

# ***Interactive comment on “Assessing inter-annual and seasonal patterns of DOC and DOM quality across a complex alpine watershed underlain by discontinuous permafrost in Yukon, Canada” by Nadine J. Shatilla and Sean Carey***

## **Anonymous Referee #1**

Received and published: 19 April 2019

Overall quality of the discussion paper

In their paper “Assessing inter-annual and seasonal patterns of DOC and DOM quality across a complex alpine watershed underlain by discontinuous permafrost in Yukon, Canada”, Shatilla and Carey utilize a nested catchment study to investigate how the seasonal and annual patterns of DOC and DOM composition vary across the Wolf Creek Research Basin.

The main new findings and contribution of this research are that: -They demonstrate

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that DOC concentrations peak during freshet, which is typical for northern watersheds. More importantly they identify a decrease in peak DOC concentrations and export compared to a decade ago at Granger Creek. -The authors find that DOM composition is most variable during the spring freshet, where overall the DOM optical properties indicate this freshet DOM is predominantly terrestrial, more aromatic and more decomposed (less fresh) than DOM in runoff later in the season. - The effect of increasing watershed scale, was to dampen the peaks and variability in DOC concentrations and composition, which suggests more contributions from groundwater -The study concludes that future vegetation, permafrost and hydrological change will shift DOM from predominantly soil derived towards increasing contributions from modern decomposing vegetation, and increase groundwater contributions to runoff.

The study makes important contributions to our understanding of recent changes in DOC fluxes in this area of the subarctic. In particular, this study fills important knowledge gaps concerning winter flows, and is the first (to my knowledge) that reports on the variability in DOC concentration and composition over the entire water year in the region. The authors present a rich and unique data set, that I believe merits publication. However, I feel that some minor revisions (inclusion of some additional figures and statistical analyses) to better illustrate their findings and support their conclusions, would really strengthen the significance of this manuscript.

Specifically, (as mentioned below) the long term data by Carey et al (2013a) should be included to illustrate the important observation of change in DOC export and concentrations, and some statistical analyses of the relationships between discharge, seasons and the optical properties.

Specific Comments:

Abstract

Line 26-27 I suggest revising the last part of this sentence to make your conclusion more evident.

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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.

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.

Line 91: Would be better to have this statement of the goal in the first paragraph or start of paragraph two.

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."

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. 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?) did you repeat samples and compare values for FI, BIX or SUVA to determine repeatability of these values?

My other concern relates to the sample collection and filtration methods. The authors

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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.

## 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.

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

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

## 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.

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

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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.

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 time series, but this does not effectively demonstrate that seasonality has a greater influence than Q on the quality of DOM.

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.

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.

## 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.

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.” No where 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.

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.

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>

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2019-81>, 2019.

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