Point-by-point response to reviewers

Comments

1. "The authors claim that the performance of droplet and bulk experiments follows natural rules in the MBL involving aerosol and cloud particles. However, this may not be entirely convincing, as droplet experiments can also simulate low ionic strength conditions. Some interfacial characteristics might be overlooked in bulk reactions, and I believe the authors should discuss these limitations (beyond just droplet vs. bulk tests) in the revised paper.

Response: We thank the reviewer for the comment.

We have revised our manuscript to clarify this (lines 74-76 and lines 311-318):

"Additionally, droplet experiments can encompass certain interfacial reaction pathways that may occur in atmospheric conditions."

"Lower sulfate formation rates were observed for bulk reactions compared to droplets reactions, which may be attributed to the accelerated reactions induced by PS at the air-water interface, as well as differences in concentrations of S(IV) and NaCl. However, given that interfacial reactions are closely linked to particle size (Wei et al., 2020; Chen et al., 2022b), and additional research is needed to better understand its influence. Our experiments involve large droplets of the size of 60μm. The interfacial effects of such large droplets may not be evident. Future work should use submicron and nanometer size particles to examine the interfacial effects."

The manuscript has been altered accordingly.

2. The discussion on direct and indirect photosensitization reactions is somewhat disorganized. In my view, some molecular oxygen may be present in the commercial or home-made HULIS samples, which could also be a limitation that should be emphasized. Additionally, the role of Ar as a carrier gas was not considered.

Response:

Some molecular oxygen may be present in the extracted BB and IS samples. However, its concentration is likely low under N_2-saturated conditions, as indicated by the absence of sulfate in the controlled experiments of IS-NaCl droplets. Hence, even if they are present, the molecular oxygen did not seem to play any appreciable role. We will address this point in our revised discussion.

Lines 268-271

"Despite initial molecular oxygen in the droplets may also participate in sulfate formation under N_2-saturated conditions, its contributions are likely minimal. Therefore, the sulfate formed under N_2-saturated condition can be considered as the upper limit of direct ^{3}PS* oxidation."

Regarding the use of argon as a carrier gas, we consider its role similar to that of nitrogen, both providing an inert atmosphere; thus, we did not conduct experiments specifically with argon.

3. Why did the authors choose Pearson correlation analysis over Spearman correlation analysis? Was the distribution of the target dataset tested?

Response: Thanks for your comment.

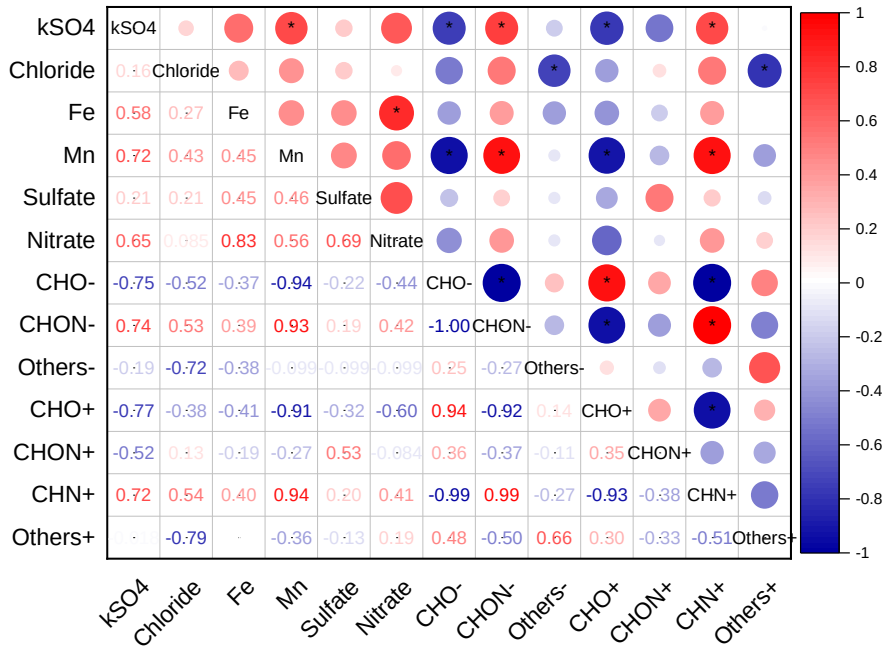
We conducted the Shapiro-Wilk test to assess the normality of the dataset, as shown in Table S4. A Shapiro-Wilk test result of $p > 0.05$ indicates that the dataset can be considered normally distributed, whereas $p \leqslant 0.05$ suggests non-normality. Given these considerations, Spearman correlation analysis is more appropriate for the heatmap analysis, while Pearson analysis is more suitable for specific parameters such as k_{SO4}, nitrate, CHN+ and others+. Consequently, we have revised Fig. S9 to Spearman correlation heatmap. The manuscript has been modified to the following:

(Lines 424-426)

"Statistical analysis using the Spearman correlation coefficients, as guided by the Shapiro-Wilk test (Table S4), revealed that the CHO, CHON, and CHN species exhibited significant correlations ($|R|>0.7$) with the sulfate formation rate ($p < 0.01$, Figure S9)."

Table S4 Shapiro-Wilk normality test results for the analysis of correlation coefficients.

Parameter	Statistic	p-value	Decision at level (5%)
k_{SO4}	0.90341	0.17551	Can't reject normality
Chloride	0.66506	3.96E-04	Reject normality
Fe	0.83678	0.02531	Reject normality
Mn	0.79415	0.00804	Reject normality
Sulfate	0.70692	9.83E-04	Reject normality
Nitrate	0.87657	0.07923	Can't reject normality
CHO-	0.80111	0.00964	Reject normality
CHON-	0.78144	0.00581	Reject normality
Others-	0.78595	0.00651	Reject normality
CHO+	0.68063	5.52E-04	Reject normality
CHON+	0.7749	0.00492	Reject normality
CHN+	0.86772	0.06114	Can't reject normality
Others+	0.88449	0.10007	Can't reject normality



* p<=0.01

Fig. S9 Heatmap of Spearman correlations between sulfate formation rate (kSO4) and other factors, including chloride, Fe, Mn, sulfate, nitrate, and different chemical species detected by ESI (-) and ESI (+) mode. Note that the calculations were based on the sulfate formation rate and the initial concentrations of the influencing factors in the bulk solution. The symbol * indicates significance, i.e., $p \leq 0.01$. Red color means positive correlation ($r > 0$) and blue color means negative correlation ($r < 0$). The darker the color, the higher the r value.

4. Regarding Figure 5: This schematic may not be of broad interest and would be better replaced by a more good-looking representation, with the primary pathways retained.

Response:

We don't know how to interpret the comment on "good-looking". This is not a TOC artwork. We view that it is useful to include these important pathways. We slightly modified it to the following:

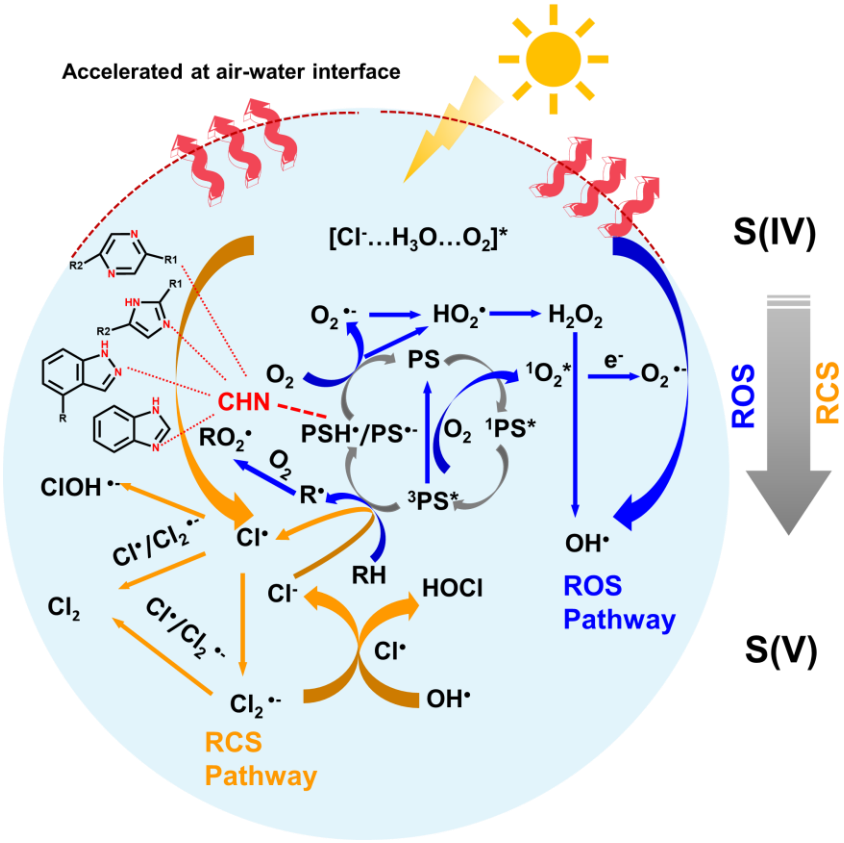


Figure 5. Conceptual diagram of PS and chloride mediated ROS and RCS production in the oxidation processes from S(IV) to S(VI)

5. I would also suggest that the authors emphasize the atmospheric implications of their findings and provide more data on the relative importance of the observed photochemical events.

Response:

In our manuscript, we focus on comparing the photosensitizing abilities of different BB and NaCl chemical systems rather than quantifying their absolute values. The significant uncertainties in atmospheric aqueous PS concentrations (2.3×10^{-13} to 1.6×10^{-10} M) (Wang et al., 2020), along with their varying photosensitizing capacities, would lead to significant uncertainties in calculating sulfate formation based on our findings. For example, we roughly estimated the sulfate formation rate under the scenario set by Cheng et al. (2016) and following the procedures proposed by Liu et al. (2021). Assuming an average PS molar mass of 170g mol^{-1} and a pH of 6, the estimated sulfate formation rate ranged from 1.29×10^{-6} μg m^{-3} h^{-1} to 0.034 μg m^{-3} h^{-1}, which spans several magnitudes. While this work serves as a foundational study for similar complex systems, further research, such as estimating PS* concentrations, is necessary for more accurate assessments.

6. Finally, additional relevant literature on atmospheric photosensitization should be cited and discussed to help readers gain a deeper understanding of this interesting topic.

Response:

We have added additional relevant literature and discussions on atmospheric photosensitization into the manuscript (lines 43-49 and lines 310-318):

"Recent studies have reported that specific BrC species from biomass burning, including vanillin (VL), acetovanillone, syringaldehyde (SyrAld), and naphthalene-derived secondary organic aerosol (Teich et al., 2016; Li et al., 2024; Liu et al., 2020; Wang et al., 2021) 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, and hence affect the sulfate formation potential (You et al., 2020; Li et al., 2019)."

"Lower sulfate formation rates were observed for bulk reactions compared to droplets reactions, which may be attributed to the accelerated reactions induced by PS at the air-water interface, as well as differences in concentrations of S(IV) and NaCl. However, given that interfacial reactions are closely linked to particle size (Wei et al., 2020; Chen et al., 2022b), additional research is needed to better understand its influence. Our experiments involve large droplets of size of 60 μm. The interfacial effects of such large droplets may not be evident. Future work should use submicron and nanometer size particles to examine the interfacial effects."

References

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Science Advances, 2, e1601530, doi:10.1126/sciadv.1601530, 2016.

Li, F., Zhou, S., Zhao, J., Hang, J., Lu, H., Li, X., Gao, M., Li, Y., and Wang, X.: Aqueous Photosensitization of Syringaldehyde: Reactivity, Effects of Environmental Factors, and Formation of Brown Carbon Products, ACS Earth and Space Chemistry, 2024.

Li, S., Jiang, X., Roveretto, M., George, C., Liu, L., Jiang, W., Zhang, Q., Wang, W., Ge, M., and Du, L.: Photochemical aging of atmospherically reactive organic compounds involving brown carbon at the air–aqueous interface, Atmos. Chem. Phys., 19, 9887-9902, 10.5194/acp-19-9887-2019, 2019.

Liang, Z., Li, Y., Go, B. R., and Chan, C. K.: Complexities of Photosensitization in Atmospheric Particles, ACS ES&T Air, 10.1021/acsestair.4c00112, 2024.

Liu, T., Chan, A. W. H., and Abbatt, J. P. D.: Multiphase Oxidation of Sulfur Dioxide in Aerosol Particles: Implications for Sulfate Formation in Polluted Environments, Environmental Science & Technology, 55, 4227-4242, 10.1021/acs.est.0c06496, 2021.

Liu, Y., Wang, T., Fang, X., Deng, Y., Cheng, H., Nabi, I., and Zhang, L.: Brown carbon: An underlying driving force for rapid atmospheric sulfate formation and haze event, Science of the Total Environment, 734, 139415, 2020.

Teich, M., van Pinxteren, D., Kecorius, S., Wang, Z., and Herrmann, H.: First quantification of imidazoles in ambient aerosol particles: potential photosensitizers, brown carbon constituents, and hazardous components, Environmental science & technology, 50, 1166-1173, 2016.

Wang, X., Gemayel, R., Baboomian, V. J., Li, K., Boreave, A., Dubois, C., Tomaz, S., Perrier, S., Nizkorodov, S. A., and George, C.: Naphthalene-derived secondary organic aerosols interfacial photosensitizing properties, Geophysical Research Letters, 48, e2021GL093465, 2021.

Wang, X., Gemayel, R., Hayeck, N., Perrier, S., Charbonnel, N., Xu, C., Chen, H., Zhu, C., Zhang, L., Wang, L., Nizkorodov, S. A., Wang, X., Wang, Z., Wang, T., Mellouki, A., Riva, M., Chen, J., and George, C.: Atmospheric

Photosensitization: A New Pathway for Sulfate Formation, Environmental Science & Technology, 54, 3114-3120, 10.1021/acs.est.9b06347, 2020.
You, B., Li, S., Tsona, N. T., Li, J., Xu, L., Yang, Z., Cheng, S., Chen, Q., George, C., Ge, M., and Du, L.: Environmental Processing of Short-Chain Fatty Alcohols Induced by Photosensitized Chemistry of Brown Carbons, ACS Earth and Space Chemistry, 4, 631-640, 10.1021/acsearthspacechem.0c00023, 2020.
Zhou, L., Liang, Z., Mabato, B. R. G., Cuevas, R. A. I., Tang, R., Li, M., Cheng, C., and Chan, C. K.: Sulfate formation via aerosol-phase SO2 oxidation by model biomass burning photosensitizers: 3,4-dimethoxybenzaldehyde, vanillin and syringaldehyde using single-particle mixing-state analysis, Atmos. Chem. Phys., 23, 5251-5261, 10.5194/acp-23-5251-2023, 2023.