Response to Anonymous Referee #1

This manuscript describes measurements of light-absorption properties and chemical composition of ambient water-soluble HULIS samples collected during haze episodes and clean periods. The measurements involve comprehensive chemical analyses including carbon analysis (OC/EC and TOC), ion chromatography for inorganic ions, and ESI FTICR MS for organics. The light absorption properties were quantified using UV-vis spectrometry.

General comments:

- The data set produced in this study, especially the ESI FTICR MS data, is extensive and informative. However, there are various instances where assertions are made that are not supported by the data, and are at some points contradictory with other assertions in different parts of the manuscript. Please see specific examples under 'Specific comments' below.

Re: We appreciated the reviewer for the constructive and valuable comments, which is of great help to improve the quality of the manuscript. According to your 'Specific comments', we have carefully and thoughtfully revised the manuscript, and responded to all comments point by point, and explained how the reviewers' comments and suggestions were addressed in the current version of the manuscript.

- The term HULIS as used in this manuscript needs to be better defined. HULIS is a vague term – much like brown carbon – that has been used to refer to different things in different studies. Here, HULIS is obtained based on an extraction procedure that isolates the less polar fraction (~50%) of WSOC. It would be helpful for the reader to explicitly indicate in the methods section that this definition is operational, and also contrast the definition of HULIS in this study with other studies. This is important because the results are compared to multiple previous studies on HULIS, and it should be noted that not all HULIS are defined the same way.

Re: Thanks. We agreed with your comments that although the term “HULIS” has been used in many literatures, this concept is still vague, which may refer to different things in different studies. Therefore, the term HULIS should be defined in the manuscript, which are important when compared it with those in previous studies.

In this study, HULIS was isolated based on a water-extraction and SPE method that has been widely used by researchers in atmospheric science and environment (Lin et al., 2012; Fan et al., 2012, 2013; Zou et al., 2020; Jiang et al., 2020; Qin et al., 2022). According to your comments, we have added the operational definition of HULIS in the Method section. The revisions stated in the revised manuscript are as below:

“It is noted that the HULIS here is the hydrophobic portion of water-soluble organic matter, which can be isolated with different types of SPE columns (e.g., HLB, C-18, DEAE, XAD-8, and PPL) (Fan et al., 2012, 2013; Lin et al., 2012; Zou et al., 2020; Jiang et al., 2020; Qin et al., 2022). Although each resin type has its special chemical properties, the hydrophobic HULIS isolated with different sorbents were similar in chemical, molecular properties based on previous studies (Fan et al., 2012, 2013; Zou et al., 2020). Therefore, for better comparison with other studies, the hydrophobic fractions isolated by SPE methods were all termed as HULIS in the present paper.” Please see Lines 151-158.

Reference:

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.

Fan, X., Song, J., Peng, P.: Comparative study for separation of atmospheric humiclike substance (HULIS) by ENVI-18, HLB, XAD-8 and DEAE sorbents: elemental composition, FT-IR, 1H-NMR and off-line thermochemolysis with tetramethylammonium hydroxide (TMAH). Chemosphere 93, 1710–1719, 10.1016/j.chemosphere.2013.05.045, 2013.

Jiang, H., Li, J., Chen, D., Tang, J., Cheng, Z., Mo, Y., Su, T., Tian, C., Jiang, B., Liao, Y., and Zhang, G.: Biomass burning organic aerosols significantly influence the light absorption properties of polarity-dependent organic compounds in the Pearl River Delta Region, China, Environ Int, 144, 106079, 10.1016/j.envint.2020.106079, 2020.

Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: 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, 10.1021/es300285d, 2012.

Qin, J., Zhang, L., Qin, Y., Shi, S., Li, J., Gao, Y., Tan, J., and Wang, X.: pH-Dependent Chemical Transformations of Humic-Like Substances and Further Cognitions Revealed by Optical Methods. Environ Sci Technol, 56, 7578-7587, 10.1021/acs.est.1c07729, 2022.

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.

Specific comments:

- Section 2.4 and 2.5 should be combined: ESI-MS is also chemical analysis.

Re: Thanks. We have combined Section 2.4 and 2.5 as “2.4. Chemical analysis” in the current manuscript. Please see Line 165.

- Line 165: The manuscript presents results of $PM_{2.5}$ concentrations, but there is not description of how the $PM_{2.5}$ concentrations are measured in the methods section.

Re: Thanks for your comments. In this study, the $PM_{2.5}$ concentrations were determined by weighing the filters before and after collection. The details have been added in the Method section of the current manuscript. Please see Lines 125-130.

- Figure 1: There are inconsistencies in the x-axis values: the distance between the major ticks changes between 1 day (e.g. 1/24 – 1/25) and 2 days (e.g. 1/10 – 1/12).

Re: Sorry for this error. We have corrected that in the Figure 1.

- Figure 1f: how come the Lev/OC value are larger than 1? Lev is one of many OC species.

Re: Sorry, it is clerical error. We have revised "Lev/OC" in the right vertical axis to "Lev/OC ($\times 10^{-3}$)" in the Figure 1f.

- Line 218-219: The statement that Lev/OC increased in haze-II is not accurate. There are 2 data point for Lev/OC in haze-II (Figure 1f): one is higher than haze-I and one is lower than haze-I.

Re: We apologized for this error. Based on your comment, we have revised that in the current manuscript. Please see Lines 241-243.

- Line 232-233: This is not valid. AAE is a measure of the wavelength dependence of light absorption, not the magnitude of light absorption.

Re: Thanks for your comment. We agreed with that AAE is a measure of the wavelength dependence of light absorption, not the magnitude of light absorption. As shown in Figure 1i, the AAE values for HULIS were higher than those for WSOC in the same sample. We think that this difference may be related with the light-absorbing organic species in the isolated HULIS fractions have strong wavelength dependence than those in the original WSOC. We have revised that in the current manuscript. Please see Lines 254-256.

- Line 248-260: The statement on line 251 that MAE of HULIS is generally higher than WSOC is not valid. The values for HULIS (1.1 +/- 0.27) and WSOC (1 +/- 0.21) are virtually the same. In Lines 254-256, MAE of HULIS (1.1 +/- 0.27) is said to be "comparable" to other values ranging between 0.91 and 1.84. Then in line 257-259, MAE of 0.91 is said to be "much lower" than MAE of 1.3. These statements are subjective and inconsistent.

Re: Thanks for your comments. At first, we agreed with the comment that the MAE_{365} values for HULIS (1.1 ± 0.27) and WSOC (1.0 ± 0.21) are virtually the same. Accordingly, we have revised this sentence to "'the average MAE_{365} value for WSOC was 1.0 ± 0.21 m^2 gC^{-1} (0.68–1.3 m^2 gC^{-1}), nearly same to 1.1± 0.27 m^2 gC^{-1} (0.77–1.8 m^2 gC^{-1}) for HULIS, during the entire sampling period" in the current manuscript. Please see Lines 271-273.

In addition, for the statement in Lines 254-256, I want to say is that the MAE_{365} values of HULIS (1.1 ± 0.27) in this study are dropped in the ranges between 0.91 and 1.84 reported in previous studies. The "comparable" is an inaccurate word, so we have revised that in the current manuscript. Please see Lines 274-275.

Finally, for the statement in Lines 257-259, we think it is right. As shown in Table S2, the MAE_{365} values for HULIS were 0.91±0.03 and 0.95 ± 0.11 m^2 gC^{-1} in haze-I and haze-II days, respectively, which were lower than those (1.3 ± 0.22 and 1.3 ± 0.27 m^2 gC^{-1}, respectively) observed in clean-I and clean-II days.

- Line 263-266: The argument that stagnant conditions lead to prolonged oxidation thus lower MAE for haze versus clean days is not convincing. It is not clear that the PM sampled during the haze days had longer atmospheric lifetime / OH exposure. What if the PM in the clean days had more contribution from long-range transported PM?

Re: Thanks for your comments. We agreed with that the argument that stagnant conditions lead to prolonged oxidation thus lower MAE for haze versus clean days is not convincing because it is not clear if the PM sampled during the haze days or the clean days had longer atmospheric lifetime. According to the variation of meteorological parameters and atmospheric trace gases (e.g., ozone) and molecular properties of HULIS during the entire sampling period, we think that the relative lower MAE_{365} values for haze HULIS may potentially contribute to the enhanced oxidation reaction that was derived by the increased ozone levels and high temperature and relative humidity during haze days (Figure 1). This stronger oxidation process would lead the chromophores containing C=C unsaturated bond to be severely degraded. Accordingly, we have revised that in the current manuscript. Please see Lines 284-288.

- Line 285-286: It is not clear how the presence of these 3 molecules suggests contribution from biomass burning and vehicular emissions.

Re: Thanks. In our study, these 3 molecules (i.e., Compounds a ($C_7H_7NO_3$) and b ($C_8H_6O_4$), and d($C_8H_{18}O_4S$) with stronger arbitrary abundance were identified, which may derived from biomass burning and vehicular emissions as reported in previous studies (Table S3) (Mohr et al., 2013; Riva et al., 2015; Blair et al., 2017). Therefore, the detection of these molecules in this study suggested some contribution from biomass burning and vehicular emissions. We have clarified that in the current manuscript. Please see Lines 303-306.

References:

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prevot, A. S., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton, J. A.: Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time, Environ Sci Technol, 47, 6316-6324, 10.1021/es400683v, 2013.

Matthieu Riva, Ellis S. Robinson, Emilie Perraudin, Neil M. Donahue, and Eric Villenave. Photochemical Aging of Secondary Organic Aerosols Generated from the Photooxidation of Polycyclic Aromatic Hydrocarbons in the Gas-Phase[J]. Environmental Science & Technology: ES&T, 49, 5407-5416, 10.1021/acs.est.5b00442, 2015.

Blair S. L., Macmillan, A. C., Drozd G. T., Goldstein A. H., Chu R. K., Ljiljana P., Shaw J. B., Tolic Nikola, Lin Peng., Laskin J., Laskin A., and Sergey A. Nizkorodov. Molecular characterization of organosulfur compounds in biodiesel and diesel fuel secondary organic aerosol. American Chemical Society. Environ. Sci. Technol., 51, 119-127, 10.1021/acs.est.6b03304, 2017

- Line 308-318: This paragraph mentions that HULIS in haze days had higher MW than in clean days, and makes the point that high MW HULIS is more resistant to chemical transformation. This is in contrast with the assertions in section 3.2 that MAE on haze days were smaller than on clean days because HULIS on haze days underwent more chemical transformation.

Re: Thanks for the good comments. As mentioned in this study, HULIS in haze days had higher MW values than those in clean days, but the MAE_{365} values on haze days were smaller than on clean days (Table S2, S4, and S5). We think these results are scientifically reasonable in the present study: (1) MAE_{365} is a key parameter signifying the light absorption ability of HULIS or BrC. According to previous studies, the MAE_{365} values were mainly affected by their unsaturated aromatic structures and they didn't exhibit significant relationship with the MW of HULIS or BrC (Song et al, 2019; Zeng et al., 2021; Jiang et al., 2021). As indicated in Table S4 and S5, although HULIS had higher MW during haze days, the AI_{mod} values of haze HULIS were relatively lower. This result indicated that the haze HULIS were characterized by comparatively lower degree of conjugation or aromaticity, therefore, the MAE_{365} values on haze days were smaller than on clean days is scientifically reasonable. (2) The HULIS is a class of highly complex organic compounds, which consists of various types of aromatic and aliphatic molecules. In general, the organic molecules

containing unsaturated bonds (e.g., aromatic structures, olefins) are relatively labile than those saturated aliphatic compounds (e.g., aliphatic acids), which are easy to be degraded during the atmospheric oxidation process (Claflin et al., 2018). Therefore, it is reasonable that the enhanced oxidation reaction during haze days degraded more aromatic structures and lead to relative lower MAE_{365} values for haze HULIS. (3) Base on previous studies, the low MW compounds are more susceptible to atmospheric oxidation processes, while the high MW compounds have relatively higher chemical resistance (Di Lorenzo et al., 2016; Wong et al., 2017), therefore the enhanced oxidation reaction during haze days also lead to the enrichment of high MW HULIS compounds in haze days than in clean days. We have clarified that in the current manuscript. Please see Lines 335-342.

References:

Claflin, M. S.; Ziemann, P. J. Identification and quantitation of aerosol products of the reaction of β-pinene with NO_3 radicals and implications for gas- and particle-phase reaction mechanisms. J Phys Chem A 2018, 122 (14), 3640-3652.

Di Lorenzo, R. A.; Washenfelder, R. A., Attwood, A. R., Guo, H., Xu, L., Ng, N. L., Weber, R. J., Baumann, K., Edgerton, E., and Young, C. J.: Molecular-Size-Separated Brown Carbon Absorption for BiomassBurning Aerosol at Multiple Field Sites. Environ Sci Technol, 51, 3128−3137, 10.1021/acs.est.6b06160, 2017.

Jiang, H., Li, J., Sun, R., Tian, C., Tang, J., Jiang, B., Liao, Y., Chen, C. E., and Zhang, G.: Molecular Dynamics and Light Absorption Properties of Atmospheric Dissolved Organic Matter, Environ. Sci. Technol., 55, 10268–10279, 10.1021/acs.est.1c01770, 2021.

Song, J., Li, M., Fan, X., Zou, C., Zhu, M., Jiang, B., Yu, Z., Jia, W., Liao, Y., Peng, P.: Molecular Characterization of Water- and Methanol-Soluble Organic Compounds Emitted from Residential Coal Combustion Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Environ Sci Technol, 53, 13607-13617, 10.1021/acs.est.9b04331, 2019.

Wong, J. P. S., Nenes, A., and Weber, R. J.: Changes in Light Absorptivity of Molecular Weight Separated Brown Carbon Due to Photolytic Aging, Environ Sci Technol, 51, 8414-8421, 10.1021/acs.est.7b01739, 2017.

Zeng, Y., Ning, Y., Shen, Z., Zhang, L., Zhang, T., Lei, Y., Zhang, Q., Li, G., Xu, H., Ho, S. S. H., Cao, J.: 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. J Geophys Res Atmos, 126, 10.1029/2021JD034791, 2021.

- Line 319-330: This paragraph makes the point that lower AI_mod for haze days can be due to photooxidation during haze days and explain that lower MAE for haze days. How is this assertion reconciled with the larger MW and resistance to oxidation mentioned in the previous paragraph?

Re: Thanks for your comment. As discussed above, we think it is scientific reasonable. As indicated in this study, the molecular properties of HULIS in different stages of haze process exhibited some observable differences. The HULIS samples in haze days presented relatively higher MW and relatively lower $AI_{mod,w}$ values than those in clean days (Table S4). These results indicated that the haze HULIS have relatively higher molecular weight, but their aromaticity were lower than the clean HULIS. We think that these results could be related to the evolution of different types of HULIS molecules during atmospheric oxidation process. On the one hand, the organic molecules containing unsaturated aromatic structures are relatively labile than those saturated aliphatic molecules, which are easy to be degraded during the atmospheric oxidation process (Claflin et al., 2018). Therefore, the enhanced oxidation during haze days would degrade more aromatic structures and lead to relative lower $AI_{mod,w}$ values for haze HULIS. On the other hand, the low molecular weight compounds are more susceptible to atmospheric oxidation processes, while the high MW organic compounds have relatively higher chemical resistance (Di Lorenzo et al., 2016; Wong et al., 2017), therefore the enhanced oxidation reaction during haze days also lead to the haze HULIS are characterized with relative higher MW values. Therefore, the

haze HULIS have relative lower AI_{mod} and higher MW values than the clean HULIS is scientific reasonable.

References:

Claflin, M. S.; Ziemann, P. J. Identification and quantitation of aerosol products of the reaction of β-pinene with NO_3 radicals and implications for gas- and particle-phase reaction mechanisms. J Phys Chem A 2018, 122 (14), 3640-3652.

Wong, J. P. S., Tsagkaraki, M., Tsiodra, I., Mihalopoulos, N., Violaki, K., Kanakidou, M., Sciare, J., Nenes, A., and Weber, R. J.: Atmospheric evolution of molecular-weight-separated brown carbon from biomass burning, Atmos Chem Phys, 19, 7319–7334, 10.5194/acp-19-7319-2019, 2019.

- Line 374-378: It does not look like the statement "relatively low BBOA content" is supported by the data in Figure 3. Most of the molecules are clustered in the region identified as BBOA. In any case, previous parts of the manuscript mention BBOA as being an important contributor to HULIS measured in this study, but this paragraph mentions that traffic sources are more important.

Re: We apologized for this error. At first, we agreed with your comment that "relatively low BBOA content" is an inaccurate description. Accordingly, we have removed that in the current manuscript.

In addition, we also agreed with your comment "BBOA is an important contributor to HULIS as measured in this study", however some HULIS species derived from the traffic sources were also identified. As shown in Table S6 and Figure 3, relative contents of traffic sources in haze days are higher than in clean days, but BBOA is still the most important contributor to HULIS in the present study. We have revised that in the current manuscript. Please see Lines 389-391, 397-400.

Minor comments:

- Line 80-83: The statement talks about ‘recent years’ but is supported by a reference from 2014. A newer reference is needed.

Re: Thanks. We have added three new references in the current manuscript. Please see Lines 86-87.

References:

An, Z., Huang, R. J., Zhang, R., Tie, X., Li, G., Cao, J., Zhou, W., Shi, Z., Han, Y., Gu, Z., and Ji, Y.: Severe haze in northern China: A synergy of anthropogenic emissions and atmospheric processes, Proc Natl Acad Sci USA, 116, 8657-8666, 10.1073/pnas.1900125116, 2019.

Li, K., Jacob, D. J., Liao, H., Shen, L., Zhang, Q., and Bates, K.H.: Anthropogenic drivers of 2013 – 2017 trends in summer surface ozone in China, P. Natl. Acad. Sci. USA, 116, 422 – 427, https://doi.org/10.1073/pnas.1812168116, 2019.

Yang, X., Lu, K., Ma, X., Gao, Y., Tan, Z., Wang, H., Chen, X., Li, X., Huang, X., He, L., Tang, M., Zhu, B., Chen, S., Dong, H., Zeng, L., and Zhang, Y.: Radical chemistry in the Pearl River Delta: observations and modeling of OH and HO_2 radicals in Shenzhen in 2018. Atmos. Chem. Phys., 22, 12525-12542, 10.5194/acp-22-12525-2022, 2022

- Line 91: What is meant by ‘exact’?

Re: We are sorry for this inaccurate word. We have deleted it in the current manuscript. Please see Line 101.

- Line 99-102: This sentence is not comprehensible.

Re: Thanks. We have rewritten this sentence in the current manuscript. Please see Lines 109-112.

- Line 180-182: This statement is not valid. Wind speed alone does not dictate stability (See stability classifications by Turner 1970). In fact, for an unstable atmosphere, increasing wind speed makes the atmosphere less unstable.

Re: Thanks for your comments. We have deleted it in the current manuscript.

- Line 277-279: Vague statement. In what sense are the peaks "comparable" with peaks from other studies?

Re: Sorry for this vague statement. We have deleted that in the current manuscript.

- Line 337-339: I assume you mean biomass burning aerosol (not biomass burning mixture). In any case, what does "comparable" mean here?

Re: Yes. It is biomass burning aerosol. In addition, the "comparable" is an inaccurate word. We have rewritten that in the current manuscript. Please see Lines 361-363.