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 1

This study analyzes the characteristic of the DMB and VL as photosensitizers reacting with GUA for aqSOA formation, including kinetic analysis, product distributions and chemical characteristics, as well as optical properties. Meanwhile, the effect of AN for aqSOA formation was analyzed. In general, the paper is well written and conclusions are convincing in terms of rational and rigorous experimental design and analyses. I just have several minor comments on it.

1. In terms of abundance of products, for GUA+DMB, the abundance of products in the presence of AN is less than that in the absence of AN, however, for GUA+VL, the results are the opposite. Please elaborate.

Response: It is very common to compare the relative abundance of products based on peak areas from mass spectrometry (MS) results (e.g., Lee et al., 2014; Romonosky et al., 2017; Wang et al., 2017; Fleming et al., 2018; Song et al., 2018; Klodt et al., 2019; Ning et al., 2019) to show the relative importance of different types of compounds (K. Wang et al., 2021). However, comparisons of relative abundance among different compounds can be subject to uncertainties as ionization efficiencies in soft ionization, such as ESI, may significantly vary between different compounds (Kebarle, 2000; Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Kruve et al., 2014). **In our previous work (Mabato et al., 2022), we introduced the normalized abundance of products ([P], unitless).** The calculation assumes equal ionization efficiencies of different compounds, which is commonly used for estimation of O:C ratios of SOA (e.g., Bateman et al., 2012; Lin et al., 2012; Laskin et al., 2014; De Haan et al., 2019). **This allows us to have a better comparison with the literature results.** It is therefore emphasized that the normalized abundance of products is a semi-quantitative analysis of the detected products under different experimental conditions, instead of absolute concentrations of them.

Moreover, as stated in the footnote of Table 1, the normalized abundance of products was calculated using only the positive ion mode data as the GUA signal from the negative ion mode was weak and thus may present large uncertainties during normalization. Therefore, products that may not give signals or may have weak signals in the positive ion mode were possibly underestimated in the normalized product abundance. The contrasting trends of the normalized abundance of products for GUA+DMB and GUA+VL in the absence and presence of AN may therefore be related to the differences in the ionization efficiencies of the products formed. Nevertheless, the much higher normalized abundance of products for

GUA+DMB vs. GUA+VL is consistent with the other more quantitative measurements in this work (i.e., faster GUA decay and stronger light absorption by reaction products in GUA+DMB vs. in GUA+VL).

Sect. 2.2 has been revised to give more information about the normalized abundance of products as follows:

Section 2.2 Calculation of ~~the~~ normalized abundance of products

Several recent studies have used comparisons of relative abundance of products based on peak areas from mass spectrometry (MS) results (e.g., Lee et al., 2014; Romonosky et al., 2017; Wang et al., 2017; Fleming et al., 2018; Song et al., 2018; Klodt et al., 2019; Ning et al., 2019) to show the relative importance of different types of compounds (K. Wang et al., 2021). However, comparisons of relative abundance among different compounds can be subject to uncertainties as ionization efficiencies in soft ionization, such as ESI, may significantly vary between different compounds (Kebarle, 2000; Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Kruve et al., 2014). ~~The normalized abundance of products ([P], unitless) was introduced in our previous work (Mabato et al., 2022).~~ In our previous work (Mabato et al., 2022), we introduced the normalized abundance of products ([P], unitless) (Eq. 2) as ~~Nevertheless, it is~~ a semi-quantitative analysis that gives an overview of how the signal intensities changed under different experimental conditions but not the quantification of the absolute product concentration. ~~Briefly,~~ The calculation assumes equal ionization efficiencies of different compounds, which is commonly used to estimate O:C ratios of SOA (Bateman et al., 2012; Lin et al., 2012; Laskin et al., 2014; De Haan et al., 2019) ~~was assumed for the calculation~~:

$$[\mathrm{P}] = \frac{\mathrm{A}_{P,t}}{\mathrm{A}_{GUA,t}} \cdot \frac{[\mathrm{GUA}]_t}{[\mathrm{GUA}]_0} \qquad \text{(Eq. 2)}$$

where $A_{P,t,}$ and $A_{GUA,t}$ are the extracted ion chromatogram (EIC) peak areas of the product P and GUA from UHPLC-HESI-Orbitrap-MS analyses at time *t*, respectively; $[GUA]_t$ and $[GUA]_0$ are the GUA concentrations (μM) determined using UHPLC-PDA at time *t* and 0, respectively. Note that the normalized abundance of products has intrinsic uncertainties due to the variability in ionization efficiencies for various compounds. Moreover, it should be noted that the normalized abundance of products was calculated using only the positive ion mode data as the GUA signal from the negative ion mode was weak and thus may present large uncertainties during normalization. Therefore, products that may not give signals or may have weak signals in the positive ion mode were possibly underestimated in the normalized product abundance. Nevertheless, it enables the comparison of MS results among different experiments. As demonstrated in our previous work (Mabato et al., 2022) and the current study, a higher normalized abundance of products generally correlates with higher efficiency of oxidation. The reported uncertainties were propagated from the changes in [GUA] measured using UHPLC-PDA and the MS signal intensities.

2. For Fig.4, why choose an absorbance wavelength of 180 min for the study? What is the change of absorbance during the whole reaction process, and is the effect of AN obvious on the change of absorbance?

Response: We apologize for the confusion. In Figure 4, the absorbance enhancement was based on the integrated area of absorbance from 350 to 550 nm, and 180 min refers to the total irradiation time. An irradiation time of 180 min was chosen for this study as it was sufficient to show the differences in the extent of the 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. 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. This information has been added to the discussion of 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.

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. As mentioned in lines 353-358, the effect of AN was not evident on the absorbance enhancement. For GUA+DMB+AN, the N-containing products may have offset the decrease in oligomers to maintain the absorbance enhancement noted from GUA+DMB. For GUA+VL+AN, the decrease in monomers may have counteracted the increased oligomers and the generated N-containing products.

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:

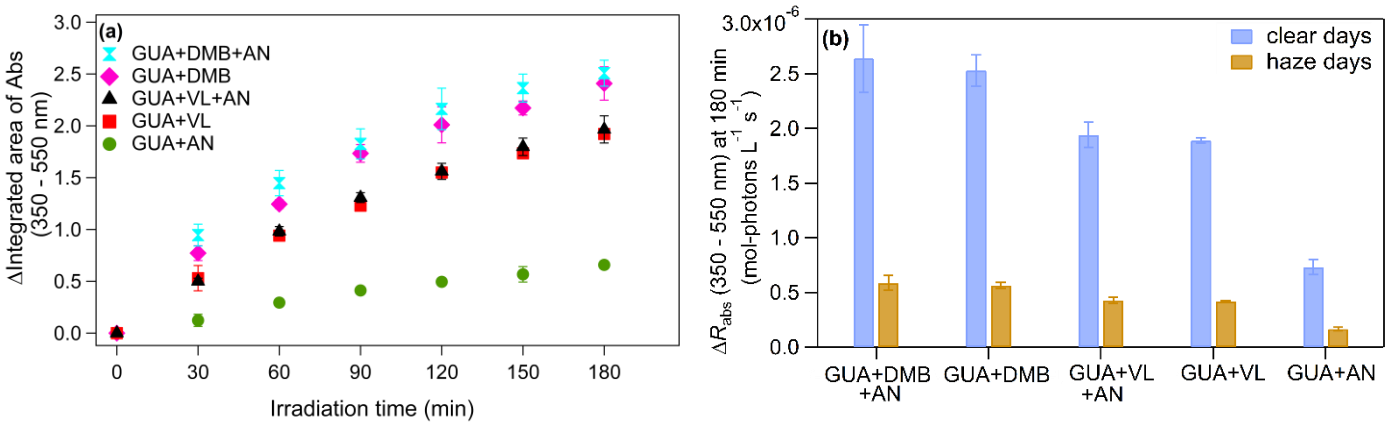

Figure 4. (a) Increase in light absorption throughout 180 min of irradiation for all reaction systems studied and (b) Change in the rate of sunlight absorption (ΔR_{abs}) from 350-550 nm at 180 min during typical clear and haze days in Beijing, China for aqSOA from GUA+DMB+AN, GUA+DMB, GUA+VL+AN, GUA+VL,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

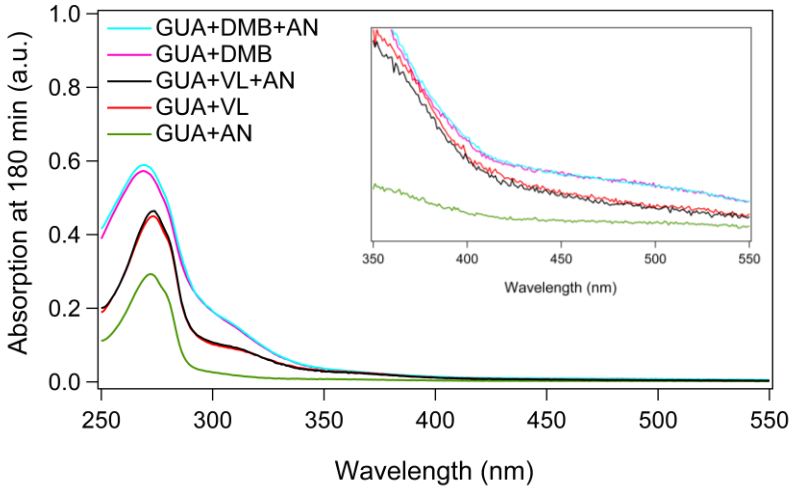

Figure S7. UV-Vis absorption spectra of GUA+DMB+AN, GUA+DMB, GUA+VL+AN, GUA+VL, and GUA+AN after 180 min of irradiation. The inset is the expanded view from 350 to 550 nm.

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).

3. (a) Why the entire reaction time of this study was 180 minutes, and (b) did the precursors get reacted completely?

Response: (a) As mentioned in our response to question #2, 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. To clarify this in the text, the discussion of product distributions has been amended, as shown in the response to question #2.

(b) No, GUA and the photosensitizers were not fully consumed within the 180 min irradiation. The estimated fraction of GUA and the photosensitizers that remained after irradiation were as follows:

Reaction conditions	**Estimated fraction of GUA and the photosensitizers that remained after 180 min of irradiation**
GUA+AN	84% GUA
GUA+DMB	39% GUA and 89% DMB
GUA+DMB+AN	40% GUA and 89% DMB
GUA+VL	79% GUA and 46% VL
GUA+VL+AN	78% GUA and 47% VL

References for responses to Reviewer 1:

Bateman, A. P., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Applications of high-resolution electrospray ionization mass spectrometry to measurements of average oxygen to carbon ratios in secondary organic aerosols, Environ. Sci. Technol., 46, 8315–8324, https://doi.org/10.1021/es3017254, 2012.

De Haan, D.O., Pajunoja, A., Hawkins, L. N., Welsh, H.G., Jimenez, N. G., De Loera, A., Zauscher, M., Andretta, A. D., Joyce, B. W., De Haan, A. C., Riva, M., Cui, T., Surratt, J. D., Cazaunau, M., Formenti, P., Gratien, A., Pangui, E., and Doussin, J-F.: Methylamine's effects

on methylglyoxal-containing aerosol: chemical, physical, and optical changes, ACS Earth Space Chem., 3, 1706–1716, https://doi.org/10.1021/acsearthspacechem.9b00103, 2019.

Fleming, L. T., Lin, P., Laskin, A., Laskin, J., Weltman, R., Edwards, R. D., Arora, N. K., Yadav, A., Meinardi, S., Blake, D. R., Pillarisetti, A., Smith, K. R., and Nizkorodov, S. A.: Molecular composition of particulate matter emissions from dung and brushwood burning household cookstoves in Haryana, India, Atmos. Chem. Phys., 18, 2461–2480, https://doi.org/10.5194/acp-18-2461-2018, 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.

Laskin, J., Laskin, A., Nizkorodov, S. A., Roach, P., Eckert, P., Gilles, M. K., Wang, B., Lee, H. J., and Hu, Q.: Molecular selectivity of brown carbon chromophores, Environ. Sci. Technol., 48, 12047–12055, https://doi.org/10.1021/es503432r, 2014.

Lee, H. J., Aiona, P. K., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Effect of solar radiation on the optical properties and molecular composition of laboratory proxies of atmospheric brown carbon, Environ. Sci. Technol., 48, 10217–10226, https://doi.org/10.1021/es502515r, 2014.

Leito, I., Herodes, K., Huopolainen, M., Virro, K., Künnapas, A., Kruve, A., and Tanner, R.: Towards the electrospray ionization mass spectrometry ionization efficiency scale of organic compounds, Rapid Commun. Mass Sp., 22, 379–384, https://doi.org/10.1002/rcm.3371, 2008.

Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: a study by ultra-high-resolution mass spectrometry, Environ. Sci. Technol., 46, 13118–13127, https://doi.org/10.1021/es303570v, 2012.

Kebarle, P. A.: A brief overview of the mechanisms involved in electrospray mass spectrometry, J. Mass Spectrom., 35, 804−817, https://doi.org/10.1002/9783527628728.ch1, 2000.

Klodt, A.L., Romonosky, D.E., Lin, P., Laskin, J., Laskin, A., and Nizkorodov, S.A.: Aqueous photochemistry of secondary organic aerosol of α-pinene and α-humulene in the presence of hydrogen peroxide or inorganic salts, ACS Earth Space Chem., 3, 12, 2736–2746, https://doi.org/10.1021/acsearthspacechem.9b00222, 2019.

Kruve, A., Kaupmees, K., Liigand, J., and Leito, I.: Negative electrospray ionization via deprotonation: predicting the ionization efficiency, Anal. Chem., 86, 4822–4830, https://doi.org/10.1021/ac404066v, 2014.

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.

Ning, C., Gao, Y., Zhang, H., Yu, H., Wang, L., Geng, N., Cao, R., and Chen, J.: Molecular characterization of dissolved organic matters in winter atmospheric fine particulate matters (PM2.5) from a coastal city of northeast China, Sci. Total Environ., 689, 312–321, https://doi.org/10.1016/j.scitotenv.2019.06.418, 2019.

Perry, R. H., Cooks, R. G., and Noll, R. J.: Orbitrap mass spectrometry: instrumentation, ion motion and applications, Mass Spectrom. Rev., 27, 661–699, https://doi.org/10.1002/mas.20186, 2008.

Romonosky, D. E., Li, Y., Shiraiwa, M., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Aqueous photochemistry of secondary organic aerosol of α-Pinene and α-Humulene oxidized with ozone, hydroxyl radical, and nitrate radical, J. Phys. Chem. A, 121, 1298–1309, https://doi.org/10.1021/acs.jpca.6b10900, 2017.

Schmidt, A-C., Herzschuh, R., Matysik, F-M., and Engewald, W.: Investigation of the ionisation and fragmentation behaviour of different nitroaromatic compounds occurring as polar metabolites of explosives using electrospray ionisation tandem mass spectrometry, Rapid Commun. Mass Sp., 20, 2293–2302, https://doi.org/10.1002/rcm.2591, 2006.

Song, J., Li, M., Jiang, B., Wei, S., Fan, X., and Peng, P.: Molecular characterization of water-soluble humic like substances in smoke particles emitted from combustion of biomass materials and coal using ultrahigh-resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Environ. Sci. Technol., 52, 2575–2585, https://doi.org/10.1021/acs.est.7b06126, 2018.

Wang, K., Huang, R-J., Brüggemann, M., Zhang, Y., Yang, L., Ni, H., Guo, J., Wang, M., Han, J., Bilde, M., Glasius, M., and Hoffmann, T.: Urban organic aerosol composition in eastern China differs from north to south: molecular insight from a liquid chromatography–mass spectrometry (Orbitrap) study, Atmos. Chem. Phys., 21, 9089–9104, https://doi.org/10.5194/acp-21-9089-2021, 2021.

Wang, X., Hayeck, N., Brüggemann, M., Yao, L., Chen, H., Zhang, C., Emmelin, C., Chen, J., George, C., and Wang, L.: Chemical characterization of organic aerosols in Shanghai: A study by ultrahigh-performance liquid chromatography coupled with orbitrap mass spectrometry, J. Geophys. Res. Atmos., 122, 11703–11722, https://doi.org/10.1002/2017JD026930, 2017.

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.