Response to reviewer#1

We are very grateful for the reviewer's critical comments, which have helped us improve the paper quality substantially. We have addressed all of the comments carefully as detailed below in our point-by-point responses. Our responses start with "R:".

General comments

This paper aims at studying the optical characteristics and sources of CDOM in the seasonal snow. The paper is generally well written. Please find below my general comments.

R: Thanks for the reviewer's comments, we have addressed all of the comments carefully as detailed below.

1. A large proportion of the introduction is devoted to present various usages of spectrometry indices. Rather, authors should use this space to better present the problems they are trying to address.

R: We have totally rewritten the introduction. The discussions about the CDOM in aquatic environments and the usages of spectrometry indices have been weakened, and replaced by the scientific progress on the characteristics of DOM and CDOM in the cryosphere.

2. In the methods section, authors said they frozen water samples before optic measurements. Freezing DOM samples are problematic because of sedimentation/precipitation processes that are further causing scattering (Thieme et al. (2016); Fellman, D'Amore, and Hood (2008)). Authors need to carefully address this issue. To cite Fellman, D'Amore, and Hood (2008):

> We further show that when surface water samples were frozen, there was a decrease in the specific ultraviolet absorbance (SUVA) of DOC that is particularly evident

with high concentrations of DOC.

R: We have added the discussion of the uncertainties due to the freeze-thaw process into the method section (lines 5-22, page 8). We agreed with the reviewer that the freeze-thaw process may lead to biases of the optical properties for the DOM samples. According to the previous studies, Fellman et al. (2008) reported that there was a decrease of specific ultraviolet absorbance (SUVA) for stream water DOM after frozen, with a median of approximately 8%. A study of peatland DOC found that the change of light absorption at 254 nm after freeze and thaw was less than 5% in median (Peacock et al., 2015). Thieme et al. (2016) assessed the changes of fluorescence properties for several types of DOM samples. The results showed the decreased relative percentages of terrestrial humic-like fluorophores (-3% on average) and HIX (-2% on average), and the increased percentage of fluvic-like fluorophore (+6% on average). However, various types of DOM in previous studies were shown that their optical properties (light absorption and fluorescence) were not affected significantly by frozen effect, such as ocean water, pore water, spring and cave water (Birdwell and Engel, 2010; Del Castillo and Coble, 2000; Otero et al., 2007; Yamashita et al., 2010). As discussed above, the freeze-thaw process may influence the relative contributions of PARAFAC components slightly, and the effects on a_{280} and the fluorescence indices can be neglected. It seems that the impact of freezing to optical properties of DOM samples varies largely with the sample types, preservation methods, DOC concentrations and optical parameters. There is limited study focuses on the preservation effects on snow DOM, which is frozen in the nature. Therefore, it is urgent to fill in this gap to minimize the artifacts of freezing in future studies.

3. Many figures in the manuscript are used to present the relationships among the calculated optical indices. These do not contribute to increasing our knowledge about DOM in the snowpack. Actually, there are many studies that compared optical indices. Hence, these figures are not interesting in the context of the current study. Authors should carefully review the objectives of the paper and use appropriate figures.

R: We have replotted nearly all of the figures except Fig. 8 and Fig. 13. We have also rewritten the introduction, and restructured the results and discussion section. The discussions about the sources of CDOM have been moved to Sec. 3.3 in the revised manuscript. We hope that these modifications can improve the quality of our manuscript significantly.

4. In relation with my previous comment, I found the ratio between the length of the paper and new knowledge to be rather high. I believe that the results/discussion section could be shortened by at least 50%.

R: We have shortened the results and discussion section.

Specific comments

Introduction

5. Page 4, line 4: Helms et al. (2008) did not show that. It was already known in the 1960's. This is the same for the next citation.

R: We have removed the citation and rewritten lines 3-6 in page 3, as follows: "Chromophoric dissolved organic matter (CDOM), widely known as the light-absorbing constituent of DOM, can absorb light from ultraviolet to visible (UV-vis) wavelengths (Bricaud et al., 1981)."

6. Page 5, line 16: Do not start a paragraph with however.

R: We have rewritten the introduction and modified the grammar mistake.

7. Page 6, lines 10-14: Please review the sentences (2 times however). I do not understand the sentence at line 10. I thought you were talking about CDOM in the snow, not in the atmosphere or in water bodies.

R: (1) We have rewritten the introduction, and the improper expression have been removed.

(2) Sorry for the misleading, we indicated that the CDOM had been widely studied

in aerosol and water bodies, but rarely investigated in seasonal snow. The corresponding description has been changed in lines 10-12, page 4, as follows:

"However, these studies neglected CDOM, which is rarely studied in snow but has been proved as an effective light absorber whether in the atmosphere (i.e., brown carbon, BrC) (Hecobian et al., 2010) or water bodies (Bricaud et al., 1981)."

8. Page 6, line 20: Why 280 nm? This is rather unusual in the literature. Most people use either 275 nm or 254 nm.

R: We agreed with the reviewer, and the sentence has been modified in line 20, page 5 to line 1, page 6, as follows:

"The absorption coefficient at a certain wavelength within the UV band, for instance, 254 nm, 280 nm or 350 nm (Spencer et al., 2012; Zhang et al., 2010, 2011), usually serve as an indicator of CDOM abundance.".

9. Page 6, lines 17: This paragraph on the use UV-vis spectroscopy could be shortened.

R: The description of the UV-vis and fluorescence spectroscopy has been combined together and shortened greatly. Please see line 19, page 5 to line 17, page 6 in the revised manuscript.

10. Page 7, lines 9-14: These advantages are also valid for absorption measurements.

R: The advantages of fluorescence and absorption measurements has been rewritten in lines 19-20, page 5, as follows:

"UV-vis absorption and fluorescence spectroscopies are both rapid and effective methods of characterizing the optical properties and sources of CDOM."

11. Page 7, lines 15-16: Authors should be a clear distinction between CDOM and FDOM (EEMs). FDOM is a sub-fraction of the CDOM.

R: The "CDOM" has been replaced by "fluorescent DOM (FDOM)" in line 8, page 6.

Methods and materials

12. Page 9, lines 10-13: Freezing DOM samples is problematic. See my general comments. Also, at line 15, it is said that samples were analyzed within 24h. It is not clear how samples were processed.

R: (1) Please see our response to comment 2.

(2) The procedure of snow samples has been described in more detail in lines 2-7, page 9, as follows:

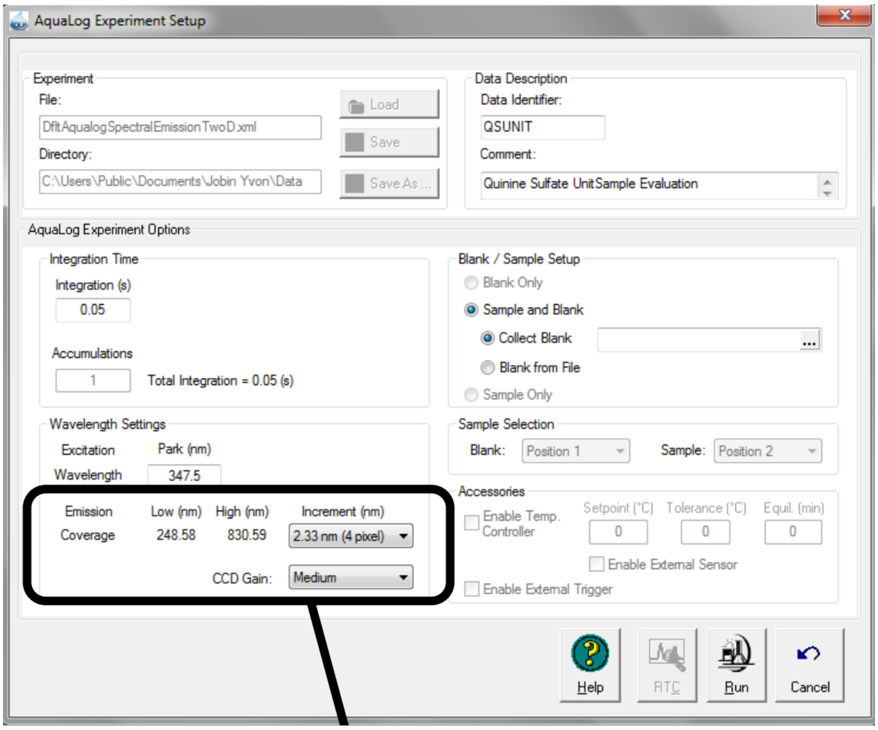
"The snow samples were firstly melted under the room temperature. Then, the snow water samples were filtrated using 0.22 μm PTFE syringe filters (Jinteng, Tianjin, China), and stored in prebaked glass vials (450 ℃ for 4 h) at 4 ℃ in a freezer. All the samples were measured for UV-Vis and fluorescence spectroscopies within 24 hours after filtration. The ultrapure water (18.2 MΩ·cm) filtrated by the PTFE syringe filters exhibited no clear fluorescence signal."

13. Page 9, line 19: ~~determined~~ measured

R: Changed as suggested in line 8, page 9.

14. Page 9, line 21:8 What are the 8 pixels? I never heard about that term.

R: In the software of Aqualog spectrofluorometer, the increment of emission wavelength was measured in pixels with a conversion to nm, as shown in the black box of the following picture. To minimize the readout noise of the CCD detector, we use the maximum increment (8 pixels, 4.65 nm) in the experiment.



15. Page 10: Equations are not written correctly. For example, I_{370}^{450} is the integrated fluorescence between these two wavelengths. Please use the appropriate notation.

R: We have changed the notations in the Eq. (1-3) as follows:

FI = I (Ex = 370, Em = 450) / I (Ex = 370, Em = 499);

BIX = I (Ex = 310, Em = 379) / I (Ex = 310, Em = 430);

HIX = I (Ex = 255, Em = 434-480) / I (Ex = 255, Em = 300-345);

16. Page 11, lines 16-21: How the exponential fit was performed? Was a background coefficient K used? If so it is problematic to fit a non-exponential function of such narrow spectral range with a background coefficient.

R: The equation used in this study has been presented as Eq. (5): $a(\lambda)= a(\lambda_r)e^{-S(\lambda-\lambda_r)}$, given by Twardowski et al. (2004). The background coefficient K was not used to perform the exponential fit. This equation and its corresponding description have been added in line 21, page 11 to line 2, page 12.

17. Page 12, equation 5: More details should be given about this metric since it is not widely used by the community.

R: More details have been added in lines 6-9, page 12, as follows:

"The absorption Ångström exponent (AAE) is used to describe the wavelength dependence of light absorption for aerosol (Bond, 2001), which was also applied to characterize the ILAPs and CDOM in snow and ice (Doherty et al., 2010; Niu et al., 2018; Wang et al., 2013; Yan et al., 2016)."

18. Page 13, lines 3-8: It is not clear how the clustering was performed. What are the multiple correlation coefficients?

R: Sorry for the misleading. The "multiple correlation coefficients" in the text does not represent a term, we indicated the various cophenetic correlation coefficients for different clustering methods (e.g., weighted average method, centroid method, and so on). The cophenetic correlation coefficient is a criterion of the efficiency of clustering methods (Saracli et al., 2013). Higher cophenetic correlation coefficient indicates that the clustering method is better. Sec. 2.5 has been rewritten in lines 1-8, page 14.

19. Page 13, lines 9-17: This is the first time authors talk about fires. How is it related to the current study? This is an example where authors should better use the introduction to present the problem and what they did to address it.

R: Sec. 2.6 has been rewritten, and the details about air mass backward trajectories and fire location map have been added in line 10, page 14 to line 2, page 15.

Results and discussion

20. Figure 3: Why results from Qinghai region are not presented?

R: All the samples sites in Xinjiang and Qinghai are shown in Fig. 3. To avoid such ambiguity, we have updated Fig. 1 and Fig. 3. We believe that the revised figures could be much friendlier to the readers who are not familiar with the geography of China.

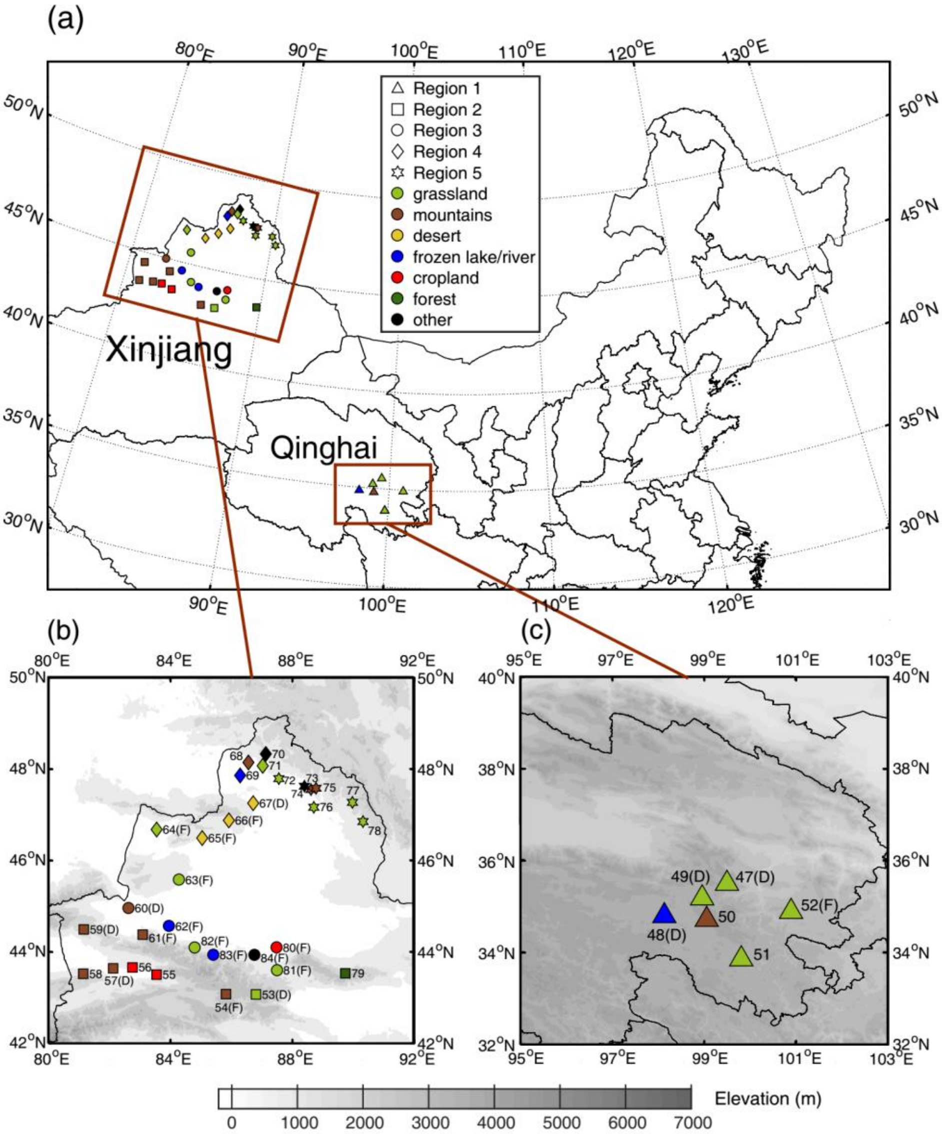


Figure 1. (a) The location of study area and sample site distribution across northwestern China. The site numbers and regional groupings are shown in panel (b) for Xinjiang and (c) for Qinghai. Sample areas are divided into five regions indicated by different symbol shapes, and the land cover types of sample sites are represented in different colors, as shown in the legend in panel (a). The "D" indicates that the sample was collected from a snow drift, and the "F" indicates that the surface sample was fresh snow. The elevation is shown in the contour plot.

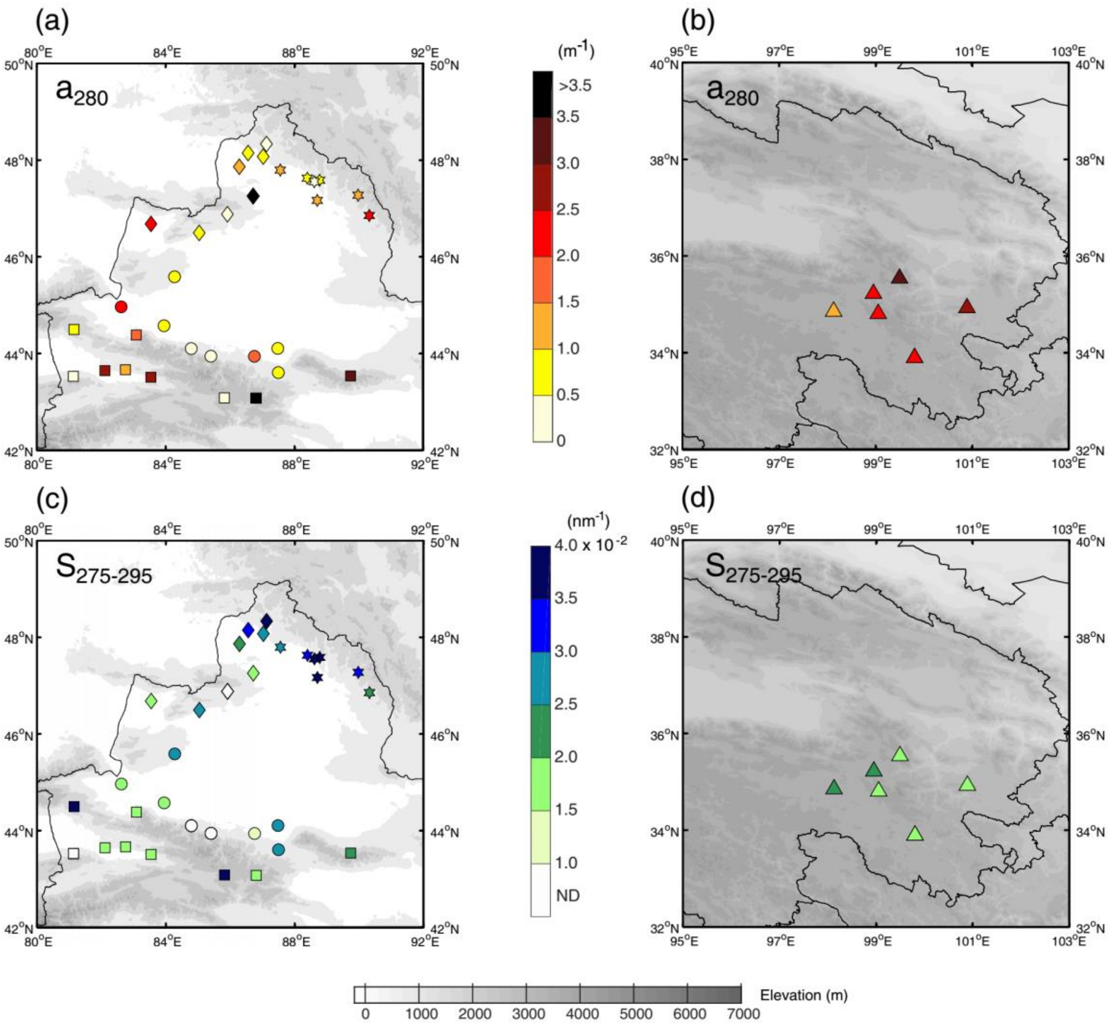


Figure 3. a_{280} and $S_{275\text{-}295}$ for sites in (a, c) Xinjiang and (b, d) Qinghai, respectively. The five regions are indicated by different symbols (same as Fig. 1).

21. Page 14, lines 1-2: In Fig. 3, a280 varies between 0 and 4.5, not between 0.15 and 10.57 as said in the text.

R: Sorry for the misleading. The symbols in black color shown in Fig. 3 represents a_{280} higher than 3.5 m^{-1}. To make the figure more clearly, the color bar has been updated in the revised manuscript.

22. Page 14, lines 13-15: Why comparing S measured in snow and S measured in oceans? This sentence is detached from the rest of the text.

R: The values of $S_{275\text{-}295}$ were rarely reported in the cryosphere in previous studies. Hence, we compared our results to the values of various types of aquatic environments summarized by Hansen et al. (2016). There is a large difference of $S_{275\text{-}295}$ between oceanic and terrestrial systems (0.020-0.030 nm^{-1} and 0.012-0.023 nm^{-1}, respectively) due to the different CDOM sources. We noted that the $S_{275\text{-}295}$ in snow showed a broad range of 0.0129-0.0389 nm^{-1}, which covered the value ranges of different aquatic environments, may indicating complex sources. We have rewritten these sentences in line 17, page 15 to line 3, page 16, as follows:

"$S_{275\text{-}295}$ is never reported in the terrestrial snow and ice samples before, but is widely measured in the aquatic environments. For example, Hansen et al. (2016) summarized the $S_{275\text{-}295}$ for oceanic and terrestrial systems, the values range of 0.020-0.030 nm^{-1} for ocean, 0.010-0.020 nm^{-1} for coastal water, and 0.012-0.023 nm^{-1} for terrestrial systems. The $S_{275\text{-}295}$ in this study covered the typical values in different types of natural water bodies, indicating complex compositions and sources of CDOM in seasonal snow across northwestern China."

23. Figure 4: There is a relation (which is already known in the literature) between S275-350 and a280. What does it mean in the context of this study? As I said, this relation is already known, so I am not sure that this figure is needed.

R: We agreed with the reviewer. Fig. 4 and the corresponding description have been removed.

24. Page 14, line 22: What is HULIS?

R: "HULIS" is the abbreviation of "humic-like substances". We have updated this information in the introduction in line 20, page 4 to line 1, page 5, as follows:

"while humic-like substances (HULIS), which is a type of macromolecular organic substances defined for aerosol with certain similar chemical properties to terrestrial and aquatic humic and fulvic substances (Graber and Rudich, 2006), and unknown chromophores each accounted for approximately half of the total absorption."

25. Page 15, lines 2-6: Why AAE values not presented in a map like for S and a?

R: The AAE values were calculated from 240-550 nm. Because the light absorption within the visible wavelengths of some samples were below the detection limit of the spectrometer, approximately half of the samples were available for the AAE calculation. This has been mentioned in lines 15-17, page 12. Due to the missing values appeared, the AAEs were not shown as a figure in this study but summarized in Table 1, which could be useful for further studies.

26. Pages 15-17: These results are site specific and cannot be generalized. The Editor should check if this is in line with the scope of the journal. Since authors are interested in presenting differences among regions, I suggest using boxplots instead of Fig. 3 and Fig. 7. Then, ANOVA or t-test could be used.

R: We have replotted Fig. 3 and Fig. 7. The results in pages 16-17 were also revised. We tried to assess the optical properties and sources of snow CDOM across northwestern China, not only the differences among regions. The sample sites were grouped based on the geographical distributions, because we suggested that the geographical locations combined with the local land cover and topography might be the major mechanisms for the variations of sources and optical properties of CDOM in snow. Our previous study has proved that the sources of insoluble light-absorbing particles show regional variations in the same field campaign (Pu et al., 2017). Additionally, in the following discussion (Sec. 3.3), we really found variations of sources for snow CDOM among some regions, for instance, regions 1, 3 and 4; meanwhile, some regions also showed similar characteristics, like regions 1 and 2, regions 4 and 5. As suggested by the reviewer, ANOVA have been used to assess the differences among regions in Sec. 3.3.

27. Section 3.3: These results are not related to paper objectives that aim to study DOM in the snow.

R: We agreed with the reviewer. Sec. 3.3 has been removed in the revised manuscript.

28. Table S1 same results as in Fig. S5.

R: We have visualized Table S1 as pie charts and added them into Fig. S4 in the revised

Supplement.

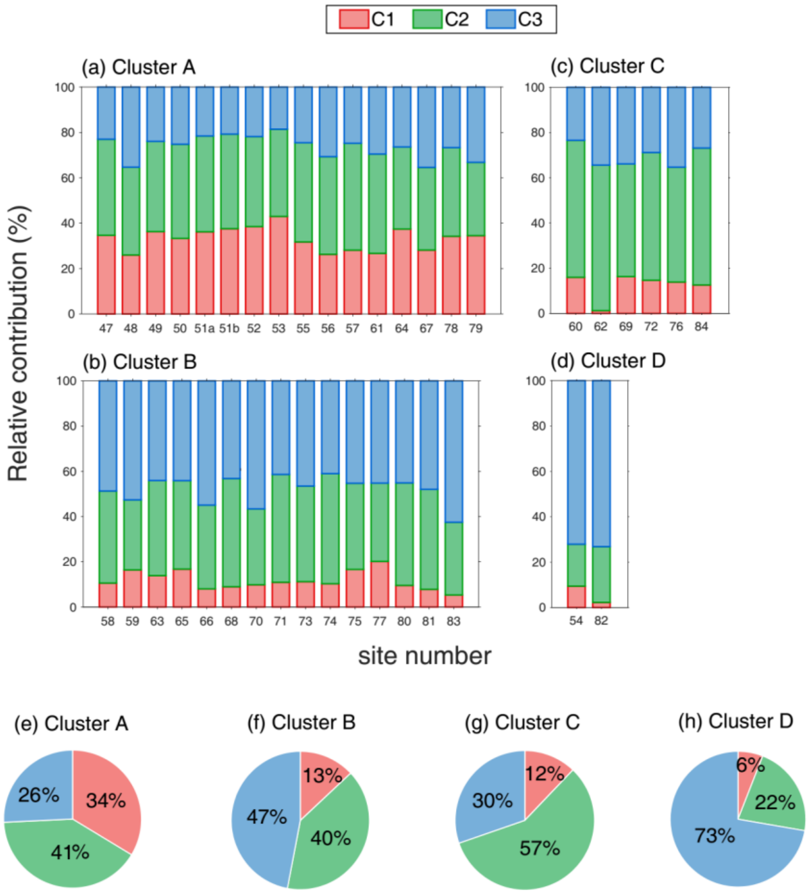


Figure S4. (a-d) The results of cluster analysis, and (e-h) the average %C1-%C3 in each cluster (pies).

29. Fig. 5: This should be in the appendix.

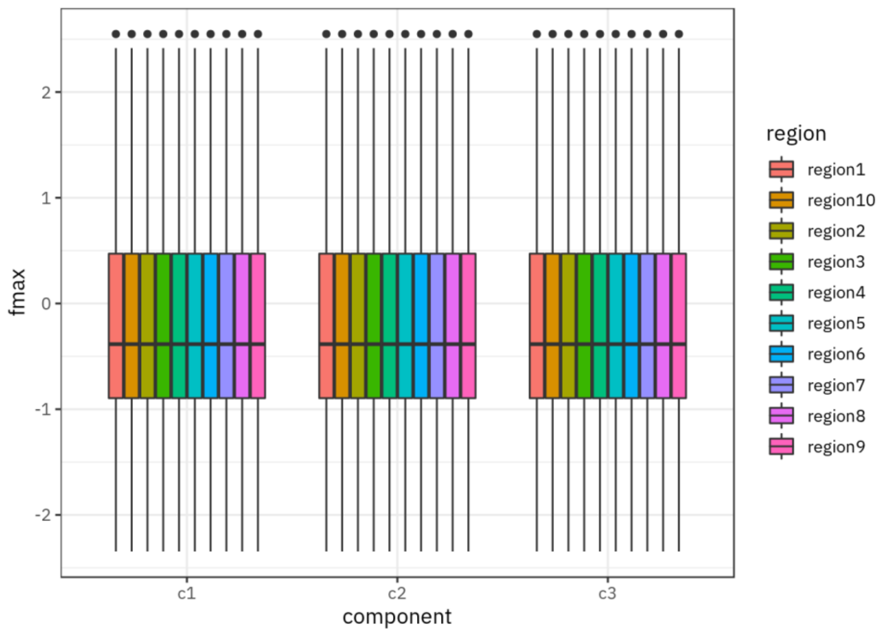
R: We should admit that the fingerprints of EEM components decomposed by PARAFAC method were widely used to discuss the CDOM in aquatic environments. However, the potential readers of this manuscript are likely to be the scientists who are expert in the cryosphere. The EEMs combined with the PARAFAC analysis is rarely used in this research field, and Fig. 5 (Fig. 4 in the revised manuscript) can give a visualization of the fluorescent components appeared in the snow of northwestern China. Therefore, we have kept the panels a-c in the main text and removed the panels d-f.

30. Section 3.2.1: Three pages are dedicated to present PARAFAC components. Once

again, what kind of information this brings in the context of the paper?

R: We have shortened Sec 3.2.1, and the correlation analysis among PARAFAC components has been moved to Sec. 3.3 in the revised manuscript. The EEM combined with the PARAFAC analysis is the key analytical tool in this study. Since these components do not appear frequently in the studies of snow and ice, we suggested that the thorough discussion of the present knowledge of PARAFAC components is needed. Besides, the correlation analysis is a useful method to identify the potential sources of the PARAFAC components (e.g., Murphy et al., 2008; Zhang et al., 2011), which is also very important in this study.

31. Fig. 7: This figure is very difficult to interpret. It is rarely a good idea to present pie chart because human eyes are very bad at judging angles. I suggest a figure like this:



With such figure, regional variations will be better visualized.

R: Fig. 7 has been replotted as Fig. 5 in the revised manuscript, and the information from Table 3 has been added into Fig. 5 as pie charts.

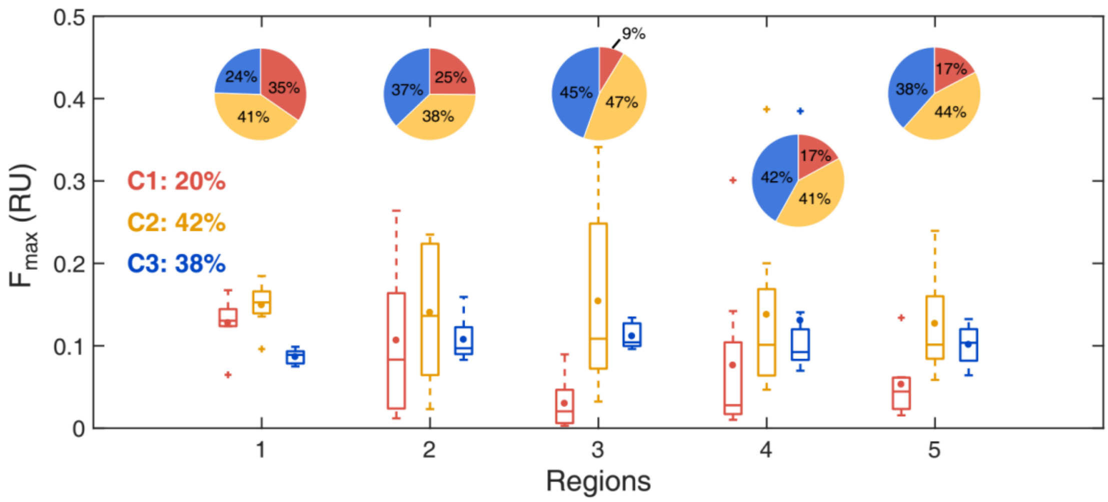


Figure 5. Variations of the fluorescent components among regions. The boxplots show the intensities of components. The boxes denote the 25th and 75th quantiles, and the horizontal lines represent the 50th quantiles (medians), the averages are shown as dots; the whiskers denote the maximum and minimum data within 1.5 times of interquartile rang, and the datapoints out of this range are marked as "+". The pie charts show the average relative contributions of three components in each region. C1, C2, and C3 are represented in red, yellow, and blue, respectively, both for the boxplots and pie charts. The percentages on the left of the panel are the averages of %C1-%C3 for the whole dataset.

32. Figure 8: The clustering should be done using all optical indices (S, AAE, a280).

R: Due to missing values of S and AAE, cluster analysis is not available for such parameters. In this study, the cluster analysis is used to assess the compositions or sources variations among samples, however, a_{280} does not contain such information and was not involved into the cluster analysis. Furthermore, in previous studies, the input dataset of cluster analysis was usually derived from the same types of measurement, such as EEM-PARAFAC (Dubnick et al., 2010; Maie et al., 2012; Zhao et al., 2016), Fourier transform infrared (FT-IR) spectroscopy (Yang et al., 2015) or high-resolution mass spectrometry (HR-MS) (Chen et al., 2016). Therefore, we used the relative contributions of three fluorescent components in the cluster analysis.

33. Figure 9: Any reasons to present sites in that specific order? This can be confusing

if there is no link among regions. What are the a and b letters under stations 51 and 52?

R: (1) These sites were grouped by regions and arranged in the order of regions 1 to 5 in Fig. 9. We have updated Fig. 9 to the boxplot as Fig. 7 in the revised manuscript using the data in Table 4 (Table 4 has been removed). The values in each site can be found in Table 1. In this way, the variations among regions could be clear.

(2) To assess the variations of CDOM properties in a same snowpack, we collected two snow profiles at site 51 marked as sites 51a and 51b. The results showed that the properties of CDOM at sites 51a and 51b were quite similar.

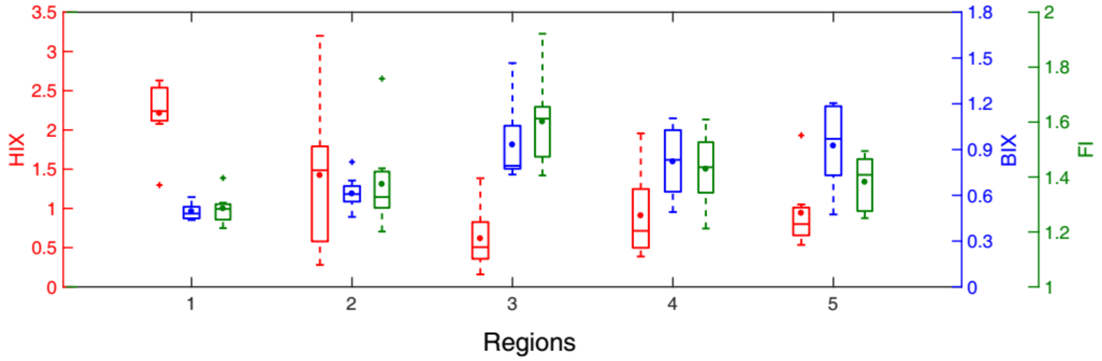


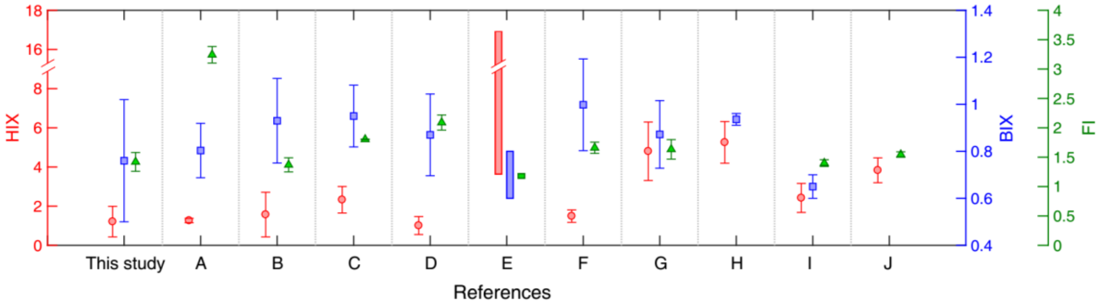
Figure 7. HIX (shown in red), BIX (shown in blue) and FI (shown in green) of surface snow samples among regions. The meaning of each part of box is same as that in Fig. 5.

34. Figure 10: See my other comments about showing how optical indices compare and the aim of the study.

R: Sec.3.3 has been removed as mentioned in our response to comment 27, correspondingly, Fig.10 has also been deleted in the main text. Fig.10 (a-c) has been moved to the Supplement as Fig. S5.

35. Tables 3, 4 and 5: This data could be presented using boxplots are better than tables for visualization. Raw data should be given in the appendix.

R: As shown in our responses to comments 31 and 33, the data in Table 3 has been added into Fig. 5 in the revised manuscript, and Table 4 has been plotted as Fig. 7 in the revised manuscript based on the reviewer's suggestions. For Table 5, we have also drawn a boxplot for visualizing the data as the following figure shown, however, we noted that Table 5 could also provide useful information for the comparison among studies. Hence, we suggested that Table 5 could be retained in the revised manuscript if the reviewer also agreed.



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