Response to acp-2025-561-RC2

Comment on acp-2025-561

Anonymous referee #2

The research component of this manuscript examines the changes in optical properties, fluorophores, and molecular composition of WSOM from biomass and coal combustion during aqueous photolysis and hydroxyl radical (·OH) photo-oxidation. The results show that the ·OH photo-oxidation process leads to the degradation of more WSOM molecules, producing products with higher molecular weights and higher levels of oxidation, including tannins and newly formed black carbon analogs. While the photolysis products show relatively little change. These findings provide new insights into the photochemical evolution of WSOM from combustion and help predict its impact on the environment and climate change. In conclusion, this manuscript is highly recommended to be accepted for publication with a few modifications:

Re: Thank you for your valuable criticisms and comments, which are of great help for improving the quality of the manuscript. According to your comments, we have revised the manuscript and provided a point-by-point response to all the comments and explained how the comments and suggestions were addressed in the current version of the manuscript.

1. Line 102-103: Please provide basic information about the two fuels.

Re: Thanks. We have provided the basic information about the two fuels in the revised manuscript. The detailed information please refer to Lines 101-103 in revised main text, Text S1 and Table S1 in the supporting information (SI).

The details are as follows:

"The detailed information of RS and YL were provided in Text S1 and Table S1 in the supporting information (SI)." (Lines 101-103 in revised main text);

"Rice straw (RS) and Yulin coal (YL) were selected as representative biomass and coal fuel materials for the preparation of combustion-derived WSOM samples. RS was

collected in Chuzhou, Anhui Province. As shown in Table S1, the carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and ash contents of RS were 38.3%, 5.74%, 43.8%, 1.90% and 10.3%, respectively. Prior to combustion, the RS was sorted and cut into smaller sections to enhance the efficiency of the combustion process. YL coal was collected from Yulin, Shanxi Province. The maturity and volatile content of YL coal were determined to be 0.58% and 34.4%, respectively, confirming its classification as high volatile bituminous coal. Additionally, the ash content of YL coal was measured at 4.22% and the C, H, O, N and S contents of YL coal were 77.0%, 6.07%, 11.6%, 1.01% and 0.17%, respectively." (Text S1. Sample information in SI)

Table S1. Basic information and elemental composition of RS and YL (%)

	Biomass (RS)	Coal (YL)
C (%)	38.3	77.0
H (%)	5.74	6.07
O (%)	43.8	11.6
N (%)	1.90	1.01
S (%)	-	0.17
Ash (%)	10.3	4.22
Maturity (%)	-	0.58
Volatile (%)	-	34.4
Rank	-	High volatile bituminous coal

2. Line 116-119: Please present the WSOC measurement protocol in the manuscript or SI: instrumentation, general experimental methods.

Re: Thanks. According to your suggestion, the WSOM measurement protocol have been added in SI. The detailed information please refer to Lines 116-122 in the manuscript and Text S2 in the SI.

The detailed revision are as follows:

"The organic carbon concentration of WSOM solution was measured by a total organic carbon analyzer (VCPH analyzer, Shimadzu, Kyoto, Japan) following the non-purgeable organic carbon protocol. After the removal of inorganic carbon, the sample

was oxidized at high temperature (680 °C) to generate CO_2 and then determined by non-dispersive infrared detector. Before photochemical reaction, WSOM solution was diluted to 20 mgC/L by ultrapure water. The detailed information can be found in Text S2 of SI." (Lines 116-122 in the revised manuscript)

"The weighted smoke filters were fragmented into small pieces and subsequently placed into a pre-baked 100 mL glass bottle. Then, 60 mL of ultrapure water was added, and the mixture was subjected to sonication at a constant temperature of 25°C for a duration of 30 min. The supernatant was filtered through a 0.22 μm PTFE membrane, resulting in a solution that serves as the stock solution of water-soluble organic matter (WSOM). The concentration of the WSOM stock solution was quantified using a total organic carbon analyzer (VCPH analyzer, Shimadzu, Kyoto, Japan) in accordance with the non-purgeable organic carbon protocol. After the removal of inorganic carbon, the sample underwent oxidation at a high temperature of 680°C, and the peak area of CO_2 was measured using a non-dispersive infrared detector. The WSOM stock solution was subsequently diluted to approximately 20 mgC/L with ultrapure water, based on the measured concentration. Photolysis experiments will be conducted utilizing this diluted solution." (Text S2 in the SI)

3. Line 129-132: What is the approximate OH concentration during the corresponding oxidation time? How much H_2O_2 is consumed in this process? Is there any estimate?

Re: Thanks for these good questions. In the ·OH photooxidation experiment, WSOM was subjected to continuous reaction with ·OH generated from hydrogen peroxide (H_2O_2) under light exposure. The concentration of ·OH in the reaction solution was determined using benzoic acid as a chemical probe, as described by Tong et al. (2015) and Hems et al. (2018). The results shown that the ·OH concentration in the reaction solution varied between 9.3×10^{-14} to 1.3×10^{-13} mol/L.

In the present study, the initial concentration of H_2O_2 in the reaction solution was set at 3 mM, which falls within the range of 0.1 mM to 10 mM reported in prior studies (Fan et al., 2023; Zhao et al., 2015; Ye et al., 2019). In addition, it was observed that about 35.6%±4.6% of H_2O_2 was consumed after a 24h reaction period in the present

study, as measured by a N,N-diethyl-p-phenylenediamine (DPD) chemical probe method. This result suggests that there was an adequate supply of ·OH available to react with WSOM in the ·OH photooxidation experiment.

Accordingly, we also clarified that in the revise manuscript (Lines 137-140).

"Based on the conditional experiment, it was found that approximately 35.6%±4.6% of H_2O_2 was consumed after a 24-hour reaction period. This indicates that there was a sufficient amount of ·OH present to react with WSOM during the ·OH photooxidation experiment." (Lines 137-140)

Reference:

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, The Science of the total environment, 912, 169290, 10.1016/j.scitotenv.2023.169290, 2024.

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 and Space Chemistry, 2, 225-234, 10.1021/acsearthspacechem.7b00123, 2018.

Tong, M., Yuan, S., Ma, S., Jin, M., Liu, D., Cheng, D., Liu, X., Gan, Y., and Wang, Y.: Production of Abundant Hydroxyl Radicals from Oxygenation of Subsurface Sediments, Environmental science & technology, 50, 214-221, 10.1021/acs.est.5b04323, 2015.

Ye, Z., Qu, Z., Ma, S., Luo, S., Chen, Y., Chen, H., Chen, Y., Zhao, Z., Chen, M., and Ge, X.: A comprehensive investigation of aqueous-phase photochemical oxidation of 4-ethylphenol, Science of The Total Environment, 685, 976-985, 10.1016/j.scitotenv.2019.06.276, 2019.

Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F., and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric brown carbon, Atmospheric Chemistry and

Physics, 15, 6087-6100, 10.5194/acp-15-6087-2015, 2015.

4. Line 184-185: What physical properties of WSOC can be characterized by α254 and α365?

Re: Thanks. In this study, α_{254} and α_{365} refer to the absorbance coefficients of organic substances at 254 and 365 nm (Fan et al., 2019; Zhao et al., 2023). The α_{254} value indicate the content of aromatic structures and double bonds, which are associated with π electron clouds that are prone to transition under ultraviolet light excitation at around 254 nm. In general, it was positively correlated with the amounts and properties of aromatic components of organic matter and had been widely applied to indicate the light absorption of WSOM in previous studies (Fan et al., 2019). The α_{365} represent the light absorption of WSOM in near ultraviolet and visible ranges. Previous research has demonstrated a strong correlation between α_{365} and the cumulative absorption measured between 300 and 400 nm, which had been widely to indicate BrC in atmospheric environments (Hecobian et al., 2010; Jiang et al., 2021). Accordingly, we have added a brief description in the revised SI. Please refer to Text S3 in the SI.

"The α_{254} value indicates the content of aromatic structures and double bonds, which was positively correlated with the amounts and properties of aromatic components. The α_{365} value represents the light absorption of WSOM in near ultraviolet and visible ranges, which had been widely used to characterize BrC in atmospheric environments (Hecobian et al., 2010; Jiang et al., 2021b)." (Text S3 in SI)

Reference:

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.

Hecobian, A., Zhang, X., Zheng, M., Frank, N., Edgerton, E. S., and Weber, R. J.: Water-Soluble Organic Aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States, Atmospheric

Chemistry and Physics, 10, 5965-5977, 10.5194/acp-10-5965-2010, 2010.

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, Environmental science & technology, 55, 10268-10279, 10.1021/acs.est.1c01770, 2021.

Zhao, Y., Kumar, A., Wang, K., Lin, J., Yu, Z., Cheng, S., Zhang, S., Yu, Z., and Liu, D.: Spatial heterogeneity of soil dissolved organic matter characteristics in the riparian zone of the Three Gorges Reservoir, Ecohydrology, 17, 10.1002/eco.2570, 2023.

5. Line 350-354: The results in this section show that the content of condensed aromatic compounds increases after photolysis, but the results of α254 and α365 of rice straw calculated in the absorption section show that the aromaticity decreases. Is there any connection or difference between the results in these two sections? Please explain

Re: Thank you for your question. We agreed with your observation that the content of condensed aromatic compounds increases after photolysis, but the results of α_{254} and α_{365} of RS WSOM decreased. These differences can be explained by the fact that these two parameters characterize different fraction of WSOM. The α_{254} and α_{365} of WSOM indicate the light absorption properties of total WSOM. Therefore, the results of α_{254} and α_{365} of RS WSOM calculated in the absorption section showed that the aromaticity of WSOM decreased after photolysis. However, the condensed aromatic compounds only contributed 1.08% and 4.86% of all identified molecules for fresh and ·OH protoxidized RS WSOM, which are too small to represent the total molecular properties of WSOM. The content of condensed aromatic compounds increases after photolysis only indicated the formation of condensed aromatic fraction rather than the aromaticity changes of total WSOM. Therefore, we think these different results for the changes of the content of condensed aromatic compounds and the α_{254} and α_{365} values of RS WSOM after photolysis and ·OH photooxidation are scientifically reasonable.

6. Figure 4: It is recommended that the sub-graphs in Figure 4 be numbered to make

it easier to distinguish the results for coal and biomass.

Re: Thanks. In the revise manuscript, we have numbered the sub-graphs in Figure 4. In addition, we also revised the manuscript based on the revised Figure 4. The detailed revision please refer to Lines 373, 388, 394, and the revised Figure 4.

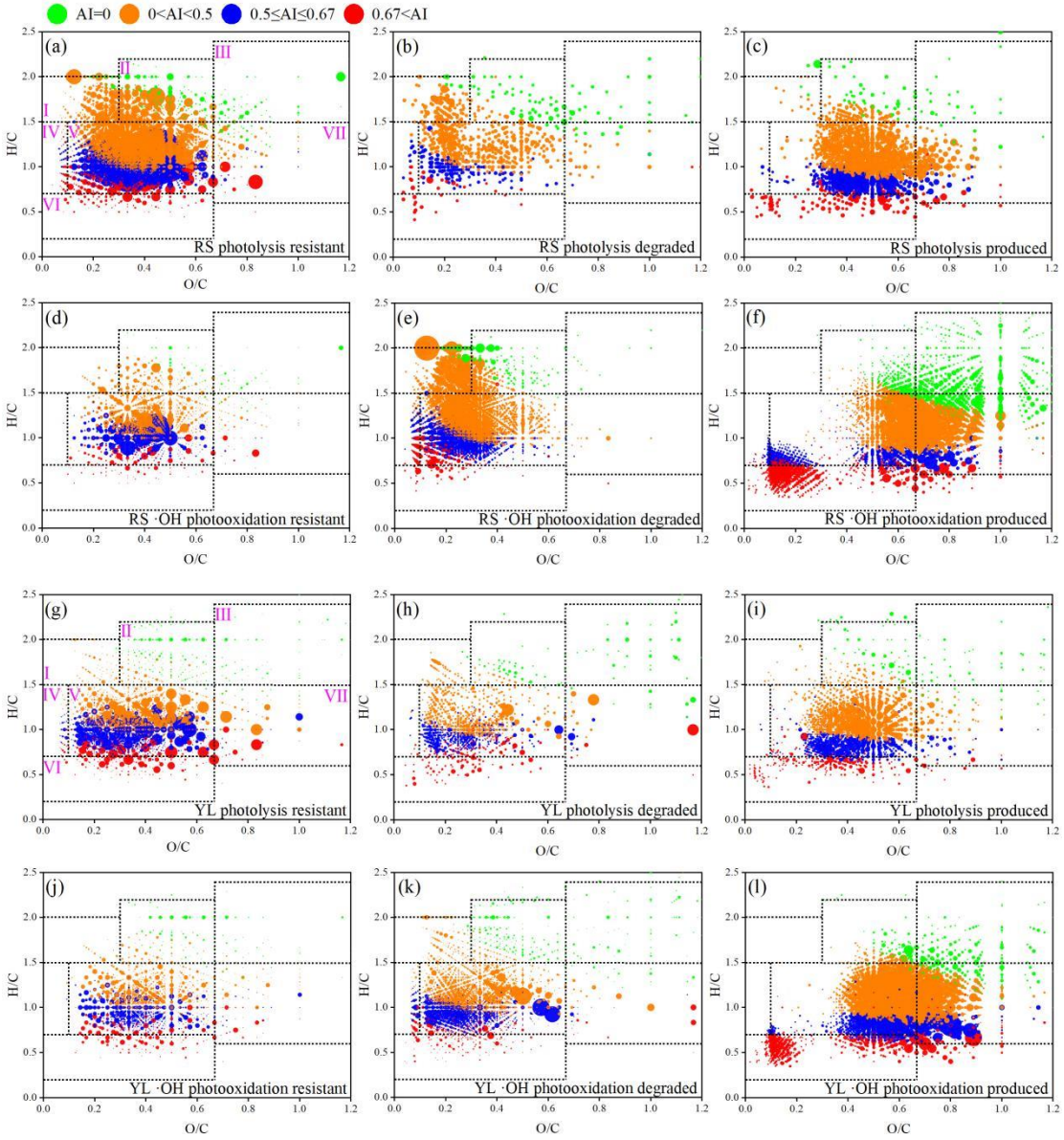

Figure 4. Van Krevelen diagrams for molecules resistant, degraded and produced after photolysis and ·OH photooxidation for RS WSOM (upper) and YL WSOM (bottom).