

Response to acp-2025-561-RC1

Comment on acp-2025-561

Anonymous referee #1

This paper investigated the changes in the optical properties, fluorophores, and molecular composition of WSOM derived from the combustion of biomass (RS) and coal (YL) during aqueous photolysis and hydroxyl radical ($\cdot\text{OH}$) photooxidation. Results show distinct photochemical aging effects for RS and YL WSOM, characterized by photobleaching in RS WSOM and photoenhancement in YL WSOM. Additionally, $\cdot\text{OH}$ photooxidation induces more substantial alterations than photolysis, degrading 61.6% of RS and 65.0% of YL WSOM molecules, compared to 14.9% and 23.1% during photolysis, respectively. The oxidation products were characterized by larger molecular weights and higher oxidation levels, including tannin-like substances and a type of black carbon-like compounds, whereas photolysis causes minor changes. These findings are helpful for us to understand the photochemical evolution of combustion-derived WSOM and its environmental and climate impacts. However, I have some questions should be addressed:

Re: We appreciated the reviewer for the valuable comments and suggestions, which are of great help for improving the quality of our manuscript. We have carefully revised the manuscript based on the comments and provided a point-by-point response to all the comments and explained how the comments and suggestions by the reviewer were addressed in the current version of the manuscript.

1. Line 127-128: How about the difference between the light intensity under laboratory conditions (290-400 nm, 12.5 mW/cm²) and the actual solar exposure? How about the actinic flux of the Xe lamp used in present study.

Re: Thanks. In this study, the spectra of Xe lamp and the actual solar exposure were measured using a spectrometer USB2000+ (Ocean Optics, FL, U.S.A.), and the light

intensity of both Xe lamp and solar radiation were measured by an optical power meter (PL-MW2000, Perfect light). As shown Figure S1, the spectrum of Xe lamp is similar with that of the actual solar exposure obtained at noon of May 20, 2023, Guangzhou. The measured light intensity of Xe lamp is 12.5 mW/cm^2 (290–400 nm), which is about 5.2 times higher than that of the actual solar exposure.

In addition, the average actinic flux of the Xe lamp was $5.4 \times 10^{-5} \text{ Einstein/cm}^2/\text{s}^1$ (290–400 nm), as determined by the p-nitroanisole/pyridine actinometer method (Laszakovits et al., 2016).

Accordingly, we have added the detailed information in section 2.2 of the present manuscript (Lines 130-135) and Figure S1 in the supporting information (SI).

“The irradiation energy at the water surface is 12.5 mW/cm^2 (290–400 nm), which is about 5.2 times higher than the light intensity of actual solar exposure (Figure S1, obtained at noon of May 20, 2023, Guangzhou) and the actinic flux of Xe lamp is $5.4 \times 10^{-5} \text{ Einstein/cm}^2/\text{s}^1$ as determined by the p-nitroanisole/pyridine actinometer method (Laszakovits et al., 2016).” (Lines 130-135)

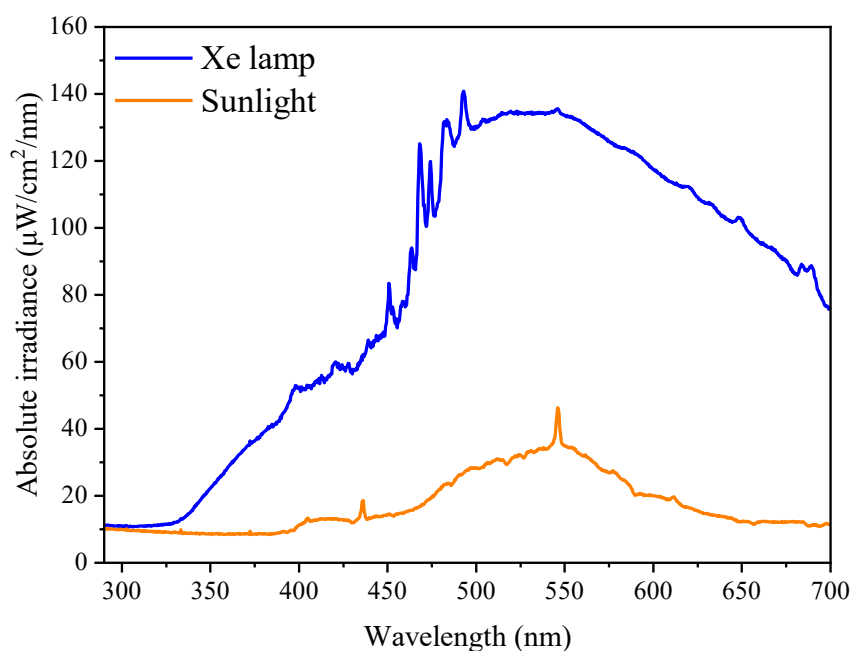


Figure S1. Spectra of Xe lamp and actual Sunlight (obtained at noon of May 20, 2023, Guangzhou)

Reference:

Laszakovits, J. R., Berg, S. M., Anderson, B. G., O'Brien, J. E., Wammer, K. H., and Sharpless, C. M.: p-Nitroanisole/Pyridine and p-Nitroacetophenone/Pyridine Actinometers Revisited: Quantum Yield in Comparison to Ferrioxalate, *Environmental Science & Technology Letters*, 4, 11-14, 10.1021/acs.estlett.6b00422, 2016.

2. For the photolysis and $\cdot\text{OH}$ photooxidation, how many experiments were repeated in the present study?

Re: Thanks. In the present study, the photolysis and $\cdot\text{OH}$ photooxidation experiments were both repeated for three times. We have clarified it in the revised manuscript (Line 125).

3. Authors are strongly suggested to use the more detailed index: nominal oxidation state of carbon (NOSC) (*Geochimica et Cosmochimica Acta* Volume 75, Issue 8, 15 April 2011, Pages 2030-2042), rather than the simplified index: state of carbon oxidation.

Re: Thanks. According to your suggestion, we have calculated the value of nominal oxidation state of carbon (NOSC) according to the following formula (LaRowe et al., 2011) and used NOSC to replace the simplified index (oxidation state of carbon) in the present manuscript.

$$NOSC = 4 - \frac{4c + h - 3n - 2o - 2s}{c}$$

Here, c, h, n, o, s represents the number of C, H, N, O, S in the formula.

The detailed revisions please refer to Lines 308-324 in main text, and Text S4, Table S2, S5, and S6 in SI.

References:

LaRowe, D.E. and Van Cappellen, P.: Degradation of natural organic matter: A thermodynamic analysis. *Geochimica et Cosmochimica Acta*, 75, 2030-2042,

4. Line 202: present -> presented

Re: Thanks. We have revised that in the present manuscript. (Line 205)

5. Line 305: The logical subject of the 'with' structure is unclear, it is recommended to replace it with 'while'.

Re: Thanks. We have revised it with “while” in the present manuscript. (Line 307)

6. Line 330: Confirm the spelling of professional terms (such as "condensed" vs. "condensated")

Re: Thanks. We are sorry for this wrong spelling. It should be corrected to “condensed”. Accordingly, we have carefully checked the full text and corrected those wrong spelling to “condensed” in the present manuscript. (Lines 330, 347, 349, 352, 393-396, 404, 504).

7. Line 407: What are the similarities between the newly produced condensated aromatic compounds which assigned as BC-like substances and the traditional DBC?

Re: Thanks. It is a good question. According to previous studies, traditional DBC is defined as the water-soluble fraction of black carbon that originates from the incomplete combustion of biomass and fossil fuels (Coppola et al., 2022). The molecular composition of DBC is characterized by high proportion of condensed aromatic compounds and various oxygen-containing functional groups, including carbonyl, carboxyl, and phenolic hydroxyl groups (Liu et al., 2022; Li et al., 2024; Tian et al., 2022). For example, FT-ICR MS analysis of DBC revealed that they are dominated by conjugated aromatic structures and always characterized with low H/C_w ratio (0.15-0.72) and high aromaticity index (AI_{mod,w}) values (0.63-0.76) (Fan et al., 2023; Liu et al., 2022; Yan et al., 2022; Tian et al., 2022). In this study, the newly produced condensed aromatic compounds are also displayed with low H/C_w (0.60 and 0.56 for

RS and YL fresh WSOM) and higher $AI_{mod,w}$ values (0.76 and 0.77 for RS and YL WSOM). Obviously, the newly produced condensed aromatic substances (i.e., BC-like substances) and traditional DBC have many similarities in molecular characteristics, such as lower H/C_w ratios and higher $AI_{mod,w}$ values and all comprised of extensive conjugated aromatic structures. Accordingly, we have clarified that in the present manuscript. The detailed revision please refer to Lines 404-409.

“According to previous studies, the condensed aromatic compounds are usually assigned to traditional dissolved black carbon (BC) molecules derived from combustion (Fan et al., 2023; Liu et al., 2022; Yan et al., 2022). These compounds share similar molecular characteristics, such as lower H/C_w ratios and higher $AI_{mod,w}$ values. However, our study suggesting that $\cdot OH$ photochemical oxidation may also contribute to the formation of BC-like molecules.” (Lines 404-409)

References:

- Coppola, A. I., Wagner, S., Lennartz, S. T., Seidel, M., Ward, N. D., Dittmar, T., Santín, C., and Jones, M. W.: The black carbon cycle and its role in the Earth system, *Nature Reviews Earth & Environment*, 3, 516-532, 10.1038/s43017-022-00316-6, 2022.
- Fan, J., Duan, T., Zou, L., and Sun, J.: Characteristics of dissolved organic matter composition in biochar: Effects of feedstocks and pyrolysis temperatures, *Environmental Science and Pollution Research*, 30, 85139-85153, 10.1007/s11356-023-28431-x, 2023.
- Li, L., Cheng, W., Xie, X., Zhao, R., Wang, Y., and Wang, Z.: Photo-Reactivity of dissolved black carbon unveiled by combination of optical spectroscopy and FT-ICR MS analysis: Effects of pyrolysis temperature, *Water research*, 251, 10.1016/j.watres.2024.121138, 2024.
- Liu, Y., Wang, M., Yin, S., Xie, L., Qu, X., Fu, H., Shi, Q., Zhou, F., Xu, F., Tao, S., and Zhu, D.: Comparing Photoactivities of Dissolved Organic Matter Released from Rice Straw-Pyrolyzed Biochar and Composted Rice Straw, *Environmental science & technology*, 56, 2803-2815, 10.1021/acs.est.1c08061, 2022.

Tian, Y. X., Guo, X., Ma, J., Liu, Q. Y., Li, S. J., Wu, Y. H., Zhao, W. H., Ma, S. Y., Chen, H. Y., and Guo, F.: Characterization of biochar-derived organic matter extracted with solvents of differing polarity via ultrahigh-resolution mass spectrometry, *Chemosphere*, 307, 10.1016/j.chemosphere.2022.135785, 2022.

Yan, W., Chen, Y., Han, L., Sun, K., Song, F., Yang, Y., and Sun, H.: Pyrogenic dissolved organic matter produced at higher temperature is more photoactive: Insight into molecular changes and reactive oxygen species generation, *Journal of hazardous materials*, 425, 10.1016/j.jhazmat.2021.127817, 2022.

8. The $\cdot\text{OH}$ oxidation of WSOM in atmosphere can happen in light and dark conditions. Could you add a discussion between the $\cdot\text{OH}$ photooxidation and dark $\cdot\text{OH}$ oxidation in the paper?

Re: Thanks for your kindly suggestion. In real atmospheric environment, the $\cdot\text{OH}$ oxidation of WSOM can occur under both light and dark conditions. Compared with the results reported in previous studies, some similarities and differences can be observed between the $\cdot\text{OH}$ photooxidation and dark $\cdot\text{OH}$ oxidation. At first, a significant reduction in the light absorbance of WSOM, indicative of photobleaching, was observed during the $\cdot\text{OH}$ oxidation in both light and dark conditions (Fan et al., 2019). In addition, similar changes at the molecular level were also identified by the ultrahigh resolution mass spectrometry, such as an increase in the average O/C ratio and oxidation state of carbon in WSOM, and a decrease in the aromaticity index (AI) values during both oxidation processes (Fan et al., 2024). These observations suggest that similar oxidation reactions may happened during the $\cdot\text{OH}$ oxidation of WSOM in both light and dark conditions. However, distinct differences were also noted between the $\cdot\text{OH}$ photooxidation and dark $\cdot\text{OH}$ oxidation. For example, the continued photooxidation by $\cdot\text{OH}$ resulted in the formation of conjugated aromatic compounds, which share molecular characteristics with traditional DBC and are thus classified as BC-like substances. In contrast, the dark $\cdot\text{OH}$ oxidation, which is initiated through Fenton chemistry, did not yield these condensed BC-like compounds (Fan et al., 2024). This finding implies that the formation of highly aromatic molecules may require

both $\cdot\text{OH}$ oxidation and photoreactions to occur. Accordingly, we have added the detailed discussion in the revised manuscript. (Please refer to Lines 193-195, Lines 266-269, Lines 289-293, Lines 304-305, Lines 312-316, Lines 409-413).

The details are as follows:

“These results are consistent with earlier studies on dark $\cdot\text{OH}$ oxidation of BB WSOM, indicating that the presence of $\cdot\text{OH}$ radicals accelerate the degradation of aromatic structures within WSOM (Fan et al., 2024; Ye et al., 2020).” (Lines 193-195)

“As shown in Figure 3, CHO and CHON compounds are the dominant compounds (95.8%-98.4%) in RS WSOM, with minor fluctuations following photolysis and $\cdot\text{OH}$ photooxidation. Similar changes were also observed for BB WSOM under dark $\cdot\text{OH}$ oxidation (Fan et al., 2024).” (Lines 266-269)

“These observations in molecular weight aligned with findings related to the aqueous-phase photochemical oxidation of wood smoke WSOM, but no significant change in molecular weight was observed in the aqueous-phase dark $\cdot\text{OH}$ oxidation of BB WSOM (Fan et al., 2024; Wong et al., 2019).” (Lines 289-293)

“This significant decreasing in $\text{AI}_{\text{mod,w}}$ values of BB WSOM was also observed during the dark $\cdot\text{OH}$ oxidation (Fan et al., 2024).” (Lines 304-305)

“These observations are consistent with findings related to BB WSOM under dark $\cdot\text{OH}$ oxidation and the photochemical transformation of DOM (Gu et al., 2024; Zhang et al., 2022; Fan et al., 2024), suggesting a substantial incorporation of O-containing functional groups into carbon structures during the photolysis and $\cdot\text{OH}$ oxidation.” (Lines 312-316)

“In contrast, the $\cdot\text{OH}$ oxidation that without the presence of light, initiated by Fenton chemistry, does not produce these BC-like substances (Fan et al., 2024). This possibly indicates that the formation of highly aromatic BC-like molecules requires both $\cdot\text{OH}$ oxidation and photoreactions to occur.” (Lines 409-413)

References:

Fan, X., Xie, S., Yu, X., Cheng, A., Chen, D., Ji, W., Liu, X., Song, J., and Peng, P.:
Molecular-level transformations of biomass burning-derived water-soluble

organic carbon during dark aqueous OH oxidation: Insights from absorption, fluorescence, high-performance size exclusion chromatography and high-resolution mass spectrometry analysis, Science of the total environment, 912, 169290, 10.1016/j.scitotenv.2023.169290, 2024.

Fan, X., Yu, X., Wang, Y., Xiao, X., Li, F., Xie, Y., Wei, S., Song, J., and Peng, P. a.: The aging behaviors of chromophoric biomass burning brown carbon during dark aqueous hydroxyl radical oxidation processes in laboratory studies, Atmospheric Environment, 205, 9-18, 10.1016/j.atmosenv.2019.02.039, 2019.

9. Fig 3: the name of vertical axis should revised to “Relative intensity”.

Re: Thanks. According to the suggestion, we have revised the name of vertical axis to “Relative intensity” in the revised Figure 3.

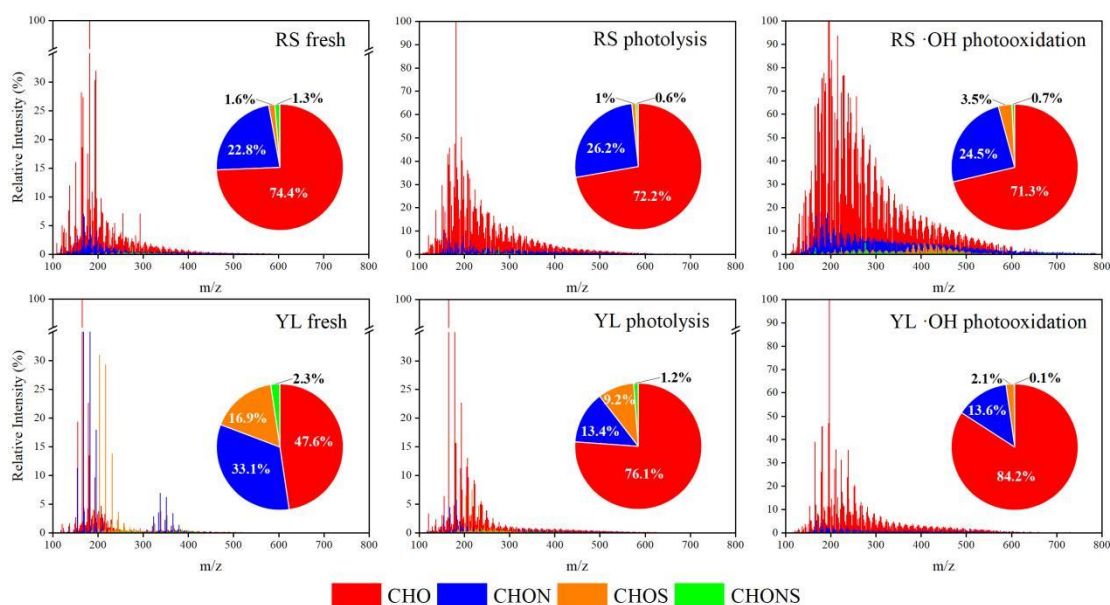


Figure 3. Reconstructed mass spectra of RS and YL WSOM for fresh (left), photolysis (middle) and ·OH photooxidation (right). Pie charts inserted represent the relative content of different formula groups in each sample by sum of intensities of all identified peaks.