Response to Anonymous Referee #2

This manuscript reports the measurements of the water-soluble organic carbon (WSOC) and WS-HULIS fraction of $PM_{2.5}$ samples collected in a developed region with dense populations during a haze event; the authors conducted a comprehensive analysis of the chemical composition and light absorption with their samples. They investigated the evolution of light absorption and molecular properties of these samples during one haze cycle (clean-haze bloom-haze decay-clean). While I think the subject is very interesting, there are several issues with this manuscript, including the analysis and conclusions, which are detailed below.

Re: Thanks for the constructive and valuable comments, which is of great help to improve the quality of the manuscript. According to your 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 are handled in the current manuscript.

General comments:

- It will be necessary for the author to provide more details in the results and discussion, especially when making deductions and conclusions. This manuscript provides a very comprehensive dataset of the chemical and optical analysis of their samples. However, in the data interpretation, some of their conclusions/statements are given too simply and vaguely, which needs to be supported with more details and be more specific. For example, in explaining the variance in properties (MW, MAE, etc) of HULIS and WSOC obtained during different stages of the haze event (e.g., haze day vs clean days), the authors mostly attribute these differences to statements such as “effects of aging/oxidation/degradation” without further explanations or details. Since the aging process involves many different pathways and mechanisms, the authors will need to be more specific in the results when explaining the data other than just simply stating “aging”.

Re: Thanks for your comments. We agreed to your comments that some of statements are given too simply and vaguely in the data interpretation, especially for the variance in properties (MW, MAE, etc) of HULIS and WSOC obtained during different stages of the haze event. In the current manuscript, we have revised that and provided more specific interpretations in the results and discussion. Please see Lines 284-288, 335-342, 361-363, 543-545, 592-593, 598.

- The "HULIS fraction" used in this manuscript needs to be better described and defined since this is the major substance studied here. Adding some brief descriptions in the introduction would be necessary. HULIS was first reported as macromolecular organic substances in atmospheric aerosol particles; and when used to refer to the light absorbing properties of the atmospheric aerosols, "HULIS" – humic-like substance, is more describing the similarities in the light absorption of the light absorbing organic carbons (e.g., brown carbon) with humic substances, which is a light absorption that sharply decreases from UV to visible wavelength. Also, many different methods for the extraction/isolation of HULIS have been reported, and the potential effects of the extraction/isolation procedure on the chemical/physical nature of HULIS have aroused concerns as well. For instance, the HULIS part could be large molecules formed by intermolecular force (aggregates) and the procedure (extraction solvent, PH adjustment, SPE, etc.) would largely change it. I think a discussion of the nature of HULIS and a brief explanation of your choice for the isolation method, at least under the circumstances of this manuscript, is important for the data interpretation later in the result section.

Re: Good comments. We agreed with your comments that a discussion of the nature of HULIS and a brief explanation of the isolation method should be added in the manuscript. This is important for the data interpretation later in the result section and compared it with those in previous studies. According to your comments, we have added some descriptions in the Introduction and Method sections. The revisions stated in our revised manuscript are as below:

"Water-soluble humic-like substances (HULIS), belonging to a class of highly complex organic compounds with physical/chemical properties similar to humic substances in natural environments" and "They are thought to be comprised of aromatic structures containing aliphatic side side chains and oxygenated functional groups such as hydroxyl, carboxyl, nitrate, and organosulfate groups". Please see Lines 42-44, 47-50.

"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.

- In order to highlight the novelty of this manuscript, it's better to have a brief summary of the work about HULIS fractions/WSOC of $PM_{2.5}$ in the Pearl River Delta with emphasis on the major contributions of this manuscript to the current state of knowledge regarding this topic. I do notice there is one sentence mentioning that there are previous works regarding this topic (line 83-86), however, I think brief descriptions of the referred studies are necessary. Also, is this the only work studying the chemical/optical evolution of WSOC/HULIS/Brown carbon collected in PRD? If not, what have the other studies done?

Re: Thanks. According to your comments, we have added brief descriptions of the referred studies. In addition, we also added new references related with the chemical/optical evolution of WSOC/HULIS/Brown carbon collected in PRD in the current manuscript. The detailed revisions are:

"Several studies have investigated the optical, chemical, and molecular properties of HULIS in the PRD region (Lin et al., 2010, 2012; Fan et al., 2016; Liu et al., 2018;

Jiang et al., 2020, 2021a,b). For example, the studies on the temporal variations of water-soluble HULIS in Guangzhou indicated that HULIS had higher concentrations and mass absorption efficiencies (MAE365) in the winter, which were attributed to the increasing contribution of BB and secondary nitrate formation in the winter monsoon period (Fan et al., 2016; Jiang et al., 2020, 2021a). In addition, the molecular composition of HULIS (and BrC) in the PRD region were also investigated and demonstrated that the levels of unsaturated and aromatic structures are the important factor influencing their light absorption properties (Jiang et al., 2020, 2021b)." Please see Lines 87-96.

References:

Fan, X., Song, J., and Peng, P.: Temporal variations of the abundance and optical properties of water soluble Humic-Like Substances (HULIS) in $PM_{2.5}$ at Guangzhou, China, Atmos Res, 172-173, 8-15, doi:10.1016/j.atmosres.2015.12.024, 2016.

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.

Jiang, H., Li, J., Sun, R., Liu, G., Tian, C., et al. Determining the sources and transport of brown carbon using radionuclide tracers and modeling, J Geophys Res Atmos, 126, e2021JD034616, doi:org/10.1029/2021JD034616, 2021a.

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, https://doi.org/10.1021/acs.est.1c01770, 2021b.

Lin, P.; Engling, G.; Yu, J. Z.: Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China. Atmos Chem Phys, 10, 6487−6500, 10.5194/acp-10-6487-2010, 2010.

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.

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.

Specific comments:

Line 37: comment for writing — "stronger" than what?

Re: This is inaccurate word. We have deleted it in the current manuscript.

Line 44: "natural environment" It is better to be more specific here about what environment (e.g., natural aquatic / soil environment).

Re: Thanks. We revised it to "natural aquatic/soil environment" in the current manuscript. Please see Line 44.

Line 45-46: "> 70% of light absorption in water-soluble brown carbon (BrC)" This need to be more specific about the wavelength/wavelength range or what parameters they used to compare (e.g., mass absorption coefficients, etc), if possible.

Re: Thanks. In this study, "> 70% of light absorption in water-soluble brown carbon (BrC)" was calculated by light absorption at 365 nm. We have clarified it in the current manuscript. Please see Line 46.

Line 114: "Field blank samples were collected without power on." Does this mean that the blank filter is "conditioned" in the air sample holder rather than conditioned in the sampling environment (e.g., passing particle-free air through the filter)? If so, can you explain why you chose this way as "blank control"?

Re: Yes. In this study, the blank filter is "conditioned" in the air sample holder on the sampling site. This method was chosen because: (1) In this study, field blank samples were collected in the air sample holder and then were analysed exactly as the procedure for the $PM_{2.5}$ samples. This is a good method for estimating the potential pollution during the $PM_{2.5}$ sampling operation and the lab's operation (including filter sample weighting, water extraction, SPE isolation, etc.) and has been recommended by US EPA (Watson et al., 1998) and widely used for correcting the filter $PM_{2.5}$ samples in many studies (Li et al., 2020; Zhu et al., 2020; Jiang et al., 2021; Deng et al., 2022; Zhan et al., 2022). (2) in this study, the $PM_{2.5}$ sampler is a high-volume sampler (1.0 m^3 min^{-1}), therefore, it is impracticable to collect blank filter using a particle-free air during 24-h field sampling period. Therefore, "conditioned in the air sample holder" was used as "blank control" in this study.

References:

Deng, J. J., Ma, H., Wang, X. F., Zhong, S. J., Zhang, Z. M., Zhu, J. L., Fan, Y. B., Hu, W., Wu, L. B., Li, X. D., Ren, L. J., Pavuluri, C. M., Pan, X. L., Sun, Y. L., Wang, Z. F., Kawamura, K., and Fu, P. Q.: Measurement report: Optical properties and sources of water-soluble brown carbon in Tianjin, North China insights from organic molecular compositions, Atmos Chem Phys, 22, 6449-6470, 10.5194/acp-22-6449-2022, 2022.

Jiang, H., Li, J., Sun, R., Liu, G.,Tian, C., Tang, J., Cheng Z., Zhu S., Guangcai Zhong G., Ding X., and Zhang G.. Determining the sources and transport of brown carbon using radionuclide tracers and modeling. Journal of Geophysical Research: Atmospheres, 126, e2021JD034616. https://doi. org/10.1029/2021JD034616, 2021.

Li, J. J., Zhang, Q., Wang, G. H., Li, J., Wu, C., Liu, L., Wang, J. Y., Jiang, W. Q., Li, L. J., Ho, K. F., and Cao, J. J.: Optical properties and molecular compositions of water-soluble and water-insoluble brown carbon (BrC) aerosols in northwest China, Atmos Chem Phys, 20, 4889-4904, 10.5194/acp-20-4889-2020, 2020.

Watson, J.G., J.C. Chow, H. Moosmüller, M. Green, N. Frank, and M. Pitchford: Guidance for Using Continuous Monitors in PM2.5 Monitoring Networks: Draft 03/06/98. Prepared for Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 27711 by Desert Research Institute, Reno, Nev, 1998.

Zhan, Y. A., Li, J. L., Tsona, N. T., Chen, B., Yan, C. Q., George, C., and Du, L.: Seasonal variation of water-soluble brown carbon in Qingdao, China: Impacts from marine and terrestrial emissions, Environ Res, 10.1016/j.envres.2022.113144, 212, 2022.

Zhu, C. S., Li, L. J., Huang, H., Dai, W. T., Lei, Y. L., Qu, Y., Huang, R. J., Wang, Q. Y., Shen, Z. X., and Cao, J. J.: n-Alkanes and PAHs in the Southeastern Tibetan Plateau: Characteristics and Correlations With Brown Carbon Light Absorption, J Geophys Res-Atmos, 125, 10.1029/2020JD032666, 2020.

Line 121-122: "Briefly, portions of the $PM_{2.5}$ samples (100 cm^2) were ultrasonically extracted with 50 mL of ultrapure water for 30 min. The extracts were filtered through a 0.22-µm PTFE syringe filter and then adjusted to pH of 2 with HCl…". I didn't find the description of the WSOC fraction here. Or is the extraction of WSOC the same as described for HULIS except for the PH adjustment and following procedure? I think this needs to be clarified here.

Re: Thanks. In this study, portions of the $PM_{2.5}$ samples (100 cm^2) were ultrasonically extracted with 50 mL of ultrapure water for 30 min. The extracts were filtered through a 0.22-µm PTFE syringe filter to remove the suspended insoluble particles. About 50 mL of water extracts were obtained from each sample, of which 20 mL was used for the isolation and analysis of HULIS, 20 mL for analysis of water soluble organic carbon (WSOC), and the remainder for the analysis of inorganic ions, respectively. Then the 20 mL water extracts were adjusted to 2 with HCl and introduced into a pre-conditioned HLB cartridge. The hydrophilic fraction (i.e., inorganic ions, high-polar organic acids, etc) was removed with ultrapure water, whereas the relatively hydrophobic HULIS fraction was retained and eluted with 2% (v/v) ammonia/methanol. Finally, HULIS solution was evaporated to dryness with a gentle

N_2 stream and redissolved with ultrapure water for the analysis. We have clarified it in the current manuscript. Please see Lines 138-144.

Line 232-233 “This difference may be related to the higher enrichment of light-absorbing organic species in HULIS.” The statement is oversimplified and needs more specific explanation and evidence to describe why the enrichment of light-absorbing OC doesn’t simply enhance the light absorption at certain wavelengths but the wavelength dependence (AAE).

Re: Thanks for your comments. In this study, 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 263-265: it might need to be more specific about the “secondary oxidation reaction” and “photolytic aging” here. It is "prolonged" or "enhanced" oxidation during haze? for example, the increased ozone levels associated with high levels of $PM_{2.5}$ could be a drive for oxidation during haze days.

Re: Thanks for your comments. We agreed with that it need to be more specific about the “secondary oxidation reaction” and “photolytic aging” here. Although it is not clear if the PM sampled during the haze days or the clean days had longer atmospheric lifetime, we think the "enhanced" oxidation during haze could lead to strong aging of HULIS, which was mainly derived by the increased ozone levels and high temperature and relative humidity during the haze days. Accordingly, we have revised that in the current manuscript. Please see Lines 284-288.

Line 315-318: The author needs to mention that the samples used in Dasari and Wong’s work are from different sources (mostly biomass burning aerosols) and are different from the samples used in this manuscript. In addition, the method for molecular weight estimation used in Wong's paper is also very different from this method (size-exclusion chromatography), in which the MW is estimated by the SEC column retention time, and it's also highly dependent on the column, the mobile phase, and the sample itself (e.g., polarity, aggregation, etc). Also, line 317-318 is a bit self-contradictory: HULIS in haze undergo stronger oxidation, which usually leads to fast degradation. However, "a longer aging process" means higher stability (longer lifetime), which means the HULIS is more stable during haze days. Or, is the "longer aging" simply implying that because they have a higher MW, they will have a longer lifetime in the atmosphere? There needs some clarification.

Re: Thanks for your comments. We agreed with that the samples used in the references are different from the samples used in this manuscript and the method for molecular weight estimation is also different the method in our study. We have clarified that in the current manuscript. Please see Lines 335-339.

For Lines 317-318: We are sorry for this vague interpretation. In this study, the MW values for HULIS during haze days were higher than those in clean days, as indicated in Table S4 and S5. These differences may be related to the enhanced oxidation reaction of HULIS during the haze days. In general, HULIS is class of highly complex organic compounds, with MW ranges from dozens to thousands. According to previous studies, the low MW fractions are more susceptible to bleaching and high MW fractions are recalcitrant under atmospheric oxidation processes of biomass burning aerosols (Di Lorenzo, et al., 2017; Wong et al., 2017; Dasari et al., 2019). Therefore, the enhanced oxidation reaction during haze days would lead to the enrichment of high MW compounds in HULIS during haze days. We have clarified that in the current manuscript. Please see Lines 335-342.

References:

Dasari, S., Andersson, A., Bikkina, S., Holmstrand, H., Budhavant, K., Satheesh, S., Asmi, E., Kesti, J., Backman, J., Salam, A., Bisht, D. S., Tiwari, S., Hameed, Z., and Gustafsson, Ö.: Photochemical degradation affects the light absorption of water-soluble brown carbon in the South Asian outflow, Sci Adv, 5, eaau8066, doi: 10.1126/sciadv.aau8066, 2019.

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.

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.

Even if the author wanted to use these two references to support their inference about the higher stability of HULIS in this manuscript, they didn't try to explain the variance in HULIS MW from different stages of the haze event (haze days vs clean days).

Re: Thanks for your comments. We have explained the variance in HULIS MW from different stages of the haze event in the current manuscript. Please see Lines 335-342.

Line 324-325: "These differences can be attributed to bleaching or degradation of aromatic compounds." As I understand it, "degradation" is one pathway that leads to bleaching, i.e., the degradation/oxidation of aromatic compounds could result in the bleaching of HULIS. There might need some clarification or rephrasing.

Re: Thanks for your comments. We have revised that in the current manuscript. Please see Lines 348-350.

Line 573-574: It is unclear if the “longer aging process” here means “a longer lifetime." Is this an inference or an observation?

Re: Thanks for your comments. The “longer aging process” is an inaccurate statement. In this study, the HULIS compounds should undergo relatively stronger oxidation during the haze days. We have revised that in the current manuscript. Please see Lines 592-593.