Author Response for “Aqueous SOA formation from photosensitized guaiacol oxidation: Comparison between non-phenolic and phenolic methoxybenzaldehydes as photosensitizers in the absence and presence of ammonium nitrate” by Mabato et al.

We thank the Reviewer for their thorough comments. We have revised the manuscript accordingly, and below are our point-by-point responses (in blue) to the comments (in black) and changes to the manuscript (in red). In those changes that begin with line numbers, the original text is also in blue. In addition, please note that the line numbers in the responses correspond to those in the original manuscript.

Reviewer 2

This paper systematically investigated the physicochemical properties of aqueous SOA formed from the photosensitized guaiacol oxidation by using DMB and VL as photosensitizers in the presence and absence of AN. In general, this paper is well written, readable and logical. Before accepted for publication, some revisions should be made. The specific comments are listed as follows:

1. Why did not show aqSOA yields in this work? In my opinion, these data are very useful for readers to understand the importance of these oxidation processes. When these data were described in the paper, the comparison between these date and other similarly reported results should be made.

Response: Since this work mainly focused on the analyses of the reaction products and product distribution, we did not perform measurements of aqSOA mass yields. As similar aqSOA mass yields have been reported from the photosensitized oxidation of syringol (another non-carbonyl phenol) by ^{3}DMB* (111%) and ^{3}VL* (114%) (Smith et al., 2014, 2016) (mentioned in lines 57-59), we assumed that aqSOA mass yields from guaiacol photo-oxidation by ^{3}DMB* and ^{3}VL* would also be comparable.

2. As mentioned in section 2.1, the samples were collected every 30 min for 180 min for offline analyses. Therefore, authors can provide more information about the changes of signal-weighted distributions and visible light absorption of aqSOA formed under different conditions during the whole reaction processes. In addition, the concentration changes of small organic acids during the whole reaction processes should be also supplemented.

Response: Thank you for pointing this out. We apologize for the confusion regarding the samples subjected to offline analyses. In this work, the samples collected every 30 min were analyzed using only UHPLC-PDA and UV-Vis spectrophotometry for GUA and photosensitizers decay kinetics and absorbance changes, respectively. The absorbance enhancement from 0 to 180 min for all reaction systems studied have been added to Figure 4(a). Based on suggestions from Reviewer 4, the original Figure 4 (now Figure 4b) has also been replaced with the change in the rate of sunlight absorption (ΔR_{abs}) from 350-550 nm at 180 min during typical clear and haze days in Beijing, China. Moreover, the absorption spectra after 180 min of irradiation for each solution have been added to the supplement (Figure S7) based on suggestions from Reviewer 4.

The updated Figure 4 and added Figure S7 are shown below:

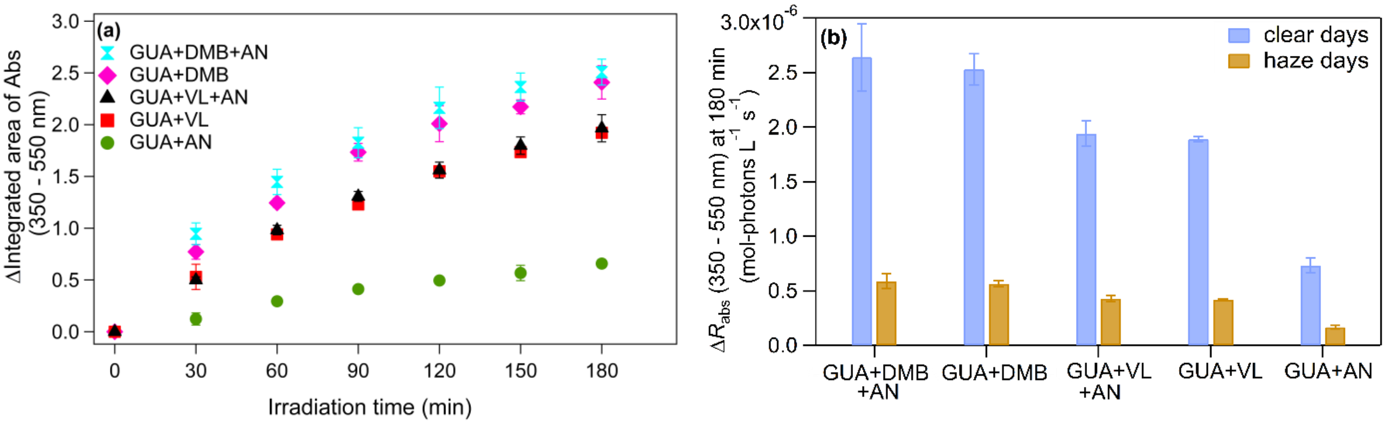

Figure 4. (a) Increase in light absorption throughout 180 min of irradiation for all reaction systems studied and (b) Change in the rate of sunlight absorption (ΔR_{abs}) from 350-550 nm at 180 min during typical clear and haze days in Beijing, China for aqSOA from GUA+DMB+AN, GUA+DMB, GUA+VL+AN, GUA+VL, and GUA+AN. ~~Increase in visible light absorption for aqSOA from GUA+DMB, GUA+VL, GUA+DMB+AN, and GUA+VL+AN.~~ Error bars represent one standard deviation of triplicate experiments.

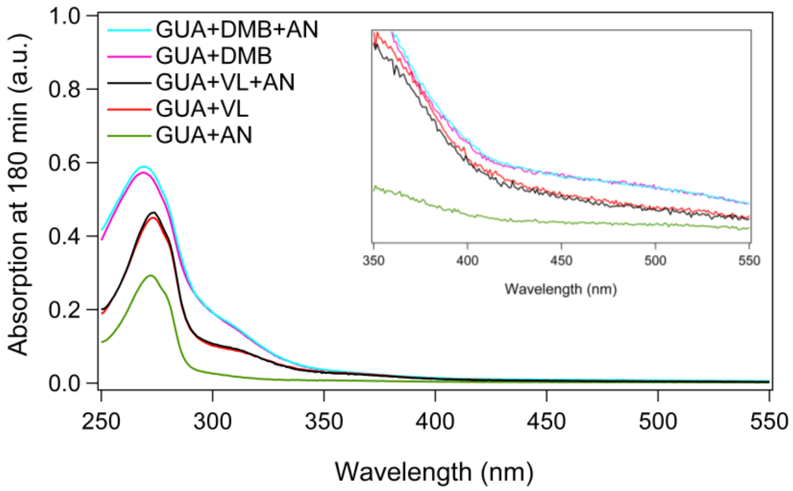

Figure S7. UV-Vis absorption spectra of GUA+DMB+AN, GUA+DMB, GUA+VL+AN, GUA+VL, and GUA+AN after 180 min of irradiation. The inset is the expanded view from 350 to 550 nm.

The corresponding revisions in the text are as follows:

Lines 253-260: The increase in light absorption throughout 180 min of irradiation and the change in the rate of sunlight absorption (ΔR_{abs}) (Jiang et al., 2021) from 350 to 550 nm at 180 min during typical clear and haze days in Beijing, China for all the reaction systems studied are provided in Figure 4. Figure S7 shows the absorption spectra after 180 min of irradiation for each reaction system studied. In this work, the absorbance enhancement of GUA+DMB and GUA+VL (Fig. 4a) could be due to ~~correlates with~~ oligomers and functionalized monomers, which are the highest contributors to the product signals. Identifying the chromophores responsible for the absorbance enhancement may be beneficial in understanding the impact of aqSOA on the Earth's radiative balance and determining the reactions that affect light absorption by aqSOA (Mabato et al., 2022). However, the detected products did not exhibit distinct peaks in the UHPLC-PDA chromatograms, likely due to the concentration of the chromophores being below the detection limit of PDA. Nevertheless, the higher absorbance enhancement and ΔR_{abs} for GUA+DMB than GUA+VL was ~~most likely associated with~~ probably due to the higher contribution and normalized abundance (by ~6 times) of oligomers in the former.

Line 353: The presence of AN also did not appreciably affect the absorbance enhancement and ΔR_{abs} for both GUA+DMB+AN and GUA+VL+AN (Fig. 4).

Moreover, the detection of products and small organic acids was performed only for the samples collected before and after irradiation (180 min). To clarify these differences, section 2.1 has been revised as follows:

Lines 132-137: Samples were collected every 30 min~~s~~ for 180 min~~s~~ for offline analyses of (1) GUA, DMB, and VL concentrations using ultra-high-performance liquid chromatography with photodiode array detector (UHPLC-PDA)~~;~~ and (~~4~~2) absorbance measurements using UV-Vis spectrophotometry. Moreover, the samples collected before and after irradiation (180 min) were analyzed for (~~2~~3) reaction products using UHPLC coupled with heated electrospray ionization Orbitrap mass spectrometry (UHPLC-HESI-Orbitrap-MS) operated in positive and negative ion modes~~;~~ and (4~~3~~) concentrations of small organic acids using ion chromatography (IC)~~;~~.

Other revisions in the text were as follows:

Line 213: The IC analyses also indicate the formation of small organic acids (e.g., formic acid), which appeared to have higher concentrations in the presence of DMB than in VL (Fig. S4~~3~~). Although no data is available for the concentration changes (every 30 min) of small organic acids during the reaction, it is likely that an increasing trend would be observed as fragmentation, which leads to the decomposition of initially formed oligomers and the generation of smaller oxygenated products, becomes important at longer irradiation times (Huang et al., 2018). This trend has also been observed in our previous work on the direct photosensitized oxidation of VL (Mabato et al., 2022), as well as other studies on photosensitized oxidation of non-carbonyl phenols and phenolic carbonyls (e.g., Yu et al., 2016; Jiang et al., 2021).

Line 382: The major aqSOA formation processes for GUA+DMB and GUA+VL were oligomerization and functionalization, but functionalization appeared to be more significant in GUA+VL due to VL transformation products. The photochemical evolution of aqSOA from GUA+DMB has been reported by Yu et al. (2016). Similar experiments for aqSOA from GUA+VL should be conducted in the future to better understand photosensitized reactions involving phenolic carbonyl photosensitizers.

3. Please provide the reason why selected the whole reaction times as 180 min.

Response: An irradiation time of 180 min was chosen for this work as it was sufficient to show the differences in the extent of reaction of GUA among the reaction systems studied. Moreover, the same irradiation time was applied to all experiments as we were trying to evaluate the product distributions after a certain time of photosensitization.

This information has been added to the discussion of the product distributions as follows:

Lines 194-197: The products detected using UHPLC-HESI-Orbitrap-MS were used to ~~represent~~ characterize the aqSOA formed in this work. The signal-weighted distributions of aqSOA calculated from combined positive (POS) and negative (NEG) ion modes MS results are summarized in Figure 2. The signal-weighted distributions calculated separately from POS and NEG ion modes MS results are available in Figures S2~~1~~ and S3~~2~~. It should be noted that in this work, the product distributions for all experiments were based on the same irradiation time of 180 min. An irradiation time of 180 min was chosen as it was sufficient to show the differences in the extent of reaction of GUA among the reaction systems studied. For reaction systems with precursors of different reactivities, chemical analysis at a fixed reaction time may be looking at different generations of products of each precursor, as Yu et al. (2014) reported. Measuring the product distribution at a fixed time might have missed the information on what/how many products are formed at the similar amounts of precursors reacted. The situation could be even more complicated if different precursors had major differences in pathways and dominant intermediates. However, comparing the product distributions after a certain time of light exposure, as is the case for this study, is useful to evaluate what products would form after a certain time of photosensitization.

4. There are still some language mistakes, please carefully check.

Response: Thank you for pointing this out. We have carefully checked the text for language mistakes.

References for responses to Reviewer 2:

Huang, D. D., Zhang, Q., Cheung, H. H. Y., Yu, L., Zhou, S., Anastasio, C., Smith, J. D., and Chan, C. K.: Formation and evolution of aqSOA from aqueous-phase reactions of phenolic carbonyls: comparison between ammonium sulfate and ammonium nitrate solutions, Environ. Sci. Technol., 52, 9215–9224, https://doi.org/10.1021/acs.est.8b03441, 2018.

Jiang, W., Misovich, M. V., Hettiyadura, A. P. S., Laskin, A., McFall, A. S., Anastasio, C., and Zhang, Q.: Photosensitized reactions of a phenolic carbonyl from wood combustion in the aqueous phase—chemical evolution and light absorption properties of aqSOA, Environ. Sci. Technol., 55, 5199−5211, https://doi.org/10.1021/acs.est.0c07581, 2021.

Mabato, B. R. G., Lyu, Y., Ji, Y., Li, Y. J., Huang, D. D., Li, X., Nah, T., Lam, C. H., and Chan, C. K.: Aqueous secondary organic aerosol formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate, Atmos. Chem. Phys., 22, 273−293, https://doi.org/10.5194/acp-22-273-2022, 2022.

Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of atmospheric phenols with an organic triplet excited state, Environ. Sci. Technol., 48, 1049–1057, https://doi.org/10.1021/es4045715, 2014.

Smith, J. D., Kinney, H., and Anastasio, C.: Phenolic carbonyls undergo rapid aqueous photodegradation to form low-volatility, light-absorbing products, Atmos. Environ., 126, 36−44, https://doi.org/10.1016/j.atmosenv.2015.11.035, 2016.

Yu, L., Smith, J., Laskin, A., Anastasio, C., Laskin, J., and Zhang, Q.: Chemical characterization of SOA formed from aqueous-phase reactions of phenols with the triplet excited state of carbonyl and hydroxyl radical, Atmos. Chem. Phys., 14, 13801−13816, https://doi.org/10.5194/acp-14-13801-2014, 2014.

Yu, L., Smith, J., Laskin, A., George, K. M., Anastasio, C., Laskin, J., Dillner, A. M., and Zhang, Q.: Molecular transformations of phenolic SOA during photochemical aging in the aqueous phase: competition among oligomerization, functionalization, and fragmentation, Atmos. Chem. Phys., 16, 4511−4527, https://doi.org/10.5194/acp-16-4511-2016.