A letter to reply the comments

Title: Aqueous OH-initiated photooxidation of smoke extracts from maize straw and coal combustion: optical character and molecular composition

Dear editor

We thank very much for the valuable comments and suggestions from the reviewer, which is of great help to improve the quality of the manuscript. The comments were carefully considered and revisions have been made in response to suggestions. Following is our point-by-point responses to the comments and corresponding revisions.

Reviewer #1

1. Line 251-259, for the reported inorganic ion and transition metal measurements, it would be helpful to specify detection limits.

Response： Thanks for your helpful suggestion. We agree that providing the detection limits for inorganic ions and transition metals can improve analytical reliability of the measurements. In the revised manuscript, we have added the method detection limits for all reported inorganic ions and transition metals **in Section 2.3 (lines 152-154).** These detection limits were determined based on three times the standard deviation of blanks.

2. In Section 3.1, the manuscript reports changes in molecular weight and elemental composition during photooxidation, but it would be helpful to include a brief discussion on the possible mechanisms driving the different trends observed between coal and maize WSOM (e.g., why MW decreases in coal but remains stable in maize).

Response： Thanks for your valuable suggestions. We totally agree that the different trends in molecular weight (MW) evolution between coal- and maize-derived WSOM require clearer mechanistic interpretation. In revised manuscript **Line 440-456**, we added discussion such as: “At the molecular-class level, CHON compounds in maize smoke initially exhibit a relatively high average molecular weight (MW, 329.45 g/mol) and DBE (10.52). Upon photolysis, the average MW decreases to 301.07 g/mol (11 h) and 296.44 g/mol (23 h), while the DBE declines to 6.59 and 4.14, respectively. These changes reflect the progressive breakdown of conjugated structures and a corresponding reduction in aromaticity, consistent with the observed decrease in light absorbance (Fig.2 b). For coal smoke, a considerable fraction of CHONS species undergoes transformation into CHON compounds with lower aromaticity and DBE during photolysis. This conversion increases the relative abundance of CHON species

while contributing to a decrease in overall molecular weight. In addition, the MW of CHO compounds in coal smoke decreases progressively with photolysis. In contrast, maize-smoke WSOM is dominated by CHO compounds, whose MW remains relatively unchanged during photolysis, resulting in only minor variation in the bulk molecular weight. This contrast primarily reflects differences in the initial WSOC compositions between coal and maize smoke. Overall, the marked decreases in AI and DBE for CHON compounds in both smokes indicate substantial loss of aromaticity, which in turn contributes to the reduction in light absorption."

3. In Section 3.3, the analysis of CHON compounds suggests different N-containing product formation between coal and maize WSOM. It would be useful to specify which types of N-containing compounds are likely responsible (e.g., nitroaromatic degradation products) and cite relevant literature to support this interpretation.

Response：Thanks. We agree that the discussion of CHON compounds would benefit from a more specific identification of likely N-containing species and supporting literature. Previous study from Song et al. (2018) suggested that biomass burning smoke contain a high abundance of CHON species with oxidized nitrogen functional groups such as nitro compounds and/or organonitrates. In contrast, coal smoke enriched in aromatic organosulfates with high double bond equivalent (≥4). In the revised manuscript (**Section 3.3, lines 440-449**), we have expanded the discussion to specify the probable classes of N-containing compounds contributing to the observed CHON signals. **Such as:** At the molecular-class level, CHON compounds in maize smoke initially exhibit a relatively high average molecular weight (MW, 329.45 g/mol) and DBE (10.52). Upon photolysis, the average MW decreases to 301.07 g/mol (11 h) and 296.44 g/mol (23 h), while the DBE declines to 6.59 and 4.14, respectively. These changes reflect the progressive breakdown of conjugated structures and a corresponding reduction in aromaticity, consistent with the observed decrease in light absorbance (Fig.2 b). For coal smoke, a considerable fraction of CHONS species undergoes transformation into CHON compounds with lower aromaticity and DBE during photolysis. This conversion increases the relative abundance of CHON species while contributing to a decrease in overall molecular weight. **We have also incorporated relevant literature to support these assignments and pathways (Song et al., 2018).**

4. The manuscript reports changes in MW and elemental composition during photooxidation, but it would be helpful to include a brief discussion on the possible mechanisms driving the different trends observed between coal and maize WSOM (e.g., why MW decreases in coal but remains stable in maize).

Response： We totally agree with you. A clearer mechanistic explanation is needed to account for the different MW trends observed between coal- and maize-derived WSOM during photooxidation. These additions provide a more mechanistically grounded explanation for the observed differences and strengthen the interpretation of molecular evolution during aqueous-phase photooxidation. **In revised manuscript, we added more detailed explanation in many section,** including **Section 3.2, 3.6.2 and conclusion**.

5.The authors added 10 mM H_2O_2 to the reaction system, and therefore the conclusions mainly reflect the contribution of •OH radicals. It is suggested to discuss whether using a lower H_2O_2 concentration might lead to a greater contribution from singlet oxygen ($^1O_2$). The authors could consider including experiments with different H_2O_2 concentrations to examine the relative contributions of • OH, $^1O_2$, and $^3C^*$.

Response： We thank the reviewer for this insightful suggestion. We agree that the use of 10 mM H_2O_2 in our experiments favors the production of •OH and thus emphasizes •OH-driven oxidation pathways. In the revised manuscript, we have clarified that the selected H_2O_2 concentration was intended to ensure sufficient •OH generation within a practical experimental timescale and to enable systematic investigation of molecular transformation mechanisms. We have also expanded the discussionto address how different H_2O_2 concentration influence the relative importance of ROS. **The results are presented in Table S5**. **Added text descriptions were as follows** (**Section 3.6.1, lines 764–777**)**:** Surely, different H_2O_2 concentrations might influence the relative role of ROS. To assess this effect, we examined the ROS concentrations and their contributions under five different H_2O_2 levels (0.5, 1, 3, 5, and 10 mM). The results are presented in Table S5. As shown in Table S5, increasing the H_2O_2 dosage leads to higher •OH concentrations and relative contributions, accompanied by a corresponding decrease in the contribution of triplet excited states ($^3C^*$). The measured •OH concentrations generally fall within a relatively narrow range under five different H_2O_2 concentration, with average values of $(0.7-9.1)\times10^{-14}$ M and $(1.3-8.3)\times10^{-14}$ M, for coal and maize smoke WSOM, respectively. Specifically, we also noted that the $^1O_2$ contribution is only weakly affected by the H_2O_2 concentration. Given that this study mainly focuses on the role of •OH, all subsequent experiments were conducted at a relatively high H_2O_2 concentration. While additional experiments at varying H_2O_2 concentrations would provide valuable quantitative constraints on these processes, they are beyond the scope of the present study.

The following figure presents the detailed results of the supplementary experiment with 0.5 mM H_2O_2, which is used as a representative case to demonstrate the feasibility of conducting experiments with different H_2O_2 concentrations.

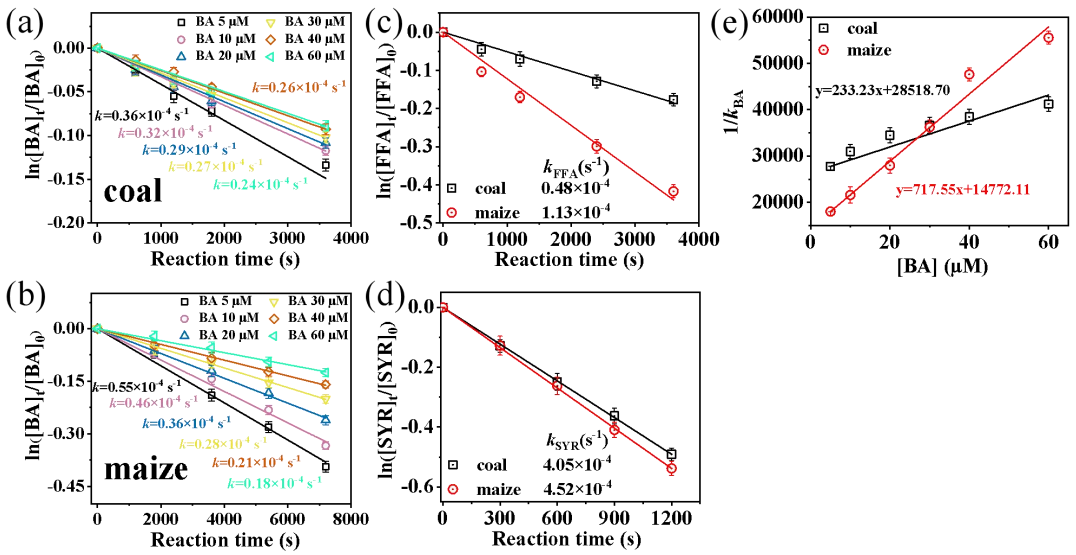

Figure Loss of (a, b) BA, (c) FFA, (d) SYR and (e)plot of $1/k_{BA}$ and BA concentration for two smoke WSOM under 0.5 mM H_2O_2 adding.

Table S5 Concentration and contribution to WSOM photodegradation of each ROS under different H_2O_2 concentration

Samples	$[H_2O_2]$ (mM)	[ROS] (M)			Contribution ratio (%)		
		$[•OH]_{ss}$ ($\times10^{-14}$)	$[^1O_2]_{ss}$ ($\times10^{-13}$)	$[^3C^*]_{ss}$ ($\times10^{-13}$)	•OH	$^1O_2$	$^3C^*$
coal	0.5	0.7	4.0	1.0	25.8	0.5	73.7
	1	1.6	3.4	1.0	46.6	0.3	53.1
	3	5.7	3.5	2.1	58.8	0.1	41.1
	5	8.7	4.1	2.6	63.5	0.1	36.4
	10	9.1	3.5	9.0	86.4	0.8	12.8
maize	0.5	1.3	9.4	1.2	37.2	0.8	62.0
	1	2.2	8.7	1.8	39.3	0.5	60.2
	3	3.8	2.5	1.3	60.9	0.1	39.0
	5	7.3	7.2	2.3	62.2	0.2	37.6
	10	8.6	0.2	7.1	80.9	3.1	16.0

6. Section 3.4: Lin 520-526, the authors employed HR–AMS to compare the temporal evolution of aqSOA produced from WSOM of two types of fuel combustion during aqueous-phase photochemical aging. They observed that the aqSOA yield from biomass was significantly lower than that from coal. It is recommended to relate these

findings to the FT-ICR-MS results, rather than merely stating that the coal sample is more efficient at generating low-volatility species compared to maize."

Response： Thanks. We agree that the discussion of aqSOA formation would benefit from a more explicit linkage to the molecular-level information obtained from FT-ICR MS. In the revised manuscript**,** we have strengthened the discussion by connecting the higher aqSOA yield from coal-derived WSOM to its initial molecular composition **(Section 3.4, lines 555–564)**: The possible reasons why coal-derived aqSOA is higher than that from maize are as follows. First, the fresh coal-derived CHOS compounds are dominated by species such as $C_{17}H_{28}O_3S$ and $C_{18}H_{30}O_3S$, which are mainly organosulfates. These compounds have relatively high saturation and stability, and undergo little change upon photolysis, resulting in a high SOA mass yield measured by HR-AMS. In contrast, maize-derived WSOM is primarily composed of lignin-like substances with high DBE values, which are more susceptible to OH functionalization, forming saturated fatty acids or polyhydroxy acids (e.g., $C_9H_{18}O_6$ and $C_9H_{10}O_7$). These products can further undergo fragmentation into smaller, more volatile products (e.g., low-molecular-weight acids), leading to a lower aqSOA mass yield.

7.While the manuscript cites a substantial number of references, some interesting explorations conducted by researchers may be valuable for reference. However, these are all neglected by the authors, for example, Atmos. Chem. Phys., 20, 2513–2532, 2020; Environ. Sci. Technol. 2016, 50, 11815−11824

Response： Thanks for your suggestion. We appreciate the suggestion and have carefully reviewed the studies (Atmos. Chem. Phys., 20, 2513–2532, 2020; Environ. Sci. Technol., 2016, 50, 11815–11824), which provide important insights into aqueous-phase oxidation processes and the formation and evolution of organic aerosols. In the revised manuscript, we have incorporated these references into the Introduction and Discussion sections (**Section 3.2.2: lines 346; Section 3.3: line 423-424, 1014 and 1048**) to better contextualize our findings.

Specific Comments:

1.For the pie charts in Fig. 8, it is recommended to standardize the values and retain one decimal place throughout.

Response: Done.

2.The font size in the attached figures needs to be standardized, and there are some minor errors. For example, in the title of Table S4, 'Chemical properties and SOA

mass yield of both coal-/maize-aqSOA,' there is a missing space between the words yield and of.

Response: Done.

3.Given that the properties of WSOM in both fuels can vary by region, it is recommended to specify their origin used in this study.

Response： Thanks. In the revised manuscript, we have provided the sources of both coal- and maize-derived samples in Section 2.2 "**Sample collection and experiment preparation", including that "**Coal and maize straw were collected from Lingwu (Ningxia) and Shangqiu (Henan Province), respectively, and combusted in a self-built stove designed to simulate domestic fuel burning conditions. Smoke particle collection followed the procedures described in our previous study (Ye et al., 2025).**"**.