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

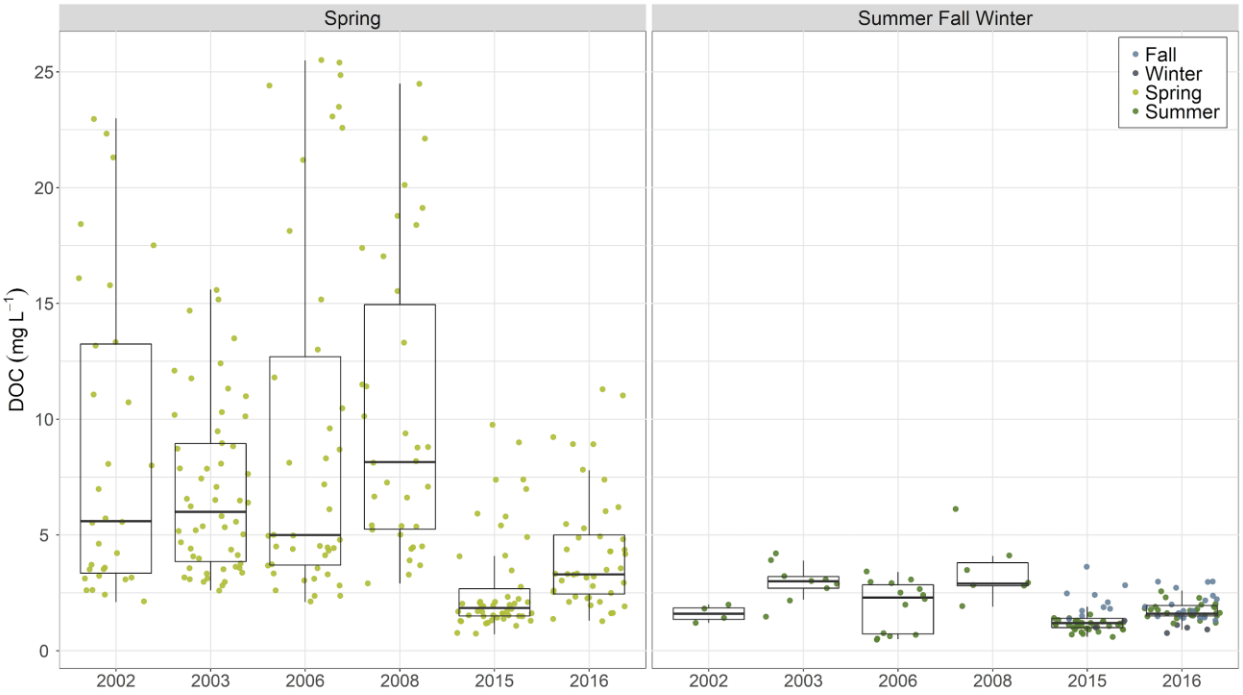
and then more or less plateaus overall (there is one sample that is higher than the rest, and there is some minor variability but it is difficult to discern a clear decrease?), while in 2016 the BIX values keep increasing steadily after the minimum during freshet.
Our response: The sentence has been 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 <u>data Carey et al 2013a data</u> 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.

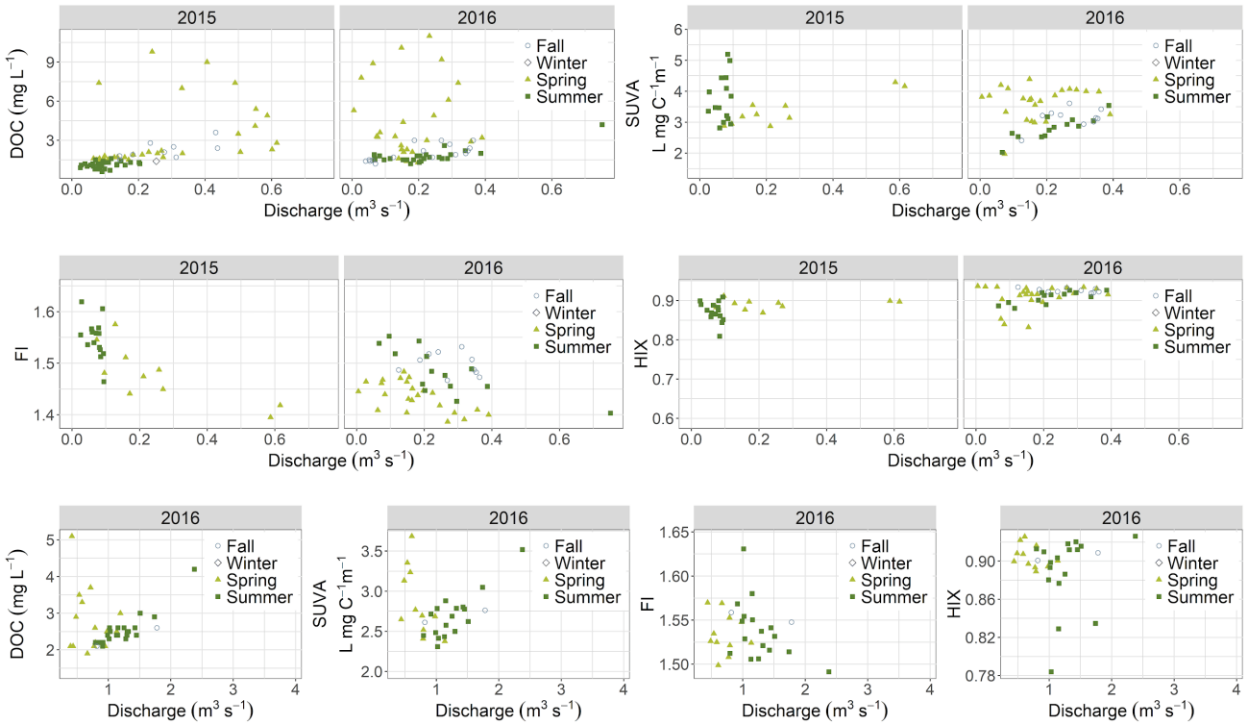
Fig 7.



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.

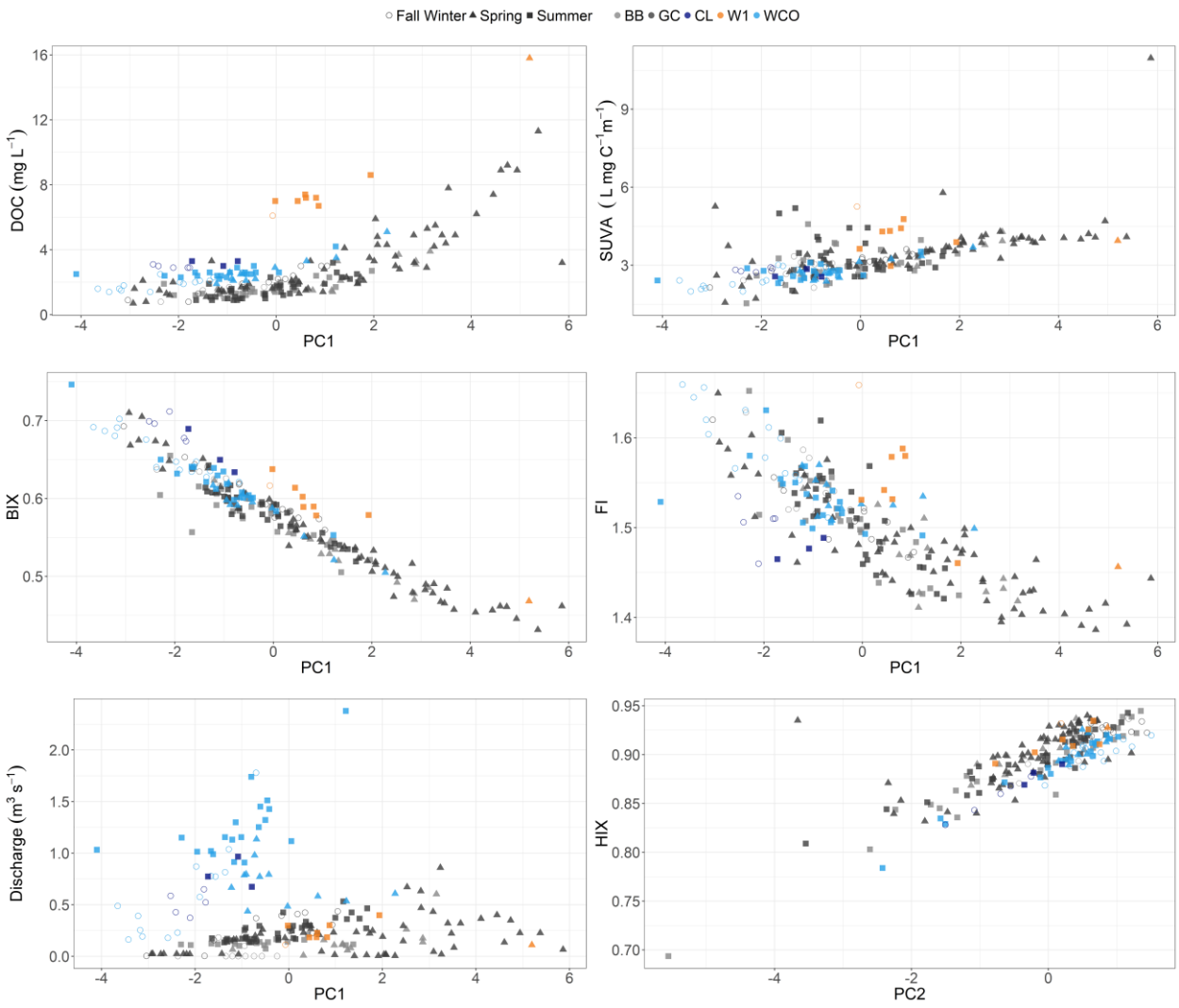
Fig 8.



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.

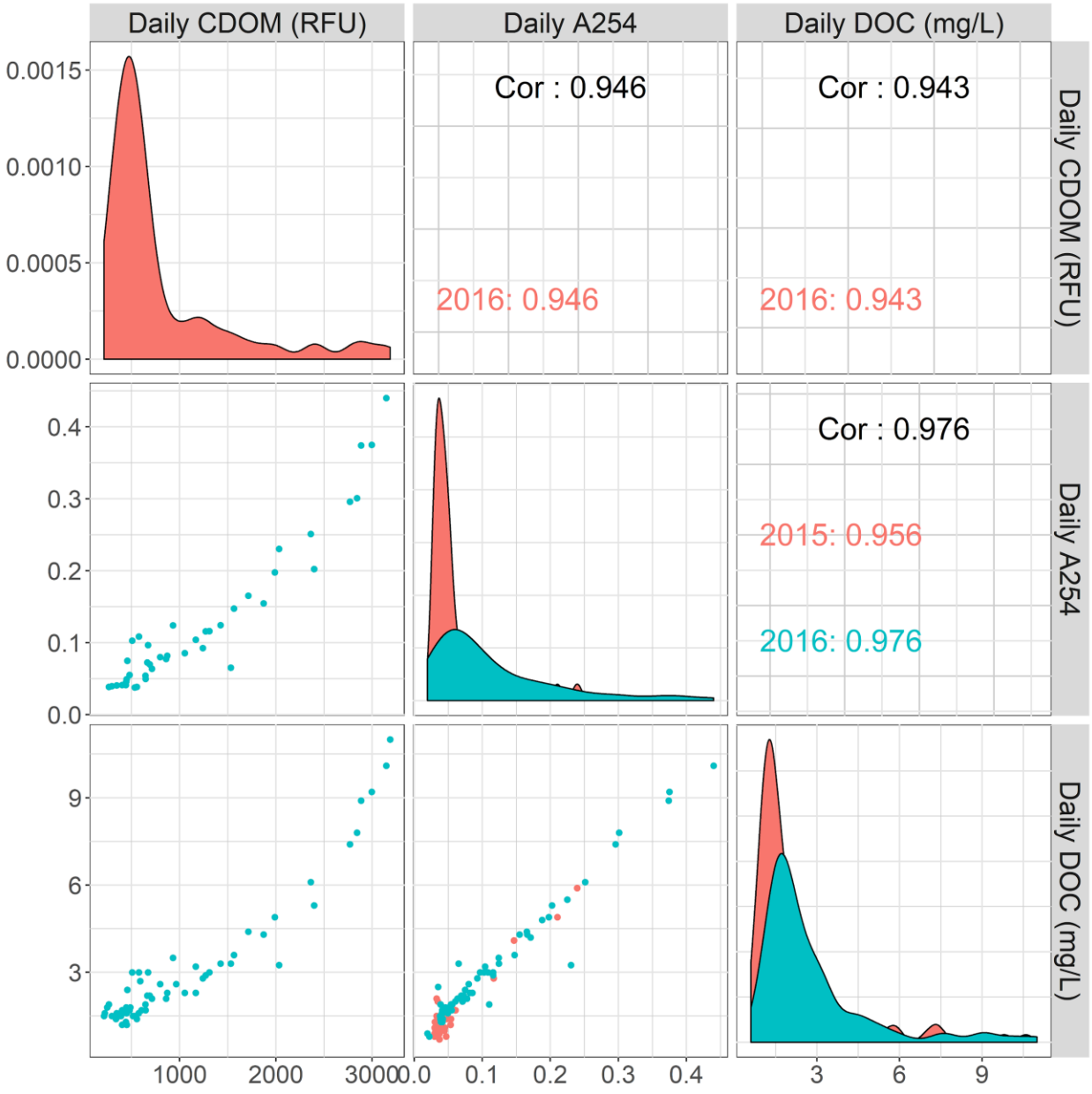
Our response: We have added the C-Q plots mentioned above to help clarify our point about seasonality having a greater influence than flow magnitude although there is some relationship between the two. We meant to communicate that the range of flow was greatest during spring and fall, however, the range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

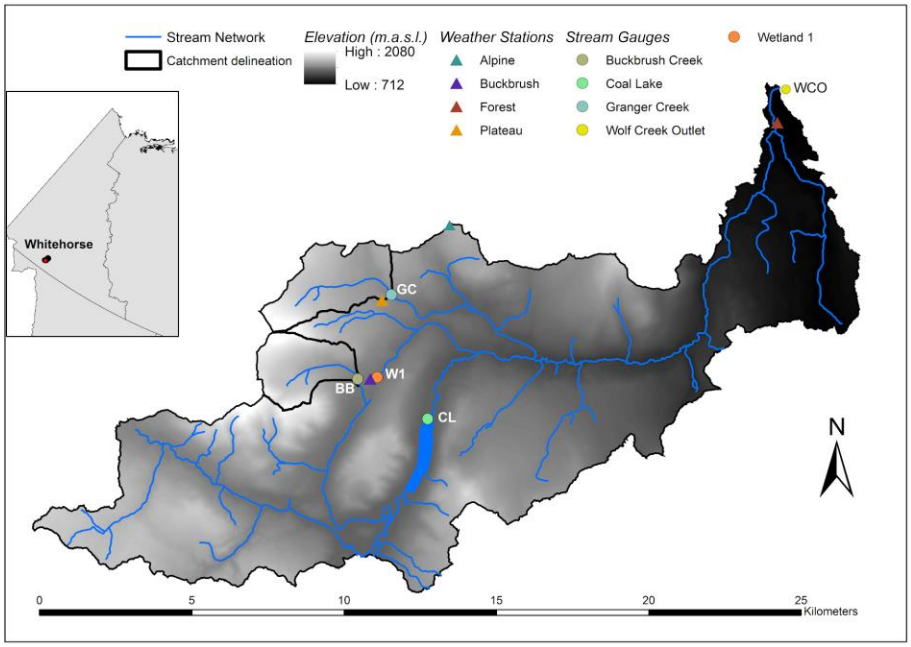


Figure 2. We have added titles at the top of each panel to indicate the location of the data: Whitehorse and Buckbrush weather stations.

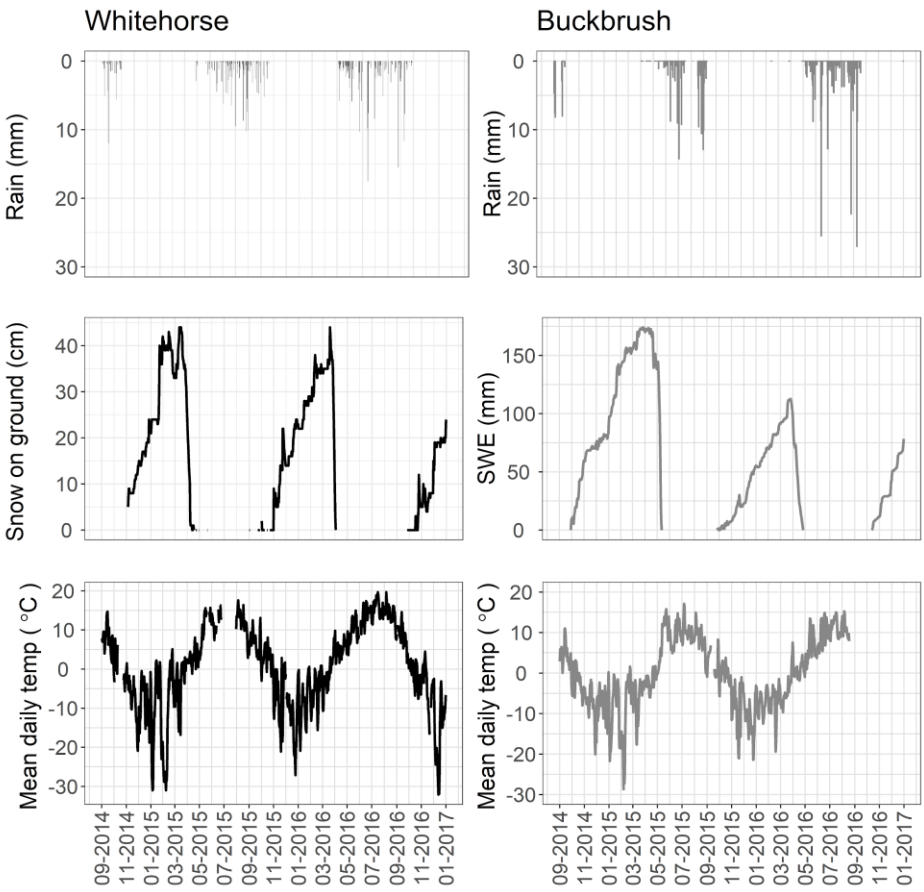


Figure 3: Referee #1 noticed an error wherein symbols in different panels had differing opacities and mentioned that the blue + for WCO was difficult to pick up in some panels.
Our response: We apologize for the oversight and the differences between panels of Figure 3. We have redone the figure with 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:

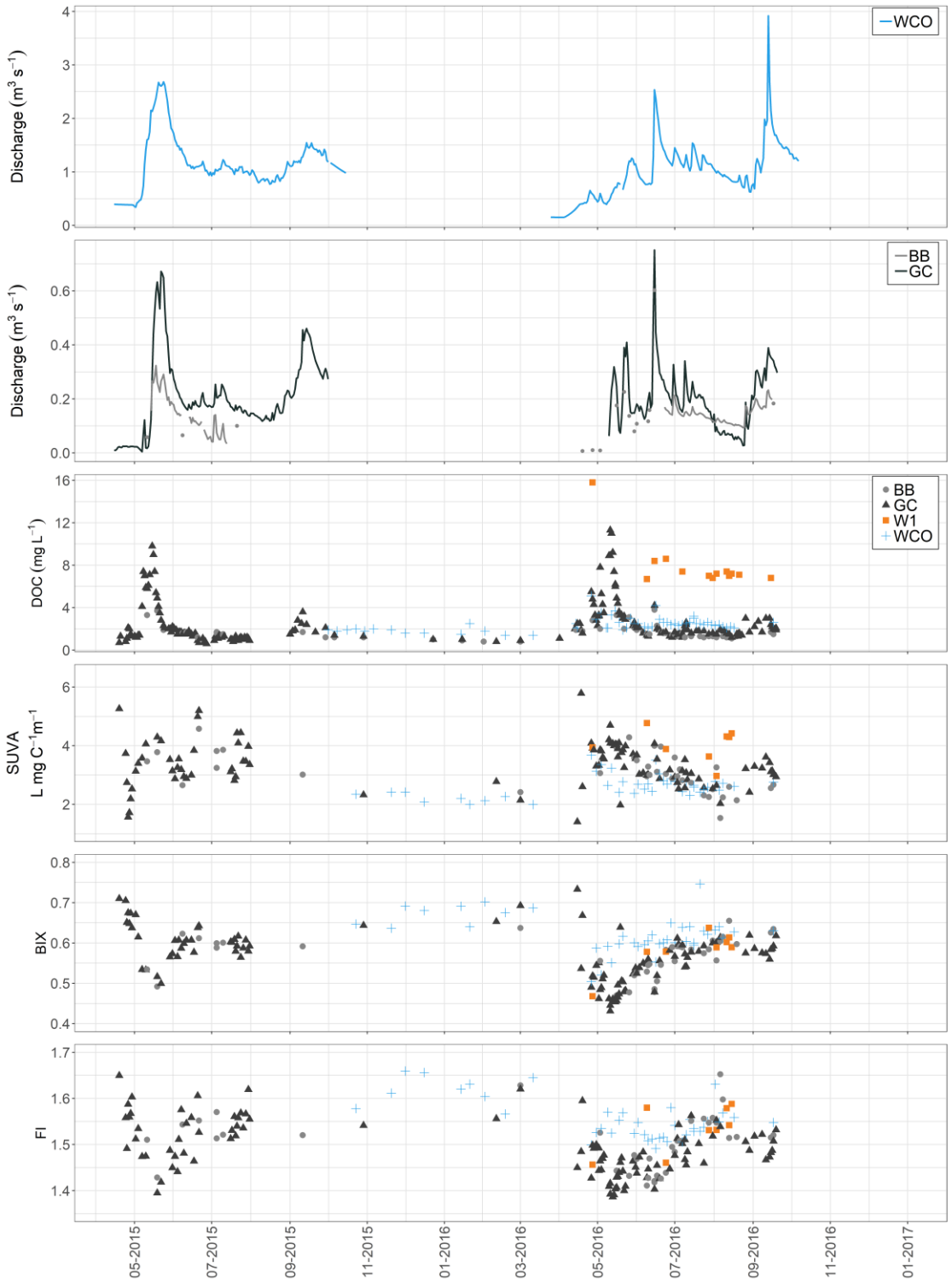
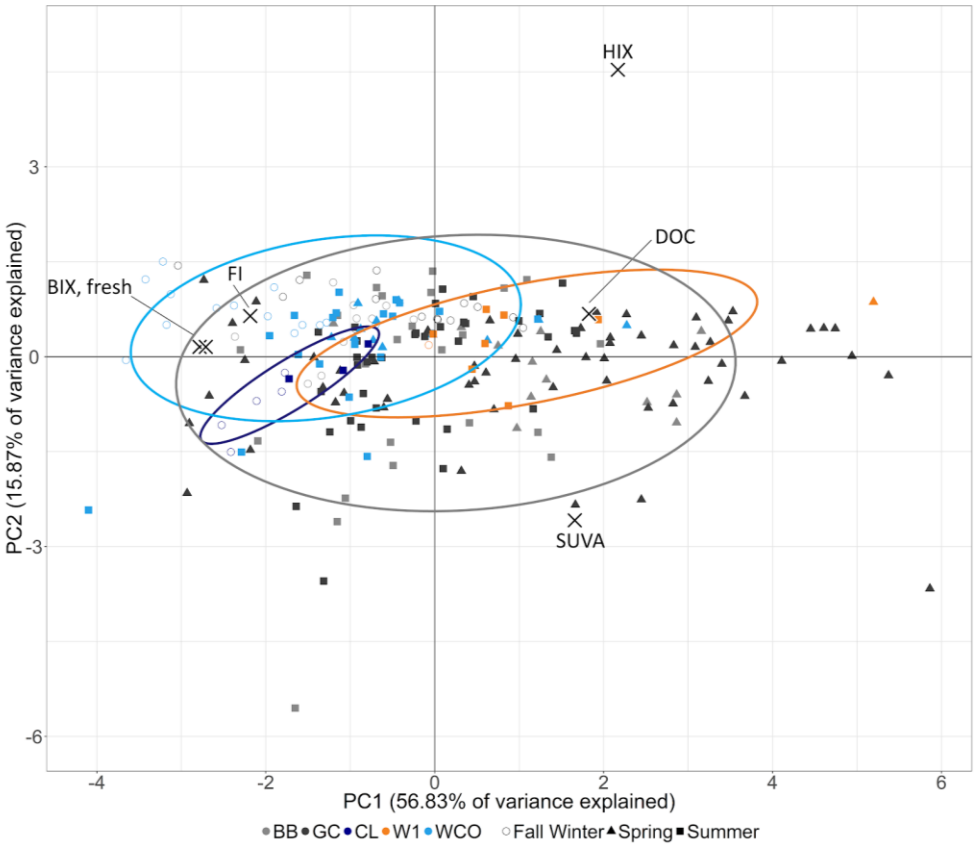


Figure 4: Referee #1 suggested changing the symbols to be able to clearly differentiate between the seasons.

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 km^2.*

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.

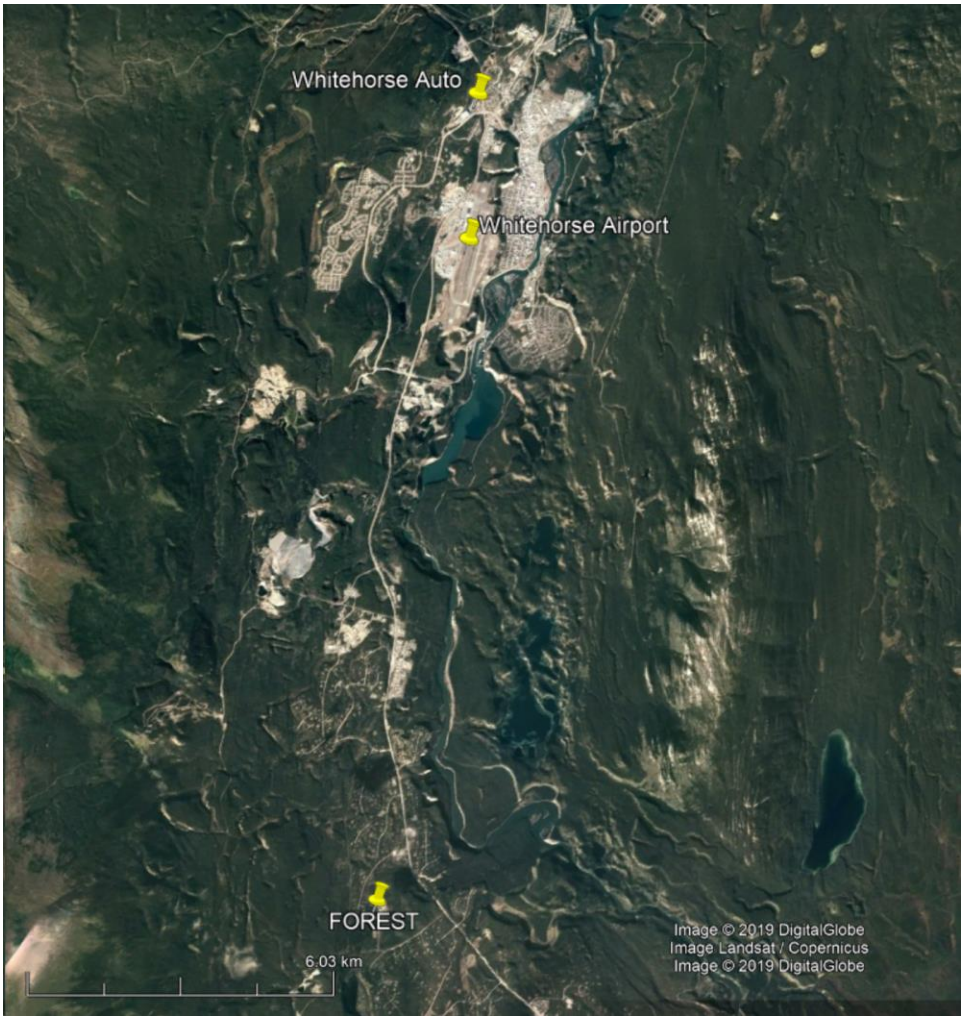
L233 "resulted"

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 (℃) 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 (℃), 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):

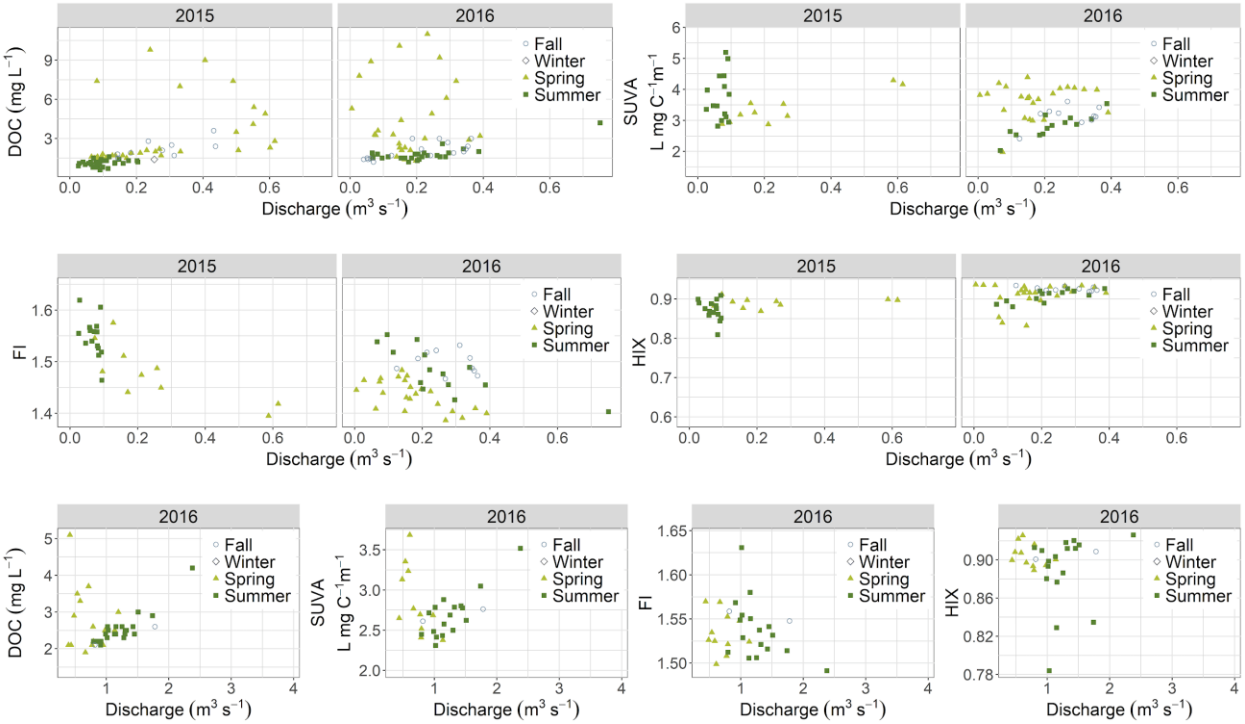
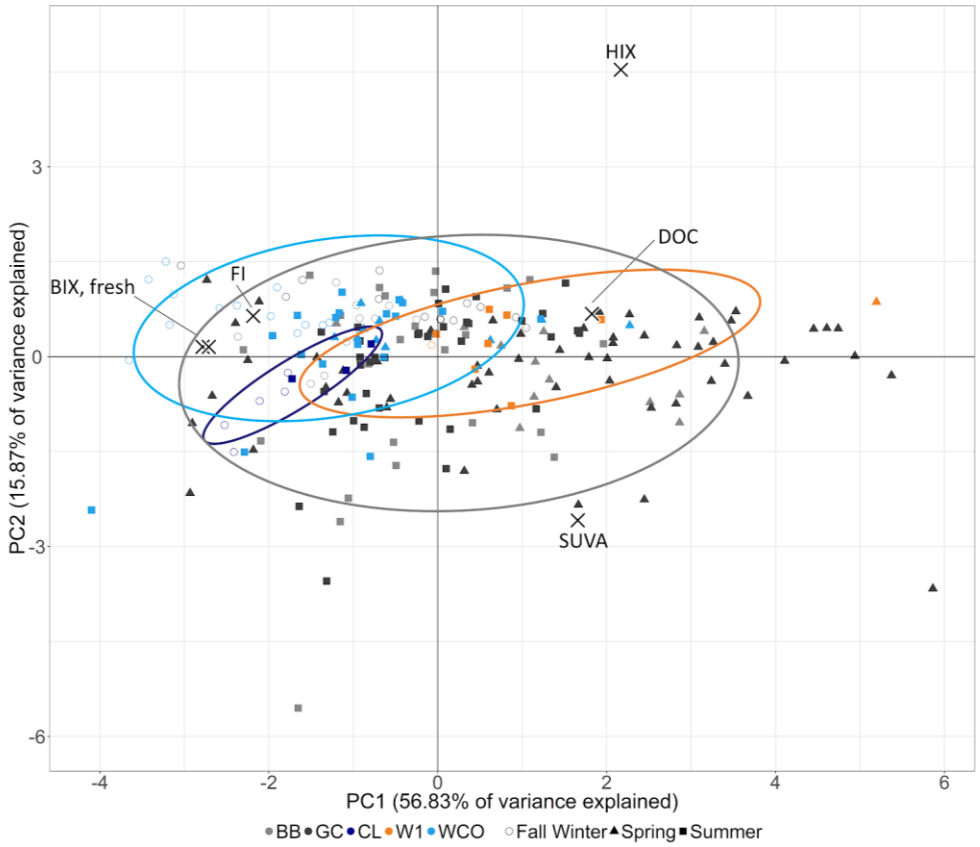


Figure 4: Similar to Figure 5, why not use different shadings of grey for BB and GC? This would allow the reader to differentiate between these catchments (or, see the of overlap between catchments within a landscape type) if they wish.

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).

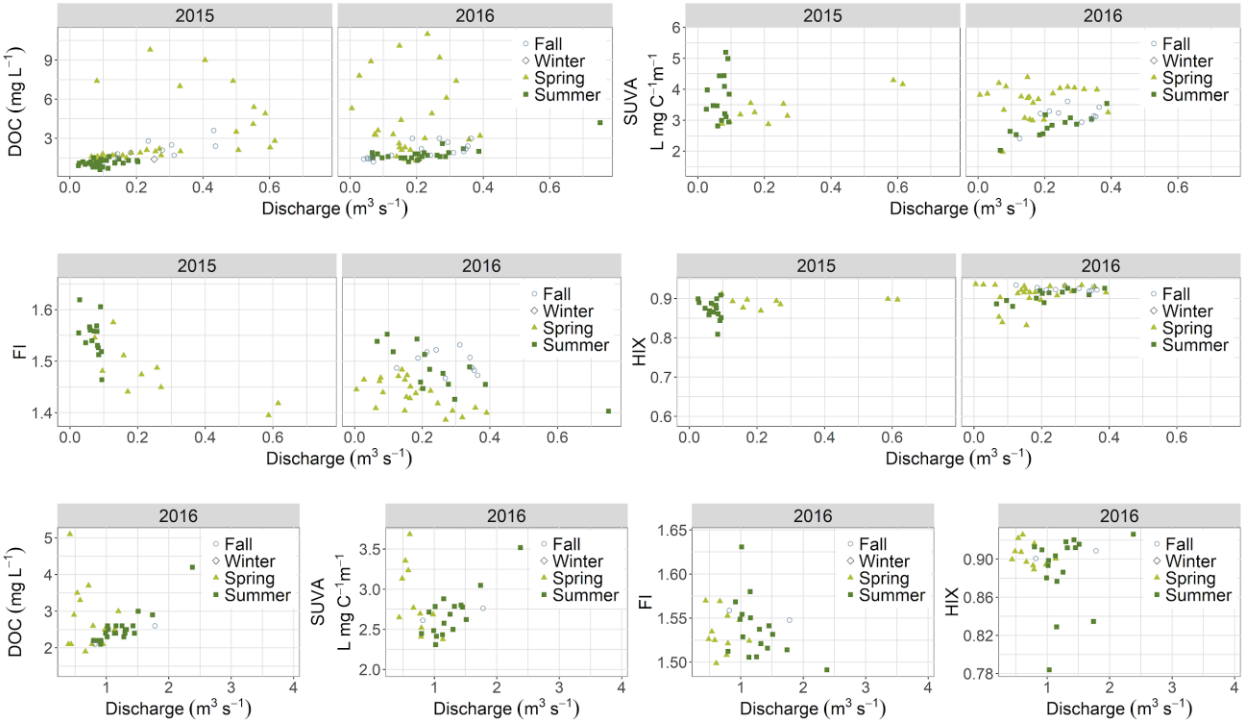


Figure 8. Concentration-discharge (C-Q) plots of DOC concentration, SUVA, FI and HIX for GC (2015-6) and WCO (2016). Season is indicated by shape and color (light green/filled triange -

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 R2 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).

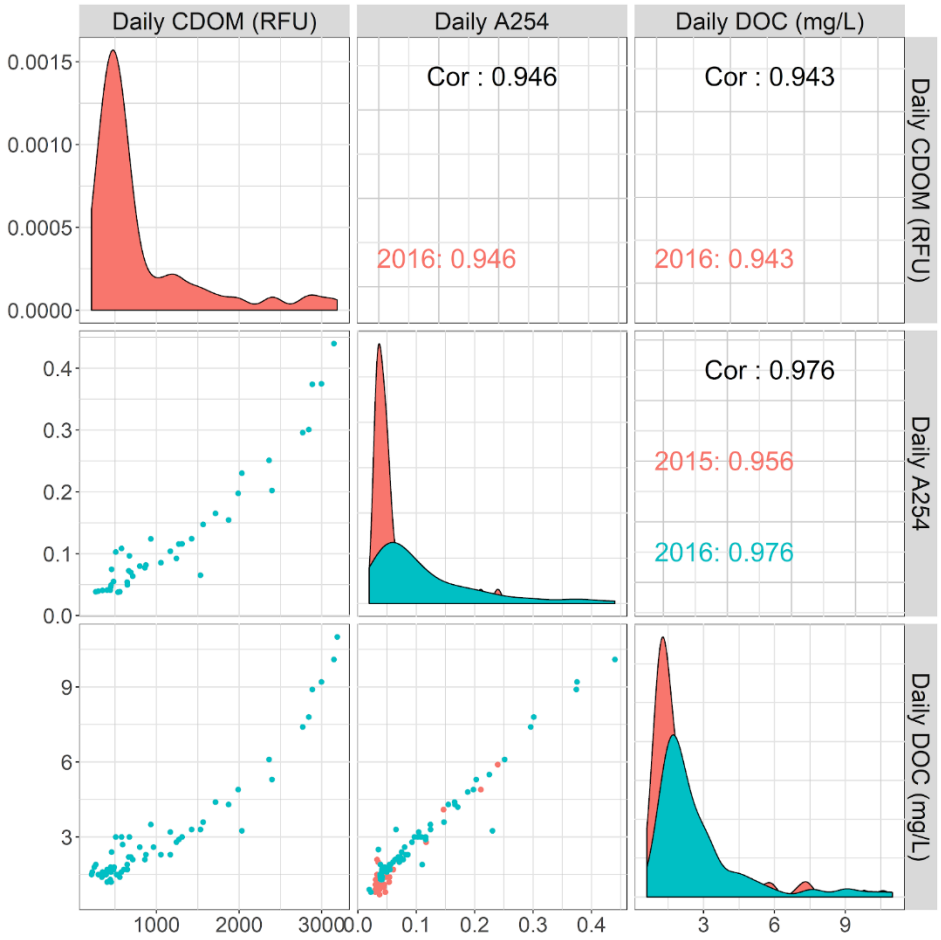


Figure S1. Correlation matrices of average daily CDOM (RFU), A254 (nm^{-1}) and DOC concentration (mg L^{-1}). No CDOM was measure in 2015 so it was not possible to separate out that year. Correlation was calculated using Pearson at 95% significance level ($p<0.001$ in all cases).

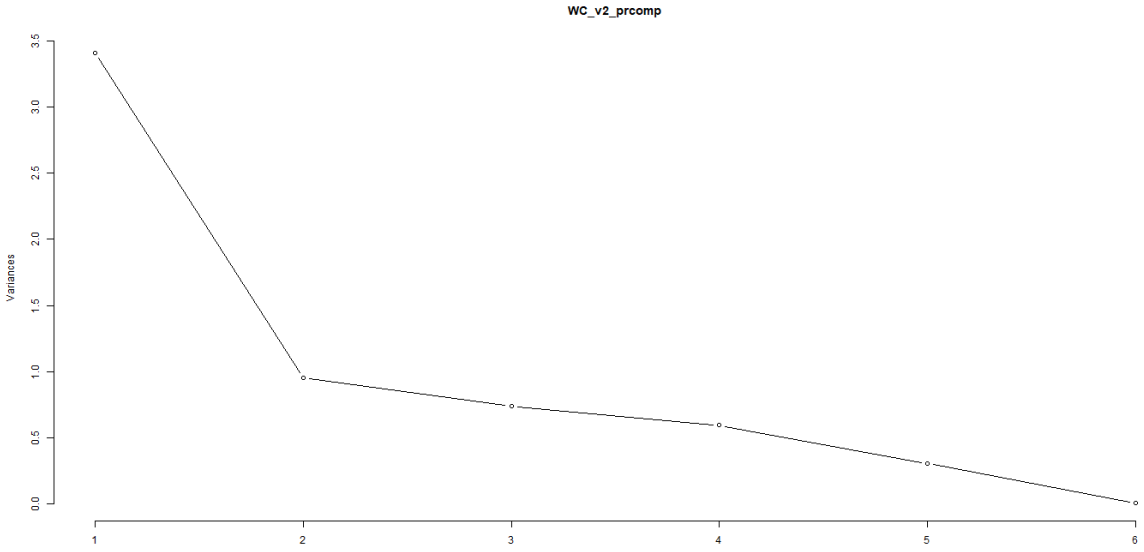
Year	*Site*	Spring (R^2)	Summer (R^2)	Fall (R^2)	Spring & Summer (R^2)	Spring, Summer & Fall (R^2)
2002	*GC*	0.047	0.180		0.063	
2003	*GC*	0.041	0.001		0.034	
2006	*GC*	0.021	0.175		0.029	
2008	*GC*	0.024	0.215		0.005	
2015	*GC*	0.263	0.004	0.547	0.316	0.314
2016	*GC*	0.115	0.536	0.551	0.039	0.048
2016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

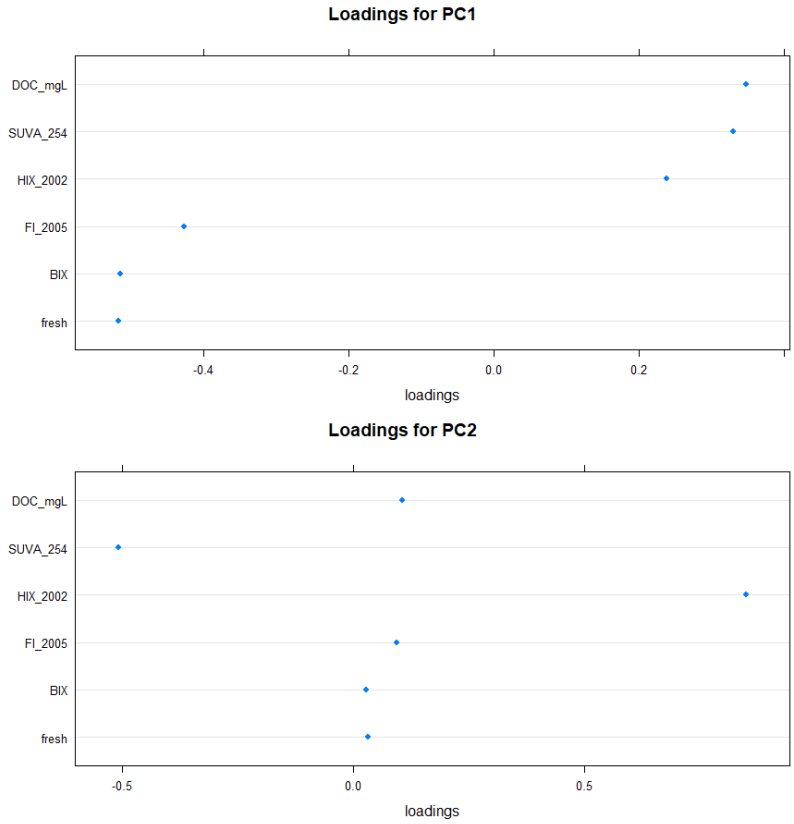


Figure S3. Dot plots of loadings per PC in PCA.