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1 **Assessing inter-annual and seasonal patterns of DOC and DOM quality across a complex alpine**
2 **watershed underlain by discontinuous permafrost in Yukon, Canada**
3

4 Nadine J. Shatilla[1], Sean Carey[1]

5 [1]Watershed Hydrology Group, School of Geography and Earth Sciences, McMaster University,
6 Hamilton, Canada, L8S 4K1

7 *Correspondence to*: Nadine J. Shatilla (n.j.shatilla@gmail.com)

8 **Abstract**

9 High latitude environments store approximately half of the global organic carbon pool in peatlands,

10 organic soils and permafrost while large arctic rivers convey an estimated 18-50 Tg C a^{-1} to the Arctic

11 Ocean. Warming trends associated with climate change affect dissolved organic carbon (DOC) export

12 from terrestrial to riverine environments. However, there is limited consensus as to whether exports will

13 increase or decrease due to complex interactions between climate, soils, vegetation, and associated

14 production, mobilization and transport processes. A large body of research has focused on large river

15 system DOC and DOM lability and observed trends conserved across years, whereas investigation at

16 smaller watershed scales show that thermokarst and fire have a transient impact on hydrologically-

17 mediated solute transport. This study, located in the Wolf Creek Research Basin situated ~20 km south

18 of Whitehorse, YT, Canada, utilises a nested design to assess seasonal and annual patterns of DOC and

19 DOM composition across diverse landscape types (headwater, wetland, lake) and watershed scales. Peak

20 DOC concentration and export occurred during freshet per most northern watersheds, however, peaks

21 were lower than a decade ago at the headwater site Granger Creek. DOM composition was most variable

22 during freshet with high A254, SUVA$_{254}$ and low FI and BIX. DOM composition was relatively

23 insensitive to flow variation during summer and fall. The influence of increasing watershed scale and

24 downstream mixing of landscape contributions was an overall dampening of DOC concentrations and

25 optical indices with increasing groundwater contribution. Forecasted vegetation shifts, permafrost thaw

26 and other changes due to climate change may alter DOM sources from predominantly organic soils to

27 decomposing vegetation, and facilitate transport through deeper flow pathways with an enhanced

28 groundwater role.

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1 Introduction

High latitudes, particularly north-western regions of North America, are experiencing some of the most rapid documented warming on the planet (Serreze and Francis, 2006; DeBeer et al., 2016). This warming has intensified the Arctic freshwater cycle (Bring et al., 2016) and resulted in landscape disturbance and change that alters biogeochemical cycles (Vonk et al., 2015; Wrona et al., 2016). Carbon storage and cycling have been the focus of considerable attention, as northern high latitudes are estimated to store approximately half of the global belowground organic carbon pool in peatlands, organic soils and permafrost (Tarnocai et al., 2009; Schuur et al., 2015) and deliver ~10 % of the total freshwater input to global oceans (Gordeev et al., 1996; Opsahl et al., 1999; Shiklomanov, 2000). The mobilization and delivery of this terrestrial organic carbon has been identified as critical to the global carbon cycle given initial estimates that Arctic rivers convey 18-26 Tg C a^{-1} to the Arctic Ocean (Dixon et al., 1994; Dittmar and Kattner, 2003). More recent studies estimate between 25 and 50 Tg C a^{-1} are exported (Raymond et al., 2007; McGuire et al., 2009; Johnston et al., 2018).

Changes in DOC export associated with warming are uncertain, often contradictory and largely associated with analysis of data from large rivers. Striegl et al. (2005) documented a 40% decline between 1978-1980 and 2001-2003 for the Yukon River, whereas Tank et al. (2016) report a 39% increase for the Mackenzie River between 1978 and 2012. In a more recent analysis of the Yukon River, Toohey et al. (2016) suggest that from 2001-2014, there has been no trend in DOC whereas weathering solutes have increased, reflecting deeper flowpaths as permafrost degrades. Typically, DOC flux estimates are derived from limited spot water quality sampling and rely on a relationship between water yield and DOC concentration to calculate loads (Raymond et al., 2007; McClelland et al., 2007; Manizza et al., 2009;

50 Holmes et al., 2012; Tank et al., 2016). While the influence of changing mean annual temperature on

51 DOC production and transport across 49 northern watersheds was summarized by Laudon et al. (2012),

52 northern landscapes are also susceptible to fire and thermokarst. These disturbances have a transient

53 influence on hydrologically-mediated DOC transport that confounds spatial and temporal patterns of

54 DOC flux from terrigenous sources to the river-ocean continuum (Larouche et al., 2015; Littlefair et al.,

55 2017; Burd et al., 2018).

56 In northern and permafrost landscapes, the link between hydrological and biogeochemical cycles and the

57 role of frozen ground and organic matter has been well documented in process-based studies (e.g. Maclean

58 et al., 1999; Carey, 2003; O'Donnell and Jones, 2006; Petrone et al., 2006; Carey et al., 2013a; Koch et

59 al., 2013; Olefeldt and Roulet, 2014; Burd et al., 2018). While wetlands have been highlighted as a source

60 of DOC, particularly in Scandinavian catchments, in permafrost environments the presence of thermally-

61 mediated flowpaths are critical. DOC export is greatest during snowmelt freshet when DOC from organic

62 rich layers is mobilized, resulting in a large annual 'flush' (Boyer et al., 2000; Carey, 2003; Finlay et al.,

63 2006). As flowpaths descend in response to soil thaw, DOC mobilization typically declines and flow in

64 mineral layers provides more opportunity for immobilization and adsorption (MacLean et al., 1999;

65 review by Kalbitz et al., 2000; Carey, 2003; Kawahigashi et al., 2004, 2006; Frey and Smith, 2005). In

66 some environments, an increase in late fall DOC flux has been ascribed to freezing processes in the soil

67 column (Johnson et al., 2018). How this temporal relationship varies across scales is less certain as few

68 studies provide nested datasets yet analysis by Tiwari et al. (2014, 2017), and synthesis by Creed et al.

69 (2015), suggest downstream mixing and deeper subsurface sources of DOC mask process drivers as scale

70 increases. In addition, the role of photodegradation and oxidation of DOC to CO_2 in large Arctic rivers

71 has received considerable attention (Cory et al., 2014; Ward and Cory, 2016).

72 The lability (i.e. biodegradability) of dissolved organic matter (DOM) is a key regulator of ecosystem

73 function and primarily linked to molecular structure and environmental factors such as temperature,

74 vegetation, oxygen availability and microbial activity (Schmidt et al., 2011). DOC is a fraction of the

75 DOM pool whose weight, aromaticity and origins can in part be characterized using optical techniques.

76 DOM exported from large Arctic rivers during spring freshet has previously been reported as highly labile

77 (Raymond et al., 2007; Holmes et al., 2008; Spencer et al., 2008) with more refractory DOM during

78 recession periods (Holmes et al., 2008; Wickland et al., 2012). DOM quality is expected to shift in

79 response to permafrost thaw, thermokarst, vegetation shifts, wildfire and increasing precipitation during

80 summer months associated with climate warming (Davidson and Janssens, 2006; Frey and McClelland,

81 2009; Schuur et al., 2015). Spectral indices and multi-dimensional analysis of large optical data sets from

82 northern landscapes have resulted in important insights into how DOM quality varies seasonally (e.g.

83 Striegl et al., 2005; Neff et al., 2006; Finlay et al., 2006; Spencer et al., 2008, 2009; Prokushkin et al.,

84 2011; Mutschlecner et al., 2018), and is linked to source material, landscape characteristics (Kawahigashi

85 et al., 2004; Harms et al., 2016) and disturbance (Balcarczyk et al 2009; Kokelj et al., 2013; Abbott et al.,

86 2015; Littlefair et al., 2017; Burd et al., 2018).

87 While information from large rivers is critical for estimates of DOM loading to the Arctic Ocean, research

88 at headwater scales that identifies controls on DOC production and transport is relatively scarce and often

89 points to multiple process mechanisms (Maclean et al., 1999; Temnerud and Bishop, 2005; Larouche et

90 al., 2015). Furthermore, much of our understanding of DOC is biased towards lowland ecosystems, with

91 relatively scarce information from northern alpine systems. The goal of this paper is to enhance our

92 understanding of coupled hydrology-DOC sources and dynamics with additional context from DOM

93 optical properties in a well-studied, discontinuous permafrost alpine research catchment in subarctic

94 Yukon, Canada, ~~over multiple years.~~ We collected samples over two consecutive years from freshet to

95 late fall from two headwater catchments, a lake, wetland and the outlet of a mesoscale catchment in a

96 nested design to explore seasonal and annual variability in DOC concentrations and DOM composition.

97 Impacts of increasing catchment scale and differing landscape types on DOM optical indices were also

98 assessed.

99 The specific questions addressed in this work are:

100 1) How do DOC concentration and DOM composition vary over multiple seasons across a diverse

101 mountain watershed, and 2) what are the factors that drive this variability across scales. This study

102 provides important insights into how season and scale influence the sources and transport of DOM in a

103 cold alpine setting.

2 Materials and methods

2.1 Study area

106 Several headwater streams, a wetland and a ~~high elevation~~ lake outlet were studied within the Wolf Creek

107 Research Basin (WCRB, 61°310 N, 135°310 W) located ~20 km south of Whitehorse in Yukon Territory,

108 Canada (Fig. 1). WCRB is a long-term research watershed located at the edge of the Coast Mountains

109 and spans an elevation ranging from 712 m a.s.l. to 2080 m a.s.l. and drains an area ~179 km^2. WCRB

110 straddles three ecological zones with boreal forest at lower elevations (predominantly White Spruce

111 (*Picea glauca var. porsildii*)) covering ~28% of the watershed; at intermediate elevations shrub taiga

112 comprises ~47 %, and at elevations above ~1500 m, alpine tundra and bare rock surfaces predominate.

113 WCRB has a relatively dry Subarctic climate (Koppen classification *Dfc*) with 30-year climate normals

114 (1981-2010) reported for Whitehorse Airport (706 m). Average airport air temperature is -0.1 °C and

115 precipitation is 262.3 mm, with 161 mm falling as rain. However, considering that WCRB covers a large

116 elevation gradient, colder temperatures and considerably larger volumes of precipitation have been

117 reported for high-elevation sub-watersheds (Pomeroy et al., 1999; Carey et al., 2013b; Rasouli et al.,

118 2019). The geological setting of WCRB is sedimentary sandstone, siltstone, limestone and conglomerate.

119 Atop bedrock, thick stony till and glacial drift covers most of the basin. Soils in the top metre are generally

120 sandy to silty and at higher elevations (taiga and lower tundra ecozones), a veneer of surface organic soils

121 with variable thickness predominate. Permafrost underlies much of the basin (~43 %), particularly at

122 higher elevations and on north-facing slopes in the taiga and alpine ecozones (Lewkowicz and Ednie,

123 2004).

124 Much of this study focussed on the headwater catchment of Granger Creek (GC), which drains an area of

125 7.6 km^2 and ranges in elevation from 1355 to 2080 m a.s.l. (McCartney et al., 2006; Carey et al., 2013a)

126 (Fig. 1). GC is above treeline (~1200 m) and is dominated by Willow (*Salix* Sp.) and Birch (*Betula* Sp.)

127 shrubs at lower elevations with dwarf shrubs, lichen and bare rock above 1500 m. South facing slopes

128 have a thin organic layer overtop sandy soils whereas north slopes have thicker organic layers (10-30 cm)

129 and are underlain with discontinuous permafrost. A wide riparian zone (50 to 100 m) with a consistently

130 high water table in the lower reaches of GC lies between the slopes. Buckbrush Creek (BB, 60°31'18.01"

131 N, 135°12'17.27" W), another headwater catchment, drains an area of 5.75 km^2 and is located

132 approximately 2 km west of GC (Fig. 1). BB ranges in elevation from 1324 to 2080 m a.s.l. with similar

133 physiographic characteristics to GC. However, Buckbrush Creek is less incised than GC and the riparian

134 zone shows evidence of multiple overbank channels during high flow events.

135 The site Wetland 1 (W1, 60°31'18.72" N, 135°11'34.71" W) is located at the edge of a wetland complex

136 located downstream of BB with an indeterminate drainage area. The vegetation is dominantly sedges,

137 with ponded water covering 200 m^2. Coal Lake (CL, 60°30'36.65" N, 135° 9'44.47" W) is a long-term

138 hydrometric station located approximately at the mid-point in the watershed at the outlet of an ~1 km^2

139 lake (Rasouli et al., 2019). A large wetland complex is located upstream of CL, which is surrounded by

140 steep slopes and vegetation that transitions from boreal forest at lake level to alpine tundra at the top of
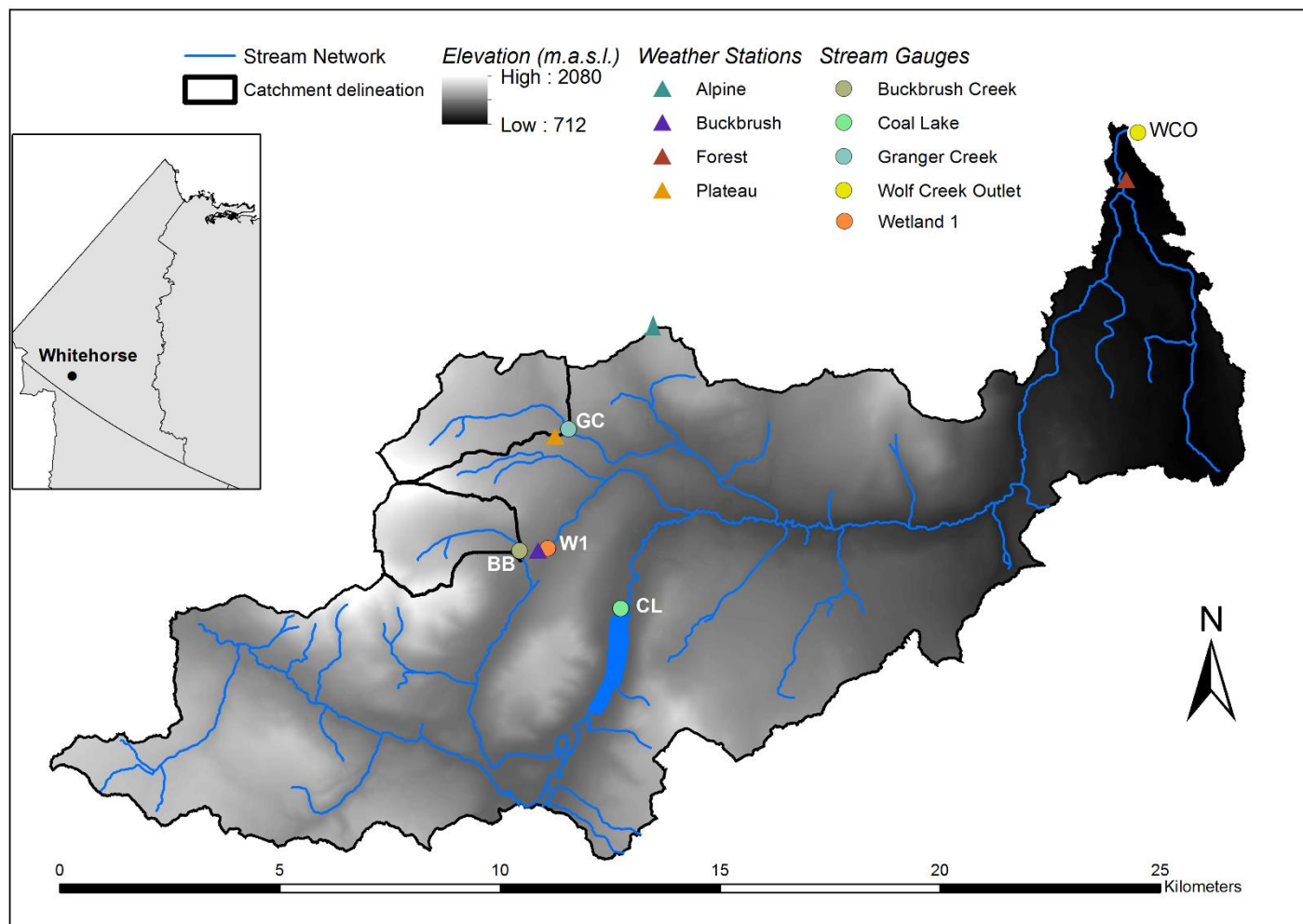
141 surrounding slopes.

Figure 1. Map of Wolf Creek Research Basin (WCRB) with BB and GC catchments delineated. All stream gauges (BB, GC, CL, W1 and WCO) are indicated by circles; weather stations within WCRB are shown as triangles.

142

2.2. Field measurements

143

144 Discharge was measured using rating curves developed for each study season at all sites except the WCRB

145 outlet (WCO) and CL, which has retained a stable curve for the past several years (discharge

146 measurements at the WCRB outlet exist from 1992). Stilling wells at each site were instrumented with

147 Solinst Levelloggers and compensated with adjacent Solinst Barologgers measuring stage/pressure every

148 15 minutes to provide continuous flow records. Manual flows were taken frequently using a SonTek

149 Flowtracker during high and low flows with salt-dilution gauging during periods when the channels were

150 beneath ice.

151 WCRB has three long-term weather stations to characterize the climate in each ecozone. All radiation

152 components, air temperature, wind speed, vapour pressure and total precipitation are measured year-round

153 at each site with some gaps due to power loss (Rasouli et al., 2019). Concomitant measurements of soil

154 temperature and moisture exist at each site. Monthly snow courses are completed in each ecozone to

155 determine snow water equivalent (SWE), and on-site continuous measurements supplement these and

156 provide information on melt rates. A fourth meteorological tower (Plateau) in GC watershed has been

157 operating since 2015.

158 **2.3 Surface water sample collection and preparation**

159 Surface water samples were collected from April 2015 to December 2016, with the bulk of collection

160 between April and September of each year with most samples collected at GC and frequent sampling at

161 BB and WCO. Only a few samples were taken at W1 from 2015 to 2016. For DOC, samples were field

162 filtered with single use plastic syringes submersed in the sample water immediately prior to sampling.

163 Water was displaced through a 0.45 µm VWR polyethersulfone syringe filter and collected in a 60 ml

164 opaque amber HDPE bottle. Duplicates were taken approximately every 10 samples. All samples were

165 kept cool and out of direct light before being shipped for analysis. DOM water samples were filtered in

166 situ and stored cool in 40 ml glass amber vials.

2.4 DOC and DOM fluorescence analysis

Water samples were sent to the Biogeochemical Analysis Service Laboratory (University of Alberta) for analysis on a Shimadzu 5000A TOC analyzer for DOC concentration. In total, 330 surface water samples were collected from 2015 to 2016 as outlined in Table 1. Of the 330 DOC samples, ~215 were analysed for DOM quality using fluorescence spectroscopy. Seven additional samples from CL in 2017 were analysed for DOC concentration and DOM quality.

Fluorescence excitation emission matrices (EEMs) were obtained from 0.45 µm filtered water samples using a Yvon Jobin Aqualog Benchtop Spectrofluorometer (HORIBA Scientific, Edison, NJ, USA). Fluorescence spectra were recorded at an excitation range of 240-600 nm in steps of 5 nm with an emission range of 212-620 nm, in steps of 3 nm. The integrated Raman spectrum was checked before each run and compared to prior values to ensure consistent lamp intensity. Fluorescence spectra were normalized to the area under the Raman scatter peak (peak excitation wavelength 397 nm) of a sealed Milli-Q water sample prior to all sample runs. Scatter from the Raman Milli-Q sample was subtracted from each sample fluorescence spectrum. The correction and normalization of samples to the Raman standard resulted in normalized intensity spectra being expressed in Raman units (R.U., nm^{-1}).

Blank subtraction, Rayleigh scatter and inner filter effects were corrected using the Aqualog(R) software. Subsequent EEM corrections and smoothing were done using the DrEEM toolbox (Murphy et al., 2013) in Matlab (Mathworks Inc., Massachusetts, USA). Results were considered comparable to each other since all data were collected from a single instrument and the Raman standard emission intensity was verified for each data run.

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187 Optical data obtained from the Aqualog(R) was used to calculate fluorescence indices. $SUVA_{254}$ (L mg

188 C^{-1} m^{-1}) is calculated as UV absorbance at 254 nm (m^{-1}) divided by DOC concentration (mg L^{-1})

189 (Weishaar et al., 2003) with a unit correction based on the cuvette path length. $SUVA_{254}$ is commonly

190 reported along with DOC concentration and is used to determine the degree of aromaticity in bulk DOM

191 (Weishaar et al., 2003). Higher $SUVA_{254}$ values (sometimes greater than 6.0 L mg C^{-1} m$^-$1) indicate more

192 aromatic carbon with a strong terrestrial signal (Jaffé et al., 2008) or potential absorption at 254 nm due

193 to colloids or iron (Weishaar et al., 2003; Hudson et al., 2007). Research in northern peatlands associated

194 peat soil leachates with relatively lower $SUVA_{254}$ values of 3.0 L mg C^{-1} m^{-1} (Olefeldt et al., 2013).

195 ~~Autotochtonou~~s or modified terrestrial DOM (microbial and soil-derived DOM) is associated with

196 decreased aromaticity and a lower $SUVA_{254}$ value. The biological index (BIX) is the ratio of emission

197 intensities at 380/430 nm at an excitation wavelength of 310 nm (Huguet et al., 2009). Higher BIX values

198 indicate greater autotrophic productivity (Huguet et al., 2009) or greater relative freshness of bulk DOM

199 (Wilson and Xenopoulos, 2009) while lower values indicate older, more terrestrial DOM. The

200 fluorescence index (FI) is calculated as the ratio of fluorescence emission intensities at 470/520 nm at an

201 excitation wavelength of 370 nm (Cory and McKnight, 2005). FI is used to differentiate between DOM

202 derived from microbial sources (1.7-2.0) or higher terrestrial plant sources (1.3-1.4) with intermediary

203 values indicative of mixing (McKnight et al., 2001; Jaffé et al., 2008; Fellman et al., 2010). Typical values

204 reported for inland rivers are between 1.3-1.8 (Brooks and Lemon, 2007).

205 In addition to the DOM quality indices reported and discussed throughout this paper, absorbance at 254

206 nm (A254), the freshness index (Parlanti et al., 2000) and the modified humification index (HIX: Ohno,

207 2002) were also calculated and compared with the other indices. BIX and the freshness index were highly

208   correlated (r^2 : 0.99, p<0.001) for all sites, years and seasons. A254 and DOC concentrations also showed

209   high correlation (r^2 : 0.95-7, p<0.001). Due to similarity in temporal trends of DOM indices, HIX was not

210   reported independently of the parameters mentioned above. HIX is calculated by summing the peak area

211   under emission intensities from 435-480 nm divided by that of 300-345 nm at an excitation of 254 nm

212   (Zsolnay et al., 1999). Higher HIX values are related to an increased degree of humification (Huguet et

213   al., 2009; Fellman et al., 2010).

214   **2.5 Statistical analysis**

215   General descriptive statistics including the mean and standard deviation were calculated for DOC,

216   $SUVA_{254}$ and the fluorescence indices and compiled in Table 1. To better assess differences between

217   landscape units (e.g. headwaters, wetland, lake, catchment outlet), principal component analysis (PCA)

218   was performed using DOC concentrations and optical indices (i.e. FI, BIX, Freshness, HI, $SUVA_{254}$).

219   These variables were scaled and then standardized into a covariance matrix to avoid larger magnitudes

220   exerting greater influence than smaller magnitudes.

Year	Sites	DOC (mg/L)			SUVA$_{254}$			BIX			FI		
		Spring	Summer	F/W	Spring	Summer	F/W	Spring	Summer	F/W	Spring	Summer	F/W
2015													
	BB	2.44±0.98(5)	1.25±0.31(11)	1.19±0.39(9)	3.30±0.58(3)	3.88±0.55(4)	2.72±0.42(2)	0.55±0.04	0.60±0.01	0.60±0.03	1.49±0.06	1.54±0.03	1.57±0.76
	GC	2.89±2.29(52)	1.07±0.21(36)	1.75±0.76(17)	3.21±0.84(22)	3.81±0.75(14)	2.42±0.33(3)	0.69±0.06	0.60±0.02	0.65±0.02	1.52±0.06	1.54±0.04	1.57±0.04
	W1	15.8(1)			3.94(1)			0.468 (1)			1.46(1)		
	WCO			1.79±0.90(14)			2.21±0.17(10)			0.66±0.03			1.62±0.03
2016													
	BB	2.34±0.87(14)	1.42±0.27(23)	1.50±0.20(3)	3.56±0.48(10)	2.81±0.59(16)	2.45±0.28(3)	0.513±0.03	0.58±0.03	0.62±0.02	1.45±0.04	1.52±0.06	1.52±0.00
	GC	4.32±2.56(43)	1.71±0.34(32)	2.00±0.57(20)	3.86±1.40(37)	2.86±0.38(17)	3.14±0.32(11)	0.513±0.06	0.58±0.03	0.60±0.04	1.45±0.04	1.50±0.04	1.50±0.02
	W1	6.7(1)	7.37±0.64(10)	6.95±0.21(2)	4.77(1)	4.04±0.60(7)		0.58(1)	0.63±0.05		1.58(1)	1.54±0.04	
	WCO	2.69±0.80(18)	2.58±0.44(22)	2.35±0.35(3)	2.83±0.42(12)	2.70±0.28(19)	2.69±0.11(2)	0.582±0.04	0.60±0.02	0.66±0.03	1.53±0.02	1.54±0.03	1.55±0.01

Table 1. Summary statistics for DOC, SUVA, BIX and FI at all sites over 2015-6. Seasons are separated with spring (15 April - 15 June); Summer (16 June - 15 August); Fall/Winter (16 August - 14 April).

221

13

222

223 The PCA was performed using R software version 3.4.0 (R Core Team 2017) in RStudio with R function

224 princomp(), and packages ggplot2, GGally, ggpubr, lubridate, magrittr, grid, dplyr and tidyr for

225 calculating descriptive statistics, correlations, data manipulation and visualization.

226 **3 Results**

227 **3.1 Climate**

228 For 2015 and 2016, the average annual air temperature as recorded at the Whitehorse airport weather

229 station was 1.4 and 2.4 °C respectively, which is warmer than the 30-year normal (1980-2010). May

230 average monthly temperatures in both years were well above the normal, with an average air temperature

231 of 11.8 °C in May 2015 compared with a normal of 7.3 °C. Average annual air temperatures measured at

232 the Buckbrush weather station (mid-basin) were -0.6 and -0.0 °C respectively for the two years (Fig. 2).

233 Persistent inversions in winter result in warmer temperatures at higher elevations from December through

234 to February. Accurate measurements of total precipitation have not been recorded at Whitehorse airport

235 for several years, limiting long-term context but rainfall values from a nearby (~ 3 km) station were used

236 for 2015-6 as well as rainfall from the Buckbrush weather stations (Fig. 2).

237
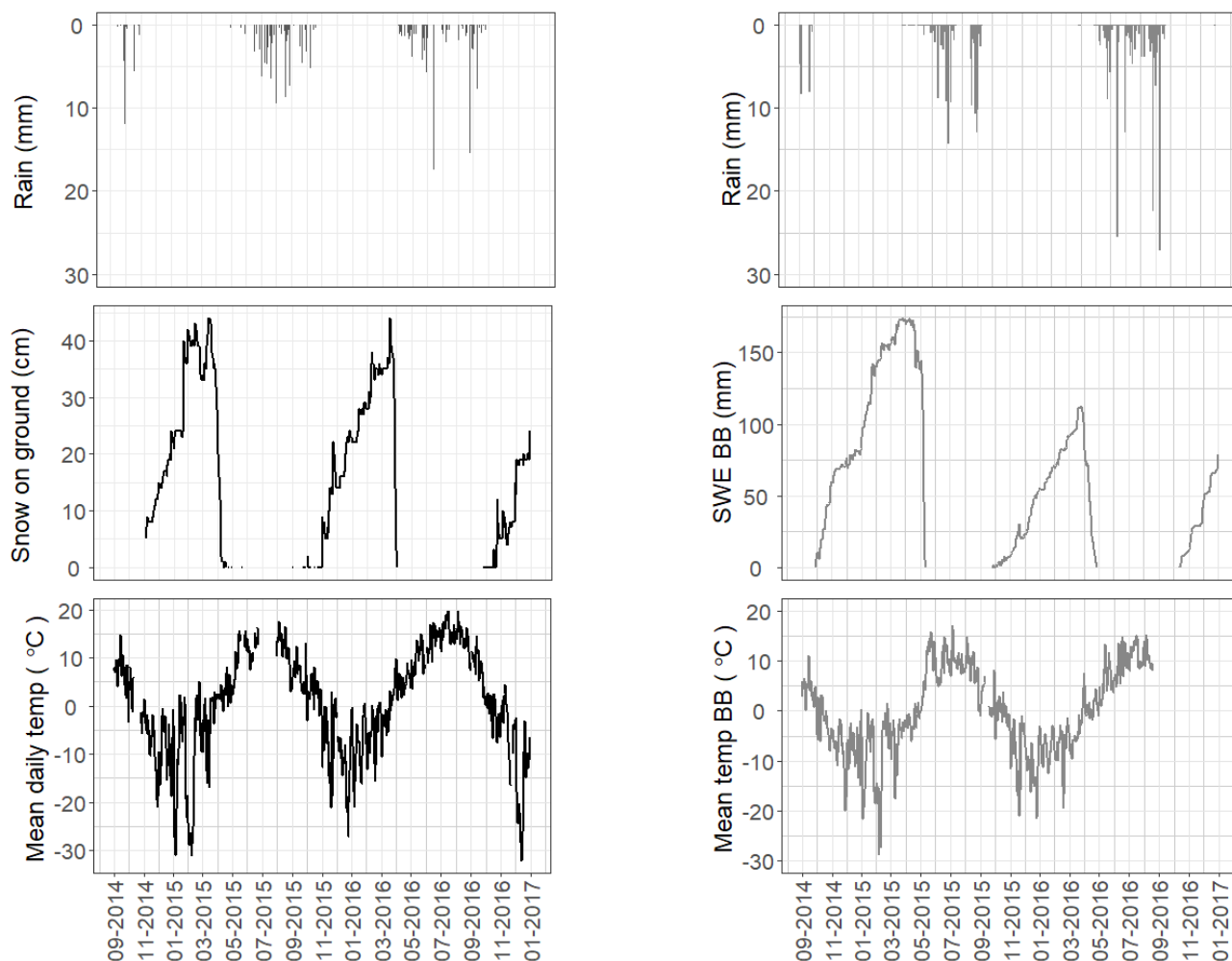
Figure 2. Climate variables from Whitehorse Airport and Buckbrush weather stations. (Left) Rain (measured in mm), snow on ground (in cm) and mean daily air temperature (°C) from the Environment Canada Airport weather station (YXY, Climate ID: 2101300). (Right) Rain measurements were summed to daily totals in mm, snow water equivalent (SWE) in mm ~~was taken as the cumulative total~~ based on 3 hour measurements from a snow pillow beside Buckbrush weather station. 30 minute air temperature measurements were averaged to get daily values.

3.2 Discharge

The 2015 and 2016 hydrographs for GC and the Wolf Creek outlet (WCO) exhibited patterns typical of

northern watersheds but were distinct in that both years have a late-season increase (Fig. 3), which is rare

247   in the GC and WCO historical record (Carey et al., 2013a,b; Rasouli et al., 2019). Summer flows were

248   also greater than typically observed. For GC, in 2015 while there was an early measurable stream response

249   on 9 May, freshet began on 14 May when flows increased from ~0.02 m^3s^{-1} to daily flows averaging ~0.5

250   m^3s^{-1} over 9 days. Peak 2015 daily discharge was 0.67 m^3s^{-1} on 22 May, thereafter flows began to decline

251   to summer levels ~0.2 m^3s^{-1}. In response to ~125 mm of rain between 17 August and 11 September, flows

252   increased to ~0.46 m^3s^{-1} on 14 September before gradually declining. Discharge at BB for 2015 and 2016

253   were slightly lower magnitude than GC with delayed flow response to both freshet and summer rainfall.

254   Data loss resulted in incomplete discharge data for both years at BB. Manual measurements are shown in

255   Fig. 3 to supplement continuous measurements. Discharge at WCO followed a similar pattern to GC,

256   rising from a winter baseflow of ~0.4-0.5 m^3s^{-1} on 3 May to a peak freshet of 2.68 m^3s^{-1} on 24 May. As

257   with GC, flows increased in September prior to the removal of the transducer on 1 October.

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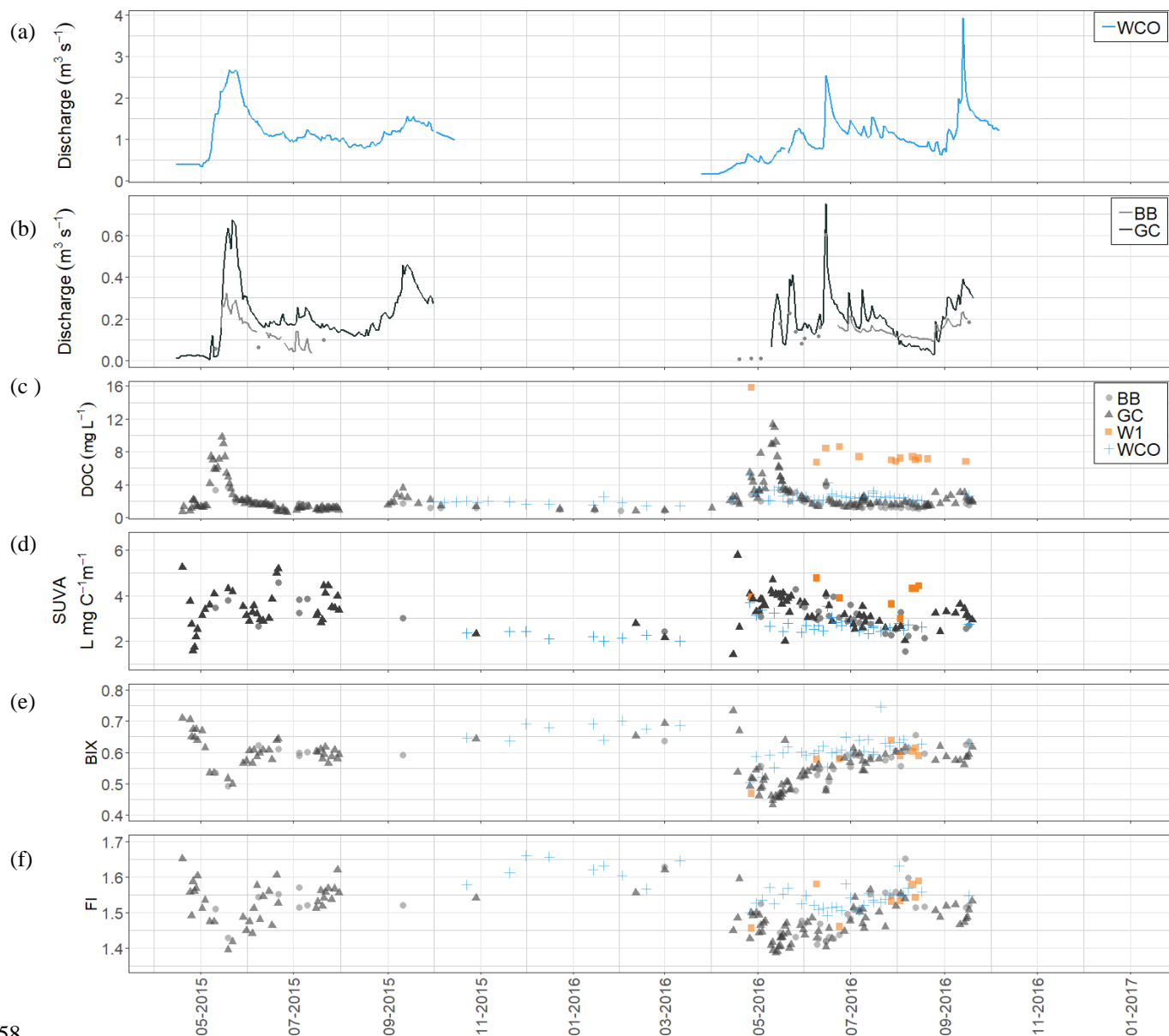
Figure 3. Flow, DOC and fluorescence indices for WCRB study sites. (a) Daily discharge data from WCO shown from April 2015 to October 2016. (b) Daily discharge data from GC (dark grey) and BB (light grey). (c) DOC concentrations in mg/L from grab samples over the study period with BB (light grey, circle), GC (dark grey, triangle), Wetland 1 or W1 (orange, square), WCO (light blue, +).

Flows in 2016 were distinct at both GC and WCO compared with 2015 and the historical record, and

exhibitied flashier behaviour early in the season (Fig. 3). There was no distinct snowmelt freshet event,

17

265   instead a gradual increase in flows was punctuated with hydrograph rises that corresponded with

266   snowmelt and summer rainfall events. Flows were of the same general magnitude to those in 2015, and

267   once again large late season rainfalls (~115 mm between 17 August and 10 September) resulted in high

268   September flows, with peak discharge at WCO of 3.9 m^3s^{-1} recorded on 13 September. Flows declined

269   again until the transducers were removed on 17 October, yet were very high compared with mid-season

270   flows.

3.3 Dissolved Organic Carbon (DOC)

272   DOC was sampled over two years at four sites: GC, WCO, BB and W1, a wetland complex in the taiga

273   ecozone near the Buckbrush tower (Fig. 1). Sampling in 2015 was largely confined to GC and BB with

274   more extensive sampling at other sites in 2016. For GC, similar patterns were observed in both years with

275   over-winter and pre-freshet DOC concentrations below 1 mg L^{-1} and rising to ~10 mg L^{-1} on the rising

276   limb of the first snowmelt flush followed by a rapid decline to levels between 1 and 2 mg L^{-1} throughout

277   the summer and with a slight rise in the fall. Seasonal statistics for DOC are presented in Table 1. In 2015,

278   the single freshet event corresponded with the rise in DOC, yet the rise and fall in DOC concentration

279   occurred fully on the rising limb of the freshet hydrograph between 7 May and 29 May. The maximum

280   DOC concentration of 9.8 mg L^{-1} on 15 May corresponded to a 13.8 mm rain event atop a sporadic

281   snowpack with largely frozen soils. After June, DOC concentrations continued to decline with slight

282   increases corresponding to rainfall events. Towards the end of the measurement period in 2015, DOC

283   concentrations rose to a maximum of 3.6 mg L^{-1} with increasing discharge in response to sustained

284   precipitation. Over-winter values in December and January declined to ~1 mg L^{-1}. This pattern of DOC

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285 behaviour was remarkably similar at the adjacent BB catchment which had more limited sampling. In

286 2016, the spring rise in DOC at GC and BB corresponded to the period immediately after the first small

287 snowmelt pulse but prior to the bulk of the freshet signal (Fig. 3). Concentrations again rose to ~11 mg

288 L^{-1} with a steep recession to summer levels where rainstorms would occasionally increase concentrations

289 above 2 mg L^{-1}. As in 2015, a wet late season with a large hydrograph increase resulted in increased DOC

290 concentrations near 3 mg L^{-1} but concentrations were much less than for corresponding freshet flows.

291 Sampling at WCO began in late fall 2015 with DOC concentrations of ~2 mg L^{-1} and remained near this

292 level through April 2016. Concentrations increased during the early phases of open water freshet, yet only

293 rose to ~5 mg L^{-1} on 26 April and then declined to summer levels between 2 and 3 mg L^{-1}, with some

294 variability related to rainfall events. While sampling was limited, there did not appear to be a notable

295 increase at WCO during the wet fall in 2016. At W1, DOC was ~16 mg L^{-1} on the first sampling date of

296 27 April, and then post-freshet samples in June through September had concentrations between 7 and 9

297 mg L^{-1}. Concurrent DOC and fluorescence samples were only collected from CL post-freshet during

298 summer and fall of 2017.

299 **3.4 Fluorescence Indices**

300 While there exists a large number of fluorescence indices in the literature (see Hansen et al. 2016), in this

301 work we report the widely utilized SUVA$_{254}$, biological index (BIX) and fluorescence index (FI) to help

302 infer the source and composition of DOM (Table 1).

303 For GC, SUVA$_{254}$ exhibited considerable variability compared with DOC concentrations. In 2015,

304 SUVA$_{254}$ declined from > 5 to ~ 1 L mg C^{-1} m^{-1} rapidly between 19 and 26 April in response to loss of

305 channel ice, and then rose to reach a local maximum of ~4.1 L mg C^{-1} m^{-1} on 10 May that corresponds to

306 the annual peak in stream discharge. $SUVA_{254}$ then declined on the receding freshet limb yet increased

307 markedly in June in response to 18 mm of rain (11 to 18 June), whereupon it ranged between 2.8 and 4.5

308 L mg C^{-1} m^{-1}. Limited under-ice sampling suggests $SUVA_{254}$ remained relatively consistent between 2

309 and 3 L mg C^{-1} m^{-1} before falling to 1 L mg C^{-1} m^{-1}, prior to the onset of freshet when values rose

310 dramatically to 5.2 L mg C^{-1} m^{-1} before gradually declining through August with considerable variability.

311 Following the wet fall in 2016, $SUVA_{254}$ began to rise to values > 3 L mg C^{-1} m^{-1}. Patterns of $SUVA_{254}$

312 for BB were similar to GC in both years. $SUVA_{254}$ started low in spring 2015 at the headwater catchments

313 before rising slightly in summer whereas the opposite occurred in 2016. For WCO, samples over the

314 2015-16 winter declined slightly from 2.5 to 2 L mg C^{-1} m^{-1}, and then during freshet increased to ~3.7 L

315 mg C^{-1} m^{-1} and then gradually declined to ~2.5 L mg C^{-1} m^{-1} with some increases associated with rising

316 discharge. $SUVA_{254}$ at W1 was on average higher compared with other sites, although limited sampling

317 makes it uncertain as to any temporal pattern.

318 BIX tended to be inversely related to discharge (and DOC concentration) during freshet at the headwater

319 sites (GC, BB) (Fig. 3). For GC in 2015, BIX fell from just above 0.7 to 0.49 during peak freshet and then

320 increased to between 0.55 and 0.65 during summer. Values increased over winter to a maximum of 0.71

321 prior to 2016 freshet where a steep decline to values < 0.45 occurred during the early phase of runoff in

322 May and then gradually returned to values between 0.55 and 0.65 with declines associated with rainfall-

323 driven spikes in the hydrograph. The late season increase in discharge did not strongly influence BIX at

324 GC. BIX exhibited inconsistencies between 2015 and 2016 at the headwater sites with lower spring values

325 in 2016 and an increase in summer whereas 2015 showed a decrease during summer to lower or 'older'

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326 values. BIX for WCO increased over winter before also declining during early melt in 2016 and then rose

327 to values ~0.65 with some large increases (as opposed to decreases at GC) during storm events. Timing

328 of declines to rainfall events was slightly offset between the headwater sites and the outlet WCO. At W1,

329 BIX values increased slightly throughout the sampling period in 2016 (Fig. 3).

330 FI at GC and BB exhibited patterns similar to BIX but inverse to $SUVA_{254}$ (Fig. 3). In 2015, FI declined

331 from 1.65 to 1.4 as DOC rose on the rising freshet limb, and then declined to values between 1.5 and 1.6

332 during summer. In 2016, FI values again declined from 1.6 to 1. during freshet yet were on average lower

333 than 2015 but also gradually increased throughout summer with a small decline during the wet late

334 summer. For WCO, winter FI ranged between 1.55 and 1.65 and more gradually declined during freshet

335 to ~ 1.5 and then increased slightly with more limited variability throughout the summer. A small decline

336 during the wet period in late September was observed. Over the two study years at GC, BB and WCO,

337 mean FI was lowest during spring, and higher in summer (2015, 2016) than in fall 2016. For W1, FI was

338 low at 1.45 on the first sampling date in spring 2016 when DOC was high, and then increased with some

339 variability but values were on average greater than those at GC and BB.

340 3.3 Principal Component Analysis

341 A principal component analysis (PCA) using 216 samples from across WCRB over three years was

342 completed to explore landscape and seasonal climate controls on DOC concentration and quality (Fig. 4).

343 DOC concentrations and fluorescence indices at BB (2015-7), CL (2017), GC (2015-7), W1 (2016-7) and

344 WCO (2015-7) were introduced into the PCA for insight into how landscape type influences DOM quality

345 at WCO (Table S1). The first principal component (PC1) explained 56.8 % of the variance in the data and

346 was selected based on screeplot analysis, a drop in the proportion of variance explained and the Kaiser

347 criterion (Kaiser and Rice, 1974). The remaining principal components (PCs) explained much less of the

348 variance than PC1. PC1 predominantly represents the relationship among DOM quality and concentration

349 and is positively and negatively correlated with all DOM fluorescence indices except for HIX. PC2

350 explained 15.8% of the variance and was most closely related to a single variable (HIX) with little

351 relationship to the other analytes (Fig. 4). Further PCs were not explored.
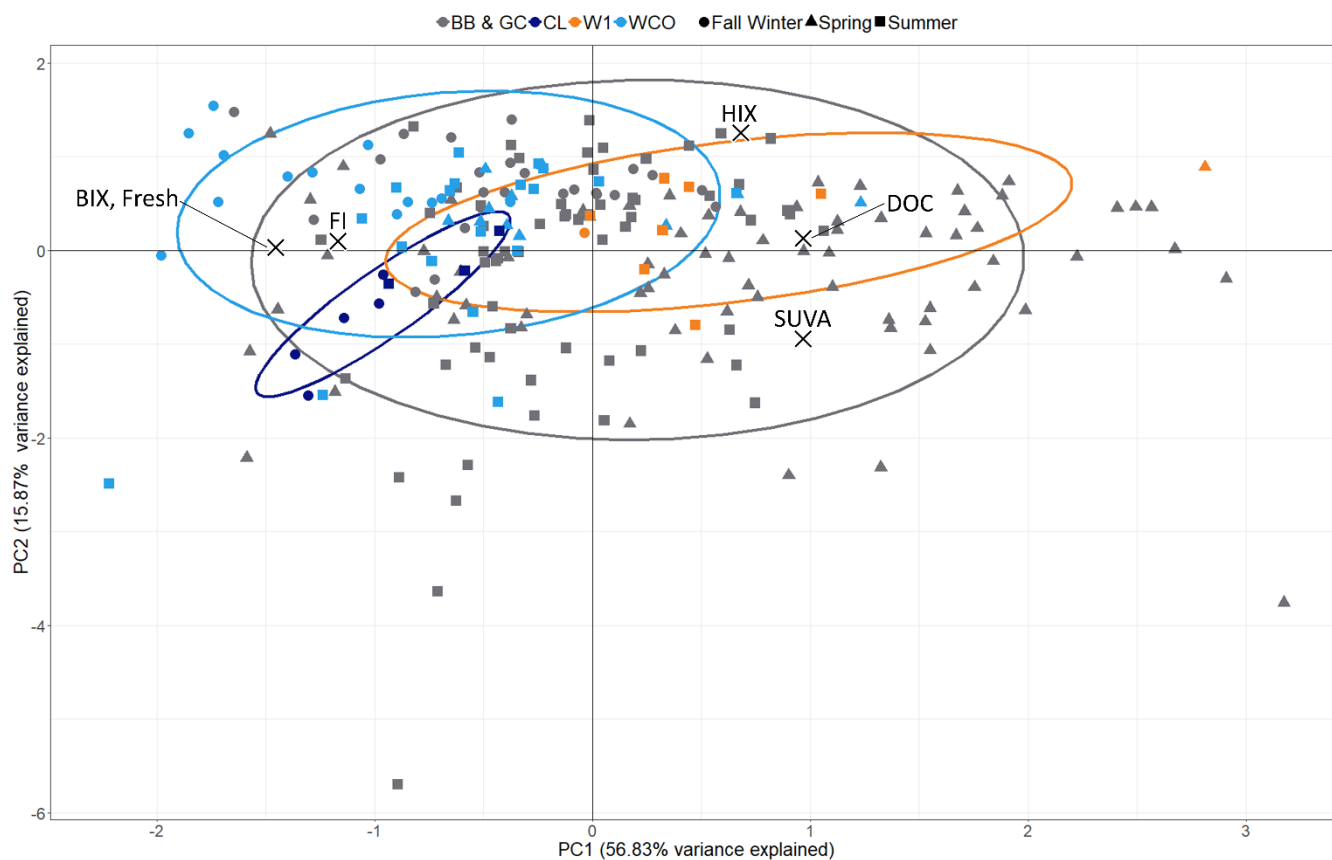
352

353 **Figure 4.** Biplots from PCA. Ellipses represent 0.8 probability of sample values being within the shape.

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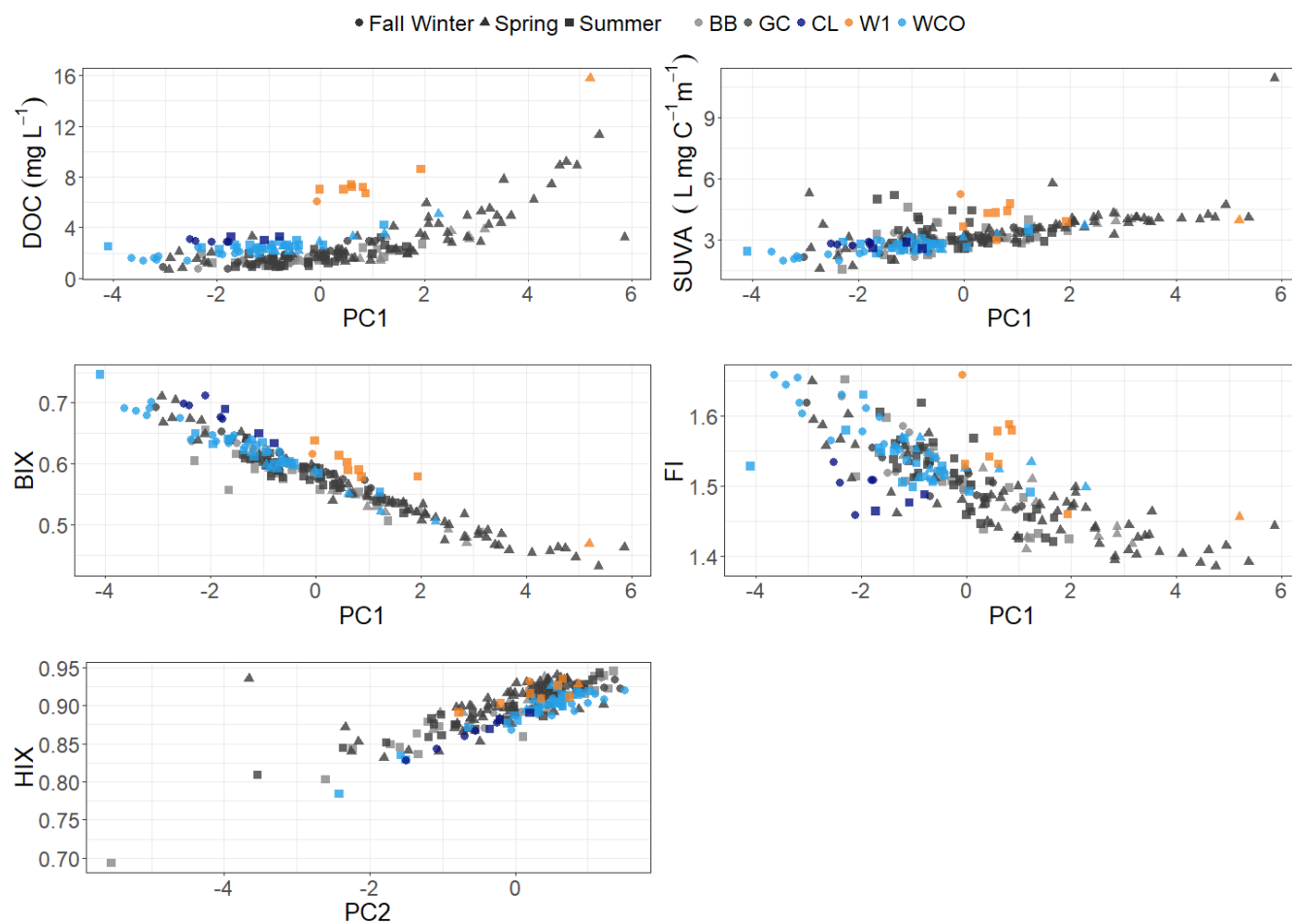
Figure 5. Regressions of principal components to DOC concentrations and DOM indices. Regression of PC1 to DOC concentrations implies some non-linear behaviour. Samples are grouped by season: Triangles = Spring (15 April-15 June); Squares = Summer (16 June-15 August); Circles = Fall/Winter (16 August-14 April). Samples are also grouped by landscape type: Bright blue = Mesoscale outlet (WCO); Dark blue = Lake (CL); Orange = Wetland (W1); Grey = Headwaters (light grey – BB, dark grey – GC).

BB and GC plotted similarly and are shown together (Fig. 4) to highlight differences between the landscape types rather than between the two headwater sites. DOC concentrations and SUVA$_{254}$, BIX/Freshness and HIX most strongly distinguish the samples in the PCA. Spring samples from the headwaters and wetland plot mostly to the right along PC1 due to high DOC concentrations and SUVA$_{254}$ measured during that time period. Headwater samples span almost the entire PC1 axis due to the high

366 variability in spring-time DOC and streamflow. Fall/winter samples are predominantly located left of the

367 zero-line (Fig. 4) for all sites. All CL samples cluster together. Some separation of DOC concentrations

368 and DOM indices is shown due to high DOC, BIX and/or SUVA$_{254}$ values (Fig. 6).

369

370 **4 Discussion**

371 **4.1 DOC quantity and timing in streams**

372 The most distinct feature of OC export in northern watersheds is the sudden increase in DOC

373 concentration on the rising limb of the freshet hydrograph (Striegl et al., 2005; Raymond et al., 2007;

374 Holmes et al., 2012). This is particularly well resolved in headwater catchments where there is limited

375 mixing of signals and sources (Ågren et al., 2007). For GC, DOC concentrations have now been observed

376 over freshet for six years (2002, 2003, 2006, 2008, 2015, 2016 - see Carey et al., 2013a; Fig. 4 for data

377 on early years). There is a considerable variability in freshet timing and volume as some years show a

378 single, rapid event (e.g. 2015) while others have a staggered response in relation to multiple spring

379 warming events (e.g. 2003, 2016). Regardless of freshet timing and volume, DOC concentrations always

380 rise in response to the first onset of flows and are insensitive to the volume of water exported during

381 freshet. While there are notable contrasts in both 2015 and 2016 freshets, in both cases, the initial DOC

382 response to flows is similar (Fig. 3), and corresponds with those reported in earlier years. The implication

383 of these historical and recent observations is that while DOC exported during spring is hydrologically

384 mediated via the transport pathways, DOC concentrations are not related to flow volumes at the headwater

385 scale. Although investigation into headwaters is relative rare (Bishop et al., 2008), studies have reported

386 greater variation in DOC at the headwater scale than in large rivers (Sedell and Dahm, 1990; Wolock et

387 al., 1997; Temnerud and Bishop, 2005; Temnerud et al., 2010). Relatively small amounts of water are

388 sufficient to extinguish the available pool of OM responsible for DOC peak concentration in the spring

389 at this headwater catchment. For GC, estimates of DOC export between 15 April-15 June over the six

390 years range between 0.46 and 1.49 mg C m^{-2} with 2015 and 2016 on the lower end. For WCO, the pattern

391 of DOC during freshet was similar to GC, yet dampened with lower values during freshet over a longer

392 period from mixing of various landscapes that integrate three distinct ecosystems and a small lake over a

393 large elevation range.

394 Following freshet, DOC was remarkably consistent across the sampling sites. The headwater GC and BB

395 values were ~1.5 mg L^{-1} whereas those at WCO were typically 2-3 mg L^{-1}, suggesting that additional

396 sources such as wetlands and Coal Lake contributed slightly to downstream increases in DOC. There

397 were small increases in DOC concentration associated with rainfall events. A notable feature of both 2015

398 and 2016 were the substantial late season rains that generated flows outside the typical range at both GC

399 and WCO (Fig. 5). Despite these large flows, DOC concentrations did not rise to the levels observed

400 during freshet, suggesting either alternate runoff pathways/flow generation mechanisms or a reduced

401 source of soluble OM in soils available for transport. Considering water tables were very high during this

402 period, we presume that the available pool of OM in shallow organic layers was less than in spring.

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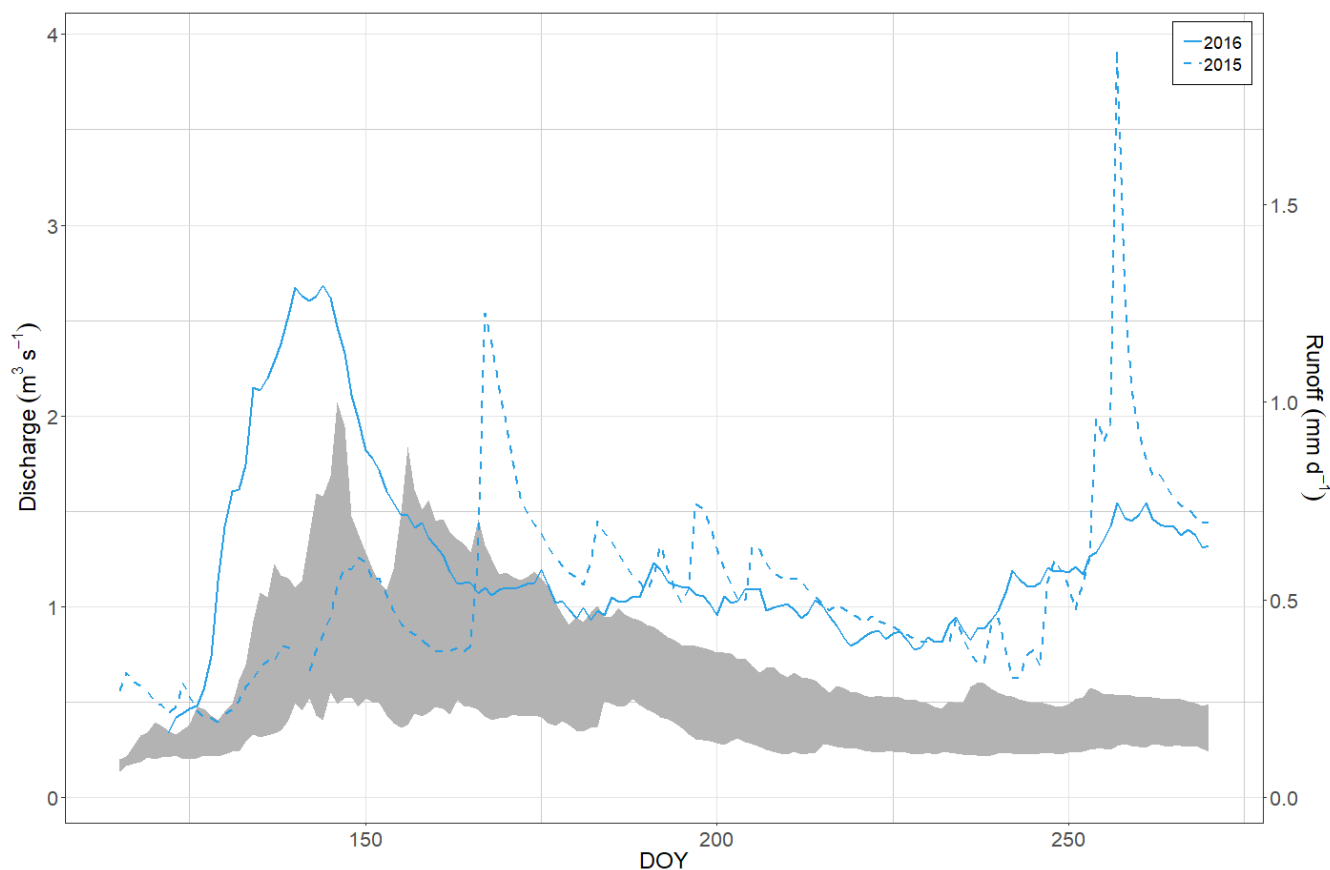
Figure 6. Historical flow at WCO with 2015-6 flows superimposed. Grey area represents inter-quartile range of 1993-2013 data. Dashed line = 2015; Solid line = 2016. Day of year along x-axis.

Unlike results elsewhere (Petrone et al., 2006, 2007; Raymond et al., 2007; Striegl et al., 2007; Balcarczyk et al 2009; Prokushkin et al., 2011; Holmes et al., 2012), there is no robust relationship between discharge and DOC over multiple years or within single years, suggesting that for this environment and at the headwater scale, discharge is a poor predictor of DOC on an annual basis at the GC catchment. However, on a seasonal basis, the relationship between DOC and discharge was stronger, particularly for summer, fall and winter when concentrations were relatively low. We caution the use of regression equations relating DOC and flow to predict DOC loads, at least on an annual basis. However, for larger streams

26

413 such as WCO, this approach may be more tractable due to mixing of sources and process integration

414 (Buffam et al., 2007; Creed et al., 2015; Peralta-Tapia et al., 2015a).

415 A curious result was a notable decline in freshet DOC concentrations between the four years in the 2000s

416 (Carey et al., 2013a) and the 2015-2016 study years. In each of the early years, peak DOC concentrations

417 ranged between 17 and 27 mg L^{-1} with overall higher concentrations during freshet, whereas the

418 maximum DOC values for GC were 9.5 and 11.3 mg L^{-1} in 2015 and 2016, respectively. The reason for

419 this decline is uncertain, yet is not related to freshet conditions as flows and climate during freshet were

420 similar among certain years. We have also largely ruled out instrumentation or sampling as a source of

421 this difference as mid-season values were unchanged. Tiwari et al. (2018), using 23 years of data from

422 the Krycklan research catchment in central Sweden, suggest that peak DOC concentrations are most

423 closely related to warm fall temperatures, cold winter conditions and shallow snowpacks. In addition,

424 Ågren et al. (2010a) used 15 years of data from boreal catchments also located in the Krycklan research

425 catchment to show that high export of DOC in the snow-free season led to decreased export in the

426 subsequent year. For six years of data at GC catchment, winter (Nov-Mar) temperatures show a weak

427 correspondence with DOC export, in that warmer winters tend to have lower DOC export during the

428 following spring, which is supported by Scandinavian research (Ågren et al., 2010a,b; Haei et al., 2010).

429 However, there was no relation between snow depth and peak DOC concentration for the six years. A

430 final possibility may be that increased summer and fall wetness that has occurred in recent years is

431 reducing decomposition as outlined by Balacarcyzk et al. (2009).

432 **4.2 DOM indices in streams**

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433 Optical indices are closely aligned with seasonal hydrological patterns in northern rivers across scales

434 (Neff et al., 2006; Striegl et al., 2007; Spencer et al., 2008; Holmes et al., 2012). An expanding knowledge

435 base linking optical indices with OM sources and biodegradability (Balcarczyk et al., 2009; Kellerman et

436 al., 2018) and catchment processes exists with observations from both temperate and northern study sites.

437 A number of widely-used indices (reviewed in Hansen et al. 2016) facilitate comparison among sites, and

438 chemometric components through the ever-expanding library OpenFluor (http://www.openfluor.org). We

439 applied the widely used drEEM toolkit (Murphy et al., 2013) to our dataset, yet we were unable to validate

440 the model using a split-half approach to the dataset. However, the overall relationship between CDOM

441 and DOC is robust in WCRB as observed in other rivers (Stedmon et al., 2011; Spencer et al., 2012; Frey

442 et al., 2015), with a strong relationship between A254 and DOC (r^2: 0.97, p<0.001).

443 The predominant signals in DOM indices observed in WCRB streams correspond well with those reported

444 in the literature for northern and permafrost basins (Walker et al., 2013; Cory et al., 2014), and support

445 conceptual models of coupled runoff generation and DOM transport (Mu et al., 2017). At the onset of

446 freshet and the rise in DOC, SUVA$_{254}$ rises while both BIX and FI decline to annual minima. This freshet

447 response is attributed to the mobilization of DOM derived from leaf litter and older terrestrial precursor

448 material with high molecular weight and aromatic DOM (Wickland et al., 2012). This pattern is

449 particularly clear at GC, where BIX and FI are closely correlated with each other and negatively correlated

450 with SUVA$_{254}$. At this time, near-surface pathways across frozen ground are the only mechanism to

451 rapidly transport OM and water to the stream. Once DOC declines, SUVA$_{254}$ decreases and FI and BIX

452 begin to increase. A number of mechanisms can be attributed to these changes: an increase in more

453 microbial DOM as thaw depths increase and soil temperatures warm, and an increased ability of mineral

28

454   soils to adsorb DOM with high organic weight and large aromatic structures along flow pathways (Ussiri

455   and Johnson, 2004). The gradual change in the three fluorescence indices as summer progresses suggests

456   a continual decline in high molecular weight, older DOM (lower $SUVA_{254}$) and a greater proportion of

457   recently produced DOM. During the unusually wet fall periods, rising water tables and activation of near-

458   surface and overland flow pathways resulted in increases in SUVA and declines in BIX and FI, yet not to

459   the same magnitude as spring when flows were of similar volume. The smaller influence of wet fall

460   periods on changing DOM composition can be explained in part by a much wider range of flow pathways

461   across deeply thawed soils and also considerable adsorption sites for DOM. In addition, sources of leaf

462   decomposition compounds located in upper soil horizons leached in spring have had less time to replenish

463   prior to leaf-fall. As with DOC concentration, the important implication is that seasonality as opposed to

464   flow magnitude has a greater influence on the quality of DOM. By early November, temperatures

465   throughout WCRB are below freezing and a long winter recession occurs. Limited over-winter sampling

466   at WCO and GC show $SUVA_{254}$ values declining to their lowest values prior to freshet with a

467   corresponding maxima in BIX and FI. This pattern corresponds to those reported elsewhere in the Yukon

468   River Basin and other watersheds in Alaska (Striegl et al., 2007; O'Donnell et al., 2010; Mutschlecner et

469   al., 2018).

470   **4.3 Patterns across space and time**

471   Understanding the integration of biogeochemical signals across temporal and spatial scales is a

472   fundamental challenge in diverse catchments such as WCRB. The link between catchment processes and

473   spatial scale to control coupled hydrological-biogeochemical processes has garnered considerable

474   attention (Ågren et al., 2007; Buffam et al., 2007; Creed et al., 2015; Tiwari et al., 2017). Whereas

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475 flowpaths at the headwater catchments (GC, BB) are well documented (Quinton and Carey, 2008; Carey

476 et al., 2013a), the dominant hydrological pathways at the scale of WCRB shift from the supra- and intra-

477 permafrost pathways to one that is more groundwater driven. In addition, a ~1 km^2 lake in the centre of

478 the basin has an important storage and mixing effect. The impact of these changes on the pattern of DOM

479 indices at WCO is complex and not easily resolved back to component landscape types.

480 From the PCA, a host of controls act to influence DOC and fluorescence indices throughout WCRB (Fig.

481 4, Fig. 6). As scale increases, DOC concentrations increase during summer and low flows yet are more

482 muted during freshet at the outlet compared with headwater streams. WCO had lower $SUVA_{254}$, greater

483 BIX and FI compared with both headwater and wetland systems. The lower $SUVA_{254}$ at WCO

484 corresponds to an increasing dominance of groundwater or greater baseflow along with deeper subsurface

485 pathways due to a lesser extent of frozen ground (Walvoord and Striegl, 2007; O'Donnell et al., 2010). In

486 contrast, higher FI and BIX likely reflect the influence of these deeper flow pathways and any processes

487 and production that occur in Coal Lake, which sits in the approximate mid-point of WCRB. Most FI

488 values at the headwater catchments are between 1.4 and 1.6, reflecting terrestrial plants as the dominant

489 source of DOM. By contrast, values in excess of 1.6 at WCO, particularly during winter and low flow

490 periods, suggest some microbial DOM sources. The high values of BIX in winter at WCO supports some

491 moderate autotrophic production, yet certainly not at the levels of many aquatic ecosystems (Kellerman

492 et al., 2018).

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PCs	DOY	Q ($m^3 s^{-1}$)	Degree days > 0°C	Riparian SM (5-15 cm avg)	Riparian ST (5-15 cm avg)	Midslope SM (5-15 cm avg)	Midslope ST (5-15 cm avg)	Air temp – BB weather station
PC1	-0.26***	-0.11*	-0.36***	0.20**	-0.23***	0.32***	-0.13*	0.23***
PC2	0.081	0.12*	0.14*	-0.032	-0.049	-0.15*	-0.092	-0.19**
PC3	-0.024	-0.019	-0.07	0.28***	0.13*	0.41***	0.22**	0.26***

Table 2. Correlations between principal components (PCs) with DOY (day of year), degree days > 0 Celsius, average riparian soil moisture between 5 to 15cm depth, average riparian soil temperature between 5 and 15 cm depth, average soil moisture at midpoint of north-facing slope between 5-15 cm depth, average soil temperature at the midpoint of north-facing slope between 5 and 15 cm depth and air temperature recorded at the BB weather station. *p<0.05, **p<0.01, ***p<0.001

493 Changes in DOC export as a result of climate change in permafrost regions are uncertain for aquatic

494 ecosystems and in the overall carbon balance of northern regions (Striegl et al., 2005, 2007; Raymond et

495 al., 2007; Frey and McClelland, 2009; Guo et al., 2012; Laudon et al., 2013; Kicklighter et al., 2013;

496 Abbott et al., 2015; Johnston et al., 2018). DOC concentration, optical properties and associated

497 biodegradability change with source, residence time and processing, all of which vary with thaw depth

498 (review by Kalbitz et al., 2000; Wickland et al., 2007). Results from this work compare well with others

499 in permafrost regions that are not experiencing rapid thermokarst, suggesting a gradual decrease in

500 biodegradability and changes in DOM likely due to mineralization and adsorption as thaw increases

501 (Striegl et al., 2007; Mu et al., 2017). Whereas most conceptual models have focussed on the implications

502 of thaw and thermokarst on DOM (Mu et al., 2017), in this study we had the opportunity to evaluate the

503 influence of increased late summer and fall precipitation, which is a notable feature in fall across much

504 of subarctic Canada (Spence and Rausch, 2005; Spence et al., 2015; DeBeer et al., 2016). Despite late-

505 season wetness and flow conditions similar to freshet in both years, which is anomalous in the WCRB

506 record (Fig. 5), the change in DOC concentration and DOM indices were small compared to changes

507 observed during snowmelt. Large late-season rain events on deeply thawed soils did not transport the

508 same volume of DOM as freshet despite high water tables due to a depleted DOM source and increased

509 adsorption potential. FI and BIX were typically higher at the outlet than the headwater and wetland sites,

510 which is attributed to lake influences and greater autotrophic production with increasing stream order.

511 While there was an increase in concentrations and a shift to heavier, more aromatic DOM during fall,

512 values were still closer to those experienced during summer baseflow.

513 The implication is that changes in precipitation, particularly in summer, will have a limited influence on

514 changing DOC export and quality compared to changes that result from emergent flow pathways,

515 thermokarst or factors that influence values during freshet. From DOC concentrations that have been

516 measured intermittently over the course of 15 years, we report a recent decline in freshet DOC

517 concentrations at a headwater catchment, which is difficult to reconcile with permafrost thaw (which has

518 not been observed or documented). Possible explanations are warmer winters and winter soils (Haei et

519 al., 2010; Tiwari et al., 2017), or that the increase in fall wetness results in a decline in spring DOC

520 concentrations through a second, albeit smaller, flushing event (similar to Ågren et al., 2010b).

521 **5 Conclusions**

522 This study reports patterns of DOC concentration and DOM quality derived from optical indices over

523 several years in a subarctic alpine watershed where hydrological processes have been studied for

524 approximately two decades. We show that DOC concentration and optical indices have a strong temporal

525 variability associated with seasonality, and that A254 and CDOM were reliable proxies for DOC

526 concentrations. Observations from nested watersheds with drainage areas of ~6 to 179 km^2 indicate that

527 mixing and complex process interactions dampen variability in downstream responses and result in a

528 gradual shift in DOM characteristics. Despite considerable fluctuations among years, DOC concentrations

529 and export are consistently highest during freshet despite differences in timing and magnitude of

530 hydrological response during six years of coupled DOC and discharge measurements.

531 Optical indices also showed the largest variation during freshet and were relatively insensitive to flow

532 volumes despite large differences in freshet between 2015 and 2016. At the headwater scale, DOM is less

533 responsive to rainfall events in summer when the water table descends into deeper mineral soil layers.

534 Mobilization and transport mechanisms operating at the headwater scale are linked to stream

535 hydrochemistry while material inputs from different landscape types causes mixing and dilutes DOM

536 signals at increasing watershed scales.

537 Recent years have shown an increase in late fall streamflow that is uncommon in the long-term

538 hydrometric record that is more often observed across northern watersheds. DOC flux in recent years falls

539 on the low end of the range reported a decade ago.

540 Other factors that have the capacity to influence the availability, movement and export of DOC and DOM

541 are forecasted to change with rapid warming in this environment (DeBeer et al., 2016). Factors at play

542 are a longer growing season, a shift in vegetation community composition and spatial extent, warmer

543 winters, increased baseflow with greater groundwater input, earlier freshet or disruption of the typical

544 northern hydrograph and an altered precipitation regime. Ultimately, watershed scale and the arrangement

545 of landscape types will play important roles in determining how DOC flux and DOM lability change

546 under a warming climate, and altered precipitation, disturbance and vegetation regimes.

547 *Data availability.* Streamflow datasets used for this study are available on the GWF/CCRN database

548 (http://giws.usask.ca/meta/) per the outlined data policy. For DOC/fluorescence, please contact the

549 corresponding author as a data repository is currently being developed.

550 *Competing Interests.* There are no competing interests.

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