Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2019-9-AC2, 2019

Interactive comment on "Characterizing organic matter composition in small Low and High Arctic catchments using terrestrial colored dissolved organic matter (cDOM)" *by* Caroline Coch et al.

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Received and published: 12 May 2019

We appreciate and are encouraged by the detailed feedback of Reviewer 2. We carefully revised and addressed the comments below. Our responses are given in a line by line list below.

Reviewer #2 General Comments:

In this study, Coch et al. undertake a comparative assessment of dissolved organic carbon and optical (as a350, SUVA, and spectral slopes) measurements. The authors use measurements from catchments on Herschel Island and Cape Bounty, using a

transect design to explore changes in DOC concentration and DOM character across regions and with movement downstream. As described below (and, as discussed by the authors) there are some issues with the optical data that appear to be still outstanding. As described in greater detail in the overarching comments, it would also be nice to see the authors more clearly elucidate how their study represents a step forward in DOM dynamics in sub-Arctic and high Arctic regions.

Overarching comments My most significant comment on the manuscript is the concerns related to Fe interference. Given the large scatter in SUVA and slope results for Cape Bounty, even across the stream sites that appear to not be affected by particularly long residence times, I think that this is an issue that must be dealt with before these data can be interpreted soundly. I don't have great confidence that the authors' approach of discarding samples that had evidence of flocculation was able to fully ameliorate this issue. Perhaps there is some residual sample that could be analyzed for Fe? A high level of confidence in the optical measurements is quite critical for the integrity of the manuscript.

-We agree with the reviewer that the confidence in the optical measurements is essential for this work. We unfortunately do not have any residual sample for additional measurements.

In comparison to the Herschel site, the Cape Bounty site indeed shows a larger range of values. As the reviewer correctly notes, this is not due to different residence times. We found that the range in SUVA and slopes at the sampling sites is due to the different nature of the sites themselves (e.g. influenced by permafrost degradation, pulse of rainfall delivering fresh DOM). We found different water types with different transparency, which regulate the photodegradation of cDOM. Thus, changes in absorption, SUVA and cDOM slope can be explained by catchment properties and/or rainfall events (see Figure 3). It might also be interesting to note that catchments at Herschel cover an area of 3 km2 in total, whereas the sampled area at Cape Bounty covered about 30 km2. This naturally results in a greater heterogeneity (and range) of optical parameters.

We looked again carefully on the raw absorption data from all samples to check for elevated absorption in long wavelengths which can be a result of high scattering by particles (in our case e.g. iron colloids). The Figure (attached, Fig. 1) shows the relationship between cDOM350 and DOC and the colors indicate the raw absorption at 700nm. Samples which we excluded from this study show high absorptions (>1 m-1) caused by particle scattering in the cuvette. This result supports the lab-notes which was used as a basis to exclude samples from this dataset. We are very confident that discarding samples based on flocculation notes actually did ameliorate the issue. To support this argument, we added a figure to the supplementary material showing DOC vs. acDOM350 for all included and excluded samples across the sites. At Cape Bounty many of the samples had SUVA values above 6, meaning that the cDOM values were too high for the low DOC concentrations. The maximum SUVA recorded in the excluded samples amounted to 59.5 L mg-1 m-1.

Furthermore, the relationship between cDOM350 and DOC of all included samples from both study sites are within the error range of other published samples from similar arctic aquatic environments (Fig. S3). If cDOM absorption data used in this study had been strongly interfered by iron colloids, the goodness regression of the relationship would be significantly lower.

A second high level comment is that I would like to see the authors do a better job of putting their work in the context of what has been done previously in the arena of DOC and cDOM in Arctic stream networks and elsewhere. At some points (see specific comments below) it seemed as if the text was focusing more on re-iterating previous findings, and less on carving out how the results from this study advance our knowledge. Ideally, a revised manuscript would have a much clearer emphasis on the latter.

-We followed the recommendations and revised the manuscript accordingly. Please

see detailed responses to the comments below.

Some editing for English grammar is also needed throughout the manuscript. I certainly have sympathy for non-native English speakers who are having to write in a second language! Perhaps some of the co-authors could assist with this sort of an edit.

-We edited the manuscript accordingly.

Figure quality could be improved, particularly for figures 3 – 6. Lake residence time: there is some discussion on effects of lakes vs. streams on cDOM in the two regions. Presumably photobleaching is more prevalent at Cape Bounty. Knowing something about the residence time (or, even rough volume / mean depth of these systems) early on in the manuscript would help greatly with this interpretation. My understanding is that the ‘lakes’ on Cape Bounty are relatively large: perhaps the Herschel systems have a very low residence time by comparison? I see that this information is provided towards the end of the paper, but it would be helpful to have it

-We added this information to the study area description.

Specific comments (as page / line number): 1/16, 2/13: What is small? The catchments being studied are very small indeed, for catchments discharging straight to the Arctic Ocean. It is not correct to state that direct export catchments of this size cover 40

-Unfortunately, there is no study available showing the actual size distribution of “small” catchments. In this case “small” means “smaller than the large Arctic rivers”. We appreciate that the catchments studied here are not representative for all of the remaining 47% of the drainage area. To clarify this, we added that the actual size distribution remains unknow in the introduction.

1/20: you don’t test for variation with SOCC and vegetation cover: “consistent with variation in vegetation cover and SOCC between the two sites”?

-We edited the sentence to “can be explained by differences in vegetation cover and SOCC. . .”

1/21: I would keep lignin out of the abstract, seeing as you don't measure this at all

-We edited the sentence according to the suggestion.

2/20-21: cDOM, or CDOM? I'm not a strong proponent for one vs. the other, but it would be good to make sure you're being consistent. We checked the manuscript for consistency.

-We changed it to cDOM in all cases.

2/32: The Spence et al. 2015 reference is incorrect here. Perhaps a mis-placement?

-This is correct. Thanks for noticing this misplacement.

3/15: add "cm" to specification of active layer depth.

-We added the unit.

3/17 and elsewhere: better specified as "C: N"

-We followed the recommendation of the reviewer.

4/5: Mean July temperature? A bit confusing if not specified.

-Edited for clarification.

4/6: "with baseflow re-establishing"?

-Good suggestion.

4/21: Manual outlet samples taken at what frequency?

-We added the frequency when specifying the manual sampling.

4/22: Can you clarify this sampling design? How many sampling points along this transect? Was there a pre-determined distance between points? Adding a reference to Fig. 1 would help here.

-We clarified the sampling design.

4/27: Herschel bottles were also triple-rinsed? It might be useful to start with a general sampling scheme at the top of this section. Also see comments above on clarifying the sampling scheme.

-We added a general sampling scheme introduction to the paragraph.

5/23: One technique to deal with particles is to subtract the average 700-800 nm base. This is a good practice for all samples, to correct for interference from colloids, etc., that might not be easily visible to the eye. See also 5/27 below.

-To our knowledge, subtracting the 700 nm base will have the same effect. We have done this as specified in the methods description.

5/27: This subtraction will correct for scatter (see above) but not for drift in instrument output across the range of wavelengths measured over hours of instrument use. The latter can be corrected for by measuring blanks (or, other standards) at specified time periods, and correcting measurements to this change.

-We measured blanks to monitor the drift of the instrument output. We clarified this in the methods description.

5/31: Were SUVA corrected for Fe? Substantial Fe could present challenges to your ability to interpret these results. Other studies have found fairly high Fe levels in the western Canadian Arctic, and Fe can also be one instigator of DOM flocculation. Some of your higher SUVA values do suggest possible interference from Fe. Reading on, I see you have some text on this below; see my later comments on this issue.

-Please find our comments below.

Section 3.2: Specify statistical packages used?

-We used the basic functions in R, so no packages need to be specified.

6/16: Here and elsewhere, please specify what your +/- values indicate. Standard error? 95

-It indicated mean +/- standard deviation. We indicated it in the methods section.

6/27: Difference in slopes is not significant, given your error bounds? In addition, you might find it useful to express your slopes as values x 103 .This is not uncommon in the literature, and might help with visualizing differences between sites, etc.

-We decided to express slopes as values x 10ˆ-3 as suggested. We changed it throughout the manuscript.

7/8-9: Separation into two groups: In Figure 3c, however, it looks like you only provide statistics for a single slope. Why not calculate both slopes, and test – statistically – whether they are different?

-We conducted a one-way ANCOVA (F-statistic and p) to test whether they are statistically different. We added "statistically" to the text.

7/13: This significant difference finding is interesting, because your error bounds overlap. It's difficult to assess this as a reader without knowing what's being presented as a metric for dispersion in the data. I'm not sure I would analyze the data in this way given that (from Figure 5) your slope values cover a similar (wide) range at each of the two sites. You also have substantially different n for your two sites, which could confound your statistical analyses.

-We agree that the current presentation of the data does not make sense in this way. We put the emphasis rather on the wider range that is covered by Cape Bounty samples in comparison to Herschel.

Section 4.4 / Figure 6: What about using C-Q (i.e., hysteresis) plots to illustrate these responses. I think this would help elucidate better what is happening across the three events. For some of these events, I'm not sure I see much of a response, or at least – it's a bit difficult to tease out with the current presentation.

-We have tried presenting the data as hysteresis in an earlier version. Unfortunately, the sampling frequency in Ice Creek East is not high enough to detect a response. We

edited the figure for improved readability.

Section 5.1 / first paragraph: Again, this makes me concerned about interference from Fe.

-Please see above.

Page 9 / line 25: Ah – yes! I see you get to Fe here. At the bottom of this paragraph (8/10): I'm really not sure you have eliminated all of the problematic samples. If you have extra water from these sites, it would be great to have this analyzed for Fe, if you haven't already. It seems you are using precipitation as a proxy for Fe interference? You may certainly have high Fe in non-precipitate samples. Particularly given the scatter in your data for a series of samples taken upstream of a lake (e.g., West River vs. East River in Figure 4c), I think you need to be concerned about whether some of the patterns you're observing are 'real'. For the Herschel Island samples, where it appears that Fe data are available, it would be great to correct for this.

-Please see above.

5.2.1, first paragraph: I agree that you see higher DOM quantity at Herschel. From Figure 4 and 5, however, I don't think you can conclude there's any difference in quality. The quality values span across a similar range at both sites, with values from Cape Bounty showing a wider range. However how this paragraph is written whether this analysis is contributing anything new. If there is something novel that's being presented in this particular ms, it would be good to structure the text in a way that really highlights that fact.

-We changed the first paragraph accordingly.

Section 5.2.2, third paragraph: it seems to me that this is perhaps the novel information that's being presented in this section; the second paragraph, as written, also seems to largely summarize findings from previous studies. Why not flesh this out a bit and focus here? For example – what is the evidence for increased permafrost DOM export with increasing baseflow; I may have missed this discussion above, but it would be nice to have this laid out very clearly. It would also be useful to cite the Spence et al. publication that seemed to be mis-placed above in this section.

-The section above leads to this conclusion. We put more emphasis on this section and also incorporated the studies by Spence et al.

12/23: See also the conceptual work on headwater to mainstem gradients by Drake et al.

-Thanks for pointing this out.

12/25: IE – temporal variation? Within sampling dates, the SUVA and slopes are fairly consistent along the transect; the values are certainly much more variable across time than across space.

-This paragraph focuses on the upstream to downstream patterns. However, it is correct that the temporal variation was not sufficiently discussed. We added this into the "rainfall events" discussion.

14/4: cDOM as a good proxy for DOC concentration. This is true (and quite well established) in cases where most DOM is terrestrial in origin, and not overly degraded. There are a few references you could cite here for studies that have made this point using pretty extensive datasets. It's not necessarily true universally, however; there's also some good papers showing a lack of relationship between DOC and colour for sites where DOM is highly reworked / photobleached – see for example work by Arts et al., Osburn et al. and others on prairie / great plains lakes.

-Thanks for pointing this out. We added the reference.

14/7: What about the relationship between CDOM and soil organic carbon content in the catchment of study? Presumably there is a strong relationship here (see, for example Connolly et al. 2018, ERL). It seems likely that climate / latitude is a controlling variable in the sense that it has such an important influence on soils. Ah – I see you

have this in the paragraph below. It would be good to look at the recent work by Connoly et al, who also examine this relationship across a variety of watershed sizes.

-This is indeed a very interesting study, especially with regard to upscaling results to the circumarctic region. Since they linked both, SOCC and DOC to slope, and not directly to each other, we decided not using the reference here.

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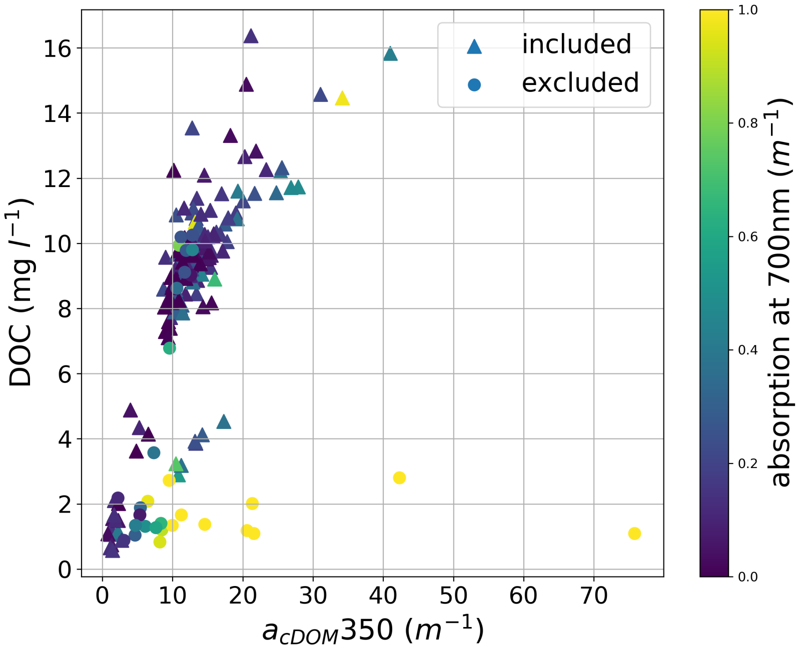

Fig. 1. Relationship between aCDOM350 and DOC concentration for all samples (included and excluded). Absorption at 700nm is color coded.