

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 3

This manuscript describes a comparative study of the photosensitization by phenolic and non-phenolic methoxybenzaldehydes in reactions of guaiacol (another phenolic compound, but without an aldehyde functional group), with and without the presence of ammonium nitrate salts. The experiments were conducted in bulk aqueous phase samples in a solar simulator.

The combination of photosensitizing reactions of methoxybenzaldehyde species with ammonium nitrate photochemistry in a series of experiments is especially interesting. The primary conclusion is that the non-phenolic species DNB is approximately 4 times more effective as a photosensitizer than the phenolic species vanillin, and produces slightly more brown carbon. The manuscript includes a great number of qualitative comparisons, but the authors highlight the most important ones in the abstract and conclusion. It will be of interest to atmospheric scientists studying mechanisms of formation of brown carbon and aqueous secondary organic aerosol.

(a) My first concern is that the authors may have oversimplified the complex task of comparing the photosensitizing abilities of VL and DNB, when VL is reacting away at  $\sim 20\times$  the rate of DNB (a factor of  $8 \times 2.4$ ). The reactivity of VL is so great that it successfully competes with GUA in the reaction with the VL triplet ( ${}^3\text{VL}^*$ ), reacting with it 24% of the time over the course of the reaction even though the VL concentration is  $10\times$  less than GUA. (I estimated this reaction fraction from the stated  $2.4\times$  faster decay rate of VL times the VL / GUA concentration ratio of  $0.01\text{mM}/0.1\text{mM}$ , resulting in a relative loss rate for VL of 0.24 if GUA loss rate = 1.) If one takes into account  ${}^3\text{VL}^*$  reactions with both VL and GUA, DNB would be at most only 3 times faster than VL at promoting photosensitization reactions in general. A more nuanced kinetics analysis would thus be helpful for GUA + VL and GUA + VL + AN reactions. Furthermore, it could allow some qualitative statements in the paper, such as those in line 204 and 207, to become quantitative: (b) when integrated over the full course of the reaction, what is the impact of the loss of the reactant VL on the total amount of products generated?

Response: (a) Thank you for pointing this out. We would like to emphasize that the kinetics analysis and apparent quantum efficiency of GUA photodegradation suggested faster GUA oxidation in GUA+DMB vs. GUA+VL, which we attributed to two reasons: (1) DMB having a stronger photosensitizing ability than VL based on its higher quantum yield of  ${}^3\text{C}^*$  formation and longer lifetime of  ${}^3\text{DMB}^*$  compared to  ${}^3\text{VL}^*$  (Felber et al., 2021) and (2) VL being highly reactive towards oxidation as it is also a phenolic compound, similar to GUA. However, these

trends **do not indicate that DMB is 4 times more effective as a photosensitizer** compared to VL. Also, during GUA oxidation, the calculated decay rate constant of VL was only 4.6 times higher (not ~20 times) than that of DMB (VL decay rate constant in GUA+VL:  $3.6 \text{ min}^{-1}/\text{s}^{-1}$  vs. DMB decay rate constant in GUA+DMB:  $0.78 \text{ min}^{-1}/\text{s}^{-1}$ ; note that the decay rate constants were corrected for internal light screening due to DMB and VL light absorption, and normalized to the experimental photon flux).

The Reviewer is correct that comparing photosensitizing abilities is a complex task. However, a detailed quantitative analysis of the photosensitizing abilities which necessitates more experiments, e.g., determining the intersystem crossing quantum yield for VL (Smith et al., 2014) or using time-resolved absorption spectroscopy (Felber et al., 2021) is beyond the scope of the paper. Nonetheless, the estimated decay rate constants and apparent quantum efficiency of GUA photodegradation indicate that GUA oxidation in GUA+DMB was overall more efficient than in GUA+VL. These measurements can be useful for comparison with GUA oxidation by other oxidants or photosensitizers. Our kinetic analysis focused on the decay rate constants of the aqSOA precursor (GUA) and the photosensitizers (DMB and VL) during photosensitization under the same experimental conditions (same aqSOA precursor and concentration, same photosensitizer concentration, and same lamp photon flux). The effects of other factors (e.g., intersystem crossing efficiency) on the rate constants were not examined. Hence, lacking rate constants that are either universal or specific for a number of experimental conditions in the literature, we hope that these parameters obtained in our study can provide first-order estimates for modeling since the experimental conditions (GUA+DMB, GUA+VL, GUA+DMB+AN, GUA+VL+AN, and GUA+AN based on concentrations relevant to cloud and fog conditions at pH 4 in air) are atmospherically relevant. Explicit kinetic studies (e.g., Smith et al., 2014, 2015) that measure second-order rate constants should be conducted in the future to extend the applicability of the kinetic parameters to other conditions.

The following sentences have been added at the end of Sect. 3.1.1 to clarify these:

Line 192: It should be noted that the differences in the GUA decay rate constants among different reaction systems are not quantitatively equivalent to photosensitizing efficiencies, and a detailed quantitative analysis of which is beyond the scope of this study. Nonetheless, these results suggested that GUA oxidation in GUA+DMB was overall more efficient than in GUA+VL. Our kinetic analysis focused on the decay rate constants of the aqSOA precursor (GUA) and the photosensitizers (DMB and VL) during photosensitization under the same experimental conditions (same aqSOA precursor and concentration, same photosensitizer concentration, and same lamp photon flux). The effects of other factors (e.g., intersystem crossing efficiency) on the rate constants were not examined. Explicit kinetic studies (e.g., Smith et al., 2014, 2015) that measure second-order rate constants should be conducted in the future to extend the applicability of the kinetic parameters to other conditions.

Moreover, it should be noted that in this work, we mainly focused on the analyses of the reaction products and product distributions.

The title of the paper has been revised to 'Comparison of aqueous SOA product distributions from guaiacol oxidation by non-phenolic and phenolic methoxybenzaldehydes as

photosensitizers in the absence and presence of ammonium nitrate' to better reflect the focus of the work.

Furthermore, the following sentences have been added to the text to clarify the focus of this work:

Line 96: The precursor and photosensitizer decay kinetics, detected products, and absorbance enhancement were used to characterize the reactions. **However, it should be noted that we mainly focused on the analyses of the reaction products and product distribution.**

(b) We have given a lot of thought to this comment. We assumed that the question pertains to the normalized abundance of products. The calculation of the normalized abundance of products involves the absolute GUA concentration changes measured before and after irradiation using UHPLC-PDA, which is related to the loss of the photosensitizers. Therefore, the estimated normalized abundance of products already covers the loss of the photosensitizers. The following are mentioned in lines 207-208: "In addition, the normalized product abundance for GUA+DMB was ~4 times higher than that for GUA+VL (Table 1), further suggesting more efficient photosensitized GUA oxidation by <sup>3</sup>DMB\* than by <sup>3</sup>VL\*." However, we would like to emphasize that the normalized abundance of products in this work represents a semi-quantitative analysis of products in different experiments rather than absolute concentration of products.

Other comments:

1. Line 95: How are products counted if they appear in both positive and negative modes of ionization?

Response: For the signal-weighted distributions in Figure 2, the peak area of each product (whether it appeared in either positive or negative ion mode only, or it appeared in both ion modes) was normalized to the total signal areas summed from positive and negative ion modes. For reference, the signal-weighted distributions calculated separately from positive and negative ion modes are provided in Figures S2 and S3 (formerly Figures S1 and S2).

2. Line 335: What could highly oxidized species decompose into, that would not be detected and therefore not contribute to the measured O/C ratio? Is this statement alluding to CO<sub>2</sub> production?

Response: We apologize for the confusion. Lines 334-335 are based on an earlier work on photo-oxidation of phenolic carbonyls in ammonium nitrate (AN) and ammonium sulfate solutions using a time-of-flight aerosol mass spectrometer (AMS) and therefore involved the aerosolization of samples before analysis (Huang et al., 2018). In that study, highly oxidized species such as small carboxylic acids with O:C =1 (e.g., acetic acid) possibly formed but may have evaporated during aerosolization as they are too volatile. As a result, these species cannot be detected by the AMS. Solutions with AN had a higher concentration of organic acids (without atomization) in the aqueous samples compared to ammonium sulfate solutions, ascribable to nitrate photolytic products promoting the reactions. In brief, the study by Huang et al. (2018) suggested that AN promoted the formation of oxygenated and oxidized products.

As mentioned in lines 340-342, AN generally increased the average  $OS_c$  values for both GUA+DMB and GUA+VL, indicating the formation of more oxidized products, similar to the findings by Huang et al. (2018). In this work, AN also possibly promoted the formation of oxygenated products. The lower average O:C for GUA+DMB+AN and GUA+VL+AN than those in the absence of AN could be due to the formation of N-heterocycles, altering the elemental ratios.

The corresponding revisions in the text are as follows:

Line 334: The  $\langle O:C \rangle$  for GUA+DMB+AN and GUA+VL+AN were lower than those in the absence of AN (Table 1), ~~likely due to the rapid formation of highly oxidized species followed by their decomposition (Huang et al., 2018)~~ possibly due to the formation of N-heterocycles, altering the elemental ratios.

Line 340: Nonetheless, AN generally increased the  $\langle OS_c \rangle$  for both GUA+DMB and GUA+VL, with a more noticeable increase for the former, suggesting more oxidized products. Similarly, in a previous work, the more oxygenated and oxidized aqSOA from the photo-oxidation of phenolic carbonyls in AN solutions than in ammonium sulfate solutions has been ascribed to nitrate photolytic products promoting the reactions (Huang et al., 2018).

3. Figure 3: at the top right, C12 and C11 products are referred to as functionalized monomers. How is this different from a ring-opened dimer? How exactly do the authors distinguish functionalization from dimerization?

Response: The dimers in this work have minimum carbon atoms of 12 for 2 benzene rings, and considering demethylation of both  $-OCH_3$  groups of typical guaiacol dimer ( $C_{14}H_{14}O_4$ ; #1 to  $C_{12}H_{10}O_4$ ; #17; Table S1). The C12 and C11 products in Figure 3 were referred to as functionalized monomers and not ring-opened dimers as the substituents (other than  $-OH$  and  $-OCH_3$ ) in these products have carbon atoms  $<6$  which were not enough to form another aromatic ring. These substituents were more likely to be highly oxygenated small species (carbon atoms  $<6$ ) from oxidation and fragmentation reactions which have also been reported in previous studies on similar reaction systems (e.g., Yu et al., 2014, 2016).

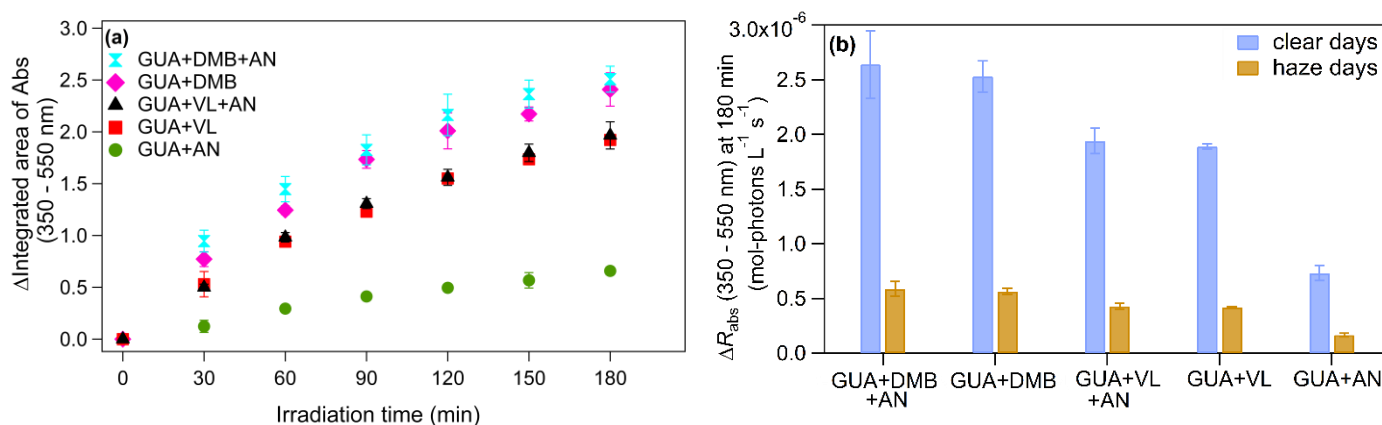
Functionalization involves the addition of polar oxygenated functional groups (e.g., hydroxyl, carbonyl, carboxyl etc.) as well as highly oxygenated small species (carbon atoms  $<6$ ) from oxidation and fragmentation reactions to the aromatic ring. Dimerization is characterized by two covalently bound units of the aromatic compounds studied.

4. Figure 4: In this graph, does 1 or zero = no change in integrated absorbance? In other words, is it normalized somehow?

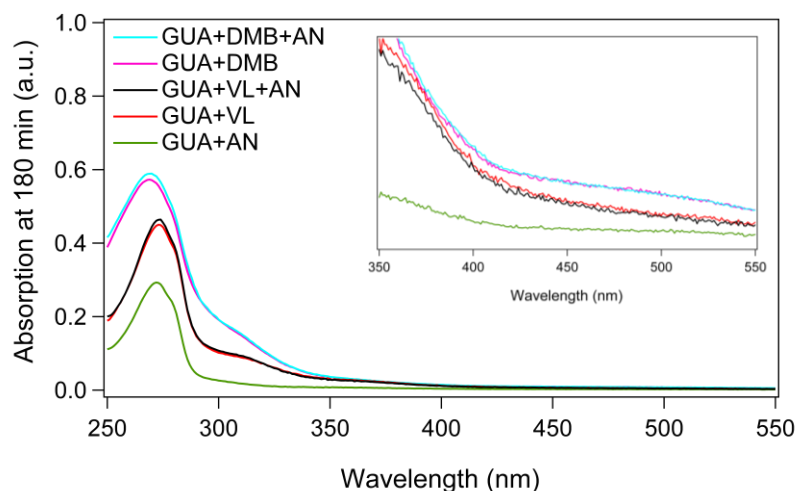
Response: In the original Figure 4, a value of zero means that at 180 min, there was no change in the integrated area of absorbance from 350 to 550 nm compared to 0 min (before irradiation). The integrated area of absorbance from 350 to 550 nm at 180 min was normalized by subtracting the corresponding values at 0 min (before irradiation). For all experiments in this work, we measured the absorbance every 30 min from 0 to 180 min and observed an increase in visible light absorption from 350 to 550 nm.

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 ( $\Delta R_{\text{abs}}$ ) 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 reaction system 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 ( $\Delta R_{\text{abs}}$ ) 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 ( $\Delta R_{\text{abs}}$ ) (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  $\Delta R_{\text{abs}}$  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  $\Delta R_{\text{abs}}$  for both GUA+DMB+AN and GUA+VL+AN (Fig. 4).

Technical corrections

1. Line (1)94: “represent” should be “characterize”

Response: Thank you for the correction. “represent” has been replaced by “characterize”

2. Line 328: should this say “likely has a furanone group”? Otherwise, how do the authors know this is the correct structure from the many possibilities?

Response: The Reviewer is correct. The text has been revised accordingly.

### References for responses to Reviewer 3:

Felber, T., Schaefer, T., He, L., and Herrmann, H.: Aromatic carbonyl and nitro compounds as photosensitizers and their photophysical properties in the tropospheric aqueous phase, *J. Phys. Chem. A*, 125, 5078–5095, <https://doi.org/10.1021/acs.jpca.1c03503>, 2021.

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.: Aqueous benzene-diols react with an organic triplet excited state and hydroxyl radical to form secondary organic aerosol, *Phys. Chem. Chem. Phys.*, 17, 10227–10237, <https://doi.org/10.1039/C4CP06095D>, 2015.

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>.