Dear Prof. Battin,

Thank you for your message dated 15 May. We have carefully reviewed the comments and have revised the manuscript accordingly. Our responses are given in green in a line by line list below. The revised manuscript with tracked changes as well as a clean version is attached to this version.

We are looking forward to hearing from you.

Best regards,

Caroline Coch

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Author responses to reviews and edits to Biogeosciences manuscript bg-2019-9 "Characterizing organic matter composition in small Low and High Arctic catchments using terrestrial colored dissolved organic matter (cDOM)".

Response to Anonymous Referee #1, 07 Feb 2019

We are very grateful for the time invested and the constructive comments, which helped to improve the paper tremendously.

General Comments:

The manuscript, "Characterizing organic matter composition in small Low and High Arctic catchments using terrestrial colored dissolved organic matter (cDOM)," presents a good body of work collected in vastly different Arctic catchments. The original data is strong and is mostly presented in a well-structured manner. Comparisons between the two sample locations show very different patterns with vegetation, latitude, rainfall events, and permafrost disturbance. Where the work requires attention is in the language used, sentence structure, some figure reorganizations/enhancements, and section reorganization. Following the major and minor revision suggestions below will greatly strengthen the manuscript.

Scientific significance: Does the manuscript represent a substantial contribution to scientific progress within the scope of Biogeosciences (substantial new concepts, ideas, methods, or data)?
EXCELLENT
Scientific quality: Are the scientific approach and applied methods valid? Are the results discussed in an appropriate and balanced way (consideration of related work, including appropriate references)?
BETWEEN GOOD AND FAIR
The scientific approach and applied methods are valid
GOOD.
The results are not discussed in a very balanced way
FAIR
Presentation quality: Are the scientific results and conclusions presented in a clear, concise, and well-structured way (number and quality of figures/tables, appropriate use of English language)?
GOOD AND FAIR
See comments regarding strong language, reevaluation, and reorganization that will improve the results and discussion sections, and the conclusion section should be reevaluated upon the completion of the rest of the edited sections.
The number of Figures should be reevaluated based on the restructuring of the discussion section.

Major revisions points include:
Adjusting weak language to strong scientific language. Examples are provided in the Line by Line revision points. The introduction is written well, but the results and discussion sections are written in a different style, with a narrative tone, that reads a bit too casually. Narrative writing styles are being encouraged in a great many manuscripts as long as the main messages of each sentence, section, and manuscript aren't lost. The recommendation under this point is to adjust the sentence structure to improve clarity, remove redundancy, and provide stronger scientific language. Briefly, language such as "There was, there are, we saw

an initial drop in values. . .” should be replaced with less wordy narrative components where stating what was observed can lead to more clearer understanding. See comments below.

We adjusted the language according to the line by line revision points. Many thanks for giving such thorough feedback.

Some figures require extra attention to improve readability and understanding. Those comments can be found below the main text comments. Some figures are included and not very well discussed in the text. Check through your figure list, decide which are very important for this work (including the possibility of moving figure S2 into the main text), and write appropriately about them. Figures that are included with little to no discussion should be deleted or moved to the supplemental section. Colors/symbols on most figures need to be improved (detailed comments below). Also Figures and Tables require all terms to be defined in the captions to avoid confusion. All acronyms and abbreviations should be written out as standalone text in the manuscript.
We revised the figures according to the detailed suggestions below. We decided to move figures 7 and 8 to the supplementary material.

Some results regarding understanding the composition of DOM from SUVA, etc. are written inconsistently. Please re-read the results and discussion section to make sure this information is accurate and not just typos. Also, the flow of the discussion section will benefit from reorganizing the sections.
We revised the respective sections according to the detailed comments below.

Some important sections are listed last with figures as well, which doesn’t strengthen the work. Think about the main message of the manuscript, adjust the title and flow of ideas throughout the manuscript to match the main message. Important points should be made up front (earlier in the discussion section) and even within paragraphs, not at the end. Consider making the important points first in the text, and then support the findings or contrast the findings with the literature information afterward.
Please find the comments in the sections below.

Title What is terrestrial colored dissolved organic matter? Using the word terrestrial in the title is misleading. Consider a revision that highlights the strength of the conclusions. Rainfall events? Permafrost disturbances? Suggestion: Comparisons of chromophoric dissolved organic matter composition in small low and high Arctic catchments OR Comparisons of cDOM composition with permafrost disturbance in small low and high Arctic catchments
This is a very good suggestion. We revised the title to: “Comparisons of chromophoric dissolved organic matter composition in small low and high Arctic catchments”

Line by Line revision points (major and minor included).

The comments are organized by sections of the manuscript, including Figures, Tables, and Supplemental material. Page numbers and Line number are provided. Note: Check the manuscript for fluctuating usage of colored and coloured.
We checked for consistency.

Abstract

Line 20 Please define SOCC

We defined SOCC in the text.

Line 28-29 How are permafrost-derived DOM vs fresh derived DOM being defined in this study?
Permafrost-derived DOM is sourced from deeper in the active layer whereas fresh derived DOM is sourced at the surface of the active layer. We added a definition for clarification.

Line 30 What does fresher DOM prone to degradation mean? Photo? Microbial? Combination? The abstract does not describe the composition of the DOM. Stronger color of DOM does not describe more aromatic and/or lignin-type constituents. What are the absorption results besides "things change downstream"? Consider a more specific details.
"Fresh" DOM means near-surface derived and therefore prone to degradation. We added more specific details.

Line 31 "This work shows that optical properties of DOM will be a useful tool for understanding DOM sources and quality at a pan-Arctic scale" Yes, the work does, but the abstract doesn't. Consider blending the ideas together so that the abstract matches the measurements made, chemical interpretations, and conclusions from the work.
We edited the abstract according to the suggestions.

Introduction
The introduction is nicely written and sets the stage very well. Consider a stronger ending so that it will tie in well with the discussion points and the relevance of small watershed importance with global carbon budgets and vulnerable environments with climate change.
This was changed accordingly.

Page 2 Line 21 Typo CDOM instead of cDOM. Please check.
This was changed accordingly.

Page 2 Line 25 What is cDOM-DOC? Concentration?
They refer to ratios. The text is changed accordingly to "Previous studies have focused on characterizing cDOM-DOC **ratios** for the large Arctic rivers and shelf areas"

Page 3 Line 6-7 This sentence could be improved by describing the importance of this contribution to global carbon budgets as the climate warms. Consider ending with a stronger contribution statement.
This was changed accordingly.

Study Area

Page 3 Line 15 Add SOCC here.
We added SOCC.

Methods

Page 5 Line 28 Typo CDOM instead of cDOM. Please check.
It was changed according to the suggestion.

Results

Page 6 Line 23 Consider revising the subheading to DOC concentration and cDOM absorption characteristics. Usually with a heading that lists specific items, they then appear in that order in the text. Think about this heading and whether it makes more sense to report DOC concentration before the absorbance data. Page 6 Line 23, 24, and 27 Typo CDOM instead of cDOM. Please check.
It was changed according to the suggestion.

Page 6 Line 27 Will CDOM slope or spectral slope be used? Also, the spectral slope of both are within the same boundaries if accounting for the standard deviation. Will this similarity be discussed? The sentence as currently written suggests that they are significantly different. Please clarify.
During the study we use spectral slopes of cDOM for the wavelength ranges 275 to 295nm (S275-295) and 350 to 400nm (S350-400). Further the ratio of both is reported as slope ratio SR (S275-295 : S350-400). In case of line 27, we decided to report the slope ratio. The sentence is changed accordingly. Differences in cDOM spectral slopes and slope ratio are discussed later on.

Page 7 Line 2 Revise the sentence to list concentration at the beginning of the sentence for improved sentence structure. Then that word can be deleted in the next line.
It was changed according to the suggestion.

Page 7 Line 3 It appears as though the lowercase L and the number one are very near identical or identical looking to read. Consider using a capital L for Liters.
Although it would indeed improve readability, we decided to stay with the SI units as suggested by the journal.

Page 7 Line 5 Consider using the word significantly in this results section when a significance value has been calculated. In this sentence it makes sense and it also makes sense in Line 1, however, this word is used in every sentence thus far on this page. Edit the results section accordingly to use the word significantly or significant when it is appropriate. Also, in this line, an open parenthesis is missing.
We carefully went through the results section to check the use of the word "significant". In most cases, significance values were calculated, making the use of the word appropriate (see Table 2). We changed it where possible (lines 14,

Page 7 Line 9 refers to different slopes in Figure 3c. Might adding the slope line/trend line or some kind of calculated slope help readers visualize this difference? This relationship is not clear from the data in Figure 3c with overlapping flowing water and standing water symbols. The overlapping data is at low DOC concentration and low absorbance at 350nm. When those values are increased, there may be a change in the grouping. Can that be reported and highlighted in the figure more clearly? Consider a reevaluation of the data and how those results will be reported.
We considered adding a slope/trend line to this figure. However, the data is not normally distributed, hence, the use of Spearman's rho. Using a straight line would suggest a regression curve and that the data is normally distributed. We added ellipses to show the "grouping".

Page 7 Line 13-14 This information is already reported in the first paragraph and commented on above.

We deleted this sentence.

Page 7 Line 14-15 Consider reporting in the text that this is a negative relationship.
The sentence was changed according to the suggestion.

Page 7 Line 16 We jumped from Figure 3c to Figure 4b. Please correct.
A reference to Figure 4a was inserted.

Page 7 Line 16-17 Redundant sentence, please delete. What outliers?
The sentence was changed according to the suggestion.

Page 7 Line 21 Same comment as the subheading for 4.2 Consider inserting the word concentration after DOC and a descriptive term for the cDOM measurement reported. This also comes up in Section 4.4 and the reason why it's misleading is because the DOC measurement is a quantitative value and the cDOM measurement involves both qualitative information and some quantitative normalization. Is the usage of cDOM all the time in these headings the best idea? What about using DOM and then describing the quantitative and qualitative information below? For example, 4.3 DOM patterns along longitudinal transects AND 4.4 DOM temporal trends with rainfall
This is a valid point. We changed headings 4.2, 4.3 and 4.4 referring to DOM instead of DOC and cDOM individually.

Page 7 Line 23-24 This information seems to be in correct based on the figure for both the characterization of DOC concentration in Ice Creek East and West.
We changed the wording to make the meaning clearer.

Page 7 Line 26-27 The usage of the word "low" in this sentence is misleading. Please describe the data more accurately. Yes, it is lower than Herschel Island, which is what it is assumed to be compared to, but the wording is weak. Describe the trends of the DOC concentration in Cape Bounty first, then make comparisons. Plenty of streams and rivers have DOC concentrations below 1 mg/L, so think about specific word usage when reporting the results.
We edited the sentences according to the suggestions.

Page 7 Line 27 Consider this revision to improve clarity, ". . .levels of DOC concentration compared to other Cape Bounty rivers. . ." Also, this is the same trend as the other West River DOC concentration data (without the rainfall event) and that is important to note.
The sentence was changed accordingly.

Page 7 Line 28-29 How is that information supported from the figure shown? It looks like three data points are right on top of each other, which suggests they are not longitudinally or hydrologically separated. This information should be clarified.
The points seem on top of each other, because they are only a few metres away. They are indeed hydrologically connected. We

Page 7 Line 30 No clear pattern was detected in Boundary River? The figure shows two data points here which suggests that a pattern would be tough to determine. Perhaps report the similarities between concentrations of Boundary River and Robin Creek?
We edited the sentences according to the suggestions.

Page 8 Line 1 Good – we should hope so given the positive relationship. Consider strengthening this sentence by noting the strong relationship between these two parameters. For example, "This confirms the strong positive relationship between both parameters."
We added "strong" to the sentence.

Page 8 Line 2-3 Same comment regarding the usage of the word low. Describe the data as remaining constant or with very little variation. Using the word low assumes a comparison. If the intention is to make a comparison, then describe it clearly.
We edited the sentence according to the suggestions.

Page 8 Line 4 Didn't DOC and absorbance also show different trends between these river systems? Consider revising this sentence to flow better with the previous text.
Less datapoints are available for the absorption measurement than there were for DOC. This is why no further trends can be described here.

Page 8 Line 4-6 Why isn't the increasing trend at ~1300m reported and discussed for DOC concentration, absorbance, and SUVA in the Herschel Island system?
We added this description. This is due to another

Page 8 Line 5-6 This is a clear sentence highlighting a comparison between rainfall events. The manuscript can be strengthened by making this point clearer throughout the results and discussion sections with these types of comparisons highlighted on the figures. Use this as a strength moving forward.

Page 8 Line 8 Certainly this could be due to some inputs?
Yes, we think so too.

Page 8 Line 9-14 Slope values? Spectral slopes? Or flow gradients? A notation of which figure is being discussed here should be included.
We inserted the reference to the figure.

Page 8 Line 16 "Electrical conductivity was found to increase. . ." This is weak scientific writing. Consider using less words to be clearer and strengthen the main message, e.g., "Electrical conductivity increased from. . ."
We changed it accordingly.

Page 8 Line 16-18 A notation of which figure is being discussed here should be included.
We inserted the reference to the figure.

Page 8 Line 22-24 Please reference the specific part of the figure.
We inserted the reference to the figure.

Page 8 Line 24 The word "drop" is weak scientific language. Consider using "decrease" in this sentence.
We changed the wording accordingly.

Page 8 Line 20-26 This section describes the results organized in Figure 6 a-f, yet the results are written a bit out of order ending with information seen in 6a. Annotate the text with the specific parts of the figure that is being discussed.

We referenced the figure parts accordingly.

Page 8 Line 27 "The hydrochemical response to the following rainfall event (Event-3, 12.7 mm) was different to the previous one." This is a weak opening sentence. Be more specific to hold the reader's attention. The response of Event 3 was different than the response of Event 2, correct? State that using stronger scientific language. This type of writing continues on in "Here, we saw an initial drop in. . .". DOC, absorbance, and Spectral slope decreased after the event, followed by a sharp increase. . . This section is difficult to follow with the events only listed on one part of the figure. Consider marking all a-f figures with a vertical line highlighting the rainfall events.
We changed the wording accordingly.

Page 8 Line 28-29 What does this mean? "SUVA shows an increase with two positive peaks." All the values are positive, so please describe increases and spikes in the data to higher values using stronger scientific language.
We changed the wording accordingly.

Page 8 Line 30 "No continuous slope records are available for this event as two outliers occurred in this event" This can't be evaluated without seeing the data or reading about how outliers were determined. Consider showing the data in the SI or discussing how outliers were calculated and extracted.
We adjusted the scale to capture the full variability. We reworded the sentence to make this clear.

Discussion

Page 9 Line 3 Typo measurement should be measurements. Also, limitations in the measurement itself or the sample? The next sentence discusses precipitates. Clarify the limitation because certainly there are limitations in absorbance measurements to infer biogeochemical relationships.
We changed the wording as suggested.

Page 9 Line 3-5 Redundant language and weak writing. Consider stronger language, for example, "Some samples formed small precipitates, which partly remained in suspension or accumulated at the bottom of the bottles."
We changed the sentence structure accordingly.

Page 9 Line 5-6 Consider being more specific with the end of this sentence. Precipitation occurred after filtration during storage, correct? Note the time of storage and any other conditions that are relevant. The way the sentence currently reads assumes immediate precipitation, which probably did not happen.
This is true. We added the storage time to the methods description.

Page 9 Line 6 "In the absorption spectra, these samples showed extraordinarily high acDOM values. . ." This is redundant. Consider this revision, "These samples had very high absorbance values at 350nm. . ." and consider reporting those values. None of this data can be evaluated so "extraordinarily high" holds no water for the reader. A comparison to the DOC concentration level – what is meant by this? Were the samples settled before running the

absorbance measurements? Or were the precipitates blocking, filtering, or absorbing some of the light?
We added clarifications to the paragraph.

Page 9 Line 6-8 "As described in the methods section (3.1), they were therefore excluded from the study based on the laboratory notes." This type of writing is redundant and without understanding what the values were before exclusion or any of these laboratory notes, the reader cannot evaluate or confirm any of this information.
We added specific values and a figure to the supplementary material.

Page 9 Line 8 "At Cape Bounty, this was the case for 25 out of 55 samples." This is very disappointing. Was no redissolution or shaking attempted? This is practically half the data set!
Unfortunately not.

Page 9 Line 13 Meaning absorbance interferences due to the sample and not the method?
This was added to the sentence.

Page 9 Line 14 "The cut off between solid and dissolved fraction in a solution is normally made. . ." Use caution here. Dissolved organic matter is operationally defined as material that can pass through a 1.0µm filter poresize. What is listed here is just a few examples of filter poresize used commonly in the DOM aquatic community. Please revise this language.
We edited the sentence accordingly.

Page 9 Line 15 Please add a comma after e.g.
Comma added.

Page 9 Line 18 Please add a reference to this statement.
We added the reference.
Page 9 Line 21-22 For what environments? 12% cannot be evaluated without an environmental reference and ties to comparisons of the percentage range or difference in the outlier values.
We added that it was a terrestrial water body.

Page 9 Line 24 There is no filter difference in this study, correct? What is meant with this statement?
We revised the sentence for clarification: We therefore assume that colloid complexes between 22 µm and 0.7 µm have a minor influence on cDOM absorption in our samples.

Page 9 Line 26-27 "Dissolved iron in terrestrially dominated waters is dominantly complexed with humic and fulvic acids" Wouldn't this suggest that the "outliers" could also have been influenced by this effect? Was iron measured in this study? Are there any references to iron concentrations in this region?
We revised this section for clarification. Iron data from a previous study only shows total iron (Fe(II) and Fe(III). Correction coefficients by Poulin et al. 2014 are based on Fe(III) values.

With regard to the "outliers": In comparison to the Herschel site, the Cape Bounty site indeed shows a larger range of values. 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 km^2 in total, whereas the sampled area at Cape Bounty covered about 30 km^2. This naturally results in a greater heterogeneity (and range) of optical parameters. We added that information to the study site description.

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. $a_{cDOM}350$ 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.

Page 9 Line 27-28 Did pH and temp change? The reference to Table 2 this late in the manuscript seems a bit out of place. This is good information that should be known before the discussion. Consider moving this table to the results section.
We referenced the table in the results section.

Page 10 Line 5-6 This is the first mention of iron concentrations being measured in this study. Please revise Table 1 or Table 2 to include this important information. Add a methods section describing these measurements. Also, the iron concentration figure in the supplemental (S2) is great and should be added to the main text.
Measurements of iron are available from a previous study. We inserted the correct reference. See the detailed comment above.

Page 10 Line 9 "Therefore, all problematic samples were removed from this study." Understandable, but the work would be strengthened if the reader could see all these data and relationships, and then this discussion section would make a lot more sense. This section defines limitations regarding data that isn't presented.
We added the data to the manuscript and expanded the discussion.

Page 10 Line 12 Is this a typo? "Our both study sites. . ."? Use Our or Both our to start this sentence.
Thanks for pointing it out. It was indeed a typo.

Page 10 Line 17-20 Is the 195 a typo?
Thanks for pointing it out. It was indeed a typo.

Page 10 Line 20 Please insert a reference.

The references for the entire paragraph are found in the end.

Page 11 Line 4 What is a full response of a rainfall event? This sentence is very confusing.
We edited the sentence for clarity.

Page 11 Line 6-7 Consider revising this sentence to improve clarity. This indicates a decrease in aromaticity and a shift to lower molecular weight, which suggests. . . Also, please define what is meant by labile material. Labile from a microbial perspective?
We revised the sentence for clarity.

Page 11 Line 8 What is a clear increase?
The sentence was edited for clarity.

Page 11 Line 10-11 Confusing sentence. The meaning is meant to be about the rain itself or the river? During the event or after?
It meant the runoff during the event. We edited the sentence to make this clear.

Page 11 Line 16 The duration of the rainfall event seems very important. This point should be included earlier in the text, added into a table, or gray shading can indicate the duration in Figure 6.
We added the onset of the rainfall events to the figure.

Page 11 Line 23-24 A tremendous increase? Compared to what?
Compared to the pre-rainfall conditions - Sentence was edited to make this clear.

Page 12 Line 16 Redundant portion of the sentence - delete “across the Arctic”
This was done according to the suggestion

Page 13 Line 1 “. . .constant proportion of bioavailable DOC. . .” Meaning concentration or qualitative nature? The meaning of DOC is dissolved organic carbon and doesn’t inherently imply concentration so the usage of DOC in this manuscript should be clarified where appropriate and this section of the discussion needs to include more descriptive qualitative or quantitative language.
This is a very good point. We edited the sentence.

Page 13 Line 4-6 Example of weak language and very confusing ideas. How was the influence of ice wedge polygons assessed? The information is provided after the confusing sentence. Please reorganize and use concise language.
We reorganized the paragraph.

Page 13 Line 6-7 But not upstream? This sentence does not make sense as written.
This section was also reorganized and rewritten.

Page 13 Line 8-9 How does this make sense from the previous statements? The flow of this paragraph is very confusing.
This section was also reorganized and rewritten.

Page 13 Line 10-11 Why is rainfall discussed again in this permafrost impact section? Is that the disturbance? Clearer ideas need to be presented.
This pattern only becomes apparent after the rainfall event.

Page 13 Line 13 "SUVA and S275-295 do not show strong differences downstream in the West River." This is a result. Why is this? Is this discussed?
We edited the section.
Page 13 Line 18 What does a shallow S275-295 mean?
We replaced it with "low".

Page 13 Line 20 In this sentence, low aromaticity is linked with SUVA increases, yet a few sentences ago it is linked with decreases in SUVA. This is very confusing. Greater SUVA values mean???
This was a typo. Greater SUVA and low S275-295 mean high aromacity and higher molecular weight (and vice versa).

Page 13 Line 20-30 This section was difficult to read and understand the flow of the main discussion points. Please reorganize and put main discussion points up front in the section, then provide supporting evidence throughout the paragraph.
We revised the paragraph

Page 13 Line 31 What is cDOM-DOC? And this section seems really important. Can it be reorganized earlier in the discussion section. If the figures are being kept in this section, then they will appear earlier. A reference to Figure1 might also assist in the terrestrial/nature argument of the different catchments.
We reorganized the section.

Page 13 Line 32-33 This is another example of weak language. Consider this revision to improve scientific language and flow of ideas. "Strong positive correlations between DOC and acDOM350 were previously reported in similar Arctic rivers and globally (insert references).
We revised the sentence accordingly.

Page 13-14 Line 1-2. This information stops the flow of the discussion. Consider removing the sentence, keep the references, and reorganize the next sentence to include them.
This was revised.

Page 14 Line 4 "This means that. . .." is an example of weak language. Consider revising these two thoughts into one sentence with a connecting word like "indicating" so that unnecessary words are removed, and the main messages are clear.
It was revised as suggested.

Page 14 Line 4-6 Why is the point of stating this?
They were removed.

Page 14 Line 1-6 Is the point of this section to state the good correlation and proxy for DOC concentration using absorbance? Figure inclusion and discussion should be an important component of the manuscript. Why is it important in this work? Think about the distributions of the data and the relationships to the other work. Does the other comparative work have similar geographical features? Ice-wedges? Etc.?
We expanded here. The figure was moved to the supplementary material.

Page 14 Line 7-8 Very confusing sentence. Another example of weak language. Is this referring to concentration and a directional trend?
We changed the wording.

Page 14 Line 9 Delete "where a large range of absorption values is covered". This is redundant. Check each sentence for repetition and redundant ideas.
We deleted the phrase.

Page 14 Line 11 Going back to Figure 7? Consider keeping Figure 7 discussion in the same section.
We edited the section accordingly.

Page 14 Line 17 "higher aromaticity, which suggests that the material is fresh and prone to degradation" and fresh material? Fresh from what? Fresh as considered by what? Light? Microbes? Terrestrial soils?
"Fresh" is used as "less altered" permafrost DOC (Vonk et al. 2015 - Biodegradability of dissolved organic carbon in permafrost soils and aquatic systems: a meta-analysis

Page 14 Line 18-23 This seems like important information to put in the results section. Then it can be discussed in this section. Consider reorganizing this section.
We moved this section earlier into the discussion.

Page 14 Line 26-27 This point was just made in the discussion section and not fully developed to be included yet in this conclusion section. How are the linkages supported?
We expanded on this topic in the discussion section 5.2.1
Page 14 Line 29-31 These points needs to be clearer in the results and discussion section. Please reorganize.

Page 15 Line 2-3 Redundant sentence. Please delete.
We deleted the sentence.

Page 15 Line 4 Fresher DOM prone to degradation means what? How is fresh defined? What type of degradation?
We added clarification to this sentence.

Page 15 Line 7 This idea needs further development in this work and cannot be a standalone conclusion. The same comment can be applied for the remaining conclusion statements.
We extended the discussion on rainfall event impacts to support this conclusion.

Figure 1 In (a) it is a little confusing that ocean and glaciers are white? Is that correct? Where are the glaciers? Consider using line and dotted line symbols in the legend for catchment and subcatchment areas so that readers don't look for boxed regions. Can river flow direction be added to these (b) and (c) figures? The legend is written well and was easy to read. Consider two revisions to include the word "concentration" when referring to DOC measurements and define CAVM in the caption.
Thanks for pointing this out. In fact, the glaciers are not visible / existent at this scale or in this area respectively. We therefore decided, to remove them from the map. We changed the symbology of the catchments and subcatchments as suggested. Adding the flow direction made the figures appear very crowded and covered too much of the image. Instead, we added the flow direction to the text of the caption.

Figure 2 Very aesthetically pleasing, well done. In the caption, please revise the opening statement to "Dissolved organic matter (DOM) absorption characteristics from Herschel. . ." so that all the terms are defined.
We revised the caption as suggested, and also removed the gridlines from the figure.

Figure 3 Great ideas here, just need slight improvements to enhance understanding and readability. Define the terms in the caption, DOM, DOC, ICE, ICW, etc. Next, the symbols of circles and triangles indicating flowing and standing water are good, but too small in all these figures. Also, triangles and circles overlapping each other look like blobs. Consider open and closed symbols to improve readability. The data blobs are hardest to read in (a). The choice of pink and red or purple and pink colors are too close together to visualize clearly in (b) and (c). Consider using light green and dark green (or some similar color tone gradient) for upstream and downstream to keep that data grouped together aesthetically. Add trend lines for (c) to show the different slopes or box/circle the two different groups to help visualize the differences discussed in the text.
Many thanks for these detailed suggestions. We improved the caption, increased the size of the symbols, changed the pink and purple symbols and added an outline to all data points. We further removed the grid lines. The color scheme as it stands enables people with colour-blindness to see the differences. We therefore decided against using a color-tone gradient for grouping data together. We, however, circled the different groups to visualize the differences.

Figure 4 Same comments as Figure 3 with caption definitions, data point size, circles and triangles, and color tones. Also, is the variability of Cape Bounty discussed in the text? These figures should really tight groupings for Herschel but not Cape Bounty.
We revised the figure accordingly.

Figure 5 Similar comments to Figure 3 and 4. Same sites should use colors that fall in the same family with different gradients so they can be linked visually on the figures. Shades of green IC East on different sample dates will help. Keep acronyms similar among figures, e.g., IC East vs. ICE. These figures have a lot of gridlines on them which makes the dotted line hard to follow. Consider removing the gridlines or thickening the dotted lines. Also, consider using different symbols for different river samples. Define the terms in the caption.
Also in this case, the colour scheme was selected to make them accessible to people with colour blindness. Instead of changing the colours, we decided to change the symbology to group same sites together. We removed the gridlines as suggested and defined the terms in the caption.

Figure 6 The gridlines wash out the green data points and lines. Consider changing the color scheme and increasing the size of the connected lines and data points. Adding a vertical line through all figures for each rain event will improve these figures. Missing data should be notated in the caption. If all the data was collected in 2016, please remove the 2016 date indicator on the x-axis because it is very crowded. The legend also includes IC west and IC East. Please make this consistent with the other notations in the previous figures and define all the terms.

We removed the grid lines, defined all terms, increased the size of the connecting lines, and added vertical lines at the beginning of each rainfall event. We also removed the "missing data" label and added this information to the caption.

Figure 7 Good figure. If it is needed still in the manuscript, since only two to three sentences discuss parts of it, then keep it with some improvements. Keep the reference on the figure but put the regions for the samples it is referring to in the figure caption and remove these words from the figure (it crowds the data). Define the terms in the figure caption. There are multiple data sets with the same color assigned to them. Please select different colors to see the different groups represented on this figure. Also, consider including the slope calculated from this work as a comparison to the literature calculated slope.
As this Figure is not needed anymore, we decided to move it to the Supplementary Material.

Figure 8 Good figure. If it is needed still in the manuscript, since only two to three sentences discuss parts of it, then keep it with some improvements. Define the terms in the caption. Is it possible to put black outlines around the Permafrost extent legend colors? The isolated patches color is very difficult to read in the legend. Also, mark the color of the ocean, since it is nearly identical to the isolated patches color, or change the ocean color to something darker?
As this Figure is not needed anymore, we decided to move it to the Supplementary Material.

Table 1 Define the term CAVM in the caption. Some formatting of this table is confusing like the dark thick line near the top and then a defining line combining ICW, ICE, and CB. Consider using indents for the sample names under the low and high Arctic categories, using another horizontal row divider (as in Table 2), or separate columns.
We edited the table and caption as suggested.

Table 2 Define the terms in the caption (all abbreviations and acronyms) and provide an explanation for underlining as a useful tool for these statistical comparisons. Typo at the bottom line "He" should read "HE"
We edited the table and caption as suggested.

Table 3 Define the terms in the caption. Supplemental Information Define the terms in the figure and table captions.
We edited the table and caption as suggested.

Consider moving **S2** to the main manuscript.
We decided to leave it in the supplementary material as it only contributes to the discussion of limitations and not to the story itself.

Response to Anonymous Referee #2, 18 Feb 2019

We appreciate and are encouraged by the detailed feedback of Reviewer 2. We carefully revised and addressed the comments 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.

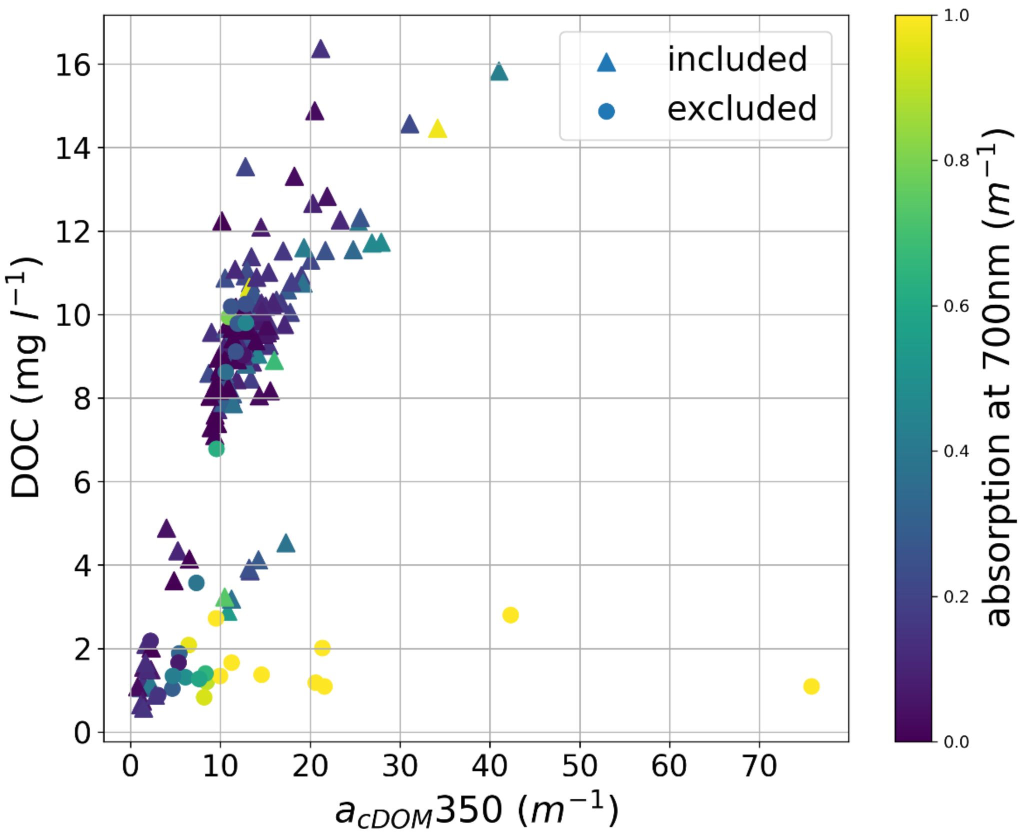
Overarching comments

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 km^2 in total, whereas the sampled area at Cape Bounty covered about 30 km^2. 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 below 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. $a_{cDOM}350$ 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 10^-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.

Comparisons of chromophoric dissolved organic matter (cDOM) composition in small low and high Arctic catchments

~~Characterizing organic matter composition in small Low and High Arctic catchments using terrestrial colored dissolved organic matter (cDOM)~~

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Abstract. Climate change is an important control of carbon cycling, particularly in the Arctic. Permafrost degradation through deeper thaw and physical disturbances result in the release of carbon dioxide and methane to the atmosphere and to an increase in riverine dissolved organic matter (DOM) fluxes. Whereas riverine DOM fluxes of the large Arctic rivers are well assessed, knowledge is limited with regard to small catchments that cover more than 40 % of the Arctic drainage basin. Here, we use absorption measurements to characterize changes in DOM quantity and quality in a Low Arctic (Herschel Island, Yukon, Canada) and a High Arctic (Cape Bounty, Melville Island, Nunavut, Canada) setting with regard to geographical differences, impacts of permafrost degradation and rainfall events. We find that DOM quantity and quality is controlled ~~is controlled~~ by differences in vegetation cover and soil organic carbon content (SOCC). The Low Arctic site has higher ~~SOCC~~ SOCC and greater abundance of plant material ~~introducing higher lignin concentrations into the aquatic system and~~ resulting in ~~a stronger color of DOM~~higher chromophoric dissolved organic matter (cDOM) than in the High Arctic. ~~There is a strong relationship between d~~Dissolved organic carbon (DOC) concentration and ~~absorption characteristics (~~cDOM~~)~~ ~~for~~ in surface waters at both sites show strong relationships similar to the one for the great Arctic rivers. We used the optical characteristics of DOM such as cDOM absorption, Specific UltraViolet Absorbance (SUVA), UltraViolet (UV) Slope~~,~~ and Slope Ratio (SR) for assessing quality changes downstream, at baseflow and stormflow conditions and in relation to permafrost disturbance. DOM in streams at both sites demonstrated optical signatures indicative of photo~~photo~~degradation downstream processes, even over short distances of 2000 m. ~~It was determined that fl~~Flow pathways and the connected hydrological residence time control DOM quality. Deeper flow pathways allow the export of permafrost-derived DOM (i.e. from deeper in the active layer), whereas shallow pathways with shorter residence times lead to the export of fresh surface and near-surface derived ~~DOM.~~DOM. Compared to the large Arctic rivers, DOM quality exported from the small catchments studied here is much fresher and therefore prone to degradation. This has important implications for the carbon cycle, especially with regard to climate change.

~~This work shows that~~O ~~o~~ptical properties of DOM will be a useful tool for understanding changes in DOM sources and quality at a pan-Arctic scale.~~.~~

1 Introduction

Climate change has important impacts on carbon cycling, particularly in the Arctic. Approximately 1300 Gt of organic carbon are stored in permafrost soils in the northern hemisphere (Hugelius et al., 2014), which is 40 % more than currently circulating in the atmosphere. Thawing permafrost and deepening of the active layer leads to the mobilization of this carbon (Osterkamp, 2007; Woo et al., 2008), the release of carbon dioxide (CO_2) and methane (CH_4) to the atmosphere (Schaefer et al., 2014), and to an increase in riverine dissolved organic carbon (DOC) fluxes (Frey and Smith, 2005; Le Fouest et al., 2018). Associated with warming is also the development of surface (physical) disturbances such as active layer detachments or retrogressive thaw slumps (Lacelle et al., 2010; Lamoureux and Lafrenière, 2009; Lewkowicz, 2007; Ramage et al., 2018), and thermal perturbation of the subsurface (Lafrenière and Lamoureux, 2013). As these processes influence freshwater systems, they ultimately have impacts on the biological production and the biogeochemistry of the Arctic Ocean. The six largest arctic rivers (Mackenzie, Yukon, Ob, Yenisey, Lena, Kolyma) drain 53 % of the Arctic Ocean drainage basin (Holmes et al., 2012) and transport huge amounts of nutrients and dissolved organic matter (DOM) into the ocean. However, there are limited flux estimates and information on DOM quality available for the remaining 47 %, which are sourced by smaller watersheds. “Small” in this context refers to smaller than the large Arctic rivers as the actual size distribution remains unknown.

Terrigenous DOM is an important source of DOC originating from allochthonous (terrestrial such as soil and plants) and autochthonous (in situ production) sources (Aiken, 2014). It is modified by biotic and abiotic processes during its lateral transport to the ocean (Tank et al., 2018; Vonk et al., 2015a; Vonk et al., 2015b). Yet, little is known about the transformation of DOM along short distances in small catchments. The composition and the vulnerability to transformation of riverine DOM is influenced by several factors such as soil organic matter and vegetation, sorption processes in the mineral layers, and biodegradation and photodegradation processes (Cory et al., 2014; Mann et al., 2012; Vonk et al., 2015b; Ward and Cory, 2015; Ward et al., 2017). Chromophoric or colored dissolved organic matter (cDOM) is a fraction of DOM, which absorbs light in the ultraviolet and visible wavelengths (Green and Blough, 1994). Optical characteristics of ~~C~~cDOM such as absorption coefficients and spectral slopes can serve as proxies for DOM molecular weight and aromaticity, which in turn can help to characterize the lability of DOM (Helms et al., 2008; Neff et al., 2006; Spencer et al., 2009; Striegl et al., 2005; Weishaar et al., 2003).

Previous studies have focused on characterizing cDOM-DOC ~~relationships~~ ratios for the large Arctic rivers and shelf areas, which exhibit a strong seasonality (Spencer et al., 2008; Stedmon et al., 2011; Walker et al., 2013). This was also shown by a global synthesis (Massicotte et al., 2017a). A handful of studies have investigated cDOM-DOC relationships in smaller Arctic catchments: Dvornikov et al. (2018) examined cDOM characteristics in surface waters of the Yamal Peninsula and cDOM-DOC relationships were examined in studies of Subarctic catchments (Balcarczyk et al., 2009; Cory et al., 2015; Larouche et al., 2015; O'Donnell et al., 2014) and the High Arctic (Fouché et al., 2017; Wang et al., 2018). Optical parameters have also been used to assess the impact of permafrost disturbance on stream geochemistry in Alaska (Abbott et al., 2014; Larouche et al., 2015) and~~,~~ NWT Canada (Littlefair et al., 2017)~~ and Siberia (Spence et al., 2015)~~. As most studies focused on downstream reaches, knowledge on the spatial variability across catchments is limited. To our knowledge, no study has examined this relationship in a Low Arctic setting or attempted to resolve geographic differences between the Low and High Arctic.

Here, we study cDOM and DOC in surface waters in the Low Arctic (Herschel Island, Yukon, Canada) and the High Arctic (Cape Bounty, Melville Island, Nunavut, Canada). The aim of this study is to (1) compare the variability and relation of DOC concentration and cDOM in High and Low Arctic surface water environments, and (2) to investigate changes in DOM composition along longitudinal stream profiles and with regard to permafrost disturbance and rainfall events. Climate change will substantially alter Arctic freshwater systems and carbon budgets. This study helps to understand and anticipate these changes.

~~This study will contribute to assessing riverine transport from small watersheds to the coastal Arctic Ocean.~~

2 Study Area

This study was carried out in two Arctic locations, Herschel Island in the Low Arctic and at the Cape Bounty Arctic Watershed Observatory, Melville Island in the High Arctic (Fig. 1a). Herschel Island (Yukon, Canada) is located at 69°35' N and 139°05' W in the Beaufort Sea off the Yukon coast. The island is composed of unconsolidated and fine-grained marine and glaciogenic sediments as it was formed by the Laurentide Ice Sheet (Mackay, 1959; Pollard, 1990). The island is situated in the zone of continuous permafrost with ground ice content between 30 and 60 % for the entire island. Physical permafrost degradation typically occurs in the form of retrogressive thaw slumps (Lantuit and Pollard, 2008) and active layer detachments (Coch et al., in review). Ramage et al. (2019) reported mean active layer depths of 52.2 ± 20.2 cm. Soil organic carbon content (SOCC) for valleys on the eastern side of Herschel Island was estimated to be 11.4 ± 3.7 kg m^2 at 0 - 30 cm depth and 26.4 ± 8.9 kg m^2 at 0 - 100 cm depth with a C:N ratio of 12.9 ± 2.2 in 0 - 100 cm depth (Ramage et al., 2019). The dominant vegetation type is lowland tundra (Myers-Smith et al., 2011; Smith et al., 1989) and can be classified into subzone E (CAVM, 2003), which corresponds to the Low Arctic. The mean annual air temperature and yearly precipitation between 1971 and 2000 at Komakuk Beach, the nearest long-term meteorological station ~40 km away from our study site, are -11 °C and 161.3 mm respectively. The mean July temperature is 7.8 °C and average precipitation is 27.3 mm (Environment and Climate Change Canada, 2018). Snowmelt is the largest hydrological event of the year occurring in May to early June. Summer baseflow from mid-June onwards is controlled by rainfall events (Coch et al., 2018). The active layer freezes up by mid-November (Burn, 2012). The studied catchments unofficially named Ice Creek West (1.4 km^2) and Ice Creek East (1.6 km^2) are adjacent to each other and merge into an alluvial fan before draining into the Beaufort Sea (Fig. 1b, Table 1). Both sampled ponds in Ice Creek West are below 1 ha large. There are degrading ice-wedge polygons present in the headwaters of Ice Creek West (Coch et al., in review).

The Cape Bounty Arctic Watershed Observatory (CBAWO) is situated on the south coast of Melville Island (Nunavut, Canada) at 74° 55' N and 109° 35' W. The geology is characterized by Devonian sandstone and siltstone bedrock overlain by Quaternary marine and glacial sediments (Hodgson et al., 1984). The soils are categorized as cryosols with a thin organic horizon. The site is situated in the zone of continuous permafrost, and active layer depths typically range from 50 to 70 cm (Lafrenière et al., 2013). Permafrost degradation such as deep thaw and physical disturbances have altered hydrochemical fluxes of the rivers (Lamoureux and Lafrenière, 2017). The vegetation cover is patchy with polar semi-desert, mesic tundra and wet sedge meadows (Edwards and Treitz, 2018), and falls into subzones B and C (CAVM, 2003). Soil organic carbon is estimated to be 3.0 kg m^2 in 0 - 30 cm depth, and 10.2 kg m^2 in 0 - 100 cm depth (Hugelius et al., 2013), with a C:N ratio of 10.0 in 0 - 100 cm depth (ADAPT, 2014). The nearest long-term meteorological station is located ~ 300 km away, at Mould Bay (NWT). Between 1971 and 2000, the mean annual air temperature and precipitation were -17.5°C and 111 mm, respectively. The average July temperature is 4.0 °C, whereas mean precipitation is 13.5 mm. Snowmelt and nival flow typically start in early to mid-June with baseflow establishing around mid-July. Refreezing of the active layer starts mid- to late August (Lamoureux and Lafrenière, 2017; Lewis et al., 2012). Samples were taken downstream in Boundary River (152.5 km^2), its sub-catchment Robin Creek (14.8 km^2), and the neighboring watersheds West River (8.8 km^2) and East River (12.4 km^2) There is an active retrogressive thaw slump in the Robin Creek watershed, and a number of recent (since 2007) active layer detachments and other disturbances in the West River watershed. The sampled lakes and ponds cover a range of sizes from below 1 ha in West River, to the larger West and East lakes (~120-140 ha).

3 Methods

3.1 Field methods and hydrochemistry

To explore downstream changes in DOM across regions, we used a transect approach in this study. Samples were taken along longitudinal stream profiles in catchments at Herschel Island and Cape Bounty (Fig. 1). Additionally, samples from standing water bodies (ponds and lakes) were collected. We further obtained discharge recordings and water samples from the outflow of both catchments at Herschel Island over the course of the summer as detailed below.

Field work on Herschel was carried out in July-August 2016. We measured discharge using a cutthroat flume equipped with a U20 Onset Hobo level logger in Ice Creek West. Discharge data at 30 minute intervals is available from 15 May 2016 and at 5 minute intervals after 22 July 2016 (Coch et al., 2018; Coch et al., in review). In Ice Creek East, discharge was determined using the area velocity method in combination with a U20 Onset Hobo level logger (see Coch et al. in review for a detailed description). Data in Ice Creek East is available at 5 minute intervals after 25 July 2016. Weather data is available from the local Environment and Climate Change Canada Station, and from a station deployed in Ice Creek West during the summer. Water samples were collected after triple rinsing the sampling bottle at the outflow of both streams between 20 July and 10 August. At the outflow of Ice Creek West, water samples were collected using an automatic water sampler (ISCO 3700) at a 12-hour interval between 25 July and 10 August and more frequently during rainfall events (between 1-3 hours). Prior to the automatic sampling, and also in Ice Creek East, water samples were taken manually once per day. We collected water samples (11 in Ice Creek West, 12 in Ice Creek East) along longitudinal profiles of the channels starting in the headwaters (~ 2000 m distance from the outflow) and following the river downstream (Fig. 1). This was done 3 times in Ice Creek West (20, 25 and 30 July) and once in Ice Creek East (30 July). Samples of flowing waters are available from Ice Creek West (n=90), Ice Creek

East (n=32) and the alluvial fan (n=8). Standing water samples (n=4) were collected from 2 ponds in the Ice Creek West catchment.

The field work at Cape Bounty took place in August 2017. All water samples were collected manually after triple rinsing the sampling bottle. Similarly to the Herschel field work, we collected samples along longitudinal stream profiles. Robin Creek is a subcatchment of Boundary River (Fig. 1), where stream samples were collected at six locations downstream of a retrogressive thaw slump. Three lakes were also sampled in the Boundary river catchment, and 2 samples from the main river channel. A total of 21 river samples and 9 samples from lakes and ponds are available from the West River catchment, some of which were collected after the rainfall event on 12 August 2017. In East River, 4 samples are available from the stream and 8 samples from standing water bodies.

Within 24 hours of sampling, electrical conductivity and pH were measured in the field lab. After collection, water samples were filtered through pre-rinsed 0.7 µm GF/F syringe filters and where then stored cool and dark for transport to the Alfred-Wegener-Institute, University of Hamburg and Geoscience Research Centre GFZ, Germany, where analysis for DOC and cDOM were carried out. Samples for DOC analyses were acidified with HCl (30 % suprapur) prior to the measurements. In 2016, DOC measurements were performed on a Shimadzu TOC-L analyzer with a TNM-L module (University of Hamburg), whereas a Shimadzu TOC-VCPH analyzer was used in 2017 (AWI). The error for these measurements is below 10 %.

Inorganic carbon (TIC) was sparged out using synthetic air prior to the measurement. As we had a shortage of HCl in the field in 2016, 82 of the samples were frozen and acidified upon return to Germany. After new acid was acquired later in the summer, sample duplicates (n=47) were processed directly in the field and also frozen. The frozen duplicate was thawed and acidified upon return to determine the effect of different sample treatment (Coch et al. 2018). There is a significant linear relationship ($p < 0.05$, $n = 47$, $R^2 = 0.87$) between DOC concentrations of unfrozen and frozen sample duplicates. Samples that were frozen in the field, and subsequently thawed and acidified upon return to Germany showed lower DOC concentrations (by 13%) than samples that were acidified directly in the field and kept unfrozen. We corrected the frozen samples for this offset (Supplementary S1). In both years, deionized water used in the field was also analyzed as blank following the same procedure.

The absorbance of cDOM was measured on a LAMBDA 950 UV/Vis Spectrophotometer (GFZ Potsdam) for the wavelength from 200 to 800 every 1 nm (average of duplicates) using a 5cm cuvette and Milli-Q water as a reference to check for instrument drift. Some of the water samples showed fine particles precipitated in the sample bottle. They appeared in the form of small thin flakes, which partly remained in suspension or accumulated at the bottom of the flask. This precipitation occurred after the samples were filtered through 0.7 µm glass fiber filters~~, and~~ transported to the laboratory for storage of about 4 weeks. This was noted down in the lab, and absorbance spectra were not further analyzed for those samples as interference of the spectral characteristics by the particles might have occurred. This was the case for 25 (out of 55) samples at Cape Bounty and for 8 samples (out of 134) at Herschel Island.

The Naperian spectral absorption coefficient of cDOM ($a_{cDOM}(\lambda)$) was calculated with

$$a_{CDOM}(\lambda)\ (m^{-1}) = \frac{2.303 * A_\lambda}{L}, \quad (1)$$

where A_λ is the absorbance and L the optical path length of the used cuvette in the spectrophotometer. The absorption was corrected for scatter using a baseline correction by subtracting $a_{cCDOM}(700)$ (Hancke et al., 2014; Helms et al., 2008). At that wavelength, absorption by cCDOM is assumed to be negligible (Mitchell et al, 2002). Spectral slopes of a_{cCDOM} for wavelength ranges from 275 to 295nm (S275-295) and 350 to 400nm (S350-400) were calculated using Eq. (2) and a non-linear fit. These slopes indicate photochemical or microbial alteration of DOM (Helms 2008). The ratio of both slopes (S275-295 : S350-400) defines the slope ratio (SR). The SUVA (mg L^{-1} m^{-1}) was calculated by dividing the decadal absorption (A_{254} / L) at 254 nm (m^{-1}) by DOC (mg l^{-1}). Both parameters have been related to the relative molecular weight and aromaticity of DOM (Helms et al., 2008; Weishaar et al., 2003).

$$a_{CDOM}(\lambda)(\lambda) = a_{CDOM}(\lambda_0) * e^{-S(\lambda-\lambda_0)}, \quad (2)$$

Where λ_0 is the absorption coefficient at reference wavelength and S is the spectral slope of $a_{CDOM}(\lambda)$ for the chosen wavelength range. To compare our data with different studies we converted absorption coefficient reported in various studies to $a_{cDOM}350$ using an interpolation method developed by Massicotte et al. (2017a).

Throughout the manuscript all data is reported as mean ± standard deviation.

3.2 Statistical Analyses

We used RStudio (Version 1.0.153) to perform statistical tests (RStudio Team, 2016). Normality was tested using the Shapiro-Wilk normality test. To determine the difference in means of two populations, we applied the Welch's two sample t-test if the data was normally distributed with unequal variances. In the case of not normally distributed data, we used the Wilcoxon-Mann-Whitney test. To measure the relationship between two variables, we used the Pearson correlation coefficient for normally distributed data and the Spearman rank correlation if the data was not normally distributed.

4 Results

4.1 Meteorological conditions and general hydrochemistry

The mean annual air temperature on Herschel Island was -6.3 °C in 2016 with mean temperatures of 9.4 °C in July and 7.7 °C in August. During the monitoring period, rainfall events of 33.9 mm (19 July), 9.3 mm (30 July) and 12.7 mm (5 August) were recorded. CABWO had a mean annual air temperature of -15.3 °C in 2017, with mean air temperatures of 4.5 °C in July and 1.6 °C in August. During the monitoring period, two rainfall events of 0.2 mm (4 August) and 1.2 mm (8 August) occurred.

Electrical conductivity (EC) and pH are significantly higher ($p < 0.05$) in surface waters on Herschel Island (1050 ± 370 µS cm^{-1} and 8.2 ± 0.2 µS cm^{-1}) than at Cape Bounty (137 ± 136 µS cm^{-1} and 7.2 ± 0.5 µS cm^{-1}). Whereas no difference was found for these parameters between standing and flowing water on Herschel Island, pH and EC were significantly higher in standing water at Cape Bounty than in flowing water (Table 2). Robin Creek showed highest EC values and the largest variability (145 ± 213 µS cm^{-1}) of the Cape Bounty rivers, whereas West River showed the overall lowest EC values (60 ± 17 µS cm^{-1}). On

Herschel Island, both adjacent rivers show EC and pH values in the same order of magnitude with a slight decrease at the alluvial fan outflows.

4.2 DOC and CDOM cabsorption characteristics

The cCDOM absorption spectra between 250 and 700 nm follow different patterns on Herschel Island and Cape Bounty (Fig. 2, Table 2). Absorption is significantly higher ($p < 0.05$) on Herschel Island than on Cape Bounty across the entire spectrum. The absorption at 350 nm wavelength (Fig. 2b) is significantly higher ($p < 0.01$) on Herschel Island (14.5 ± 5.1 m^{-1}) than on Cape Bounty (5.5 ± 4.9 m^{-1}). S275-295 amounts to 16.4 ± 1.5 x 10^{-1} nm^{-1} on Herschel Island and 14.8 ± 3.2 x 10^{-1} nm^{-1} on Cape Bounty. The same applies to the CDOM slope S275-295, which amounts to 0.016 ± 0.001 on Herschel Island and 0.015 ± 0.003 on Cape Bounty.

We found a significant positive relationship (rho = 0.78, $p < 0.05$) between the cDOM absorption at 350 nm and DOC concentration for all samples at both sites (Fig. 3a). Average DOC concentrations in surface water samples from Herschel Island amounted to 10.0 ± 1.6 mg l^{-1} on average, which is significantly higher than DOC concentrations fromon Cape Bounty water samples (2.5 ± 2.0 mg l^{-1}). Comparing the rivers on Herschel Island (Fig. 3b), highest DOC and a_{cDOM}350 values were found in the headwaters of Ice Creek West. Ice Creek West had significantly higher ($p < 0.05$) values in DOC (10.4 ± 1.5 mg l^{-1}) and a_{cDOM}350 (16.1 ± 5.4 m^{-1}) than Ice Creek East, which were 8.7 ± 1.1 mg l^{-1} and 11.1 ± 1.8 m^{-1}, respectively. No significant difference was found between the SUVA values for the two creeks. The relationship between a_{cDOM}350 and DOC at Cape Bounty is broadly separated into two groups, namely flowing and standing water. Both correlations are significant (< 0.05) and show different slopes of the regression (Fig. 3c). DOC and SUVA are significantly different for standing water relative to flowing water. No significant difference between these water types was found for a_{cDOM}350. Within the group of standing water, samples from the East River catchment show the highest DOC and a_{cDOM}350 values. The highest values of DOC and a_{cDOM}350 values of flowing water were recorded in West River after the August 8 rainfall event.

There is a significant difference ($p < 0.05$) between the mean cDOM slopes S275-295 for samples from Herschel Island (0.016 ± 0.001 nm^{-1}) and Cape Bounty (0.015 ± 0.003 nm^{-1}). Compared to the SUVA values, we found a moderate negative significant relationship between SUVA and the mean S275-295 of cDOM slopes all water samples from both locations (rho = -0.64, $p < 0.05$, Fig. 4a). The S275-295 slopes on Herschel Island showed a narrow spread (Fig. 4b) with. This means that they remained within a small range with changing SUVA, except for two outliers in Ice Creek East. They exhibited a clear negative relationship (rho = -0.72, $p < 0.05$). The headwaters in both rivers showed slightly smaller slopes than the samples taken downstream. Samples from Cape Bounty (Fig. 4c) showed a negative relationship (rho = -0.66, $p < 0.05$) between SUVA and S275-295. Standing water samples showed significantly larger slopes ($p < 0.05$) and significantly smaller SUVA ($p < 0.05$) than flowing water samples.

4.3. Downstream ~~patterns of DOC and c~~DOM patterns along longitudinal transects

The studied rivers on Herschel Island and Cape Bounty followed different hydrochemical patterns from upstream to downstream (Fig. 5). At Herschel Island, DOC concentration (Fig. 5a) decreased from upstream to downstream for Ice Creek West at all times of sampling, whereas it varies very little ~~remained on a similar level~~ from upstream to downstream in Ice Creek East. On 30 July 2016, when both rivers were sampled simultaneously, Ice Creek East showed significantly lower ($p < 0.05$) DOC concentrations than Ice Creek West throughout the entire profile. At ~1300 m from the outflow, Ice Creek West shows a slight increase in DOC concentration. At Cape Bounty, DOC concentrations remain at a ~~low~~ similar level (< 2 mg l^{-1}) in all streams, except after the rainfall event in West River. Here, we found higher levels of DOC compared to ~~the~~ other Cape Bounty rivers, and also a more pronounced downstream increase of DOC. East River shows a slight downstream decrease of DOC. In Robin Creek, we found an increase in DOC from 1.3 mg l^{-1} to 1.7 mg l^{-1} as the stream gets impacted by a retrogressive thaw slump. DOC drops directly thereafter. ~~No clear pattern was detected in~~ Boundary river shows similar concentrations to Robin Creek.~~.~~

Similar patterns as for DOC were found for $a_{cDOM}350$. This confirms the strong relationship between both parameters (Fig. 3) which is especially high at Herschel Island. At Cape Bounty $a_{cDOM}350$ followed the same pattern as DOC in West River. For the remaining rivers, $a_{cDOM}350$ remained ~~at a low level~~with little variation throughout the profiles.

SUVA values showed different trends in the rivers of Herschel Island and Cape Bounty (Fig. 5c). At Herschel Island, SUVA values remained at the same level along the profiles of both streams and did not show strong differences between rainfall and post rainfall conditions. They follow similar patterns as DOC concentrations and $a_{cDOM}350$. In contrast, at Cape Bounty, West River (sampled after rainfall) showed higher SUVA than the remaining rivers (sampled before the rainfall). Further, an increase in SUVA downstream was visible in Robin Creek and Boundary River, although the number of available data points is limited.

Slope values (S275-295) at Herschel Island were variable in the headwaters and showed an increase downstream (Fig. 5d). They were smallest after the first rainfall event in Ice Creek West and increase progressively over the course of the season. We found lows in the headwaters of Ice Creek West at ~2000 and ~1250m distance from the outflow. Overall, Ice Creek West showed smaller slope values along the stream profile compared to Ice Creek East on 30 July 2016. The rivers on Cape Bounty showed highest slopes for East River (~~0.0~~16.1 ± 1.6~~0.001~~ x 10^{-3} nm^{-1}) and the lowest for West River (~~0.012~~11.9 ± ~~<0.001~~0.8 x 10^{-3} nm^{-1}). Robin Creek showed a decrease in slope from 16.8 x 10^{-3}~~0.017~~ nm^{-1} at ~2100 m distance to ~~0.0~~1~~4~~3.4 x10^{-1} nm^{-1} at the outflow. In contrast, a slight downstream increase in slope was recorded in West River.

Electrical conductivity ~~was found to~~ increased from upstream to downstream in Ice Creek West, whereas ~~they~~ it remained at a similar level in ~~ICE~~Ice Creek East (Fig. 5e). It remained below 200 µS cm^{-1} at all times, except for the upstream location in Robin Creek where an active retrogressive thaw slump is hydrologically connected to the stream. It ~~dropped~~ decreased substantially thereafter.

4.4 Temporal trends of DOM ~~of DOC and cDOM~~ with changing meteorological conditions

Changes in discharge, DOM composition and conductivity over the summer season were observed for both rivers at Herschel Island ~~(Fig. 6)~~. Rainfall response is direct with steep rising hydrographs and elongated falling limbs (Fig. 6a) in both streams (detailed presentation of rainfall response in Coch et al. 2018). After the peakflow following the 33.9 mm rainfall event (Event-1), both streams showed a decline in DOC accompanied by a decline in a_{cDOM}350, SUVA, and an increase in S275-295 (Fig. 6b-e). EC is steadily increasing after peakflow in both streams (Fig. 6f).

The subsequent rainfall event (Event-2, 9.3 mm) led to an increase of DOC, a_{cDOM}350 and S275-295, and a ~~drop~~ decrease in SUVA (Fig. 6b-e) in Ice Creek West. This dynamic was not captured in Ice Creek East, which was sampled at a longer time interval. Baseflow had increased after this rainfall event (Fig. 6a).

The hydrochemical response to rainfall Event-3 (12.7 mm) ~~The hydrochemical response to the following rainfall event (Event-3, 12.7 mm)~~ was different ~~to the previous one~~than the response to Event-2. ~~Here, we saw a~~An initial ~~drop~~ decrease in DOC, a_{cDOM}350 and S275-295~~, and then~~ is followed by a sharp~~n~~ increase of these parameters in Ice Creek West. SUVA ~~shows an~~ increases with two ~~positive peaks~~spikes in the data. Ice Creek East had a different response showing an increase in DOC and a_{cDOM}350 and a drop in SUVA. The scale depicts only S275-295 values below 18 x 10^{-3} nm^{-1} to capture the variability, hence the two gaps in the Ice Creek East data.

~~No continuous slope records are available for this event as two outliers occurred in this event.~~

5 Discussion

5.1 Limitations of cDOM measurements from terrestrial sources

There are a few constraints to optical DOM measurements and the samples themselves that we encountered in this study. As described in the methods section, ~~a number of~~some samples ~~showed~~ formed precipitates ~~precipitation~~ inside the bottles in the form of small thin flakes, which partly remained in suspension or accumulated at the bottom. All samples were filtered in the field through 0.7 µm glass fiber filters, and the precipitation occurred after filtration during storage.~~-~~ At Cape Bounty, these problematic samples had very high a_{cDOM} values of 13.9 ± 13.8 m^{-1} with a maximum of 75.8 m^{-1}, and SUVA values of 10.1 ± 11.5 L mg^{-1} m^{-1} with a maximum of 59.5 L mg^{-1} m^{-1}. Those values are significantly higher ($p < 0.05$) than the mean values reported in Table 2 and are not realistic for natural surface waters. At Herschel Island, a_{cDOM} and SUVA did not differ significantly from the mean (11.8 ± 0.8 m^{-1} and 3.5 ± 0.4 L mg^{-1} m^{-1} respectively). ~~(Hansen et al., 2016; Weishaar et al., 2003)In the absorption spectra, these samples showed extraordinarily high a_{cDOM} values when compared to their DOC concentration level.~~ As described in the methods section (3.1), samples showing precipitates in the laboratory were excluded from the study, even if the absorption values were plausible when compared to the corresponding DOC concentration (Fig 7). ~~they were therefore excluded from the study based on the laboratory notes.~~ At Cape Bounty, this was the case for 25 out of 55 samples. We assume that absorbance measurements are high as a result of scattering by newly formed colloid complexes and precipitates. Also, Hansen et al. (2016) and Weishaar et al. (2003) report thatUnfortunately, we do not have any supporting data for these sampling sites, such as dissolved solids or turbidity. We assume that high absorption values are a result of multiple other absorbers beside cDOM and scattering by particles. SUVA values above 6.0 L mg^{-1} m^{-1} are indicative for absorption from other constituents in the sample (Hansen et al., 2016; Weishaar et al., 2003). This might have played a role also for other samples, even if they did not show precipitation in the sample bottles. We find that at Cape Bounty, 7 samples stand out in terms of higher a_{cDOM}350 compared to their DOC values – samples from West River and East River standing water (Fig. 3c). Possible influences of absorbance measurements are going to be discussed here.

We assume that the absorption interference could be due to polymeric iron (hydr)oxides or high concentrations of dissolved iron. Dissolved iron in terrestrially dominated waters is dominantly complexed with humic and fulvic acids. Therefore, with changing temperature and changing pH of the sample filtrates, redox reaction can result in colloid formation and phase changes, which then strongly affect the optical properties of the sample filtrate by scattering. Poulin et al (2014) describe how iron (Fe(II,III)) is known to interfere with the absorption of cDOM with a linear dependency of increasing a_{cDOM} with increasing Fe(III) concentration in the water. Poulin et al. (2014) suggest to correct cDOM absorption coefficients according to the iron concentrations using correction coefficients. Coch et al. (2018) report total aqueous dissolved iron concentrations from Herschel Island. High total iron concentration is found to occur in high a_{cDOM}350 (Fig. S2), which indicates a potential influence of iron concentration on the absorption. Fraction of Fe(II) and Fe(III) on the total iron concentration was not measured as a standard hydrochemistry measurement, thus the correction could not be performed. However, Figure 7 clearly shows that the samples that were removed fell into the problematic group (circled), where cDOM was overestimated compared to DOC concentration. This conservative approach removed also other samples with reasonable cDOM to DOC ratios.

The cut off between solid and dissolved fraction in a solution is normally made at 0.22, 45 µm or 0.7 µm depending on the scientific community (e.g. among others, operational water quality, biogeochemistry, aquatic optics). Therefore, the operational definition of DOM varies between studies and the choice of the filter pore sizes. In our study, we filtered the water samples through 0.7 µm GF/F because this is the least organic-rich filter material and finest glass fibre filter that is offered on the market. Colloid complexes between 22 µm and 0.7 µm are in solution and may influence the absorbance spectra(Massicotte et al., 2017b). Massicotte et al. (2017b) compared $a_{cDOM}(\lambda)$ for 1734 sample filtrates from different environments for its difference in 0.22 µm and 0.7 µm filter pore sizes. The result shows that water samples from environments with terrestrial dominated DOM are not as strongly affected as other water environments. Watanabe et al. (2015) found the difference between $a_{cDOM}(\lambda)$ between 0.22 µm and 0.7 µm to be about 12 %. Both studies conclude that the influence of different filter size on the absorbance spectra is relatively low. Most samples from our study were taken in streams of small watersheds with a clear terrestrial dominated DOM source. For most of our samples, we assume that the filter difference has a minor influence on cDOM absorption.

However, a possible source of absorption interference could be due to polymeric iron (hydr)oxides or high concentrations of dissolved iron. Iron (Fe(II,III)) is known to interfere with the absorption of cDOM (Poulin et al., 2014). Dissolved iron in terrestrially dominated waters is dominantly complexed with humic and fulvic acids. With changing temperature and changing pH of the sample filtrates, redox reaction can result in phase changes which then strongly affect the optical properties of the sample filtrate by scattering. We observed fine flakes in suspension or deposited at the bottom of some of the samples prior to absorbance measurements. These particles could be precipitation of iron-organic acid colloids and thus a large source of overestimation of a_{cDOM} in those cases. Poulin et al. (2014) describes a linear dependency of increasing a_{cDOM} with increasing Fe(III) concentration in the water. The influence of iron is expected to be especially high in the spectral parameter of cDOM such as slopes and SR as well as SUVA. The study also showed that the fraction of Fe(II) and Fe(III) of the total iron concentration inverts the two when pH increases from ~5.5 to 6.3. Table 2 shows the pH values for the different streams and catchments from this study. Lowest pH values were found in West River (6.9 ± 0.3), which is higher than the values reported by Poulin et al. (2014). This hypothesis needs thorough testing in a future study by analyzing dissolved solids along with optical characteristics. Poulin et al. (2014) further suggest to correct absorption coefficients according to the iron concentrations using correction coefficients. For this study, only samples from Herschel Island were analyzed for total aqueous dissolved iron concentration. High total iron concentration is found to occur in high $a_{cDOM}350$ (Supplementary S2), which indicates an influence of iron concentration on the absorption. Fraction of Fe(II) and Fe(III) on the total iron concentration was not measured as a standard hydrochemistry measurement. Due to the lack of Fe hydrochemistry data from Cape Bounty, a uniform correction of all samples is therefore not possible. Therefore, all problematic samples were removed from this study.

5.2 Nature of the cDOM to DOC relationship across the terrestrial Arctic

Strong positive correlations between DOC and $a_{cDOM}350$ as found in this study (Fig. 3a) were previously reported in the large Arctic rivers (Walker et al., 2013) and globally (Massicotte et al., 2017a). DOC and cDOM values are available from surface waters in northeastern Canada (Breton et al., 2009), Scandinavia (Forsström et al., 2015; Kellerman et al., 2015) and the Alaskan Arctic (Cory et al., 2015; Larouche et al., 2015). Comparing our sites to those found in the literature confirms the strong positive relationship (rho = 0.85, $p < 0.05$) between DOC and $a_{cDOM}350$ (Fig. S3), indicating the robustness for using the optical parameter a_{cDOM} as a proxy for DOC concentration in terrestrial freshwater systems. However, this relationship holds not true for sites where dissolved organic matter is strongly altered, for example through photodegradation (Osburn et al., 2017).

We linked cDOM and $a_{cDOM}350$ from this study and the literature (Table 3; Supplementary Table S1, S2) to latitude and the soil organic carbon content (SOCC) in 0-30 cm and 0-100 cm depth as retrieved from Hugelius et al. (2013). We found a positive correlation (rho = 0.53/0.51, $p < 0.05$) between SOCC and DOC concentration. The relationship between $a_{cDOM}350$ and SOCC is also significant, although weaker (rho = 0.26 / 0.34, $p < 0.05$). It is important to bear in mind that the northern circumpolar soil carbon database is a product of upscaling and will most likely not cover the spatial variability reported in the studies. Nevertheless, the data shows a decrease of SOCC at higher latitudes, influenced by climate to a certain degree. DOM and SOCC are further linked to watershed slope: Longer residence times in low relief terrain and high hydrologic connectivity facilitate leaching and export of DOM from soil organic matter (Connolly et al., 2018; Harms et al., 2016). Also, several of the studies contain data on lakes in large river floodplains with very large catchment sizes. For example, Skorospekhova et al. (2016) report high cDOM and DOC concentrations for tundra lakes in the Lena Delta, which are influenced by the spring flood delivering organic material into the lakes.

Walker et al. (2013) report SUVA for three different flow regimes of the large Arctic rivers: peakflow (spring freshet), midflow (summer) and baseflow (winter). The SUVA values reported in this study (2.9 ± 0.4 L mg^{-1} m^{-1} for Herschel Island and 2.8 ± 1.1 L mg^{-1} m^{-1} for Cape Bounty) are higher than the mean mid-flow SUVA for the five Arctic rivers (2.4 L mg^{-1} m^{-1}), which ranges between 2.0 L mg^{-1} m^{-1} in the Mackenzie River and 2.7 L mg^{-1} m^{-1} in the Ob'. This confirms the hypothesis proposed by Vonk et al. (2015b), that DOM exported from smaller rivers has a higher aromaticity, which suggests that the material is fresh (less altered) and prone to degradation. The large Arctic rivers cover approximately half of the Arctic drainage basin, whereas the other half is covered by smaller catchments. Although the exact size distribution remains unknown, our results suggest that these smaller rivers could potentially deliver material that is "fresher" and more prone to degradation, compared to the large Arctic rivers.

5.32 Catchment processes and biogeochemical cycling

5.32.1 Regional catchment properties

Our study sites show strong differences in DOM quantity and quality possibly related to their geographic location and environmental setting. Herschel Island (Low Arctic) shows on average significantly higher values in DOC, a_{cDOM}350, and SUVA than Cape Bounty (High Arctic). Although catchment slope is an important driver of DOC concentrations (Connolly et al., 2018), also vegetation type and soil characteristics play an important role (Harms et al., 2016). Greater abundance of plant material in the Low Arctic (Fig. 1) results in high lignin concentration that can be introduced into the aquatic system (Sulzberger and Durisch-Kaiser, 2009), resulting in high DOC and a_{cDOM}350 values.

The variability and range of SUVA and S275-295, indicating the molecular weight and aromaticity, is greater on Cape Bounty than it is on Herschel Island. The greater ranges of SUVA and S275-295 at Cape Bounty indicates a greater variability of DOM quality there. High SUVA in combination with low S275-295 indicate "fresh" DOM, or systems of shorter residence time receiving a greater input of fresh DOM from the catchment area. In contrast, low SUVA and high S275-195 might be an indicator of limited fresh DOM inputs, a higher relative contribution of autochthonous DOM, greater exposure to photobleaching and longer residence time (Anderson and Stedmon, 2007; Fichot and Benner, 2012; Fichot et al., 2013; Helms et al., 2008; Whitehead et al., 2000).

At Cape Bounty, two different water types were identified based on the cDOM to DOC ratios (Fig. 3c). Group 1, dominated by standing water bodies, showed lower cDOM to DOC ratios compared to group 2. We explain this difference in ratios by different turbidity and residence times. In surface waters photodegradation of DOM is a dominant process (Vonk et al., 2015b). Short residence times, but specifically turbidity through sediment inputs or resuspension might limit photodegradation processes (Cory et al., 2015; Cory et al., 2014).

~~(Cory et al., 2015; Cory et al., 2014)~~

~~5.2.1 Regional catchment properties~~

~~Our both study sites show strong differences in DOM quantity and quality possibly related to their geographic location and environmental setting. Herschel Island (Low Arctic) shows on average significantly higher values in DOC, a_{cDOM}350, and SUVA, and lower values for S275-295 and SR than Cape Bounty (High Arctic). DOM in the Low Arctic is stronger coloured (i.e. higher a_{cDOM}350) than in the High Arctic. This is a result of the greater abundance of plant material in the Low Arctic and a resulting high lignin concentration that can be introduced into the aquatic system (Sulzberger and Durisch-Kaiser, 2009).~~

~~The variability and range of SUVA and S275-195, indicating the molecular weight and aromaticity, is greater on Cape Bounty than it is on Herschel Island. The greater ranges of SUVA and S275-195 at Cape Bounty indicates a greater variability of DOM quality there. High SUVA in combination with low S275-195 indicate "fresh" DOM, or systems of shorter residence time receiving a greater input of fresh DOM from the catchment area. In contrast, low SUVA and high S275-195 might be an indicator of limited fresh DOM inputs, a higher relative contribution of autochthonous DOM, greater exposure to~~

~~photobleaching and longer residence time (Anderson and Stedmon, 2007; Fichot and Benner, 2012; Fichot et al., 2013; Helms et al., 2008; Whitehead et al., 2000).~~

~~In lakes, increased residence time of DOC in the system leads to a domination of partial photodegradation and an increase in bacterial respiration. Only two standing water bodies (small ponds) at Herschel Island were sampled for DOC and optical properties. Although not statistically different, they showed higher a_{cDOM}350, DOC and S275-295 than flowing water bodies. At Cape Bounty, the difference between standing and flowing water bodies is more pronounced. Higher S275-295 and SR are explained by higher residence time resulting in more intense photodegradation and bacterial respiration. We will discuss downstream patterns in the different rivers in section 5.2.3.~~

5.~~2~~3.2 Rainfall events

Rain magnitude, intensity and antecedent conditions play~~s~~ an important role for mobilizing DOM from permafrost catchments. At Herschel Island, we captured the response to three different rainfall events through continuous sampling at the outflow and repeated sampling along the longitudinal stream profile in Ice Creek West. Rainfall Event-1 (33.9 mm) was captured only at the receding hydrograph at the outflow (Fig. 6), but along the stream profile in Ice Creek West (Fig. 5). This event of high magnitude and intensity led to high SUVA and low S275-295 values indicating "fresh" plant derived DOM that is prone to degradation. After this event, the hydrograph recedes, and the DOM signature during the "post rain" conditions suggests a sourcing from deeper in the active layer (decreasing SUVA and increasing S275-295 at the outflow and throughout the profile). ~~Whereas the full response of rainfall event 1 was not captured at the outflow, t~~The contrasting response of Ice Creek West to rainfall events 2 and 3, suggests different sourcing of DOM and controlling factors~~of DOM~~. During the second rainfall event (9.3 mm), as DOC increased, we found a decrease in SUVA accompanied by an increase in S275-295. This indicates a decrease in aromaticity and a lower molecular weight, ~~which suggests~~indicative of more decomposed ~~, labile~~ material. The following event of 12.7 mm led to a ~~drop~~ decrease in DOC and S275-295 and an ~~clear~~ increase in SUVA indicating an increase in aromaticity and a higher molecular weight – suggesting more lignin rich plant derived DOM. A change in water sources for these two rainfall events was examined by Coch et al. (in review). Whereas ~~the~~ runoff during the 9.3 mm rainfall event showed the signature of supra-permafrost water, which was forced out during that rainfall event, runoff during the subsequent 12.7 mm rainfall event reflected the isotopic signature of rain. Thus, the DOM was first sourced from the surface and through the entire active layer and had a longer residence time than the rain event after. This indicates that antecedent (pre-rainfall) conditions play a crucial role for the sourcing of DOM. The second rainfall event (9.3 mm) occurred about 10 days after the first one (33.9 mm), whereas the time difference between the second and the third one was less than 4 days. In addition to the antecedent conditions, the magnitude and intensity of the rainfall event might also play an important role here. The 9.3 mm rainfall event occurred over a period of 3 days. Thus, the flow pathways during this event might be deeper in the active layer mobilizing more decomposed OM (Marín-Spiotta et al., 2014). In contrast, the subsequent 12.7 mm event occurred within 1 day, which presumably led to increased overland flow and the mobilization of surface OM. Baseflow in this catchment is increasing with summer rainfall and as the summer season progresses (Coch et al., 2018). The authors also reported a linear increase of DOC export with increasing runoff. Our dataset shows that the quality of exported DOC depends on the intensity of rainfall and the antecedent conditions, which in turn determine hydrological flow pathways and sourcing of DOM. Although only one river was sampled before and after rainfall on Cape Bounty (West River), we found a tremendous substantial increase in DOC there compared to the pre-rainfall concentrations. Fouché et al. (2017) conducted an extensive study of DOM quality in four headwater streams of West River (Cape Bounty) and also reported an increase in DOC concentrations and fluxes during stormflow. They observed a change in DOM quality: enrichment in fresh low molecular weight (LMW), microbially-derived, components as indicated by an increase in S275-295 and a decrease in SUVA during rainfall. Although we do not have data on the optical properties for West River before the rainfall event, similar concentrations of DOC in West River and East River point towards similar optical characteristics at that time. Baseflow in undisturbed High Arctic headwater streams seems therefore characterized by more high molecular weight (HMW) humic-like components with high aromaticity (low slope and increase in SUVA) relative to stormflow DOM. In turn, stormflow leads to an export of DOM characterized by lower molecular weight and decreased aromaticity (high slope, decreased SUVA). Fouché et al. (2017) explain this pattern by a change in flow pathways from shallow active layer soils (baseflow) to subsurface runoff (rainfall), where soluble components from mineral soils deeper in the active layer are mobilized. Associated with the change in DOM quality, they also found an increase in total dissolved solids (TDS) supporting this hypothesis. Impacts of changing flow pathways on DOM quality are also reported from a Subarctic setting by Balcarczyk et al. (2009). The increased residence time of percolating water through the active layer leads to a selective sorption of compounds to mineral soil particles. The authors describe that hydrophobic compounds are absorbed, while hydrophilic compounds remain in the solution, and are therefore exported from the catchment (Balcarczyk et al., 2009). Further, an increased residence time and subsurface flow mobilizes DOC that is more microbially degraded (Striegl et al., 2005; Ward and Cory, 2015).

Different studies anticipate a shift towards deeper flow pathways as active layer depths increase with climate change (Drake et al., 2018; Mann et al., 2015; O'Donnell et al., 2014; Ward and Cory, 2015). (Mann et al., 2015; O'Donnell et al., 2014; Ward and Cory, 2015). These studies found that permafrost-derived DOM is more labile compared to surface (organic mat) DOM. HereAs described above, we show that stormflow at the Low and High Arctic locations alter flow pathways and therefore the quality of DOM exported. At the Low Arctic setting our data suggests that more permafrost-derived DOM is exported with increasing baseflow during the season and during a rainfall event of smaller magnitude and lower intensity. Based on the optical properties, this material shows low molecular weight and aromaticity, i.e. it is already altered and not prone to degradation. In contrast, rainfall events of high magnitude and intensity that act on saturated soil lead to shorter residence time in the flow path and thus export more fresh (less altered) near-surface-derived DOM (higher SUVA and lower S275-295). As summer rainfall is projected to increase across the Arctic (Bintanja, 2018; Bintanja and Andry, 2017), we are expecting an increase in DOC export (Coch et al. 2018) export across the Arctic. Small catchments in the subarctic Canadian Shield already shift towards a nival-pluvial flow regime leading to substantial increases in organic matter fluxes during fall and winter (Spence et al., 2011; Spence et al., 2015). TThe DOM quality will depend on the residence time and thus, flow pathways within the catchment, which in turn is controlled by the frequency and magnitude of the rainfall events and the thaw depth of the active layer.

5.~~2~~3.3 Downstream patterns and impact of permafrost disturbance

Transport and degradation of DOC is a dynamic process. Vonk et al. (2015b) showed that the degradability decreased from small streams towards larger rivers within the continuous permafrost zone. The fate of DOC along lateral flow pathways from headwater streams through lakes and large rivers to the ocean is connected to photochemical and biological oxidation (Cory et al., 2015; Cory et al., 2014). Studies show the importance of headwater systems where photodegradation (Cory et al., 2014) and bacterial respiration of ancient permafrost-derived DOC are prevalent (Mann et al., 2015). Our objective was therefore to investigate the upstream to downstream patterns in small coastal catchments in the Low and High Arctic.

At Herschel Island, we found a high variability of DOC, SUVA and S275-295 in the headwaters of Ice Creek West. The locations at 2000 m and 1300 m distance from the outflow show high DOC, S275-295 and low SUVA compared to the other locations. This is due to ~~There are~~ degrading ice-wedge polygons ~~present~~, which heavily influence ~~the~~ DOM in the headwaters of the stream (Coch et al. in review). The location at 1300 m marks the inflow of another headwater tributary impacted by ~~where~~ degrading ice-wedge polygons ~~are present~~. Thus, main expected sources for fresh mobilized DOM are headwaters and water from the tributary. ~~This is clearly reflected in~~ DOC and a_{cDOM}350 ~~with~~ show highest values in the headwaters ~~and~~ decreasing towards the outflow ~~with another peak at the location of the tributary inflow~~. Increasing S275-295 ~~shows~~ along both streams stream is indicative of a gradual~~ly~~ photochemical degradation of DOM with distance ~~and an interruption where fresh DOM is provided by the tributary channel (1300m)~~. S275-295 has been found a good indicator for photodegradation of DOM (Fichot and Benner, 2012; Fichot et al., 2013; Helms et al., 2008), and also been observed along a flow-path continuum of the Kolyma river basin (Frey et al., 2016). Here, they found a relative constant proportion of bioavailable DOM~~C~~ along the entire flow path, indicating an acclimatization of aquatic microorganisms to downstream DOM changes and/or the generation of labile DOM for microbial processing through photodegradation. SUVA values show a similar pattern to DOC and a_{cDOM}350 including the distinct increase at 1300 m. ~~In Ice Creek East, the influence of degrading ice-wedge polygons is minimal, so that we do not see a clear downstream pattern of DOC. At locations where ice-wedge polygon degradation is present, we see a high aromaticity and higher molecular weight than further downstream from that location. We assume that microbial and photochemical degradation or both processes are altering the DOM downstream.~~ Cory et al. (2014, 2015) show at a Subarctic site that DOC in headwater streams, which are directly sourced by soil water, have low prior exposure to light and is therefore prone to photodegradation to CO_2. The temporal variation of the DOM parameters across the stream profile is in line the onset

At Cape Bounty, optical data of upstream to downstream patterns is more limited (see section 5.3). West River shows an increase in DOC downstream ~~after the rainfall event~~ (3 August 2017), which is also reflected in an increase of a_{cDOM}350. As discussed by Fouché et al. (2017) and Wang et al. (2018), West ~~r~~River is characterized by a downstream increase in autochthonous DOM. SUVA and S275-295 do not show strong differences downstream in the West River suggesting little modification of DOM through microbial and/or photodegradation processes. A retrogressive thaw slump at Robin Creek heavily impacts DOM quality.The adjacent catchment East River shows a smaller cDOM slope at the location 4000 m from the outflow, accompanied with an increase in SUVA and low DOC concentration. The greatest measured differences are found in Robin Creek, which represents the outflow from an active retrogressive thaw slump. At ~2100 m distance from the outflow, closest to the slump, we see the highest DOC, S275-295 and EC values and lowest SUVA. This is indicative of low aromaticity and lower molecular weight. Abbott et al. (2014) found that DOM is most biodegradable during active disturbance at sites in the Subarctic. SUVA values at thermokarst outflows in that study are half as high as in undisturbed reference waters indicating less aromatic DOC. High S275-295 and SR were observed in conjunction with geomorphic disturbance in headwater streams of West River by Fouché et al. (2017). Downstream of this point, at the outflow of Robin Creek draining into Boundary river, high SUVA and a shallow S275-295 are found. The first sampling point, at about 1600 m upstream marks the point before both rivers merge. It is visible, that, after Robin Creek merges SUVA increased downstream. This reflects low aromaticity downstream. Abbott et al. (2014) found that DOM is most biodegradable during active disturbance at sites in the Subarctic. SUVA values at thermokarst outflows in that study are half as high as in undisturbed reference waters indicating less aromatic DOC. Fouché et al. (2017), who studied headwater streams of West River found greater microbial activity with an increase in the magnitude of geomorphic disturbance indicated by an increase of less-humified and degradable protein-like components. S275-295 and SR significantly increased in those cases. Impact of retrogressive thaw slumps on DOM quality was also studied in the Subarctic Peel Plateau by Littlefair et al. (2017). They reported similar dynamics at modestly sized slumps as we observed at Robin Creek: DOC concentration is highest directly at the slump outflow and is lower downstream compared to the undisturbed site before the slump impacted the stream. The authors attribute low SUVA and high S275-295 within the disturbed site to deep permafrost flow pathways. Our SUVA values within the slump and downstream are very similar to the ones reported by Littlefair et al. (2017), despite the great geographical difference.

5.3 Nature of cDOM-DOC across the terrestrial Arctic

(Walker et al., 2013; Massicotte et al., 2017a; Breton et al., 2009)There is a strong relationship between DOC and a_{cDOM}350 across our study sites, which has been reported previously for the large Arctic rivers by Walker et al. (2013), and globally by Massicotte et al. (2017a). Breton et al. (2009) report DOC and cDOM values for thaw ponds in northeastern Canada across different vegetation zones, and this data s also available from Scandinavia (Forsström et al., 2015; Kellerman et al., 2015) and the Alaskan Arctic (Cory et al., 2015; Larouche et al., 2015). Comparing our sites to those found in the literature confirms the strong positive relationship (rho = 0.85, $p < 0.05$) between DOC and a_{cDOM}350 (Fig. 7). This means that the optical parameter a_{cDOM} acts as a good proxy for DOC concentration. The highest values for DOC and a_{cDOM}350 are found in Sweden (Kellerman et al., 2015) and the Canadian Subarctic (Breton et al., 2009). Figure 8 includes also sites from Siberia (Dvornikov et al., 2018; Skorospekhova et al., 2016; Skorospekhova et al., 2017), where only a_{cDOM}350 is available. There is a weak significant negative relationship between latitude and a_{cDOM}350 (rho = -0.22, $p < 0.05$) pointing towards a decrease in cDOM and therefore DOC as going north. The great variability of a_{cDOM}350 within study regions is especially visible in Yamal and Scandinavia, where a large range of absorption values is covered independent from latitude. This is due to different catchment sizes of the water bodies sampled.

It is remarkable that the DOC-a_{cDOM}350 relationships from surface water bodies across the Arctic are similar to the one established for the five large Arctic rivers (Mackenzie, Lena, Kolyma, Ob', Yenisei) (Fig. 7, Walker et al. (2013)). The authors also report SUVA for three different flow regimes: peakflow (spring freshet), midflow (summer) and baseflow (winter). The SUVA values reported in this study (2.9 ± 0.4 L mg^{-1} m^{-1} for Herschel Island and 2.8 ± 1.1 L mg^{-1} m^{-1} for Cape Bounty) are higher than the mean mid-flow SUVA for the five Arctic rivers (2.4 L mg^{-1} m^{-1}), which ranges between 2.0 L mg^{-1} m^{-1} in the Mackenzie River and 2.7 L mg^{-1} m^{-1} in the Ob'. This confirms the hypothesis proposed by Vonk et al. (2015b), that DOM exported from smaller rivers has a higher aromaticity, which suggests that the material is fresh and prone to degradation.

We linked cDOM and a_{cDOM}350 from this study and the literature (Table 3; Supplementary Table S1, S2) to latitude and the soil organic carbon content (SOCC) in 0-30 cm and 0-100 cm depth as retrieved from Hugelius et al. (2013). We found a positive correlation (rho = 0.53/0.51, $p < 0.05$) between SOCC and DOC concentration. The relationship between a_{cDOM}350 and SOCC is also significant, although weaker (rho = 0.26 / 0.34, $p < 0.05$). It is important to bear in mind that the northern circumpolar soil carbon database is a product of upscaling and will most likely not cover the spatial variability reported in the studies.

6 Conclusion

This study investigates DOM optical properties in Low and High Arctic surface water environments and downstream patterns with regard to permafrost disturbance and rainfall events. We find that both Arctic locations exhibit a distinct signature of DOC concentration and a_{cDOM}350 linked to the differences in vegetation cover and SOCC content. Compared to the High Arctic, a_{cDOM}350 DOM in the Low Arctic is stronger highercoloured due to the greater abundance of plant material and higher lignin concentrations introduced into the aquatic system. SOCC is higher in the Low Arctic than in the High Arctic. This results in higher DOC and a_{cDOM}350 values in the Low Arctic (Herschel Island) than in the High Arctic (Cape Bounty).

In both regions, the strong terrestrial signature of DOM is apparent in the optical properties, which is typical for small headwater catchments. The relationship between a_{cDOM}350 and DOC is very strong across both regions and including data from the literature, proving the applicability of cDOM as a tracer for DOC throughout different aquatic Arctic environments (rivers, streams and lakes). It agrees very well with the a_{cDOM}350 to DOC relationship established for the great five Arctic rivers. However, examining DOM optical characteristics (SUVA, S275-295 and SR) for those large rivers and our sites, we find that smaller catchments in our study deliver fresh, less altereder DOM prone to degradation.

The optical characteristics of DOM prove also a useful tool for assessing downstream patterns in the streams studied. The downstream increase of S275-295 is indicative for photodegradation processes, which is apparent in most of the streams. Further, local sources of DOM such as degrading ice-wedge polygons are detected in the optical signature of DOM. Although the temporal resolution of data at Cape Bounty is limited, we found a similar response to rainfall events. Rainfall leading to runoff with a short residence time (rainfall of high magnitude and intensity, dry antecedent conditions in the catchment) leads to the export of fresh near-surface-derived DOM (higher SUVA, lower S275-295). In contrast, baseflow conditions and long residence times (including low magnitude rainfall events and a saturated catchment) favors the export of permafrost-derived DOM that has undergone microbial processing in the soil. Examining flow pathways and residence time will be crucial to assess the impacts of projected increasing summer rainfall across the Arctic. Optical properties of DOM will be a useful tool for assessing DOM ~~sources and~~ quality changes at a pan-Arctic scale.~~.~~

Data Availability

Data has been made available through PANGAEA:

Coch, Caroline; Juhls, Bennet; Lamoureux, Scott; Lafrenière, Melissa; Fritz, Michael; Heim, Birgit; Lantuit, Hugues (2019): Colored dissolved organic matter (cDOM) absorption measurements in terrestrial waters on Herschel Island (Low Arctic) and Melville Island (High Arctic) in 2016 and 2017. PANGAEA, https://doi.pangaea.de/10.1594/PANGAEA.897289

Author Contributions

C.C., H.L. and S.L. developed the study design. Field work was conducted by C.C. in 2016, and by C.C., S.L., M.L. in 2017. M.F. partly funded and supervised lab analyzes for cDOM measurements. B.J. processed the absorbance spectra and contributed to developing the manuscript. C.C. ran lab analyzes, processed and visualized the data with input from B.H., M.L., S.L. and H.L. and prepared the manuscript with editorial contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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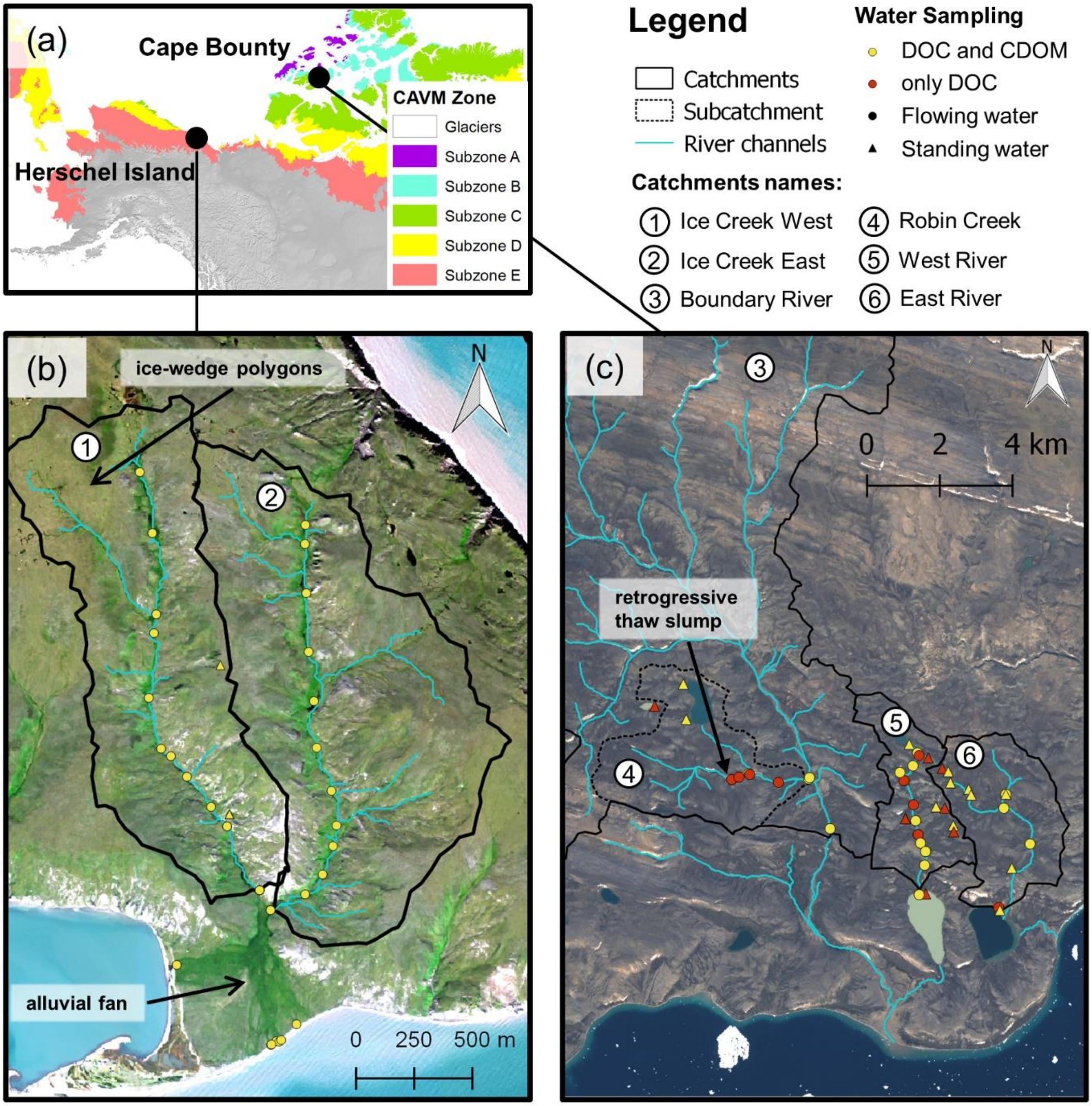
Figures


(a)
Cape Bounty
Herschel Island
CAVM Zone
Glaciers
Subzone A
Subzone B
Subzone C
Subzone D
Subzone E
Legend
Catchments
Subcatchment
River channels
Water Sampling
DOC and CDOM
only DOC
Flowing water
Standing water
Catchments names:
① Ice Creek West
② Ice Creek East
③ Boundary River
④ Robin Creek
⑤ West River
⑥ East River
(b)
ice-wedge polygons
N
alluvial fan
0 250 500 m
(c)
N
0 2 4 km
retrogressive
thaw slump

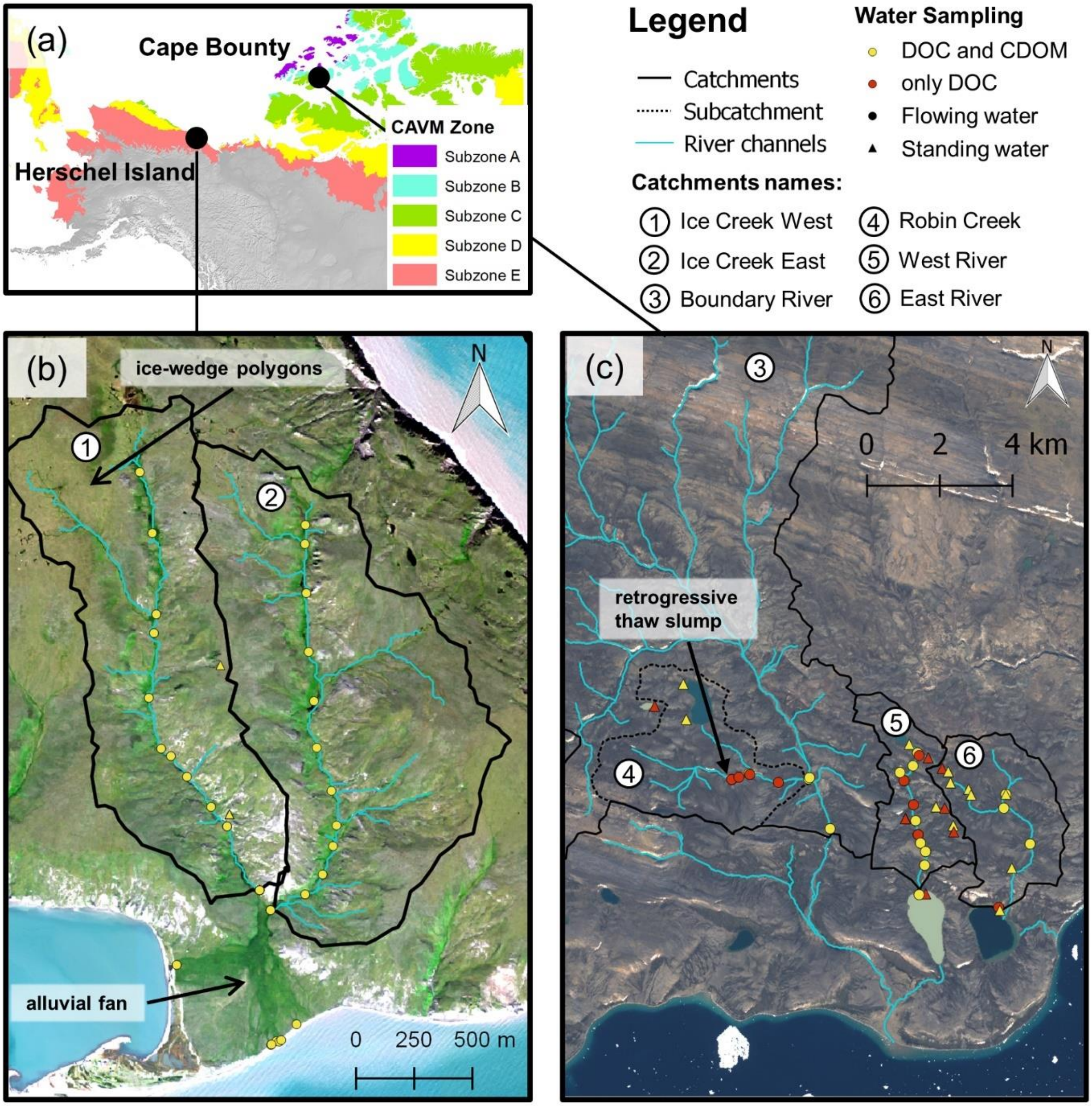
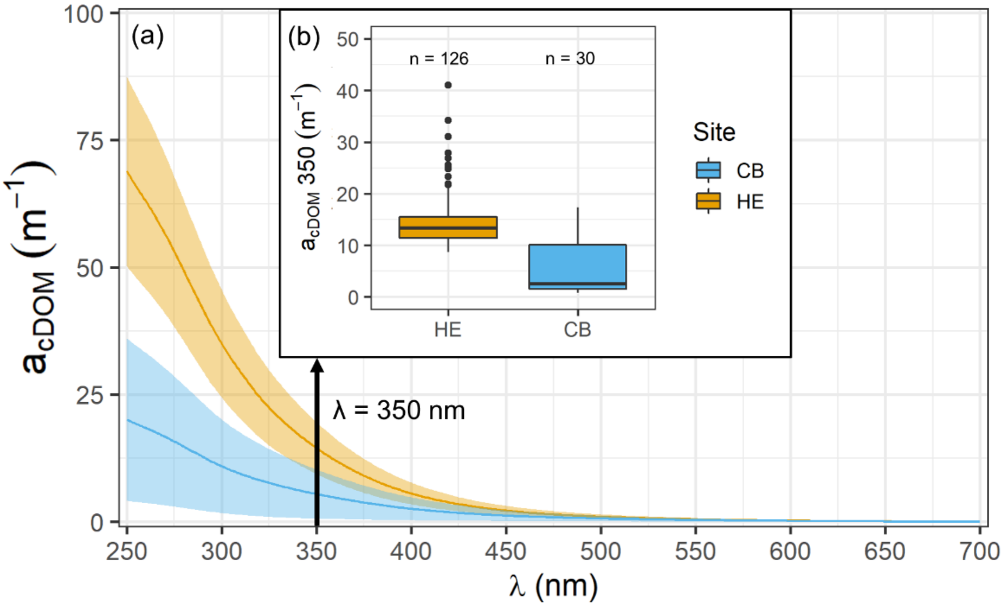


Figure 1. Maps of the study area showing (a) the location of Herschel Island and Cape Bounty in the Canadian Arctic including the Circumpolar Arctic Vegetation Map (CAVM) ~~CAVM~~ bioclimatic zones (Walker & Raymond 2016), (b) the studied catchments Ice Creek West and Ice Creek East on Herschel Island and (c) the studied catchments Boundary River with its subcatchment Robin Creek (dashed watershed), West River and East River. The watershed names are indicated with numbers, and the general flow direction is southwards towards the ocean. Note that samples from flowing water (rivers and streams) are indicated by circles, whereas samples from standing water (ponds and lakes) are indicated by triangles. Yellow colors mark locations where DOC concentration and c~~C~~DOM measurements are available, while only DOC concentrations are available at red locations. The background images are true color mosaics (Herschel Island: WorldView-3 quasi-true color RGB composite, acquired on 8 August 2015; Cape Bounty: Sentinel-2 quasi-true color RGB composite, acquired on 7 August 2016).

~~**Figure 1. Maps of the study area showing (a) the location of Herschel Island and Cape Bounty in the Canadian Arctic including the CAVM bioclimatic zones (Walker & Raymond 2016), (b) the studied catchments Ice Creek West and Ice Creek East on Herschel Island and (c) the studied catchments Boundary River with its subcatchment Robin Creek (dashed watershed), West River and East River. The watershed names are indicated with numbers. Note that samples from flowing water (rivers and streams) are indicated by circles, whereas samples from standing water (ponds and lakes) are indicated by triangles. Yellow colors mark locations where DOC and CDOM measurements are available, while only DOC values are available at red locations. The background images are true color mosaics (Herschel Island: WorldView-3 quasi-true color RGB composite, acquired on 8 August 2015; Cape Bounty: Sentinel-2 quasi-true color RGB composite, acquired on 7 August 2016).**~~



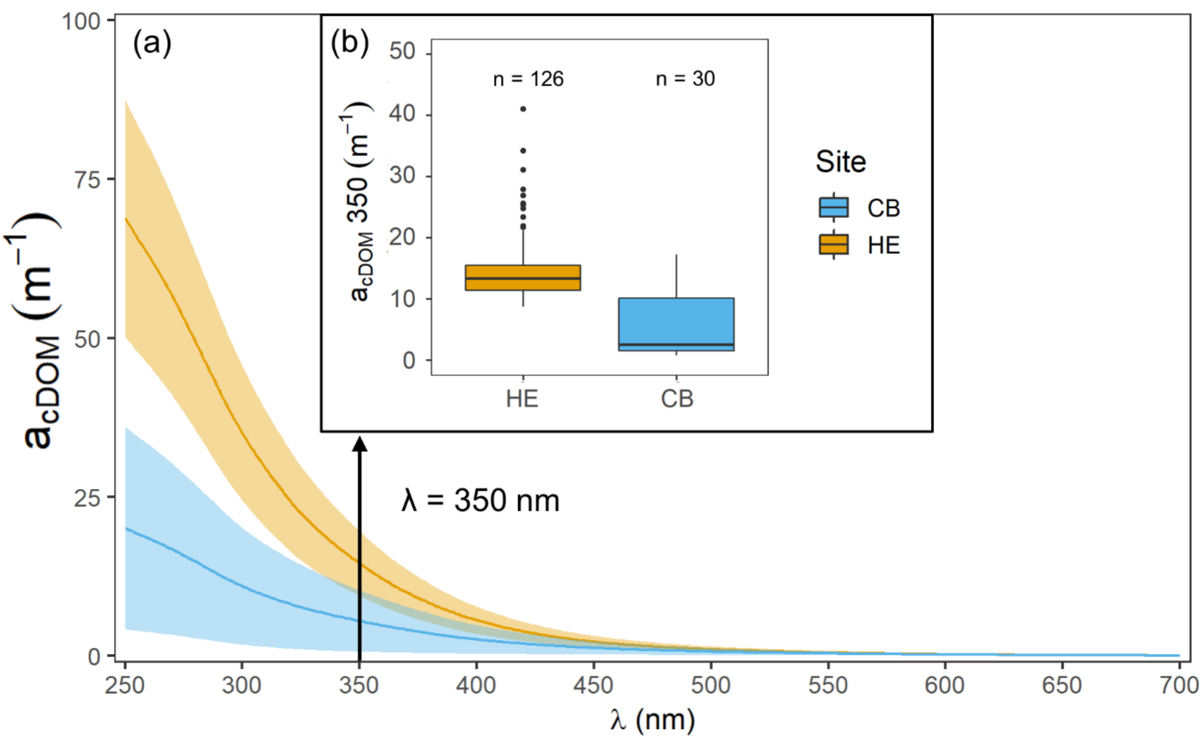
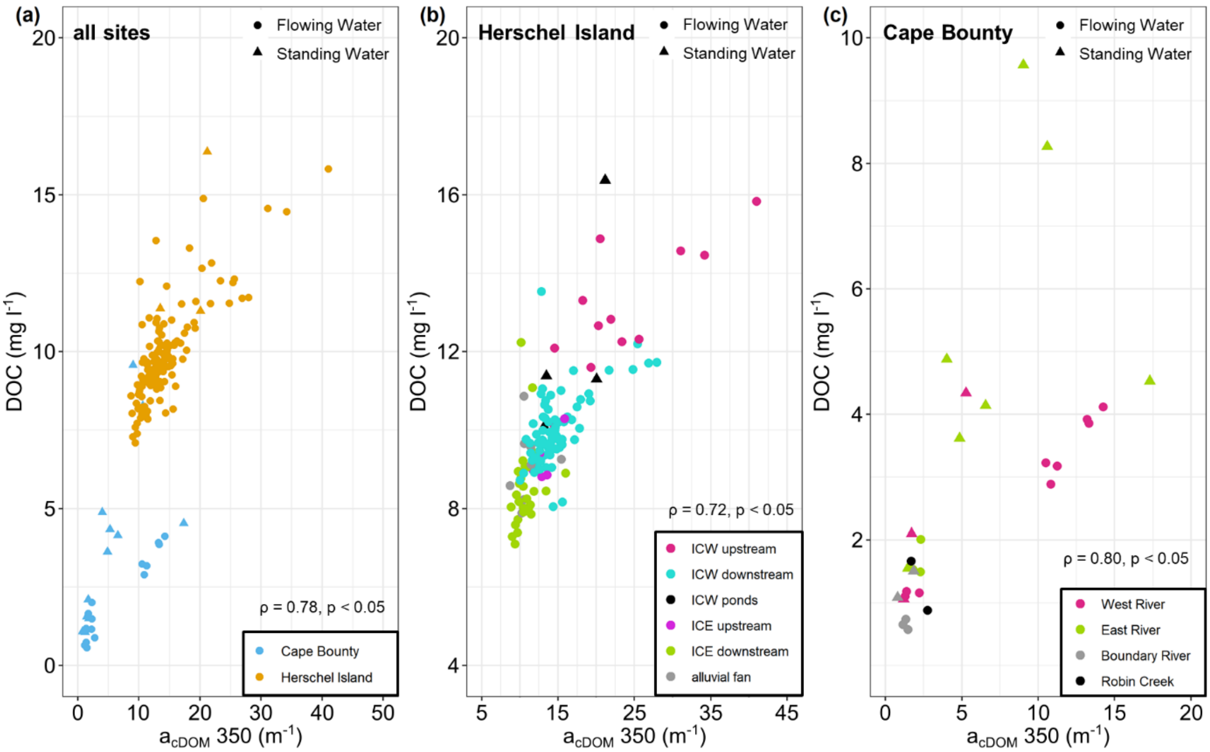


Figure 2. Dissolved organic matter (DOM) aAbsorption characteristics for the sites from Herschel Island (HE, in orange) and Cape Bounty (CB, in blue). (a) Average absorption (m^{-1}) for the wavelengths (λ) between 250 and 700 nm. The colored shaded areas represent the standard deviation from the mean (solid line). (b) boxplots of absorption at 350 nm for both sites.



(a)
all sites
Flowing Water
Standing Water
DOC (mg l-1)
ρ = 0.78, p < 0.05
Cape Bounty
Herschel Island
acDOM 350 (m-1)
(b)
Herschel Island
Flowing Water
Standing Water
DOC (mg l-1)
ρ = 0.72, p < 0.05
ICW upstream
ICW downstream
ICW ponds
ICE upstream
ICE downstream
alluvial fan
acDOM 350 (m-1)
(c)
Cape Bounty
Flowing Water
Standing Water
DOC (mg l-1)
ρ = 0.80, p < 0.05
West River
East River
Boundary River
Robin Creek
acDOM 350 (m-1)

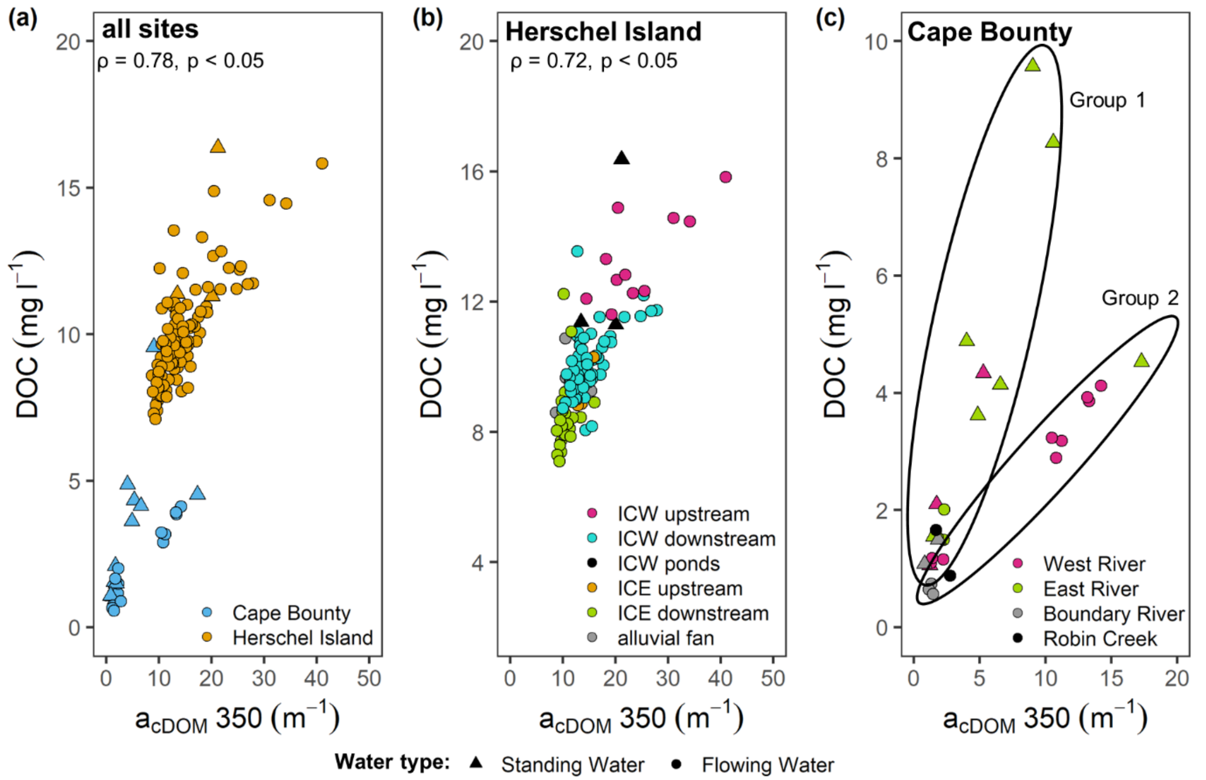
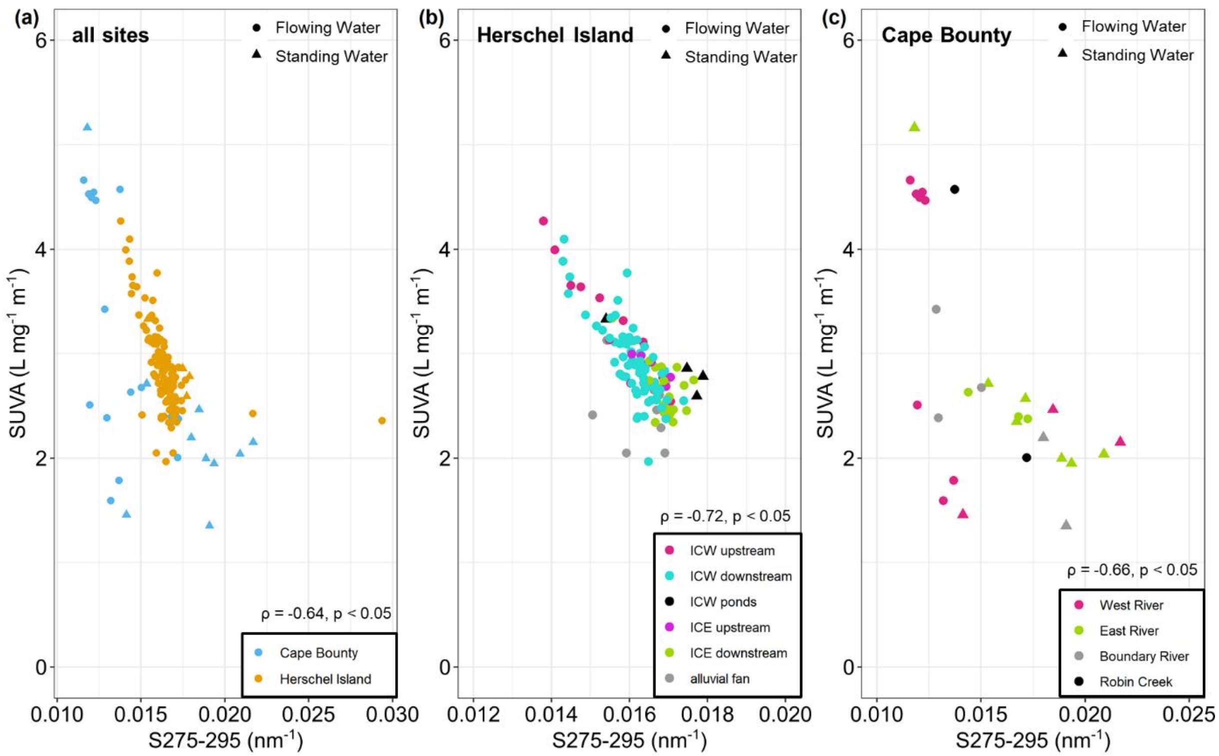


Figure 3. Absorption of colored dissolved organic matter (cDOM) at 350 nm (m^{-1}) versus dissolved organic carbon (DOC) concentration (mg l^{-1}) for (a) all sites, (b) sites on Herschel Island depicting the sampling locations Ice Creek West (ICW) upstream, downstream and ponds, Ice Creek East (ICE) upstream and downstream and alluvial fan, and (c) sites at Cape Bounty (West River, East River, Boundary River, Robin Creek). Note that flowing water is indicated by a circle while standing water such as lakes or ponds is indicated by a triangle. The cDOM to DOC relationships are divided in two different groups (c).

~~**Figure 3. Absorption of cDOM at 350 nm (m^{-1}) versus DOC concentration (mg l^{-1}) for (a) all sites, (b) sites on Herschel Island and (c) sites at Cape Bounty. Note that flowing water is indicated by a circle while standing water such as lakes or ponds is indicated by a triangle.**~~



(a)
all sites
Flowing Water
Standing Water
SUVA (L mg-1 m-1)
ρ = -0.64, p < 0.05
Cape Bounty
Herschel Island
S275-295 (nm-1)
(b)
Herschel Island
Flowing Water
Standing Water
SUVA (L mg-1 m-1)
ρ = -0.72, p < 0.05
ICW upstream
ICW downstream
ICW ponds
ICE upstream
ICE downstream
alluvial fan
S275-295 (nm-1)
(c)
Cape Bounty
Flowing Water
Standing Water
SUVA (L mg-1 m-1)
ρ = -0.66, p < 0.05
West River
East River
Boundary River
Robin Creek
S275-295 (nm-1)

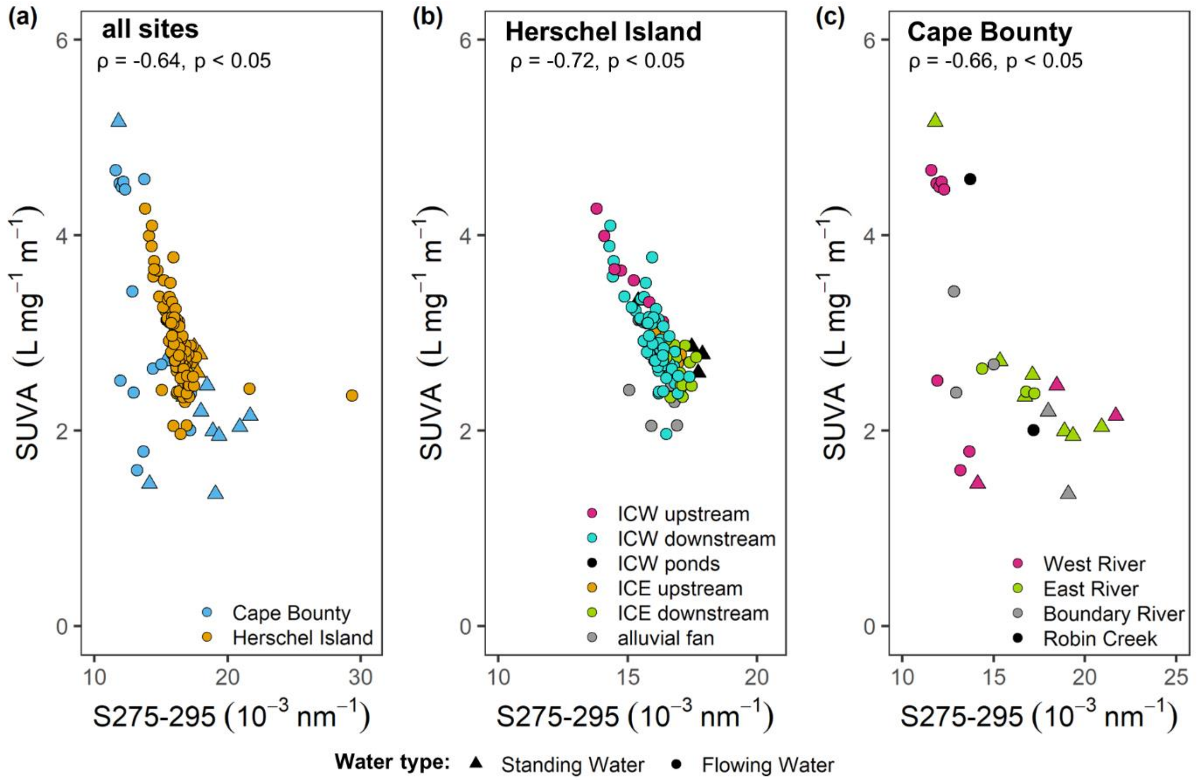
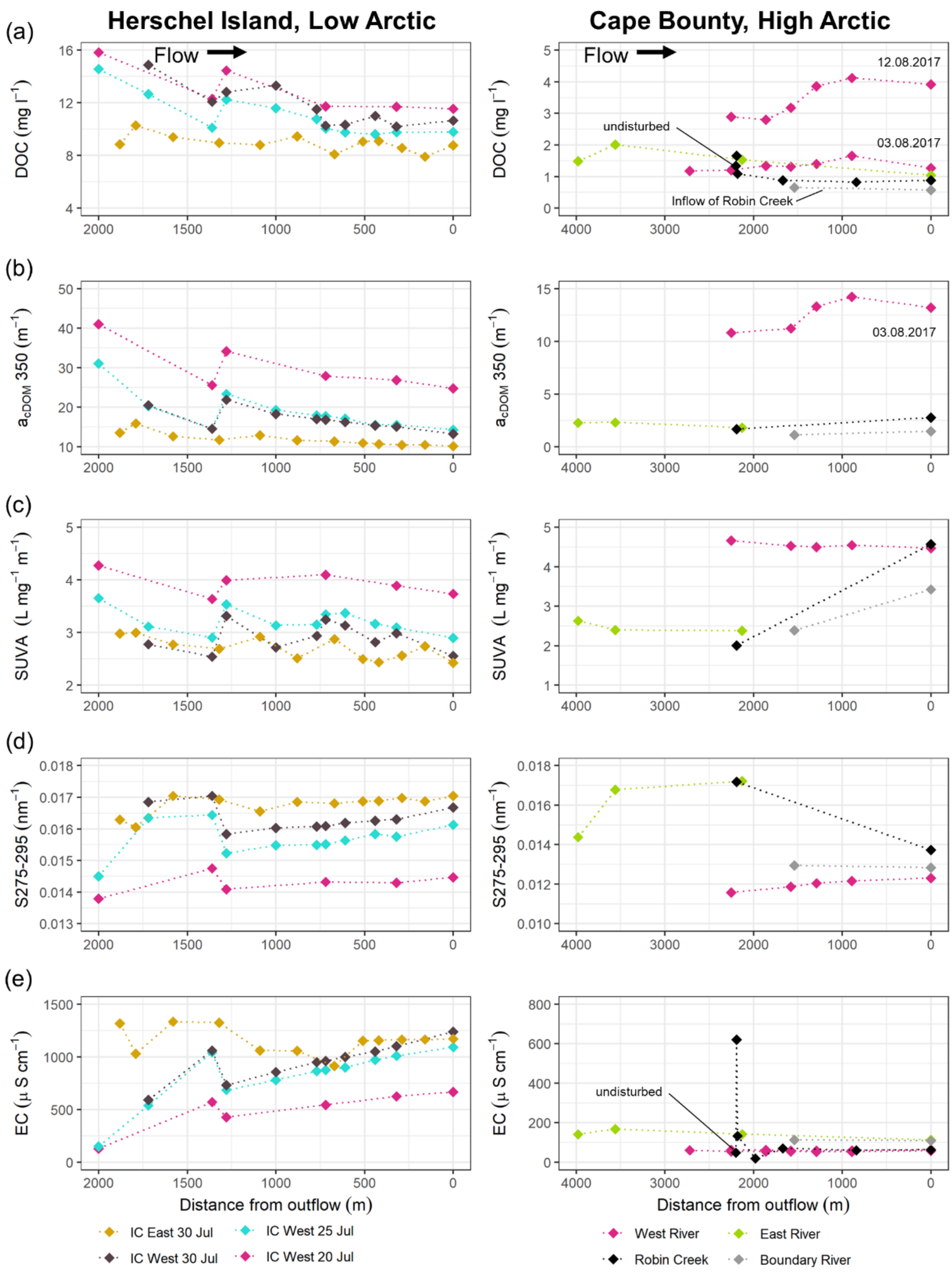


Figure 4. Slope of colored dissolved organic matter ultraviolet cDOM UV absorption 275-295 (10^{-3} nm^{-1}) versus specific ultraviolet absorbance SUVA (L mg^{-1} m^{-1}) for (a) all sites, (b) sites on Herschel Island depicting the sampling locations Ice Creek West (ICW) upstream, downstream and ponds, Ice Creek East (ICE) upstream and downstream and alluvial fan, and (c) sites at Cape Bounty (West River, East River, Boundary River, Robin Creek). Note that flowing water is indicated by a dot while standing water such as lakes or ponds is indicated by a triangle.

~~**Figure 4. Slope of cDOM UV absorption 275-295 (nm^{-1}) versus SUVA (L mg^{-1} m^{-1}) for (a) all sites, (b) sites on Herschel Island and (c) sites at Cape Bounty. Note that flowing water is indicated by a dot while standing water such as lakes or ponds is indicated by a triangle.**~~



Herschel Island, Low Arctic
Cape Bounty, High Arctic
(a)
(b)
(c)
(d)
(e)
Flow
DOC (mg l⁻¹)
12.08.2017
03.08.2017
undisturbed
Inflow of Robin Creek
a_CDOM 350 (m⁻¹)
SUVA (L mg⁻¹ m⁻¹)
S275-295 (nm⁻¹)
EC (μ S cm⁻¹)
Distance from outflow (m)
IC East 30 Jul
IC West 25 Jul
IC West 30 Jul
IC West 20 Jul
West River
East River
Robin Creek
Boundary River

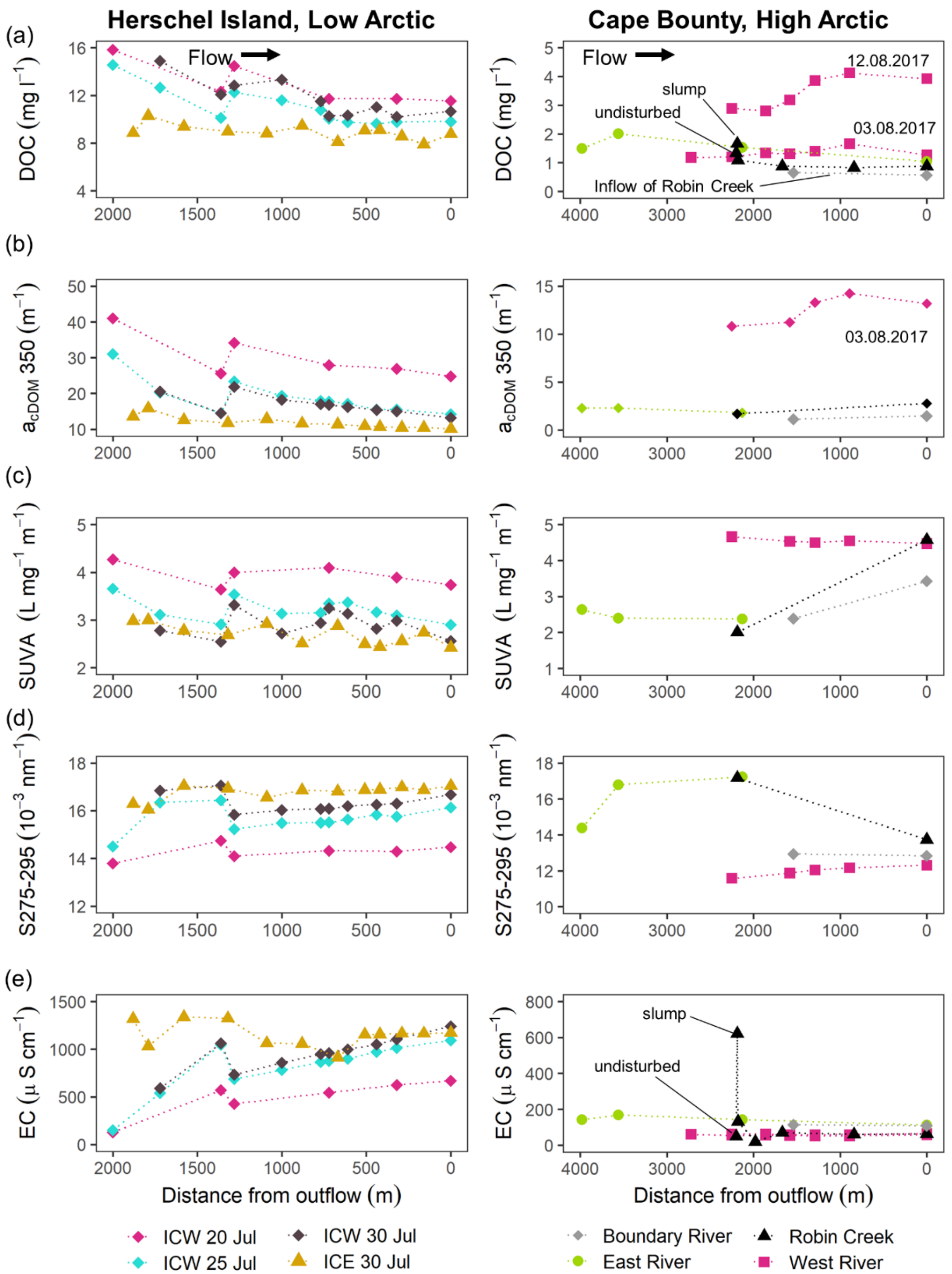
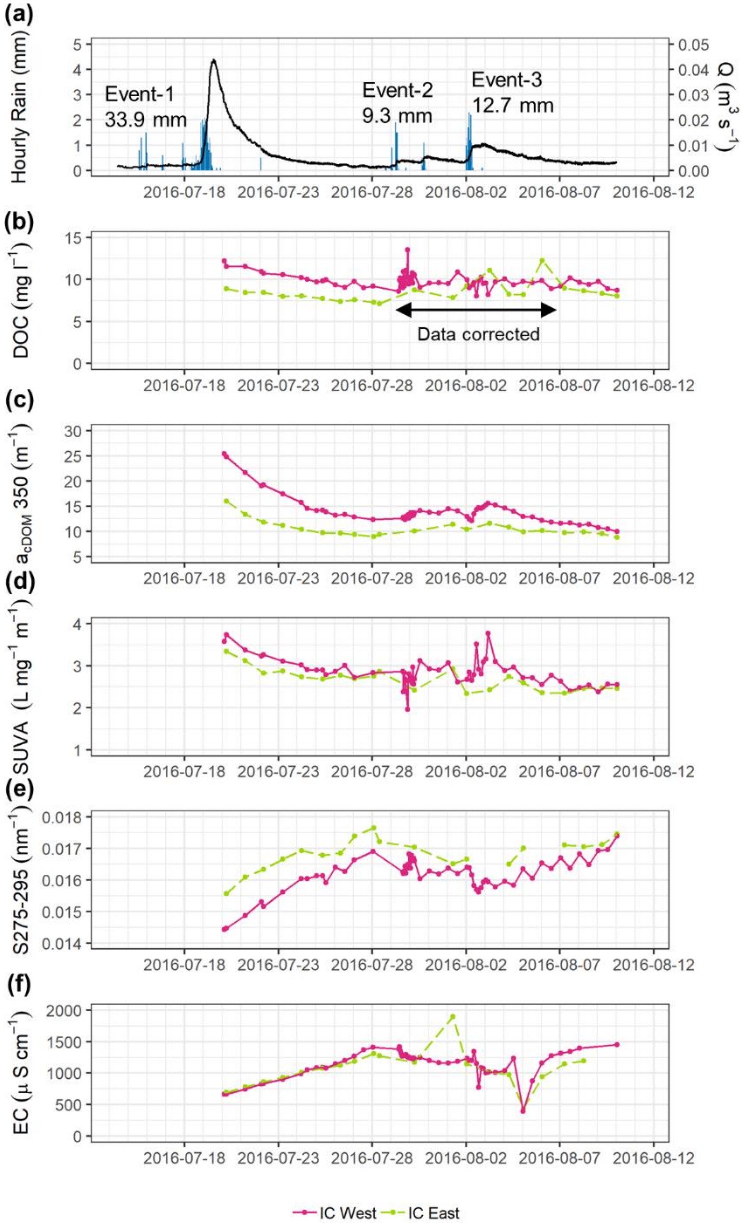


Figure 5. River transects showing values of (a) dissolved organic carbon (DOC) concentration (mg l^{-1}), (b) absorption of colored dissolved organic matter (cDOM) at 350 nm, $a_{cDOM}350$ (m^{-1}), (c) specific ultraviolet absorbance SUVA (L mg^{-1} m^{-1}), (d) cDOM Slope S275-295 (10^{-3} nm^{-1}), (e) electrical conductivity (EC) for rivers on Herschel Island (left) and Cape Bounty (right). Note that Ice Creek West (ICW) and Ice Creek East (ICE) on Herschel Island were sampled at different dates as indicated in the legend. ~~Figure 5. River transects showing values of (a) DOC (mg l^{-1}), (b) $a_{cDOM}350$, (c) SUVA (L mg^{-1} m^{-1}), (d) cDOM Slope S275-295 (nm^{-1}), (e) electrical~~

~~**conductivity for rivers on Herschel Island (left) and Cape Bounty (right). Note that IC West on Herschel Island was sampled at different dates as indicated in the legend.**~~


(a)
Hourly Rain (mm)
Q (m^3 s^-1)
Event-1
33.9 mm
Event-2
9.3 mm
Event-3
12.7 mm
(b)
DOC (mg l^-1)
Data corrected
(c)
a_cDOM 350 (m^-1)
(d)
SUVA (L mg^-1 m^-1)
(e)
S275-295 (nm^-1)
(f)
EC (μ S cm^-1)
2016-07-18
2016-07-23
2016-07-28
2016-08-02
2016-08-07
2016-08-12
IC West
IC East

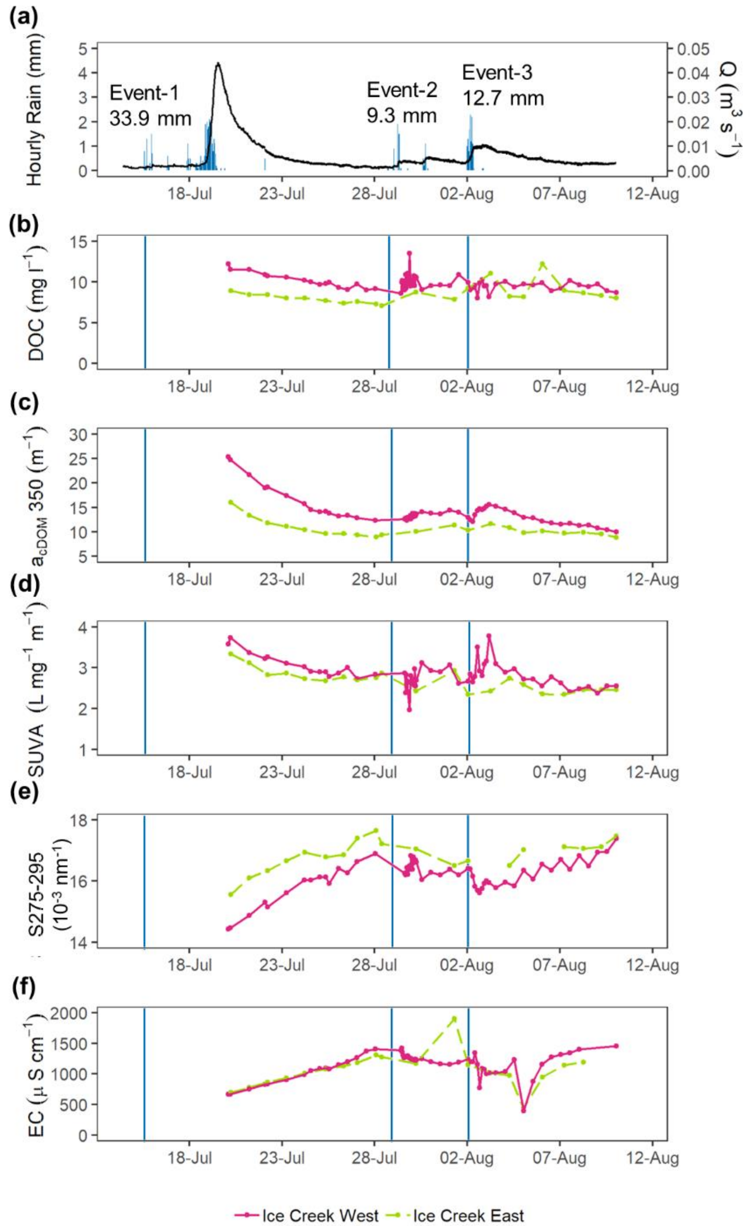


Figure 6. Time series from Herschel Island in 2016 showing (a) Discharge ($m^3\ s^{-1}$) and hourly rainfall (mm) from Ice Creek West, (b) dissolved organic carbon (DOC) concentration ($mg\ l^{-1}$), (c) colored dissolved organic matter absorption at 350 nm, $a_{cDOM}350$ (m^{-1}), (d) specific ultraviolet absorbance SUVA ($L\ mg^{-1}\ m^{-1}$) and (e) the cDOM slope S275-295 ($10^{-3}\ nm^{-1}$) over the summer season 2016 for Ice Creek West (magenta) and Ice Creek East (green) respectively. The onset of rainfall events is marked with vertical blue lines. As described in the methods, DOC concentrations were corrected between 30 July and 7 August.

~~**Figure 6. Time series from Herschel Island showing (a) Discharge ($m^3\ s^{-1}$) and hourly rainfall (mm) from Ice Creek West, (b) DOC concentration ($mg\ l^{-1}$), (c) $a_{cDOM}350$ (m^{-1}), (d) SUVA ($L\ mg^{-1}\ m^{-1}$) and (e) the S275-295 (nm^{-1}) over the summer season 2016 for Ice Creek West (magenta) and Ice Creek East (green) respectively. The label "data corrected" indicates the time period during which samples were frozen on site instead of being acidified immediately in the field.**~~

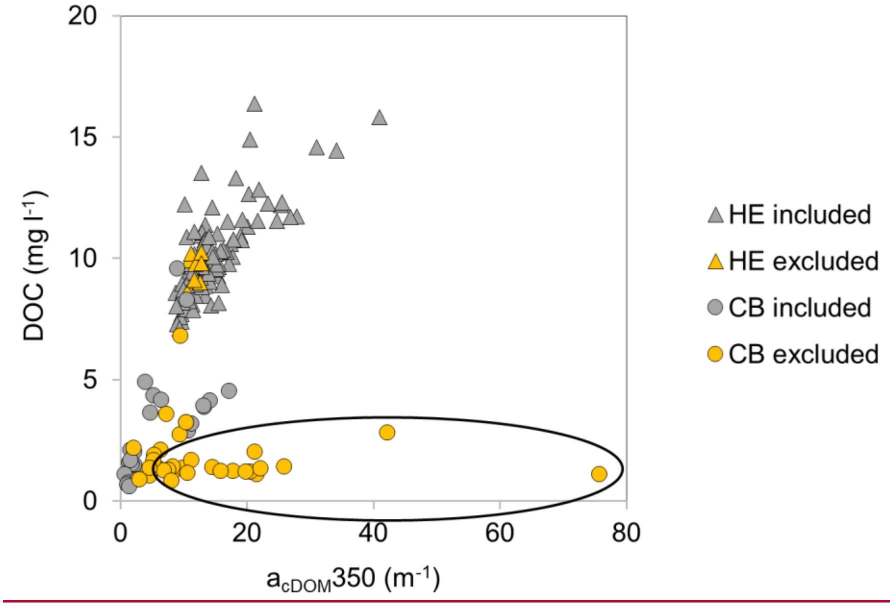
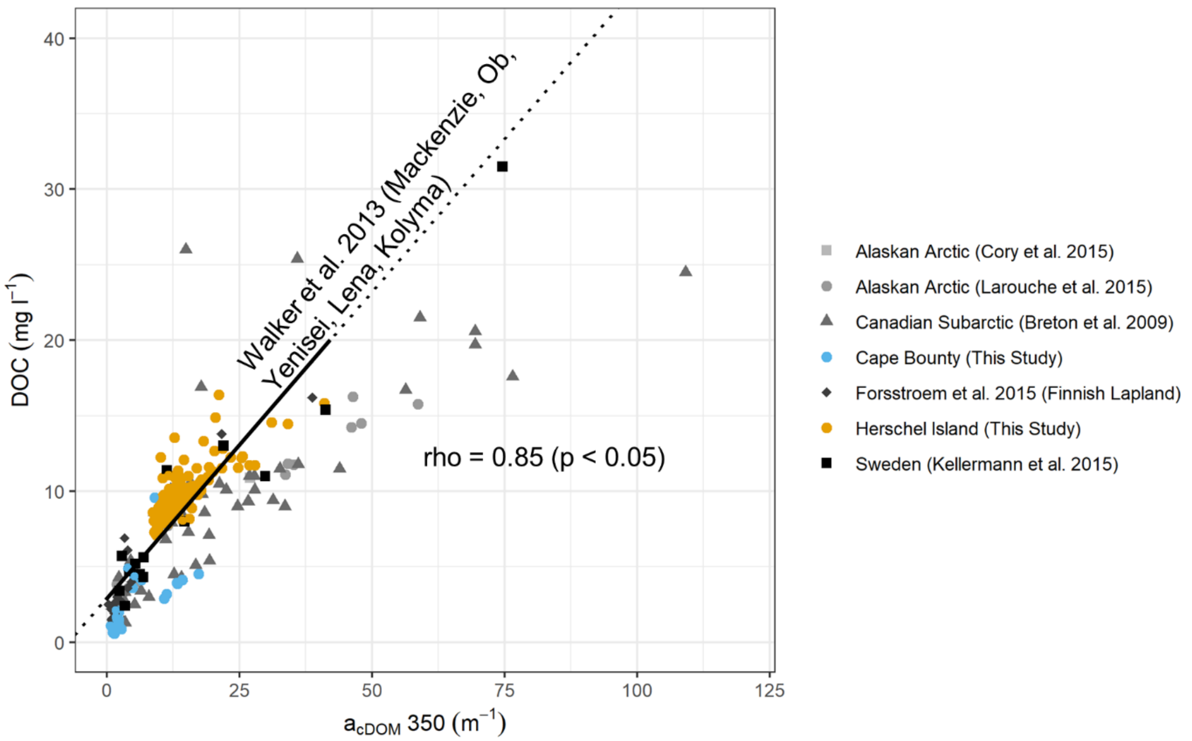


Figure 7. Relationship between colored dissolved organic matter absorption $a_{cDOM}350$ (m^{-1}) and dissolved organic matter concentration DOC (mg l^{-1}) at Herschel Island (HE) displayed as triangle and Cape Bounty (CB) shown as circle. Samples marked in orange were excluded from the study due to flocculation after filtration (section 3.1). The samples circled in black show to high absorption values in relation to the DOC concentration.



~~**Figure 7. Relationship between a_{cDOM}350 (m^{-1}) and DOC concentration ($mg\ l^{-1}$) for our study sites (Herschel Island in orange and Cape Bounty in blue) and sites retrieved from the literature. The black lines represent the regression line established for the large Arctic rivers by Walker et al. (2013). The solid section marks the validity ranges for the relationship established, whereas the dotted line is the linear continuation.**~~

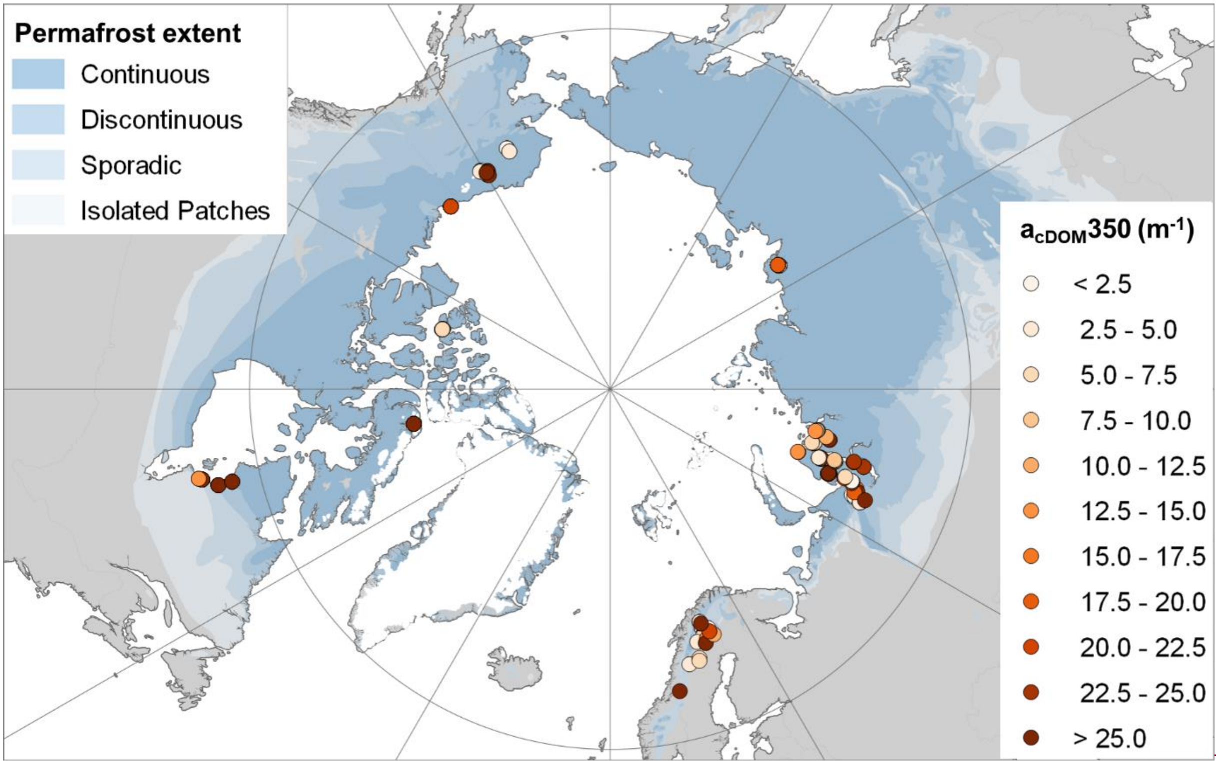


Figure 8. Values for $a_{cDOM}350$ across the Arctic region from this study and retrieved from the literature. The blue colour shows the permafrost extent (from continuous to isolated) and the color code of the points shows $a_{cDOM}350$ between < 2.5 m^{-1} and > 25 m^{-1}.

Tables

Table 1. Characteristics of studied watersheds on Herschel Island (Low Arctic) and Cape Bounty (High Arctic) showing catchment size (km^2), channel length (km), circumarctic vegetation map (CAVM) bioclimatic zone (CAVM, 2003), soil organic carbon content (SOCC) (Hugelius et al., 2013; Ramage et al., 2019) and maximum catchment elevation above sea level (m).

Site	Catchment size (km^2)	Channel length (km)	Vegetation zone (CAVM)	Soil Organic Carbon content 0-30cm/0-100cm (kg m^2)	Maximum catchment elevation (m above sea level)
Herschel Island, Low Arctic					
Ice Creek West	1.4	2.2	Subzone D	11.4 / 26.4	88
Ice Creek East	1.6	1.9	Subzone D		95
Cape Bounty, High Arctic					
Boundary River	152.5	22.7	Subzone B/C	3.0 / 10.2	213
Robin Creek	14.8	5.1	Subzone B/C		151
West River	8.8	4.2	Subzone B/C		94
East River	12.4	5.2	Subzone B/C		103

Table 2. Descriptive statistics (mean ± standard deviation) of dissolved organic carbon, DOC (mg l^{-1}), specific ultraviolet absorbance, SUVA (L mg^{-1} m^{-1}), colored dissolved organic matter absorption at 350 nm, $a_{cDOM}350$ (m^{-1}), cDOM Slope S275-295 (10^{-3} nm^{-1}), slope ratio SR, electrical conductivity EC (µS cm^{-1}), pH and the number (n) of all samples/samples with cDOM absorption measurements. The statistics are given for specific rivers, samples from flowing waters, standing waters and all samples on Herschel Island (HE) and Cape Bounty (CB) respectively. The symbols ">" and "<" indicate significant inter-group differences at the alpha = 0.95 level. When the inter-group differences are significantly different at the alpha = 0.99 level, then they are underlined. When the difference is not significant, "≈" is used.

Site	EC µS cm^{-1}	pH	DOC mg l^{-1}	SUVA L mg^{-1} m^{-1}	$a_{cDOM}350$ m^{-1}	Slope 275-295 10^{-3} nm^{-1}	SR	n
Herschel Island, Low Arctic								
Ice Creek West	1050 ± 310	8.2 ± 0.2	10.4 ± 1.5	3.0 ± 0.4	16.1 ± 5.4	16.0 ± 0.7~~0.016 ± 0.001~~	0.83 ± 0.02	90/82
Ice Creek East	1030 ± 340	8.2 ± 0.2	8.7 ± 1.1	2.7 ± 0.2	11.1 ± 1.8	17.3 ± 2.4~~0.017 ± 0.002~~	0.90 ± 0.12	32/32
Alluvial fan	970 ± 170	7.8 ± 0.2	9.2 ± 0.9	2.5 ± 0.4	11.1 ± 1.9	16.3 ± 0.7~~0.016 ± 0.001~~	0.84 ± 0.02	8/8
Flowing Water (all)	1040 ± 310	8.2 ± 0.2	9.9 ± 1.5	2.9 ± 0.4	14.5 ± 5.1	16.4 ± 1.5~~0.016 ± 0.001~~	0.85 ± 0.07	130/122
Standing Water (all)	1440 ± 1300	8.3 ± 0.1	12.3 ± 2.8	2.9 ± 0.3	17.0 ± 4.2	17.1 ± 1.2~~0.017 ± 0.001~~	0.93 ± 0.06	4/4
All samples	1050 ± 370	8.2 ± 0.2	10.0 ± 1.6	2.9 ± 0.4	14.5 ± 5.1	16.4 ± 1.5~~0.016 ± 0.001~~	0.85 ± 0.07	134/126
Standing (S) vs. Flowing (F)	S ≈ F	S ≈ F	S > F	S ≈ F	S ≈ F	S ≈ F~~S ≈ F~~	S > F	n.a.
Cape Bounty, High Arctic								
Boundary River	110 ± 3	7.1 ± 0.0	0.7 ± 0.1	2.8 ± 0.5	1.3 ± 0.2	13.1 ± 1.4~~0.014 ± 0.001~~	1.13 ± 0.06	3/3
Robin Creek	145 ± 213	7.3 ±0.6	1.1 ± 0.3	3.3 ± 1.8	2.2 ± 0.8	15.1 ± 2.3~~0.015 ± 0.002~~	1.03 ± 0.12	7/2
West River	60 ± 17	6.9 ± 0.3	2.5 ± 1.7	3.6 ± 1.4	8.5 ± 5.2	11.9 ± 0.8~~0.012 ± 0.001~~	0.86 ± 0.10	19/8
East River	141 ± 22	7.3 ± 0.1	1.5 ± 0.4	2.5 ± 0.1	2.1 ± 0.3	16.1 ± 1.6~~0.016 ± 0.002~~	0.95 ± 0.06	4/3
Flowing Water (all)	92 ± 101	7.0 ± 0.4	1.9 ± 1.5	3.2 ± 1.2	5.5 ± 5.1	13.1 ± 2.0~~0.013 ± 0.002~~	0.94 ± 0.13	33/16
Standing Water (all)	210 ± 160	7.5 ± 0.6	3.4 ± 2.4	2.4 ± 1.0	5.4 ± 4.9	17.4 ± 2.9~~0.018 ± 0.003~~	1.14 ± 0.20	20/12
All samples	137 ± 136	7.2 ± 0.5	2.5 ± 2.0	2.8 ± 1.1	5.5 ± 4.9	14.8 ± 3.2~~0.015 ± 0.003~~	1.02 ± 0.19	53/28
Standing (S) vs. Flowing (F)	S > F	S > F	S > F	S < F	S ≈ F	S > F	S > F	n.a.
He_all vs. CB_all	HE > CB	HE > CB	HE > CB	HE > CB	HE > CB	~~HE > CB~~n.a.	HE > CB	n.a.

Table 3. Correlation matrix using the Spearman's rho correlation coefficient between latitude, dissolved organic carbon concentration (DOC), colored dissolved organic carbon absorption at 350 nm ($a_{CDOM}350$), soil organic carbon content (SOCC) in 0-30 cm and 0-100 cm depth (Hugelius et al. 2014). Significance levels of $p < 0.05$ and $p \leq 0.01$ are indicated.

	Latitude	$a_{CDOM}350$	DOC	SOCC 0-30cm	SOCC 0-100cm
Latitude	1.00	**-0.22**	**-0.13**	**-0.19**	**-0.26**
$a_{CDOM}350$		1.00	**0.85**	**0.26**	**0.34**
DOC			1.00	**0.53**	**0.51**
SOCC 30cm				1.00	**0.71**
SOCC 100cm					1.00