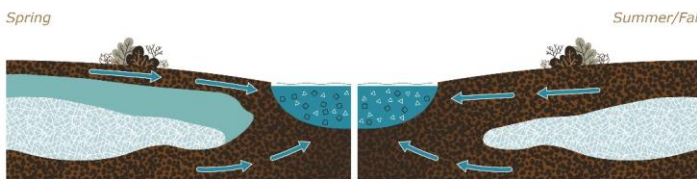
Strong Topographical Gradients

- Relative change in ion concentrations: **Mediated by permafrost extent**
- Relative change in DOC concentrations: **High**
- Average DOC concentrations: **Low**



Weak Topographical Gradients

- Relative change in ion concentrations: **Mediated by permafrost extent**
- Relative change in DOC concentrations: **Low**
- Average DOC concentrations: **High**



Stream:

- ▲ Major ions
- DOC
- Direction of ground water flow
- Stream

Soil column:

- Organic layer (DOC, OC)
- Mineral layer (Ca, Mg, SO₄, etc.)
- Seasonal frost
- Permafrost

679

680 ~~Figure 8. Seasonality in DOC concentrations is largely influenced by flushing of organic layer during~~
681 ~~freshet. This conceptual figure depicts changes in chemistry purely driven by seasonal processes other~~
682 ~~than discharge. The change in DOC concentrations is less dramatic in low gradient catchments due to a~~
683 ~~thicker organic layer. This also results in greater overall DOC concentrations.~~

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

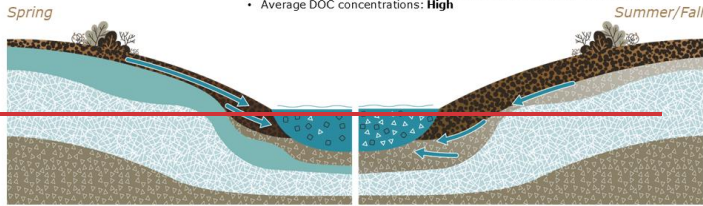
687 **4.2.2. Permafrost extent is important for major ion seasonality**

688 Unlike DOC, permafrost extent and winter groundwater contributions do influence the seasonality of
689 major ions, although the overall ~~concentration and~~ export is ~~likely more strongly~~ influenced by ~~regional~~
690 ~~variability in~~ surficial geology. ~~In general, catchments in WCRB had, which is considerable in this study.~~
691 ~~ANOVA and Tukey tests revealed higher seasonality in major ions for sites underlain with continuous~~
692 ~~permafrost than for sites underlain with sporadic and discontinuous permafrost. The lower seasonality~~
693 ~~than TWO catchments for major ions. Km 44 and Km 175 were the only exception to this, as these sites~~
694 ~~generally had low seasonality for major ions. This may in catchments with lower permafrost extent can~~
695 be explained by significant surface-groundwater connection throughout the ice-free season ~~as neither of~~
696 ~~these catchments are underlain with continuous permafrost as, as~~ outlined conceptually in ~~Fig 8~~ ~~Figure~~
697 ~~9~~. Our results are similar to Webster et al. (2022) who observed seasonal increases in NO₃ in Alaska,
698 which the authors attributed to thawing active layer in a high permafrost extent catchment but not in
699 low permafrost catchments. The authors argued that dominance of groundwater was responsible for the
700 lack of a seasonal trend in the low permafrost catchments. This supports our hypothesis for major ions,
701 where the presence of deep groundwater contributions in low-permafrost catchments can dampen
702 seasonality ~~of CQ relationships for major ions.~~ However, these results should be interpreted with
703 caution as ~~estimating~~ permafrost extent in mountain headwater catchments is uncertain. ~~The seasonality~~
704 ~~metrics for Mg at BB have low predictive power; this is likely due to limited sampling during freshet and~~
705 ~~presence of some samples that were below the detection limit.~~

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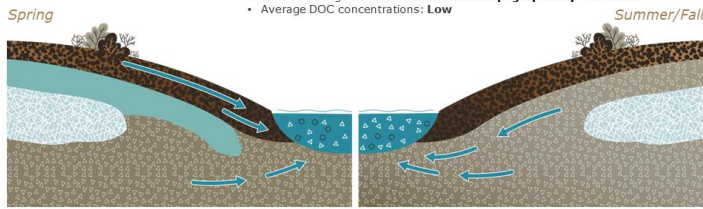
High Permafrost Extent

- Relative change in ion concentrations: **High**
- Relative change in DOC concentrations: **Topographically mediated**
- Average DOC concentrations: **High**



Low Permafrost Extent

- Relative change in ion concentrations: **Low**
- Relative change in DOC concentrations: **Topographically mediated**
- Average DOC concentrations: **Low**



Stream:

- ▲ Major ions
- DOC
- Direction of ground water flow
- Stream

Soil column:

- Organic layer (DOC, OC)
- Mineral layer (Ca, Mg, SO₄, etc.)
- Seasonal frost
- Permafrost

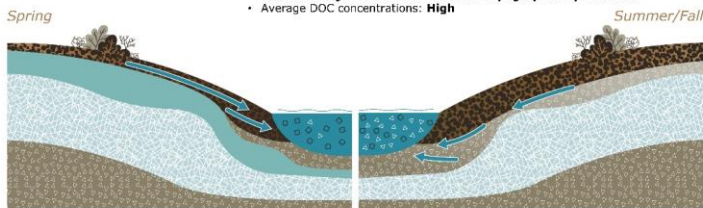
Description:

Seasonality in ion concentrations are largely influenced by changes in flow paths due to active layer thaw and seasonal discharge. This conceptual figure depicts changes in chemistry purely driven by seasonal processes other than discharge. The change ion concentrations is less dramatic in low permafrost catchments due to greater groundwater contributions muting the effect of active layer thaw. Average ion concentrations are likely driven by geology.

706

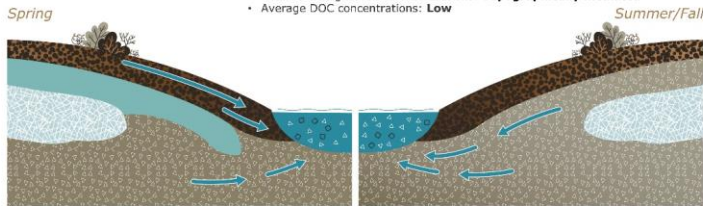
High Permafrost Extent

- Relative change in ion concentrations: **High**
- Relative change in DOC concentrations: **Topographically mediated**
- Average DOC concentrations: **High**



Low Permafrost Extent

- Relative change in ion concentrations: **Low**
- Relative change in DOC concentrations: **Topographically mediated**
- Average DOC concentrations: **Low**



Stream:

- ▲ Major ions
- DOC
- Direction of ground water flow
- Stream

Soil column:

- Organic layer (DOC, OC)
- Mineral layer (Ca, Mg, SO₄, etc.)
- Seasonal frost
- Permafrost

707

708 Figure 89. Conceptual diagram depicting the influence of permafrost extent on the relative seasonal
 709 change in ion concentrations and the mean concentration of DOC after accounting for seasonal
 710 discharge.

5. Conclusion and Future Directions

In this study, we assessed the role of catchment characteristics, seasonal active layer thaw, permafrost extent and topography on seasonality of DOC and depletion of solute stores in controlling solute export major ion concentrations in permafrost underlain watersheds/catchments. 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 suggesting permafrost extent drove variability/seasonality in chemical concentrations was found to be largely true. However, although permafrost extent was/may be 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. We found some evidence for higher DOC concentrations in catchments with continuous permafrost which supported our third hypothesis. However, we found stronger evidence for high topographical gradients leading to lower median DOC concentrations. We found no evidence of permafrost extent influencing median concentrations of weathering derived ions, which is presumably due to the diverse geology in WCRB and TWO.

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.

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

752 6. Future Directions

753 GAMs offer a valuable approach for assessing trends in solute concentrations driven by permafrost thaw,
754 while simultaneously accounting for variability in discharge. Long-term trend analysis of solute
755 concentrations in permafrost regions is often complicated by concurrent trends in specific discharge,
756 which can lead to significant data omissions (Keller et al., 2010). By leveraging partial effect plots within a
757 CQ framework, GAMs provide a powerful technique to disentangle the effects of discharge variability
758 from long-term changes in stream chemistry.

759 Water transit times may be a critical factor influencing stream chemistry, as they govern the contact time
760 between water and soil substrate, while also reflecting flow path length (Benettin et al., 2015;
761 Hrachowitz et al., 2016). This is particularly relevant in permafrost environments, where water transit
762 times can exhibit pronounced seasonality (Piovano et al., 2019). As of yet, the role of seasonal ground
763 freeze-thaw processes on water ages is poorly characterized in permafrost environments. Future work
764 should examine the influence of water transit times on seasonality of stream chemistry in permafrost
765 catchments.

766

767 Data Availability Statement

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

770 Author Contributions

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

774 Conflict of Interest

775 The authors declare that they have no conflict of interest.

776 Special Issue Statement

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

779 Acknowledgments

780 We would like to thank David Barrett, Tyler de Jong, Fiona Chapman, Joseph Desmarais, Sean Leipe,
781 Lauren Bourke, Aliana Fristensky, Anna Grunsky, Andras Szeitz, and Calvin Newbery for field assistance.
782 We would like to thank Global Water Futures, and National Science and Engineering Council of Canada
783 (RGPNS-2020-06722) for providing financial support for this project. We acknowledge the continued
784 support of the Water Resources Branch, Government of Yukon, for the operation of Wolf Creek Research
785 Basin. We thank Mike Waddington, Christopher Wellen, Alemu Gonsamo, along with the two anonymous
786 reviewers for providing important feedback, which greatly improved the manuscript.

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