We thank both referees for their comments, which have improved the clarity of key points of the manuscript as well as the figures and other aspects of data presentation. The input from both referees enabled us to better elucidate the nuance in some of our findings through new figures and better substantiate some points through statistical analyses. Their attention to detail was appreciated and we have outlined our responses to general, specific and technical comments below.

This document is structured so that Anonymous Referee comments are in **bold**, followed by our response and either a figure, table or text with changes in *italics*.

Anonymous Referee #1:
It seems like you are suggesting the DOM will shift from organic soils to more DOM from decomposing vegetation?
Suggestion: ... may alter DOM sources, shifting from DOM derived predominantly from organic soils (high aromaticity, less fresh) towards a greater contributions from decomposing vegetation (more fresh and lower aromaticity), and facilitate flow and transport through deeper flow pathways and enhance groundwater contributions to runoff.
Our response: The sentence has been changed to suggested phrasing.
Forecasted vegetation shifts, permafrost thaw and other changes due to climate change *may alter DOM sources, shifting from DOM derived predominantly from organic soils (high aromaticity, less fresh) towards a greater contribution from decomposing vegetation (more fresh and lower aromaticity). These changes may also facilitate flow and transport through deeper flow pathways and enhance groundwater contributions to runoff.*

Introduction
Line 74-75: "DOC is a fraction of the DOM pool..." This requires rephrasing. DOC is the mass of C in the entire DOM pool, so this statement is incorrect.
Our response: We have corrected this inaccuracy. Sentence has been changed to:
DOC *is the mass of C in the DOM pool* whose *lability, aromaticity and origins* can in part be characterized using optical techniques.

Line 91: Would be better to have this statement of the goal in the first paragraph or start of paragraph two.
Our response: Unfortunately, although the authors see how moving the statement of the goal upwards could be helpful, we believe flow of the paper is better maintained with its current structure.

Also I suggest rephrasing this for clarity: "The goal ... understanding of the coupled dynamics of hydrology and DOC export and composition (using optical properties of DOM), in a well studied... Yukon, Canada."

Our response: Thank you for this suggestion. The sentence has been rephrased as follows:
The goal of this paper is to enhance our *understanding of the coupled dynamics of hydrology and DOC export and composition (using optical properties of DOM), in a well-studied, discontinuous permafrost alpine catchment in subarctic Yukon, Canada.*

Methods

I have concerns about the sampling and filtration methods for the DOC and DOM analyses, and the lack of proper reporting of the precision error on these measurements. Section 2.4 the authors should report on the detection limits and uncertainty in the DOC concentrations. This is not a trivial issue when concentrations in the watersheds hover around the 1ppm level through the winter.
Our response: Thank you for your comments regarding Section 2.4 and the inclusion of detection limits and uncertainty. We have added the relevant information to that section:
Water samples were sent to the Biogeochemical Analysis Service Laboratory (BASL, University of Alberta) for analysis on a Shimadzu *TOC-5000A Total Organic Carbon analyzer for DOC concentration following the US EPA protocol 415.1. The reportable detection limit provided by BASL for these samples was 0.1 mg/L.*

Also some additional information on the repeatability of the fluorescent measurements would be helpful here – did you correct or compare to a standard (e.g. Quinine Sulfate or other?)
Our response: To address the concerns related to repeatability of fluorescence measurements as well as comparison to standards, we've separated out the reviewer's comments to clearly provide the relevant information.

The fluorescence measurements were compared to both a Raman and a Quinone Sulfate standard (and associated blank) before each sample run (one batch of samples). All of which arrived sealed from the manufacturer with the relevant certificates. Fluorescence measurements of these two standards were tracked to ensure that no instrument error or inconsistency was occurring. In addition, the Raman standard was included with every batch of samples that was run at each integration time. A lab blank of distilled water was also included in each run at each integration time.

did you repeat samples and compare values for FI, BIX or SUVA to determine repeatability of these values?
Our response: Yes, samples were selected at random to be re-run to determine repeatability.

My other concern relates to the sample collection and filtration methods. The authors report that they used plastic syringes and PES filters, which can both leach DOM.

Standard methods for DOC and DOM analysis involve use of pre-combusted glass filtration apparatus and glass fiber filters. The authors need to demonstrate that the DOC concentrations in their method blanks, and the impact of the methods on the optical properties are negligible, or cite other studies that have demonstrated these methods have little effect on background DOC and optical properties. Although I suspect the effects of the filtration methods may be trivial, given that these methods are not standard, the authors need to demonstrate this in fact the case.

In response to this concern, method blanks at a southern Ontario field site using the same syringe + filter set up and in situ filtering showed that DOC concentrations and optical properties of the samples seemed unaffected by their brief contact time with the plastic syringe and the PES filter. DOC concentrations for method blanks were <0.1 mg/L (below detection for BASL) for 6 samples and in one case, 0.4 mg/L.

In addition, the authors carried out a small intercomparison experiment using PES + plastic syringes and glass filter apparatus + GF filters to have a direct comparison of the two filter types.

We collected water from small headwater site in Southern Ontario in 4 pre-combusted 240 mL glass amber bottles. Samples were placed in cooler and returned to lab for filtration on the same day using glass filter apparatus and glass fiber filters. Pre-combusted 40mL glass amber vials were environmentalized with filtrate 3 times before being filled (no headspace). A method blank was included. Samples were analyzed the next day.

For comparison, 5 syringes and PES filters were also brought to the field site and 5 samples were collected in situ. The syringes were submersed in the stream 3-4 times before being filled. PES filters were attached. Sample water was pushed through the PES filter into pre-combusted 120 mL glass amber bottles. These bottles were environmentalized 3 times before being filled (no headspace). These samples were also placed in a cooler, returned to the lab and then placed in the fridge until analysis. Two method blanks for field filtration were included.

Once the samples were run on the Aqualog following the procedures described in the manuscript, the effects of plastic syringes and PES filters were undetectable. EEMs were extremely similar between all samples (same site, within 10 minutes) regardless of filter method, and the method blanks from GF and PES filters were also directly comparable to unfiltered DI water.

Results

Line 324: I do not see the 'inconsistency' you are describing in the figure (though I agree there are differences). It seems to me that BIX reaches a minimum at onset of melt and then increases in both years. The difference appears to be that in 2015 the BIX increases

and then more or less plateaus overall (there is one sample that is higher than the rest, and there is some minor variability but it is difficult to discern a clear decrease?), while in 2016 the BIX values keep increasing steadily after the minimum during freshet.

Our response: The sentence has been reworded for clarity.

BIX exhibited similar patterns between 2015 and 2016 at the headwater sites with minimum values during spring in both years followed by an increase, which plateaued in summer 2015 but continued to rise slightly during the 2016 summer.

Line 331: Can you provide an indication as to what constitutes a meaningful (significant) change in FI (form the repeatability or your own results, or from information derived from literature)?

We appreciate the subjective nature of what 'meaningful' or 'significant' means, particularly with regards to issues of repeated measures. From the literature and in our study, FI values can be located within a small subset of the typical range of values (1.2 to 1.8) depending on the source DOM. In our case, we calculated the average standard deviation of FI from samples measured more than once as 0.022. The range of FI values from WCRB sites was relatively small (~0.3) so we relied on nonparametric Kruskal-Wallis to determine a statistically significant shift in FI.

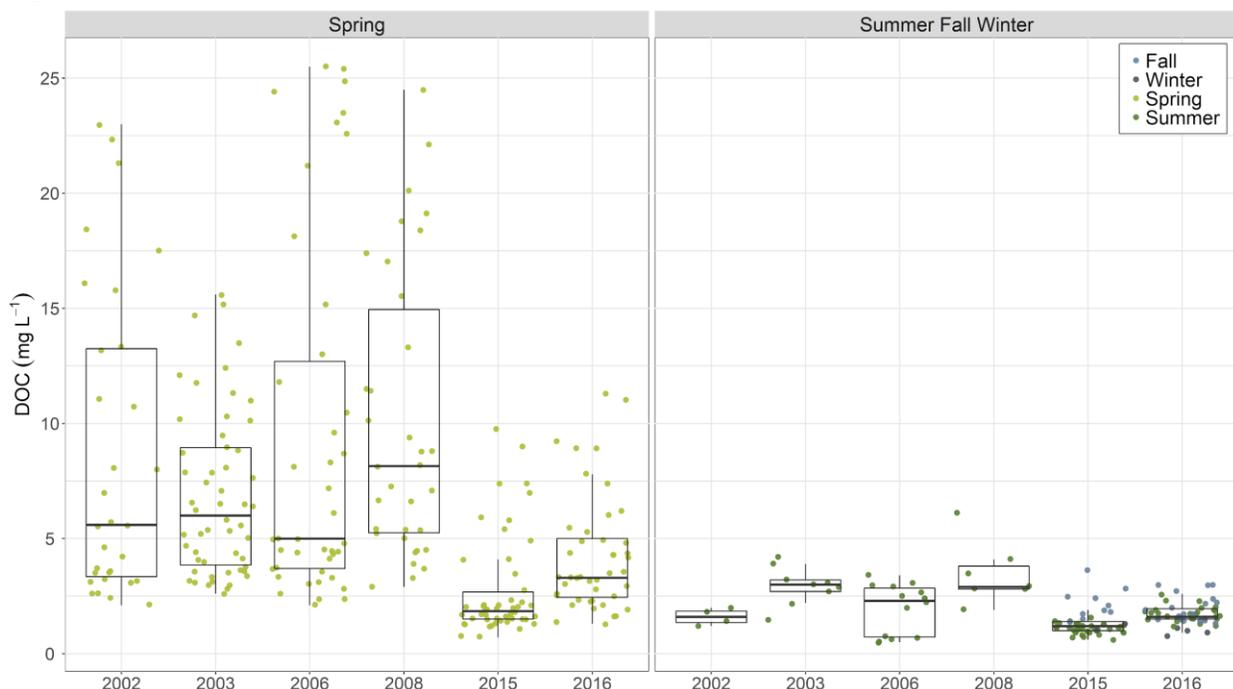
Line 347-348: Please include the full details of the PCA as supplemental information.

Our response: Although we struggled with what entails the 'full details' of a PCA, the authors have assembled some background information in the supplemental document as requested.

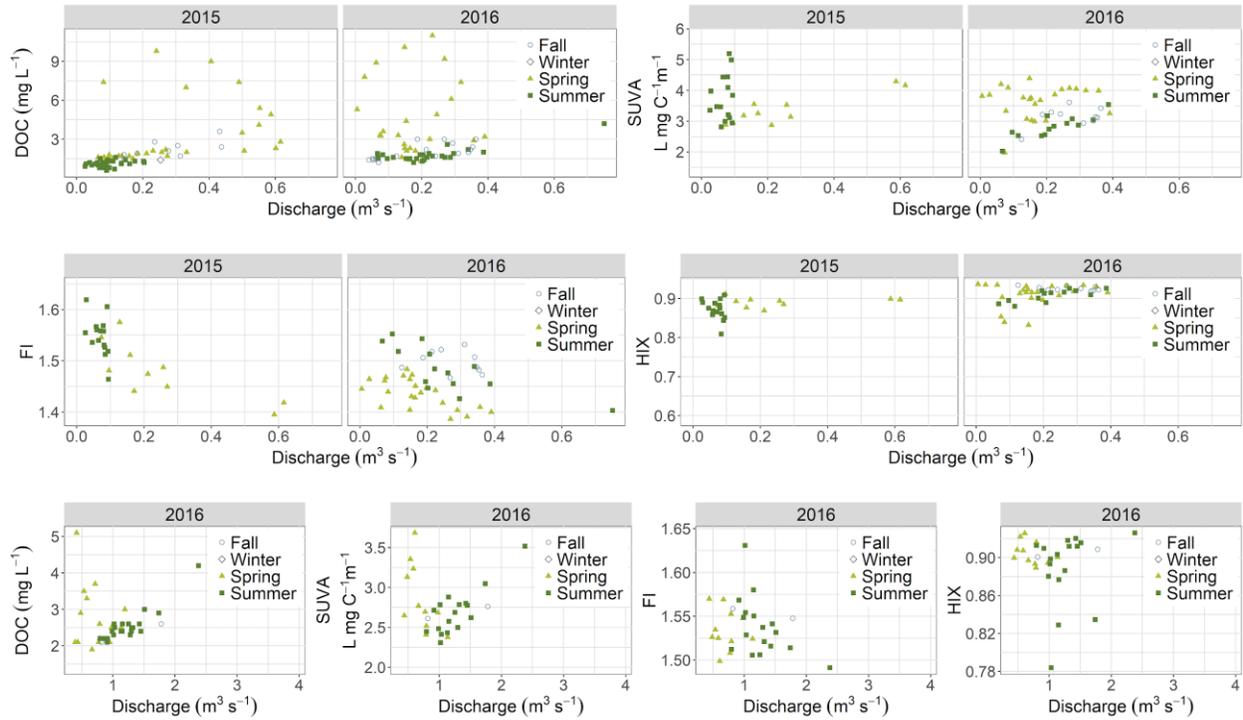
Discussion

Line 415 and 426/427: You should include the data Carey et al 2013a data here, as a table or graph. If you are using them as a basis of these arguments, you must show the data.

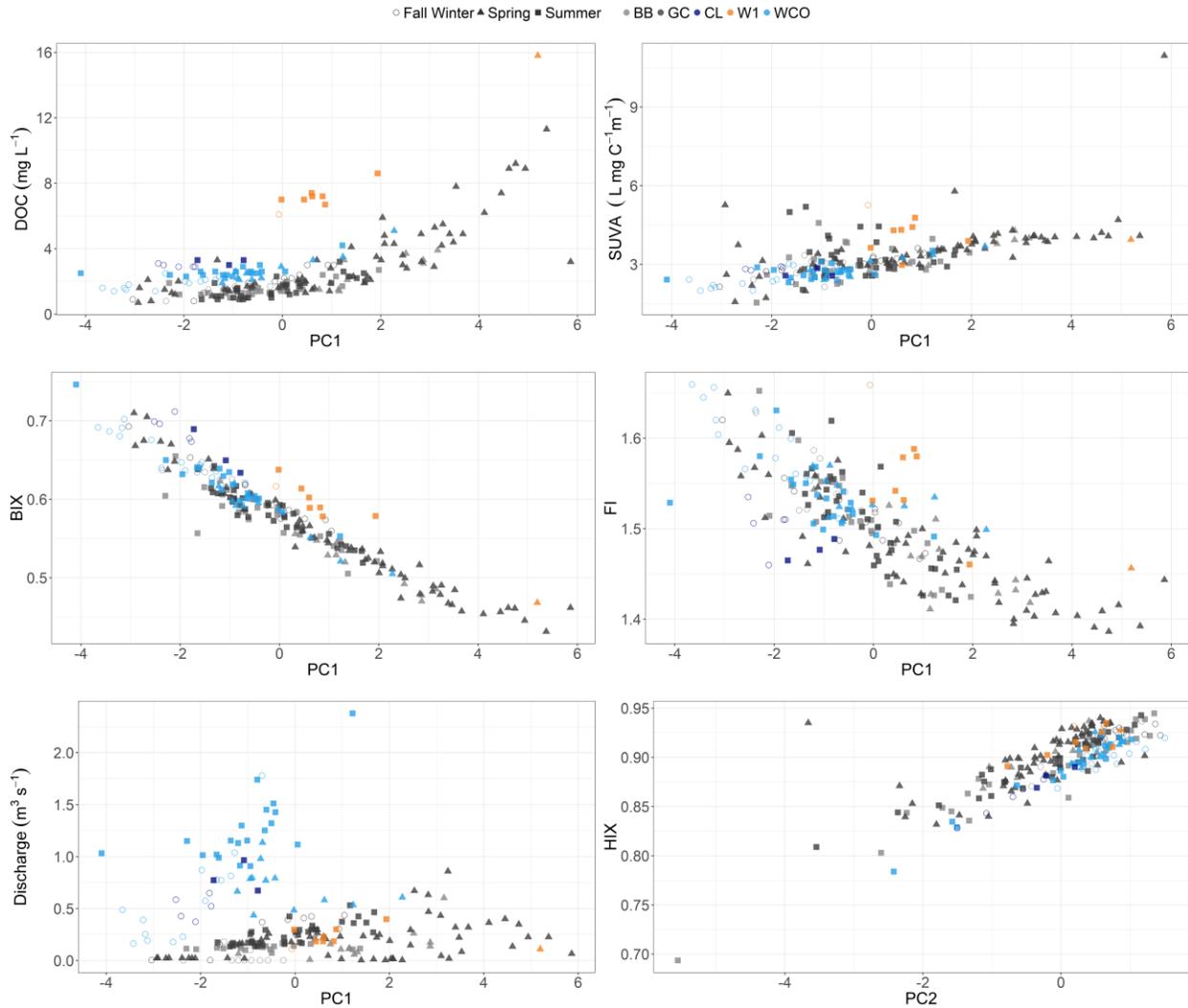
Our response: The data from Carey et al 2013a has now been included in the figure below and added to the manuscript.

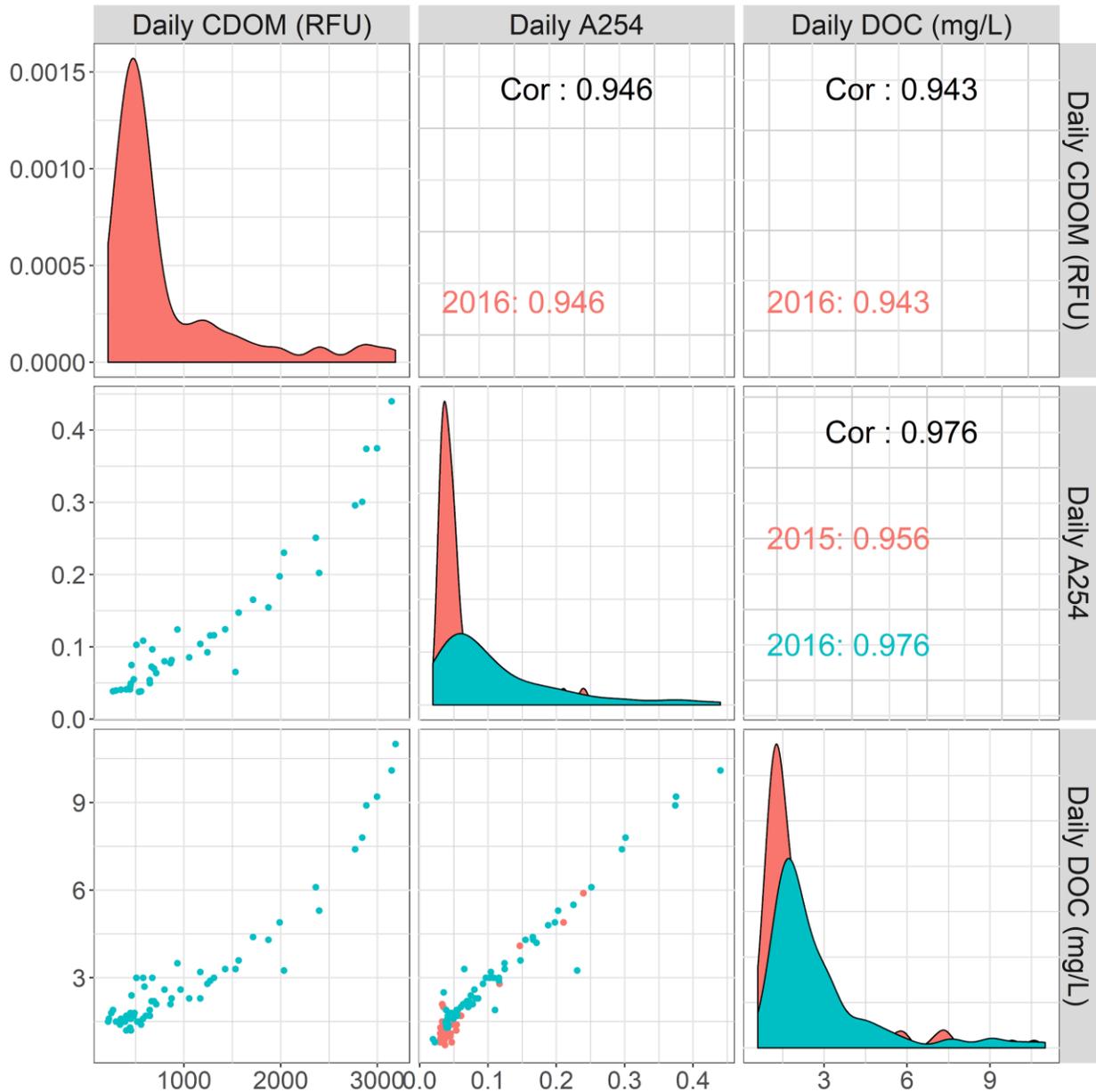
Fig 7.

Line 463-464: The authors state that "As with DOC concentration, the important implication is that seasonality as opposed to flow magnitude has a greater influence on the quality of DOM" Although I do not disagree with this statement, I do not believe the authors have demonstrated clearly or quantitatively, how the flow magnitude relates to the quality of DOM.

Our response: Thank you bringing up this point. In response to this comment as well as Referee #2's suggestion, C-Q plots of DOC and several optical indices have been added to the manuscript to better elucidate this point. We have included a table with C-Q regressions and have discussed their patterns in the revised manuscript.

Fig 8.

Can you plot Q vs PC1 and show the seasons? As you do for the fluorescence indices in Figure 4. Figure 4 shows a strong change in the PC and optical indices with seasons. But you do not show relationship between Q and the optical indices (except in the timeseries, but this does not effectively demonstrate that seasonality has a greater influence than Q on the quality of DOM.

Our response: We have added the C-Q plots mentioned above to help clarify our point about seasonality having a greater influence than flow magnitude although there is some relationship between the two. We meant to communicate that the range of flow was greatest during spring and fall, however, the range of optical indices values in fall was much less than what was measured in spring.

We have also added a panel showing Q vs PC1 with the seasons shown. This figure is below:

Line 525: I do not see where you have shown any relationships between CDOM and A254 and DOC - you need to include these relationships (correlation analyses) in the paper or in the supplemental if you are making this a principle conclusion of the work.

Our response: We have now included the key information and a plot in the supplemental material (Fig. S1) showing the Pearson correlation for the average daily DOC concentration in mg/L and the average daily CDOM in RFU (p<0.001); DOC concentration and average daily absorption at 254nm (p<0.001); average daily absorption at 254nm and CDOM (RFU) (p<0.001). New correlation figure is shown below:

Line 456: You cannot say the DOM is older, as you do not have age measurements. You can only say that there is a decline in aromaticity with lower SUVA. SUVA cannot be used to infer DOM age, unless you can demonstrate the two are correlated here. It is possible especially in permafrost systems to have very old or modern DOM with low SUVA.

Our response: We have rephrased it to avoid attributing age to the DOM. Sentence has been reworded as follows:

The gradual change in the three fluorescence indices as summer progresses suggests a continual *decline in more aromatic DOM (lower SUVA$_{254}$) and* a greater proportion of recently produced DOM.

Conclusions

Line 482-483: I see there are shifts in the indices in the figures, and Table 1. However, to strengthen your argument you should indicate whether these differences statistically significant or not. See my comment for Table 1 in pdf.

We have run nonparametric Kruskal-Wallis tests across seasons at the same site in the same year, and also across sites for the same season in the same year (per Table 1). We indicated the first case as superscript A: significantly different across seasons for same site at $p<0.05$ (*) or $p<0.001$ (**). The second case was denoted by superscript B.

Line 524-526: "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." Nowhere in this paper (or supp. Info) do you show any relationships between CDOM or A254 and DOC - you need to include these relationships in the paper or in the supplemental if you are making this conclusion.

Our response: We have added a figure (also shown above) to the supplemental information to show the correlation between daily averages of A254, DOC and CDOM.

Line 531-532: "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." You have not clearly demonstrated these relationships. You should include some statistical analyses in data tables (correlation analyses?) or an additional figure (e.g. similar to Figure 4) to support that the optical indices are less sensitive to Q than to seasons.

Our response: We believe now with the inclusion of the C-Q data this point is clear. The variability of C to Q in spring is markedly greater than in all other seasons. We have also rewritten the sentence above to better reflect the observation that the range in DOC concentration remains consistent despite much less flow in 2016 compared to 2015. We have also added that while DOC concentrations are similar, DOC export is much less in 2016.

Technical corrections: Please see the annotated pdf provided by the reviewer for suggested minor editorial and typographic corrections. Please also note the supplement to this comment:https://www.hydrol-earth-syst-sci-discuss.net/hess-2019-81/hess-2019-81-RC1-supplement.pdf

L10:
Our response: arctic changed to *Arctic*.

L25-28: Other changes such as?
Our response: Sentence has been rewritten to incorporate more details about particular aspects of climate change. Also, the original sentence has been changed to include more details about how DOM composition will be altered.

Forecasted vegetation shifts, *enhanced* permafrost *and seasonal thaw, earlier snowmelt, increased rainfall,* and other projected climate driven changes will alter DOM sources and transport pathways. *Results here support a projected* shift from DOM derived predominantly from organic soils *(high aromaticity, less fresh)* towards greater contributions from decomposing vegetation *(more fresh and lower aromaticity)*, and transport through deeper flow pathways with enhanced groundwater contributions to runoff.

L33-37: You should refer to the newer and better constrained numbers reported in Hugelius et al. 2014.

Our response: We have incorporated the newer Hugelius et al SOC estimates.

Carbon storage and cycling have been the focus of considerable attention, *as soils and sediments in the northern high latitudes are estimated to store approximately 1300 Pg (~40%) of the global belowground organic carbon pool (Hugelius et al., 2014)* and deliver ~10 % of the total freshwater input to global oceans (Gordeev et al., 1996; Opsahl et al., 1999; Shiklomanov, 2000).

L45-47: Strikethrough on weathering solutes.

Our response: Sentence changed:

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 Ca, Mg, Na, SO$_4$, and P fluxes have increased significantly over the last thirty years. These increases are attributed to deeper flowpaths as permafrost degrades, increased weathering and increased sulfate oxidation (Toohey et al., 2016).*

L52-55:

Our response: We added "non-permafrost" to describe terrigenous sources originally mentioned in this sentence. The sentence has been changed to:

These disturbances have a transient influence on hydrologically-mediated DOC transport that confounds spatial and temporal patterns of DOC flux from *non-permafrost* terrigenous sources to the river-ocean continuum (Larouche et al., 2015; Littlefair et al., 2017; Burd et al., 2018).

L67-70: Process driver such as?

Our response: In response to the request for examples of process drivers, we have added "including in-stream transformation" to the following sentence:

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 *including in-stream transformation* as scale increases.

L151: More detail about instrumentation, measurement intervals etc.

Our response: Although it was not mentioned by referee #1, we added information on how we determined when headwater streams were ice-free with this sentence:

Bushnell game cameras and in-person observation were used to document when the headwater streams and outlet were ice-free in spring to validate the use of pressure transducer measurements.

As pointed out, details were scarce concerning instrumentation, measurement intervals, snow courses, and soil moisture and temperature. We have added the following paragraph to the methods section to explain the location/position of instrumentation, provide more details about precipitation and rain measurements, and soil moisture and temperature. We also added information about the Plateau weather station (specifically the SR50 sensor) and the 2 soil moisture stations located within Granger Basin. Other instrumentation that has been collecting data at the Buckbrush weather station is well-documented in Rasouli et al., 2019.

All radiation components, air temperature, wind speed, vapour pressure and total precipitation are measured at *30 minute resolution,* year-round at each site with some gaps due to power loss (Rasouli et al., 2019). *The rainfall data reported in this study is from a tipping bucket rain gauge located at the nearby Buckbrush weather station and compared with an Alter-shielded Geonor total precipitation gauge for accuracy. A fourth meteorological tower (Plateau) in GC watershed has been operating since 2015.*

Section 2.3: Referee #1 questioned the use of syringes and PES filters rather than the standard method using pre-combusted glass fibre filters.
Our response: We have added this sentence to clarify why we used syringes at these particular sites. In particular, we were constrained by a lack of lab space in 2015 since most of our time was spent camping near WCRB at high elevation to facilitate both water sample collection as well vegetation surveys, vegetation and soil sampling etc. The sentence below was added to the end of Section 2.3:
In situ filtration with a syringe kept the time between sample collection and filtration to a minimum, particularly during spring freshet when logistical constraints meant that researchers remained in the catchment for up to two weeks at a time before returning to Whitehorse.

Section 2.4:
Our response: We want to thank Referee #1 for pointing out areas where the methodology surrounding fluorescence and absorption measurements were not well articulated. We went through this section and added detail where it was pointed to be lacking (e.g. specifying which filter was used) and have included more information about standards and blanks.

Fluorescence excitation emission matrices (EEMs) were obtained from 0.45 µm *PES*-filtered water samples using a Yvon Jobin Aqualog Benchtop Spectrofluorometer (HORIBA Scientific, Edison, NJ, USA). *Extra steps were taken to ensure that no background DOM from PES filter and syringe provided a fluorescence signature (see Supplement for further information, data and example EEMs).* 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. *A sealed Quinone Sulfate sample and blank pair were also run prior to each batch of samples and compared to prior values to ensure consistency.* Fluorescence spectra were normalized to the area under the Raman scatter peak (peak excitation wavelength 397 nm) of a sealed Raman Milli-Q water sample

prior to all sample runs. *A lab blank of distilled water was also appended to each sample run and every 4 sample runs, a sample was repeated.* 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}).*

Figure 1. Map adjustments.
Our response: We have added a point to the inset map to indicate the location of WCRB relative to Whitehorse.

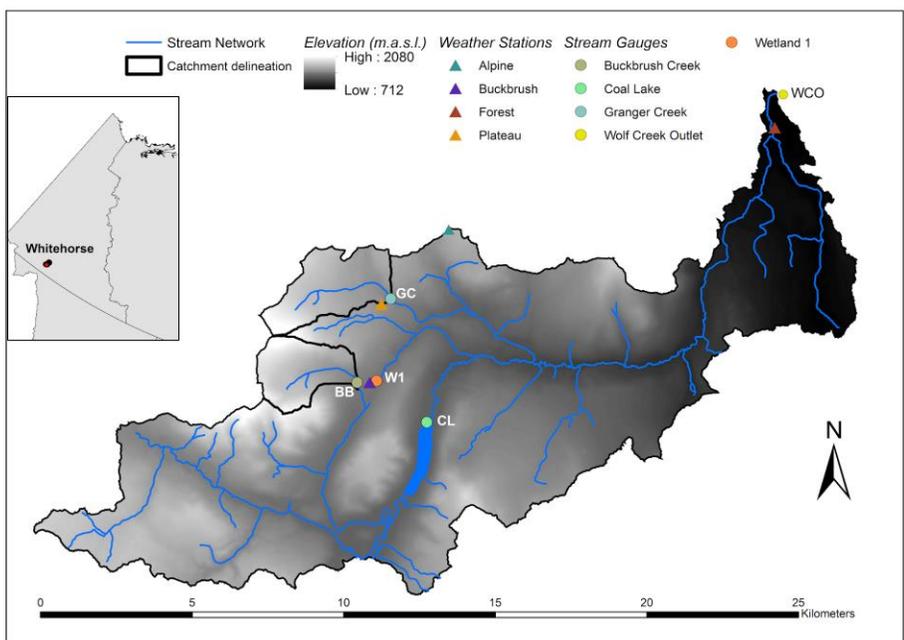



Figure 2. We have added titles at the top of each panel to indicate the location of the data: Whitehorse and Buckbrush weather stations.

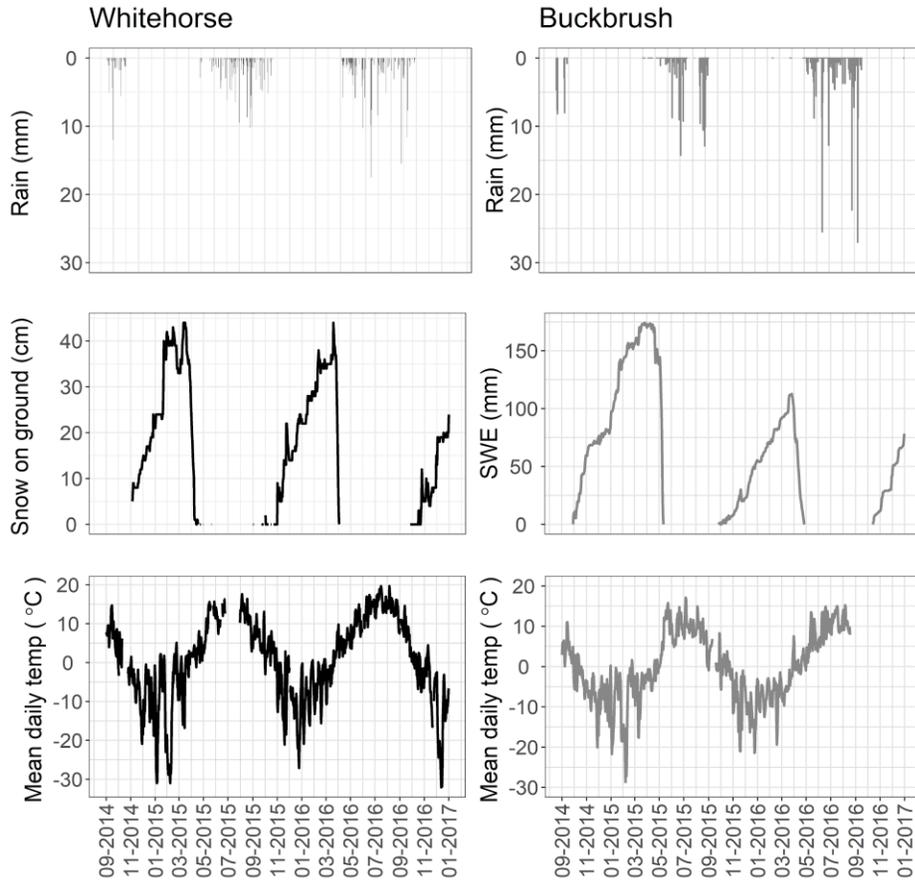



Figure 3: Referee #1 noticed an error wherein symbols in different panels had differing opacities and mentioned that the blue + for WCO was difficult to pick up in some panels. Our response: We apologize for the oversight and the differences between panels of Figure 3. We have redone the figure with zero transparency (like panel d), which we believe has helped the blue + representing WCO become more visible. Figure 3 with no transparency is shown below:

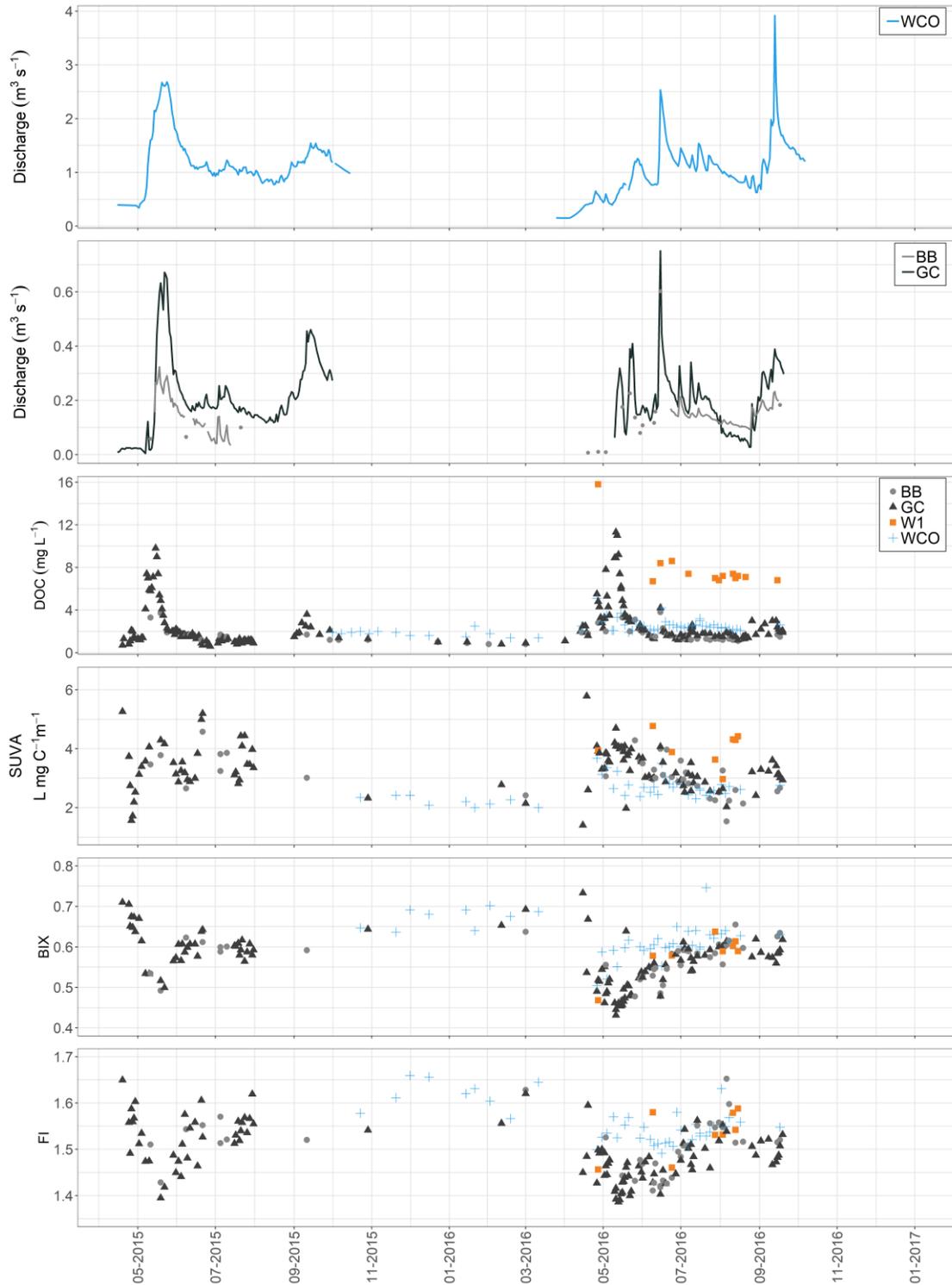
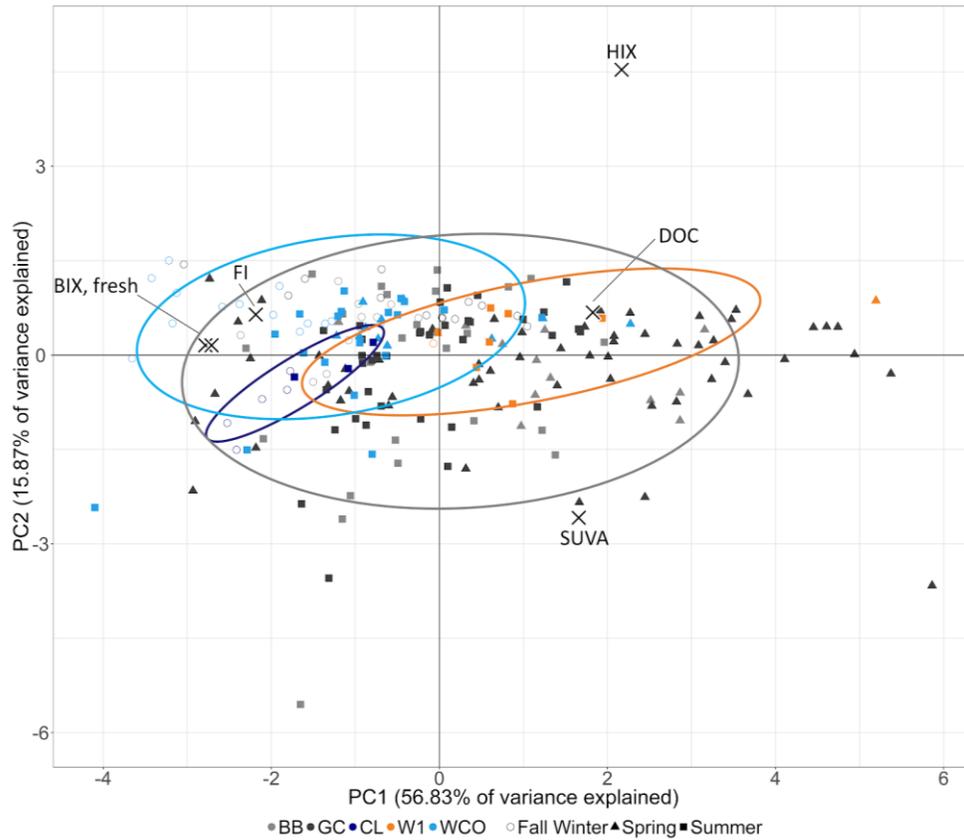



Figure 4: Referee #1 suggested changing the symbols to be able to clearly differentiate between the seasons.

Our response: We agree that the original choice of symbols did not provide an obvious differentiation of seasons. We have changed the figure so that "fall winter" is shown as an open circle while spring and summer are a filled triangle and square, respectively. Figure 4 is shown below:

Anonymous Referee #2:

Overall, I find that the authors provide useful data to help bolster our understanding of carbon cycling in northern regions. However, there were some areas of concern for me: the change in DOC concentrations documented between older studies and the present day was really quite striking; I would have liked to have seen more attention paid to ruling out analytical error. Several of the SUVA measurements were also quite high, suggesting possible iron interference. If Fe value are available for these sites, it would be useful to confirm whether these concentrations may have affected overall values, or change across seasons.

Our response: With regard to potential analytical errors, we have added information to the manuscript and to this document to address the change in DOC concentrations. For Fe, a study by Herod et al. 2016[1] in Wolf Creek provided Fe concentrations in their supplementary materials, which shows that Fe is quite low in Wolf Creek (or WCO as per the manuscript). Mean Fe for 17 samples was 0.06+/-0.09 mg/L. There were also 10 samples from WCO below detection limit.

[1]Herod, M. N., Li, T., Pellerin, A., Kieser, W. E., & Clark, I. D. (2016). The seasonal fluctuations and accumulation of iodine-129 in relation to the hydrogeochemistry of the Wolf Creek Research Basin, a discontinuous permafrost watershed. *Science of the Total Environment*, *569*, 1212-1223.

In addition to these analytical points, I found myself looking for the manuscript to delve into the data a bit further, to add to our process-based understanding of seasonal variation in DOC dynamics in sub-Arctic regions. Examining seasonal variation in C-Q plots, or plots of the various optical metrics might be one good way to do this. Making better use of what sounds to be a rich historical dataset seems like it would also be worthwhile. Finally, the authors discuss the high fall flows that are unique to the study years. While it is interesting that concentration does not change during this time,it would have been nice to have seen an assessment of this effect on overall C export: do these fall flows have a substantial effect on export from the catchment. It is not that surprising that concentration and measures of aromaticity increase during the spring freshet (as the authors point out!), but this becomes one of the main take-homes of the manuscript, as currently structured. It would be nice to see this rich dataset used in a slightly more nuanced way. Finally, I would recommend some work to create slightly higher quality figures for publication.

Our response: We appreciate the opportunity to delve more into dynamics and C export. We have adjusted sections of the discussion to better relate the DOC and DOM data to processes. More focus has been placed on C export rather than just DOC concentrations as well. We have added two plots (C-Q of DOC and other indices; boxplots of historical and current DOC concentrations before and after mid-June). Figure quality has also been increased. We have addressed these and other concerns in more detail below.

Specific comments:

L10: Reference to large Arctic rivers seems misplaced for this manuscript focused on small stream processes?

Our response: The mention of large Arctic rivers is meant to contextualize the dataset and the study catchment by alluding to research undertaken at much larger scales before coming back to process understanding at the mesoscale. Paralleling Wolf Creek Research Basin (WCRB) and areas like the Yukon River Basin are meant to highlight the complexity inherent at all scales as well as the lack of consensus in how climate change has already and will continue to alter stream and river DOC concentration and export. Although much of this manuscript focuses on ~ 6 km^2 to 179km^2 catchments, the emphasis is on the processes that are difficult to elucidate at much larger scales.

L42: Note that Striegl et al. document declines in flow weighted concentration, rather than overall flux. DOC flux was still documented to increase. Also, Frey and McClelland (2009; cited later in this work) and some other authors provide some discussion on why regions might vary in this way.

Noted.

L61: An obvious point, but it's the combination of high concentration and high flow that causes these high exports to occur; perhaps tweak your sentence here slightly for clarity? In addition, substantially elevated concentrations during the freshet are not necessarily going to occur, even if this is the typical response in western Canada. See, for example Li Yung Lung et al. 2018.
https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2018JG004659

Our response: We have changed L61 to avoid generalizing observations from some northern areas as ubiquitous after reading the article suggested above. The sentence has been changed to: DOC export is *often* greatest during snowmelt freshet when DOC mobilized from organic rich layers *result in peak concentrations and spring flows are also high*, resulting in a large annual 'flush' as is typically observed in Western Canada (Boyer et al., 2000; Carey, 2003; Finlay et al., 2006).

L64-65: Again, this is likely to be region specific, and depend upon the soil profile.
Dependent on the soil profile, as flowpaths descend in response to soil thaw, DOC mobilization can decline with depth as mineral layers provide 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).

L85: Kokelj reference might be mis-placed here? It is an excellent study, but does not examine DOM.

Our response: We have removed it this reference.

L91: Consider adding a reference for this statement. "Furthermore, much of our understanding of DOC is biased towards lowland ecosystems, with relatively scarce information from northern alpine systems."
Added Laudon et al. (2012) for support.

L99: Note two different tenses being used in this sentence.
Our response: Sentence changed to: "The specific questions addressed in this work *were:"*

L109: Some edits needed in this sentence for grammar; switch between passive and active wording about half way through
Our response: Sentence changed to: *WCRB is a long-term research watershed located at the edge of the Coast Mountains, spans an elevation ranging from 712 m a.s.l. to 2080 m a.s.l., and has a drainage area of ~179 km².*

L151: Clarify location of the three long-term weather stations.
Our response: Sentence changed to include the names of the three long-term weather weather stations so that their name and corresponding presence on the map is directly referenced.
WCRB has three long-term weather stations to characterize the climate in each ecozone *(Alpine, Buckbrush, Forest).*

L187: Note that SUVA is based on absorbance, rather than fluorescence, so the use of 'fluorescence indices' here is technically incorrect. Switch to 'optical indices'?
Our response: Thank you for the note. Fluorescence has been switched to optical.

L191: Values as high as 6 (typically, anything over~4.5) almost certainly indicates interference from Fe. See Poulain et al. 2014 ES&T for more information on correction procedures, etc.
Our response: As noted above, we have examined the possible influence of iron and values that have been reported for WCO are very low (see above). While not impossible, we cannot conclusively state that Fe is an issue and we have kept the data as-is.

We have adjusted this sentence to emphasize that Fe interference is typically responsible for values > 0.45.

 $SUVA_{254}$ is commonly reported along with DOC concentration and is *positively related to aromaticity in bulk DOM (Weishaar et al., 2003) with higher values indicative of a strong terrestrial signal (Jaffé et al., 2008). Typically, $SUVA_{254}$ values greater than 4.5 L mg C^{-1} m^{-}1 denotes high absorption at 254 nm due to colloids or iron (Weishaar et al., 2003; Hudson et al., 2007). .*

L195: Typically, terrestrially-derived DOM would have SUVA values that are higher,rather than lower; perhaps tweak the text inside the bracket? I think you're referring to modified terrestrial DOM here, but this is not necessarily clear from how the parenthetical text is worded.

Our response: Sentence has been reworded for clarity.

Allochtonous, terrestrial DOM (terrestrial DOM) is associated with increased aromaticity and a higher SUVA$_{254}$ value while lower SUVA$_{254}$ values are related to modified terrestrial DOM.

L233 "resulted"

Our response: Verb tense has been changed : The correction and normalization of samples to the Raman standard *resulted* in normalized intensity spectra being expressed in Raman units (R.U., nm^{-1}).

L234: Rework this sentence for clarity. It's also unclear to me what the nearby weather station is / where it is located, particularly in the context of Figure 2.

Our response: The Whitehorse Airport station (60°42' N 135°04' W, 706m) is located in Whitehorse and was referenced for the Environment Canada 30 year climate normal as context. The Whitehorse A station has a similar elevation to the Forest weather station albeit ~14 km NW along the Alaska Highway. Due to gaps in the Forest site climate station and no records in recent years at Whitehorse Airport, we used the Whitehorse Auto weather station (located 3km from the airport) for 2014-2016. We added a point to Figure 1 to show the location of WCRB relative to Whitehorse and changed the Figure 2 caption to clearly identify the location and differentiate between data sources.

Figure 2. Climate variables from *Whitehorse Auto (Rainfall; 60°43'59.000" N, 135°05'52.000" W135°05'52.000" W, 707 m a.s.l., Whitehorse Airport (Snow on ground, Mean daily temp; 60°42'34.200" N, 135°04'07.800" W) and Buckbrush weather stations. (Left) Rain (measured in mm) from Whitehorse Auto (Climate ID: 2101310) located 3 km from Whitehorse Airport, snow on ground (in cm) and mean daily air temperature (°C) from the Environment Canada Airport weather station (YXY, Climate ID: 2101300) located ~ 14 km NW of Forest at 706 m a.s.l.* (Right) Rainfall daily totals in mm were derived from hourly measurements, snow water equivalent (SWE) in mm based on 3 hour measurements from a snow pillow beside Buckbrush weather station. Daily average air temperature (°C), derived from 30 min measurements.

L247: Is it possible to display this long-term average, to give the reader a comparison point? (i.e., perhaps move up Figure 6).
Our response: Thank you for this suggestion. We have moved up Figure 6 to follow the time series (Figure 3). Figure 6 is now Figure 4 and we have renamed the subsequent figures.

L272: As worded, a bit repetitive with previous text (ie, from the site description).
Our response: Sentence has been deleted.

L299: See previous comment re: tweak to your terminology here; note that SUVA is an absorbance-based metric.
Our response: Fluorescence has been changed to optical.

L304: As mentioned previously, these values are somewhat high. Do you have any corresponding Fe data that might help to get a sense of Fe interference?
See above. Yes, published values by Herod et al., (2016) are low.

Plot DOM quality indices against Q, rather than time series (or, as a compliment to time series)? Would this help to think about process?

Our response: Thank you for the suggestion. Referee #1 had a similar suggestion and we have added C-Q plots for DOC, SUVA, FI and HIX for both Granger Creek and Wolf Creek Outlet with season indicated by color and shape. The plot is below (Fig. 8):

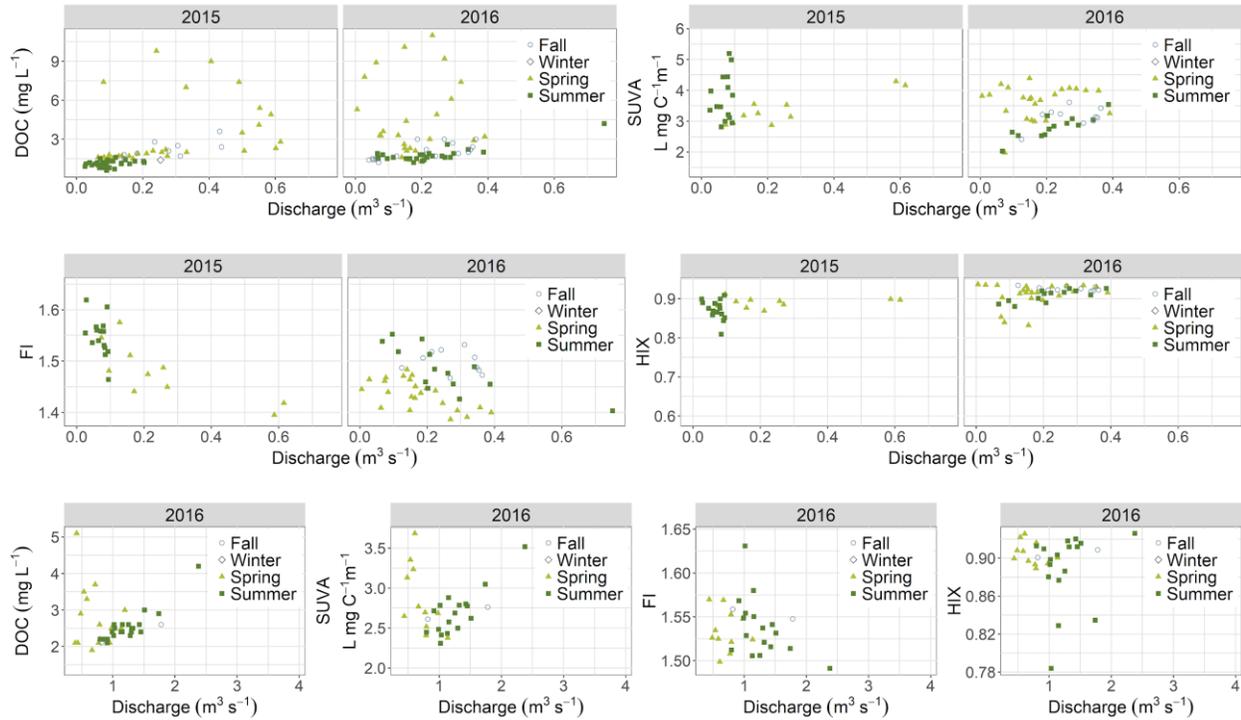
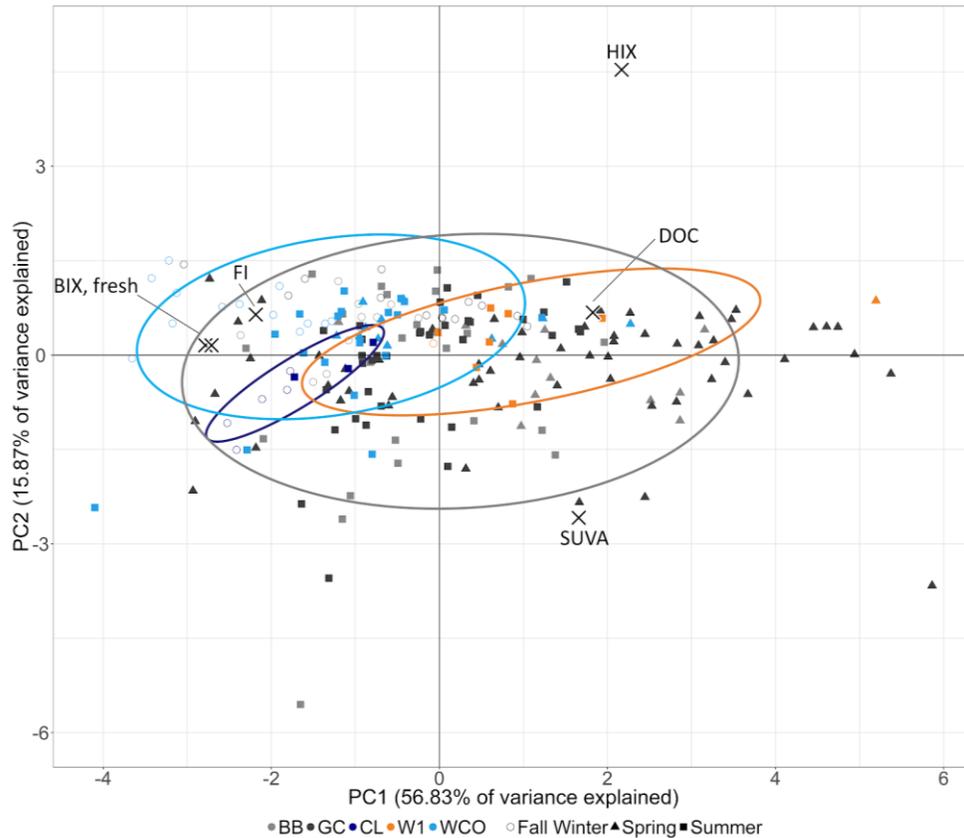



Figure 4: Similar to Figure 5, why not use different shadings of grey for BB and GC? This would allow the reader to differentiate between these catchments (or, see the of overlap between catchments within a landscape type) if they wish.

Our response: Thank you for this recommendation. We have changed the colors to reflect previous figures with BB and GC being represented with a light and dark shade of grey. Please see the revised figure below (now Fig. 5):

L372: Certainly, this will be true in systems that switch from baseflow sourced from deeper mineral layers to flow during the freshet that is sourced from organic-rich surface layers (similar to the large river studies being referred to here). But, I'm not sure it will necessarily be universal.

Our response: We have changed this sentence to avoid implying that the phenomenon is universal.

A distinct feature of OC export in *some* northern watersheds is the sudden increase in DOC concentration on the rising limb of the freshet hydrograph *as the baseflow-driven system switches to near-surface flowpaths in organic-rich soils* (Striegl et al., 2005; Raymond et al., 2007; Holmes et al., 2012).

L386: See also Creed et al. (Can J. Fish Aquat. Sci) on this point.

Our response: We have referred to the parallels in the river continuum concept and have added Creed et al. 2015 as a reference.

L390: Is this export estimate a unique calculation for this paper, or taken from elsewhere?
Our response: The original set of calculations were done using a nearest neighbour interpolation approach. To better compare between years and for better reproducibility, the authors chose to use the RiverLoad package in R (Nava et al., 2019).

If the former, then some text in the methods and results should be included. If the latter, then a reference is warranted.
Our response: Information about the RiverLoad package and the time-weighted interpolation of DOC concentrations has been added to methods as section 2.5 with reference to Nava et al (2019):

2.5 DOC Load Calculations

DOC fluxes for GC were estimated using the R package RiverLoad (Nava et al., 2019). RiverLoad provided several methods to generate estimates of DOC flux and for this paper, Method1 (time-weighted Q and C) was chosen as most appropriate. Briefly, Method1 considers the mean concentration and mean flow of each sample to obtain a load value and is biased towards underestimating load in some situations (see Nava et al. 2019, Section 2.1.1 for full details and equation). Daily discharge data and DOC concentrations (maximum of 1 measurement per day) for 2002, 2003, 2006 and 2008 were obtained from the authors of Carey et al., 2013a. DOC concentrations (maximum of 2 per day) and discharge at 15 minute resolution for 2015 and 2016 are outlined in Sections 3.2 and 3.3). Any gaps in the discharge data were filled by time-weighted interpolation, however there were no gaps greater than 3 days during springs flows for any year (2002, 2003, 2006, 2008, 2015, 2016.

L391: Given the last sentence, I'm unclear on whether DOC concentration or export is being referred to here.
Our response: We have added "concentration." Sentence has been changed to:
For WCO, the pattern of DOC *concentrations* 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.

L394: For clarity, it would be useful to refer specifically to "DOC concentration"
Our response: We have changed the wording in this sentence to specifically refer to DOC concentration.
Following freshet, DOC *concentrations* were remarkably consistent across the sampling sites.

L396: While it's somewhat self-evident that wetlands will increase DOC concentration across integrated scales, the residence time of lakes (and, associated biological /

photochemical processing) will often cause outlet DOC concentrations to be lower than inlet concentrations.

Can you provide data to support the statement that the lake might have increased integrated [DOC] at the outlet?

Our response: We agree with this statement about how lake outlet DOC concentrations are often lower than inlet concentrations. However, while lake outlet DOC concentrations were often extremely similar to headwater concentrations during spring, the lake is located downstream of a large wetland complex and not the two headwaters mentioned so it is probable that source DOC concentrations are much greater than if GC and BB 'fed' the lake. DOC concentrations measured at the lake outlet during summer were typically twice that of headwater (BB and GC) concentrations albeit less than wetland (W1) concentrations based on a comparison of 70 samples wherein BB, GC and CL DOC concentrations follow this pattern. We have adjusted the following sentence slightly to account for the lake having higher concentrations than the headwaters during summer. "The headwater GC and BB values were ~1.5 mg L^{-1} whereas those at WCO were typically 2-3 mg L^{-}, suggesting that additional sources such as wetlands and Coal Lake contributed slightly to downstream increases in DOC concentration *during summer months*."

We are principally referring to DOC concentration data from 2015-7 to support for this statement. DOC concentrations from the same day or within 1-2 days of sampling Coal Lake (CL) are more numerous in 2017, which is (mostly) outside the scope of this paper except for the PCA. A follow up to this paper that focuses on C-Q relationships from 2016-2018 is currently underway.

L399: However, if flow was substantial, this period may have been important for overall flux, even in the absence of a change in concentration?

Our response: Thank you for bringing this up. We have amended Section 4.1 in the discussion to address this point.

For GC, estimates of DOC export between 15 April-14 June over the six years range between 0.29 and 1.48 g C m^{-2} with 2015 and 2016 on the lower end (Table 2).

Year		Spring (g C m^{-2})	Summer (g C m-2)	Fall (g C m-2)	Spring & Summer (g C m^{-2})	Spring, Summer & Fall (g C m^{-2})
2002	GC	0.83	0.12		0.95	
2003	GC	0.42	0.19		0.61	
2006	GC	1.48	0.14		1.61	
2008	GC	0.97	0.31		1.28	
2015	GC	0.55	0.08	0.28	0.63	0.90
2016	GC	0.29	0.28	0.20	0.57	0.77
2016	WCO	0.06	0.09	0.09	0.15	0.24

Table 2. Load estimates for GC and WCO for 6 years by individual season, spring and summer, all relevant seasons together (spring, summer, fall) in g C m-2.

In the years that had multiple spring warming events (2003, 2016), loads were typically smaller as DOC concentrations had declined ahead of larger runoff volumes. For WCO, the pattern of DOC concentrations 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. *From an export perspective, springtime area-normalized loads were much smaller at WCO, suggesting that headwater ecosystems such as GC is where the bulk of DOC is sourced during freshet.*

Following freshet, DOC concentrations were 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 concentration *during summer months*. There were small increases in DOC concentrations associated with rainfall events *in summer*. 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. 3). Despite these large flows, DOC concentrations did not rise to the levels observed during freshet, *and the effect on DOC export varied between years (Table 2). In 2015, freshet was typical of prior observations with a large increase in both discharge and DOC concentrations with 1.9 times the DOC exported compared to fall. While DOC concentrations peaked in spring at both GC and WCO in 2016, export remained similar across all seasons. In*

both years, DOC export was consistent or approached half of spring export 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 more depleted than in spring yielding less terrestrially-derived, aromatic DOM *(Mutschlecner et al., 2018).*

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 was no robust relationship between discharge and DOC concentration over multiple years or within single years, suggesting that for this environment and at the headwater scale, discharge is a poor predictor of DOC export on an annual basis at the GC catchment (Table S2). However, on a seasonal basis, the relationship between DOC and discharge was at times stronger during summer, fall and winter when concentrations and discharge were relatively low (Table S2) (Fig. 8).

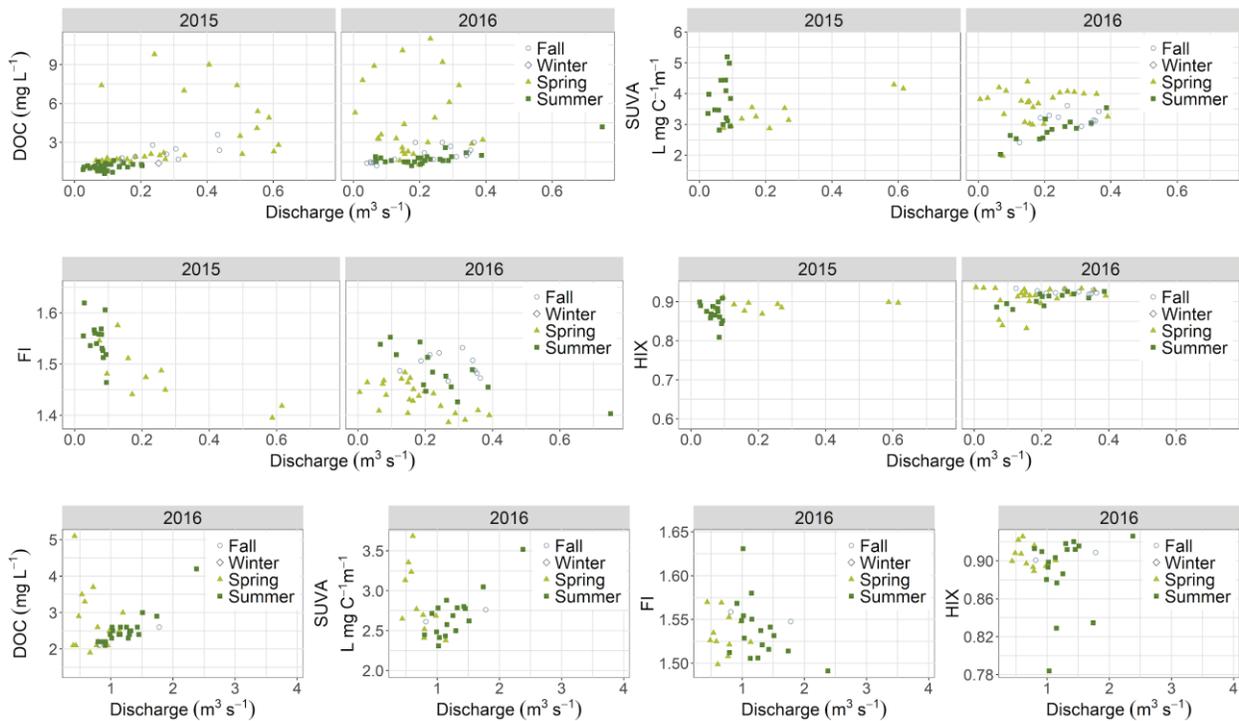



Figure 8. Concentration-discharge (C-Q) plots of DOC concentration, SUVA, FI and HIX for GC (2015-6) and WCO (2016). Season is indicated by shape and color (light green/filled triange -

Spring; dark green/filled square - Summer; light blue/open circle - Fall; dark blue/open diamond - Winter).

The lack of robust relationships between flow and DOC concentration over time is not surprising given the complex interaction of transport pathways and available organic carbon as the season progresses. The highly dynamic nature of freshet complicates C-Q patterns when concentration and export is greatest (see section 4.3), whereas later in the year as thaw increases and subsurface pathways contribute more, weaker (yet more significant) relations exist. We caution the use of regression equations relating DOC and flow to predict DOC loads, at least during spring or 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).

L402: There is some literature to support this assertion: ie, that the pool of OM will build up during dry periods, or periods when decomposition is not possible (ie, winter).This material then becomes available for flushing at the onset of rains and/or thaw. It might be useful to reference some of these studies here.
Our response: Reference was added.

L406: It would be really nice to see a plot of this data, and to see this used for a deeper consideration of process-level effects.
Our response: The statistically significant R^2 of the relationship between DOC and Q has been included in the supplemental materials (Table S2) after also being run in R using the C-Q regression function from the RiverLoad package (Nava et al., 2019). Table included below for reference:

Year	Site	Spring (R^2)	Summer (R^2)	Fall (R^2)	Spring & Summer (R^2)	Spring, Summer & Fall (R^2)
2002	GC	0.047	0.180		0.063	
2003	GC	0.041	0.001		0.034	
2006	GC	0.021	0.175		0.029	
2008	GC	0.024	0.215		0.005	
2015	GC	0.263	0.004	0.547	0.316	0.314
2016	GC	0.115	0.536	0.551	0.039	0.048
2016	WCO	0.066	0.783		0.010	0.011

Does a C-Q plot show distinct seasonal patterns, for example?
Our response: As seen in these plots, hysteresis plays a large part in DOC-Q patterns in spring, however, there is not much of a discernible relationship between DOC concentration and Q according to season. A seasonal pattern is most distinguishable during spring as prominent hysteresis. We also provided Table S2 (as shown above) to address these questions.

Swapping Q for runoff in a plot would allow comparison of multiple panels from different watershed components, which could be very instructive
Our response: Although substituting Q with runoff would be instructive, we believe that the influence of flow magnitude is of greater importance in our analysis and patterns can be observed well in the newly included C-Q plots.

L415: Similar to the comment above, it would be nice to see this data plotted, so that the reader could understand the magnitude of the effect.
Our response: Thank you for the suggestion. We have added new C-Q plots for GC and WCO (Figure 7 as shown above) to the manuscript with the season indicated using both shapes and colors.

L417: Agreed – this is a very big difference! Were early samples properly acidified to remove inorganic carbon during analyses?
Our response: Carey et al. 2003 & 2013 report sample acidification using H2SO4 to 0.035M.

Also, please tweak the sentence to clarify whether in all cases you're referring to concentrations measured at GC.
Our response: Sentence has been changed to clearly refer to DOC concentrations and we added DOC export calculations for additional context:
In each of the early years, peak DOC *concentrations* ranged between 17 and 27 mg L^{-1} with overall higher concentrations during freshet *(0.42 to 1.48 g C m^{-2} exported)*, whereas the maximum DOC *concentrations* for GC were 9.5 and 11.3 mg L^{-1} *(0.55 and 0.29 g C m^{-2} exported)* in 2015 and 2016 , respectively.

Section 4.2: As worded, this section is a bit repetitive with the results section. Consider weaking to move away from a restatement of the results, and more towards a discussion of what these optical indices can tell you about process.

We have recast this section to differentiate it from the results and provide greater reflection on processes.

Also consider cutting much of the first paragraph, where you discuss the inability to validate the PARAFAC model. If the model is not to be included, then perhaps it is best to omit its discussion from the paper?

Our response: Thank you for this comment. Any mention of the parafac model was removed from the paper.

L475: If this is well documented, this seems like an excellent opportunity to take this data and generate a more process-level understanding of DOM generation. Can knowledge of flowpaths be more directly tied to the DOC and DOM patterns being observed to more directly discuss OM generation at the sub-catchment and catchment outlet?

We have attempted to provide more process-level in the revised manuscript, although we are hesitant to reach too far. Quite often, more data asks more questions than it answers.

L481: Note that this is in agreement with expectations from the literature. See, for example Creed et al. CJFAS (as above).

Our response: We changed the sentence to mention the river continuum concept and added Creed et al 2015 as a reference:

As scale increases, DOC concentrations increase during summer and low flows yet are more muted during freshet at the outlet compared with headwater streams *in accordance with the river continuum concept (Creed et al., 2015).*

L498: To me, the change that might be expected in this catchment with permafrost thaw is not clear from the text that precedes.

Most work from permafrost regions is now suggesting that biodegradeability, at least, should increase with thaw, although it's not clear that this change will be visible at even the sub-catchment outlet scale (see, for example, work by Spencer and others).

Declines in concentration are presumably more related to soil profiles than the presence or absence of thermokarst.

" 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)."

Our response: We apologize for the confusion and meant to write increase. Thank you for the additional guidance to seek out and reread other work concerning whether these changes would be visible at the scale of our study areas. We have changed this sentence to:

At the scale of WCRB and its sub-catchments, results from other research in permafrost regions not experiencing rapid thermokarst that suggest a gradual increase in biodegradability (Spencer et al., 2008; Mann et al., 2015) are not necessarily discernable. However, changes in DOC concentrations and export are likely due to mineralization and adsorption within the soil profile as thaw increases and active layers expand (Striegl et al., 2007; Mu et al., 2017) with a warming climate.

L503: Effects of late summer / fall precipitation. I agree that this is an understudied, and worthwhile avenue of investigation.
Can you pull out this section with more clarity?
For example, it would be nice to see a more quantitative examination of effects on export – surely if discharge is increasing substantially, export is also affected? Is it possible to calculate overall effect on export?
Our response: Table 2 now displays the export from Granger Creek (GC) for each year, for each study period (spring to fall in 2015 and 2016; spring to late summer in 2002, 2003, 2006 and 2008). Mentioned in Section 4.1 rather than 4.3 with excerpt from 4.1 above.

L520: Again, I do wonder about these DOC values. Any chance you have some old, preserved (or frozen) samples that could be re-analyzed?
Our response: Unfortunately, no samples from previous years (2002-2008) were preserved so re-analysis was not possible.

A difference of ~10 mg/L is substantial, and an obvious culprit is a lack of full removal of inorganics (ie, bicarbonates) from the sample during processing.
Our response: While we agree that the differences between concentrations between the study periods in 2002-2008 and 2015-2016 are substantial, analytical error (due to collection, preservation and analysis) has been ruled out to the best of our ability. Ideally, as stated above by the referee, samples would have been preserved so that re-analysis could definitively address any possibility of analytic error but we do not have any preserved samples.

L537: Try to avoid single sentence paragraphs.
Our response: We have restructured the conclusion (according to similar input from Referee #1) to avoid single sentence paragraphs.

Supplementary Materials

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	1.77±0.66(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
	CL	2.90(1)		2.60(1)									
	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)			0.47(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
	CL		3.15±0.35(2)										
	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	6.70(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
2017	BB	2.70(1)	2.17±0.45(7)	1.15±0.14(6)		3.02±0.38(6)	3.15±0.17(6)		0.55±0.03	0.61±0.02		1.48±0.03	1.55±0.02
	CL		3.23±0.15(4)	2.96±0.09(5)		2.66±0.15(3)	2.82±0.08(5)		0.66±0.03	0.69±0.02		1.48±0.01	1.50±0.03
	GC	3.15±0.64(2)	2.33±0.71(7)	1.28±0.18(6)		3.14±0.23(5)			0.55±0.03			1.45±0.03	
	W1			6.10(1)			5.26(1)			0.62(1)			1.66(1)
	WCO	4.42±1.84(6)	2.72±0.37(5)	2.14±0.11(5)		2.83±0.25(3)	2.94±0.10(3)		0.61±0.03	0.64±0.01		1.51±0.02	1.57±0.02

Table S1. This table is similar to Table 1 in the manuscript but incorporates all samples used for principal component analysis (PCA). Additional sites (CL, W1) and additional years of data for sites BB, GC and WCO were used in the analysis to investigate influence of landscape type. Notation: Mean ± standard deviation (number of samples).

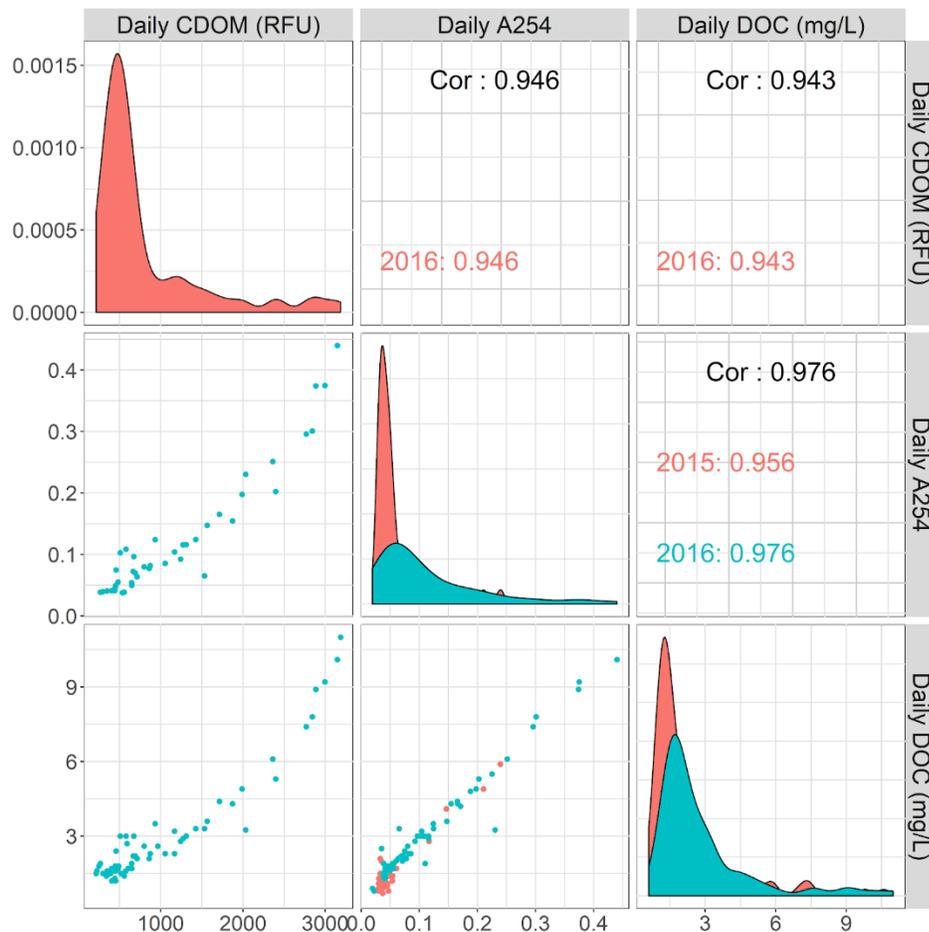



Figure S1. Correlation matrices of average daily CDOM (RFU), A254 (nm^{-1}) and DOC concentration (mg L^{-1}). No CDOM was measure in 2015 so it was not possible to separate out that year. Correlation was calculated using Pearson at 95% significance level (p<0.001 in all cases).

Year	Site	Spring (R^2)	Summer (R^2)	Fall (R^2)	Spring & Summer (R^2)	Spring, Summer & Fall (R^2)
2002	GC	0.047	0.180		0.063	
2003	GC	0.041	0.001		0.034	
2006	GC	0.021	0.175		0.029	
2008	GC	0.024	0.215		0.005	
2015	GC	0.263	0.004	0.547	0.316	0.314
2016	GC	0.115	0.536	0.551	0.039	0.048
2016	WCO	0.066	0.783		0.010	0.011

Table S2. Regressions between discharge (Q) and DOC concentrations (C) were performed using the CQregression function in the RiverLoad package (Nava et al., 2019) for GC in 2002, 2003, 2006, 2008, 2015 and 2016. A statistically significant correlation between C and Q was necessary to perform the regression.

Kaiser-Meyer-Olkin factor
Overall MSA = 0.77

MSA for each item:
FI = 0.98
Fresh = 0.68
HIX = 0.86
BIX = 0.69
SUVA = 0.91
DOC = 0.94

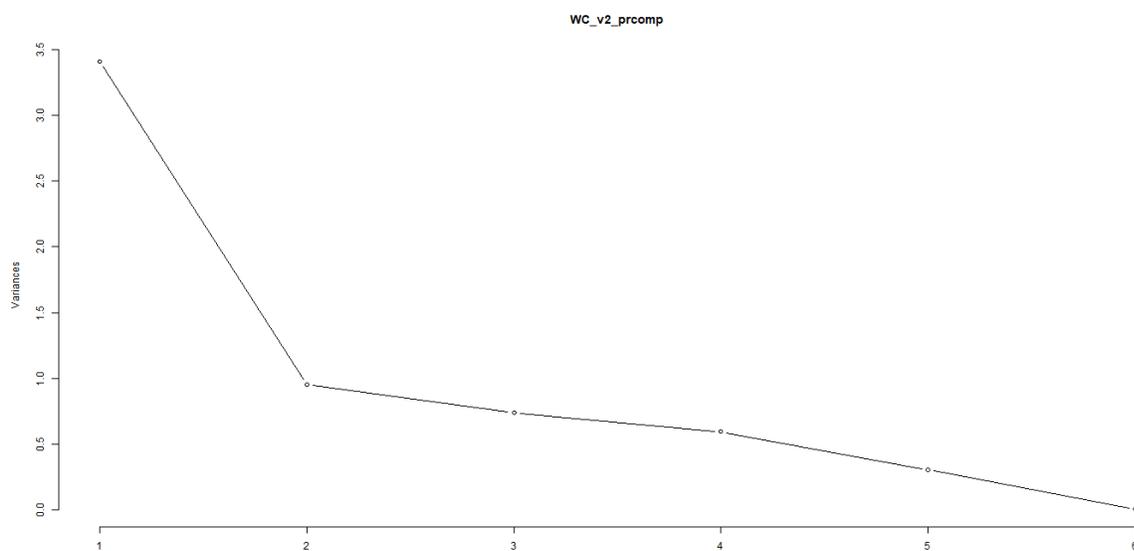
Figure S2. Scree plot for PCA.

	PC1	PC2	PC3	PC4
Standard dev	1.8472	0.9747	0.8577	0.7702
Proportion of variance	0.5687	0.1583	0.1226	0.09887
Cumulative proportion	0.5687	0.7270	0.8496	0.9485

Table S3. Standard deviation, proportion of variance explained by each PC (x100 for %) and cumulative proportion explained.

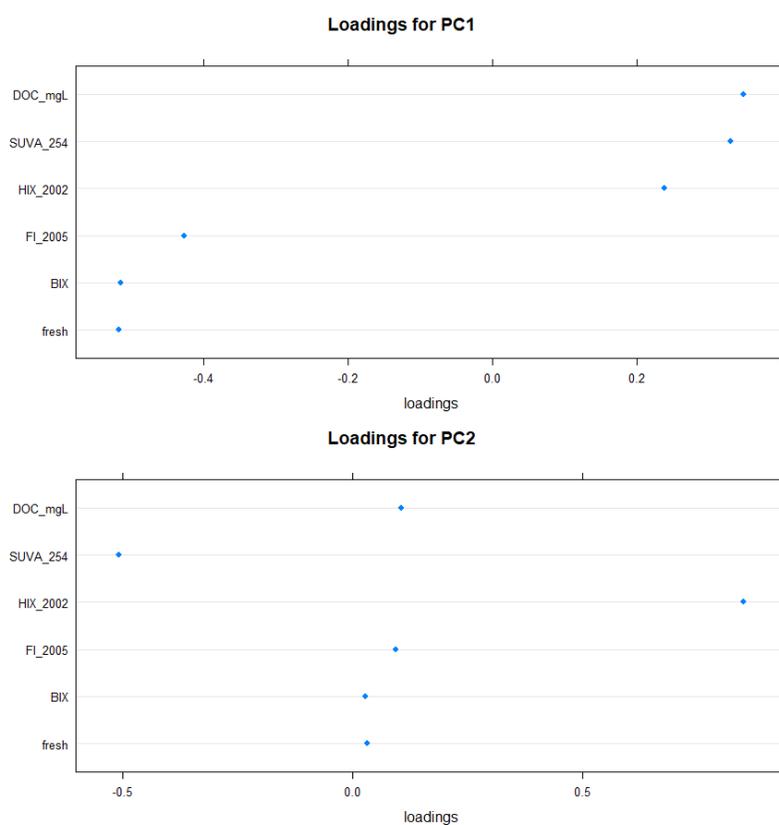



Figure S3. Dot plots of loadings per PC in PCA.

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 A~~a~~rctic 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, enhanced permafrost and seasonal thaw, earlier snowmelt, increased rainfall and other projected climate driven changes ~~due to climate change may~~will alter DOM sources and transport pathways. Results here support a projected shift from predominantly organic soils (high aromaticity, less fresh) to decomposing vegetation (more fresh and lower aromaticity)~~,~~. These changes may also ~~and~~ facilitate flow and transport through deeper flow pathways and enhance ~~with an enhanced~~ groundwater ~~role~~contributions to runoff.

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 soils and sediments in the the northern high latitudes are estimated to store approximately 1300 Pg (~40%) of the global belowground organic carbon pool (Hugelius et al., 2014) and ~~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~~ Ca, Mg, Na and SO_4 and P fluxes have ~~solutes have~~ increased significantly over the last thirty years. These increases are attributed to ~~, reflecting~~ deeper flowpaths as permafrost degrades, increased weathering and increased sulphate oxidation (Toohey et al., 2016). 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 non-permafrost 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

74 of thermally-mediated flowpaths are critical. DOC export is often greater during snowmelt freshet

75 when DOC mobilized from organic rich layers ~~is mobilized~~such that peak concentrations and high

76 spring flows result in ~~, resulting in~~ a large annual 'flush' as is typically observed in Western Canada

77 (Boyer et al., 2000; Carey, 2003; Finlay et al., 2006). Dependent on the soil profile, ~~A~~as flowpaths

78 descend in response to soil thaw, DOC mobilization typically declines and flow in mineral layers

79 provides more opportunity for immobilization and adsorption (MacLean et al., 1999; review by Kalbitz

80 et al., 2000; Carey, 2003; Kawahigashi et al., 2004, 2006; Frey and Smith, 2005). In some

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

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

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

84 (2015), suggest downstream mixing and deeper subsurface sources of DOC mask process drivers

85 including in-stream transformation as scale increases. In addition, the role of photodegradation and

86 oxidation of DOC to CO_2 in large Arctic rivers has received considerable attention (Cory et al., 2014;

87 Ward and Cory, 2016).

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

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

90 vegetation, oxygen availability and microbial activity (Schmidt et al., 2011). DOC is the mass of C in

91 the DOM~~a fraction of the DOM~~ pool whose lability, aromaticity and origins~~weight, aromaticity and~~

92 ~~origins~~ can in part be characterized using optical techniques. DOM exported from large Arctic rivers

93 during spring freshet has previously been reported as highly labile (Raymond et al., 2007; Holmes et al.,

94 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 relatively scarce information from northern alpine systems (Laudon et al., 2012). The goal of this paper is to enhance our understanding of the coupled dynamics of hydrology and ~~-~~DOC export and composition (using optical properties of DOM) in a well-studied, discontinuous permafrost alpine catchment in subarctic Yukon, Canada. ~~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

116 DOM composition. Impacts of increasing catchment scale and differing landscape types on DOM

117 optical indices were also assessed.

118 The specific questions addressed in this work weare:

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

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

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

122 cold alpine setting.

123 **2 Materials and methods**

124 **2.1 Study area**

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

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

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

128 Mountains, and spans an elevation ranging from 712 m a.s.l. to 2080 m a.s.l., and has a drainage

129 areadrains an area of ~179 km^2. WCRB straddles three ecological zones with boreal forest at lower

130 elevations (predominantly White Spruce (*Picea glauca var. porsildii*)) covering ~28% of the watershed;

131 at intermediate elevations shrub taiga comprises ~47 %, and at elevations above ~1500 m, alpine tundra

132 and bare rock surfaces predominate. WCRB has a relatively dry Subarctic climate (Koppen

133 classification *Dfc*) with 30-year climate normals (1981-2010) reported for Whitehorse Airport (706 m).

134 Average airport air temperature is -0.1 ºC and precipitation is 262.3 mm, with 161 mm falling as rain.

135 However, considering that WCRB covers a large elevation gradient, colder temperatures and

136 considerably larger volumes of precipitation have been reported for high-elevation sub-watersheds

137 (Pomeroy et al., 1999; Carey et al., 2013b; Rasouli et al., 2019). The geological setting of WCRB is

138 sedimentary sandstone, siltstone, limestone and conglomerate. Atop bedrock, thick stony till and glacial

139 drift covers most of the basin. Soils in the top metre are generally sandy to silty and at higher elevations

140 (taiga and lower tundra ecozones), a veneer of surface organic soils with variable thickness

141 predominate. Permafrost underlies much of the basin (~43 %), particularly at higher elevations and on

142 north-facing slopes in the taiga and alpine ecozones (Lewkowicz and Ednie, 2004).

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

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

145 2013a) (Fig. 1). GC is above treeline (~1200 m) and is dominated by Willow (*Salix* Sp.) and Birch

146 (*Betula* Sp.) shrubs at lower elevations with dwarf shrubs, lichen and bare rock above 1500 m. South

147 facing slopes have a thin organic layer overtop sandy soils whereas north slopes have thicker organic

148 layers (10-30 cm) and are underlain with discontinuous permafrost. A wide riparian zone (50 to 100 m)

149 with a consistently high water table in the lower reaches of GC lies between the slopes. Buckbrush

150 Creek (BB, 60°31'18.01" N, 135°12'17.27" W), another headwater catchment, drains an area of 5.75

151 km^2 and is located approximately 2 km west of GC (Fig. 1). BB ranges in elevation from 1324 to 2080

152 m a.s.l. with similar physiographic characteristics to GC. However, Buckbrush Creek is less incised

153 than GC and the riparian zone shows evidence of multiple overbank channels during high flow events.

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

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

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

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

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

159 steep slopes and vegetation that transitions from boreal forest at lake level to alpine tundra at the top of

160 surrounding slopes.

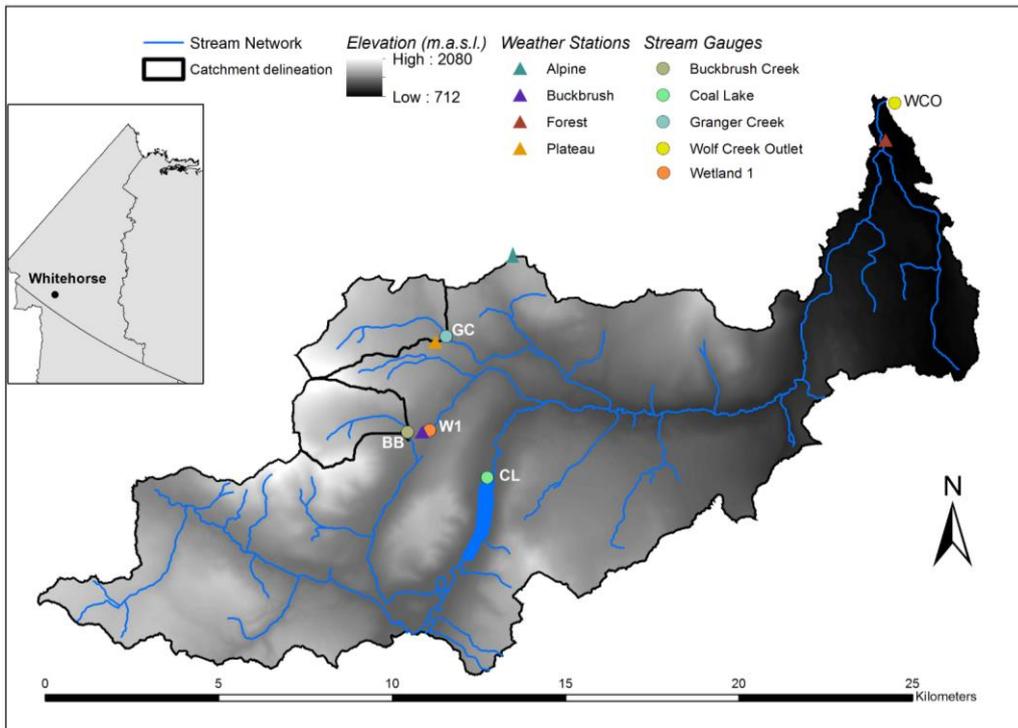
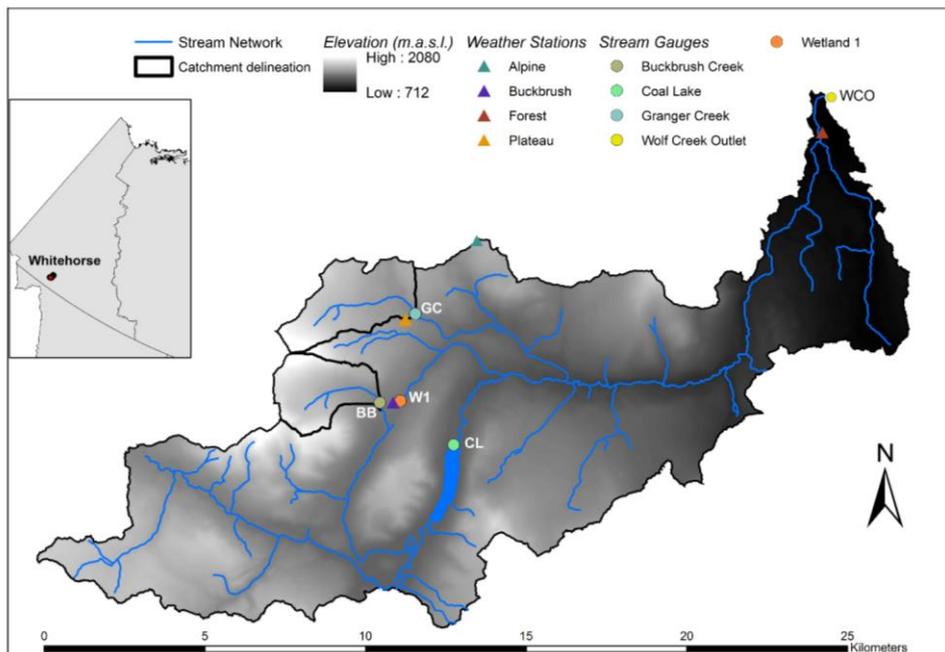



Figure 1. Map of Wolf Creek Research Basin (WCRB) with BB and GC catchments delineated. All stream gauges (BB, GC, CL, W1 and WCO) are indicated by circles; weather stations within WCRB are shown as triangles.

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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. Bushnell game cameras and in-person observation were used to document when the headwater streams and outlet were ice-free in spring to validate the use of pressure transducer measurements.

WCRB has three long-term weather stations to characterize the climate in each ecozone (Alpine, Buckbrush, Forest). All radiation components, air temperature, wind speed, vapour pressure and total precipitation are measured at 30 minute resolution, year-round at each site with some gaps due to power loss (Rasouli et al., 2019). The rainfall data reported in this study is from a tipping bucket rain gauge located at the nearby Buckbrush weather station and have been compared with an Alter-shielded Geonor total precipitation gauge for accuracy. 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. Monthly snow courses are completed in each ecozone to determine snow water equivalent (SWE), and on-site continuous measurements from a SR50 sensor at Plateau along with snow pillow

183 measurements from Buckbrush (Rasouli et al., 2019 provide instrumentation details) supplement these

184 and provide information on melt rates.

185

186 **2.3 Surface water sample collection and preparation**

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

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

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

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

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

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

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

194 situ and stored cool in 40 ml glass amber vials. In situ filtration with a syringe kept the time between

195 sample collection and filtration to a minimum, particularly during freshet when logistical constraints

196 meant that researchers remained in the catchment for up to two weeks at a time before returning to

197 Whitehorse.

198 **2.4 DOC and DOM fluorescence analysis**

199 Water samples were sent to the Biogeochemical Analysis Service Laboratory (University of Alberta) for

200 analysis on a Shimadzu 5000A Total Organic Carbon TOC analyzer for DOC concentration following

201 the US EPA protocol 415.1. The reportable detection limit provided by BASL for these samples was 0.1

202 mg/L. In total, 330 surface water samples were collected from 2015 to 2016 as outlined in Table 1. Of

203 the 330 DOC samples, ~215 were analysed for DOM quality using fluorescence spectroscopy. Seven

204 additional samples from CL in 2017 were analysed for DOC concentration and DOM quality.

205 Fluorescence excitation emission matrices (EEMs) were obtained from 0.45 µm PES-filtered water

206 samples using a Yvon Jobin Aqualog Benchtop Spectrofluorometer (HORIBA Scientific, Edison, NJ,

207 USA). Extra steps were taken to ensure that no background DOM from the PES filter and syringe

208 provided a fluorescence signature (see Supplemental Materials for further information). Fluorescence

209 spectra were recorded at an excitation range of 240-600 nm in steps of 5 nm with an emission range of

210 212-620 nm, in steps of 3 nm. The integrated Raman spectrum was checked before each run and

211 compared to prior values to ensure consistent lamp intensity. A sealed Quinone Sulfate sample an blank

212 pair were also run prior to each batch of samples and compared to prior values to ensure consistency.

213 Fluorescence spectra were normalized to the area under the Raman scatter peak (peak excitation

214 wavelength 397 nm) of a sealed Milli-Q water sample prior to all sample runs. A lab blank of distilled

215 water was also appended to each sample run and every 4 sample runs, a sample was repeated. Scatter

216 from the Raman Milli-Q sample was subtracted from each sample fluorescence spectrum. The

217 correction and normalization of samples to the Raman standard resulted in normalized intensity spectra

218 being expressed in Raman units (R.U., nm^{-1}).

219 Blank subtraction, Rayleigh scatter and inner filter effects were corrected using the Aqualog(R)

220 software. Subsequent EEM corrections and smoothing were done using the DrEEM toolbox (Murphy et

221 al., 2013) in Matlab (Mathworks Inc., Massachusetts, USA). Results were considered comparable to

222 each other since all data were collected from a single instrument and the Raman standard emission

223 intensity was verified for each data run.

224 Optical data obtained from the Aqualog(R) was used to calculate ~~fluorescence~~ optical indices. $SUVA_{254}$

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

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

227 reported along with DOC concentration and is positively related to aromaticity in bulk DOM ~~and is~~

228 ~~used to determine the degree of aromaticity in bulk DOM~~ (Weishaar et al., 2003) with higher values

229 indicative of a strong terrestrial signal. ~~Higher SUVA$_{254}$ values (sometimes greater than 6.0 L mg C^{-1} m^{-}~~

230 ~~1) indicate more aromatic carbon with a strong terrestrial signal~~ (Jaffé et al., 2008). ~~or poten~~Typically,

231 SUVA values greater than 4.5 L mg C^{-1} m^{-1} denote high~~tial~~ absorption at 254 nm due to colloids or iron

232 (Weishaar et al., 2003; Hudson et al., 2007). Research in northern peatlands associated peat soil

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

234 A~~llochton~~utotochtonous, terrestrial ~~or modified terrestrial~~ DOM ~~(microbial and soil-derived DOM)~~ is

235 associated with in~~de~~creased aromaticity and a ~~lower~~ higher $SUVA_{254}$ value while lower SUVA values

236 are related to modified terrestrial DOM. The biological index (BIX) is the ratio of emission intensities at

237 380/430 nm at an excitation wavelength of 310 nm (Huguet et al., 2009). Higher BIX values indicate

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

239 and Xenopoulos, 2009) while lower values indicate older, more terrestrial DOM. The fluorescence

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

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

242 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 DOC Load Calculations

DOC fluxes for GC were estimated using the R package RiverLoad (Nava et al., 2019). RiverLoad provided several methods to generate estimates of DOC flux and for this paper, Method1 (time-weighted Q and C) was chosen as most appropriate. Briefly, Method1 considers the mean concentration and mean flow of each sample to obtain a load value and is biased towards underestimating load in some situations (see Nava et al. 2019, Section 2.1.1 for full details and equation). Daily discharge data and DOC concentrations (maximum of 1 measurement per day) for 2002, 2003, 2006 and 2008 were obtained from the authors of Carey et al., 2013a. DOC concentrations (maximum of 2 per day) and discharge at 15 minute resolution for 2015 and 2016 are outlined in Sections 3.2 and 3.3). Any gaps in

264 the discharge data were filled by time-weighted interpolation, however there were no gaps greater than

265 3 days during springs flows for any year (2002, 2003, 2006, 2008, 2015, 2016.

266 **2.65 Statistical analysis**

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

268 SUVA$_{254}$ and the fluorescence indices and compiled in Table 1. To better assess differences between

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

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

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

272 exerting greater influence than smaller magnitudes.

Year	Sites	DOC (mg/L)			SUVA₂₅₄			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(1)	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±0.76	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
	WI	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)	0.51±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)	0.51±0.06	0.58±0.03	0.60±0.04	1.45±0.04	1.50±0.04	1.50±0.02
	WI	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).

274
275 The PCA was performed using R software version 3.4.0 (R Core Team 2017) in RStudio with R

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

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

278

279 **3 Results**

280 **3.1 Climate**

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

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

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

284 temperature of 11.8 °C in May 2015 compared with a normal of 7.3 °C. Average annual air

285 temperatures measured at the Buckbrush weather station (mid-basin) were -0.6 and -0.0 °C respectively

286 for the two years (Fig. 2). Persistent inversions in winter result in warmer temperatures at higher

287 elevations from December through to February. Accurate measurements of total precipitation have not

288 been recorded at Whitehorse airport for several years, limiting long-term context but rainfall values

289 from a nearby (~ 3 km) station were used for 2015-6 as well as rainfall from the Buckbrush weather

290 stations (Fig. 2).

291

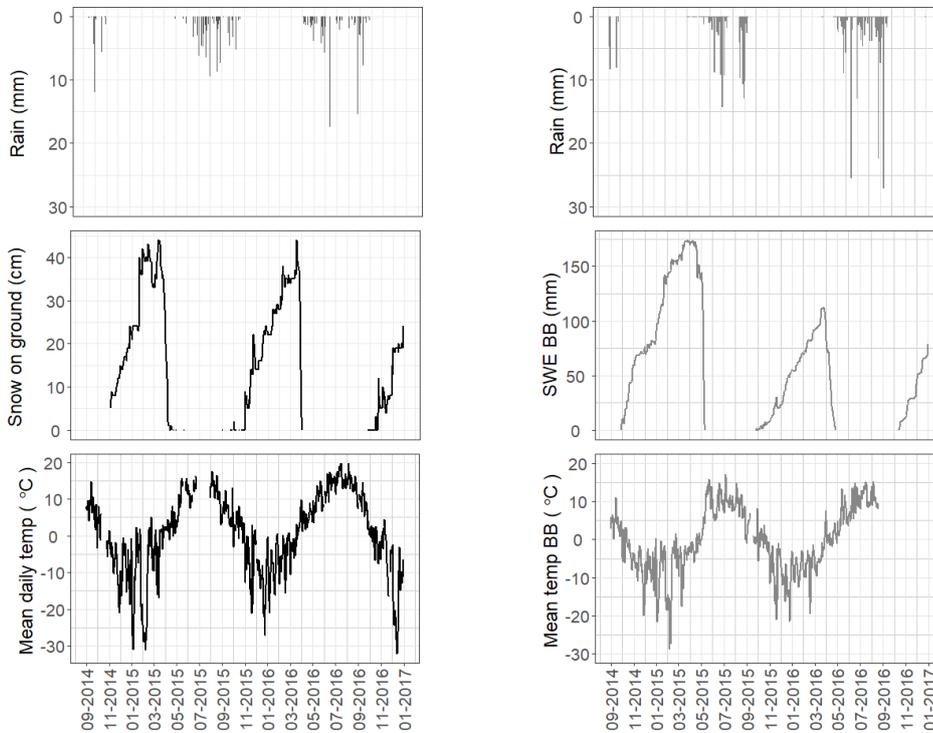



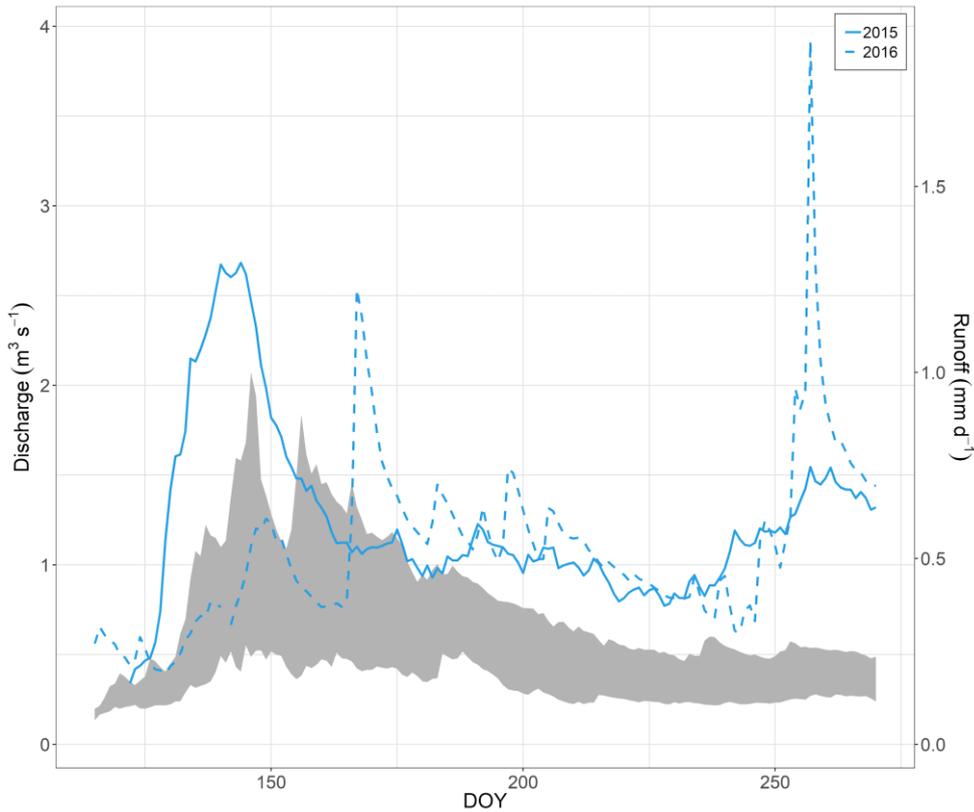
Figure 2. Figure 2. Climate variables from *Whitehorse Auto (Rainfall; 60°43'59.000" N, 135°05'52.000" W135°05'52.000" W, 707 m a.s.l., Whitehorse Airport (Snow on ground, Mean daily temp; 60°42'34.200" N, 135°04'07.800" W) and Buckbrush weather stations. (Left) Rain (measured in mm) from Whitehorse Auto (Climate ID: 2101310) located 3 km from Whitehorse Airport, snow on ground (in cm) and mean daily air temperature (°C) from the Environment Canada Airport weather station (YXY, Climate ID: 2101300) located ~ 14 km NW of Forest at 706 m a.s.l. (Right) Rainfall daily totals in mm were derived from hourly measurements, snow water equivalent (SWE) in mm based on 3 hour measurements from a snow pillow beside Buckbrush weather station. Daily average air temperature (°C), derived from 30 min measurements.* ~~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~~

304 ~~was taken as the cumulative total based on 3 hour measurements from a snow pillow beside Buckbrush~~
305 ~~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).

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310

311 **Figure 3.** Historical flow at WCO with 2015-6 flows superimposed. Grey area represents inter-quartile

312 range of 1993-2013 data. Solid line = 2015; dashed line = 2016. Day of year (DOY) along x-axis.

313 Summer flows were also greater than typically observed. For GC, in 2015 while there was an early

314 measurable stream response on 9 May, freshet began on 14 May when flows increased from ~0.02 m³s⁻¹

315 to daily flows averaging ~0.5 m³s⁻¹ over 9 days. Peak 2015 daily discharge was 0.67 m³s⁻¹ on 22 May,

316 thereafter flows began to decline to summer levels ~0.2 m³s⁻¹. In response to ~125 mm of rain between

317 17 August and 11 September, flows increased to ~0.46 m³s⁻¹ on 14 September before gradually

318 declining. Discharge at BB for 2015 and 2016 were slightly lower magnitude than GC with delayed

319 flow response to both freshet and summer rainfall. Data loss resulted in incomplete discharge data for

320 both years at BB. Manual measurements are shown in Fig. 3 to supplement continuous measurements.

321 Discharge at WCO followed a similar pattern to GC, rising from a winter baseflow of ~0.4-0.5 m^3s^{-1} on

322 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

323 removal of the transducer on 1 October.

(a)
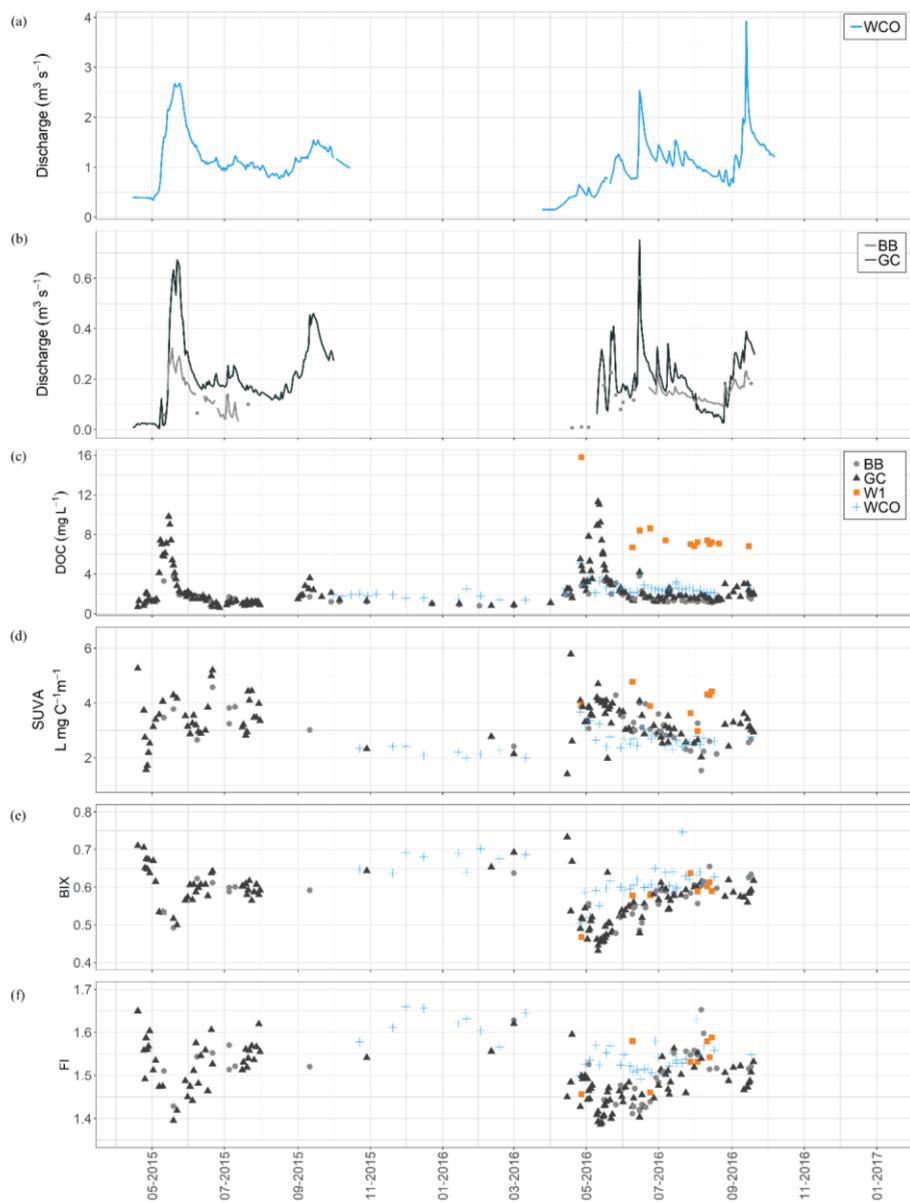
Figure 3. Flow, DOC and ~~fluorescence~~ optical indices for WCRB study sites. (a) Daily discharge data from WCO shown from April 2015 to October 2016. (b) Daily discharge data from GC (dark grey) and BB (light grey). (c) DOC concentrations in mg/L from grab samples over the study period with BB (light 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 when compared with 2015 and the historical record, exhibiting a more pronounced response to snowmelt than 2015 that occurred much earlier in the year in comparison to the 25 year record (Fig. 3). There was no distinct snowmelt freshet event in 2016, instead a gradual increase in flows was punctuated with hydrograph rises that corresponded with both 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 recorded at 3.9 m^3s^{-1} on 13 September. ~~Flows in 2016 were distinct at both GC and WCO compared with 2015 and the historical record, and exhibited 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) Concentrations

~~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

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

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

349 throughout the summer and with a slight rise in the fall. Seasonal statistics for DOC are presented in

350 Table 1. In 2015, the single freshet event corresponded with the rise in DOC, yet the rise and fall in

351 DOC concentration occurred fully on the rising limb of the freshet hydrograph between 7 May and 29

352 May. The maximum DOC concentration of 9.8 mg L^{-1} on 15 May corresponded to a 13.8 mm rain event

353 atop a sporadic snowpack with largely frozen soils. After June, DOC concentrations continued to

354 decline with slight increases corresponding to rainfall events. Towards the end of the measurement

355 period in 2015, DOC concentrations rose to a maximum of 3.6 mg L^{-1} with increasing discharge in

356 response to sustained precipitation. Over-winter values in December and January declined to ~1 mg L^{-1}.

357 This pattern of DOC behaviour was remarkably similar at the adjacent BB catchment which had more

358 limited sampling. In 2016, the spring rise in DOC at GC and BB corresponded to the period

359 immediately after the first small snowmelt pulse but prior to the bulk of the freshet signal (Fig. 3).

360 Concentrations again rose to ~11 mg L^{-1} with a steep recession to summer levels where rainstorms

361 would occasionally increase concentrations above 2 mg L^{-1}. As in 2015, a wet late season with a large

362 hydrograph increase resulted in increased DOC concentrations near 3 mg L^{-1} but concentrations were

363 much less than for corresponding freshet flows.

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

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

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

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

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

369 date of 27 April, and then post-freshet samples in June through September had concentrations between

370 7 and 9 mg L^{-1}. Concurrent DOC and fluorescence samples were only collected from CL post-freshet

371 during summer and fall of 2017.

372 **3.4 DOC Loads**

373

374 Export estimates for the six years of available data from GC range from 0.29 to 1.48 g C m^{-2} during

375 spring (15 April to 14 June); between 0.08 to 0.31 g C m^{-2} in summer (15 June to 14 August); 0.28 and

376 0.20 g C m^{-2} during fall in 2015 and 2016, respectively (Table 2). No estimates were made for fall in

377 2002, 2003, 2006 and 2008 due to a lack of concentration data. Spring DOC export was lowest during

378 2003 (0.42 g C m^{-2}) and 2016 (0.29 g C m^{-2}), two years characterized by a staggered snowmelt leading

379 to relatively low discharge during peak DOC concentrations (Fig. 4abc; Fig 4 in Carey et al., 2013a).

380 Total export during summer was relatively consistent across 2002, 2003, 2006 and 2015 at 0.12, 0.19,

381 0.14 and 0.08 g C m^{-2} while it was appreciably higher in 2008 and 2016 at 0.31 and 0.28 g C m^{-2},

382 respectively. Fall DOC export estimates for 2015 and 2016 were 0.28 g C m^{-2} and 0.20 g C m^{-2}. DOC

383 export estimates for WCO in 2016 were 0.06 g C m^{-2} in spring, 0.09 g C m^{-2} in summer and 0.09 g C

384 m^{-2} for fall (Table 2).

385 **3.5~~4~~ ~~Fluorescence~~ Optical Indices**

386 While there exists a large number of optical ~~fluorescence~~ indices in the literature (see Hansen et al.

387 2016), in this work we report the widely utilized SUVA$_{254}$, biological index (BIX) and fluorescence

388 index (FI) to help infer the source and composition of DOM (Table 1).

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

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

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

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

393 increased markedly in June in response to 18 mm of rain (11 to 18 June), whereupon it ranged between

394 2.8 and 4.5 L mg C^{-1} m^{-1}. Limited under-ice sampling suggests $SUVA_{254}$ remained relatively consistent

395 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

396 rose dramatically to 5.2 L mg C^{-1} m^{-1} before gradually declining through August with considerable

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

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

399 headwater catchments before rising slightly in summer whereas the opposite occurred in 2016. For

400 WCO, samples over the 2015-16 winter declined slightly from 2.5 to 2 L mg C^{-1} m^{-1}, and then during

401 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

402 increases associated with rising discharge. $SUVA_{254}$ at W1 was on average higher compared with other

403 sites, although limited sampling makes it uncertain as to any temporal pattern.

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

405 headwater sites (GC, BB) (Fig. 43). For GC in 2015, BIX fell from just above 0.7 to 0.49 during peak

406 freshet and then increased to between 0.55 and 0.65 during summer. Values increased over winter to a

407 maximum of 0.71 prior to 2016 freshet where a steep decline to values < 0.45 occurred during the early

408 phase of runoff in May and then gradually returned to values between 0.55 and 0.65 with declines

409 associated with rainfall-driven spikes in the hydrograph. The late season increase in discharge did not

410 strongly influence BIX at GC. BIX exhibited similar patterns inconsistencies between 2015 and 2016 at

411 the headwater sites with lower minimum values during spring in both years followed by an increase,

412 which plateaued in summer 2015 but continue to rise slightly during the 2016 summer spring values in

413 ~~2016 and an increase in summer whereas 2015 showed a decrease during summer to lower or 'older'~~

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

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

416 Timing of declines to rainfall events was slightly offset between the headwater sites and the outlet

417 WCO. At W1, BIX values increased slightly throughout the sampling period in 2016 (Fig. 4~~3~~).

418 FI at GC and BB exhibited patterns similar to BIX but inverse to $SUVA_{254}$ (Fig. 4~~3~~). In 2015, FI

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

420 1.5 and 1.6 during summer. In 2016, FI values again declined from 1.6 to 1. during freshet yet were on

421 average lower than 2015 but also gradually increased throughout summer with a small decline during

422 the wet late summer. For WCO, winter FI ranged between 1.55 and 1.65 and more gradually declined

423 during freshet to ~ 1.5 and then increased slightly with more limited variability throughout the summer.

424 A small decline during the wet period in late September was observed. Over the two study years at GC,

425 BB and WCO, mean FI was lowest during spring, and higher in summer (2015, 2016) than in fall 2016.

426 For W1, FI was low at 1.45 on the first sampling date in spring 2016 when DOC was high, and then

427 increased with some variability but values were on average greater than those at GC and BB.

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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	1.77±0.66(5)**	1.25±0.31(11) A*	1.19±0.39(9)^A B*	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±0.01	1.49±0.06	1.54±0.03	1.57±0.76
	CL GC	2.90(1) 2.89±2.29(52) A**	1.07±0.21(36) A**	2.60(1) 1.75±0.76(17) A**B*	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 WCO	15.8(1)		1.79±0.90(14) B*	3.94(1)		2.21±0.17(10)	0.47(1)		0.66±0.03	1.46(1)		1.62±0.03
2016	BB	2.34±0.87(14) A**B**	1.42±0.27(23) A**B**	1.50±0.20(3)	3.56±0.48(10) A**B**	2.81±0.59(16) A**B**	2.45±0.28(3)	0.513±0.03 A**B**	0.58±0.03 A**B**	0.62±0.02 A**B**	1.45±0.04 A**	1.52±0.06 A**B*	1.52±0.00
	CL GC	3.15±0.35(2) 4.32±2.56(43) A**B**	1.71±0.34(32) A**B**	2.00±0.57(20) A**	3.86±1.40(37) A**B**	2.86±0.38(17) A**B**	3.14±0.32(11) A**B	0.513±0.06 A**B**	0.58±0.03 A**B*	0.60±0.04 A**	1.45±0.04 A**B**	1.50±0.04 A**B*	1.50±0.02 A**
	W1	6.70(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) A**B**	2.58±0.44(22) A**B**	2.35±0.35(3)	2.83±0.42(12) A**B**	2.70±0.28(19) A**B**	2.69±0.11(2)	0.582±0.04 A**B**	0.60±0.02 A**B**	0.66±0.03	1.53±0.02 A**B*	1.54±0.03 A**B*	1.55±0.01

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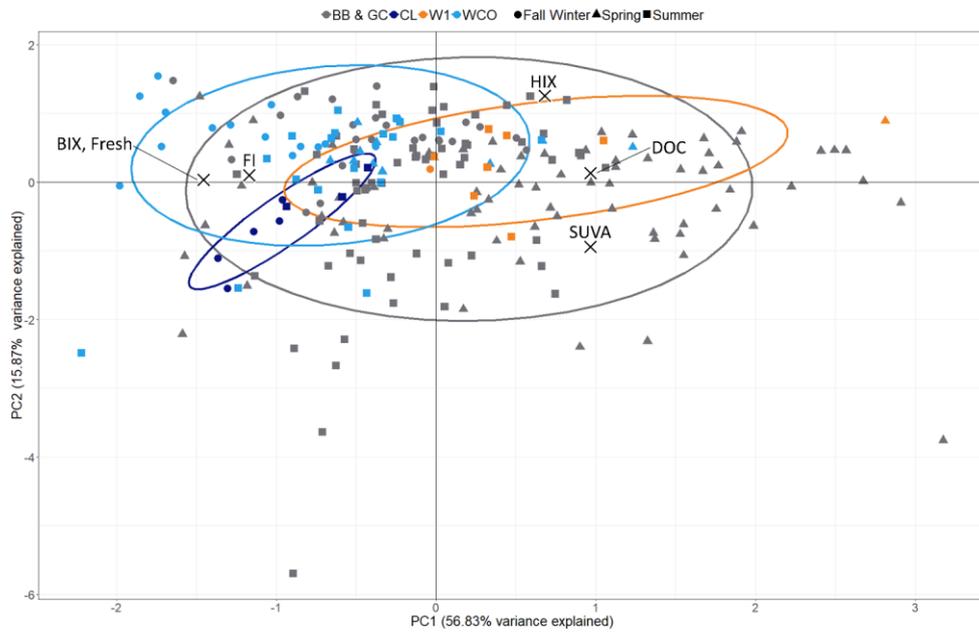
3.65 Principal Component Analysis

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.

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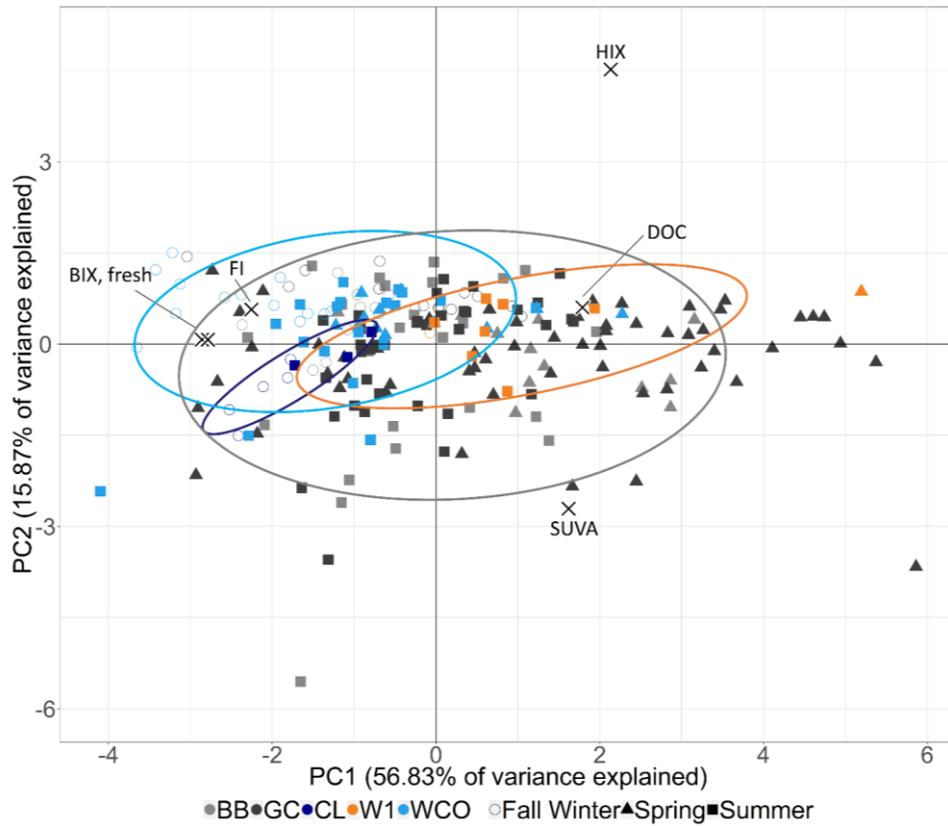
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478 **Figure 5.** Biplot from PCA. PC1 on the x-axis and PC2 along the y-axis. X indicates where the point of
479 the loadings with the applicable index written nearby. Samples are grouped by season: Triangles =
480 Spring (15 April-15 June); Squares = Summer (16 June-15 August); Circles = Fall/Winter (16 August-
481 14 April). Samples are also grouped by landscape type: Bright blue = Mesoscale outlet (WCO); Dark
482 blue = Lake (CL); Orange = Wetland (W1); Grey = Headwaters (light grey – BB, dark grey – GC).
483 ~~**Figure 4.** Biplots from PCA. Ellipses represent 0.8 probability of sample values being within the shape.~~

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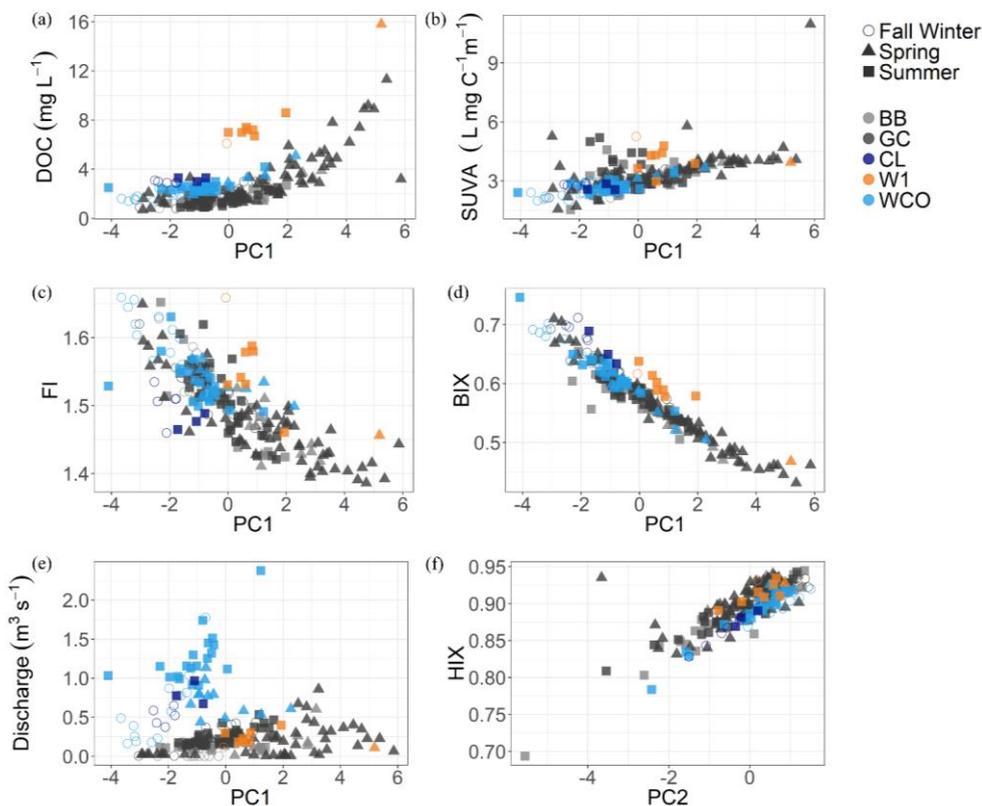
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486 **Figure 5̶6.** Regressions of principal components to DOC concentrations and DOM indices. Regression
487 of PC1 to DOC concentrations implies some non-linear behaviour. Samples are grouped by season:
488 Triangles = Spring (15 April-15 June); Squares = Summer (16 June-15 August); Circles = Fall/Winter
489 (16 August-14 April). Samples are also grouped by landscape type: Bright blue = Mesoscale outlet
490 (WCO); Dark blue = Lake (CL); Orange = Wetland (W1); Grey = Headwaters (light grey – BB, dark
491 grey – GC).

492 BB and GC plotted similarly and are shown together (Fig. 5̶4) to highlight differences between the

493 landscape types rather than between the two headwater sites. DOC concentrations and SUVA$_{254}$,

494 BIX/Freshness and HIX most strongly distinguish the samples in the PCA. Spring samples from the

495 headwaters and wetland plot mostly to the right along PC1 due to high DOC concentrations and

496 SUVA$_{254}$ measured during that time period. Headwater samples span almost the entire PC1 axis due to

497 the high variability in spring-time DOC and streamflow. Fall/winter samples are predominantly located

498 left of the zero-line (Fig. 54) for all sites. All CL samples cluster together. Some separation of DOC

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

500

501 **4 Discussion**

502 **4.1 DOC quantity and timing in streams**

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

504 concentration on the rising limb of the freshet hydrograph as the baseflow-driven system switches to

505 near-surface flowpaths in organic-rich soils (Striegl et al., 2005; Raymond et al., 2007; Holmes et al.,

506 2012). The most distinct feature of OC export in northern watersheds is the sudden increase in DOC

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

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

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

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

511 for data on early yearsFig. 7).

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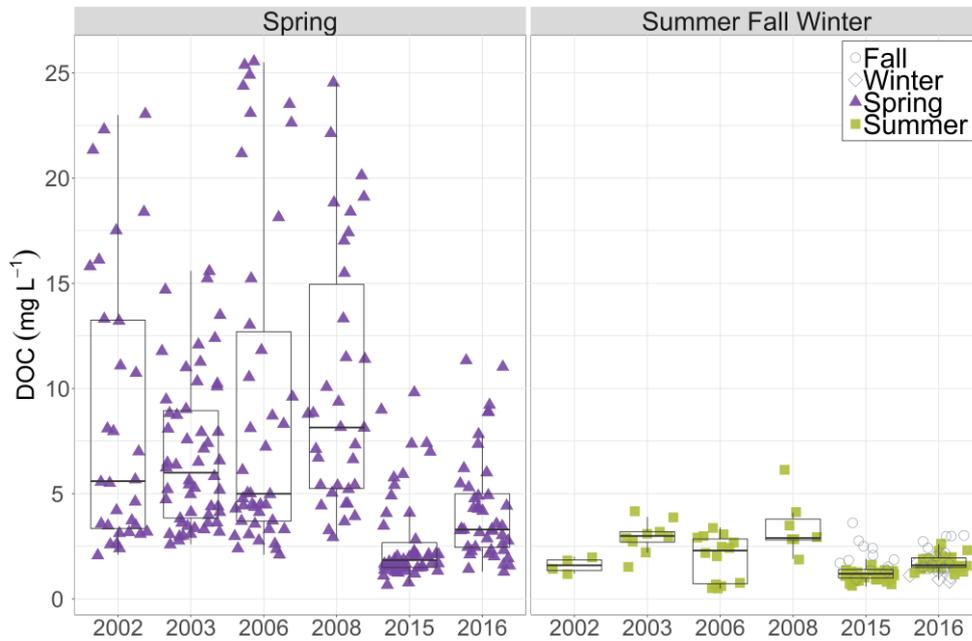


Figure 7. DOC concentration in mg/L is displayed on the y-axis with the left panel showing DOC concentrations measured in 2002, 2003, 2006, 2008, 2015 and 2016 during spring (April 15 to June 14). The right panel displays DOC concentrations for the same years during summer, fall and winter (prior to April 15; June 15 to Dec 31). Season is additionally indicated by shape and color (purple/filled triangle - Spring; light green/filled square - Summer; open circle - Fall; open diamond - Winter).

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

524 similar (Fig. 43), and corresponds with those reported in earlier years (Carey et al, 2013a). The

525 implication of these historical and recent observations is that while DOC exported during spring is

526 hydrologically mediated via the transport pathways, DOC concentrations are not related to flow

527 volumes at the headwater scale. Although investigation into headwaters is relatively rare (Bishop et al.,

528 2008), studies have reported greater variation in DOC at the headwater scale than in large rivers (Sedell

529 and Dahm, 1990; Wolock et al., 1997; Temnerud and Bishop, 2005; Temnerud et al., 2010; Creed et al.,

530 2015). Relatively small amounts of water are sufficient to extinguish the available pool of OM

531 responsible for DOC peak concentration in the spring at this headwater catchment. For GC, estimates of

532 DOC export between 15 April-14 June over the six years range between 0.29 and 1.48 g C m^{-2} with

533 2015 and 2016 on the lower end (Table 2).

Year	Site	Spring (g C m^{-2})	Summer (g C m^{-2})	Fall (g C m^{-2})	Spring & Summer (g C m^{-2})	Spring, Summer & Fall (g C m^{-2})
2002	GC	0.83	0.12		0.95	
2003	GC	0.42	0.19		0.61	
2006	GC	1.48	0.14		1.61	
2008	GC	0.97	0.31		1.28	
2015	GC	0.55	0.08	0.28	0.63	0.90
2016	GC	0.29	0.28	0.20	0.57	0.77
2016	WCO	0.06	0.09	0.09	0.15	0.24

534

535 **Table 2.** Load estimates for GC and WCO for 6 years by individual season, spring and summer, all
536 relevant seasons together (spring, summer, fall) in g C m^{-2}.
537

538 In the years that had multiple spring warming events (2003, 2016), loads were typically smaller as DOC

539 concentrations had declined ahead of larger runoff volumes. For WCO, the pattern of DOC

540 concentrations during freshet was similar to GC, yet dampened with lower values during freshet over a

541 longer period from mixing of various landscapes that integrate three distinct ecosystems and a small

542 lake over a large elevation range. From an export perspective, springtime area-normalized loads were

543 much smaller at WCO, suggesting that headwater ecosystems such as GC is where the bulk of DOC is

544 sourced during freshet.

545 Following freshet, DOC concentrations were remarkably consistent across the sampling sites. The

546 headwater GC and BB values were ~1.5 mg L$_{-1}$ whereas those at WCO were typically 2-3 mg L$_{-1}$,

547 suggesting that additional sources such as wetlands and Coal Lake contributed slightly to downstream

548 increases in DOC concentration during summer months. There were small increases in DOC

549 concentrations associated with rainfall events in summer. A notable feature of both 2015 and 2016 were

550 the substantial late season rains that generated flows outside the typical range at both GC and WCO

551 (Fig. 3). Despite these large flows, DOC concentrations did not rise to the levels observed during

552 freshet, and the effect on DOC export varied between years (Table 2). In 2015, freshet was typical of

553 prior observations with a large increase in both discharge and DOC concentrations with 1.9 times the

554 DOC exported compared to fall. While DOC concentrations peaked in spring at both GC and WCO in

555 2016, export remained similar across all seasons. In

556 25both years, DOC export was consistent or approached half of spring export suggesting either alternate

557 runoff pathways/flow generation mechanisms or a reduced source of soluble OM in soils available for

558 transport. Considering water tables were very high during this period, we presume that the available

559 pool of OM in shallow organic layers was more depleted than in spring yielding less terrestrially-

560 derived, aromatic DOM (Mutschlecner et al., 2018).

561 For WCO, the pattern of DOC during freshet w similar to GC, yet dampened with lower values during

562 freshet over a longer period from mixing of various landscapes that integrate three distinct ecosystems

563 and a small lake over a large elevation range.

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

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

566 additional sources such as wetlands and Coal Lake contributed slightly to downstream increases in

567 DOC. There were small increases in DOC concentration associated with rainfall events. A notable

568 feature of both 2015 and 2016 were the substantial late season rains that generated flows outside the

569 typical range at both GC and WCO (Fig. 5). Despite these large flows, DOC concentrations did not rise

570 to the levels observed during freshet, suggesting either alternate runoff pathways/flow generation

571 mechanisms or a reduced source of soluble OM in soils available for transport. Considering water tables

572 were very high during this period, we presume that the available pool of OM in shallow organic layers

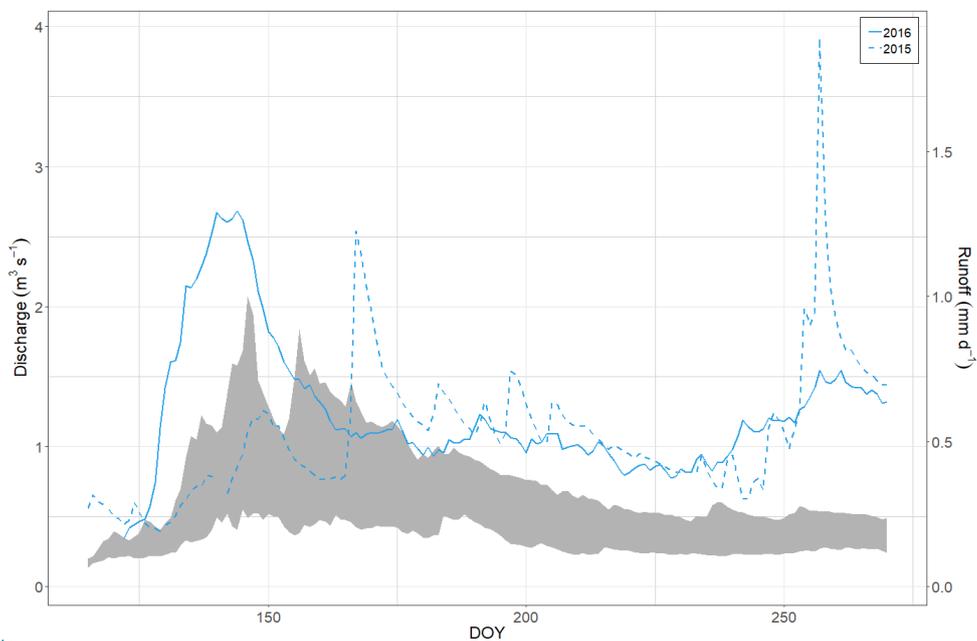
573 was less than in spring.

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Figure 6. ~~Historical flow at WCO with 2015-6 flows superimposed. Grey area represents inter-quartile~~
575
576 ~~range of 1993-2013 data. Dashed line = 2015; Solid line = 2016. Day of year along x-axis.~~

577 Unlike results elsewhere (Petrone et al., 2006, 2007; Raymond et al., 2007; Striegl et al., 2007;

578 Balcarczyk et al 2009; Prokushkin et al., 2011; Holmes et al., 2012), there is no robust relationship

579 between discharge and DOC over multiple years or within single years, suggesting that for this

580 environment and at the headwater scale, discharge is a poor predictor of DOC export on an annual basis

581 at the GC catchment (Table S2). However, on a seasonal basis, the relationship between DOC and

582 discharge was at times stronger~~, particularly for~~ during summer, fall and winter when concentrations

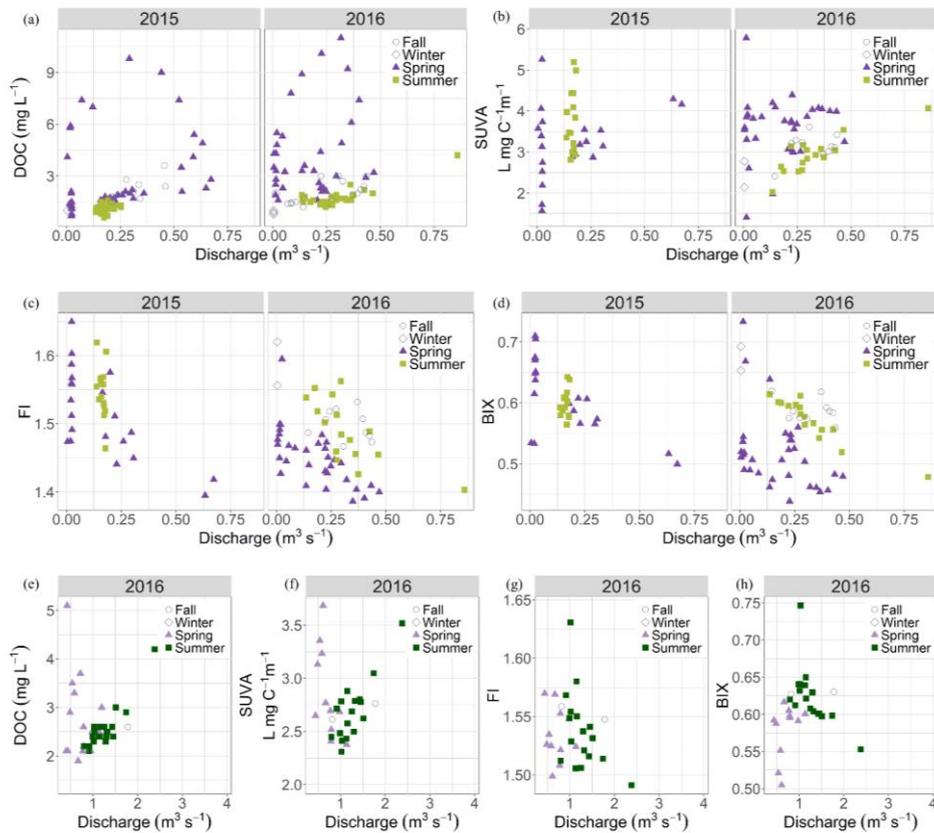
583 and discharge were relatively low (Table S2; Fig. 8).

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Figure 8. Concentration-discharge (C-Q) plots of DOC concentration, SUVA, FI and HIX for GC (2015-6) and WCO (2016). Panels a, b, c, d show DOC concentration, SUVA254, FI and HIX optical indices in relation to discharge for 2015 and 2016 at Granger Creek (GC). The bottom four panels (e, f, g, h) show the same sets of concentration-discharge relationships for 2016 at Wolf Creek Outlet (WCO). Season is indicated by shape and color (purple/filled triangle - Spring; green/filled square - Summer; open circle - Fall; open diamond - Winter). Y-axis values differ for each plot.

591

592 The lack of robust relationships between flow and DOC concentration over time is not surprising given

593 the complex interaction of transport pathways and available organic carbon as the season progresses.

594 The highly dynamic nature of freshet complicates C-Q patterns when concentration and export is

595 greatest (see section 4.3), whereas later in the year as thaw increases and subsurface pathways

596 contribute more, weaker (yet more significant) relations exist. We caution the use of regression

597 equations relating DOC and flow to predict DOC loads, at least on an annual basis. However, for larger

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

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

600 A curious result was a notable decline in freshet DOC concentrations between the four years in the

601 2000s (Carey et al., 2013a) and the 2015-2016 study years (Fig. 7). In each of the early years, peak

602 DOC concentrations ranged between 17 and 27 mg L^{-1} (0.42 to 1.48 g C m^{-2} exported) with overall

603 higher concentrations during freshet, whereas the maximum DOC values for GC were 9.5 and 11.3 mg

604 L^{-1} (0.55 and 0.29 g C m^{-2} exported) in 2015 and 2016, respectively. The reason for this decline is

605 uncertain, yet is not related to freshet conditions as flows and climate during freshet were similar among

606 certain years. We have also largely ruled out instrumentation or sampling as a source of this difference

607 as mid-season values were unchanged. Tiwari et al. (2018), using 23 years of data from the Krycklan

608 research catchment in central Sweden, suggest that peak DOC concentrations are most closely related to

609 warm fall temperatures, cold winter conditions and shallow snowpacks. In addition, Ågren et al.

610 (2010a) used 15 years of data from boreal catchments also located in the Krycklan research catchment

611 to show that high export of DOC in the snow-free season led to decreased export in the subsequent year.

612 For six years of data at GC catchment, winter (Nov-Mar) temperatures show a weak correspondence

613 with DOC export, in that warmer winters tend to have lower DOC export during the following spring,

614 which is supported by Scandinavian research (Ågren et al., 2010a,b; Haei et al., 2010). However, there

615 was no relation between snow depth and peak DOC concentration for the six years (data not shown,

616 snow data available in Rasouli et al., 2019). A final possibility may be that increased summer and fall

617 wetness that has occurred in recent years is reducing decomposition as outlined by Balcarcyzk et al.

618 (2009).

619 **4.2 DOM indices in streams**

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

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

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

623 Kellerman et al., 2018) and catchment processes exists with observations from both temperate and

624 northern study sites. A number of widely-used indices (reviewed in Hansen et al. 2016) facilitate

625 comparison among sites, and chemometric components through the ever-expanding library OpenFluor

626 (http://www.openfluor.org). We applied the widely used drEEM toolkit (Murphy et al., 2013) to our

627 dataset, yet we were unable to validate the model using a split-half approach to the dataset. However,

628 the overall relationship between CDOM and DOC is robust in WCRB as observed in other rivers

629 (Stedmon et al., 2011; Spencer et al., 2012; Frey et al., 2015), with a strong relationship between A254

630 and DOC (r^2: 0.97, p<0.001).

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

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

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

634 onset of freshet and the rise in DOC, $SUVA_{254}$ rises while both BIX and FI decline to annual minima.

635 This freshet response is attributed to the mobilization of DOM derived from leaf litter and older

636 terrestrial precursor material with high molecular weight and aromatic DOM (Wickland et al., 2012).

637 This pattern is particularly clear at GC, where BIX and FI are closely correlated with each other and

638 negatively correlated with $SUVA_{254}$. At this time, near-surface pathways across frozen ground are the

639 only mechanism to rapidly transport OM and water to the stream. Once DOC declines, $SUVA_{254}$

640 decreases and FI and BIX begin to increase. A number of mechanisms can be attributed to these

641 changes: an increase in more microbial DOM as thaw depths increase and soil temperatures warm, and

642 an increased ability of mineral soils to adsorb DOM with high organic weight and large aromatic

643 structures along flow pathways (Ussiri and Johnson, 2004). The gradual change in the three

644 fluorescence indices as summer progresses suggests a continual decline in high molecular weight, older

645 DOM (lower $SUVA_{254}$) and a greater proportion of recently produced DOM. During the unusually wet

646 fall periods, rising water tables and activation of near-surface and overland flow pathways resulted in

647 increases in SUVA and declines in BIX and FI, yet not to the same magnitude as spring when flows

648 were of similar volume. The smaller influence of wet fall periods on changing DOM composition can

649 be explained in part by a much wider range of flow pathways across deeply thawed soils and also

650 considerable adsorption sites for DOM. In addition, sources of leaf decomposition compounds located

651 in upper soil horizons leached in spring have had less time to replenish prior to leaf-fall. As with DOC

652 concentration, the important implication is that seasonality as opposed to flow magnitude has a greater

653 influence on the quality of DOM. By early November, temperatures throughout WCRB are below

654 freezing and a long winter recession occurs. Limited over-winter sampling at WCO and GC show

655 SUVA$_{254}$ values declining to their lowest values prior to freshet with a corresponding maxima in BIX

656 and FI. This pattern corresponds to those reported elsewhere in the Yukon River Basin and other

657 watersheds in Alaska (Striegl et al., 2007; O'Donnell et al., 2010; Mutschlecner et al., 2018).

4.4 Patterns across space and time

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

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

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

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

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

664 Carey et al., 2013a), the dominant hydrological pathways at the scale of WCRB shift from the supra-

665 and intra-permafrost pathways to one that is more groundwater driven. In addition, a ~1 km^2 lake in the

666 centre of the basin has an important storage and mixing effect. The impact of these changes on the

667 pattern of DOM indices at WCO is complex and not easily resolved back to component landscape types.

668 From the PCA, a host of controls act to influence DOC and fluorescence indices throughout WCRB

669 (Fig. 4, Fig. 6, Table 3). As scale increases, DOC concentrations increase during summer and low flows

670 yet are more muted during freshet at the outlet compared with headwater streams in accordance with the

671 river continuum concept (Creed et al., 2015). WCO had lower SUVA$_{254}$, greater BIX and FI compared

672 with both headwater and wetland systems. The lower SUVA$_{254}$ at WCO corresponds to an increasing

673 dominance of groundwater or greater baseflow along with deeper subsurface pathways due to a lesser

674 extent of frozen ground (Walvoord and Striegl, 2007; O'Donnell et al., 2010). In contrast, higher FI and

675 BIX likely reflect the influence of these deeper flow pathways and any processes and production that

676 occur in Coal Lake, which sits in the approximate mid-point of WCRB. Most FI values at the headwater

677 catchments are between 1.4 and 1.6, reflecting terrestrial plants as the dominant source of DOM. By

678 contrast, values in excess of 1.6 at WCO, particularly during winter and low flow periods, suggest some

679 microbial DOM sources. The high values of BIX in winter at WCO supports some moderate autotrophic

680 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 3. 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

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

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

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

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

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

686 (review by Kalbitz et al., 2000; Wickland et al., 2007). At the scale of WCRB and its sub-catchments,

687 results from other research in permafrost regions not experiencing rapid thermokarst that suggest a

688 gradual increase in biodegradability (Spencer et al., 2008; Mann et al., 2015) are not necessarily

689 discernable. However, changes in DOC concentrations and export are likely due to mineralization and

690 adsorption within the soil profile as thaw increases and active layers expand (Striegl et al., 2007; Mu et

691 al., 2017) with a warming climate. ~~Results from this work compare well with others in permafrost~~

692 ~~regions that are not experiencing rapid thermokarst, suggesting a gradual decrease in biodegradability~~

693 ~~and changes in DOM likely due to mineralization and adsorption as thaw increases (Striegl et al., 2007;~~

694 ~~Mu et al., 2017).~~ Whereas most conceptual models have focussed on the implications of thaw and

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

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

697 Canada (Spence and Rausch, 2005; Spence et al., 2015; DeBeer et al., 2016). Despite late-season

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

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

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

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

702 adsorption potential. FI and BIX were typically higher at the outlet than the headwater and wetland

703 sites, which is attributed to lake influences and greater autotrophic production with increasing stream

704 order.

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

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

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

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

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

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

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

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

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

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

715 **5 Conclusions**

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

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

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

719 temporal variability associated with seasonality, and that A254 and CDOM were reliable proxies for

720 DOC concentrations. Observations from nested watersheds with drainage areas of ~6 to 179 km^2

721 indicate that mixing and complex process interactions dampen variability in downstream responses and

722 result in a gradual shift in DOM characteristics. Despite considerable fluctuations among years, DOC

723 concentrations and export are consistently highest during freshet despite differences in timing and

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

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

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

727 less responsive to rainfall events in summer when the water table descends into deeper mineral soil

728 layers.

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

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

731 signals at increasing watershed scales.

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

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

734   falls on the low end of the range reported a decade ago.

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

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

737   play are a longer growing season, a shift in vegetation community composition and spatial extent,

738   warmer winters, increased baseflow with greater groundwater input, earlier freshet or disruption of the

739   typical northern hydrograph and an altered precipitation regime. Ultimately, watershed scale and the

740   arrangement of landscape types will play important roles in determining how DOC flux and DOM

741   lability change under a warming climate, and altered precipitation, disturbance and vegetation regimes.

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

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

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

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

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