# 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.

 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 lightabsorbing 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.

 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)."

 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."

- 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  $\mu$ m PTFE syringe filters (Jinteng, Tianjin, China), and stored in prebaked glass vials (450 °C for 4 h) at 4 °C in a freezer. All the samples were measured for UV-Vis and fluorescence spectroscopies within 24 hours after filtration. The ultrapure water (18.2 M $\Omega$ ·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.

Experiment	Data Description
DfttAqualogSpectralEmissionTwoD.xml	QSUNIT
Directory: C:\Users\Public\Documents\Jobin Yvon\Data Save As	Comment:     Quinine Sulfate UnitSample Evaluation
quaLog Experiment Options	
Integration Time Integration (s) 0.05 Accumulations 1 Total Integration = 0.05 (s)	Blank / Sample Setup Blank Only Sample and Blank Gollect Blank Blank from File Sample Only
Wavelength Settings Excitation Park (nm) Wavelength 347.5	Sample Selection Blank: Position 1 v Sample: Position 2 v
Emission Low (nm) High (nm) Increment (nm) Coverage 248.58 830.59 2.33 nm (4 pixel) • CCD Gain: Medium •	Accessories  Enable Temp. Controller  Enable External Sensor  Enable External Trigger

- 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  $S_{275-295}$  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<sup>-1</sup>. 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  $S_{275-295}$  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  $S_{275-295}$  between oceanic and terrestrial systems (0.020-0.030 nm<sup>-1</sup> and 0.012-0.023 nm<sup>-1</sup>, respectively) due to the different CDOM sources. We noted that the  $S_{275-295}$  in snow showed a broad range of 0.0129-0.0389 nm<sup>-1</sup>, 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<sub>275-295</sub> 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<sub>275-295</sub> for oceanic and terrestrial systems, the values range of 0.020-0.030 nm<sup>-1</sup> for ocean, 0.010-0.020 nm<sup>-1</sup> for coastal water, and 0.012-0.023 nm<sup>-1</sup> for terrestrial systems. The S<sub>275-295</sub> 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 25<sup>th</sup> and 75<sup>th</sup> quantiles, and the horizontal lines represent the 50<sup>th</sup> 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<sub>280</sub> 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.



# References

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and seasonal drivers of dissolved organic matter composition: Sources and physical disturbance controls, Appl. Geochem., 27, 917-929, 2012.

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- Zhao, Y., Song, K., Li, S., Ma, J., and Wen, Z.: Characterization of CDOM from urban waters in Northern-Northeastern China using excitation-emission matrix fluorescence and parallel factor analysis, Environ. Sci. Pollut. R., 23, 15381-15394, 2016.

# Response to reviewer#2

We are very grateful for the reviewer's insightful comments, which are helpful and valuable for greatly improving our manuscript. 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 work describes the results of a field campaign on surface snow chemical properties, lead in northwestern China. More specifically, it investigates the colored dissolved organic matter (CDOM) in seasonal snow, trying to evaluate its different components, their sources, and overall importance for light absorption by snow, which is a very important topic, linked to the climate impact of snow. The subject treated is thus highly relevant for The Cryosphere and is worth publishing, once the authors take care of the following remarks.

R: Thanks very much for the reviewer's comments. We have carefully responded the following remarks.

My major issue with this work is related to clarity. Although generally well written, I truly think the authors should make a distinct effort on two aspects:

1. Have a clearer presentation of the PARAFAC method. Although as stated by the authors, it has become very mainstream in the aquatic chemistry community, and is starting to be used in the aerosol community, it is still a novelty for most readers of The Cryosphere. It would be good, in this case, to have a clear reminder of what the PARAFAC methods gives (what are the Components, the Fmax, ...). If the authors are somewhat familiar with the PMF method, they might even want to draw a parallel, which might (arguably) help.

R: Thanks for the reviewer's insightful comments. We have added a brief introduction of PARAFAC method in lines 19-22, page 9, and also added the interpretations of the theory and several terms of PARAFAC method in the Supplement, such as the components,  $F_{max}$  and loadings. We hope that it can be helpful for the scientists who

#### are not familiar with this method.

2. Maybe draw a clearer separation between actual results, and their interpretation in terms of sources and comparison with previous studies. This could be done by adding a "discussion" section. In particular, this might help clarifying the case on sources. In its current form, the paper discusses sources through the analyses of PARAFAC components, and then though the analyses of back trajectories and other data such as the ion data. I feel that the case of the authors on sources would much stronger if raw results were presented first (PARAFAC components, clusters, ion ratios, maybe back trajectories) and then discussed together: this would help synthesis, and avoid losing the reader between two different discussions on the same topics.

R: We have reconstructed the results and discussion section. The discussion of CDOM sources have moved to Sec. 3.3.1 and Sec. 3.3.2. Considering the consistency of this paper, the discussion about the optical characteristics (Sec. 3.1, Sec. 3.2, and Sec. 3.4) were still after or together with the results.

#### **Specific comments:**

- P7 line 14: there were studies on EEM application to aerosols before the recent papers cited here. Please refer to the appropriate literature (probably not exhaustive):
- Duarte, R. M. B., Pio, C. A. et Duarte, A. C.: Synchronous scan and excitation emission matrix fluorescence spectroscopy of water-soluble organic compounds in atmospheric aerosols, Journal of Atmospheric Chemistry, 48(2), 157–171, 2004.
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- Mladenov, N., Alados-Arboledas, L., Olmo, F. J., Lyamani, H., Delgado, A., Molina,
   A. et Reche, I.: Applications of optical spectroscopy and stable isotope analyses to
   organic aerosol source discrimination in an urban area, Atmospheric Environment,

45(11), 1960-1969, doi:10.1016/j.atmosenv.2011.01.029, 2011.

R: All of the above literatures have been cited in lines 10-11, page 6.

4. P8 line 18: "grouping scheme presented by Pu et al. (2017)": Pu et al actually just refer to "geographical distribution" as a grouping scheme. Reading further in the article, there is a logic, in terms of north or south of a mountain range, on this or that side of strong potential human sources, ... I suggest this logic should be somewhat detailed here, rather than reporting to a reference where it is actually not clearly presented.

R: We agreed with the reviewer. Reasons for such grouping scheme have been presented in more detail in lines 5-12, page 7. As the reviewer said, "north or south of a mountain range" or "this or that side of strong potential human sources", actually, the logic for such grouping scheme is still the geographical distribution, we noted that the different geographical locations combined with the land cover and topography can be the major mechanisms in leading to the variously optical properties and sources for CDOM. In addition, our previous study found clearly regional variations of insoluble lightabsorbing impurities in the same field campaign (Pu et al., 2017).

5. P10 line 9-10: "In addition, the emission wavelengths longer than 650 nm were removed to eliminate the uncertainty of measurement". It is not clear what uncertainty is eliminated here. Please be more specific.

R: Because the emission signals were mainly within 250-650 nm, those at longer wavelengths were week and more likely to be noises, which might influence the performance of PARAFAC model. The corresponding description has been added in lines 3-6, page 10.

6. P10 line 10-15: as in any statistical factor analysis (PARAFAC, PMF, ...) the choice of factor number is quite critical, and thus must be very carefully argued. Here, the choice of 3 components is based on residual error analysis. Yet, although going from 2 to 3 decreases strongly this error, there is still (fig S1) a large error around 270 nm which disappears when going from 4 to 5 factors. The authors "confirm" the 3 factor

analysis with some splitting method, but they do not reject the 4 or 5 factor analysis with this method. To me, it seems at this point, the choice of 3 factors is largely arbitrary. R: We agreed with the reviewer that the model validation is the most important step in PARAFAC method. The split-half analysis is the most powerful way to confirm the factor numbers of the model (Murphy et al., 2013). The data set is firstly divided into two random, typically equal sized groups and conducting a PARAFAC model on both halves independently. If the correct number of components is chosen, the loadings from both the models will be the same (Stedmon et al., 2003). Many studies used the splithalf analysis alone to validate the model (e.g., Yamashita et al., 2008; Zhang et al., 2010; Zhao et al., 2016). Although there were both significant decreases of residual error when component number increased from 2 to 3 and 4 to 5; when subsequently conducting splithalf method for 2- to 7-component model, only the 2- and 3- component models passed the analysis. Therefore, the 3-component model was confirmed and the 5-component model was rejected. The corresponding description has been changed in lines 6-11, page 10.

7. P10: I may have missed it, but did the authors mention the number of samples used in the PARAFAC analysis? Is that number sufficient for such a statistical method? There are quality guidelines for PMF studies from filters and offline tracers analysis (Belis et al, 2014), I would expect similar guidelines to exist for PARAFAC, as these methods are mathematically very close (if not equivalent).

R: Yes, there is a recommended sample number for PARAFAC analysis. As shown in Stedmon and Bro (2008), at least 20 samples are required. Of course, if more data is used, easier for getting a robust model. In this study, 78 EEMs were measured, and 76 of them were involved into the PARAFAC model (removed 2 contaminated samples), which is sufficient for this method. We have added the number of measured samples (n = 78) in line 8, page 9 and line 6, page 11.

8. P11 line 17-19: the reason put forward by the authors for choosing one fitting method rather than the other seems statistically weak to me. Of course, as any point where the

choice would actually matter is anyway rejected in advance, it is of minor importance. Yet, could the authors be more specific here?

R: Actually, the variation of results for these two fitting methods was approximately 3% on average. This was consistent with Helms et al. (2008), who first introduced  $S_{275-295}$  into the CDOM research field. Due to fits were conducted in a narrow wavelength band (275-295 nm), the data points were much fewer than the whole band. It can lead to a better performance of linear fit than the exponential fit, which was proved by the higher  $R^2$  of linear fit. Therefore, we chose the linear fit here. The description has been added in lines 2-3, page 12.

9. P11 line 17-25: confidence on fits? this translates in uncertainties in the reported slopes and AAE, which might impact interpretations. So it is of some importance! R:  $R^2$  of all the fits (S<sub>275-295</sub> and AAE) were higher than 0.9 and most of them were higher than 0.95. Hence, we noted that these results are credible and accurate. We have added the corresponding description in lines 13-14, page 12.

10. P12 line 20: nss-K is reportedly calculated after Tao et al 2016 following nss-K = K - 0.159 Mg. Tao et al 2016 actually claim they used Cheng et al, 2000 definition of nss-K, reported as nss-K = K - 0.037 Na, which they claim they took from Hitchcock et al, 1980. I would suggest being more precise on the calculation really made, and its origin. In any case, I also have some reservations on this approach, as it was originally used for coastal sites (North Carolina for Hichcock et al., 1980; Hong Kong for Cheng et al., 2000). In more continental areas, with significant input of terrestrial dust, there might be a sizable portion of either Mg2+ and/or Na+ coming from dust, which would distort the relation used. An example of such distortion and the way to analyse it is presented in Pio et al, 2007. I suggest to take these points into account.

R: We agreed with the reviewer and corrected the  $K^+$  to nss-ndust- $K^+$ , the details can be seen in the main text in lines 5-20, page 13.

11. P13 line 7-8: how was the choice of 4 clusters decided to be relevant?

R: The determination of cluster number is also an important and difficult issue. Because only three parameters were used in the analysis, solutions with too many clusters can lead to difficulty of results interpretation. In this study, 3- to 5-cluster solutions were taken into consideration. The following figure shows the relative contributions of three fluorescent components in each cluster for 3- to 5-cluster solutions. The clusters B and C of 4-cluster solution (panel b) were decomposed from cluster B of 3-cluster solution (panel a). The relative intensities of C2 and C3 in clusters B and C (4-cluster solution) were significantly different (ANOVA, p<0.001), therefore, the 4-cluster solution is appropriate and better than the 3-cluster solution. As for 5-cluster solution (panel c), only sample no. 62 was isolated as the cluster E. The cluster contained very few data should be avoided for determination of cluster numbers. Hence, the 5-cluster solution was rejected., and 4-cluster solution was adopted here.



12. Fig 5: replace "excitation" with "excitation"; it is not quite clear to me what "excitation (emission) loading" is. I suspect it is the sum over emission (excitation) of the EEM matrix of each component. Am I right? maybe it should be precise either here in the caption, or somewhere in the text (or both).

R: (1) Sorry for the negligence, the wrong word in Fig. 5 has been replaced (Fig. 4 in the revised version).

(2) To explain the term "loading", we should go back to the theory of this method. PARAFAC decomposes a three-way dataset into a set of trilinear terms and a residual array:

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + \varepsilon_{ijk},$$
  
(R1)  
 $i = 1, ..., I; j = 1, ..., J; k = 1, ..., K.$ 

In Eq. (R1), x is the original data set, i is the sample number, j and k are the excitation and emission wavelength numbers, respectively; f is the number of fluorescent components,  $\varepsilon$  is the residual containing noise and other unmodeled variation. Parameters a, b and c represent the concentration, emission spectra and excitation spectra of each fluorophore, respectively. Actually, "loadings" are the parameters b and c calculated from the model, these two parameters showed the basic information of each component. Details can be seen in Stedmon and Bro (2008). Because the term "loading" cannot be explained easily, we have given a brief description in the Supplement (Sec. S1.1), and also deleted Fig. 5d-f since Fig. S2 shows the same information.

13. P19 line 4-8: It is not clear to a non-PARAFAC aficionado what Fmax is. I feel that it is the fraction of the observed total fluorescence that is explained by a given component, so that it should be somewhat proportional to the concentration of this component in the mixture that the sample is made of. It would be really helpful to clarify this point.

R:  $F_{max}$  represents the max fluorescence intensity of each component, which is calculated by parameters *a*, *b* and *c* in Eq. (R1) and with the same unit of the original EEMs.  $F_{max}$  is truly proportional to the concentration of corresponding composition.

However, the intensity of fluorescence does not only dependent on the concentration, as well as the molar absorptivity and fluorescence quantum efficiency. In other words, if species A has higher  $F_{max}$  than species B, we cannot conclude that A is more abundant than B. If certain PARAFAC component can be identified as any known chemical species, then the quantification can be performed. Nonetheless, the changes of  $F_{max}$  for a certain component and the ratios between components can be used to investigated the differences among samples qualitatively and quantitively. Details can be seen in Stedmon and Bro (2008) and Murphy et al. (2013). We have also added a brief description of  $F_{max}$  in the Supplement (Sec. S1.2).

14. P21 line 9: the picture presented by the authors looks much like lichens to me, more than algae. I also thought that algae only lived in aquatic media (including snow), except when associated with fungi in lichens.

R: We have changed the corresponding text in lines 10-11, page 20 as "We found lichens near these two sample sites (Fig. S3), providing evidence for the latter reason".

15. P22 line 18: I feel that figure 9 is not very informative as such.

R: Fig. 9 has been changed to a box plot as Fig. 7 in the revised manuscript, which exhibits the regional variations of fluorescence indices.



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.

16. P23 line 2-5: Figure S6 should be considered as a replacement for figure 10: it is

more informative, while not being really more clustered. Maybe it could be made even better by reducing slightly the font size of the red equations and drawing dashed red lines, thus using size and line type and color to make stress which correlation is important and which one is rejected.

R: We found that Sec. 3.3 seems not very relate to the aim of this study. Therefore, Sec.3.3 and Fig. 10 have been deleted. Based on the reviewer's suggestions, we have replotted Fig. S3 as Fig. 8 in the revised manuscript.



**Figure 8.** The linear relationships between intensities of (a) C1 and C2, (b) C1 and C3, (c) C2 and C3. The red dashed lines show the fit of the entire dataset, and the blue solid lines show the fit of data excluded site 67 (shown as markers in red). The corresponding fitting parameters are exhibited in the same color, including the equations, correlation coefficients and p-values.

17. P25 line 20: see my previous comment on  $nss-K^+$ . how is the authors discussion here sensitive to the objection raised in that previous comment?

R: We have corrected  $K^+$  to nss-ndust- $K^+$  following Pio et al. (2007), please see our response to comment 10. The related results have also been changed, such as Fig. 9b and Table 4 in the revised manuscript. We can see that the results varied slightly, and also supported our conclusions.

18. P26: I have a hard time evaluating whether the backtrajectory analysis presented here is relevant. Obviously, fires location from MODIS can be active or not when a

back trajectory passes over it. Here, it seems that any back trajectory can overpass any fire location, and be taken into account in the analysis, even if the backtrajectory overpasses on day n, and the fire was only active from day n+3 to day n+10. This seems to weaken a lot the analysis presented here.

R: We have modified the method. To better combined the backward trajectory and the active fire data, only the fire points that were active during the trajectory calculation period (72 h) were taken into consideration. Then, the trajectories were separated into "passed" and "not passed" groups (red and blue lines in Fig. 10, respectively) to assess the potential influence of biomass burning to the receptor regions.



**Figure 10.** 72-h air mass backward trajectories at 500 m above ground level with the initial positions at representative sites (shown as yellow pentagrams) in each region. Trajectories were calculated four times per day for a period of 30 days preceding the sampling date at a given site by HYSPLIT (version 4, NOAA) except for panel (c). Since the snow was fresh at site 84, the trajectories were derived for 5 days preceding the sampling date. The red lines show the airmasses passed through the active fires before reaching the receptor sites, and the blue lines are those did not pass the fires. The white dots represent the typical industrial cities in Xinjiang, i.e., Karamay, Kuytun, Shihezi and Urumqi from west to east.

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# The optical characteristics and sources of chromophoric dissolved organic matter (CDOM) in seasonal snow of northwestern China

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# Abstract.

Chromophoric dissolved organic matter (CDOM) plays an important role in the global carbon cycle and energy budget-, but is rarely studied in seasonal snow. A field campaign was conducted across northwestern China from January to February 2012,

- 5 and surface seasonal snow samples were collected at 39 sites in Xinjiang and Qinghai provinces. <u>Light-absorption measurements, Absorption and</u> fluorescence measurements and <u>spectroscopies along with</u> chemical analysis were <u>conductedused</u> to investigate the optical <u>propertiescharacteristics</u> and potential sources of CDOM in <u>seasonal</u>-snow. The abundance of CDOM (<u>shown as</u> the absorption coefficient at 280 nm, a<sub>280</sub>) and the
- 10 spectral slope from 275 to 295 nm ( $S_{275-295}$ ) ranged from 0.15-10.57 m<sup>-1</sup> and 0.0129-0.0389 nm<sup>-1</sup>, respectively. The highest average  $a_{280}$  (2.30±0.52 m<sup>-1</sup>) andwas found in Qinghai and the lowest average  $S_{275-295}$  (0.0188±0.0015 nm<sup>-1</sup>) in Qinghai indicated that the snow CDOM in this region had strongly terrestrial characteristic. Relatively low regional averageaverages of  $a_{280}$  values were found inat sites located to the north
- of the Tianshan Mountains and northwestern Xinjiang along the border of China (0.93  $\pm 0.68 \text{ m}^{-1}$  and  $0.80 \pm 0.62 \text{ m}^{-1}$ , respectively). Parallel factor analysis (PARAFAC) analysis identified three types of chromophores fluorophores that were attributed to two humic-like substances (HULIS, C1 and C2) and one protein-like material (C3). C1 was mainly from soil HULIS, C3 was a type of autochthonously labile CDOM, while the
- 20 potential sources of C2 were complex and included soil, microbial activities, anthropogenic pollution, and biomass burning. The good relationship between  $a_{280}$ and the intensity of C1 ( $\mathbb{R}^2 = 0.938$ , p<0.001) indicated that the CDOM abundance in

the surface snow across northwestern China was mainly controlled by terrestrial sources. In additionFurthermore, the regional variations of sources for CDOM in snow were further assessed by the analysisanalyses of chemical species (e.g., soluble ions)), fluorescent components and air mass backward trajectories combined with the satellite

5 active fire locations.

#### **<u>1</u>** Introduction

Dissolved organic matter (DOM) is widely distributed in natural aquatic ecosystems and plays a key role in the global carbon cycle (Massicotte et al., 2017). Chromophoric dissolved organic matter (CDOM), widely known as the light-absorbing constituent of

- 5 DOM (Helms et al., 2008),, can absorb light from ultraviolet to visible (UV-vis) wavelengths (Bricaud et al., 1981) Stedmon et al., 2000). CDOM in aquatic ecosystems originates from the microbial decomposition of plant matter and is released by organisms within the ecosystems (autochthonous), as well as is imported from surrounding terrestrial environments (allochthonous) (Yao et al., 2011; Zhang et al.,
- 2010). Due to its light-absorbing properties, CDOM is important in biological processes
   (Seekell et al., 2015; Thrane et al., 2014), photochemical processes (Helms et al., 2013;
   Vaehaetalo and Wetzel, 2004), and the energy budget (Hill and Zimmerman, 2016;
   Pegau, 2002) in natural water bodies.\_

The light absorbing properties, composition, and sources of CDOM in lakes, rivers, wetlands, coasts, estuaries and ocean have been studied all over the world (Andrew et al., 2013; Chen and Jaffe, 2014; Coble, 1996; Organelli et al., 2014; Shao et al., 2016; Stedmon et al., 2011; Wang et al., 2014). Massicotte et al. (2017) summarized the distribution of DOM concentrations, CDOM absorption and their relationship based on more than 12000 measurements across rivers, lakes and oceans globally. Their study

20 showed that the CDOM from wetlands has the highest absorption coefficients at 350 nm (a<sub>CDOM</sub>(350)) with a median value of 87.2 m<sup>-1</sup>, while the median a<sub>CDOM</sub>(350) of oceans was 0.08 m<sup>-1</sup> and CDOM absorption decreased from fresh water to oceans. A

strong logarithmic relationship between DOC concentrations and  $a_{CDOM}(350)$  (n = 12808,  $R^2 = 0.92$ ) was also found.

Compared to the aquatic <u>ecosystemsenvironments</u>, there were <u>far feweronly limited</u> studies evaluating <u>CDOMDOM</u> in the cryosphere <u>(Barker et al., 2009; Dubnick et al.,</u>

- 5 2010; Feng et al., 2016; Norman et al., 2011). However, Whereas the global glacier ecosystem is a large organic carbon pool and exports approximately 1.04±0.18 TgC yr<sup>-</sup>
  - <sup>1</sup> of <u>DOCdissolved organic carbon (DOC)</u> into freshwater and marine ecosystems<u>environments</u> (Hood et al., 2015). <u>Dubnick et al. (2010)</u> separated the <u>CDOM of ice samples from several glacial environments into five components, namely,</u>
- 10 four protein-like components and one humic-like component, using fluorescence spectrometry. According to the results of a field experiment conducted in Canada, biological fluorophores represented the main species of CDOM in subglacially routed meltwater (Barker et al., 2009). Feng et al. (2016) found that the CDOM in cryoconite samples in Tibetan Plateau glaciers was mainly derived from microbial activity using
- 15 light absorption and fluorescence measurements. In general, CDOM in glacial environments In addition, the glacier-derived DOM shows high bioavailability, and can be a source of labile organic matter for the downstream ecosystems (Hood et al., 2015). However, to the best of our knowledge, there is no study focusing on the CDOM in snow seasonal (Hood et al., 2009; Lawson et al., 2014; Singer et al., 2012). The DOM in snow
- 20 in midlatitude regions. As the largest component of theand ice originates from the insitu microbial processes (autochthonous) (Anesio et al., 2009), as well as is imported from the surrounding terrestrial environments (allochthonous), including soil,

vegetations (Bhatia et al., 2010), and anthropogenic activities (Stubbins et al., 2012). eryosphere (Brutel-Vuilmet et al., 2013), seasonal snow can cover up to 40% of Earth's surface during the Northern Hemisphere winter (Hall et al., 1995). For its ecological functions, snowfall\_

- 5 <u>Snowfall</u> is an important carbon and nutrient input for land ecosystems (Mladenov et al., 2012) and a crucial freshwater reservoir (Jones, 1999<u>)</u>, especially for barren regions (e.g., northwestern China). In addition<u>. Besides</u>, snowpack is also an active field for photochemical (Beine et al., 2011; Domine et al., 2013) and biological processes (Liu et al., 2009; Lutz et al., 2016). Unlike <u>the</u> aquatic environments, the high surface
- 10 albedo is the most obvious physical property of snow (IPCC, 2013). Once lightabsorbing impurities are deposited on the snow surface, the albedo can be significantly reduced, and the regional and global climate are further affected (Hadley and Kirchstetter, 2012). Several field campaigns covering the Arctic, Russia, North America and northern China have been conducted to measure insoluble light-absorbing particles
- (ILAPs) in seasonal snowsnow, for instance, black carbon (BC), insoluble organic carbon (ISOC) and mineral dust (MD) (Doherty et al., 2010, 2014, 2015; Huang et al., 2011; Pu et al., 2017; Wang et al., 2013, 2015, 2017; Warren and Wiscombe, 1980; Ye et al., <u>2012; Y. Zhou et al., 2017</u>)2012; Zhou et al., 2017a). However, these studies neglected CDOM, which is also an effective light absorber, whether in the atmosphere
- 20 (i.e., brown carbon, BrC) or water bodies. However, Dang and Hegg (2014) suggested that the absorption coefficients of soluble chromophores in Arctic snow are lower than those of black carbon (BC) by several orders of magnitudes at visible wavelengths.

Compared to the Arctic, the results might be different in seasonal snow across northwestern China due to the much higher level of anthropogenic activity and dry deposition of local soil there (Pu et al., 2017). However, these studies neglected CDOM, which has been proved as an effective light absorber whether in the atmosphere (i.e.,

- 5 brown carbon, BrC) (Hecobian et al., 2010) or water bodies (Bricaud et al., 1981), but is rarely studied in snow. To constrain the photochemistry of snow soluble chromophores, Anastasio and Robles (2007) first quantified the light absorption of dissolved organic chromophores in melted snow samples from the Arctic and Antarctica. They found that in addition to NO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, approximately half of the light
- 10 absorption at 280 nm and above was responsible for unknown chromophores, probably organics. After that, Beine et al. (2011) analyzed more than 500 snow samples in Alaska. They exhibited that the contributions of  $H_2O_2$  and  $NO_3^-$  to the total absorption within 300-450 nm were slight (combined < 9%); while Humic-like substances (HULIS), which is a type of macromolecular organic substances defined for aerosol with certain
- 15 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. Recently, several studies have started to focus on the optical properties and radiative forcing of CDOM in glaciers on the Tibetan Plateau. Yan et al. (2016) measured the mass absorption cross section (MAC) of CDOM
- 20 <u>in snow (1.4  $\pm$  0.4 m<sup>2</sup> g<sup>-1</sup> on average at 365 nm) at Laohugou glacier, northern Tibetan</u> <u>Plateau, and further calculated the radiative forcing of CDOM which accounted for</u> approximately 10% relative to that of BC. Niu et al. (2018) showed a quite high MAC
value of CDOM ( $6.31 \pm 0.34 \text{ m}^2 \text{ g}^{-1}$  on average at 365 nm) for snow and ice samples collected on Mt. Yulong, southeastern Tibetan Plateau. Moreover, it is surprising that the light absorption of CDOM within 330 to 400 nm was approximately 4 times higher than that of BC, although with high uncertainty. In above studies, the CDOM showed

- 5 significant effects on the energy budget of surface snow and ice on glaciers. Until now, the study of CDOM in snow and ice is still in its infancy, and much more work is imperative to improve our understanding of them. In northern China, the snowpack is affected by more anthropogenic activities or sunlight than those at higher elevation or latitude, thus the effects of CDOM may be more remarkable. Therefore, we conducted
- 10 a large field campaign to investigate the CDOM in seasonal snow of northwestern China from January to February 2012.

UV-vis absorption spectral analysis is a<u>and fluorescence spectroscopies are both</u> rapid and effective <u>methodmethods</u> of characterizing the optical properties and sources of CDOM. The abundance of CDOM is usually described by the light<u>The</u> absorption

- 15 of DOMcoefficient at a certain wavelengthswavelength within the UV band, for instance, 254 nm, 280 nm (or 350 nm (Spencer et al., 2012; Zhang et al., 2010, 2011)., usually serves as an indicator of CDOM abundance. The absorption spectrum of CDOM decreases approximately exponentially with increasing wavelength (Helms et al., 2008), and is usually described by the spectral slope (S) is used to describe the wavelength
- 20 dependence of absorption (Twardowski et al., 2004). Helms et al. (2008) used the spectral slope between 275 and 295 nm (S<sub>275-295</sub>) and the ratio of the spectral slopes (S<sub>R</sub>) of two narrow bands (275-295 nm and 350-440 nm) to investigate the molecular

weight and sources of CDOM (terrestrial or marine origin). Then,), lower S<sub>275-295</sub> was used as a tracer of terrigenous DOC importvalues correspond to marine environments and applied to the Arctic Ocean by remote sensing (Fichot and Benner, 2012; Fichot et al., 2013). Fichot and Benner (2011) presented a method to retrieve the DOM

5 concentration using S<sub>275 295</sub> for northern Gulf of Mexico marine water.

terrestrial and higher molecular weight CDOM. The fluorescence excitation-emission matrix (EEM) offers multiple advantages, such as high sensitivity, easy sample preparation and non-destructivity to samples (Birdwell and Valsaraj, 2010), and has been widely used to identify the <u>sourcesources</u> and <u>compositioncompositions</u> (humic-

- 10 like or protein-like) of CDOMfluorescent DOM (FDOM) in natural waterbodies (Birdwell and Engel, 2010; Coble, 1996; Zhao et al., 2016), rainwater (Y. Q. Zhou et al., 20172017b), fog water (Birdwell and Valsaraj, 2010) and aerosols (ChenDuarte et al., 2004; Lee et al., 2013; Mladenov et al., 2011).2016a, 2016b; Fu et al., 2015). However, the CDOM in nature is composed of complicated chromophores and shows
- 15 overlapping signals with EEMs. To precisely extract the useful information from the very-large dataset of EEMs, Stedmon et al. (2003Bro (1997) successfully applied parallel factor analysis (PARAFAC) analysis to decompose the EEMs into several independent fluorescent components. Due to the great advantageadvantages of PARAFAC analysis in interpreting the results of EEMs, this has been a "mainstream"
- approach in recent natural CDOM studies (Murphy et al., 2013). In addition, three fluorescence derived indices are widely used to identify the potential sources of CDOM.
   Zsolnay et al. (1999) presented a humification index (HIX) to describe the relative

humification of DOM. The fluorescence index (FI) is used to identify the sources of DOM from terrestrial or microbial origins (McKnight et al., 2001), and the biological index (BIX) can be an indicator of autochthonous productivity (Huguet et al., 2009). However, the application of EEM combined with PARAFAC analysis in the cryosphere

5 is scarce. Therefore, we try to employ it to characterize the CDOM in snow.

In this study, surface snow samples collected for the first time, with the aim of presenting a comprehensive understanding of CDOM in seasonal snow across northwestern China-, the samples were subjected to UV-vis absorption, fluorescence, and chemical analyses. For the first time, with the aim of presenting an understanding

10 of CDOM in seasonal snow, to investigate the abundances, optical properties, and potential sources of CDOM and as well as their spatial distributions were investigated.

# 2 Material and methods

### 2.1 Sample collection

During January to February 2012, snow samples were collected at 7 sites (no. 47-51a,

- 15 51b, 52) in Qinghai and 32 sites (no. 53-84) in Xinjiang, which are located in northwestern China. The distribution of sample sites, which are numbered chronologically, is shown in Fig. 1. The sampleBased on Pu et al. (2017), these sites were separated into five regions by their geographical distribution to investigate the spatial variations of CDOM abundance, optical properties and their potential sources.
- 20 One group of sites was Region 1 is in the southeastern part of Qinghai with high altitude, and four groupsother regions were in Xinjiang, following the grouping scheme

presented by Pu et al. (2017). Region 2 is along the Tianshan Mountains; region 3 is located to the north of the Tianshan Mountains and close to the industrial city belt in central Xinjiang. Regions 4 and 5 are in the northwestern and northeastern Xinjiang, respectively, and both along the border of China.

- 5 The sample sites were chosen to be upwind and far enough away from roads, railways, cities and villages to minimize the effects of local pollution. Hence, the collected samples can be representative offor a wide range of areas. Pictures of some of these veral sample sites are shown in Fig. 2. At each site, snow Snow samples were collected every 5 cm from top to bottom at each site, and if there was a melt layer or fresh snow on the
- 10 top layer, such a sample was collected individually. A pair of two adjacent vertical profiles of snow were gathered ("left" and "right") for assessing the variability of the same snowpack and to enhance the accuracy of the measurements. During this campaign, 13 fresh snow samples that had fallen during the sampling time were collected. In addition, at some sites, the snow was thin and patchy and the wind was
- 15 strong; hence, thethese samples were gathered from snow drifts. These samples were, and potentially influenced by the deposition of local soil dust (Ye et al., 2012). More details on the sampling methods have been reported previously (Doherty et al., 2010; Wang et al., 2013; Ye et al., 2012).

After being returned to the laboratory in Lanzhou University, all the samples were stored in a freezer at -20C° or lower for subsequent analysis. <u>Although the previous</u> <u>studies indicated that the freeze-thaw process may lead to biases of the optical</u> <u>properties for DOM samples. For instance, Fellman et al. (2008) reported that there was</u> 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

- 5 properties for several types of DOM samples. The results showed the decreased relative percentages of terrestrial humic-like fluorophores (-3% on average) and humification index (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
- 10 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<sub>280</sub> and fluorescence indices can be neglected. More details on the sampling methods have been
- 15 reported previously (Doherty et al., 2010; Wang et al., 2013; Ye et al., 2012).

### 2.2 Fluorescence measurement

20

The snow <u>samples were firstly melted under the room temperature. Then, the snow</u> water samples were first-filtrated using 0.22 µm PTFE syringe filters (Jinteng, Tianjin, China), and the filtrates were stored in prebaked glass vials (450 C° for 4 h) at 4 C° <u>until measurementin a freezer. All the samples were measured for UV-Vis and</u> fluorescence spectroscopies within 24 hhours after filtration. The ultrapure water (18.2 M $\Omega$ ·cm) filtrated by the PTFE syringe filters exhibited no clear fluorescence signal.

The EEMs (n = 78) of surface snow samples were determined measured by an Aqualog spectrofluorometer system (Horiba Scientific, NJ, USA) in a 1 cm quartz cell. The scanning ranges were 240 to 600 nm in 5 nm intervals for excitation and 250 to

825 nm in 4.65 nm (8 pixelpixels) intervals for emission, and with the integrating time
 wasof 5 s. An ultrapure water blank was subtracted to remove the water Raman scatter peaks.

The inner filter effect (IFE) of EEM was corrected using the method shown in Kothawala et al. (2013). The fluorescence intensities were calibrated by the Raman

peak of the ultrapure water reference at a 350 nm excitation wavelength following the method presented by Lawaetz and Stedmon (2009). The Rayleigh scatter peaks of EEMs were addressed by the EEMscat MATLAB toolbox (version 3) (Bahram et al., 2006)-using an interpolation algorithm-(Bahram et al., 2006).

ThePARAFAC is a multi-way method for modeling the data with three- or higher-

- 15 order arrays (Murphy et al., 2013). For the EEMs, the three dimensions are samples, excitation and emission wavelengths. After PARAFAC analysis, the EEMs can be decomposed into several components with clear chemical interpretations. The details about the theory of PARAFAC analysis can be found in the Supplement. In this study, the PARAFAC analysis was performed by the DOMFluor toolbox (version 1.7) in
- 20 MATLAB (Stedmon and Bro, 2008). In additionIn addition, because the emission signals were mainly in the range of 240-650 nm, those at longer wavelengths were weak and more likely to be noises, hence, the emission wavelengths longer than 650 nm were

removed to eliminate the uncertainty of measurement.not considered into the model. According to the analysis of residual error, <u>split-half method</u> and visual inspection, the <u>three3</u>-component PARAFAC model was selected. The residual error decreased distinctly when the <u>components component number</u> increased from <u>two2</u> to <u>three 3 and</u>

- 5 from 4 to 5 (Fig. S1). The three-component model was alsoCombined with the splithalf analysis for 2- to 7-component models, only 2- and 3-component models were validated by the split-half analysis with the "S4C4T2" split scheme (Murphy et al., 2013) (Fig. S2).2013). Therefore, the 3-component model was chosen here. The fluorescence intensity of the fluorescence each fluorescent component was expressed as F<sub>max</sub>F<sub>max</sub> in
- Raman unit (RU) (Stedmon and Markager, 2005a). 2005b). The relative contributions
  of intensity for components to the total fluorescence are given as %C1-%C3 hereinafter.
  In addition, thethree fluorescence-derived indices were calculated by Eq. (1-3)are
  widely used to identify the potential sources of CDOM. Zsolnay et al. (1999) presented
  a humification index (HIX) to describe the relative humification of DOM. The
- 15 fluorescence index (FI) is used to identify the sources of DOM from terrestrial or microbial origins (McKnight et al., 2001), and the biological index (BIX) can be an indicator of autochthonous productivity (Huguet et al., 2009).; McKnight et al., 2001; Zsolnay et al., 1999): These three indices are calculated by the following formulas:

$$-FI = I \frac{450}{370} / I \frac{499}{370}, \qquad (1)$$
20
$$-BIX = I \frac{379}{310} / I \frac{430}{310}, \qquad (2)$$

$$HIX = I \frac{434}{255} / I \frac{300}{255}, \qquad (2)$$

$$FI = I (Ex = 370, Em = 450) / I (Ex = 370, Em = 499), \qquad (1)$$

$$\underline{HIX} = I (\underline{Ex} = 255, \underline{Em} = 434 - 480) / I (\underline{Ex} = 255, \underline{Em} = 300 - 345),$$
(3)

where I is the fluorescence intensity, the subscript denotes Ex and Em are short for the excitation wavelength and the superscript denotes the correspondingand emission

5 wavelength or wavelength rangewavelengths, respectively. We note that the wavelengths used in the calculation were changed slightly (1 nm or less) due to different instruments.

#### 2.3 UV-vis absorption measurement

The UV-vis absorption spectra (n = 78) of snow samples were derived from 240 to 600

- 10 nm in 5 nm intervals while the fluorescence measurements were conducted by an Aqualog spectrofluorometer system (Horiba Scientific, NJ, USA), and an ultrapure water blank was used as a reference. The absorbance of CDOM was assumed to be zero above 550 nm, and the average absorbance between 550-600 nm was subtracted from the whole spectrum to correct the baseline shifts and scattering effects of the 15 measurement. The absorbances of the samples were converted to absorption
  - coefficients using the following equation:

20

$$a(\lambda) = \ln(10) \cdot A(\lambda) / L, \qquad (4)$$

where A is the absorbance of the sample,  $\lambda \lambda$  is the wavelength, L is the path length of cuvette (0.01 m), and a is the absorption coefficient (m<sup>-1</sup>). The abundance of CDOM is presented by the absorption <u>coefficients\_coefficient</u> at 280 nm (a<sub>280</sub>) (Zhang et al., 2010).

The spectral slope between 275-295 nm ( $S_{275-295}$ ) was determined <u>both</u> by a linear

regression between logarithmic absorbance<u>fit</u> and <u>wavelengths since</u><u>an exponential fit</u>. <u>The exponential fit was performed as Eq. (5) (Twardowski et al., 2004):</u>

	$\underline{\qquad}a(\lambda) = a(\lambda_r)e^{-S(\lambda-\lambda_r)}, \tag{5}$
	where the correlation $\underline{a}(\lambda_r)$ is the absorption coefficient at a reference wavelength $\lambda_r$ , S
5	is the spectra slope. The variation of these two fitting methods was approximately 3%
	on average. Finally, linear fit was adopted due to the higher fitting coefficients were
	higher than that of the exponential fit. If. Additionally, if the difference in S275-295
	between the linear and exponential regressionsmethods was higher than 10%, indicating
	a high uncertainty for absorption measurement, such data were removed. The
10	absorption Ångström exponents (AAEs, from 240exponent (AAE) is used to 550
	mm)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). The AAEs were
	calculated using power-law fit-from Eq. (5), as follows:

15 —  $a(\lambda) = K \cdot \lambda^{-AAE}$ , (5 (6)

where a is the absorption coefficient (m<sup>-1</sup>), K is a constant and  $\lambda\lambda$  is the wavelength (from 240 to 550 nm). The R<sup>2</sup> of all the fits (S<sub>275-295</sub> and AAE) were higher than 0.9 and most of them were higher than 0.95.

Because the light absorption within the visible wavelengths of some samples were

20 too low to be measured bybelow the detection limit of the spectrometer, 19 of 39 samples were available for the calculation of AAE.

Furthermore, the "left" samples of sitesites 51b and 58, which showed abnormal

absorption and fluorescence spectra compared to the other samples, and were supposed to be contaminated, and hence, thereby these two samples were not used in the absorption and fluorescence analyses.

### 2.4 Soluble ions

- 5 The major soluble ions of surface snow water samples were analyzed with an ion chromatograph (Dionex, Sunnyvale, CA, USA) using an AS11 column for the anions  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $Cl^-$ , and  $F^-$  and a CS12 column for the cations  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and NH<sub>4</sub><sup>+</sup>. The soluble ions showed no obvious differences between filtered and unfiltered samples (Pu et al., 2017). In addition, the concentration of non-sea-salt K<sup>+</sup>
- $(nss-K^{+})$  was corrected by  $Mg^{2+}$  (a sea salt indicator) using the following formula (Tao 10 et al., 2016): According to Pio et al. (2007), the  $K^+$  can be separated into three fractions: sea salt (ss), dust and others (the fraction not related to sea salt and mineral dust, nssndust). The nss-ndust- $K^+$  is a good maker for biomass burning (Pio et al., 2007). The Ca<sup>2+</sup>concentrations of our samples were mostly larger than that of Na<sup>+</sup>, leading to much larger mass ratios of  $Ca^{2+}/Na^{+}$  than that in sea water (0.038) (Pio et al., 2007). 15 Therefore,  $Ca^{2+}$  is dominated by the dust fraction and not corrected to nss- $Ca^{2+}$  in this study. nss-ndust- $K^+$  is calculated using the following formulas (Pio et al., 2007):

$$nss - K^{+} = -K^{+} - 0.159 Mg^{2+}.$$
(6)  

$$nss - ndust - K^{+} = -K^{+} - ss - K^{+} - dust - K^{+},$$
(6)  

$$ss - K^{+} = 0.038 \times ss - Na^{+},$$
(7)  

$$ss - Na^{+} = -Na^{+} - 0.14 \times Ca^{2+},$$
(8)

$$\underline{s} - Na^{\dagger} = Na^{\dagger} - 0.14 \times Ca^{2^{\dagger}}, \qquad (8)$$

In Eq. (7), 0.038 is the mass ratio of  $K^+/Na^+$  in the sea water (Pio et al., 2007). In Eq. (8), the lowest mass ratio of  $Na^+/Ca^{2+}$  of our samples (0.14) is used to evaluate the dust fraction of  $Na^+$ . Similarly, the lowest mass ratio of  $K^+/Ca^{2+}$  (0.028) is used in Eq.

5 (9) to calculate the dust fraction of  $K^+$ .

#### 2.5 Hierarchical cluster analysis

A hierarchical cluster analysis was used to classify the CDOM in snowsamples based on the relative abundances of three PARAFAC components. Euclidean distance was used to estimate the distances between samples, and. Before determining the

- 10 unweighted average distance was chosen for<u>clustering method</u>, the hierarchical cluster analysis by comparing the multiplecophenetic correlation coefficients for the <u>cluster</u> trees created by different methods were calculated, including unweighted average, weighted average, centroid, farthest neighbor, shortest neighbor, weighted center of mass and Ward's <u>distance.methods</u>. Finally, the unweighted average method was
- 15 <u>chosen due to the highest correlation coefficients.</u> A total of four clusters were determined and labeled <u>as</u> clusters A-D.

# 2.6 Active fire data and air Air mass backward trajectories and active fire data

Active fire data (MCD14DL) from Moderate Resolution Imaging Spectroradiometer (MODIS) Collection 6 were used to capture potential fire source distributions. <u>Air mass</u>

20 <u>backward trajectory has been widely used to identify the sources of air pollution (Stein</u> et al., 2015), and also successfully applied to the studies of impurities in snow (Hegg et al., 2010; Wang et al., 2015; Zhang et al., 2013). In this study The data are available online: http://carthdata.nasa.gov/firms.-To further analyze the potential sources of CDOM, 72-h air mass backward trajectories were conducted by the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, http://ready.arl.noaa.gov/HYSPLIT.php)) model (version 4<del>).</del>, http://ready.arl.noaa.gov/HYSPLIT.php). The model was run at 500 m above ground level four times a day for a period of 30 days preceding the sampling date at a given site. Combined with the satellite fire location map, the backward trajectories pass through the fires can be identified as the sources of biomass burning particles to the

10 receptor sites (Antony et al., 2014; Hegg et al., 2010; Zhang et al., 2013). We used the active fire data from the Moderate Resolution Imaging Spectroradiometer (MODIS) Collection 6 (MCD14DL) and the Visible Infrared Imaging Radiometer Suite (VIIRS) (VNP14IMGTDL\_NRT) to capture potential fire location distributions. The data are available online: http://earthdata.nasa.gov/firms.

## 15 **3 Results and discussion**

5

### 3.1 The absorption characteristics of CDOM (a<sub>280</sub>, S<sub>275-295</sub> and AAE)

The distributions of  $a_{280}$  and  $S_{275-295}$  are shown in Fig. 3. and the corresponding values are summarized in Table 1.  $a_{280}$  ranged widely from 0.15 to 10.57 m<sup>-1</sup> with an average of  $1.69 \pm 1.80$  m<sup>-1</sup>. The highest value appeared at site 67 (10.57 m<sup>-1</sup>), followed

20 by sites 53, 79 and 47 (5.25 m<sup>-1</sup>, 3.13 m<sup>-1</sup> and 3.11 m<sup>-1</sup>, respectively). Most of these samples were collected from the snow drifts<u>-under strong wind.</u> These values were

higher than the  $a_{280}$  of snow, ice and cryoconite CDOM on the Tibetan Plateau (typically lower than 2.0 m<sup>-1</sup>;-) (Feng et al., 2016, 2017). The lowest value was found at site 66 (0.15 m<sup>-1</sup>), followed by sites 70, 82, 73, and 83 (0.21 m<sup>-1</sup>, 0.23 m<sup>-1</sup>, 0.30 m<sup>-1</sup>, and 0.31 m<sup>-1</sup>, respectively), and these values were compared to the absorption of soluble

- 5 light-absorbing species in <u>Alaskan</u> snow-at Alaska with typical values of 0.1-0.15 m<sup>-1</sup> at 250 nm (Beine et al., 2011). Some of these samples comprised freshly fallen snow and some were collected at remote sites in northern Xinjiang, which that were far from pollution sources (Pu et al., 2017). The values of  $S_{275-295}$  ranged from 0.0129 to 0.0389 nm<sup>-1</sup> with an average of 0.0243 ± 0.0073 nm<sup>-1</sup>.  $S_{275-295}$  is never reported in the
- 10 terrestrial snow and ice samples before, but is widely measured in the aquatic environments. For example, Hansen et al. (2016) summarized the values of  $S_{275-295}$ for oceanic and terrestrial systems, and the values range from of 0.020-0.030 nm<sup>-1</sup> for ocean, 0.010-0.020 nm<sup>-1</sup> for coastal water, and 0.012-0.023 nm<sup>-1</sup> for terrestrial river systems. The wide range of  $S_{275-295}$  indicates in this study covered the typical values
- 15 <u>in different types of natural water bodies, indicating</u> complex <u>compositions and</u> sources of CDOM in seasonal snow across northwestern China. Furthermore, as shown in Fig. 4,  $S_{275-295}$  decreases logarithmically with increasing  $a_{280}$  ( $R^2 = 0.586$ , p<0.001). As presented by Helms et al. (2008), lower  $S_{275-295}$  values correspond to terrestrial and higher molecular weight CDOM. Therefore, the higher  $a_{280}$  values of our samples may
- 20 be due to greater inputs of terrestrially derived CDOM with high molecular weights, such as HULIS (Zhou et al., 2013). Similar negative relationships between absorption coefficients and S<sub>275-295</sub> was also found in estuarine (Asmala et al., 2012) and marine

water (Zhou et al., 2013). The AAEs of 19 CDOM samples are also shown in Table 1-The values, which ranged from 4.41–8.91 with an average of  $5.55\pm1.11$ . This value is comparable with the average AAE of HULIS (6.11, from 300 to 550 nm), the major CDOM species in snow (Beine et al., 2011), extracted from Alaskan snow (6.11, from

5 <u>300 to 550 nm</u>) (Voisin et al., 2012).

The detailed results of each region are discussed below. Region 1 (sites 47-52) is located in the eastern Tibetan Plateau-in Qinghai province, which is typically higher than 4000 m above sea level. In this region, the snowpack was usually patchy and thin (Fig. 2a). During windy time, local soil can be blown and deposited on the snow surface,

- 10 this which had been observed by previous studies (Pu et al., 2017; Ye et al., 2012), and). Moreover, the filters for samples in this region were in yellow color due to high loading of soil <u>dust</u>. The average  $a_{280}$  was highest among all five regions (2.30±0.52 m<sup>-1</sup>), and the S<sub>275-295</sub> fell in the range of 0.0170–0.0212 nm<sup>-1</sup> (mean: 0.0188±0.0015 nm<sup>-1</sup> on <u>average)</u>. The lowest regional average and slight variation of S<sub>275-295</sub> clearly
- 15 indicates<u>which shows</u> the <u>similar values of leaching for permafrost on the Tibetan</u> <u>Plateau (Wang et al., 2018).</u> dominant contribution of a terrestrial source (e.g., local soil) to snow CDOM (Fichot and Benner, 2012; Helms et al., 2008).\_

RegionIn region 2 (sites 53-59, 61, and 79) is along the Tianshan Mountains. Within this region, ), snow at some sites was patchy (e.g., sites 53, 57, 61 and 79, Fig. 2b) and

some sites were farmland (e.g., sites 55 and 56) (, Fig. 2c), which <u>all</u> can be influenced by local <u>soil due to strong wind or agriculture activities (e.g., crop and grass burning).</u>
 The snow at some other sites (e.g., sites 53, 57 and 79) was patchy (Fig. 2b), and

blowing soil have been an important source of CDOM. Thus, the  $a_{280}$  values of these sites (were in the range of 1.66-5.25 m<sup>-1</sup>) were higher than those at the other. Several sites in this region showed lower  $a_{280}$  (0.41-0.54 m<sup>-1</sup>) with high snow coverage rates, e.g., sites 54, 58 and 59), might resulting from new fallen snow or long distances from human activities (high altitude) (e.g., sites 54, 58 and 59). Overall, region 2 showed a high average  $a_{280}$  (2.00±1.50 m<sup>-1</sup>), and the average  $S_{275-295}$  was 0.0229±0.0073 nm<sup>-1</sup>.

5

Region 3 (sites 60, 62, 63 and 80-84) is located to the northmost developed part of the Tianshan MountainsXinjiang, and close to the major industrial city belt in central

- 10 Xinjiang. Hencecities are located here (e.g., Urumqi, Shihezi, Kuytun and Karamay). Therefore, human activities may dominate the contribution of CDOM in snow in this region. However, the  $a_{280}$  values were mostly less than 1.0 m<sup>-1</sup> except for at sites 60 and 84, and the average value was low ( $0.93 \pm 0.68 \text{ m}^{-1}$ ). Because samples of these sites were almost new fallen snow, the deposition of pollutants to the snowpack can be quite
- 15 slight. Sites 60 and 84 were both close to industrial cities (Fig. 1 in Pu et al., (2017)), and the transportation and deposition of locally anthropogenic pollutants may be responsible for the high  $a_{280}$  (2.39 m<sup>-1</sup> and 1.65 m<sup>-1</sup>, respectively). The average  $S_{275-295}$  was  $0.0218\pm0.0057$  nm<sup>-1</sup> and was comparable to that in this region -2.

Region 4 (sites 64-71) is located in northwestern Xinjiang. In this region, the snow
 depth increased from south to north. At sites 64-67, the snow was thin due to the low
 snowfall in sample year (Ye et al., 2012). TheIn region 4 (sites 64-71), the maximal and
 minimal a<sub>280</sub> values of the entire campaign, 10.57 m<sup>-1</sup> (site 67, snow drift, Fig. 2e) and

0.15 m<sup>-1</sup> (site 66, new snow), were found in this area. Sites 68-71, which were the northmost sites during this campaign, were far from industrial areas, and the snow depth and coverage rate were high, which led to low  $a_{280}$  values.<u>here.</u> Generally, the  $a_{280}$  was in the range of 0.5-2.0 m<sup>-1</sup> with an average of  $0.80\pm0.62$  m<sup>-1</sup> (excluded site 67),

5 which was the lowest compared to the values in the other four regions. The mean value of  $S_{275-295}$  (0.0255±0.0060 nm<sup>-1</sup>) was higher than that in regions 2 and 1-3. The low  $S_{275-295}$  of site 67 (0.0169 nm<sup>-1</sup>) suggested a strongly terrestrial input of CDOM.

RegionIn region 5 (sites 72-78) is located in northeastern Xinjiang along the border of China. Thethe average value of  $a_{280}$  was  $1.17\pm0.63$  m<sup>-1</sup>, which was intermediate

10 among five regions. However, the The  $S_{275-295}$  was typically higher than 0.0300 nm<sup>-1</sup> with an average of  $0.0324 \pm 0.0060$  nm<sup>-1</sup>. These values indicated that non-terrestrial sources were dominant for snow CDOM in this region This value was highest among five regions.

## 3.2 The fluorescence characteristics of CDOM

### 15 **3.2.1 PARAFAC components**

20

The EEMs of snow water samples were analyzed by PARAFAC <u>model</u>, and three separate fluorescent components (C1-C3) were identified (Fig. <u>4).5a-c</u>). Figure 5d-f present the <u>The</u> corresponding excitation and emission loading spectra of each component is shown in the Supplement as Fig. S2. The excitation/emission (Ex/Em) wavelengths of each component's fluorescence peaks are summarized in Table 2. The spectral characteristics of three components in this study are similar to the fluorophores

identified in aquatic environments in previous studies (Stedmon and Markager, 2005a; Stedmon et al., 2003; Zhang et al., 2010, 2011).

C1 showed a primary peak at <240/453 nm for Ex/Em, which was similar to the component 1 reported by Stedmon and Markager (2005b)2005a). (Ex/Em = <250/448). This kind of fluorophore absorbs light mainly in the UVC band and shows a broad emission peak, andwhich is usually identified as terrestrial CDOMFDOM (Stedmon et al., 2003). However, in our study, The appearance of a secondary peak was also presented at longer excitation wavelength (Ex/Em = 305/453 nm). The appearance of an

excitation peak at longer wavelengths) may indicate that C1 is more aromatic and has

5

20

- 10 higher molecular weight (Coble et al., 1998). C1 also resembled another terrestrial fluorophore, namely, component 4 in Stedmon and Markager (2005a2005b) (Ex/Em = <250,-(360/)/440), which has been widely found in nature fresh water environments and even water-extracted organic matter in aerosols (Chen et al., 2016b2016; Mladenov et al., 2011; Zhang et al., 2009; Zhao et al., 2016). C1 in our study showed blue shifted</p>
- 15 excitation wavelengths, which likely corresponded to a lower molecular weight (Coble et al., 1998).

C2 had a primary (secondary) peak at <240(300)/393 nm (Ex/Em), namely, peak M, thatwhich was first measured in the oceanic system by Coble (1996). Hence, this component is usually identified as marine HULIS. However, the marine sources of CDOM can be nearly ignored in this study because the sample sites were several thousand kilometers away from the ocean. Subsequently, Stedmon et al. (2003) found a similar fluorophore (component 4 therein) that showed terrestrial source in a terrestrially dominated estuary region. The subsequent<u>following</u> studies suggested that the C2-like component is also linked to microbial activity and phytoplankton degradation in natural aquatic systems (Yamashita et al., 2008; Zhang et al., 2009) or DOM in wastewater from anthropogenic sources (Stedmon and Markager,

5 <u>2005a2005b</u>).

C3 is a typical fluorophore that is categorized as tyrosine-like CDOMFDOM and that exhibits Ex/Em pairs of <240(270)/315 nm. C3 reflects autochthonously labile CDOMDOM produced by biological processes (Stedmon et al., 2003) and has been commonly reported in previous studies of natural water bodies and the water extraction

of aerosols (Chen et al., 2016b2016; Murphy et al., 2008; Stedmon and Markager,
 2005b2005a).

To analyze the mutual relationships between three components, linear correlation analyses were conducted (Fig. 6). The F<sub>max</sub> values of C3 at site 67 were much higher than those of any other sample (shown as red markers in Fig. S3), which can strongly influence the results of the correlation analysis. When excluding the data of site 67, the R<sup>2</sup>-between F<sub>max</sub>(C1) and F<sub>max</sub>(C3) fell from 0.316 to 0.082, and the linear relationship became nonsignificant (Fig. S3). Therefore, we chose to use the dataset that excludes site 67 in the analysis, and the results are shown below. F<sub>max</sub>(C1) and F<sub>max</sub>(C2) exhibited a significant and positive correlation (R<sup>2</sup> = 0.332, p<0.001); however, this value was much lower than that in previous studies of natural water, for instance, R<sup>2</sup> = 0.63 for

inland lakes (Zhao et al., 2016) and  $R^2 = 0.88$  for inland rivers (Zhang et al., 2011). This result indicated that two humic-like components might only share partially common

sources. The relationships between the two humic-like components and the protein-like component are quite different. Not surprisingly,  $F_{max}(C1)$  and  $F_{max}(C3)$  showed no correlation ( $R^2 = 0.082$ , p>0.05), while a significant linear relationship ( $R^2 = 0.364$ , p<0.001) was found between  $F_{max}(C2)$  and  $F_{max}(C3)$ , which implied a potential

5 microbial source for C2, consistent with the finding of Yamashita et al. (2008).

### **3.2.2 Regional variation in PARAFAC components**

Figure 7<u>5</u> shows the <u>relative intensities variations</u> of <u>the</u> three <u>fluorescencefluorescence</u> fluorescent components at each site, <u>among regions</u>, including the intensities and <u>Table 3 exhibits</u> the regional average of the relative <u>intensity and  $F_{max}$  for each component</u> contributions.

- 10 Overall, C2 was the most intense fluorophore and accounted for 42% on average of the total fluorescence intensity of all samples, followed by C3 (38% on average) and C1 (20% on average). Compared to glacial snow and ice samples, which were dominated by protein-like substances (Dubnick et al., 2010; Feng et al., 2016), the seasonal snow samples in this study showed fewer microbial characteristics. According to Thieme et
- 15 al. (2016), although we might underestimate the %C1 (approximately -3%) and overestimate the %C2 (approximately +6%) due to the preservation artifacts, it only slightly changes the results showed here.

In Qinghai (region 1), the most obvious feature was that C1 accounted for approximately 35% of the total fluorescence intensity <u>on average</u>. This value was significantly higher than the other regions. As mentioned in Sect. 3.1, the snowpack of these sites was strongly influenced by the local soil, hence clearly implying that C1 was mainly from the soil HULIS. This finding confirmed the constantly terrestrial source of the C1-like fluorophore, regardless of whether the sample was collected from natural water bodies, aerosol water extraction or snow. The relative contribution of <u>In</u> <u>contrast, %</u>C3 (the protein-like component) in region 1 was much lower than that in

5 other regions.quite low (24% on average). This result was mainly due to the high  $F_{max}(F_{max}(C1))$  in region 1 since the regional variation of  $F_{max}(F_{max}(C3))$  was slight (Table 3Fig. 5).

In Xinjiang, the relative intensity of <u>(regions 2-5)</u>, %C1 varied by region, while %C2 and %C3 accounted for were roughly equal contributions. In region 2, the

- 10 relative contribution of <u>%</u>C1 was <u>also</u> high (25% on average), which implied a substantial amount of CDOM originating from local soil. In). However, <u>%C1 showed</u> the lowest value (9% on average) in region 3, where most of the samples were new fallen snow (7 of 8 sites), the CDOM showed much fewer terrestrial characteristics as demonstrated by the lowest relative intensity of C1 (9% on average).). The great
- 15 difference between relative contributions of <u>%</u>C1 and <u>%</u>C2 in this region indicated that the<u>different</u> sources of these two humic-like components-were different. In regions 4 and 5, the contributions of <u>%</u>C1 (both were approximately 17%) were nearly double <u>of</u> that in region 3. As the snow samples collected in northern Xinjiang were more aged than those in region 3, the deposition of soil was more significant, which led to a higher

## 20 C1 fraction. (both were approximately 17%).

At <u>sitesites</u> 54 and 82, the <u>fractional intensityrelative abundance</u> of C3 exceeded 70%. This value was approximately twofold higher than the average of <u>all samples.the</u> whole <u>dataset (38%).</u> This result can be explained by two possible reasons, (1) lower inputs of C1 and C2-were present at these sites, and (2) much-greater microbialbiological activities were available in the snowpack at <u>these</u> sites <u>54</u> and <u>82</u>. We found <u>algal</u> <u>communitieslichens</u> near the samplethese two sites (Fig. <u>S4S3</u>), providing evidence for

5 the latter reason.

At site 67, the fluorescence intensities of C1, C2 and C3 were all highest among all samples (0.30 RU, 0.39 RU, and 0.38 RU for C1, C2, and C3, respectively), especially for C3. The average intensity of  $F_{max}$  (C3 for samples excluding site 67) was 0.10 RU, (excluded site 67), with a low standard deviation of 0.02 RU, and this value was

10 approximately one-fourth of that at site 67. Therefore, rather than owing to microbial activity alone, the extremely high  $F_{max}(F_{max}(C3))$  of site 67 may be due to other sources, for instance, some organic compounds released from diesel combustion may show similar spectra (Mladenov et al., 2011).

To assess the similarities and differences between samples from different regions, a 15 hierarchical cluster analysis based on the relative intensities of three fluorescencefluorescent components was conducted (Fig. <u>86</u>). The snow samples were separated into four clusters (clusters A-D) (Fig. <u>S5S4</u>). Samples classified into clusters A and B were dominant. The high relative contribution of <u>%</u>C1, which was 34% on average, was the most remarkable feature of cluster A and led to a low relative abundance of %C3 (26% on average) (<u>Table S1Fig. S4</u>). All samples in region 1 and

20 abundance of %C3 (26% on average) (Table S1Fig. S4). All samples in region 1 and most samples in region 2 were assigned to cluster A. For cluster B, the contribution of %C1 was low (13% on average), and the abundance of %C3 (47% on average) was slightly higher than that of <u>%</u>C2 (40% on average). For sites in northern Xinjiang (regions 4 and 5), most samples were classified into cluster B. The samples assigned to cluster C, including those of sites 60, 62, 69, 72, 76 and 84, showed dominant contributioncontributions of C2 (57% on average). Half of these samples were found in

- 5 region 3, and the others were dispersed in regions 4 and 5. Pu et al. (2017) analyzed the concentrations and sources of ILAPs in snow in the same field campaign. They found that the dominant source of ILAPs at these sites was industrial pollution. This result indicates that the humic-like fluorophore C2 may partly originate from anthropogenic pollution. Cluster D contained only two samples from sites 54 and 82. The difference
- 10 between cluster D and <u>the</u> others was an extremely high relative contribution of proteinlike component C3 (73% on average), which indicated the high bioavailability of snow CDOM-there.

#### 3.2.3 Fluorescence-derived indices

The valuesregional variations of the three established fluorescence-derived indices for
surface snow samples are shown in Fig. 9. The regional average7 and the values of each
site are shown in Table 41. The HIX of samples in this study fell into the range of 0.163.20 with an average of 1.21±0.78. The highest average HIX appeared in region 1 (2.21
±0.42), which was highly consistent with the low S<sub>275-295</sub> and high relative intensity
of C1 and further demonstrated the large terrestrial contribution in this
region.demonstrating high degree of humification of snow CDOM. The lowest average
HIX was found in region 3 (0.62±0.37 on average), which suggests that the CDOM

was fresh. This finding is easily explained <u>asby</u> the <u>fact that nearly all of</u> snow samples in this region were <u>nearly from</u> new fallen snow. Compared to the HIX of other types of samples (Table <u>53</u>), the HIX of snow across northwestern China was higher than that of spring water (Birdwell and Engel, 2010); comparable to cryoconite in glaciers from

- 5 the Tibetan Plateau (Feng et al., 2016), inland lakes (Zhang et al., 2010), cave water (Birdwell and Engel, 2010) and north Pacific Ocean water (Helms et al., 2013); and was lower than cave water (Birdwell and Engel, 2010), estuarine water (Huguet et al., 2009), fog water (Birdwell and Valsaraj, 2010), groundwater (Huang et al., 2015), water extraction of alpine aerosol (Xie et al., 2016) and urban aerosol (Mladenov et al., 2011).
- 10 According to McKnight et al. (2001) and Huguet et al. (2009), the values of  $\underline{FI} > 1.9$ or BIX > 1.0 or  $\overline{FI} > 1.9$  indicate microbially derived DOM. The values of BIX and FI for the snow samples were typically below 1.0 and 1.9, respectively, implying unremarkably autochthonous characteristics. The regional distributions of BIX and FI corresponded with that of HIX. The samples with highest average BIX and FI were in
- 15 region 3 (0.93±0.25 and 1.60±0.15, respectively), and the samples in region 1 exhibited the lowest average values of BIX and FI (0.49±0.05 and 1.29±0.05, respectively). The BIX and FI of different types of samples changed little, and the only exception was the FI of cryoconite in glaciers from the Tibetan Plateau (3.24, Feng et al., 2016), which was approximately twice as high as those of the other samples.

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### **3.3 Correlation between light absorption and fluorescence properties.**

The relationships between the  $a_{280}$  and  $F_{max}$  of each component and the fluorescencederived indices are shown in Fig. 10. Similar to Fig. 6, we used the dataset excluding site 67 in the analysis, and the comparisons with the results using the entire dataset are shown in Fig. S6. The  $F_{max}(C1)$  exhibited a strong and positive linear relationship with  $a_{280}$  ( $R^2 = 0.938$ , p<0.001), while the correlation coefficients between  $a_{280}$  and  $F_{max}(C2)$  ( $R^2 = 0.464$ , p<0.001),  $F_{max}(C3)$  ( $R^2 = 0.152$ , p<0.05) were much lower. These

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results suggested that the variation of CDOM in northwestern China seasonal snow was mainly controlled by terrestrially derived HULIS. This finding is different from those results found for inland lakes and rivers (Zhang et al., 2010, 2011; Zhao et al., 2016),

10 in which the correlations between CDOM absorption and C1- and C2-like fluorophores were comparable and both strong.

The relationships between a<sub>280</sub> and the three fluorescence derived indices are also shown (Fig. 10d-f). The results showed considerable similarity to that between a<sub>280</sub> and F<sub>max</sub>. a<sub>280</sub> and HIX exhibited a significant and positive correlation (R<sup>2</sup> = 0.828, p<0.001). This result suggested that the CDOM abundance in northwestern China seasonal snow increases with the degree of humification. Negative log-log correlations were found between a<sub>280</sub> and BIX (R<sup>2</sup> = 0.269, p<0.001), FI (R<sup>2</sup> = 0.547, p<0.001), which indicates that a higher CDOM abundance corresponds to higher terrestrial inputs. The AAE of CDOM also showed a significant correlation with the fluorescence-

20 derived indices (Fig. S7). HIX was negatively and linearly correlated with AAE (R<sup>2</sup> = 0.396, p<0.005), indicating that the AAE can decrease with the increasing humification degree of snow CDOM, which can be characterized by the higher aromaticity (Bayer

et al., 2000). This result was consistent with a study of BrC in aerosol from the Los Angeles Basin (Zhang et al., 2013). They suggested that compared to water-soluble BrC, the lower AAE of methanol-extracted BrC can be explained by the higher aromaticity of insoluble organic components. In contrast, positive correlations were found between AAE and BIX ( $R^2$  = 0.814, p<0.001) and FI ( $R^2$  = 0.463, p<0.005), which implied that the microbial-derived CDOM has a higher AAE than terrestrial CDOM.

#### 3.4 Source distributions of CDOM

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As discussed in Sect. 3.2.1, C2 shared partially common sources with C1 and C3, which represented soil and microbial origins, respectively. Furthermore, the F<sub>max</sub>(C2) and F<sub>max</sub>(C3) varied slightly among regions, while the variation of F<sub>max</sub>(C1) was dramatic (Table 3). This phenomenon clearly reflected that the HULIS fluorophore C2 may originate from sources besides soil and microbial activity. To further analyze the potential sources of PARAFAC components, the correlation coefficients between three major ions and F<sub>max</sub> of fluorescence components were calculated. The results are shown
 in Table 6. F<sub>max</sub>(C2) showed a significant and positive correlation with three ions

- (p<0.001). The secondary ions SO<sup>2</sup>/<sub>4</sub> and NO<sup>-</sup>/<sub>3</sub> are commonly considered as the markers of anthropogenic emissions from the burning of fossil fuel, such as oil and coal (Doherty et al., 2014; Oh et al., 2011; Pu et al., 2017), and nss K<sup>+</sup> is widely used as a tracer of biomass burning (Tao et al., 2016). Therefore, C2 may also originate from anthropogenic pollution and biomass burning; in other words, there were two additional
- potential sources of snow CDOM in this study. Since the contribution of microbial-

derived C3 to a<sub>280</sub> was low (Fig. 10c), three major sources of snow CDOM were identified, namely, soil, biomass burning and anthropogenic pollution. The regional variations of CDOM sources are discussed below using analyses of chemical species and air mass backward trajectories. In addition, the sources of CDOM in snow are also

5 compared with those of particulate light absorption of ILAPs.

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In Qinghai (region 1), the backward trajectories to a typical site (site 47, Fig. 11a) were mostly from the west, and very few fire locations were encountered. Combined with the low ratio of  $(SO_4^2 + NO_3^2)/nss - K^{\pm}$  (Fig. 12), the CDOM produced by biomass burning and anthropogenic pollution is negligible in region 1. As mentioned in Sect. 3.1, the snowpack in Qinghai was strongly influenced by local soil, and hence, the soil HULIS was clearly the primary source of CDOM. In region 2, the contribution of soil to CDOM was also significant, which was confirmed by the high relative intensity of C1, as discussed in Sect. 3.2.2. For the results of the backward trajectories, along the

paths of the air masses to site 55 in region 2 (Fig. 11b), the local fire spots due to the

agricultural activities could also be important contributors to snow CDOM. Additionally, the value of (SO<sup>2</sup>/<sub>4</sub>+NO<sup>-</sup>/<sub>3</sub>)/nss-K<sup>±</sup> was also low in region 2, which indicated an insignificant role of anthropogenic pollution. Therefore, in region 2, a mixed source of soil and biomass burning is reasonable. In region 3, the extremely high ratio of (SO<sup>2</sup>/<sub>4</sub>+NO<sup>-</sup>/<sub>3</sub>) to nss K<sup>±</sup> implied a strong contribution of anthropogenic pollution to snow CDOM. Additionally, the mass ratio of Cl<sup>-</sup> and Na<sup>+</sup> (2.48, Fig. S8) was also significantly higher than that in sea water (1.18, Hara et al., 2004), which indicated that Cl<sup>-</sup> might originate from other sources in addition to sea salt, such as coal

combustion (Wang H. L. et al., 2008; Wang Y. et al., 2006), while the values in other regions were comparable to 1.18. These results, again, confirmed that the CDOM from anthropogenic pollution was dominant in region 3 but inapparent in other regions. The backward trajectories also showed consistent results (Fig. 11c). Most of the trajectories to site 84 came from the northwest and passed through the cities with heavy industry (e.g., Karamay and Shihezi). Therefore, air pollutants can be transported to the sample area and deposited in the surface snow. In region 4, the ratios of  $(SO_4^2 + NO_3^2)$  to  $nss K^+$ were much lower than those in region 3, and the air masses originated from Siberia (Fig. 11d and e), where significant crop and grass burning take place (Hegg et al., 2010),

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- 10 strongly influenced this region. In region 5, the value of (SO<sup>2-</sup>+NO<sup>-</sup><sub>3</sub>)/nss-K<sup>+</sup> was comparable with that in region 4, which suggested CDOM from biomass burning rather than pollution. Although the backward trajectories were more dispersive (Fig. 11f), the amount of air mass from the Siberia was also respectable which can explain this finding. Furthermore, the low mass ratios of Cl<sup>-</sup> and Na<sup>+</sup> in region 4 and 5 also implied the slight
- 15 influence of anthropogenic pollution. Overall, biomass burning was the dominant source of CDOM in snow in both regions 4 and 5.

Pu et al. (2017) identified the potential sources of particulate light absorption of ILAPs (denoted as  $C_{BC}^{max}$ ) in snow during the same field campaign, using a positive matrix factorization (PMF) model. The comparison of  $C_{BC}^{max}$  and  $a_{280}$  among regions

20 is shown in Fig. S9. In regions 1 and 5, there were no correlation between  $C_{BC}^{max}$  and  $a_{280}$ , which indicated entirely different sources of CDOM and particulate absorption of ILAPs. As reported by Pu et al. (2017), the dominant sources of  $C_{BC}^{max}$  were biomass

burning and industrial pollution in regions 1 and 5, respectively, while those of CDOM were soil and biomass burning in our study. Much higher correlation coefficients were found in regions 2-4 ( $R^2 = 0.72$ , 0.95 and 0.81, respectively), especially for region 3, which implied consistency for sources of CDOM and particulate absorption of ILAPs.

5 The relative weaker relationship presented in region 2 may have resulted from the mixed sources of CDOM (soil and biomass burning); however, biomass burning was the primary source for particulate absorption of ILAPs.

# 3.3 Source attribution of CDOM

### 3.3.1 Source identification of PARAFAC components

- In Qinghai, As mentioned in Sec. 3.1, the snow packs were strongly influenced by the local soil dust, which was confirmed by the lowest average S<sub>275-295</sub>, leading to a high %C1 (35% on average). This result implied that the terrestrial fluorophore C1 was mainly from the soil HULIS, and confirmed the invariably terrestrial source of the C1-like fluorophores, regardless of whether in the natural water bodies, aerosol water
- 15 <u>extraction or snow.</u>

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Correlation analyses were conducted to assess the potential sources of C2. The mutual relationships between PARAFAC components were shown in Fig. 8. The  $F_{max}(C3)$  of site 67 were much higher than those of any other sample (shown as red markers in Fig. 8), which can strongly influence the results of the correlation analysis. When excluding the data of site 67, the R<sup>2</sup> between  $F_{max}(C1)$  and  $F_{max}(C3)$  fell from 0.316 to 0.082, and the linear relationship became nonsignificant (Fig. 8b). Therefore, we used the dataset that excludes site 67 in the analysis, and the results are shown below.  $F_{max}(C1)$  and  $F_{max}(C2)$  exhibited a significant and positive correlation ( $R^2 = 0.332$ , p<0.001); however, this value was much lower than those in previous studies of natural water, for instance,  $R^2 = 0.63$  for inland lakes (Zhao et al., 2016) and  $R^2 = 0.88$  for inland rivers (Zhang et al., 2011). This result indicated that soil dust only partly accounted for the source of C2. Meanwhile, a significant linear relationship ( $R^2 = 0.364$ ,

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p<0.001) was found between  $F_{max}(C2)$  and  $F_{max}(C3)$ , which implied a potential microbial source for C2, consistent with the finding of Yamashita et al. (2008). Not surprisingly,  $F_{max}(C1)$  and  $F_{max}(C3)$  showed no correlation ( $R^2 = 0.082$ , p>0.05).

- 10 Furthermore, the correlation coefficients between  $F_{max}$  and three major ions were calculated. The results are shown in Table 4.  $F_{max}(C2)$  showed significant and positive correlations with three ions (p<0.001). The secondary ions  $SO_4^{2-}$  and  $NO_3^{-}$  are commonly considered as the markers of anthropogenic emissions from the burning of fossil fuel, such as oil and coal (Doherty et al., 2014; Oh et al., 2011; Pu et al., 2017),
- 15 and nss-ndust-K<sup>+</sup> is a good tracer of biomass burning (Pio et al., 2007). Therefore, C2 may also originate from anthropogenic pollution and biomass burning. Overall, there are four potential sources of snow CDOM in our study, since the contribution of microbial-derived C3 to a<sub>280</sub> was low compared to C1 and C2 (Fig. S5), three major sources were identified, i.e., soil dust, biomass burning and anthropogenic pollution.
- 20 The ratios of intensities for PARAFAC components can be a useful tool to trace the <u>CDOM sources (Murphy et al., 2008). In this study, the ratio of  $F_{max}(C2)$  and  $F_{max}(C1)$ </u> was applied to assess the relative contributions of soil and non-soil (biomass burning

and anthropogenic pollution) sources for snow CDOM (Fig. 9a). An analysis of variations (ANOVA) was used to test the differences among regions. Regions 1 and 2 showed low ratios of  $F_{max}(C2)$  and  $F_{max}(C1)$  (1.20±0.14 and 1.76±0.82 on average, respectively), indicating the strong influence from local soil dust. The values of

5  $F_{max}(C2)/F_{max}(C1)$  for regions 3, 4 and 5 were significantly higher (ANOVA, p<0.05) with averages of  $5.57\pm2.26$ ,  $3.17\pm1.47$  and  $3.02\pm1.22$ , respectively. This result implies that the snow CDOM in these regions were different from those in regions 1 and 2, and mainly from the non-soil sources.

# **3.3.2 Regional variations**

10 The regional variations of CDOM sources are discussed below using analyses of absorption and fluorescence characteristics, chemical species, and air mass backward trajectories. In addition, the sources of CDOM in snow are also compared with those of particulate light absorption of ILAPs.

In Qinghai (region 1), the lowest regional average and slight variation of S<sub>275-295</sub>
 indicated the dominant contribution of terrestrial sources for snow CDOM (e.g., local soil dust) (Fichot and Benner, 2012; Helms et al., 2008). This result is also verified by the fluorescence properties (highest HIX and %C1, lowest F<sub>max</sub> (C2)/F<sub>max</sub> (C1)). Although some of trajectories to site 47 passed through the active fires (Fig. 10a), compared to the strongly local soil input, the influence of long-range transportation of biomass burning aerosol was much fewer. Combined with the low value of (SO<sup>2</sup><sub>4</sub>-±NO<sub>3</sub>)/nss-ndust-K<sup>+</sup> (Fig. 9b), the CDOM produced by anthropogenic pollution

is negligible in region 1. Above all, the soil dust is clearly the primary source of CDOM. In region 2, the high relative intensities of C1 and low values of  $F_{max}(C2)/F_{max}(C1)$ indicated that the contribution of soil to snow CDOM was also remarkable. Along the paths of the air masses to site 55 (Fig. 10b), very few trajectories encountered the fires.

5 Additionally, the average of (SO<sub>4</sub><sup>2</sup>+NO<sub>3</sub>)/nss-ndust-K<sup>+</sup> was also low, which showed an insignificant role of anthropogenic pollution. Therefore, in region 2, a major source of soil is reasonable.

In region 3, the extremely high averages of  $F_{max}$  (C2)/  $F_{max}$  (C1) and  $(SO_4^2 + NO_3^2)/nss$ -ndust-K<sup>+</sup>, which were significantly higher than those in other regions

- 10 (ANOVA, p<0.05), implied a strong influence of anthropogenic pollution. The mass ratio of Cl<sup>-</sup> and Na<sup>+</sup> (2.48, Fig. S6) was approximately 2 times higher than that in sea water (1.18, Hara et al., 2004), which indicated that Cl<sup>-</sup> might originate from other sources in addition to sea salt, such as coal combustion (H. L. Wang et al., 2008; Y. Wang et al., 2006), while the values in other regions were comparable to 1.18. This
- 15 result, again, confirmed that the CDOM from pollution was dominant in region 3 but inapparent in other regions. The backward trajectories also showed consistent results (Fig. 10c). Most of the trajectories to site 84 came from the northwest and passed through the cities with heavy industry (e.g., Karamay and Shihezi). Therefore, the air pollutants can be transported to the sample area and deposited on the surface snow.
- 20 In regions 4 and 5, the non-soil sources of snow CDOM were predominant due to the high regional averages of  $F_{max}(C2)/F_{max}(C1)$ . In region 4, many of air masses, which originated from the central Asia (west), Siberia (north) and central Xinjiang (south),

passed through the active fires, and strongly influenced this region (Fig. 10d). The ratios of  $(SO_4^{2^-}+NO_3^-)$  and nss-ndust-K<sup>+</sup> were significantly lower than those in region 3 (ANOVA, p<0.05), indicating a major source of biomass burning. Coincidentally, in region 5, the value of  $(SO_4^{2^-}+NO_3^-)/nss-ndust-K^+$  was comparable, which suggested

- 5 CDOM from biomass burning rather than pollution. The respectable amount of air mass encountered the fires (Fig. 10e) can explain this finding. Furthermore, the low mass ratios of Cl<sup>-</sup> and Na<sup>+</sup> in region 4 and 5 also implied the slight influence of anthropogenic pollution. Overall, biomass burning is the dominant source both in regions 4 and 5. Pu et al. (2017) used a positive matrix factorization (PMF) model to identified the
- 10 sources of particulate light absorption of ILAPs (denoted as C<sup>max</sup><sub>BC</sub>) in snow during the same field campaign. The comparison of C<sup>max</sup><sub>BC</sub> and a<sub>280</sub> among regions is shown in Fig. S7. In regions 1, 2, and 5, there were no significant correlation between C<sup>max</sup><sub>BC</sub> and a<sub>280</sub>, which indicated the entirely different sources of CDOM and particulate absorption of ILAPs. As reported by Pu et al. (2017), the major sources of C<sup>max</sup><sub>BC</sub> were biomass
- 15 burning in regions 1-2 and industrial pollution in region 5; while those of CDOM were soil dust and biomass burning, respectively. Robust linear correlations were found in regions 3 and 4 ( $R^2 = 0.95$  and 0.75, respectively), which implied high consistency for sources of CDOM and particulate absorption of ILAPs (i.e., anthropogenic pollution and biomass burning, respectively).

## 20 **3.54** Comparing the light absorption by CDOM and BC

Figure 1311 shows the relative contributions of CDOM and BC to light absorption. As

mentioned above, light absorption within visible wavelengths was available for 19 samples. The BC concentrations in surface snow were obtained from Pu et al. (2017), and the mass absorption coefficient (MAC) at 550 nm and the AAE of BC used in the calculation were  $6.3 \text{ m}^2 \text{ g}^{-1}$  and 1.1, respectively (Pu et al., 2017).

- 5 The light absorption of CDOM was 0.02-1.17 times ( $0.34\pm0.34$  on average) of that for BC at 400 nm-with an average of  $0.34\pm0.34$ . At 500 nm, this value decreased quickly to  $0.10\pm0.11$  on average and ranged from 0.005-0.40. The CDOM absorption at 400 nm was comparable to or even slightly higher than the absorption by BC at sites 50, 52 and 79. This finding is quite different from the results for Alaskan snow. Dang
- 10 and Hegg (2014) converted the CDOM absorption in snow at Barrow, Alaska, reported by Beine et al. (2011), into equivalent BC mixing ratios of 0.14 ng g<sup>-1</sup> at 400 nm and 0.07 ng g<sup>-1</sup> at 550 nm. As presented by Doherty et al. (2013), the mixing ratio of BC in Barrow snow ranged from 10-30 ng g<sup>-1</sup>. Hence, the absorption of CDOM in Alaskan snow can be safely ignored, but this does not appear reasonable for some sitesareas
- 15 across northwestern China.

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Previous studies on impurities in seasonal snow have focused on insoluble particles (e.g., BC, insoluble OCISOC and dust) (Doherty et al., 2010, 2014; Pu et al., 2017; Wang et al., 2013). The above discussion indicated indicates that in some specific areas of northwestern China, the absorption of CDOM in snow was remarkable. What is the common feature of such sites? Most of them were classified into cluster A (16 of 19 sites). The average  $S_{275-295}$  (0.0187 ± 0.0022) of these 19 sites was the lowest compared to the five regional averages, and the average of regions 1-5. The averages

of BIX ( $0.60\pm0.20$ ) and FI ( $1.31\pm0.09$ ) and F<sub>max</sub>(C2)/F<sub>max</sub>(C1) ( $1.66\pm1.03$ ) were lower than those of region 2, in which the influence of local soil was obvious; in additionBesides, the average valuesaverages of HIX ( $1.87\pm0.57$ ) and relative contribution of %C1 ( $30\pm8\%$ ) were higher than those of region 2. These results

5 indicated that the CDOM of these sites was undoubtedly offrom terrestrial originorigins (e.g., wind-blown soil dust). Hence, we suggest that the absorption by CDOM in the snowpack, which is heavily affected by soil, cannot be ignored.

### **4** Conclusions

SurfaceSeasonal snow samples waswere collected across northwestern China from

- 10 January to February 2012. The  $a_{280}$  and  $S_{275-295}$  of snow water samples<u>CDOM</u> ranged from 0.15-10.57 m<sup>-1</sup> and 0.0129-0.0389 nm<sup>-1</sup>, respectively. The average value of  $a_{280}$  (1.69±1.80 m<sup>-1</sup>) was approximately 10 times higher than that of snow in Alaska (Beine et al., 2011). Samples in Qinghai (region 1) exhibited the highest average  $a_{280}$ (2.30±0.52 m<sup>-1</sup>) and lowest average  $S_{275-295}$  (0.0188±0.0015 nm<sup>-1</sup>) resulting from the
- 15 strong influence of local soil <u>dust</u>. Low average a<sub>280</sub> appeared in central Xinjiang (region 3, 0.93±0.68 m<sup>-1</sup>), where <u>almost all</u> the samples were <u>nearly</u> collected from new fallen snow, and northwestern Xinjiang (region 4, 0.80±0.62 m<sup>-1</sup> when excluded site 67) which was far from industrial areas. In the Tianshan Mountains (region 2) and northeastern Xinjiang (region 5), the average <u>values of a<sub>280</sub> values</u> were 2.00±1.50 m<sup>-1</sup>
- <sup>1</sup> and  $1.1617\pm0.63$  m<sup>-1</sup>, respectively. For all sites in Qinghai and some of the sites in Xinjiang (19 of 39 sites), the light absorption of CDOM cannot be neglected and even

was remarkable at some sites compared to that of BC ( $0.34\pm0.34$  times relative to BC at 400 nm on average) due to the high contribution of soil <u>dust</u> to <u>snow</u> CDOM in snow. Hence, we suggest that the CDOM absorption <del>at</del> in the visible wavelengths at such sites should be taken into consideration in future studies.

- 5 Based on PARAFAC <u>analysis</u>, two humic-like fluorophores (C1 and C2) and one protein-like fluorophore (C3) were identified. C2 showed partially common sources with terrestrially derived C1 ( $R^2 = 0.332$ , p<0.001). The positive relationship between  $F_{max}(C2)$  and  $F_{max}(C3)$  ( $R^2 = 0.364$ , p<0.001) indicated a potential microbial source of C2. In region 1, the relative intensity of C1 (35%) was much higher than that of the
- 10 other regions, and combined with the highest HIX and lowest BIX and FI, indicated a clearly terrestrial origin of C1. In contrast, the contribution of C1 to total fluorescence was lowest in region 3 (9%), and the values of fluorescence-derived indices also showed the consistent results. The high correlations between  $a_{250}$  and  $F_{max}(C1)$  ( $R^2 = 0.938$ , p<0.001), HIX ( $R^2 = 0.828$ , p<0.001) indicated that the CDOM abundance in surface
- 15 snow across northwestern China was mainly controlled by the terrestrial sources. In Qinghai (region 1), %C1 (35% on average) was much higher than those of the other regions, and the highest HIX, lowest BIX and FI were also found. In Xinjiang (regions 2-5), %C1 varied among regions. In region 2, C1 accounted for approximately 25% to the total fluorescence, followed by regions 4 and 5 (both were 17% on average). In
- 20 region 3, the C1 contribution was lowest (9% on average), and the values of fluorescence-derived indices also showed the consistent results (the lowest HIX, highest BIX and FI). A hierarchical cluster analysis was used to classify samples into

four clusters (A-D) <u>based</u> on the <u>basis</u> of the relative <u>intensityintensities</u> of three fluorescent components. All samples in region 1 and most samples in region 2 were assigned to cluster A (a high contribution of C1). The number of samples assigned to cluster B (roughly equal contributions of C2 and C3) and cluster C (a dominant

5 contribution of C2) were nearly even in region 3. For regions 4 and 5, most samples were classified into cluster B. Only two samples were assigned to cluster D due to the dominant contribution of C3.

According to the correlation analysis between three major ions and the  $F_{max}$  of PARAFAC components, in addition to soil and microbial activity, C2 exhibited

potential sources of anthropogenic pollution and biomass burning. Furthermore, the spatial variation of CDOM sources was assessed by using regional variations of (SO<sup>2</sup>/<sub>4</sub>+NO<sup>-</sup>/<sub>3</sub>)/nss K<sup>+</sup>, Cl<sup>-</sup>/Na<sup>+</sup> and air mass backward trajectory analysis. In regions 1 and 3 - 5, the dominant sources were soil, anthropogenic pollution, biomass burning and biomass burning, respectively, while there may be a soil-biomass-burning mixed source
 in region 2.

According to the correlation analysis between  $F_{max}(C2)$  and three major ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and nss-ndust-K<sup>+</sup>), as well as the mutual relationships among the fluorescent components, C2 exhibited potential sources of soil, microbial activity, anthropogenic pollution and biomass burning. Furthermore, the regional distribution of CDOM

20 <u>sources was assessed by using variations of  $(SO_4^2 + NO_3)/nss-ndust-K^+, Cl^/Na^+, F_{max}(C2)/F_{max}(C1)$  and air mass backward trajectory analysis. The major sources for the five regions were soil dust in regions 1-2, anthropogenic pollution in region 3, and</u>
biomass burning in regions 4-5.

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This study investigated the <u>light absorption</u>, <u>fluorescence propertiesoptical</u> <u>characteristics</u> and potential sources of CDOM in seasonal snow across northwestern China. Future studies should focus on the molecular characteristics <del>and the</del>

5 relationships between of snow CDOM and its relationship with the optical properties, which is of CDOM in snow. Understandinggreat importance to the structures, chemistry, energy budget of snowpack and sources of snow CDOM and its effects on the global carbon cycle-is important.

Data availability. All datasets and codes used to produce this study can be obtained by

10 contacting Xin Wang (wxin@lzu.edu.cn). The elevation data used in this study are available at http://rda.ucar.edu/datasets/ds759.3/#!access.

Competing interests. The authors declare that they have no conflict of interest.

*Acknowledgements.* This research was supported by the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (41521004), the National Natural Science Foundation of China under grant (41522505 and 41775144), and the Fundamental Research Funds for the Central Universities (lzujbky-2018k05k02). We thank Jinsen Shi of Lanzhou University, Hao Ye of Texas A&M University, and Rudong Zhang of Nanjing University for their assistance in field sampling.





Figure 1. <u>Sample(a)</u> The location of study area and sample site distribution, across northwestern China. The site numbers and regional groupings are shown in (a) Qinghai and panel (b) for Xinjiang and (c) for Qinghai. Sample areas are divided into five regions

5 indicated by different symbol shapes, and the land cover types of sample sites are represented in different colors, as shown in the legend-<u>in panel (a)</u>. 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 2. Pictures of typical sample sites.



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



Figure 4. The fluorescent components identified by the PARAFAC analysis.

Relationship between log-transformed  $a_{280}$  and  $S_{275-295}$ 



**Figure 5. (a-c)** The EEM components identified by the PARAFAC model and **(d-f)** the corresponding excitation and emission loadings of each component; the orange line indicates the excitation (Ex) loading, and the blue line indicates the emission (Em)

5 loading.



Figure 6. The linear relationships between the intensities of (a) C1 and C2, (b) C1 and

C3, (c) C2 and C3.



**Figure 7.** Distribution of relative intensities for three fluorescence components in **(a)** Qinghai and **(b)** Xinjiang. The red, yellow and blue in each pie represent C1, C2 and C3, respectively, and the size of each pie shows the total fluorescence intensity as a sum

5 of the three components.



**Figure 5.** Variations of the fluorescent components among regions. The boxplots show the intensities of components. The boxes denote the 25<sup>th</sup> and 75<sup>th</sup> quantiles, and the horizontal lines represent the 50<sup>th</sup> quantiles (medians), the averages are shown as dots;

5 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

10 <u>dataset.</u>



Figure 8. Figure 6. Hierarchical cluster analysis based on the relative intensities of the

three PARAFAC fluorescent components.



Figure 97. HIX (<u>shown in red y axis and circles</u>), BIX (<u>shown in blue y axis and</u> squares) and FI (<u>shown in green y axis and triangles</u>) of surface snow samples-<u>among</u>

5 regions. The meaning of each part of box is same as that in Fig. 5.

The sample sites in regions 1-5 are separated by black



**Figure 8.** The linear relationships between intensities of (a) C1 and C2, (b) C1 and C3, (c) C2 and C3. The red dashed lines show the fit of the entire dataset, and the blue solid lines. \_\_\_\_\_\_ show the fit of data excluded site 67 (shown as markers in red). The

5 corresponding fitting parameters are exhibited in the same color, including the equations, correlation coefficients and p-values.



**Figure 9.** The regional averages of the ratios for (a)  $F_{max}(C2)$  and  $F_{max}(C1)$ , (b)

 $(SO_4^{2-}+NO_3^{-})$  and nss-ndust-K<sup>+</sup>.



Figure 10. The relationships between a<sub>280</sub> and the intensities of (a) C1, (b) C2, and (c)

C3 and the fluorescence-derived indices (d) HIX, (e) BIX, and (f) FI.



(c) Region 3: site 84



(e) Region 4: site 72













**Figure 11.** Figure 10. 72-h air mass backward trajectories (blue lines) at 500 m above ground level with the initial positions at representative sites (shown as yellow dotspentagrams) in each region. Trajectories were calculated four times per day for a period of 30 days preceding the sampling date at a given site by HYSPLIT (version 4, NOAA) except for panel (c). Since the snow was fresh at site 84, the trajectories were derived for 5 days preceding the sampling date. The blackThe red lines show the airmasses passed through the active fires before reaching the receptor sites, and the blue

<u>lines are those did not pass the fires. The white</u> dots represent the typical industrial cities in Xinjiang, <u>namely, i.e.</u>, Karamay, Kuytun, Shihezi and Urumqi from west to east. <del>The</del> <del>red dots are MODIS active fire locations.</del>











Figure 11. The relative absorption contributions of CDOM (yellow bar) and BC (gray

bar) at (a) 400 nm and (b) 500 nm.

Site	Lat. (N)	Lon. (E)	$a_{280}$ (m <sup>-1</sup> )	S <sub>275-295</sub> (nm <sup>-1</sup> )	AAE	HIX	BIX	FI
47	35.54	99.49	3.11	0.0174	4.66	2.24	0.51	1.3
48	34.85	98.13	1.32	0.0212	5.12	1.30	0.59	1.40
49	35.22	98.95	2.14	0.0206	5.20	2.24	0.47	1.29
50	34.80	99.05	2.38	0.0194	4.91	2.08	0.48	1.2
51a	33.89	99.80	2.44	0.0183	4.87	2.44	0.44	1.2
51b	33.89	99.80	2.02	0.0175	4.91	2.57	0.44	1.2
52	34.92	100.89	2.71	0.0170	4.63	2.63	0.53	1.2
53	43.07	86.81	5.25	0.0178	4.53	3.20	0.48	1.2
54	43.08	85.82	0.41	0.0350	N.A.	0.28	0.82	1.7
55	43.51	83.54	2.52	0.0178	5.13	1.90	0.61	1.3
56	43.66	82.75	1.38	0.0192	5.77	1.39	0.61	1.3
57	43.64	82.11	2.66	0.0168	5.31	1.75	0.59	1.3
58	43.52	81.13	0.42	N.A.	N.A.	0.54	0.70	1.4
59	44.49	81.15	0.54	0.0357	N.A.	0.59	0.65	1.4
60	44.96	82.63	2.39	0.0174	8.91	1.38	1.24	1.4
61	44.38	83.09	1.66	0.0189	6.06	1.49	0.59	1.3
62	44.57	83.96	0.80	0.0194	N.A.	0.52	1.47	1.6
63	45.58	84.29	0.81	0.0264	N.A.	0.71	0.78	1.4
64	46.68	83.54	2.01	0.0194	5.54	1.96	0.49	1.2
65	46.49	85.04	0.64	0.0291	N.A.	0.77	0.82	1.3
66	46.88	85.92	0.15	N.A.	N.A.	0.39	0.84	1.6
67	47.26	86.71	10.57	0.0169	4.41	1.47	0.63	1.3
68	48.15	86.56	0.57	0.0301	N.A.	0.59	1.10	1.5
69	47.86	86.29	1.41	0.0221	7.70	1.02	1.04	1.4
70	48.33	87.13	0.21	0.0351	N.A.	0.41	0.62	1.3
71	48.07	87.03	0.61	0.0255	N.A.	0.66	1.01	1.5
72	47.79	87.56	1.49	0.0259	N.A.	1.05	1.20	1.4
73	47.55	88.61	0.30	0.0381	N.A.	0.54	1.12	1.4
74	47.63	88.40	0.55	0.0337	N.A.	0.63	1.20	1.4
75	47.58	88.78	0.81	0.0376	N.A.	0.74	0.79	1.3
76	47.17	88.70	1.21	0.0389	N.A.	0.89	0.97	1.4
77	47.27	89.97	1.50	0.0301	N.A.	0.80	0.71	1.2
78	46.85	90.32	2.32	0.0221	5.52	1.93	0.48	1.2
79	43.53	89.74	3.13	0.0221	5.52	1.65	0.46	1.2
80	44.10	87.49	0.54	0.0292	N.A.	0.49	0.74	1.6
81	43.60	87.51	0.72	0.0255	N.A.	0.45	0.80	1.6
82	44.09	84.80	0.23	N.A.	N.A.	0.16	0.88	1.9
83	43.93	85.41	0.31	N.A.	N.A.	0.27	0.77	1.6
84	43.93	86.76	1.65	0.0129	6.66	0.95	0.79	1.5

Table 1. Statistics on absorption and fluorescence parameters for surface snow at each

Component number	Excitation maximal wavelength (nm)	Emission maximal wavelength (nm)	Descriptions	References
C1	<240 (305)	453	Terrestrial humic-	Stedmon and
			like substances_	Markager,
				<del>2005a</del> 2005b;
				Stedmon et al.,
				2003
C2	<240 (300)	393	Microbial,	Murphy et al.,
			anthropogenic or	2011; <u>Zhang</u> et
			terrestrial humic-	al., 2010
			like substances	
C3	<240 (270)	315	Tyrosine-like	Yu et al., 2015
			fluorophore_	

 Table 2. Description of the three PARAFAC components. The secondary peaks are shown in brackets.

Table 3. Regional average of relative intensity (in percent) and  $F_{max}$  of each

Regions	<del>C1 (%)</del>	<del>C2 (%)</del>	<del>C3 (%)</del>	F <sub>max</sub> (C1)	F <sub>max</sub> (C2)	F <sub>max</sub> (C3)
				(RU)	(RU)	<del>(RU)</del>
4	<del>35±4</del>	41±1	$\frac{25 \pm 5}{25 \pm 5}$	<del>0.13±0.03</del>	$0.15 \pm 0.03$	$0.09 \pm 0.01$
2	<del>25±11</del>	<del>38±8</del>	<del>37±16</del>	$0.11 \pm 0.08$	$0.14 \pm 0.08$	$0.11 \pm 0.02$
3	<del>9±5</del>	47 <u>±13</u>	4 <del>5±16</del>	$0.03 \pm 0.03$	$0.15 \pm 0.11$	$0.11 \pm 0.01$
4	$\frac{17 \pm 10}{17 \pm 10}$	4 <del>1±6</del>	$42 \pm 10$	<del>0.08±0.09</del>	$0.14 \pm 0.11$	$0.13 \pm 0.10$
5	<del>17±8</del>	44 <u>+</u> 7	<del>38±8</del>	$0.05 \pm 0.04$	<del>0.13±0.06</del>	$0.10 \pm 0.02$
Total	<del>20±11</del>	4 <del>2±9</del>	<del>38±14</del>	$0.08 \pm 0.07$	<del>0.14±0.08</del>	$0.11 \pm 0.05$

fluorescence component.

Regions	HIX	BIX	FI
1	$\frac{2.21 \pm 0.42}{2.21 \pm 0.42}$	<del>0.49±0.05</del>	$1.29 \pm 0.05$
2	$1.42 \pm 0.84$	<del>0.61±0.10</del>	$1.37 \pm 0.15$
3	$0.62 \pm 0.37$	<del>0.93±0.25</del>	$\frac{1.60\pm0.15}{1.00\pm0.15}$
4	$0.91 \pm 0.52$	$0.82 \pm 0.21$	$1.43 \pm 0.12$
5	<del>0.94±0.43</del>	$0.92 \pm 0.25$	$1.38 \pm 0.09$
Total	<del>1.21±0.78</del>	<del>0.76±0.26</del>	<del>1.42±0.16</del>

Table 4. The regional average of fluorescence derived indices.

**Table 5.** Summary of fluorescence-derived indices <u>Table 3.</u> The fluorescence-derived indices in this study and summary of that from natural water and water extraction of aerosol reported by other studies with average values for some studies are shown in brackets.

Study area	Sample type	HIX	BIX	FI	References
Northwestern	Seasonal snow	0.16-3.20	<u>0.44-1.47</u>	<u>1.20-1.92</u>	This study
<u>China</u>		(1.21)	<u>(0.76)</u>	<u>(1.42)</u>	
Tibetan Plateau	Cryoconite in	1.11-1.37	0.65-0.93	3.12-3.44	Feng et al.,
	glaciers	(1.27)	(0.80)	(3.24)	2016
Yungui Plateau,	Inland lakes	0.23-6.00	0.60-1.54	1.14-1.80	Zhang et al.,
China		(1.57)	(0.93)	(1.37)	2010
Frasassi Caves,	Cave water	1.79-3.28	0.80-1.12	~1.8	Birdwell and
Italy		(2.32)	(0.95)		Engel, 2010
Springs in USA	Spring water	0.36-1.21	0.64-1.13	1.92-2.28	Birdwell and
		(0.76)	(0.87)	(2.09)	Engel, 2010
Gironde	Estuary	~ <del>10<u>4</u>-17</del>	0.6-0.8	1.14-1.22	Huguet et
Estuary, France					al., 2009
North Pacific	Ocean water	0.92-1.80	0.88-1.38	1.54-1.77	Helms et al.,
Ocean		(1.49)	(1.0)	(1.66)	2013
Tai Mountain,	Fog water	3.23-6.79	0.64-1.02	1.42-1.83	Birdwell and
China		(4.8)	(0.87)	(1.63)	Valsaraj,
					2010
Jianghan Plain,	Ground water	2.71-7.49	0.88-0.97	-	Huang et al.,
China					2015
Colorado, USA	Aerosol in	0.72-4.75	0.54-0.75	1.18-1.57	Xie et al.,
	alpine sites	(2.42)	(0.65)	(1.4)	2016
Granada, Spain	Urban aerosol	2.79-4.89	-	1.48-1. <mark>61<u>64</u></mark>	Mladenov et
					al., 2011

**Table 64**. Pearson's correlation coefficients (r) of major ions and  $\mathbf{F}_{max}$ . F<sub>max</sub> for fluorescence fluorescent components when excluding data from site 67; the results for the entire dataset are shown in parentheses. Note: \* denotes p<0.001.

	$SO_4^{2-}$	NO <sub>3</sub>	nss-ndust-K <sup>+</sup>
$F_{max}(F_{max}(C1))$	0.01 (0.14)	-0.10 (-0.04)	0.23 (0.48)
$F_{max}(F_{max}(C2))$	$0.70^{*}(0.72)$	$0.60^{*} (0.57)$	0. <del>63</del> <u>57</u> *
			(0. <del>73<u>69</u>)</del>
$F_{max}(C3)$	0.44 (0.42)	0.34 (0.23)	0.29 (0.68)

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