## *Response to Editors and Reviewers*

Thanks for reviewers' careful reading and constructive comments and suggestions. We made every effort to respond to reviewers' questions point to point, and carefully revised our manuscript and Supporting Information based on their comments. To enhance clarity, we present the reviewers' comments in regular black font, while our responses are displayed in blue normal font. The modified content in both the manuscript and the Supporting Information is highlighted in red font.

**Anonymous Referee #2**

The authors characterized High (HMW) and Low Molecular Weight (LMW) using a combination of analytical techniques to differentiate the molecular, functional and optical properties between samples collected during summer and winter in Anhui (China). The manuscript is well written and the link between seasonal sources, HULIS functional and molecular level of information are well linked with the optical properties. The results are a bit long in some sections, and perhaps some of the material (less novel results) could be moved to the Supplementary information to avoid losing the readers and keep the manuscript clear and concise. I would recommend this manuscript for publication after addressing the major comments.

[Response]: Thanks for the reviewer's comment. The contents on FTIR analysis and results have been removed into supporting information.

General comments:

In section 2.6, are there any biases due to the use of the negative mode with ESI-MS? Can the authors estimate the fraction of HMW and LMW HULIS lost during the ESI characterization, or do they assume that most of the HMW HULIS will end up in a multiple charge state or "disassemble" (based on the statement page 32 line 596)? The idea of HMW HULIS being aggregates of smaller molecules should be developed in more details throughout the discussion instead of only mentioning it toward the end.

[Response]: Thanks for the reviewer's comment. Yes, biases can arise due to the use of the negative mode with ESI- HRMS. Electrospray ionization (ESI) is a form of soft ionization source where compounds with high molecular weight and poor stability won't decompose during the ionization process. Simultaneously, it's a selective ionization source primarily suitable for highly polar compounds containing functional groups prone to losing protons, making them more effectively detectable in the negative ESI mode (Lin et al., 2012; Song et al., 2018, 2022). Consequently, in the negative ESI mode, the detection of low-polarity substances like polycyclic aromatic hydrocarbons, aliphatic hydrocarbons, may be missed, and substances easily protonated, such as nitrogenous substances, may also be absent (He et al., 2023; Zou et al., 2023). In general, the ESI- HRMS can reveal molecular composition of a subset of organic molecules that are preferentially ionized in the negative ESI source, rather than representing the entire HULIS composition. Regarding the fraction of HULIS lost during ESI characterization, it's beyond our analysis scope due to the limitations of ESI HRMS. The concept of HMW HULIS being aggregates of small molecules has been elaborated with more details in the revised manuscript.

[Revise]: The relevant statements on biases of ESI HRMS have been added in lines 359-392, 437-439 in the revised manuscript:

"It is worth noting that the ESI- HRMS could reveal molecular composition of a subset of organic molecules that are biased ionized in the negative ESI source rather than representing the entire HULIS composition (He et al., 2023; Lin et al., 2012)."

"This difference could be explained by several factors: (1) ESI- HRMS is based towards relatively small molecules that easily protonated in negative ESI mode (He et al., 2023; Lin et al., 2012)"

The content on assembly of MW HULIS has been incorporated in lines 244-246, 356-359, 441-443 in the revised manuscript:

"In addition, the magnitude peak at 570 Da (peak i) in HMW HULIS may indicate the incorporation of small molecule through weak interactions based on π–π and/or van der Waals forces between the HULIS components (Fan et al., 2021; Piccolo, 2002)."

"The findings imply an assembly of small and heterogeneous molecules to form bulk

HULIS through weak intramolecular forces (i.e., π–π, van der Waals, hydrophobic, or hydrogen bonds) (Fan et al., 2021; Piccolo, 2002) and/or charge-transfer interactions (Phillips et al., 2017; Qin et al., 2022)."

"(3) the potential disassembly of larger molecules stabilized by weak forces during electrospray ionization of HRMS (Fan et al., 2021; Phillips et al., 2017)."

[Reference]:


(1) He, T., Wu, Y., Wang, D., Cai, J., Song, J., Yu, Z., Zeng, X., Peng, P.a., 2023. Molecular compositions and optical properties of water-soluble brown carbon during the autumn and winter in Guangzhou, China. Atmos. Environ. 296, 119573.

(2) Lin, P., Rincon, A.G., Kalberer, M., Yu, J.Z., 2012. Elemental composition of HULIS in the Pearl River Delta Region, China: results inferred from positive and negative electrospray high resolution mass spectrometric data. Environ. Sci. Technol. 46, 7454-7462.

(3) Song, J., Li, M., Jiang, B., Wei, S., Fan, X., Peng, P., 2018. Molecular Characterization of Water-Soluble Humic like Substances in Smoke Particles Emitted from Combustion of Biomass Materials and Coal Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Environ. Sci. Technol. 52, 2575-2585.

(4) Song, J., Li, M., Zou, C., Cao, T., Fan, X., Jiang, B., Yu, Z., Jia, W., Peng, P.a., 2022. Molecular Characterization of Nitrogen-Containing Compounds in Humic-like Substances Emitted from Biomass Burning and Coal Combustion. Environ. Sci. Technol. 56, 119-130.

(5) Zou, C., Cao, T., Li, M., Song, J., Jiang, B., Jia, W., Li, J., Ding, X., Yu, Z., Zhang, G., Peng, P.a., 2023. Measurement report: Changes in light absorption and molecular composition of water-soluble humic-like substances during a winter haze bloom-decay process in Guangzhou, China. Atmospheric Chemistry and Physics 23, 963-979.

Would the contribution of small molecules at 570Da (peak i) present in HMW chromatogram (similarly the fraction of HMW in the LMW, peak ii ~2200 Da) as seen in Figure 1, influence the subsequent observation, in particular the FTIR spectra?

[Response]: Thanks for the reviewer's comments. We admit that there might be a small number of small molecules in HMW HULIS and a small number of large molecules in LWM HULIS, primarily due to the following reasons: (1) Large size molecules obtained by ultrafiltration may incorporate small molecules as a result of weak interactions based on π–π and/or van der Waals forces between the HULIS components (Fan et al., 2021; Piccolo, 2002). These small molecules can be released in the high-pressure mobile phase and thus detected in the HMW fraction; (2) For small size molecules obtained by ultrafiltration, some long-chain substances may pass through the ultrafiltration membrane under pressure during the ultrafiltration process and can be detected in the LMW fraction (Fan et al., 2021; Lee et al., 2020; Wang et al., 2018). Overall, for comprehensive analysis methods such as EEM, HPSEC, FTIR and HRMS, the HMW and LMW HULIS present distinct molecular characteristics, rendering the effects of these minor components negligible.

[Reference]

(1) Fan, X., Cai, F., Xu, C., Yu, X., Wang, Y., Xiao, X., Ji, W., Cao, T., Song, J., Peng, P.a., 2021. Molecular weight-dependent abundance, absorption, and fluorescence characteristics of water-soluble organic matter in atmospheric aerosols. Atmos. Environ. 247.

(2) Lee, Y.K., Romera-Castillo, C., Hong, S., Hur, J., 2020. Characteristics of microplastic polymer-derived dissolved organic matter and its potential as a disinfection byproduct precursor. Water Res. 175, 115678.

(3) Piccolo, A., 2002. The supramolecular structure of humic substances: A novel understanding of humus chemistry and implications in soil science, Advances in Agronomy. Academic Press, pp. 57-134.

(4) Wang, K., Zhang, Y., Huang, R.-J., Cao, J., Hoffmann, T., 2018. UHPLC-Orbitrap mass spectrometric characterization of organic aerosol from a central European

city (Mainz, Germany) and a Chinese megacity (Beijing). Atmos. Environ. 189, 22-29.

Could Tar Balls influence the samples and absorption measurement?

[Response]: Tar balls are a specific type of particle produced from wood combustion, especially during biomass smoldering burning, and are abundant in the troposphere (Chen et al., 2017; Li et al., 2019). Microanalysis has revealed that tar balls are homogeneous spherical carbonaceous particles with sizes ranging from tens to hundreds nanometers. However, during their long atmospheric transport, tar balls particles occasionally form aggregates up to ten particles, including coagulation with dust particles (Hand, et al., 2005, Tóth et al., 2014). Importantly, tar balls are generally considered as water-insoluble brown carbon (Corbin et al., 2019). In the current study, the focus is on water-soluble HULIS, which allows the avoidance of the influence of tar balls.

[Reference]:

(1) Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M. S., Wang, S., Hao, J., Zhang, H., and He, C.: A review of biomass burning: Emissions and impacts on air quality, health and climate in China, Sci. Total Environ., 579, 1000 – 1034, https://doi.org/10.1016/j.scitotenv.2016.11.025, 2017.

(2) Corbin, J. C. and Gysel-Beer, M.: Detection of tar brown carbon with a single particle soot photometer (SP2), Atmos. Chem. Phys., 19, 15673 – 15690, https://doi.org/10.5194/acp-19-15673-2019, 2019.

(3) Hand, J. L., Malm, W., Laskin, A., Day, D., Lee, T. B., Wang, C., Carrico, C., Carrillo, J., Cowin, J. P., and Collett, J.: Optical, physical, and chemical properties of tar balls observed during the Yosemite Aerosol Characterization Study, J. Geophys. Res.- Atmos., 110, D21210, https://doi.org/10.1029/2004JD005728, 2005

(4) Li, C., He, Q., Schade, J., Passig, J., Zimmermann, R., Meidan, D., Laskin, A., and Rudich, Y.: Dynamic changes in optical and chemical properties of tar ball

aerosols by atmospheric photochemical aging, Atmos. Chem. Phys., 19, 139 – 163, https://doi.org/10.5194/acp-19-139-2019, 2019.

(5) Tóth, A., Hoffer, A., Nyiro-Kósa, I., Pósfai, M., and Gelencsér, A.: Atmospheric tar balls: aged primary droplets from biomass burning?, Atmos. Chem. Phys., 14, 6669 – 6675, https://doi.org/10.5194/acp-14-6669-2014, 2014.

Minor comments:

Page 6 line 109 and 110: "low-LMW" change to low-MW, and "MW MSOM" do you mean WSOM here?

[Response]: Thanks for the reviewer's comment. "low-LMW" has been changed to "low-MW", and "MW MSOM" has been changed to "MW WSOM".

Page 10 line 193: "with a scanning speed of 12,000 nm/min".

[Response]: Yes, that is right. The scanning speed for EEM spectra collection was indeed set at 12,000 nm/min.

Page 13 line 252: "lager" did the author mean larger?

[Response]: Thanks. It has been revised.

Page 18 line 343: "were divided five fluorescence regions" to "were divided in five fluorescence regions"

[Response]: Thanks. The relevant statement has been modified.

Page 13 Figure 1: Would the small percent of LMW in HMW samples and HMW in the LMW solution influence the subsequent observation?

[Response]: Thanks for the reviewer's comment. As we replied above, the relevant influence is negligible.

Page 20 line 396: "HMW HULIS generally exhibit more intense at 1721" rephrase

[Response]: Thanks. The phrase "more intense" has been replaced with "a stronger band".

[Revise]: Text S2 in the revised supporting information:

"HMW HULIS generally exhibit a stronger band at 1721 $cm^{-1}$ compared to LMW HULIS in both seasonal aerosols (Fig. S6)."

Page 23 line 436 : "an strong" please correct.

[Response]: Thanks. This sentence has been modified.

[Revise]: Text S2 in the revised supporting information:

"This provides a potential explanation for the higher $MAE_{365}$ values observed in winter HULI compared to summer HULIS."

Page 33 line 613: "HMW HULIS contain amounts of carboxylic functional groups, reduced nitrogen species (e.g., amines) and aromatic species than LMW HULIS", contain more/higher?

[Response]: Thanks for the suggestion. We have incorporated the term "higher" after "contain".

Supplement:

Figure S4: Use different type of markers between the summer and winter values of AAE vs MAE for the current study.

[Response]: After a thorough examination of the provided Figure S4 and associated descriptions, we find that these statements lack precision. Consequently, we have made the decision to delete this figure and the corresponding statements.