Response to reviewer's comments

We thank the referee for the useful comments and suggestions which have helped us to improve the manuscript. Our point-by-point responses are below. The referee's comments are in black font and our responses are in blue font.

General comments

The manuscript investigates fossil and non-fossil sources' contribution to the molecular composition of water-soluble humic-like substances (HULIS) in $PM_{2.5}$ during the summer and winter in Nanjing. In addition, the study employed radiocarbon and chemical analyses to characterize water-soluble HULIS molecular composition and to examine the different sources' influence on the molecular composition.

The authors discuss the molecular compositions and their seasonal difference. The seasonal difference was found to be originated from seasonal sources, i.e., biomass burning in the winter and biogenic emission in the summer. The study concludes that fossil and non-fossil sources are equally important in the air pollution reduction policy. I found the conclusion is overreaching. However, the results presented don't provide information on the equal contributions of fossil and non-fossil sources to the HULIS composition. This issue, along with others provided below, needs to be addressed.

R: We thank the reviewer for pointing out the issue and have answered this question together with others in the specific comments below.

Overall, the study is well within the scope of the Atmospheric Chemistry and Physics journal and is a good addition to the current knowledge. The manuscript flows logically. I found a few technical issues, as listed below. Finally, I recommend publishing the manuscript after addressing the comments.

R: We thank the reviewer for the brief summary and positive comments on our work.

Specific comments

1、Line 512 suggests the equal importance of fossil and non-fossil fuels in atmospheric aerosol in Nanjing. The fraction of non-fossil (f-nf) of HULIS-C is, on average, 39 ± 8 % in the summer and 36 ± 6 % in the winter. That means they are not equally contributing (+/- 50%: 50%) to HULIS in $PM_{2.5}$ and air pollution in general. Moreover, there is a slight difference due to seasonal sources, i.e., biogenic emission and biomass burning. That infers that the policy needs to consider the types of pollution for each season instead of generalizing the contribution of the sources. This issue needs to be addressed and clarified.

R: We changed the sentence in section 3.1 to "the radiocarbon analysis results showed that the f_{nf} of HULIS-C ranged from 30 % to 50 % with an average contribution of 39 ± 8 % in summer and ranged from 32 % to 48 % with an average contribution of 36 ± 6 % in winter, indicating the significant contributions from fossil sources to HULIS at the study site." We further supported the results by adding more explanations here. "The 48 h back trajectories (Fig. S1) showed that the study site was affected by the polluted air masses mainly from the northern cities in winter, suggesting the coal combustion contributions to HULIS in winter. In addition, significant increasing of the levoglucosan and HULIS-C mass concentrations were found from 31 December 2017 to 1 January 2018, corresponding to the W1-W3 samples and the maximum of the levoglucosan and HULIS-C mass concentrations were 552.79 ng m^{-3} and 7.40 μg m^{-3}, respectively, indicating the biomass burning impact during the periods. In summer, the study site was affected by both regional transport from the nearby cities in the north and west of Nanjing and the Donghai Sea. The anthropogenic emissions from the neighboring cities might cause the anthropogenic SOA formation, i.e., secondary N-containing and S-containing compounds with aromatic structures during the atmospheric transport processes, which was discussed in detail in section 3.4 in this study." (See lines 205-220)

We thank the reviewer for pointing out the issue on the different sources of HULIS, i.e., biogenic emission in summer and biomass burning in winter. At the end of the abstract, we pointed out that "Generally, different policies need to be considered for each season due to the different season sources, i.e., biogenic emission in summer and biomass burning in winter for non-fossil source, traffic emission and anthropogenic SOA formation in both seasons and additional coal combustion in winter. Measures to control emissions from motor vehicles and industrial processes need to be considered in summer. Additional control measures on coal power plants and biomass burning should be concerned in winter." (See lines 46-52)

2、The introduction needs more context on the study location. What has been found so far in Nanjing, what needs to be added to the current knowledge, and how does this study fit/enrich the knowledge?

R: We added new contents in the introduction section in the revised manuscript to describe the current researches at the study location. Organic matter can account for 20-40 % of $PM_{2.5}$ in the Yangtze River Delta area due to the impact of complicated sources, especially anthropogenic emissions (Wang et al., 2017; Wang et al., 2016). Studies have reported that Brown carbon (BrC) is an important contributor to aerosol light absorption in Nanjing and exhibited obvious seasonal variations, with peaks in wintertime, owing to emissions from biomass burning, fossil fuel combustion, and secondary formation (Chen et al., 2018; Cui et al., 2021; Xie et al., 2020; Wang et al., 2018). Recently, works on the field observation of nitrated aromatic compounds (NACs) were conducted to explore the light absorption contributions of NACs to BrC and help to better understand the links between the optical properties and molecular compositions of BrC (Gu et al., 2022; Cao et al., 2023). However, as far as we know, understanding of the sources of atmospheric HULIS at molecular levels was still limited. In this work, we aim to obtain the molecular characteristic differences of water soluble HULIS in summertime and wintertime and to get a better understanding of the influence of different sources on the molecular compositions of HULIS. (See lines 107-117)

3、Some clarifications for the following.

- What parameters are provided by China Environmental Monitoring Centre (Line 121)? Are the parameters the ones mentioned in Line 163?

R: The air pollutants data including $PM_{2.5}$, SO_2 and NO_2 were provided by China National Environmental Monitoring Centre. We listed the parameters in the revised manuscript. (See line 136)

- Add a brief description of the isolation and measurement of the chemical analysis before referring to previous studies/references (Line 132).

R: We added a brief description of the isolation and measurement of HULIS, as well as the water soluble ions and levoglucosan. (See lines 140-144 and lines 149-155)

- Line 168 mentions NAAQS for the first grade. I don't know "the first grade", but the phrase may not be necessary as the NAAQS level is sufficient. If that is important to mention, add some context.

R: We removed “the first grade” in the revised manuscript. (See lines 193-194)

4、Lines 435-442 discuss the abundant CHOS compounds are isoprene SOA tracers that formation is higher in the summer. Isoprene SOA enhancement in the summer is well understood. Other than enhanced isoprene SOA, what are the consistent results between this study and the previous one (Bao et al., 2022)?

R: According to the previous study reported by Bao et al. (2022), good correlations were found between HULIS with levoglucosan and K^+ in winter, suggesting the biomass burning influence on HULIS in winter, which was further supported by the positive matrix factorization (PMF) analysis. Consistent results were found in this study. In addition, the PMF results showed that anthropogenic SOA formation and fossil fuel combustions including industrial and traffic emissions significantly contributed to HULIS in summer (51%) and winter (51%), respectively. Significant fossil sources were found based on both the PMF model before and ^{14}C analysis in this study. It should be noted that the fossil source contributions derived from the PMF model were a little lower than the ^{14}C results. The PMF model results were influenced by the input parameters, which possessed definite subjectivity and had uncertainties due to the measurement errors. The ^{14}C analysis is a powerful tool for distinguishing and determining fossil and non-fossil sources of carbonaceous aerosols due to the fact that all ^{14}C atoms have completely decayed in fossil fuels, whereas non-fossil sources contain constant ^{14}C levels (Mo et al., 2018; Liu et al., 2018).

In this study, two high-intensity CHO compounds containing condensed aromatic ring structures ($C_9H_6O_7$ and $C_{10}H_5O_8$) identified in summer and winter samples were similar to those from off-road engine samples, indicating that traffic emission was one of the important fossil sources of HULIS at the study site. The presence of long-chain alkanes derived OSs supported the radiocarbon results, providing another evidence that the traffic emission was the important fossil sources at the study site. The presence of aromatic secondary N-containing and S-containing compounds provided evidence for the anthropogenic SOA formation contribution to fossil sources at the study site. These results further verified the work reported before by Bao et al. (2022) at molecular level and help a better understanding of the interaction between the sources and the molecular compositions of atmospheric HULIS. We added these descriptions in the revised manuscript in lines 407-408 and lines 563-569.

Technical comments

1、Line 63: Do you mean “increase aerosol hygroscopicity”?

R: Yes. We thank the reviewer for finding out the issue. We changed the word “produced” to “increased” in the revised manuscript. (See line 68)

2、Line 398: Both species have a DBE of 6. Unless there's a typo on the Molecular Formula.

R: We thank the reviewer for pointing out the mistake. We changed the sentence to “such as $C_6H_4N_2O_6$ and $C_7H_6N_2O_6$ both with a DBE value of 6”. (See line 445)

3、Line 406: Reverse the O/N ratios: "... 1 and 2, respectively".

R: Corrected. (See line 456)

4、Line 407: Typo "Previously, studies have found...".

R: Corrected. (See line 457)

5、Figure 4: I have a minor suggestion. It is difficult to identify the unsaturated HC and lipid-like groups because the bar line is red, which is close to the colors used for those groups. I'd suggest changing the bar line to transparent/no-line or white, similar to Fig. 2 pie charts.

R: We thank the reviewer for the useful suggestion. We changed the bar line to no-line in Figure 4 in the revised manuscript.

References:

Bao, M., Zhang, Y. L., Cao, F., Lin, Y. C., Hong, Y., Fan, M., Zhang, Y., Yang, X., and Xie, F.: Light absorption and source apportionment of water soluble humic-like substances (HULIS) in $PM_{2.5}$ at Nanjing, China, Environ. Res., 206, 112554, 10.1016/j.envres.2021.112554, 2022.

Cao, M., Yu, W., Chen, M., and Chen, M.: Characterization of nitrated aromatic compounds in fine particles from Nanjing, China: Optical properties, source allocation, and secondary processes, Environ. Pollut., 316, 120650, 10.1016/j.envpol.2022.120650, 2023.

Chen, Y., Ge, X., Chen, H., Xie, X., Chen, Y., Wang, J., Ye, Z., Bao, M., Zhang, Y., and Chen, M.: Seasonal light absorption properties of water-soluble brown carbon in atmospheric fine particles in Nanjing, China, Atmos. Environ., 187, 230-240, 10.1016/j.atmosenv.2018.06.002, 2018.

Cui, F., Pei, S., Chen, M., Ma, Y., and Pan, Q.: Absorption enhancement of black carbon and the contribution of brown carbon to light absorption in the summer of Nanjing, China, Atmos. Pollut. Res., 12, 480-487, 10.1016/j.apr.2020.12.008, 2021.

Gu, C., Cui, S., Ge, X., Wang, Z., Chen, M., Qian, Z., Liu, Z., Wang, X., and Zhang, Y.: Chemical composition, sources and optical properties of nitrated aromatic compounds in fine particulate matter during winter foggy days in Nanjing, China, Environ. Res., 212, 113255, 10.1016/j.envres.2022.113255, 2022.

Liu, J., Mo, Y., Ding, P., Li, J., Shen, C., and Zhang, G.: Dual carbon isotopes (^{14}C and ^{13}C) and optical properties of WSOC and HULIS-C during winter in Guangzhou, China, Sci. Total. Environ., 633, 1571-1578, 10.1016/j.scitotenv.2018.03.293, 2018.

Mo, Y., Li, J., Jiang, B., Su, T., Geng, X., Liu, J., Jiang, H., Shen, C., Ding, P., Zhong, G., Cheng, Z., Liao, Y., Tian, C., Chen, Y., and Zhang, G.: Sources, compositions, and optical properties of humic-like substances in Beijing during the 2014 APEC summit: Results from dual carbon isotope and Fourier-transform ion cyclotron resonance mass spectrometry analyses, Environ. Pollut., 239, 322-331, 10.1016/j.envpol.2018.04.041, 2018.

Wang, J., Ge, X., Chen, Y., Shen, Y., Zhang, Q., Sun, Y., Xu, J., Ge, S., Yu, H., and Chen, M.: Highly time-resolved urban aerosol characteristics during springtime in Yangtze River Delta, China: insights from soot particle aerosol mass spectrometry, Atmos. Chem. Phys., 16, 9109–9127, https://doi.org/10.5194/acp-16-9109-2016, 2016.

Wang, J., Nie, W., Cheng, Y., Shen, Y., Chi, X., Wang, J., Huang, X., Xie, Y., Sun, P., Xu, Z., Qi, X., Su, H., and Ding, A.: Light absorption of brown carbon in eastern China based on 3-year multi-wavelength aerosol optical property observations and an improved absorption Ångström exponent segregation method, Atmos. Chem. Phys., 18, 9061-9074, 10.5194/acp-18-9061-2018, 2018.

Wang, J., Zhao, B., Wang, S., Yang, F., Xing, J., Morawska, L., Ding, A., Kulmala, M., Kerminen, V.-M., Kujansuu, J., Wang, Z., Ding, D., Zhang, X., Wang, H., Tian, M., Petäjä, T., Jiang, J., and Hao, J.: Particulate matter pollution over China and the effects of control policies, Sci. Total. Environ., 584–585, 426–447, 10.1016/j.scitotenv.2017.01.027, 2017.

Xie, X., Chen, Y., Nie, D., Liu, Y., Liu, Y., Lei, R., Zhao, X., Li, H., and Ge, X.: Light-absorbing and fluorescent properties of atmospheric brown carbon: A case study in Nanjing, China, Chemosphere, 251, 126350, 10.1016/j.chemosphere.2020.126350, 2020.