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:

3. 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.
- Lee, H. J. (Julie), Laskin, A., Laskin, J. et Nizkorodov, S. A.: Excitation–Emission Spectra and Fluorescence Quantum Yields for Fresh and Aged Biogenic Secondary Organic Aerosols, Environ. Sci. Technol., 47(11), 5763-5770, doi:10.1021/es400644c, 2013.
- 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 light-absorbing 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 split-half 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 split-half 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 $S_{275\text{-}295}$ 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!

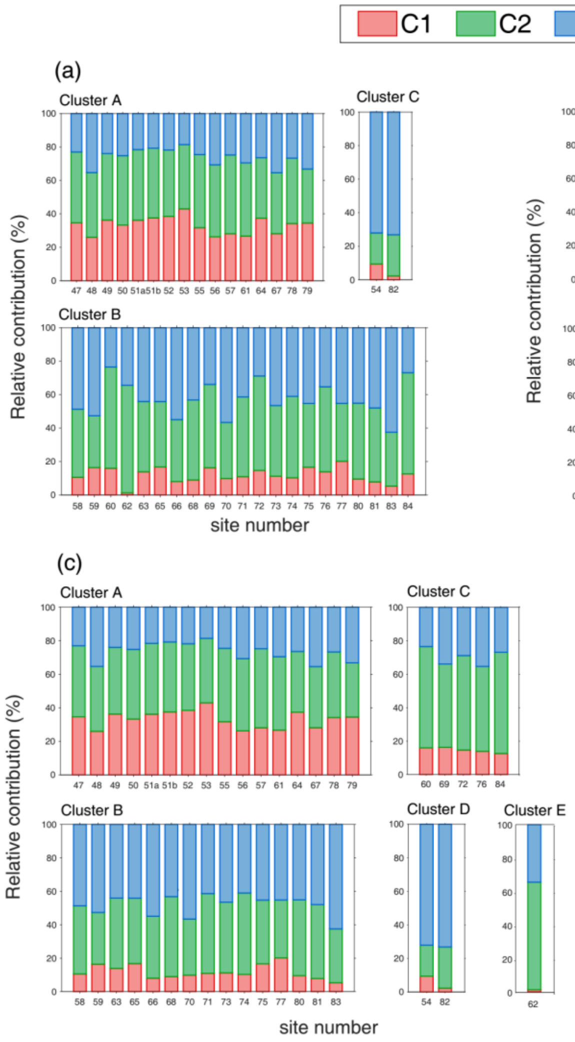
R: R^2 of all the fits ($S_{275\text{-}295}$ and AAE) were higher than 0.9 and most of them were higher than 0.95. Hence, we noted that these results are credible and accurate. We have added the corresponding description in lines 13-14, page 12.

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 “excitaition” 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:

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

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, *ε* 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.

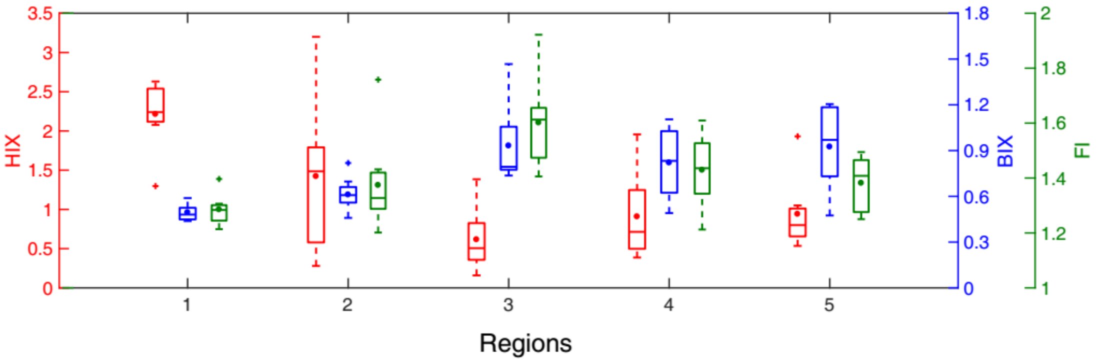


Figure 7. HIX (shown in red), BIX (shown in blue) and FI (shown in green) of surface snow samples among regions. The meaning of each part of box is same as that in Fig. 5.

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.

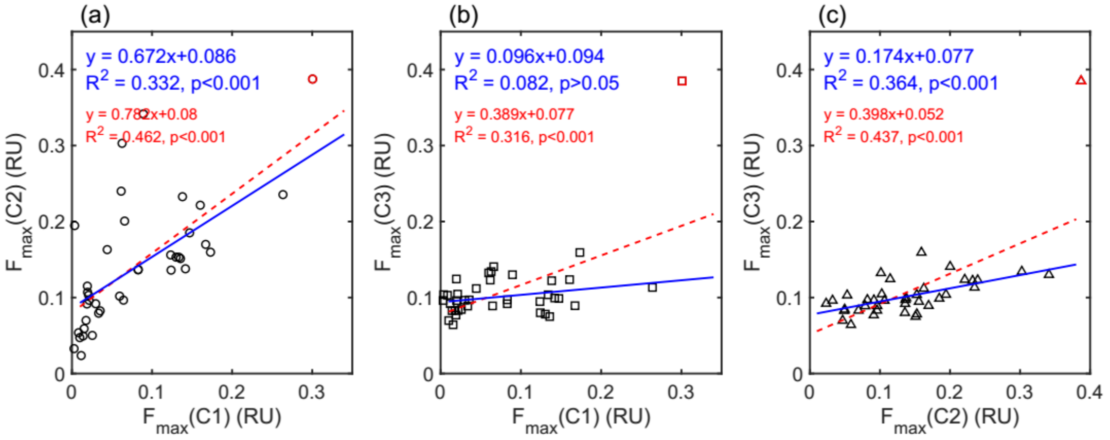


Figure 8. The linear relationships between intensities of (a) C1 and C2, (b) C1 and C3, (c) C2 and C3. The red dashed lines show the fit of the entire dataset, and the blue solid lines show the fit of data excluded site 67 (shown as markers in red). The corresponding fitting parameters are exhibited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

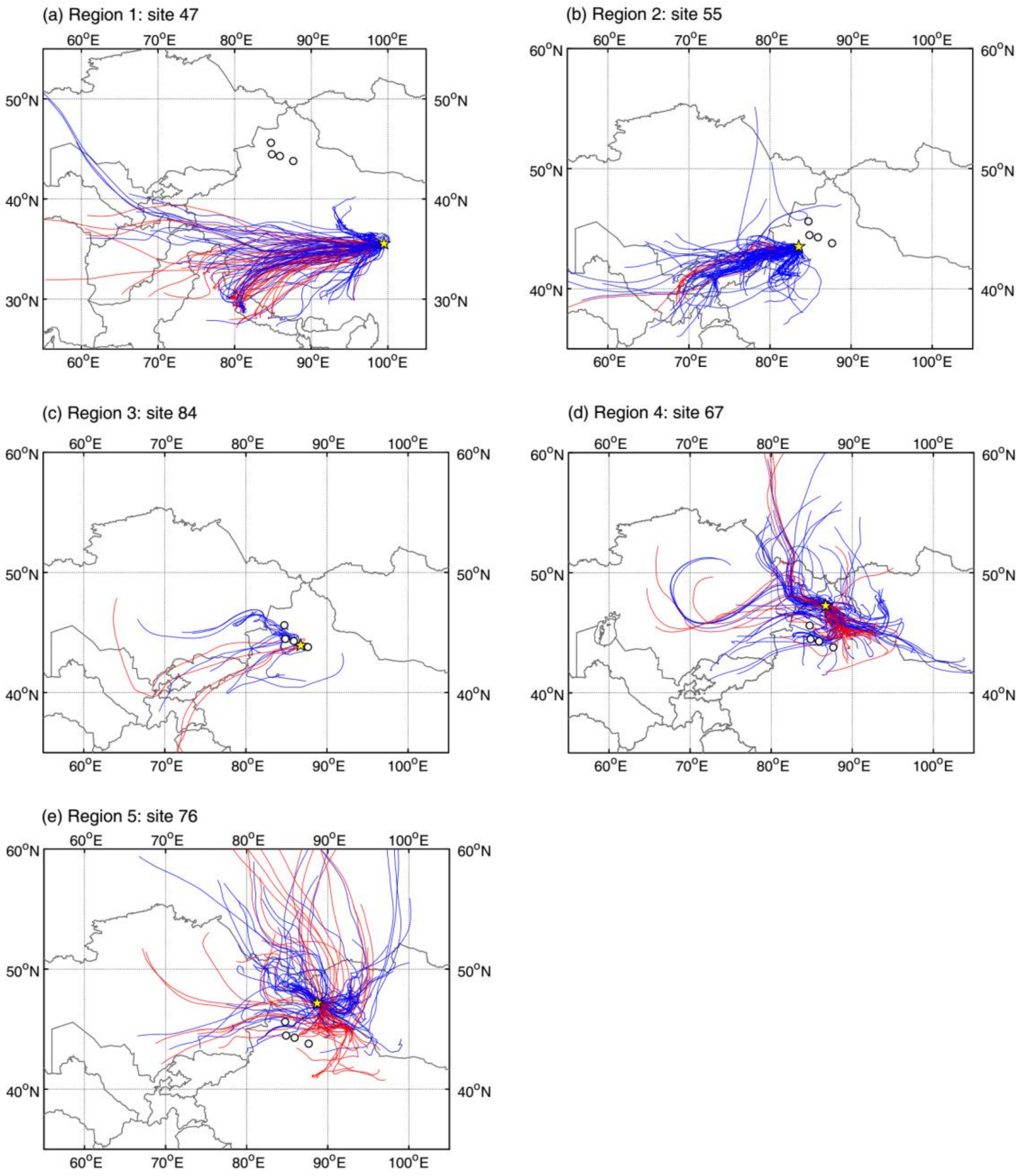


Figure 10. 72-h air mass backward trajectories at 500 m above ground level with the initial positions at representative sites (shown as yellow pentagrams) in each region. Trajectories were calculated four times per day for a period of 30 days preceding the sampling date at a given site by HYSPLIT (version 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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