Point-by-point response to reviewers

RC1:

Tang et al. reported the enhancement of sulfate production from photosensitization in biomass burning-NaCl droplets. The effects of atmospheric aging and chloride ions in photosensitization-initiated sulfate formation and the corresponding influencing mechanism were also discussed. The experimental results are solid and reliable, but the discussion is not deep enough. I have outlined some of the shortcomings below.

In this manuscript, sulfate formation in the atmosphere was investigated by mixing biomass burning and sea-salt particles. My major concern is about the environmental relevant of the designed experiments. The authors showed in detail the reported formation mechanism of sulfates and the prevalence of biomass burning in the Introduction. It is too tedious. The author does not logically explain the importance and necessity of studying sulfate formation by mixing real biomass burning extracts and NaCl. In addition, the relationship between photosensitization and biomass burning should be shown in a few words.

Response: We appreciate the reviewer's thoughtful feedback on our manuscript.

We have shortened our introduction and incorporated the importance and necessity of studying sulfate formation by mixing real BB extracts and NaCl. We also showed the link between photosensitization and biomass burning in the introduction. Overall, when BB air mass mixes with marine air mass, the interactions of BB and sea-salt components are important to atmospheric chemistry, especially multiphase reactions due to the high humidity. The introduction has been modified to the following (lines 36-89):

Recent fire outbreaks in areas like Canada, Amazonia, and Southeast Australia, together with the increased fire frequency and intensity reports in areas like western US have highlighted the risks of fire, especially biomass burning (BB), to human health and climate change (Bond et al., 2013; Andreae, 2019; Jones et al., 2022). As an agricultural powerhouse, China boasts immense agricultural crop yields, especially in rice, wheat, and corn throughout the country. These crop residues are frequently burned in rural areas for cooking and heating purposes, as well as for land preparation after harvest, resulting in the substantial production of light-absorbing species, such as brown carbon (BrC) (Chen et al., 2017). Recent studies have reported that the specific BrC species from biomass burning, including vanillin (VL), acetovanillone, syringaldehyde (SyrAld), can act as photosensitizers (PS) and oxidize SO_2 to sulfate (Zhou et al., 2023; Liang et al., 2024). Atmospheric processes like aging or long-range transport, can alter the chemical compositions and optical properties of PS, potentially affecting the sulfate formation potential.

Sea-salt aerosol (SSA), with its high particulate matter loadings and extensive surface area, plays a significant role in interfacial and multiphase reactions with reactive gases, thereby impacting global radiation balance and air quality in marine and coastal areas (Gantt and Meskhidze, 2013; Chi et al., 2015). Prior research has identified several secondary sulfate formation pathways in SSA, e.g., multiphase SO_2 oxidation by O_3 (Alexander et al., 2012), coexistence of NO_2 (Zhang and Chan, 2023), PS (Tang et al., 2023), chlorine-photosensitizer synergistic effects (Zhang and Chan, 2024), and Cl and OH radicals generated by chlorine photoactivation (Cao et al., 2024), highlighting the importance of NaCl-based photochemistry in sulfate formation.

SSA can frequently mix with organic matter through processes such as sea-to-air emission, photochemical oxidation and atmospheric transport (Liu et al., 2023). Previous studies have observed elevated sulfate concentrations in coastal regions when air masses passed through inland areas due to intensive BB or other anthropogenic emissions, suggesting the possible interactions between the SSA (primarily sodium chloride) and anthropogenic emissions (Qiu et al., 2019; Huang et al., 2018; Wu et al., 2022). Van Pinxteren et al. (2015) observed an increase in sulfate concentration (2.26 $\mu g\ m^{-3}$) during the RV MARIA S cruise as it approached the African mainland, in contrast to the marine-origin aerosol (1.59 $\mu g\ m^{-3}$), showing significant influence of BB. Hence, mixing of sea-salt and biomass burning aerosols can happen in coastal regions.

Since the sulfate formation rate depends on the intrinsic properties of the solution matrix and the two main reaction matrixes in marine boundary layer (MBL) were wet aerosol (droplet in our case) and cloud/fog (bulk aqueous), both droplet and aqueous reactions are relevant for studying the aqueous reactions in aerosols and clouds within MBL (Ruiz-Lopez et al., 2020; Herrmann, 2003). Typically, droplet experiments were characterized by high ionic strength (up to >10 M), low liquid water content (10^{-7}-10^{-3} $cm^3\ m^{-3}$) and high surface-to-volume ratio whereas aqueous reactions exhibit the opposite characteristics. Transmission electron microscopy (TEM) studies indicate that most coastal particles are internally mixed, showing a higher proportion of organic and salt mixtures in the presence of biomass burning aerosols, accompanied by an increase in sulfate (Dang et al., 2022; Li et al., 2003) However, discrepancies persist between modeled simulations and measured sulfate concentrations in MBL (Yu et al., 2023). The interactions of sea-salt and BB aerosols, especially in multiphase reactions, can potentially unravel the intricate chemistry of sulfate formation in BB affected MBL. Hence, internal mixtures of inorganic salt and water-soluble organic carbons are often used in reaction studies (Tan et al., 2024).

In this study, we performed in-situ droplet and aqueous experiments using BB extracts-NaCl mixture to explore the possible interplay between biomass burning and marine aerosols in coastal areas. BB was derived from the burning of rice straw (RS), wheat straw (WS), and corn straw (CS) as well as incense burning (IS). The aims of this study are to: (i) compare the differences in sulfate formation among different kinds of BB-NaCl particles and BB extracts; (ii) examine the impacts of the atmospheric aging (OH• aging) on sulfate formation across different BB-NaCl particles and BB extracts; (iii) investigate the role of chloride ions in BB extracts mediated sulfate formation.

The manuscript has been altered accordingly.

Minor comments:

1. *Please check carefully English statement in the whole manuscript.*

Response:

We have conducted a comprehensive check of the manuscript and made relevant modifications to enhance its quality.

2. *Line 98–100. As mentioned by the authors, the aim of this study includes three points, but the title only covered one point.*

Response:

We have modified the title to "Enhanced Sulfate Formation in Mixed Biomass Burning and Sea-salt Interactions Mediated by Photosensitization: Effects of Chloride, Nitrogen-containing Compounds and Atmospheric Aging" to cover all the aspects raised in the abstract.

3. *Line 100. "investigating".*

Response:

We have changed the "Investigating" to "investigating" into the manuscript.

The manuscript has been altered accordingly.

4. *Line 105. Did the author measure the water content of the dried biomass?*

Response:

The water contents of the dried biomass were ~10%.

We have added this information into the manuscript.

The manuscript has been altered to the following:

About 100 g of the dried biomass materials (~10% moisture content) was then introduced into a traditional iron stove commonly used in rural areas (Figure S1).

5. *Line 150. Please show more details about experimental conditions such as temperature, and pH value of the generated droplets.*

Response:

We have showed more details of the droplets experiment in response to the reviewer's suggestion. Temperature and pH information are now included in the main text (Lines 139-144).

In SO_2 uptake experiments, the stock solution of BB extracts was premixed with sodium chloride solution (1M) at a volume ratio of 1:1 and the solutions had a pH of 4-6. A droplet generator (Model 201, Uni-Photon Inc.) was then utilized to deposit droplets onto a hydrophobic substrate (model 5793, YSI Inc.) for SO_2 uptake experiments. Reactive SO_2

uptake experiments were performed via a flow cell/in-situ Raman system at controlled room temperature (23-25℃).

6. *Line 157. It would be better to give the specific value of the light intensity of xenon lamp.*

Response:

The light intensity for our xenon lamp is 1318 mW/cm^2.

We have included the information into the manuscript (lines 145-148).

The light experiment was performed using a xenon lamp (model 6258, ozone free, 300W, Newport, light intensity of 1318 mW cm^{-2}), with photon flux of 9.8 ×10^{15} photons cm^{-2} s^{-1} in 280-420 nm received by particles in the flow cell (Zhang and Chan, 2023).

7. *Line 168. The used concentration of bisulfite and BB TOC extracts are 100 ppm and 1 ppm, respectively. Are there environmental reference values for these two concentrations?*

Response:

The concentrations of 1 ppm for BB TOC extracts and 100 ppm for bisulfite have significant atmospheric relevance.

Previous studies have indicated that phenolic and non-phenolic aromatic carbonyls from biomass burning plumes can lead to concentrations of up to hundreds of micromolar humid carbonyls (potential PS) in aqueous aerosols, fogs, and clouds (Anastasio et al., 1997). In our study, the 1 ppm TOC concentration aligns well with these atmospheric-relevant ranges and serves as an appropriate representative of aqueous phase photosensitizer concentrations. Furthermore, bisulfite concentrations in ambient cloud and fog water can reach hundreds of micromolar, with total sulfur concentrations (S(IV) + S(VI)) often exceeding several millimolar (Guo et al., 2012; Shen et al., 2012; Rao and Collett, 1995). Therefore, our bisulfite concentration of 100 ppm fits well within the sulfur concentrations detected in cloud and fog water.

We have incorporated this relevant information into our manuscript. (Lines 161-165)

Note that the 1 ppm BB TOC and 100 ppm bisulfite align well with the atmospheric-relevant ranges in aqueous aerosols, fogs and clouds, where PS concentration can reach hundreds of micromolar and total sulfur concentration can exceed several millimolar. (Anastasio et al., 1997; Guo et al., 2012; Shen et al., 2012; Rao and Collett, 1995)

8. *Line 202. polycyclic aromatic hydrocarbons (PAHs)*

Response:

We have added the full name of PAHs for the first appearance.

The manuscript has been altered accordingly.

9. *Line 204. PAHs.*

Response:

The manuscript has been altered accordingly.

10. *Line 270–271. Did the aging experiments conduct under UV irradiation or OH oxidation condition? The text in lines 121–128 did not show that well, but I think it may be UV irradiation based on descriptions elsewhere, such as line 26 and line 29. If only UV irradiation, 185 nm and 254 nm are not relevant in the troposphere (λ > 290 nm). Please clarify that.*

Response:

The UV lamps are used to produce OH• to study OH• oxidation. The oxidation of hydroxyl radicals (OH•) is the predominant oxidation pathway occurring during daylight hours. Irradiation at 185 nm and 254 nm effectively generates OH radicals, leading to the aging of the filter samples, as indicated by the following reactions:

$$H_2O + h\nu(185\ \text{nm}) \rightarrow OH\bullet + H\cdot \qquad (1)$$

$$O_2 + h\nu(185\ \text{nm}) \rightarrow 2O(^3P) \qquad (2)$$

$$O_2 + O(^3P) \rightarrow O_3 \qquad (3)$$

$$O_3 + h\nu\ (254\text{nm}) \rightarrow O_2 + O(1D) \qquad (4)$$

$$O(^1D) + H_2O \rightarrow 2OH\bullet\cdot \qquad (5)$$

$$H\bullet + O_2 \rightarrow HO_2\bullet\cdot \qquad (6)$$

The illumination of UV lights creates oxygen atoms, i.e., $O(^3P)$ and $O(^1D)$, which are short-lived and highly reactive with oxygen and water, respectively. The production of ozone in the presence of 185 nm lamp initiates reactions under the presence of 254 nm, which will result in the formation of OH• radicals.

In order to avoid any misunderstanding, we have clarified this in the manuscript.

The manuscript has been altered accordingly.

Modifications in the manuscript:

Lines 26-27

The filter aging was achieved by exposing them to OH• through UV irradiation.

Lines 289-291

To investigate the aging effects across various BB materials, we subjected the collected BB filters to OH radical aging by irradiating them with UV lights at wavelengths of 185 nm and 254 nm. This combination effectively generate OH radicals (Tang et al., 2023).

Lins 109-113 To achieve atmospheric OH• aging, the collected fresh BB filter samples were placed in a pre-flushed combustion chamber (zero air, more than 24 h) and illuminated with UV lamps for 40 min. We used lamps of 185 nm and 254 nm, the combination of which have been widely used in oxidation flow reactor design and experiments for mimicking atmospheric OH• concentrations (Peng and Jimenez, 2020; Rowe et al., 2020; Tkacik et al., 2014; Hu et al., 2022).

11. Line 283–309. The topic of Sect. 3.2 is aging effects on sulfate formation across various BB materials. The text in line 289–309 provides the explanation about the accelerated sulfate formation in droplets. It would be more in line with the topic to compare whether there is a difference of aging effects between air-water interfaces and bulk phase.

Response:

Thank you for your suggestion.

Air-water interfacial reactions are not the focus of this study, and hence we have decided to remove this discussion to maintain alignment with the main narrative of the manuscript. To address this question, we will need to do experiments with different particle sizes to vary the surface to volume ratio. This would be useful future work.

12. Line 316. BrC.

Response:

We have deleted the “brown carbon” in the manuscript.

The manuscript has been altered accordingly.

13. Line 349. How to distinguish $WS_{A\text{-}BrC}$ from WS_A?

Response:

The method to distinguish $WS_{A\text{-}BrC}$ from WS_A is the same as mentioned before in distinguishing RS and CS (lines 313-318).

$WS_{A\text{-}BrC}$ is a subset of WS_A. WS_A and $WS_{A\text{-}BrC}$ are defined as the water-soluble organic species and molecularly identified water-soluble brown carbon in WS extracts, respectively. They can be differentiated based on the criteria raised by Lin et al. (2018). Efficient absorption of visible light in organic molecules necessitates continuous conjugation across a substantial portion of the molecular framework. Compounds exhibiting a Double Bond Equivalent to Carbon (DBE/C) ratio exceeding that of polyenes are promising candidates for brown carbon (BrC) chromophores. For linear polyenes with a general formula of C_xH_{x+2}, DBE=0.5×C, while fullerene-like hydrocarbons follow a DBE value of 0.9×C. Compounds with DBE/C ratio higher than polyenes and lower than fullerene-like hydrocarbons can be categorized as potential BrC chromophores. (Lin et al., 2018).

The sentence has been modified to the following to avoid ambiguity (lines 313-318):

Given the presence of chromophoric compounds in BrC (Laskin et al., 2015), we constrained the DBE values to the range of $0.5C \leqslant DBE \leqslant 0.9C$ to semi-qualitatively distinguish BrC chromophores in the dissolved organic carbon (Lin et al., 2018). $BB_{F/A}$ was defined as the water-soluble organic species while $BB_{F/A\text{-}BrC}$ represented the molecularly identified water-soluble brown carbon falling in the range of 0.5C⩽DBE⩽0.9C in BB extracts. These definitions will be consistently applied hereafter.

14. Line 373. RS extracts.

Response:

We have deleted “rice straw” in the manuscript.

The manuscript has been altered accordingly.

15. *Line 384. Confirm? More possible explanation should be provided.*

Response: We changed the phrase to the following: “On one hand, it supported the findings that chloride participated in the sulfate formation under light but no sulfate formation under dark (Cao et al., 2024; Tang et al., 2023; Zhang and Chan, 2024).”

The manuscript has been altered accordingly.

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