

## 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.

### Referee comments #1

This study analyzed radiocarbon and molecular composition of HULIS from Nanjing, China. They found both the fossil and non-fossil sources contributed substantially to HULIS. Interestingly, the different pattern of the molecular composition in CHO, CHON and CHOS compounds showed that a very different formation mechanism of HULIS in winter and summer. This paper was well organized, written and the method provided in this study was relatively new. I will recommend for a publication after they may address the following comments.

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

Line 147: did the authors analyze the blanks?

R: No field blank correction was performed for the carbon isotope analysis since the carbon content in the field blanks was negligible. However,  $^{14}\text{C}$  analysis of the oxalic acid standard (IAEA-C7), a standard material with  $f_m$  value of 0.4953, was conducted in this study and the measured  $f_m$  value of IAEA-C7A was  $0.4975 \pm 0.0018$  (Xu et al., 2021). We added the sentence “ $^{14}\text{C}$  analysis of the oxalic acid standard (IAEA-C7) was conducted in this study (Xu et al., 2021).” in the revised manuscript. (See lines 168-169)

Line 165: do S and W mean summer and winter, respectively?

R: Yes. We added the explanation of S1-S6 and W1-W6. The new sentence in the revised manuscript was changed to “The 12 samples were named as S1-S6 (summer) and W1-W6 (winter) in chronological order corresponding to the six samples in summer and winter, respectively in this study.” (See lines 187-189)

Line 178: ng or ug for Lev?

R: The unit of the levoglucosan concentrations should be  $\text{ng m}^{-3}$ . We corrected the mistake. (See line 214)

Line 182: I think fossil sources were even more important from the  $^{14}\text{C}$  analysis. So this should be stated.

R: We thank the reviewer for pointing out the issue. We adjusted the descriptions in the revised manuscript to “The radiocarbon analysis results showed that the  $f_{\text{nf}}$  of HULIS-C ranged from 30 % to 50 % with an average contribution of  $39 \pm 8$  % in summer and ranged from 32 % to 48 % with an average contribution of  $36 \pm 6$  % in winter, indicating the significant contributions from fossil sources to HULIS at the study site.” (See lines 205-209)

We also complemented the descriptions in the abstract and conclusions to support the results for the important fossil source contributions found in this study. At the end of the abstract, we stressed that “Generally, different policies need to be considered for each season due to the different season sources, i.e., biogenic emissions in summer and biomass burning in winter for non-fossil sources, 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)

In the conclusion section in the revised manuscript, we pointed out that “The presence of long-chain alkanes derived OSs supported the radiocarbon results, indicating 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 substantial contributions from anthropogenic SOA formation to fossil sources at the study site.” (See lines 563-567)

Line 182-183: this sentence was not clear.

R: We removed the sentence considering this sentence was not described logically here and we added more explanation here which was shown in the next comment.

Line 185-186: the logic was not clear, and more explanation was needed.

R: We adjusted the logic and added new descriptions to explain the sources in summer and winter, respectively from the back trajectories analysis. “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  $552.79 \text{ ng m}^{-3}$  and  $7.40 \text{ } \mu\text{g m}^{-3}$ , respectively, indicating the importance of the biomass burning contribution. 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 209-220)

Line 228: what did the higher values indicate?

R: The higher DBE<sub>w</sub> and DBE/C<sub>w</sub> values of CHO and CHON compounds indicated the higher unsaturation degree of these two groups. We added the explanation in the revised manuscript. (See lines 272-273)

Line 293-297: it seemed that the summary may not fully represent the findings.

R: We thank the reviewer for pointing out the issue. We added more contents in the summary. The new summary was shown as “In summary, both the summer and winter samples were mainly composed of compounds from biogenic origins (lignins-like, tannins-like, proteins-like, and carbohydrates-like species). More tannins-like and carbohydrates-like species were detected in summer including large amounts of highly oxidized OSs or nitrooxy-OSs, indicating biogenic SOA formation. More condensed aromatic structures in CHO and CHON compounds were detected in winter, owing to increasing anthropogenic emissions.” (See lines 338-343)

Figure 1 should add S1-S6 or W1-W6 in the figure. Or add a table

R: We added the corresponding S1-S6 and W1-W6 in Figure 1 in the revised manuscript.

### **References:**

Xu, B., Cheng, Z., Gustafsson, Ö., Kawamura, K., Jin, B., Zhu, S., Tang, T., Zhang, B., Li, J., and Zhang, G.: Compound-specific radiocarbon analysis of low molecular weight dicarboxylic acids in ambient aerosols using preparative gas chromatography: method development, *Environ. Sci. Technol. Lett.*, 8, 135-141, 10.1021/acs.estlett.0c00887, 2021.