Response to reviewer #2

Thanks to the reviewer for your careful reading and your constructive comments and suggestions on our manuscript. The reviewer's comments and suggestions are shown as *italicized font*, our response to the comments is normal font. New or modified text is in normal font and in blue. Details are as follows.

Reviewer's comments:

Reviewer #2: *This study collected atmospheric* $PM_{2.5}$ *samples during wintertime in Changchun and identified the molecular structures in HULIS, providing a new insight into the potential sources and temperature effects on the light-absorption properties of HULIS. We have gained some new insights through this study, but there is still room for improvement.*

[Response]

Thanks for the reviewer's comments on this manuscript. Please check our point-by-point response and the modified text in the manuscript.

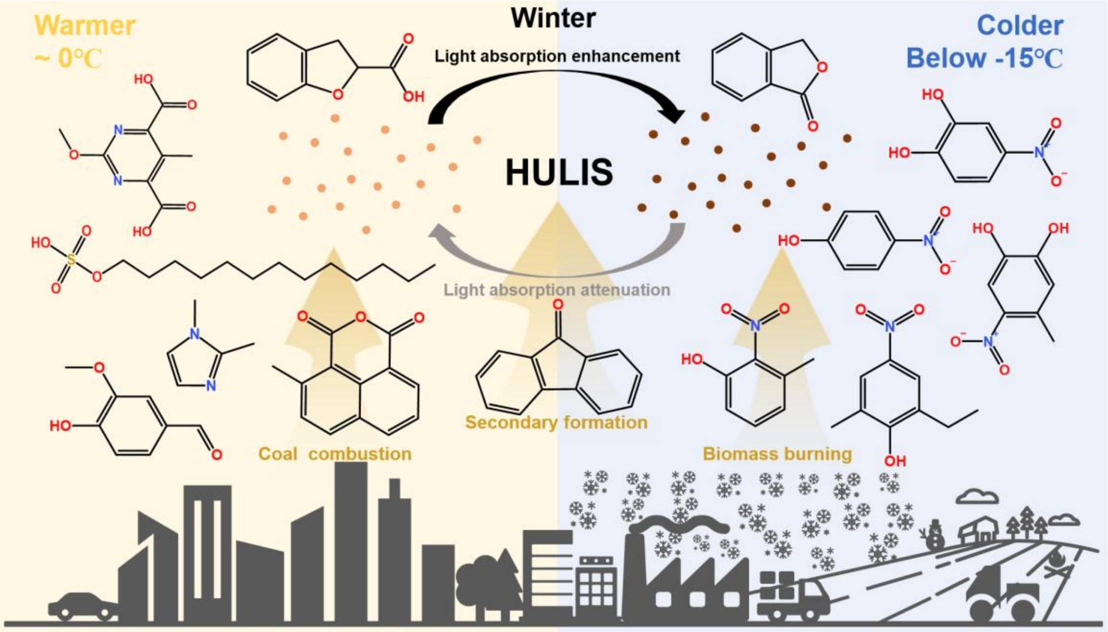
(1) Is the temperature division in Figure 3 based on the daily average temperature? Studying the impact of temperature on HULIS based on daily average temperature may be too crude. In addition, the temperature in the sampling area is generally low. How to compare the impact of high temperature on the formation of HULIS, because the so-called high temperature during the sampling period is far from the general high temperature, such as 20℃ or even 30℃ or above. Please clarify. Warm and cold need to be indicated the temperature range in the Graphical abstract.

[Response]

We sincerely thank the reviewer's comment. To address these concerns, we have implemented the following clarifications and revisions. Firstly, the 24-hour sampling period inherently precludes higher temporal resolution of ambient temperature. Each sample represents a daily average of HULIS, making daily average temperature the only operationally meaningful thermal indicator relative to the detected chemistry and optical properties of HULIS. Secondly, this study was explicitly designed to investigate HULIS evolution under severe winter conditions, not to characterize warm-season behavior. Consequently, experimentally addressing the impact of genuinely high temperatures (e.g., >20 °C) falls outside the scope of this specific field observation and its dataset. Upon reflection, we recognize that the original labels "Warm Weather" and "Cold Weather" in the Graphical Abstract, while intended to represent the relative conditions within our winter dataset, could indeed be misinterpreted as implying a comparison across seasons or to genuinely warm temperatures (e.g., >20 °C). This ambiguity was unintended. To eliminate any potential confusion and explicitly anchor the study within its exclusive wintertime context, we have revised the Graphical Abstract.

[Revised]

Graphical Abstract:



(2) *The average concentration and standard deviation of PM2.5 during the entire sampling period need to be reported in order to reflect the rationality of the selection of two typical haze events. The PM2.5 concentration of Event II is not high. Please indicate the basis for selecting these two events. The daily meteorological data and mean values of the entire sampling process also need to be presented in the attachment.*

[Response]

We sincerely appreciate the reviewer's valuable suggestions regarding event selection criteria and data transparency. In response, we have now reported the average concentration of pollutants (e.g. $PM_{2.5}$, HULIS-C, OC, EC, etc.) and meteorological data (Temperature, RH, wind speed) of the entire sampling period in **Table S6**. Event I and II were selected from all haze episodes ($PM_{2.5} > 75\ \mu g/m^3$) based on their maximal divergence in MAE_{365} values. Event I represented the most serious pollution episode (159.6 ± 53.8 $\mu g\ m^{-3}$ of $PM_{2.5}$ and 6.68 $\mu gC/m^3$ of HULIS-C) with lower light absorption efficiency of HULIS (1.56 $m^2\ gC^{-1}$ of $MAE_{365,HULIS}$), while Event II represented moderate pollution episode (83.7 ± 36.4 $\mu g\ m^{-3}$ of $PM_{2.5}$ and 4.65 $\mu gC/m^3$ of HULIS-C) but exhibited the highest $MAE_{365,HULIS}$ (2.06 $m^2\ gC^{-1}$) value. Moreover, Event I was characterized by continuous high RH (83.1 ± 4.6%) and strong emission of CO (1.56 ± 0.34 mg m^{-3}) and Event II was the Spring Festival period with a high SO_2 concentration (25.1 ± 15.1 $\mu g\ m^{-3}$) and the highest hourly SO_2 concentration reached 76 $\mu g\ m^{-3}$.

[Revised]

Line 169-177: To investigate drivers of the high concentrations and variable light absorption efficiency of HULIS in this study, we selected two samples (Event I and II) among all haze events ($PM_{2.5}$ concentration > 75 $\mu g\ m^{-3}$) that exhibited the maximal divergence in MAE_{365} values. Event I had higher

PM$_{2.5}$ (159.6 ± 53.8 μg m^{-3}) and HULIS-C (6.68 μgC m^{-3}) but lower MAE$_{365,\mathrm{HULIS}}$ (1.56 m^2 gC^{-1}), while Even II had lower PM$_{2.5}$ (83.7 ± 36.4 μg m^{-3}) and HULIS-C (4.65 μgC m^{-3}) but higher MAE$_{365,\mathrm{HULIS}}$ (2.06 m^2 gC^{-1}). These contrasting events were chosen for potential sources comparison from the perspective of molecular composition. Considering the lowest PM$_{2.5}$ and HULIS-C concentration, the sample on January 13 (PM$_{2.5}$ = 14.1 ± 11.9 μg m^{-3}, HULIS-C = 0.97 μgC m^{-3}, MAE$_{365,\mathrm{HULIS}}$ = 1.28 m^2 gC^{-1}) was selected to represent clean days. **Figure 2** exhibited the reconstructed MS spectra, the number, and concentration fraction of HULIS in both positive and negative modes.

Table S6. Meteorological parameters and concentrations of pollutants during two haze events, clean day, and overall period.

Parameters	Event I	Event II	Clean day	Overall
PM$_{2.5}$ (μg/m^3)	159.5 ± 53.8	83.7 ± 36.4	14.1 ± 11.9	50.7 ± 34.3
HULIS-C (μgC/m^3)	6.68	4.65	0.97	2.97 ± 1.54
OC (μgC/m^3)	27.8	16.6	4.6	11.7 ± 5.7
EC (μgC/m^3)	3.2	4.6	1.3	2.1 ± 0.9
OC/EC	8.7	3.6	3.6	5.7 ± 1.4
Na$^+$ (μg/m^3)	0.33	0.37	0.07	0.21 ± 0.13
K$^+$ (μg/m^3)	1.89	7.20	0.25	1.66 ± 2.43
NH$_4^+$ (μg/m^3)	20.65	4.30	1.32	4.32 ± 4.09
Cl$^-$ (μg/m^3)	5.69	7.29	0.77	3.06 ± 1.92
NO$_3^-$ (μg/m^3)	41.56	6.79	2.09	7.40 ± 8.80
SO$_4^{2-}$ (μg/m^3)	16.66	7.30	1.32	4.09 ± 3.51
SO$_2$ (μg/m^3)	20.9 ± 5.3	25.1 ± 15.1	10.6 ± 4.2	18.1 ± 8.8
NO$_2$ (μg/m^3)	69.5 ± 12.6	31.5 ± 13.3	11.3 ± 5.2	33.6 ± 19.4
O$_3$ (μg/m^3)	14.2 ± 10.4	33.1 ± 19.2	64.9 ± 7.2	35.7 ± 18.6
CO (mg/m^3)	1.56 ± 0.34	0.79 ± 0.20	0.27 ± 0.10	0.65 ± 0.36
Relative Humidity (%)	83.1 ± 4.6	61.9 ± 14.0	51.6 ± 8.7	60.9 ± 13.8
Temperature (℃)	-10.0 ± 4.1	-18.3 ± 4.3	-10.9 ± 4.4	-13.3 ± 6.8
Wind Speed (m/s)	1.6 ± 0.6	1.7 ± 0.9	1.7 ± 0.5	3.3 ± 1.8

(3) *Table S5 only shows the concentrations of K+ and SO$_2$ for two pollution events and does not compare them with other non-polluting days. How can you know that these two pollution events were strongly contributed by biomass and coal combustion?*

[Response]

We sincerely appreciate the reviewer's insightful comment regarding source attribution. To substantiate the important contribution of biomass burning and coal combustion during Event I and II, we have incorporated the clean-day sample for comparison in the revised manuscript. First, as well-established biomass burning tracer, K+ showed 7.6-fold and 28.8-fold elevations in Event I (1.89 μg m^{-3}) and Event II (7.20 μg m^{-3}) relative to clean-day (0.25 μg m^{-3}). This indicated that K+ enrichment, particularly in Event II, aligns with intensive biomass burning. Second, Event I (20.9 μg m^{-3}) and Event

II (25.1 μg m^{-3}) maintained 1.97-2.37 times higher levels of SO_2 than clean-day (10.6 μg m^{-3}), consistent with enhanced emission from coal combustion. Third, source apportionment results in our previous study identified biomass burning (13.6 – 21.1%) and coal combustion (14.5 – 17.7%) as important sources of particles in Changchun, winter via PMF model. The tracer enhancements during haze events confirmed the important contribution of biomass burning and coal combustion.

[Revised]

Line 184-192: In the positive mode, Event I and II had similar molecular composition, both dominated by CHO compounds, followed by CHON, CHN, and others. The most abundant species in Event I and II were 9-fluorenone (*m/z* 181.0643) and 2-[(1E)-1-Buten-1-yl]-5-methylfuran (*m/z* 137.0958), respectively. The former originates from diverse combustion sources such as biomass burning, coal combustion, and vehicle emission (Alves et al., 2016; Huo et al., 2021; Ma et al., 2023; Souza et al., 2014; Xu et al., 2024; Zhao et al., 2020), whereas the latter is believed to stem specifically from biomass burning (Bhattu et al., 2019; Hatch et al., 2015). High concentrations of biomass burning (K^+) and coal combustion (SO_2, **Table S6**) tracers proved the key contribution of biomass burning and coal combustion (Chen et al., 2017; Dutton et al., 2009; He et al., 2010; Liang et al., 2021), which have been confirmed in our previous study to be the main sources of air pollution in Changchun winter (Dong et al., 2023).

(4) Can the mechanism of low temperatures reducing the photobleaching of brown carbon be further explored? And is it related to relative humidity?

[Response]

We are grateful for the reviewer's insightful questions regarding the mechanisms of photobleaching suppression under low temperatures and the role of relative humidity (RH). While our field observations demonstrate the correlation between cold condition, particle phase transition, and reduced BrC photobleaching, we acknowledge that definitive mechanistic attribution requires controlled laboratory studies to decomposition the complex interactions of atmospheric factors (e.g. variable oxidant concentrations, emission sources, RH). Moreover, the role of RH is indeed multifaceted and critical to our findings. As implemented in our glass transition temperature (Tg) parameterization, RH governs aerosol liquid water content which depresses Tg by reducing the mass fraction of organic matter in aerosol. This may inhibit the transition of particles from liquid to solid state, thus indirectly promoting the possibility of atmospheric aqueous reaction. In previous studies, high RH can promote BrC photobleaching through enhanced aqueous reactions (Arangio et al., 2015; Hems and Abbatt, 2018), which aligns with our observation of low $MAE_{365,HULIS}$ in Event I. However, temperature (Pearson's R = -0.34) was more related to $MAE_{365,HULIS}$ than RH (Pearson's R = -0.19), which may indicate that temperature is more important for BrC photobleaching in northeast China, winter.

Reference

Alves, C. A., Vicente, A. M. P., Gomes, J., Nunes, T., Duarte, M., and Bandowe, B. A. M.: Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated-PAHs, nitrated-PAHs and azaarenes) in size-fractionated particles emitted in an urban road tunnel, Atmos Res, 180, 128–137, https://doi.org/10.1016/J.ATMOSRES.2016.05.013, 2016.

Arangio, A. M., Slade, J. H., Berkemeier, T., Pöschl, U., Knopf, D. A., and Shiraiwa, M.: Multiphase chemical kinetics of oh radical uptake by molecular organic markers of biomass burning aerosols: Humidity and temperature dependence, surface reaction, and bulk diffusion, Journal of Physical Chemistry A, 119, 4533–4544, https://doi.org/10.1021/JP510489Z, 2015.

Bhattu, D., Zotter, P., Zhou, J., Stefenelli, G., Klein, F., Bertrand, A., Temime-Roussel, B., Marchand, N., Slowik, J. G., Baltensperger, U., Prevot, A. S. H., Nussbaumer, T., Haddad, I. El, and Dommen, J.: Effect of Stove Technology and Combustion Conditions on Gas and Particulate Emissions from Residential Biomass Combustion, Environ Sci Technol, 53, 2209–2219, https://doi.org/10.1021/ACS.EST.8B05020, 2019.

Chen, S., Guo, Z., Guo, Z., Guo, Q., Zhang, Y., Zhu, B., and Zhang, H.: Sulfur isotopic fractionation and its implication: Sulfate formation in PM2.5 and coal combustion under different conditions, Atmos Res, 194, 142–149, https://doi.org/10.1016/J.ATMOSRES.2017.04.034, 2017.

Dong, D., Qiu, T., Du, S., Gu, Y., Li, A., Hua, X., Ning, Y., and Liang, D.: The chemical characterization and source apportionment of PM2.5 and PM10 in a typical city of Northeast China, Urban Clim, 47, 101373, https://doi.org/10.1016/J.UCLIM.2022.101373, 2023.

Dutton, S. J., Williams, D. E., Garcia, J. K., Vedal, S., and Hannigan, M. P.: PM2.5 characterization for time series studies: Organic molecular marker speciation methods and observations from daily measurements in Denver, Atmos Environ, 43, 2018–2030, https://doi.org/10.1016/J.ATMOSENV.2009.01.003, 2009.

Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E., and Barsanti, K. C.: Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography-time-of-flight mass spectrometry, Atmos Chem Phys, 15, 1865–1899, https://doi.org/10.5194/ACP-15-1865-2015, 2015.

He, J., Zielinska, B., and Balasubramanian, R.: Composition of semi-volatile organic compounds in the urban atmosphere of Singapore: Influence of biomass burning, Atmos Chem Phys, 10, 11401–11413, https://doi.org/10.5194/ACP-10-11401-2010, 2010.

Hems, R. F. and Abbatt, J. P. D.: Aqueous Phase Photo-oxidation of Brown Carbon Nitrophenols: Reaction Kinetics, Mechanism, and Evolution of Light Absorption, ACS Earth Space Chem, 2, 225–234, https://doi.org/10.1021/ACSEARTHSPACECHEM.7B00123, 2018.

Huo, Y., Guo, Z., Li, Q., Wu, D., Ding, X., Liu, A., Huang, D., Qiu, G., Wu, M., Zhao, Z., Sun, H., Song, W., Li, X., Chen, Y., Wu, T., and Chen, J.: Chemical Fingerprinting of HULIS in Particulate Matters Emitted from Residential Coal and Biomass Combustion, Environ Sci Technol, 55, 3593–3603, https://doi.org/10.1021/acs.est.0c08518, 2021.

Liang, L., Engling, G., Liu, C., Xu, W., Liu, X., Cheng, Y., Du, Z., Zhang, G., Sun, J., and Zhang, X.: Measurement report: Chemical characteristics of PM2.5 during typical biomass burning season at an agricultural site of the North China Plain, Atmos Chem Phys, 21, 3181–3192, https://doi.org/10.5194/ACP-21-3181-2021, 2021.

Ma, G., Liu, X., Wang, J., Li, M., Dong, Z., Li, X., Wang, L., Han, Y., and Cao, J.: Characteristics and health risk assessment of indoor and outdoor PM2.5 in a rural village, in Northeast of China: impact of coal and biomass burning, Environ Geochem Health, 45, 9639–9652, https://doi.org/10.1007/S10653-023-01755-W, 2023.

Souza, K. F., Carvalho, L. R. F., Allen, A. G., and Cardoso, A. A.: Diurnal and nocturnal measurements of PAH, nitro-PAH, and oxy-PAH compounds in atmospheric particulate matter of a sugar cane burning region, Atmos Environ, 83, 193–201, https://doi.org/10.1016/J.ATMOSENV.2013.11.007, 2014.

Xu, H., Gu, Y., Bai, Y., Li, D., Liu, M., Wang, Z., Zhang, Q., Sun, J., and Shen, Z.: Exploration and comparison of the relationship between PAHs and ROS in PM2.5 emitted from multiple anthropogenic sources in the Guanzhong Plain, China, Science of The Total Environment, 915, 170229, https://doi.org/10.1016/J.SCITOTENV.2024.170229, 2024.

Zhao, T., Yang, L., Huang, Q., Zhang, Y., Bie, S., Li, J., Zhang, W., Duan, S., Gao, H., and Wang, W.: PM2.5-bound polycyclic aromatic hydrocarbons (PAHs) and their derivatives (nitrated-PAHs and oxygenated-PAHs) in a road tunnel located in Qingdao, China: Characteristics, sources and emission factors, Science of The Total Environment, 720, 137521, https://doi.org/10.1016/J.SCITOTENV.2020.137521, 2020.