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.

Based on the radiocarbon analysis combining the Fourier Transform Ion Cyclotron Resonance Mass Spectrometry technique, this study reports the potential fossil and non-fossil sources and molecular compositions of water soluble humic-like at a suburb site of Yangtze River Delta, China. The research was carried out to better understand the interaction between the sources and the molecular compositions of atmospheric HULIS. There are several issues that need to be point out before publication (see additional comments):

Additional comments:

1、Line 60-62: Some recent literatures on the composition of HULIS should be cited here, such as: Optical properties, molecular characterizations, and oxidative potentials of different polarity levels of water-soluble organic matters in winter $PM_{2.5}$ in six China's megacities. Sci. Total. Environ., 853 (2022), 158600; Seasonal and diurnal variation of $PM_{2.5}$ HULIS over Xi'an in Northwest China: Optical properties, chemical functional group, and relationship with reactive oxygen species (ROS). Atmos. Environ., 268 (2022), 118782).

R: We thank the reviewer for providing the recent literatures. We added the provided references in the revised manuscript. (See line 66 and lines 959-966)

2、Line 76: The "lingin-derived products" refers to lignin-derived products?

R: Corrected. (See line 81)

3、Line 177-178: How about the difference between the concentration of HULIS-C in this study and previous literature? For example, HULIS-C in Xi'an can compare with this study. ($PM_{2.5}$ Humic-like substances over Xi'an, China: Optical properties, chemical functional group, and source identification. Atmos. Res., 234 (2020), 104784).

R: We added the description about the comparison between our results with those measured in other cities in China. The details were shown as "The averaged mass concentrations of HULIS in summer and winter during the selected periods were 1.83 ± 0.27 μg m^{-3} and 4.52 ± 2.29 μg m^{-3}, respectively. The averaged HULIS concentration in summer was comparable with those measured in other cities in China, i.e., 1.70 μg m^{-3} in Guangzhou,1.61 μg m^{-3} in Shanghai and 1.50 μg m^{-3} in Xi'an. Compared with those measured in winter samples in other cities, our result was comparable with those in Xi'an (4.50 μg m^{-3}), a little lower than those in the megacity of Shanghai (5.31 μg m^{-3}) and higher than those in the southern coastal city of Guangzhou (3.6 μg m^{-3})." (Fan et al., 2016; Zhang et al., 2020; Zhao et al., 2016). (See lines 195-202)

4、Line 185-186: "… mainly from the northern heating cities in winter, suggesting the coal combustion contributions to HULIS in winter". Additional references are needed here.

R: We added two references here which focus on HULIS in the northern cities in China and found that coal combustions was one of the important sources of HULIS to support our results. (See line 211, lines 771-773 and lines 841-843)

5、Line 191-195: "Our results are similar to those found for the ultrahigh resolution mass spectra of water-soluble organic…". Please explain what does the similarity of these mass spectra indicate?

R: Thousands of peaks were detected for each sample in this study, suggesting the chemical complexity of HULIS. Here we presented the similarity of our samples with those from source samples, ambient aerosols and cloud water samples to illustrate that the data were within a reasonable range. We added the illustration at the end of the sentence. (See line 228)

6、Line 205-208: The source profiles of molecules of HULIS from biomass burning can be used here to indicate the biomass burning contribution. (Light absorption properties and molecular profiles of HULIS in $PM_{2.5}$ emitted from biomass burning in traditional "Heated Kang" in Northwest China. Sci. Total. Environ., 776 (2021), 146014). Are biomass combustion emissions also responsible for the increased contribution of S-containing compounds in winter in this study?

R: We thank the reviewer for providing the references. We added the new references in the revised manuscript. Song et al. (2018) also found that primary HULIS emitted from biomass burning contain a high abundance of CHON compounds and S-containing compounds were the dominant component (78.1%) for HULIS in coal-smoke particles. We changed the sentences to "The CHON groups were the major components of molecular formulas, furthermore, the relative intensity of CHON groups increased significantly in winter (Fig. S2 and Fig. S3). Studies have suggested that HULIS emitted from biomass burning can produce a high abundance of CHON compounds and S-containing compounds were the dominant component for primary HULIS emitted from coal combustion (Zhang et al., 2021; Song et al., 2018). The higher intensity of CHON compounds in winter in this study further indicated the biomass burning contribution. The contributions of S-containing compounds (CHOS and CHONS groups) increased in winter which might be related to the polluted air masses transported from the northern cities with increasing coal combustions emissions in winter (Song et al., 2018).” (See lines 239-248)

In section 3.4.3, we discussed the molecular characteristics of S-containing compounds in this study. We found the S-containing compounds were mainly composed of organosulfates (OSs) derived from biogenic precursors, long-chain alkane and aromatic hydrocarbon. In addition, the aromatic OSs presented higher relative intensities in winter. However, as far as we know, we could not make sure what’s the sources of these OSs. What we can explain was the aromatic OSs in winter indicated the increasing anthropogenic emissions.

7、Line 202-206: As I have seen, the average proportions of CHO and CHON groups were higher in summer (22% and 36%, respectively) than in winter (17% and 32%, respectively). Please explain the possible reasons for this phenomenon.

R: In section 3.4.1 and 3.4.2, we discussed the molecular characteristics of CHO and CHON compounds, respectively. Large amounts of biogenic SOA species were found in summer CHO compounds, indicating the significant biogenic emissions in summer. For the CHON compounds, we found they were mainly composed of organonitrates or nitro compounds with O/N values ≥3. The increasing of biogenic emissions might cause the increasing formation of organonitrates which could be from NO_3 oxidation of biogenic VOCs. Above all, we thought the possible reason for the higher proportion of CHO and CHON groups in summer was the increasing biogenic emissions in summer.

We added the sentence in the revised manuscript to explain the higher proportions of CHO and CHON groups in summer at the end of the paragraph which was described as “Notably, the relatively higher proportions of CHO and CHON groups in summer were most probably related to the increasing biogenic emissions in summer, resulting in the formation of some high molecular weight oligomers or highly oxidized organonitrates, which was discussed in detail in section 3.4.1 and 3.4.2 in this study.” (See lines 248-251)

8、Line 227-228: What is the difference between DBE_w and DBE/C_w? In addition, what does the higher DBE and DBE/C values of CHO and CHON compounds indicate in this study?

R: DBE was the double-bond equivalent of compounds and DBE/C was the double-bond equivalent of unit carbon. We added the description of DBE/C and the indication of higher DBE and DBE/C values of CHO and CHON compounds in the revised manuscript. It was shown as "The related parameter DBE/C was the double-bond equivalent of unit carbon which can reflect the condensed ring structures in the compounds (Jiang et al., 2021). The higher DBE_w and DBE/C_w values of CHO and CHON compounds were found in this study, indicating the higher unsaturation degree of these two groups." (See lines 270-273)

9、In section 3.4, when discussed the formation of HULIS molecular, a recent study on BrC molecular formation can be used to support author conclusion.

The Roles of N, S, and O in Molecular Absorption Features of Brown Carbon in $PM_{2.5}$ in a Typical Semi-Arid Megacity in Northwestern China. Journal of Geophysical Research-Atmospheres 126.

R: We added the references at the end of section 3.4.2 to support our results on the reduced N compounds formation in summer. The details were described as "Our results were consistent with previous study conducted in Xi'an, China which also found formation of reduced N compounds in light-absorbing aerosols through ammonia involved reactions in summer (Zeng et al., 2021)." (See lines 460-462)

10、Line 431-434: "The high-intensity CHONS compounds observed in this study, such as $C_{10}H_{16}NO_{7-9}S$, $C_{10}H_{18}NO_{8-9}S$, $C_{10}H_{18}N_2O_{11}S$···". What are the differences in the abundance of these compounds in winter and summer in this study?

R: We compared the relative intensity of these compounds in summer and winter and the results were shown in Table 1 below. Some of them were higher in summer and some were higher in winter, indicating both biogenic emission contributions to HULIS in summer and winter, respectively, which was also found in CHOS compounds in this study. Despite this, some information still could be found from table 1, for instance, the compounds detected in summer contained more oxygen atoms, indicating the higher oxidation degree of these nitrooxy-OSs in summer. This information can also be seen from Fig. S2 and S3. We changed the sentence to "The high-intensity CHONS compounds observed in this study, such as $C_{10}H_{16}NO_{7-9}S$, $C_{10}H_{18}NO_{8-9}S$, $C_{10}H_{18}N_2O_{11}S$, and $C_9H_{14}NO_{8-9}S$ could be nitrooxy-OSs derived from monoterpenes such as limonene and α-terpinene of which we found the formulas in summer contained more oxygen atoms, indicating the higher oxidation degree of these nitrooxy-OSs in summer (Figure S2 and S3)." (See lines 485-487)

Table 1. Averaged relative intensity (%) of the high-intensity CHONS compounds in summer and winter, respectively.

	Summer	winter
$C_{10}H_{16}NO_7S$	13.66	14.74
$C_{10}H_{16}NO_8S$		21.68
$C_{10}H_{16}NO_9S$	56.00	26.83
$C_{10}H_{18}NO_8S$		44.39
$C_{10}H_{18}NO_9S$	61.85	47.81
$C_{10}H_{18}N_2O_{11}S$		31.79
$C_9H_{14}NO_8S$		39.97
$C_9H_{14}NO_9S$	37.72	20.70

References:

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Zhang, T., Shen, Z., Zeng, Y., Cheng, C., Wang, D., Zhang, Q., Lei, Y., Zhang, Y., Sun, J., Xu, H., Ho, S. S. H., and Cao, J.: Light absorption properties and molecular profiles of HULIS in $PM_{2.5}$ emitted from biomass burning in traditional "Heated Kang" in Northwest China, Sci. Total. Environ., 776, 146014, 10.1016/j.scitotenv.2021.146014, 2021.

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