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

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Abstract

High latitude environments store approximately half of the global organic carbon pool in peatlands, organic soils and permafrost while large arctic rivers convey an estimated 18-50 Tg C a^{-1} to the Arctic Ocean. Warming trends associated with climate change affect dissolved organic carbon (DOC) export from terrestrial to riverine environments. However, there is limited consensus as to whether exports will increase or decrease due to complex interactions between climate, soils, vegetation, and associated production, mobilization and transport processes. A large body of research has focused on large river system DOC and DOM lability and observed trends conserved across years, whereas investigation at smaller watershed scales show that thermokarst and fire have a transient impact on hydrologically-mediated solute transport. This study, located in the Wolf Creek Research Basin situated ~20 km south of Whitehorse, YT, Canada, utilises a nested design to assess seasonal and annual patterns of DOC and DOM composition across diverse landscape types (headwater, wetland, lake) and watershed scales. Peak DOC concentration and export occurred during freshet per most northern watersheds, however, peaks were lower than a decade ago at the headwater site Granger Creek. DOM composition was most variable during freshet with high A254, $SUVA_{254}$ and low FI and BIX. DOM composition was relatively insensitive to flow variation during summer and fall. The influence of increasing watershed scale and downstream mixing of landscape contributions was an overall dampening of DOC concentrations and optical indices with increasing groundwater contribution. Forecasted vegetation shifts, permafrost thaw and other changes due to climate change may alter DOM sources from predominantly organic soils to decomposing vegetation, and facilitate transport through deeper flow pathways with an enhanced 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 fa^{-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;

Holmes et al., 2012; Tank et al., 2016). While the influence of changing mean annual temperature on DOC production and transport across 49 northern watersheds was summarized by Laudon et al. (2012), northern landscapes are also susceptible to fire and thermokarst. These disturbances have a transient influence on hydrologically-mediated DOC transport that confounds spatial and temporal patterns of DOC flux from terrigenous sources to the river-ocean continuum (Larouche et al., 2015; Littlefair et al., 2017; Burd et al., 2018).

In northern and permafrost landscapes, the link between hydrological and biogeochemical cycles and the role of frozen ground and organic matter has been well documented in process-based studies (e.g. Maclean et al., 1999; Carey, 2003; O'Donnell and Jones, 2006; Petrone et al., 2006; Carey et al., 2013a; Koch et al., 2013; Olefeldt and Roulet, 2014; Burd et al., 2018). While wetlands have been highlighted as a source of DOC, particularly in Scandinavian catchments, in permafrost environments the presence of thermally-mediated flowpaths are critical. DOC export is greatest during snowmelt freshet when DOC from organic rich layers is mobilized, resulting in a large annual 'flush' (Boyer et al., 2000; Carey, 2003; Finlay et al., 2006). As flowpaths descend in response to soil thaw, DOC mobilization typically declines and flow in mineral layers provides more opportunity for immobilization and adsorption (MacLean et al., 1999; review by Kalbitz et al., 2000; Carey, 2003; Kawahigashi et al., 2004, 2006; Frey and Smith, 2005). In some environments, an increase in late fall DOC flux has been ascribed to freezing processes in the soil column (Johnson et al., 2018). How this temporal relationship varies across scales is less certain as few studies provide nested datasets yet analysis by Tiwari et al. (2014, 2017), and synthesis by Creed et al. (2015), suggest downstream mixing and deeper subsurface sources of DOC mask process drivers as scale increases. In addition, the role of photodegradation and oxidation of DOC to CO_2 in large Arctic rivers has received considerable attention (Cory et al., 2014; Ward and Cory, 2016).

The lability (i.e. biodegradability) of dissolved organic matter (DOM) is a key regulator of ecosystem function and primarily linked to molecular structure and environmental factors such as temperature, vegetation, oxygen availability and microbial activity (Schmidt et al., 2011). DOC is a fraction of the DOM pool whose weight, aromaticity and origins can in part be characterized using optical techniques. DOM exported from large Arctic rivers during spring freshet has previously been reported as highly labile (Raymond et al., 2007; Holmes et al., 2008; Spencer et al., 2008) with more refractory DOM during recession periods (Holmes et al., 2008; Wickland et al., 2012). DOM quality is expected to shift in response to permafrost thaw, thermokarst, vegetation shifts, wildfire and increasing precipitation during summer months associated with climate warming (Davidson and Janssens, 2006; Frey and McClelland, 2009; Schuur et al., 2015). Spectral indices and multi-dimensional analysis of large optical data sets from northern landscapes have resulted in important insights into how DOM quality varies seasonally (e.g. Striegl et al., 2005; Neff et al., 2006; Finlay et al., 2006; Spencer et al., 2008, 2009; Prokushkin et al., 2011; Mutschlecner et al., 2018), and is linked to source material, landscape characteristics (Kawahigashi et al., 2004; Harms et al., 2016) and disturbance (Balcarczyk et al 2009; Kokelj et al., 2013; Abbott et al., 2015; Littlefair et al., 2017; Burd et al., 2018).

While information from large rivers is critical for estimates of DOM loading to the Arctic Ocean, research at headwater scales that identifies controls on DOC production and transport is relatively scarce and often points to multiple process mechanisms (Maclean et al., 1999; Temnerud and Bishop, 2005; Larouche et al., 2015). Furthermore, much of our understanding of DOC is biased towards lowland ecosystems, with

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relatively scarce information from northern alpine systems. The goal of this paper is to enhance our understanding of coupled hydrology-DOC sources and dynamics with additional context from DOM optical properties in a well-studied, discontinuous permafrost alpine research catchment in subarctic Yukon, Canada, over multiple years. We collected samples over two consecutive years from freshet to late fall from two headwater catchments, a lake, wetland and the outlet of a mesoscale catchment in a nested design to explore seasonal and annual variability in DOC concentrations and DOM composition. Impacts of increasing catchment scale and differing landscape types on DOM optical indices were also assessed.

The specific questions addressed in this work are:

1) How do DOC concentration and DOM composition vary over multiple seasons across a diverse mountain watershed, and 2) what are the factors that drive this variability across scales. This study provides important insights into how season and scale influence the sources and transport of DOM in a cold alpine setting.

2 Materials and methods

2.1 Study area

Several headwater streams, a wetland and a high elevation lake outlet were studied within the Wolf Creek Research Basin (WCRB, 61°310 N, 135°310 W) located ~20 km south of Whitehorse in Yukon Territory, Canada (Fig. 1). WCRB is a long-term research watershed located at the edge of the Coast Mountains 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 straddles three ecological zones with boreal forest at lower elevations (predominantly White Spruce (*Picea glauca var. porsildii*)) covering ~28% of the watershed; at intermediate elevations shrub taiga comprises ~47 %, and at elevations above ~1500 m, alpine tundra and bare rock surfaces predominate. WCRB has a relatively dry Subarctic climate (Koppen classification *Dfc*) with 30-year climate normals (1981-2010) reported for Whitehorse Airport (706 m). Average airport air temperature is -0.1 ^{o}C and precipitation is 262.3 mm, with 161 mm falling as rain. However, considering that WCRB covers a large elevation gradient, colder temperatures and considerably larger volumes of precipitation have been reported for high-elevation sub-watersheds (Pomeroy et al., 1999; Carey et al., 2013b; Rasouli et al., 2019). The geological setting of WCRB is sedimentary sandstone, siltstone, limestone and conglomerate. Atop bedrock, thick stony till and glacial drift covers most of the basin. Soils in the top metre are generally sandy to silty and at higher elevations (taiga and lower tundra ecozones), a veneer of surface organic soils with variable thickness predominate. Permafrost underlies much of the basin (~43 %), particularly at higher elevations and on north-facing slopes in the taiga and alpine ecozones (Lewkowicz and Ednie, 2004).

Much of this study focussed on the headwater catchment of Granger Creek (GC), which drains an area of 7.6 km^2 and ranges in elevation from 1355 to 2080 m a.s.l. (McCartney et al., 2006; Carey et al., 2013a) (Fig. 1). GC is above treeline (~1200 m) and is dominated by Willow (*Salix* Sp.) and Birch (*Betula* Sp.) shrubs at lower elevations with dwarf shrubs, lichen and bare rock above 1500 m. South facing slopes have a thin organic layer overtop sandy soils whereas north slopes have thicker organic layers (10-30 cm) and are underlain with discontinuous permafrost. A wide riparian zone (50 to 100 m) with a consistently high water table in the lower reaches of GC lies between the slopes. Buckbrush Creek (BB, 60°31'18.01"

N, 135°12'17.27" W), another headwater catchment, drains an area of 5.75 km^2 and is located approximately 2 km west of GC (Fig. 1). BB ranges in elevation from 1324 to 2080 m a.s.l. with similar physiographic characteristics to GC. However, Buckbrush Creek is less incised than GC and the riparian zone shows evidence of multiple overbank channels during high flow events.

The site Wetland 1 (W1, 60°31'18.72" N, 135°11'34.71" W) is located at the edge of a wetland complex located downstream of BB with an indeterminate drainage area. The vegetation is dominantly sedges, with ponded water covering 200 m^2. Coal Lake (CL, 60°30'36.65" N, 135° 9'44.47" W) is a long-term hydrometric station located approximately at the mid-point in the watershed at the outlet of an ~1 km^2 lake (Rasouli et al., 2019). A large wetland complex is located upstream of CL, which is surrounded by steep slopes and vegetation that transitions from boreal forest at lake level to alpine tundra at the top of surrounding slopes.

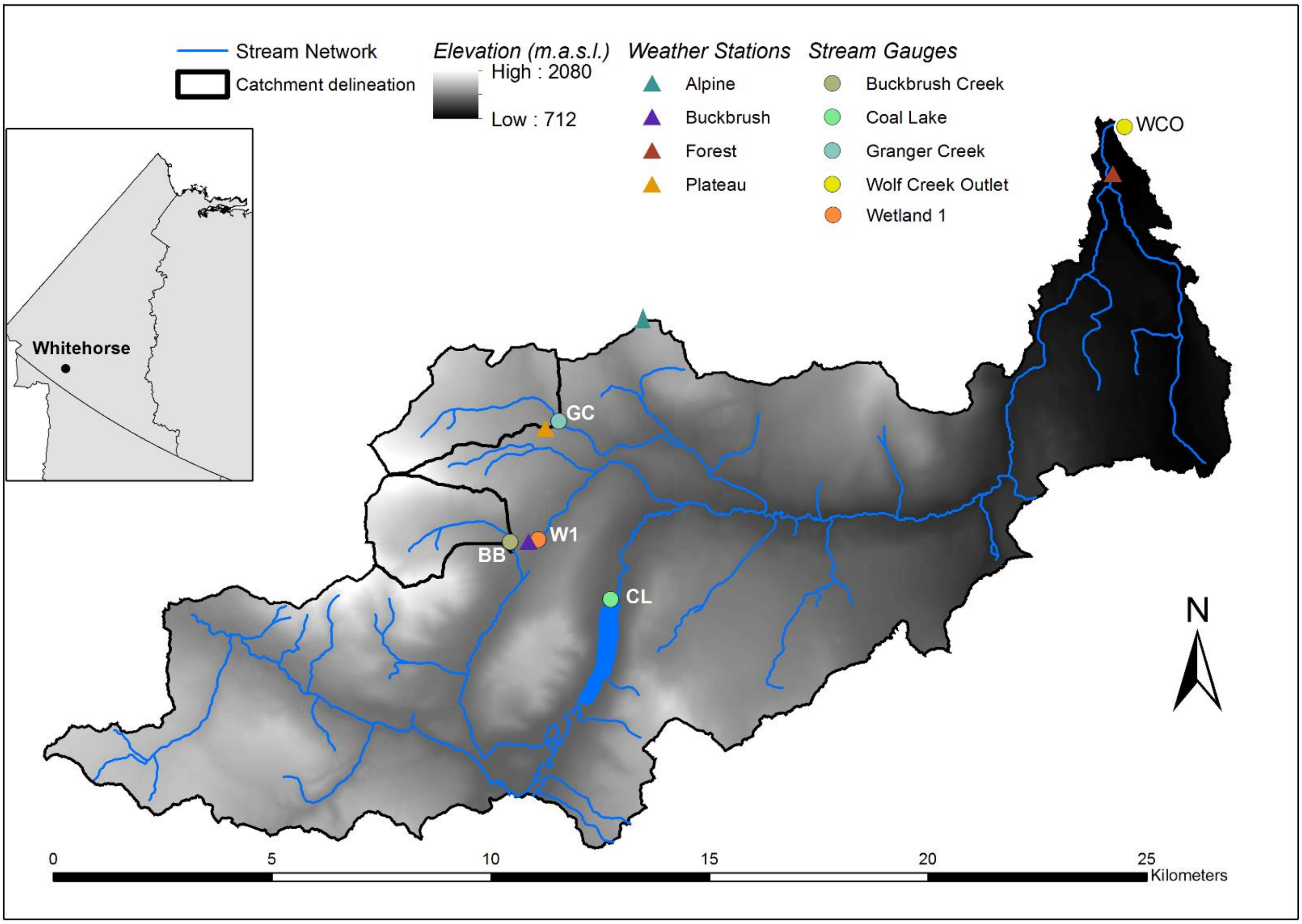

Figure 1. Map of Wolf Creek Research Basin (WCRB) with BB and GC catchments delineated. All stream gauges (BB, GC, CL, W1 and WCO) are indicated by circles; weather stations within WCRB are shown as triangles.

2.2. Field measurements

Discharge was measured using rating curves developed for each study season at all sites except the WCRB outlet (WCO) and CL, which has retained a stable curve for the past several years (discharge measurements at the WCRB outlet exist from 1992). Stilling wells at each site were instrumented with

Solinst Leveloggers and compensated with adjacent Solinst Barologgers measuring stage/pressure every 15 minutes to provide continuous flow records. Manual flows were taken frequently using a SonTek Flowtracker during high and low flows with salt-dilution gauging during periods when the channels were beneath ice.

WCRB has three long-term weather stations to characterize the climate in each ecozone. All radiation components, air temperature, wind speed, vapour pressure and total precipitation are measured year-round at each site with some gaps due to power loss (Rasouli et al., 2019). Concomitant measurements of soil temperature and moisture exist at each site. Monthly snow courses are completed in each ecozone to determine snow water equivalent (SWE), and on-site continuous measurements supplement these and provide information on melt rates. A fourth meteorological tower (Plateau) in GC watershed has been operating since 2015.

2.3 Surface water sample collection and preparation

Surface water samples were collected from April 2015 to December 2016, with the bulk of collection between April and September of each year with most samples collected at GC and frequent sampling at BB and WCO. Only a few samples were taken at W1 from 2015 to 2016. For DOC, samples were field filtered with single use plastic syringes submersed in the sample water immediately prior to sampling. Water was displaced through a 0.45 µm VWR polyethersulfone syringe filter and collected in a 60 ml opaque amber HDPE bottle. Duplicates were taken approximately every 10 samples. All samples were kept cool and out of direct light before being shipped for analysis. DOM water samples were filtered in 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.

Optical data obtained from the Aqualog(R) was used to calculate fluorescence indices. $SUVA_{254}$ (L mg C^{-1} m^{-1}) is calculated as UV absorbance at 254 nm (m^{-1}) divided by DOC concentration (mg L^{-1}) (Weishaar et al., 2003) with a unit correction based on the cuvette path length. $SUVA_{254}$ is commonly reported along with DOC concentration and is used to determine the degree of aromaticity in bulk DOM (Weishaar et al., 2003). Higher $SUVA_{254}$ values (sometimes greater than 6.0 L mg C^{-1} m-1) indicate more aromatic carbon with a strong terrestrial signal (Jaffé et al., 2008) or potential absorption at 254 nm due to colloids or iron (Weishaar et al., 2003; Hudson et al., 2007). Research in northern peatlands associated peat soil leachates with relatively lower $SUVA_{254}$ values of 3.0 L mg C^{-1} m^{-1} (Olefeldt et al., 2013). Autotochtonous or modified terrestrial DOM (microbial and soil-derived DOM) is associated with decreased aromaticity and a lower $SUVA_{254}$ value. The biological index (BIX) is the ratio of emission intensities at 380/430 nm at an excitation wavelength of 310 nm (Huguet et al., 2009). Higher BIX values indicate greater autotrophic productivity (Huguet et al., 2009) or greater relative freshness of bulk DOM (Wilson and Xenopoulos, 2009) while lower values indicate older, more terrestrial DOM. The fluorescence index (FI) is calculated as the ratio of fluorescence emission intensities at 470/520 nm at an excitation wavelength of 370 nm (Cory and McKnight, 2005). FI is used to differentiate between DOM derived from microbial sources (1.7-2.0) or higher terrestrial plant sources (1.3-1.4) with intermediary values indicative of mixing (McKnight et al., 2001; Jaffé et al., 2008; Fellman et al., 2010). Typical values reported for inland rivers are between 1.3-1.8 (Brooks and Lemon, 2007).

In addition to the DOM quality indices reported and discussed throughout this paper, absorbance at 254 nm (A254), the freshness index (Parlanti et al., 2000) and the modified humification index (HIX: Ohno, 2002) were also calculated and compared with the other indices. BIX and the freshness index were highly correlated (r^2 : 0.99, $p<0.001$) for all sites, years and seasons. A254 and DOC concentrations also showed high correlation (r^2 : 0.95-7, $p<0.001$). Due to similarity in temporal trends of DOM indices, HIX was not reported independently of the parameters mentioned above. HIX is calculated by summing the peak area under emission intensities from 435-480 nm divided by that of 300-345 nm at an excitation of 254 nm (Zsolnay et al., 1999). Higher HIX values are related to an increased degree of humification (Huguet et al., 2009; Fellman et al., 2010).

2.5 Statistical analysis

General descriptive statistics including the mean and standard deviation were calculated for DOC, $SUVA_{254}$ and the fluorescence indices and compiled in Table 1. To better assess differences between landscape units (e.g. headwaters, wetland, lake, catchment outlet), principal component analysis (PCA) was performed using DOC concentrations and optical indices (i.e. FI, BIX, Freshness, HI, $SUVA_{254}$). These variables were scaled and then standardized into a covariance matrix to avoid larger magnitudes 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).

The PCA was performed using R software version 3.4.0 (R Core Team 2017) in RStudio with R function princomp(), and packages ggplot2, GGally, ggpubr, lubridate, magrittr, grid, dplyr and tidyr for calculating descriptive statistics, correlations, data manipulation and visualization.

3 Results

3.1 Climate

For 2015 and 2016, the average annual air temperature as recorded at the Whitehorse airport weather station was 1.4 and 2.4 °C respectively, which is warmer than the 30-year normal (1980-2010). May average monthly temperatures in both years were well above the normal, with an average air temperature of 11.8 °C in May 2015 compared with a normal of 7.3 °C. Average annual air temperatures measured at the Buckbrush weather station (mid-basin) were -0.6 and -0.0 °C respectively for the two years (Fig. 2). Persistent inversions in winter result in warmer temperatures at higher elevations from December through to February. Accurate measurements of total precipitation have not been recorded at Whitehorse airport for several years, limiting long-term context but rainfall values from a nearby (~ 3 km) station were used for 2015-6 as well as rainfall from the Buckbrush weather stations (Fig. 2).

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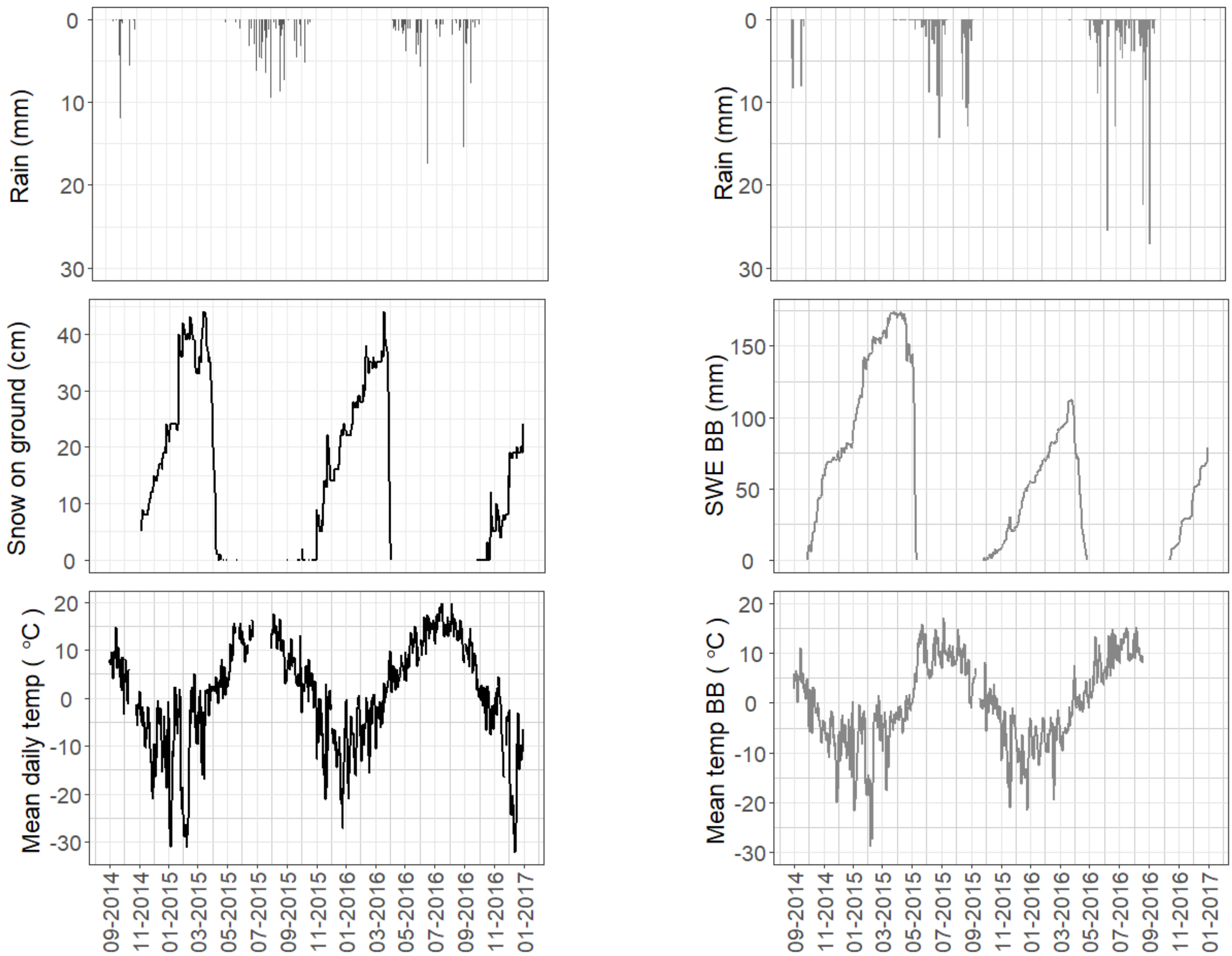

Figure 2. Climate variables from Whitehorse Airport and Buckbrush weather stations. (Left) Rain (measured in mm), snow on ground (in cm) and mean daily air temperature (°C) from the Environment Canada Airport weather station (YXY, Climate ID: 2101300). (Right) Rain measurements were summed to daily totals 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 in the GC and WCO historical record (Carey et al., 2013a,b; Rasouli et al., 2019). Summer flows were also greater than typically observed. For GC, in 2015 while there was an early measurable stream response on 9 May, freshet began on 14 May when flows increased from ~0.02 m^3s^{-1} to daily flows averaging ~0.5 m^3s^{-1} over 9 days. Peak 2015 daily discharge was 0.67 m^3s^{-1} on 22 May, thereafter flows began to decline to summer levels ~0.2 m^3s^{-1}. In response to ~125 mm of rain between 17 August and 11 September, flows increased to ~0.46 m^3s^{-1} on 14 September before gradually declining. Discharge at BB for 2015 and 2016 were slightly lower magnitude than GC with delayed flow response to both freshet and summer rainfall. Data loss resulted in incomplete discharge data for both years at BB. Manual measurements are shown in Fig. 3 to supplement continuous measurements. Discharge at WCO followed a similar pattern to GC, 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 with GC, flows increased in September prior to the removal of the transducer on 1 October.

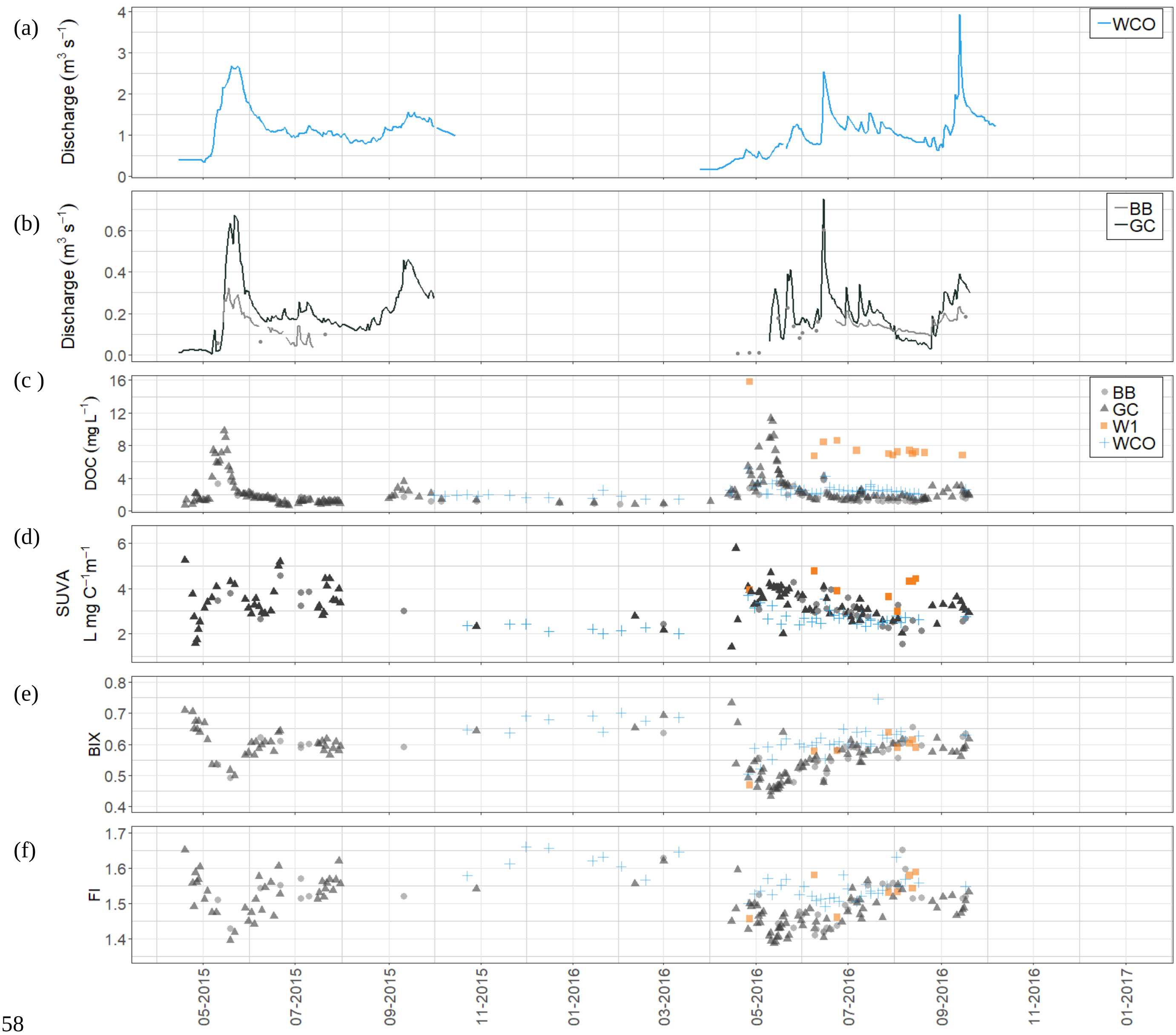

Figure 3. Flow, DOC and fluorescence indices for WCRB study sites. (a) Daily discharge data from WCO shown from April 2015 to October 2016. (b) Daily discharge data from GC (dark grey) and BB (light grey). (c) DOC concentrations in mg/L from grab samples over the study period with BB (light grey, circle), 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, instead a gradual increase in flows was punctuated with hydrograph rises that corresponded with snowmelt and summer rainfall events. Flows were of the same general magnitude to those in 2015, and once again large late season rainfalls (~115 mm between 17 August and 10 September) resulted in high September flows, with peak discharge at WCO of 3.9 m^3s^{-1} recorded on 13 September. Flows declined again until the transducers were removed on 17 October, yet were very high compared with mid-season flows.

3.3 Dissolved Organic Carbon (DOC)

DOC was sampled over two years at four sites: GC, WCO, BB and W1, a wetland complex in the taiga ecozone near the Buckbrush tower (Fig. 1). Sampling in 2015 was largely confined to GC and BB with more extensive sampling at other sites in 2016. For GC, similar patterns were observed in both years with over-winter and pre-freshet DOC concentrations below 1 mg L^{-1} and rising to ~10 mg L^{-1} on the rising limb of the first snowmelt flush followed by a rapid decline to levels between 1 and 2 mg L^{-1} throughout the summer and with a slight rise in the fall. Seasonal statistics for DOC are presented in Table 1. In 2015, the single freshet event corresponded with the rise in DOC, yet the rise and fall in DOC concentration occurred fully on the rising limb of the freshet hydrograph between 7 May and 29 May. The maximum DOC concentration of 9.8 mg L^{-1} on 15 May corresponded to a 13.8 mm rain event atop a sporadic snowpack with largely frozen soils. After June, DOC concentrations continued to decline with slight increases corresponding to rainfall events. Towards the end of the measurement period in 2015, DOC concentrations rose to a maximum of 3.6 mg L^{-1} with increasing discharge in response to sustained precipitation. Over-winter values in December and January declined to ~1 mg L^{-1}. This pattern of DOC

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Discussion started: 7 March 2019

behaviour was remarkably similar at the adjacent BB catchment which had more limited sampling. In 2016, the spring rise in DOC at GC and BB corresponded to the period immediately after the first small snowmelt pulse but prior to the bulk of the freshet signal (Fig. 3). Concentrations again rose to ~11 mg L^{-1} with a steep recession to summer levels where rainstorms would occasionally increase concentrations above 2 mg L^{-1}. As in 2015, a wet late season with a large hydrograph increase resulted in increased DOC concentrations near 3 mg L^{-1} but concentrations were much less than for corresponding freshet flows.

Sampling at WCO began in late fall 2015 with DOC concentrations of ~2 mg L^{-1} and remained near this level through April 2016. Concentrations increased during the early phases of open water freshet, yet only rose to ~5 mg L^{-1} on 26 April and then declined to summer levels between 2 and 3 mg L^{-1}, with some variability related to rainfall events. While sampling was limited, there did not appear to be a notable increase at WCO during the wet fall in 2016. At W1, DOC was ~16 mg L^{-1} on the first sampling date of 27 April, and then post-freshet samples in June through September had concentrations between 7 and 9 mg L^{-1}. Concurrent DOC and fluorescence samples were only collected from CL post-freshet during summer and fall of 2017.

3.4 Fluorescence Indices

While there exists a large number of fluorescence indices in the literature (see Hansen et al. 2016), in this work we report the widely utilized $SUVA_{254}$, biological index (BIX) and fluorescence index (FI) to help infer the source and composition of DOM (Table 1).

For GC, $SUVA_{254}$ exhibited considerable variability compared with DOC concentrations. In 2015, $SUVA_{254}$ declined from > 5 to ~ 1 L mg C^{-1} m^{-1} rapidly between 19 and 26 April in response to loss of 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 the annual peak in stream discharge. $SUVA_{254}$ then declined on the receding freshet limb yet increased markedly in June in response to 18 mm of rain (11 to 18 June), whereupon it ranged between 2.8 and 4.5 L mg C^{-1} m^{-1}. Limited under-ice sampling suggests $SUVA_{254}$ remained relatively consistent between 2 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 dramatically to 5.2 L mg C^{-1} m^{-1} before gradually declining through August with considerable variability. Following the wet fall in 2016, $SUVA_{254}$ began to rise to values > 3 L mg C^{-1} m^{-1}. Patterns of $SUVA_{254}$ for BB were similar to GC in both years. $SUVA_{254}$ started low in spring 2015 at the headwater catchments before rising slightly in summer whereas the opposite occurred in 2016. For WCO, samples over the 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 mg C^{-1} m^{-1} and then gradually declined to ~2.5 L mg C^{-1} m^{-1} with some increases associated with rising discharge. $SUVA_{254}$ at W1 was on average higher compared with other sites, although limited sampling makes it uncertain as to any temporal pattern.

BIX tended to be inversely related to discharge (and DOC concentration) during freshet at the headwater sites (GC, BB) (Fig. 3). For GC in 2015, BIX fell from just above 0.7 to 0.49 during peak freshet and then increased to between 0.55 and 0.65 during summer. Values increased over winter to a maximum of 0.71 prior to 2016 freshet where a steep decline to values < 0.45 occurred during the early phase of runoff in May and then gradually returned to values between 0.55 and 0.65 with declines associated with rainfall-driven spikes in the hydrograph. The late season increase in discharge did not strongly influence BIX at GC. BIX exhibited inconsistencies between 2015 and 2016 at the headwater sites with lower spring values in 2016 and an increase in summer whereas 2015 showed a decrease during summer to lower or 'older' values. BIX for WCO increased over winter before also declining during early melt in 2016 and then rose to values ~0.65 with some large increases (as opposed to decreases at GC) during storm events. Timing of declines to rainfall events was slightly offset between the headwater sites and the outlet WCO. At W1, BIX values increased slightly throughout the sampling period in 2016 (Fig. 3).

FI at GC and BB exhibited patterns similar to BIX but inverse to $SUVA_{254}$ (Fig. 3). In 2015, FI declined 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 during summer. In 2016, FI values again declined from 1.6 to 1. during freshet yet were on average lower than 2015 but also gradually increased throughout summer with a small decline during the wet late summer. For WCO, winter FI ranged between 1.55 and 1.65 and more gradually declined during freshet to ~ 1.5 and then increased slightly with more limited variability throughout the summer. A small decline during the wet period in late September was observed. Over the two study years at GC, BB and WCO, mean FI was lowest during spring, and higher in summer (2015, 2016) than in fall 2016. For W1, FI was low at 1.45 on the first sampling date in spring 2016 when DOC was high, and then increased with some variability but values were on average greater than those at GC and BB.

3.3 Principal Component Analysis

A principal component analysis (PCA) using 216 samples from across WCRB over three years was completed to explore landscape and seasonal climate controls on DOC concentration and quality (Fig. 4). DOC concentrations and fluorescence indices at BB (2015-7), CL (2017), GC (2015-7), W1 (2016-7) and WCO (2015-7) were introduced into the PCA for insight into how landscape type influences DOM quality at WCO (Table S1). The first principal component (PC1) explained 56.8 % of the variance in the data and was selected based on screeplot analysis, a drop in the proportion of variance explained and the Kaiser criterion (Kaiser and Rice, 1974). The remaining principal components (PCs) explained much less of the variance than PC1. PC1 predominantly represents the relationship among DOM quality and concentration and is positively and negatively correlated with all DOM fluorescence indices except for HIX. PC2 explained 15.8% of the variance and was most closely related to a single variable (HIX) with little relationship to the other analytes (Fig. 4). Further PCs were not explored.

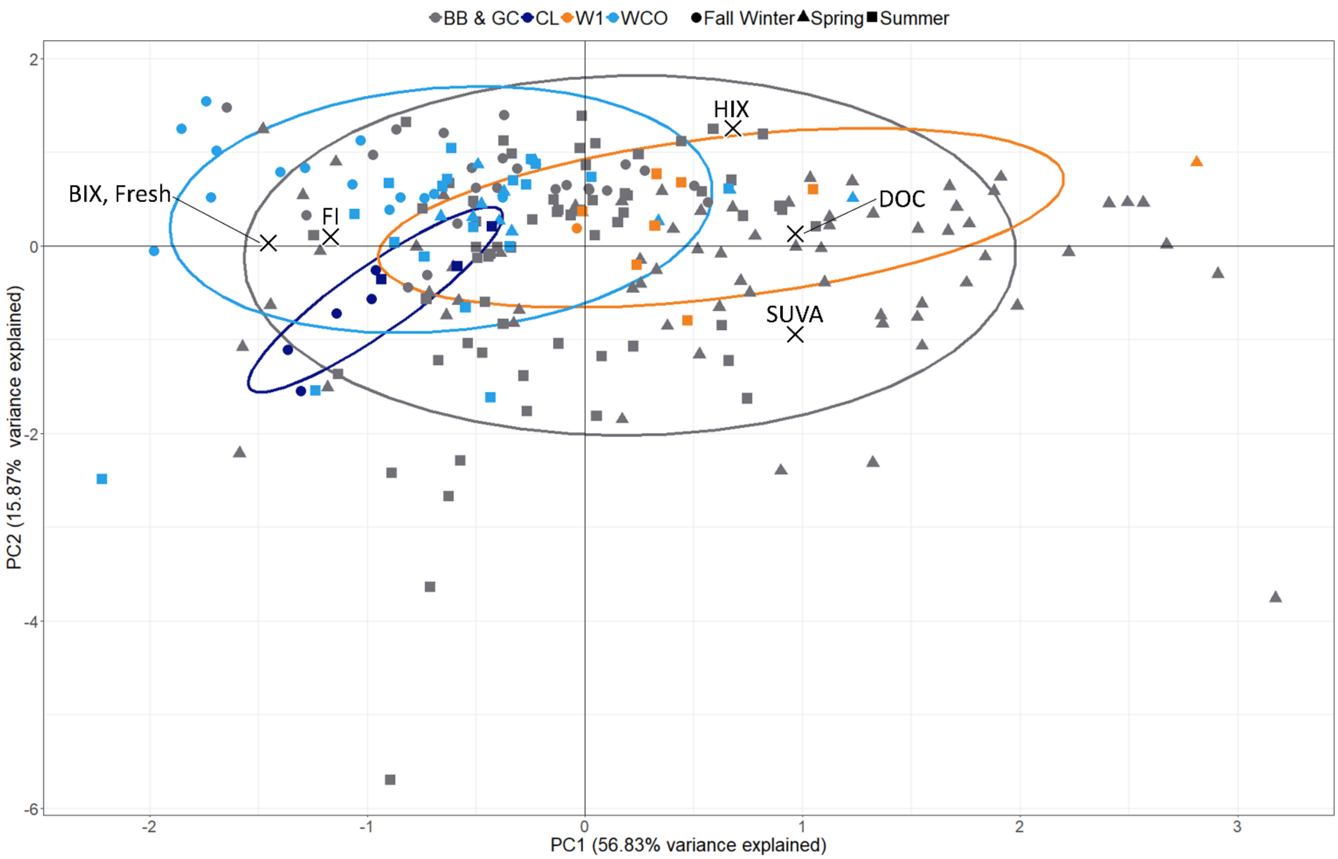

Figure 4. Biplots from PCA. Ellipses represent 0.8 probability of sample values being within the shape.

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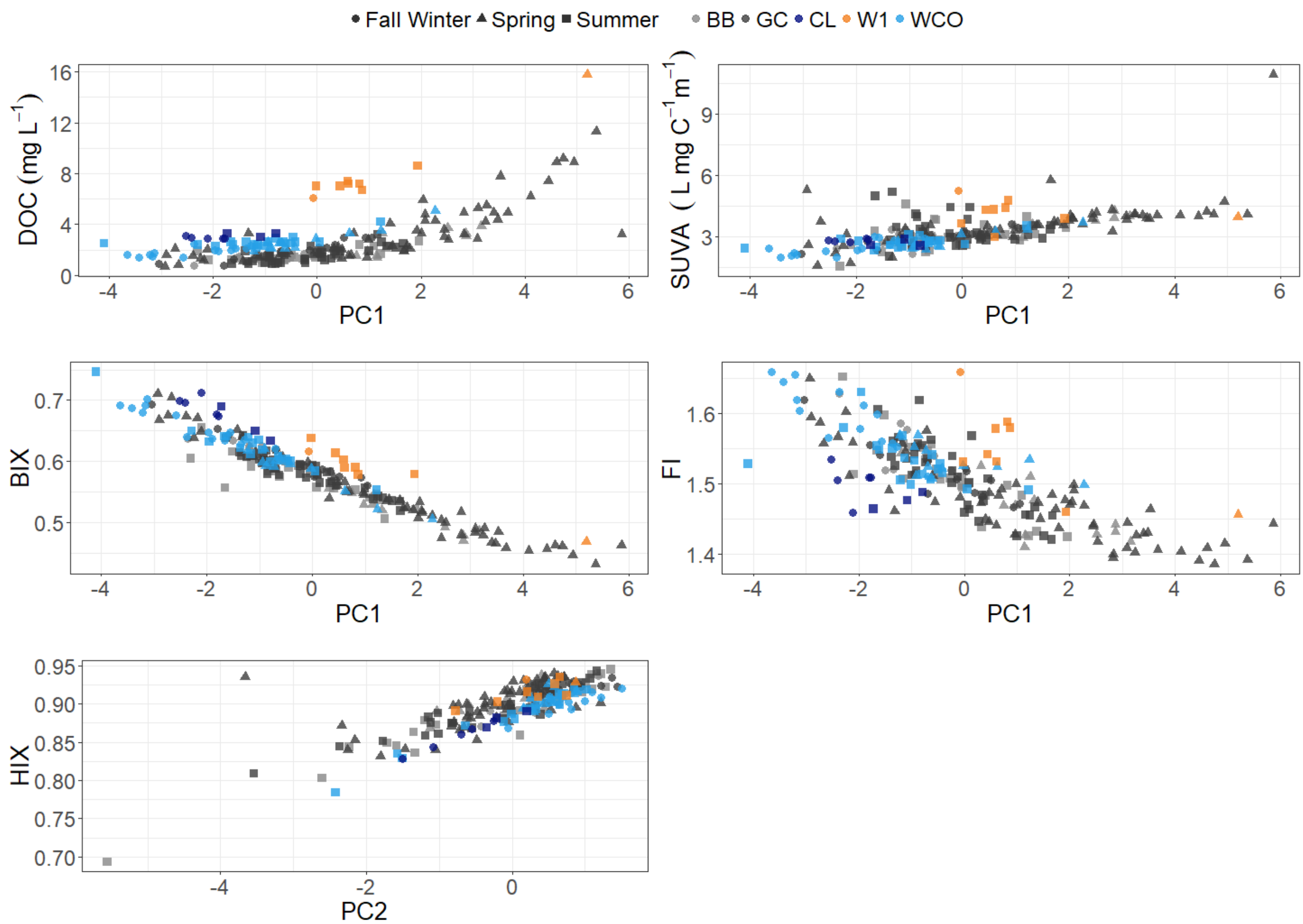

Figure 5. Regressions of principal components to DOC concentrations and DOM indices. Regression of PC1 to DOC concentrations implies some non-linear behaviour. Samples are grouped by season: Triangles = Spring (15 April-15 June); Squares = Summer (16 June-15 August); Circles = Fall/Winter (16 August-14 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

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Discussion started: 7 March 2019

variability in spring-time DOC and streamflow. Fall/winter samples are predominantly located left of the zero-line (Fig. 4) for all sites. All CL samples cluster together. Some separation of DOC concentrations and DOM indices is shown due to high DOC, BIX and/or $SUVA_{254}$ values (Fig. 6).

4 Discussion

4.1 DOC quantity and timing in streams

The most distinct feature of OC export in northern watersheds is the sudden increase in DOC concentration on the rising limb of the freshet hydrograph (Striegl et al., 2005; Raymond et al., 2007; Holmes et al., 2012). This is particularly well resolved in headwater catchments where there is limited mixing of signals and sources (Ågren et al., 2007). For GC, DOC concentrations have now been observed over freshet for six years (2002, 2003, 2006, 2008, 2015, 2016 - see Carey et al., 2013a; Fig. 4 for data on early years). There is a considerable variability in freshet timing and volume as some years show a single, rapid event (e.g. 2015) while others have a staggered response in relation to multiple spring warming events (e.g. 2003, 2016). Regardless of freshet timing and volume, DOC concentrations always rise in response to the first onset of flows and are insensitive to the volume of water exported during freshet. While there are notable contrasts in both 2015 and 2016 freshets, in both cases, the initial DOC response to flows is similar (Fig. 3), and corresponds with those reported in earlier years. The implication of these historical and recent observations is that while DOC exported during spring is hydrologically mediated via the transport pathways, DOC concentrations are not related to flow volumes at the headwater scale. Although investigation into headwaters is relative rare (Bishop et al., 2008), studies have reported greater variation in DOC at the headwater scale than in large rivers (Sedell and Dahm, 1990; Wolock et al., 1997; Temnerud and Bishop, 2005; Temnerud et al., 2010). Relatively small amounts of water are

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2019-81
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Discussion started: 7 March 2019

sufficient to extinguish the available pool of OM responsible for DOC peak concentration in the spring at this headwater catchment. For GC, estimates of DOC export between 15 April-15 June over the six years range between 0.46 and 1.49 mg C m^{-2} with 2015 and 2016 on the lower end. For WCO, the pattern of DOC during freshet was similar to GC, yet dampened with lower values during freshet over a longer period from mixing of various landscapes that integrate three distinct ecosystems and a small lake over a large elevation range.

Following freshet, DOC was remarkably consistent across the sampling sites. The headwater GC and BB values were ~1.5 mg L^{-1} whereas those at WCO were typically 2-3 mg L^{-1}, suggesting that additional sources such as wetlands and Coal Lake contributed slightly to downstream increases in DOC. There were small increases in DOC concentration associated with rainfall events. A notable feature of both 2015 and 2016 were the substantial late season rains that generated flows outside the typical range at both GC and WCO (Fig. 5). Despite these large flows, DOC concentrations did not rise to the levels observed during freshet, suggesting either alternate runoff pathways/flow generation mechanisms or a reduced source of soluble OM in soils available for transport. Considering water tables were very high during this period, we presume that the available pool of OM in shallow organic layers was less than in spring.

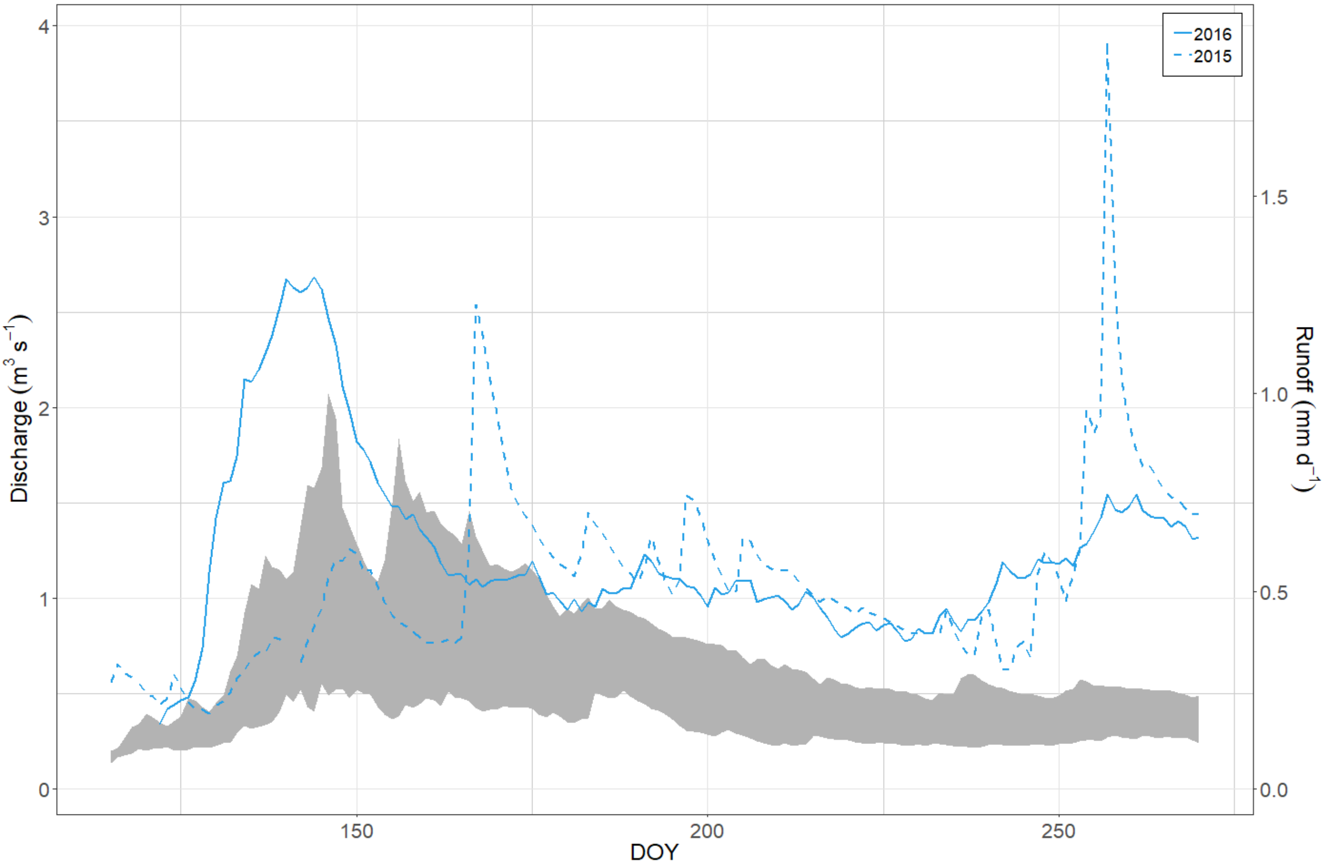

Figure 6. Historical flow at WCO with 2015-6 flows superimposed. Grey area represents inter-quartile range of 1993-2013 data. Dashed line = 2015; Solid line = 2016. Day of year along x-axis.

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 such as WCO, this approach may be more tractable due to mixing of sources and process integration (Buffam et al., 2007; Creed et al., 2015; Peralta-Tapia et al., 2015a).

A curious result was a notable decline in freshet DOC concentrations between the four years in the 2000s (Carey et al., 2013a) and the 2015-2016 study years. In each of the early years, peak DOC concentrations ranged between 17 and 27 mg L^{-1} with overall higher concentrations during freshet, whereas the maximum DOC values for GC were 9.5 and 11.3 mg L^{-1} in 2015 and 2016, respectively. The reason for this decline is uncertain, yet is not related to freshet conditions as flows and climate during freshet were similar among certain years. We have also largely ruled out instrumentation or sampling as a source of this difference as mid-season values were unchanged. Tiwari et al. (2018), using 23 years of data from the Krycklan research catchment in central Sweden, suggest that peak DOC concentrations are most closely related to warm fall temperatures, cold winter conditions and shallow snowpacks. In addition, Ågren et al. (2010a) used 15 years of data from boreal catchments also located in the Krycklan research catchment to show that high export of DOC in the snow-free season led to decreased export in the subsequent year. For six years of data at GC catchment, winter (Nov-Mar) temperatures show a weak correspondence with DOC export, in that warmer winters tend to have lower DOC export during the following spring, which is supported by Scandinavian research (Ågren et al., 2010a,b; Haei et al., 2010). However, there was no relation between snow depth and peak DOC concentration for the six years. A final possibility may be that increased summer and fall wetness that has occurred in recent years is reducing decomposition as outlined by Balacarcyzk et al. (2009).

4.2 DOM indices in streams

Optical indices are closely aligned with seasonal hydrological patterns in northern rivers across scales (Neff et al., 2006; Striegl et al., 2007; Spencer et al., 2008; Holmes et al., 2012). An expanding knowledge base linking optical indices with OM sources and biodegradability (Balcarczyk et al., 2009; Kellerman et al., 2018) and catchment processes exists with observations from both temperate and northern study sites. A number of widely-used indices (reviewed in Hansen et al. 2016) facilitate comparison among sites, and chemometric components through the ever-expanding library OpenFluor (http://www.openfluor.org). We applied the widely used drEEM toolkit (Murphy et al., 2013) to our dataset, yet we were unable to validate the model using a split-half approach to the dataset. However, the overall relationship between CDOM and DOC is robust in WCRB as observed in other rivers (Stedmon et al., 2011; Spencer et al., 2012; Frey et al., 2015), with a strong relationship between A254 and DOC (r^2: 0.97, $p<0.001$).

The predominant signals in DOM indices observed in WCRB streams correspond well with those reported in the literature for northern and permafrost basins (Walker et al., 2013; Cory et al., 2014), and support conceptual models of coupled runoff generation and DOM transport (Mu et al., 2017). At the onset of freshet and the rise in DOC, $SUVA_{254}$ rises while both BIX and FI decline to annual minima. This freshet response is attributed to the mobilization of DOM derived from leaf litter and older terrestrial precursor material with high molecular weight and aromatic DOM (Wickland et al., 2012). This pattern is particularly clear at GC, where BIX and FI are closely correlated with each other and negatively correlated with $SUVA_{254}$. At this time, near-surface pathways across frozen ground are the only mechanism to rapidly transport OM and water to the stream. Once DOC declines, $SUVA_{254}$ decreases and FI and BIX begin to increase. A number of mechanisms can be attributed to these changes: an increase in more microbial DOM as thaw depths increase and soil temperatures warm, and an increased ability of mineral soils to adsorb DOM with high organic weight and large aromatic structures along flow pathways (Ussiri and Johnson, 2004). The gradual change in the three fluorescence indices as summer progresses suggests a continual decline in high molecular weight, older DOM (lower $SUVA_{254}$) and a greater proportion of recently produced DOM. During the unusually wet fall periods, rising water tables and activation of near-surface and overland flow pathways resulted in increases in SUVA and declines in BIX and FI, yet not to the same magnitude as spring when flows were of similar volume. The smaller influence of wet fall periods on changing DOM composition can be explained in part by a much wider range of flow pathways across deeply thawed soils and also considerable adsorption sites for DOM. In addition, sources of leaf decomposition compounds located in upper soil horizons leached in spring have had less time to replenish prior to leaf-fall. As with DOC concentration, the important implication is that seasonality as opposed to flow magnitude has a greater influence on the quality of DOM. By early November, temperatures throughout WCRB are below freezing and a long winter recession occurs. Limited over-winter sampling at WCO and GC show $SUVA_{254}$ values declining to their lowest values prior to freshet with a corresponding maxima in BIX and FI. This pattern corresponds to those reported elsewhere in the Yukon River Basin and other watersheds in Alaska (Striegl et al., 2007; O'Donnell et al., 2010; Mutschlecner et al., 2018).

4.3 Patterns across space and time

Understanding the integration of biogeochemical signals across temporal and spatial scales is a fundamental challenge in diverse catchments such as WCRB. The link between catchment processes and spatial scale to control coupled hydrological-biogeochemical processes has garnered considerable attention (Ågren et al., 2007; Buffam et al., 2007; Creed et al., 2015; Tiwari et al., 2017). Whereas flowpaths at the headwater catchments (GC, BB) are well documented (Quinton and Carey, 2008; Carey et al., 2013a), the dominant hydrological pathways at the scale of WCRB shift from the supra- and intra-permafrost pathways to one that is more groundwater driven. In addition, a ~1 km^2 lake in the centre of the basin has an important storage and mixing effect. The impact of these changes on the pattern of DOM indices at WCO is complex and not easily resolved back to component landscape types.

From the PCA, a host of controls act to influence DOC and fluorescence indices throughout WCRB (Fig. 4, Fig. 6). As scale increases, DOC concentrations increase during summer and low flows yet are more muted during freshet at the outlet compared with headwater streams. WCO had lower $SUVA_{254}$, greater BIX and FI compared with both headwater and wetland systems. The lower $SUVA_{254}$ at WCO corresponds to an increasing dominance of groundwater or greater baseflow along with deeper subsurface pathways due to a lesser extent of frozen ground (Walvoord and Striegl, 2007; O'Donnell et al., 2010). In contrast, higher FI and BIX likely reflect the influence of these deeper flow pathways and any processes and production that occur in Coal Lake, which sits in the approximate mid-point of WCRB. Most FI values at the headwater catchments are between 1.4 and 1.6, reflecting terrestrial plants as the dominant source of DOM. By contrast, values in excess of 1.6 at WCO, particularly during winter and low flow periods, suggest some microbial DOM sources. The high values of BIX in winter at WCO supports some moderate autotrophic production, yet certainly not at the levels of many aquatic ecosystems (Kellerman et al., 2018).

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

Changes in DOC export as a result of climate change in permafrost regions are uncertain for aquatic ecosystems and in the overall carbon balance of northern regions (Striegl et al., 2005, 2007; Raymond et al., 2007; Frey and McClelland, 2009; Guo et al., 2012; Laudon et al., 2013; Kicklighter et al., 2013; Abbott et al., 2015; Johnston et al., 2018). DOC concentration, optical properties and associated biodegradability change with source, residence time and processing, all of which vary with thaw depth (review by Kalbitz et al., 2000; Wickland et al., 2007). Results from this work compare well with others in permafrost regions that are not experiencing rapid thermokarst, suggesting a gradual decrease in biodegradability and changes in DOM likely due to mineralization and adsorption as thaw increases (Striegl et al., 2007; Mu et al., 2017). Whereas most conceptual models have focussed on the implications of thaw and thermokarst on DOM (Mu et al., 2017), in this study we had the opportunity to evaluate the influence of increased late summer and fall precipitation, which is a notable feature in fall across much of subarctic Canada (Spence and Rausch, 2005; Spence et al., 2015; DeBeer et al., 2016). Despite late-season wetness and flow conditions similar to freshet in both years, which is anomalous in the WCRB record (Fig. 5), the change in DOC concentration and DOM indices were small compared to changes observed during snowmelt. Large late-season rain events on deeply thawed soils did not transport the same volume of DOM as freshet despite high water tables due to a depleted DOM source and increased adsorption potential. FI and BIX were typically higher at the outlet than the headwater and wetland sites, which is attributed to lake influences and greater autotrophic production with increasing stream order. While there was an increase in concentrations and a shift to heavier, more aromatic DOM during fall, values were still closer to those experienced during summer baseflow.

The implication is that changes in precipitation, particularly in summer, will have a limited influence on changing DOC export and quality compared to changes that result from emergent flow pathways, thermokarst or factors that influence values during freshet. From DOC concentrations that have been measured intermittently over the course of 15 years, we report a recent decline in freshet DOC concentrations at a headwater catchment, which is difficult to reconcile with permafrost thaw (which has not been observed or documented). Possible explanations are warmer winters and winter soils (Haei et al., 2010; Tiwari et al., 2017), or that the increase in fall wetness results in a decline in spring DOC concentrations through a second, albeit smaller, flushing event (similar to Ågren et al., 2010b).

5 Conclusions

This study reports patterns of DOC concentration and DOM quality derived from optical indices over several years in a subarctic alpine watershed where hydrological processes have been studied for approximately two decades. We show that DOC concentration and optical indices have a strong temporal variability associated with seasonality, and that A254 and CDOM were reliable proxies for DOC concentrations. Observations from nested watersheds with drainage areas of ~6 to 179 km^2 indicate that mixing and complex process interactions dampen variability in downstream responses and result in a gradual shift in DOM characteristics. Despite considerable fluctuations among years, DOC concentrations and export are consistently highest during freshet despite differences in timing and magnitude of hydrological response during six years of coupled DOC and discharge measurements.

Optical indices also showed the largest variation during freshet and were relatively insensitive to flow volumes despite large differences in freshet between 2015 and 2016. At the headwater scale, DOM is less responsive to rainfall events in summer when the water table descends into deeper mineral soil layers.

Mobilization and transport mechanisms operating at the headwater scale are linked to stream hydrochemistry while material inputs from different landscape types causes mixing and dilutes DOM signals at increasing watershed scales.

Recent years have shown an increase in late fall streamflow that is uncommon in the long-term hydrometric record that is more often observed across northern watersheds. DOC flux in recent years falls on the low end of the range reported a decade ago.

Other factors that have the capacity to influence the availability, movement and export of DOC and DOM are forecasted to change with rapid warming in this environment (DeBeer et al., 2016). Factors at play are a longer growing season, a shift in vegetation community composition and spatial extent, warmer winters, increased baseflow with greater groundwater input, earlier freshet or disruption of the typical northern hydrograph and an altered precipitation regime. Ultimately, watershed scale and the arrangement of landscape types will play important roles in determining how DOC flux and DOM lability change under a warming climate, and altered precipitation, disturbance and vegetation regimes.

Data availability. Streamflow datasets used for this study are available on the GWF/CCRN database (http://giws.usask.ca/meta/) per the outlined data policy. For DOC/fluorescence, please contact the corresponding author as a data repository is currently being developed.

Competing Interests. There are no competing interests.

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