

Response to Dr. Jacobi

We are very grateful for reviewer's constructive comments, which have helped us improve the paper quality substantially. We have addressed all comments carefully as detailed below in point-by-point responses. All referenced lines of the text are related to the revised manuscript with changes in tracking mode. Our responses start with "R:".

The authors present results from detailed measurements of the absorption determined in a number of melted snow samples collected in northwest China. The samples are grouped into different categories like rural, urban, and influenced by soil. The authors further analyzed the chemical composition of the snow samples with advanced analytical techniques to derive information on the water-soluble organic fraction at the bulk as well molecular level. This study generates a wealth of information on the composition of the snowpack in this region. Unfortunately, the number of analyzed samples and the characterization of the input sources for the different categories of organic compounds remain to limited to derive more general conclusions on the snow composition under different conditions. In a second part, the authors examined the impact of the absorption related to the organic compounds on the snow albedo and compared it to the impact of the also measured black carbon (BC). It appears that under specific circumstances the contribution of the organic compounds to the instantaneous radiative forcing can be non-negligible compared to BC. This is an important finding, especially for a region that has not received yet much attention in the literature. In summary, this manuscript describes an important exploratory study for a comprehensive chemical characterization of organics in the snow and how their impact on the absorption and the snow albedo can be analyzed. Below I have listed a number of comments that the authors may want to consider before the publication of the manuscript.

Major comments:

1. In ch. 2.1 it is mentioned that snow samples were taken in 5 cm intervals. However, no further information on these samples is later found in the manuscript. Are these

samples analyzed separately or are they mixed before or after melting? If they are analyzed separately how do the absorption or chemical profiles look like? Moreover, the parameters snow depths, snow density, and snow temperature are also mentioned. Snow depths and density are listed for each snow pit in table S3, but only an average value for the density can be found. It would be useful to provide all data for all collected samples.

R: Sorry for confusing statement. In this campaign, only surface snow, and for some sites, subsurface snow samples were collected. The sentence in line 164 has been revised as “28 surface and 8 subsurface snow samples were collected from 28 sites in Xinjiang, northwestern China during a road trip in January 2018.”

The description in lines 199-205 has been revised as “The snow samples were collected in sterile plastic bags (Whirl-Pak, Nasco, WI, USA) using clean, stainless steel utensils and by scooping ~ 3 L of snow on top 5 cm at each site, resulting in ~600 mL volume of melted snow water. For several sites with snowpack deeper than 10 cm, subsurface snow (~5-10 cm) was also collected. Snow depths, snow density, and snow temperature were also measured for each sampled snow layer (Shi et al., 2020).”

For all optical and chemical measurements, 28 surface samples were analyzed. The relevant statement has been added in line 206 as “28 surface samples were analyzed by the following analytical techniques.”

The values reported in Table S5 in the revised SI file are for surface snow only. A homogenous snowpack assumption was applied in snow albedo modeling, for both snow physical properties and pollutants concentrations. The statement has been added in lines 342-345 as “The input values of parameters for the SNICAR model, which are those for surface snow, are summarized in Table S5. For simplicity, a homogenous snowpack assumption was applied for both snow physical properties and pollutants concentrations.”

During 2018 Xinjiang campaign, the snow depths of most sites (20/28) were lower than 10 cm, hence sampling of 5 cm is a good representative for most of the snowpack. Moreover, surface layer is the most important for optical properties of snowpack. As reported by Zatko et al. (2016a), the photic zones are 4–7 cm for snowpack from the

Uintah Basin, Utah, USA, which are much shallower compared to snow in polar regions (Zatko et al., 2016b). Due to the similar geographical conditions (latitude, sampling time, etc.) of Xinjiang and Uintah Basin along with higher snow pollutants levels in Xinjiang, the shallow photic zones for our samples can be expected. Overall, we believe that the assumption of homogenous snowpack is practical in this study.

2. Ch. 3.2: The authors compare the measured absorption with absorptions obtained in other studies described in the literature. However, the snowpack properties and further conditions during the sampling in the different studies are not sufficiently described. For example, a thin or patchy snowpack is susceptible to the input of absorbing compounds by local sources. Apparently, this was the case for some of the here reported samples. What were the conditions during the sampling for the other cited studies? For example, the samples described by Voisin et al., 2012 were collected well before the melting period with a complete snow cover, while the samples in the study by Zhang et al., 2020 were collected in April and May. Were at this time the snow and sea ice cover still intact? Depending on the size of the glaciers the local impact should be much reduced for the samples examined by Yan et al., 2016. These effects should be considered for the comparison of the results of the different studies.

R: There are two separated campaigns in Zhang et al. (2020). One was conducted at Barrow, Alaska from April to May 2017 (snow on sea ice), the other one was across Alaska in April 2017 (continental surface snow). There is no significant difference on their MAC_{365} values (0.32 vs. 0.37 $m^2 g^{-1}$ for snow on sea ice and continental snow, respectively). The authors do not provide detail information for their sampling sites. To eliminate possible concern for the impact of snow metamorphism processes on MAC values, we have changed 0.32 $m^2 g^{-1}$ (April to May) to 0.37 $m^2 g^{-1}$ (April) (line 432) for discussion in our study, since snow is typically well covered at Alaska in April (Cox et al., 2017), which was also a common sampling time for earlier snow-related projects in Alaska (Beine et al., 2012; France et al., 2012). In Zhang et al. (2019), they found that the MAC values of snow WSOC increased significantly during melting season.

Relevant discussion has been added into lines 433-434. For Yan et al. (2016), they proposed that the high MAC₃₆₅ (1.3-1.4 m² g⁻¹) of their glacier snow samples was attributed to dust source, which has been mentioned in line 438.

3. Ch. 3.2: Although HULIS2 is introduced as potentially stemming from marine sources, this seems not to be tested by the authors, who attribute this fraction to anthropogenic sources. Did the authors check any correlation with the sea salt components that were also measured in the samples?

R: Sorry for the misleading. Because there are very limited literature sources on snow EEM measurement, we briefly summarized the EEM application and fluorophore identification from previously published works in lines 477-487. While HULIS-2 shows similar peak positions to the marine sourced fluorophores, they do not necessarily indicate the same sources due to large differences of the physicochemical and geochemical processes (Chen et al., 2016; Duarte et al., 2007). As suggested, we did correlation analysis between sea salt ions, i.e., sodium and magnesium ions, and HULIS-2, but there are no significant correlations ($r = 0.09$ and 0.01 , $p > 0.05$, for sodium and magnesium ions, respectively). Xinjiang is at the center of Eurasia and thousands miles away from oceans, hence marine organics are not considered as major sources of WSOC in this study. We have added clarification in lines 487-491 as:

“Of note, the fluorophores detected in our samples show the similar peak positions compared to the previous reports for aerosol or aquatic environments, but they do not necessarily have the same sources due to large differences of the physicochemical and geochemical processes (Chen et al., 2016b; Duarte et al., 2007).”

4. L. 426: “These results provide a useful framework for representing snow BrC optical properties in climate models.” This statement should be explored further or deleted.

R: This sentence has been revised in lines 474-476 as:

“These results provide a useful dataset of snow BrC light-absorbing properties which may inform climate models.”

5. Fig. 4, 6, and 7: Based on a simplistic hypothesis, one could expect that the imprint determined in the soil-influenced samples would also be reproduced in the urban and rural samples with additional compounds stemming from further, potentially anthropogenic sources. While this could be deduced from the patterns shown in Figures 4, 6, and 7 for the urban samples, this is apparently not the case for the rural samples. Do the authors have any explanation why the soil-induced pattern is not present in the rural samples? In my opinion this is a topic that should be explored in the manuscript.

R: Compared to urban (U) and soil-influenced (S) samples, less allochthonous input (aerosol and local soil depositions) of snow WSOC is expected in remote/rural (R) samples, because R samples were collected from relatively remote regions with fewer anthropogenic activities and higher snow cover rate. As a result, R samples present distinctive chemical characteristics. Figures 4b and 5a show that compounds with molecular weight of 250-300 Da are most abundant in the representative R sample, which is significantly different from U and S samples. As we discuss in Sec. 3.3.2 (lines 677-687), R samples have the highest fraction of aliphatic/proteins-like species among four groups (mean: $57\% \pm 4\%$, Table 3 and Fig. 6). These species are commonly regarded as a marker of biological-related sources, such as microbial activities and primary bioaerosols (e.g., plant debris, fungal spores, and pollen). The high contribution of aliphatic/proteins-like species in R samples is consistent with the results of our EEM-PARAFAC analysis, which showed that PRLIS fluorophore is the most abundant. In Fig. 7, the substantially fewer unique molecules in DBE vs. C+N plots for representative R sample indicate relatively low chemical complexity of its WSOC component. Overall, according to Figs. 4-7, the chemical composition of snow WSOC from R samples is quite different from that of the other groups of samples.

Minor comments:

6. Fig. 1a: The photographs are not convincing. For example, a difference between “Grassland” and “Desert” is not obvious to me and it is unclear how these sites are distinguished. The other two photographs do not contribute further information for

the sites.

R: While we agree that indeed no contrasting information can be obtained from the photographs, they do provide visual impression of the snow coverage in the area of study. Therefore, we opted to keep photographs as a part the artwork for Fig 1.

7. L. 213: “An ultrapure water (18.2 MΩ cm) was used for..” Not complete.

R: Revised as “An ultrapure water (18.2 MΩ cm, Milli-Q purification system, Millipore, Bedford, MA, USA)” (line 236).

8. L. 254: Please rephrase “...extracts were blown down to 200 μL...” and also “... and blew them down by pure N₂.” In text S1). For non-chemist this could be difficult to understand.

R: The sentence in main text has been rephrased as “Finally, the reconstituted extracts were further concentrated to 200 μL prior to HPLC analysis” (line 280). The text of S1 has also been rephrased as “Finally, we combined eluents 1 and 2 as analytes and concentrated them by pure N₂”.

9. L. 312: “**field**-measured”?

R: Sorry for the ambiguity. This sentence has been revised as “The effective snow grain size was retrieved from the spectral albedo measured in the field” (line 340).

10. L. 331: “the broadband albedo (α) of each scenario **needs** to be...”

R: Corrected in line 362.

11. L. 362: “It follows that in addition to the snow and glaciers from polar or alpine regions, the seasonal snow in Northern Xinjiang is also an important organic carbon source for the covered ecosystems.” The meaning of this phrase is unclear.

R: This sentence has been revised in lines 396-402 as:

“It has been reported that glaciers and ice sheets from polar or alpine regions store a large amount of WSOC and discharge it to their downstream terrestrial ecosystems

(Hood et al., 2009, 2015; Singer et al., 2012). Comparable or even higher concentrations of WSOC in our samples indicate that the seasonal snow in Northern Xinjiang is also an important organic carbon source for the terrestrial ecosystems during spring meltdown.”

12. L. 366: “the mass contributions of sulfate ions at U sites (Table S1, mean: 33%±7%), which is a commonly-used marker for fossil fuel burning...” This actually applies to non-sea-salt-sulfate. By looking at the sodium fractions, the sea salt sulfate appears to be limited, but it would be useful to calculate the non-sea-salt-sulfate in this context.

R: Based on our analysis results, it is unlikely that marine sources need to be considered in Xinjiang, an inland area with thousands miles away from ocean. Specifically, calcium ion concentrations in our samples were higher than that of sodium ion, leading to much larger mass ratios of calcium to sodium (mean: 7.1±5.2) than that in seawater (0.038) (Pio et al., 2007), hence the sodium ions from marine sources in our samples are at very trace levels.

13. L. 378: “... therefore, pollutants had been potentially accumulated...” So far in the manuscript, the snow was characterized in terms of WSOC. Why are the authors are here referring to pollutants?

R: Sorry for the ambiguity, “pollutants” has been revised as “WSOC” in line 418.

14. Fig. 9: I’m not convinced that this figure is needed since the strong impact of BrC on the absorption at wavelengths below 450 nm is already obvious in Fig. 8.

R: While indeed impact of BrC on the snow surface albedo at <450nm is seen in Fig 8, its contribution in comparison to other light-absorbing components is better illustrated in Fig 9 which we believe contributes to clarity of the paper. Therefore, we opted to keep Fig 9 in the manuscript itself.

15. L. 848: “This study presents a comprehensive overview of WSOC and its BrC properties in seasonal snow of northwestern China...” I am not convinced that the limited number of snow samples can constitute a comprehensive overview. Such a characterization is also contradictory to the fact that the sample from site 120 has unique absorbing and chemical features that do not fit into the patterns found at the other sites. A more cautious statement is preferable.

R: Thanks for the suggestion. This sentence in lines 922-925 has been revised as:

“This study presents a comprehensively chemical characterization of WSOC and its BrC properties in collected seasonal snow samples from Northern Xinjiang, northwestern China, which helps to better understand their characteristics, sources, and climate effects.”

16. Text S1: According to the presented data the recovered compounds account for less than 80% of the initial absorption (loss of 16% during the charging of the cartridge, another 6% loss during the two-step elution). It would be useful if the authors can explore what the potential impact of this missing fraction could be on the results and on the conclusions.

R: Compared to filter-collected aerosol samples, we cannot concentrate analytes by increasing the area of clipped filter or decreasing the volume of solvents for snow samples. Therefore, the main objective of SPE is to concentrate WSOC in snow water and derive a representative mixture of it. Only in this way, snow WSOC can be detectable for both PDA detector and HRMS. The secondary objective of SPE is desalting because salts with high concentration block the inlet of HPLC-HRMS system and decrease the ionization efficiency of ESI.

The strongly hydrophilic organics such as low molecular weight organic acids and sugars (e.g., oxalic acid, xylose, etc.) are expected to pass through the SPE cartridges, which have little light absorption (Lin et al., 2010a,b). Even if we inject them into HPLC, they probably cannot be resolved by C18 column due to very high polarity. Compounds bearing aromatic rings and multiple polar functional groups are expected to be retained, which may show strong light-absorbing properties and they are our target

materials. In addition, as shown in the table below, the efficiencies of SPE (determined by UV-Vis absorption at specific wavelength) are generally less than 80% (~40% - 80%) in the literatures. Overall, the efficiency of SPE in this study is excellent and the extracted fraction is a good representative for snow WSOC.

Cartridge type	Analytical methods	Recovery (%)	References
C-18	Abs ₂₈₀	64	Varga et al. (2001)
XAD-8	Abs ₂₅₀	72-79	Duarte and Duarte (2005)
C-18	Abs ₂₅₀	41-73	Fan et al. (2012)
C-18	Abs ₂₅₀	64-73	Fan et al. (2018)
HLB	Abs ₂₅₄	54-67	Zou et al. (2020)

17. Table S1: Like for BC and WSOC the measured concentrations of the soluble ions should be given, not only the mass fraction of the total ion mass for each specie. A further table with all measured concentrations would be useful. Moreover, all numbers should be reduced to their significant digits (also throughout the manuscript), i.e. instead of “4.53±3.06” it should be “5±3”. The mass fraction for the single site 120 should accordingly be reduced, i.e. instead of “3.98” use “4” for sodium.

R: Values of all measurements has been provided as Table S3 in the revised SI file. All numbers in the manuscript have been adjusted to appropriate decimals.

18. Fig. S4: Any unit for the “sum of squared error”?

R: Sum of squared error is unitless because it is calculated for EEM maps normalized to their total signals (Murphy et al., 2013).

References

- Beine, H., Anastasio, C., Domine, F., Douglas, T., Barret, M., France, J., King, M., Hall, S., and Ullmann, K.: Soluble chromophores in marine snow, seawater, sea ice and frost flowers near Barrow, Alaska, *J. Geophys. Res. Atmos.*, 117, D00R15, 10.1029/2011jd016650, 2012.
- Chen, Q. C., Miyazaki, Y., Kawamura, K., Matsumoto, K., Coburn, S., Volkamer, R., Iwamoto, Y., Kagami, S., Deng, Y. G., Ogawa, S., Ramasamy, S., Kato, S., Ida, A., Kajii, Y., and Mochida, M.: Characterization of Chromophoric Water-Soluble Organic Matter in Urban, Forest, and Marine Aerosols by HR-ToF-AMS Analysis and Excitation Emission Matrix Spectroscopy, *Environ. Sci. Technol.*, 50, 10351-10360, 10.1021/acs.est.6b01643, 2016.
- Cox, C. J., Stone, R. S., Douglas, D. C., Stanitski, D. M., Divoky, G. J., Dutton, G. S., Sweeney, C., George, J. C., and Longenecker, D. U.: Drivers and Environmental Responses to the Changing Annual Snow Cycle of Northern Alaska, *B. Am. Meteorol. Soc.*, 98, 2559-2577, 10.1175/bams-d-16-0201.1, 2017.
- Duarte, R. M. B. O., and Duarte, A. C.: Application of Non-Ionic Solid Sorbents (XAD Resins) for the Isolation and Fractionation of Water-Soluble Organic Compounds from Atmospheric Aerosols, *J. Atmos. Chem.*, 51, 79-93, 10.1007/s10874-005-8091-x, 2005.
- Duarte, R. M. B. O., Santos, E. B. H., Pio, C. A., and Duarte, A. C.: Comparison of structural features of water-soluble organic matter from atmospheric aerosols with those of aquatic humic substances, *Atmos. Environ.*, 41, 8100-8113, 10.1016/j.atmosenv.2007.06.034, 2007.
- Fan, X., Li, M., Cao, T., Cheng, C., Li, F., Xie, Y., Wei, S., Song, J., and Peng, P. a.: Optical properties and oxidative potential of water- and alkaline-soluble brown carbon in smoke particles emitted from laboratory simulated biomass burning, *Atmos. Environ.*, 194, 48-57, 10.1016/j.atmosenv.2018.09.025, 2018.
- Fan, X. J., Song, J. Z., and Peng, P. A.: Comparison of isolation and quantification methods to measure humic-like substances (HULIS) in atmospheric particles, *Atmos. Environ.*, 60, 366-374, 10.1016/j.atmosenv.2012.06.063, 2012.
- France, J. L., Reay, H. J., King, M. D., Voisin, D., Jacobi, H. W., Domine, F., Beine, H., Anastasio, C., MacArthur, A., and Lee-Taylor, J.: Hydroxyl radical and NO_x production rates, black carbon concentrations and light-absorbing impurities in snow from field measurements of light penetration and nadir reflectivity of onshore and offshore coastal Alaskan snow, *J. Geophys. Res. Atmos.*, 117, D00R12, 10.1029/2011jd016639, 2012.
- Lin, P., Engling, G., and Yu, J. Z.: Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China, *Atmos. Chem. Phys.*, 10, 6487-6500, 10.5194/acp-10-6487-2010, 2010a.
- Lin, P., Huang, X. F., He, L. Y., and Yu, J. Z.: Abundance and size distribution of HULIS in ambient aerosols at a rural site in South China, *J. Aerosol Sci.*, 41, 74-87, 10.1016/j.jaerosci.2009.09.001, 2010b.
- Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R.: Fluorescence spectroscopy

- and multi-way techniques. *PARAFAC, Anal. Methods*, 5, 6557-6566, 10.1039/c3ay41160e, 2013.
- Pio, C. A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez-Ochoa, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., and Schock, M.: Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a west-east transect across Europe, *J. Geophys. Res.*, 112, D23S02, 10.1029/2006jd008038, 2007.
- Varga, B., Kiss, G., Ganszky, I., Gelencsér, A., and Krivácsy, Z.: Isolation of water-soluble organic matter from atmospheric aerosol, *Talanta*, 55, 561-572, doi.org/10.1016/S0039-9140(01)00446-5, 2001.
- Yan, F. P., Kang, S. C., Li, C. L., Zhang, Y. L., Qin, X., Li, Y., Zhang, X. P., Hu, Z. F., Chen, P. F., Li, X. F., Qu, B., and Sillanpää, M.: Concentration, sources and light absorption characteristics of dissolved organic carbon on a medium-sized valley glacier, northern Tibetan Plateau, *The Cryosphere*, 10, 2611-2621, 10.5194/tc-10-2611-2016, 2016.
- Zatko, M., Erbland, J., Savarino, J., Geng, L., Easley, L., Schauer, A., Bates, T., Quinn, P. K., Light, B., Morison, D., Osthoff, H. D., Lyman, S., Neff, W., Yuan, B., and Alexander, B.: The magnitude of the snow-sourced reactive nitrogen flux to the boundary layer in the Uintah Basin, Utah, USA, *Atmos. Chem. Phys.*, 16, 13837-13851, 10.5194/acp-16-13837-2016, 2016a.
- Zatko, M., Geng, L., Alexander, B., Sofen, E., and Klein, K.: The impact of snow nitrate photolysis on boundary layer chemistry and the recycling and redistribution of reactive nitrogen across Antarctica and Greenland in a global chemical transport model, *Atmos. Chem. Phys.*, 16, 2819-2842, 10.5194/acp-16-2819-2016, 2016b.
- Zhang, Y., Kang, S., Gao, T., Schmale, J., Liu, Y., Zhang, W., Guo, J., Du, W., Hu, Z., Cui, X., and Sillanpää, M.: Dissolved organic carbon in snow cover of the Chinese Altai Mountains, Central Asia: Concentrations, sources and light-absorption properties, *Sci. Total Environ.*, 647, 1385-1397, 10.1016/j.scitotenv.2018.07.417, 2019.
- Zhang, Y., Kang, S., Gao, T., Sprenger, M., Dou, T., Han, W., Zhang, Q., Sun, S., Du, W., Chen, P., Guo, J., Cui, X., and Sillanpää, M.: Dissolved organic carbon in Alaskan Arctic snow: concentrations, light-absorption properties, and bioavailability, *Tellus B*, 72, 1-19, 10.1080/16000889.2020.1778968, 2020.
- Zou, C., Li, M., Cao, T., Zhu, M., Fan, X., Peng, S., Song, J., Jiang, B., Jia, W., Yu, C., Song, H., Yu, Z., Li, J., Zhang, G., and Peng, P. a.: Comparison of solid phase extraction methods for the measurement of humic-like substances (HULIS) in atmospheric particles, *Atmos. Environ.*, 225, 117370, 10.1016/j.atmosenv.2020.117370, 2020.