

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 4

Mabato and co-authors studied the aqueous photochemical reactions of guaiacol (GUA), a methoxyphenol from wood burning, in the presence of vanillin (VL; a phenolic carbonyl), dimethoxybenzaldehyde (DMB; a non-phenolic carbonyl), and/or ammonium nitrate (AN). They examined photochemistry in five different reaction solutions: (1) GUA + AN, (2) GUA + DMB, (3) GUA + DMB + AN, (4) GUA + VL, and (5) GUA + VL + AN. For each system, they give the kinetics of loss, information about the products formed, and some very cursory information about light absorption from the resulting reaction mixture.

There are a few interesting pieces in the manuscript, most notably the suggested interaction of AN photoproducts with triplet photoproducts, which I wish the authors had explored more. But, otherwise, the research seems to largely repeat ideas and experiments that have been reported previously. I don't see new, interesting questions that are driving the current work. In addition, I see several other important weaknesses, as described below.

Response: Thank you for the comprehensive review. In this work, our focuses were 1) to compare aqSOA formation from photosensitization by non-phenolic and phenolic methoxybenzaldehydes as photosensitizers using GUA as the dominant aqSOA precursor and 2) to examine the effects of AN on these reactions. Biomass burning smoke has been reported to have comparable concentrations of phenolic and non-phenolic carbonyls (Simoneit et al., 1993; Anastasio et al., 1997), and certain phenolic carbonyls including VL, have been shown to be capable of photosensitization, contributing to aqSOA formation (Smith et al., 2016; Mabato et al., 2022). However, compared to DMB (a non-phenolic carbonyl), the most commonly used photosensitizer in related studies, aqSOA formation using phenolic carbonyls as photosensitizers is less understood. DMB and VL were chosen to represent non-phenolic and phenolic methoxybenzaldehydes photosensitizers because (1) their structures differ only by one functional group ($-\text{OCH}_3$ for the former and $-\text{OH}$ for the latter), (2) they are both abundant in biomass burning emissions, and (3) there is available information on their photophysical properties (e.g., quantum yield of $^3\text{C}^*$ formation and $^3\text{C}^*$ lifetime) (Felber et al., 2021). Moreover, aromatic carbonyls and phenols may coexist with AN in biomass burning aerosols. However, aqSOA formation studies have investigated either photosensitization or nitrate-mediated photo-oxidation, even though these reactions can occur simultaneously. In general, studies on the effects of inorganic nitrate on aqSOA formation remain very limited. We believe that this work is one of the very few in the literature that examines this complex system. The Reviewer has given us a lot of valuable comments highlighting the complexity of the photosensitization reactions when even just a photosensitizer and a non-

phenolic carbonyl are involved in the reactions, let alone the addition of AN in the system. **It is understood that much more work needs to be done to fully unravel the interactions of photosensitization and nitrate photolysis.** We hope this work can **stimulate researchers to look into these important but rarely explored interactions in the photochemistry of aerosols.** Further information on the novelty of this work is given in the response to major comment #1.

Major Comments

1. It is not clear what is novel enough about this work that it deserves to be published in ACP. (a) A number of the systems or parts of the manuscript have been reported previously, both by this group and other groups. For example, Mabato et al. (2022) reported results for GUA + VL, while Smith et al. and Yu et al. reported results for GUA + DMB and for another phenol (SYR) with VL. (b) The addition of ammonium nitrate in the manuscript has no significant impact on kinetics or normalized product amounts, but does lead to incorporation of N into the aqSOA, a point made for VL + AN by Mabato et al. (2022) and for general carbonyl + ammonium systems by several past authors. (c) One result is that there is significant repetition of past work. Some examples: (1) the first two paragraphs on page 8 largely repeat what has been shown in previous work, (2) there's nothing new in Figure 1, as all of these molar absorptivities have been shown by previous groups, and (3) most of the pieces of Figure 3 have been shown in Mabato et al. (2022) or in past work by the Zhang group.

Response: (a) The Reviewer is correct that GUA+DMB and GUA+VL have been explored in earlier studies. Our previous study (Mabato et al., ACP, 2022) focused on aqSOA formation from the direct photosensitized oxidation of VL. GUA+VL in that study was compared with direct GUA photodegradation. We discussed the decay kinetics of both VL and GUA, absorbance changes, and a few detected products **but not product distribution.** Smith et al. (2014) and Yu et al. (2014, 2016) provided valuable information on GUA+DMB, focusing on the decay kinetics of GUA, aqSOA mass yields, product characterization, photochemical evolution of aqSOA, and aqSOA formation pathways. For VL+syringol, SYR (another non-carbonyl phenol), Smith et al. (2016) reported VL and SYR decay kinetics and absorbance changes. **However, as stated in the original manuscript, our previous experiments were performed at a higher concentration of VL (0.1 mM) compared to DMB concentration (0.005 to 0.01 mM) used by Smith et al. (2014) and Yu et al. (2014, 2016).** Moreover, different instruments were used to characterize the products in these earlier works. Thus, direct comparisons between GUA+DMB and GUA+VL based on atmospherically relevant conditions cannot be made using the above studies. **This paper is the first, to the best of our knowledge, to make such comparisons at the same concentration range with the same analytical techniques systematically.**

Moreover, previous aqSOA formation studies involving aromatic carbonyls and non-carbonyl phenols have examined either photosensitization or nitrate-mediated photo-oxidation **separately, even though these reactions can occur simultaneously.** In general, aqSOA formation **studies on multicomponent reaction systems** where inorganic and organic species are present **remain limited.** **In the current work, we attempted to address this gap by introducing AN, a common aerosol component** that is also abundant in cloud and fog waters, **into the reaction systems studied.**

We would like to emphasize that the novelty of the current work includes: 1) a thorough comparison of aqSOA formation from photosensitization by non-phenolic and phenolic methoxybenzaldehydes as photosensitizers using GUA as the dominant aqSOA precursor based on GUA and photosensitizers decay kinetics, detected products, and absorbance enhancement and 2) the examination of the effects of AN on these reactions. Despite some similar findings with earlier studies, our results offer new insights into the reaction systems examined. For instance, our results demonstrate that **the structural features of photosensitizers affect aqSOA formation** via GUA (non-carbonyl phenol) oxidation. Moreover, we found that **photosensitization by non-phenolic and phenolic methoxybenzaldehydes may be differently influenced by AN photolysis**. For example, compared to GUA+VL, the more extensive fragmentation in GUA+DMB likely resulted in a higher contribution of ring-opening products. These ring-opening species reacted with ammonia resulting in higher contributions of N-heterocycles and N-oligomers and yielding an overall higher contribution of N-containing products in GUA+DMB+AN than in GUA+VL+AN. The increase in oligomers in GUA+VL+AN could be due to the generation of phenoxy radicals from VL via H-atom abstraction by $\cdot\text{OH}$ or $\cdot\text{NO}_2$ from nitrate photolysis. Furthermore, our results suggest that **photosensitization may promote reactions by nitrate photolysis**. In particular, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ (secondary oxidants from $^3\text{DMB}^*$ or $^3\text{VL}^*$) can react with NO_2^- from nitrate photolysis to increase the formation of $\cdot\text{NO}_2$ (Pang et al., 2019; Mabato et al., 2022).

(b) The Reviewer is right that the formation of N-heterocycles which indicates the participation of ammonium in the reactions has also been reported in our previous experiments on VL+AN (Mabato et al., 2022) and for smaller carbonyls + ammonium systems in several past works (e.g., De Haan et al., 2009; Galloway et al., 2009; Nozière et al., 2009; Shapiro et al., 2009; Yu et al., 2011; Kampf et al., 2012; Gen et al., 2018; Mabato et al., 2019). **However, our present study also demonstrated that photosensitized aqSOA formation involving non-phenolic and phenolic methoxybenzaldehydes as photosensitizers may be differently influenced by AN photolysis**. In addition, we also found that **photosensitized reactions may promote nitrate-mediated photolytic reactions**. Overall, our conclusions provide a clear path forward for further work on other types of photosensitizers for aqSOA formation, which to date is **limited mainly to DMB, and indicate a potential interplay between photosensitized reactions and AN photolysis, beyond the formation of nitrated compounds**. We also revised the abstract to further highlight the novelty of the work, as shown below:

Abstract:

Aromatic carbonyls (e.g., methoxybenzaldehydes), an important class of photosensitizers, are abundant in the atmosphere. **Photosensitization and nitrate-mediated photo-oxidation can occur simultaneously, yet studies about their interactions, particularly for aqueous secondary organic aerosol (aqSOA) formation, remain limited**. This study compared non-phenolic (3,4-dimethoxybenzaldehyde, DMB) and phenolic (vanillin, VL) methoxybenzaldehydes as photosensitizers for ~~aqueous secondary organic aerosol (aqSOA)~~ aqSOA formation via guaiacol (GUA) oxidation **in the absence and presence of ammonium nitrate (AN)** under atmospherically relevant cloud and fog conditions...

(c) We thank the Reviewer for highlighting these three areas that contain a lot of information based on the literature. However, they mainly **provide background for the readers to follow the results and discussions**. We are unsure if they are the best examples for evaluating the novelty of this paper.

(1) The first 2 paragraphs on page 8 compare **the major products, average elemental ratios, and elemental distributions of products** from GUA+DMB and GUA+VL. In addition, we **discussed how this information relates to the differences in the product distributions, which are not available in previous works**.

(2) Aside from showing molar absorptivities, Figure 1 provides the structures of the compounds studied in this work, the photon flux in the photoreactor, and photon fluxes on clear or haze days. **This figure is meant to provide sufficient background information for readers. It is not a “result” figure.**

(3) The related figure by Yu et al. (2014) shows the **main pathways of aqSOA formation via photosensitized oxidation of non-carbonyl phenols by $^3\text{DMB}^*$ only**. Also, the related figure in our previous work (Mabato et al., 2022) shows the potential aqSOA formation pathways for the direct photosensitized oxidation of VL and VL+AN. **The comparisons about N-containing products in that work pertained to pH effects, not photosensitizers**. In addition, the aqSOA precursor (and photosensitizer) in that study is VL, whereas here, it is GUA. Figure 3 illustrates the **differences between GUA oxidation by $^3\text{DMB}^*$ and $^3\text{VL}^*$ in the absence and presence of AN, highlighting the major products detected in this work. The comparisons are based on the product distributions which have not been reported for GUA+VL. Moreover, the effects of AN on the product distributions of aqSOA from photosensitized reactions have not been examined previously.**

2. The results aren't quantitative in a way that they could be used to model aqSOA formation from $^3\text{VL}^*$. For example, the rate constants for decay of GUA given in Table 1 are probably specific for the experimental conditions used here. The same is true for the quantum yields given in the text - these are almost certainly a function of GUA concentration. It would be much more useful to measure fundamental quantities (e.g., second-order rate constants for $^3\text{VL}^* + \text{GUA}$) that can be used across a wide range of conditions. Can the current set of data be used to determine some fundamental quantities that are widely applicable? If not, how will people use these data to quantitatively understand these reaction systems?

Response: Agreed. Having said that, we believe this is a common limitation of laboratory kinetic studies in complex chemical systems. While there are some studies (e.g., Smith et al., 2015) citing various kinetic parameters on photosensitization based on selected experimental studies, we are unsure if there are kinetic parameters that are **proven universal** in photosensitization studies. Moreover, it should be noted that in this work, we mainly focused on the analyses of the reaction products and product distributions. 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.

We agree with the Reviewer that the apparent quantum efficiency of GUA photodegradation in the presence of DMB and likely VL as well is dependent on GUA concentration based on an earlier work (Anastasio et al., 1997). Regardless, this information would still be useful for comparison with GUA oxidation by other oxidants or photosensitizers.

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.

Line 192: 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.

3. (a) I don't see the utility of [P], the normalized product abundance. In the big picture, what does [P] indicate about a certain reaction system and what do differences in [P] between reaction systems indicate? (b) The authors present it as an equation without any in-depth discussion of its strengths and weaknesses. Since $[GUA]_t/[GUA]_0$ is the inverse of the fraction of initial GUA that is present at time t, Equation 2 for [P] could be simplified as $A(P,t)/A(GUA,0)$. Thus [P] depends on at least three variables: (1) the extent of reaction, since $A(P,t)$ probably rises initially and later falls, (2) the fraction of products that give a signal in the HPLC-Orbitrap (e.g., small organic acids probably do not), and (3) the ionization efficiency of each product in the Orbitrap. These issues need to be described in the manuscript; as part of this, the authors should say something about the IE values for the different classes of products that they see. (c) [P] also depends on what is used to normalize peak areas, e.g., VL in Mabato et al. (2022) and GUA here (making it very difficult to compare across the papers), and probably the initial concentration of the normalizing species. Given all of these variables, what do we learn from the Table 1 data of [P] after 180 min of illumination? If they authors

want to use [P] to describe products, they need to state what they think this parameter indicates, give us some experimental evidence that it's useful, and say something about its strengths and weaknesses. As it currently stands, the reported values of [P] seem to have no real utility.

Response: (a) The normalized abundance of products in this work is a semi-quantitative analysis intended to provide an overview of how the mass spectrometry (MS) signal intensities varied under different experimental conditions, but it does not quantify the absolute concentration of products from reaction systems. As demonstrated in our previous work (Mabato et al., 2022) and the current study, a higher normalized abundance of products correlates with higher efficiency of oxidation.

(b) Thank you for the suggestion. In this work and in our previous study (Mabato et al., 2022), we measured the absolute concentration changes of the precursor and photosensitizers using UHPLC-PDA. As we already have this quantitative data and given that it is a direct quantification of GUA concentration, we included the GUA concentration changes measured using UHPLC-PDA in the calculation of normalized product abundance to lessen its overall uncertainties. The simplification of the equation suggested by the Reviewer would yield the same trends in the original manuscript and would not change the conclusions. Therefore, we would like to retain the equation and the values presented in the original manuscript.

(1) We agree with the Reviewer that the [P] would depend on the extent of the reaction. However, in this work, the same irradiation time (180 min) was applied to all experiments as we were trying to compare the product distributions after a certain time of light photosensitization. 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. Moreover, our analysis of product distribution was focused only on aqSOA generated after 180 min of irradiation.

This has been clarified in the text 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 ~~S12~~ and ~~S23~~. **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.**

(2) We agree with the Reviewer that certain products may not give signals (or may have weak signals) in the UHPLC-Orbitrap. We mentioned in the discussion of product distributions that the products detected using UHPLC-HESI-Orbitrap-MS were used to characterize the aqSOA formed in this work (line 194). 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. For example, small organic acids are more likely to be detected in the negative ion mode as this mode is more sensitive to deprotonatable compounds (Ho et al., 2003).

To clarify this, the following has been added to the description of normalized abundance of products (Sect 2.2):

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.

(3) It is very common to compare the relative abundance of products based on peak areas from 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 (Kearle, 2000; Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Krueve 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 the 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. As stated in the footnote of Table 1, the uncertainties were propagated from the changes in [GUA] measured using UHPLC-PDA and the MS signal intensities.

Unfortunately, there is limited availability of measured relative ionization efficiencies (RIE) for different compounds in the literature. We are in no position to provide the RIE values for the detected products. While ESI ionization is not ideal for quantification analysis of products, Nguyen et al. (2013) (<https://doi.org/10.1039/C2AY25682G>) demonstrated a positive correlation between ESI signal and “adjusted mass” (= molecular mass × H:C). According to that study, the uncertainty would be a factor of 2 – 4 if only the “adjusted mass” is considered, and further complications of matrix effect and polarity are ignored. **However, what we compared is not the absolute concentrations (or contributions) of the detected products. The comparison was based on how the signal intensities (as normalized in Eq. 2) varied under different experimental conditions so that the responses of the same class of products**

(e.g., monomers, dimers, etc.) could be compared as the conditions varied. The ionization efficiency might not be very different within the same class according to the “adjusted mass” concept by Nguyen et al. (2013). We hope that the above discussion has addressed the Reviewer’s question.

(c) In this work, GUA was used to normalize the product peak areas as it is found in all samples, enabling comparisons among different experiments. In our previous study (Mabato et al., 2022), VL was used as it was both the dominant aqSOA precursor and the photosensitizer. Although the normalized abundance of products has inherent uncertainties due to the variability in ionization efficiencies for different compounds, **it can be used as a semi-quantitative analysis of the detected products that provides an overview of how the MS signal intensities varied under different experimental conditions.** 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. For instance, in our earlier study on the direct photosensitized oxidation of VL (Mabato et al., 2022), we found higher VL decay rate constants and higher normalized abundance of products under air-saturated conditions vs. nitrogen-saturated conditions. In this study, a higher GUA decay rate constant and higher normalized abundance of products was noted for GUA+DMB vs. GUA+VL.

Based on the responses above, Sect. 2.2 has been amended 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 (Kearle, 2000; Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Krueve 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:~~

$$[P] = \frac{A_{P,t}}{A_{GUA,t}} \cdot \frac{[GUA]_t}{[GUA]_0} \quad (\text{Eq. 2})$$

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.

4. In each of the five systems, products were measured after 180 min of illumination. But this approach ignores the fact that the systems have different reactivities and so a fixed time of analysis is looking at different generations of products in the different systems (as shown by Yu et al.). This is important because the relative amounts of products are a function of oxidation time in any given solution. So it is difficult to meaningfully compare across different solutions unless the GUA fraction reacted is very similar. This is further complicated by the much faster decay of VL compared to DMB.

Response: The Reviewer raised a good point. However, in this work, the same irradiation time was applied to all experiments as we were trying to evaluate the product distributions after a certain time of photosensitization. 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. It is true that 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. The corresponding changes in the text (lines 194-197) are shown in our response to major comment #3.

5. The presentation of light absorption data for the reaction products is insufficient. There is one figure (Fig. 4) that sums absorbance values across 350 – 550 nm. This is interesting in that it shows the presence of ammonium nitrate doesn't affect overall absorbance, but this is too coarse a tool to describe the brown carbon products by itself. It would be helpful to show spectra for each solution at 180 min in the supplement. Also, Fig. 4 should be improved by weighting each absorbance spectrum by the spectral actinic flux to properly describe light absorption. This could also be done by calculating the rate of sunlight absorption by each aqSOA for some standard sunlight condition. This matters because the number of solar photons increases enormously from 350 to 550 nm.

Response: Thank you for the suggestions. The absorption spectra after 180 min of irradiation for each reaction system have been added to the supplement (Figure S7) as shown below:

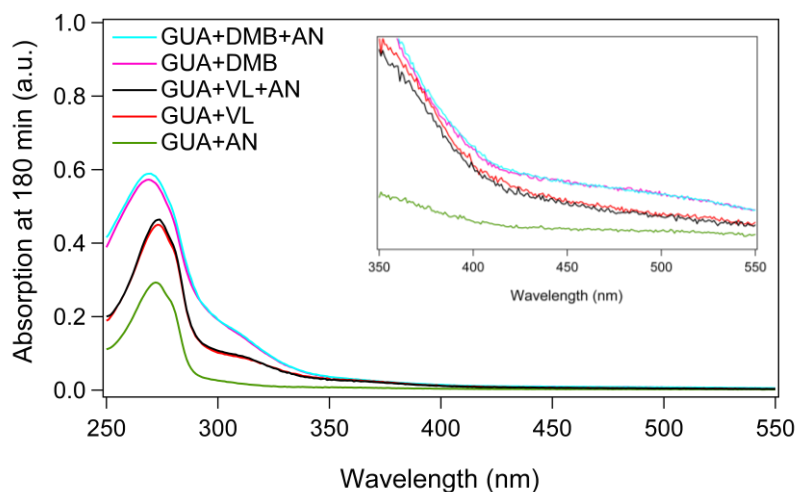


Figure S7. UV-Vis absorption spectra of GUA+DMB+AN, GUA+DMB, GUA+VL+AN, GUA+VL, and GUA+AN after 180 min of irradiation. The inset is the expanded view from 350 to 550 nm.

Moreover, the absorbance enhancement from 0 to 180 min for all reaction systems studied have been added to Figure 4(a), based on suggestions from Reviewers 1 and 2. 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. The updated Figure 4 is shown below:

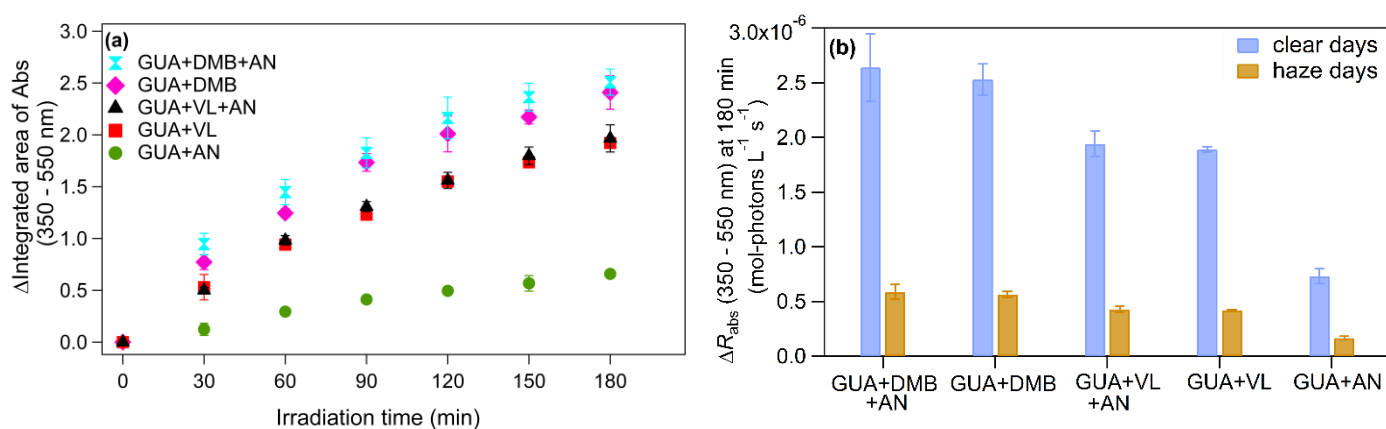


Figure 4. (a) Increase in light absorption throughout 180 min of irradiation for all reaction systems studied and (b) Change in the rate of sunlight absorption (ΔR_{abs}) from 350-550 nm at 180 min during typical clear and haze days in Beijing, China for aqSOA from GUA+DMB+AN, GUA+DMB, GUA+VL+AN, GUA+VL,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

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).

Other Comments

1. Line 125. Just a note: you don't need to bubble air through a solution to make it air saturated. Shaking the solution with air in the headspace, then opening the container, and repeating this several times is sufficient. The downside to bubbling synthetic air is that you can introduce water-soluble contaminants from the air into the solution.

Response: Thank you for the suggestion. We will keep this in mind for our future work. We performed continuous bubbling of air into the reactor to ensure that the reactions would not be limited by oxygen availability.

2. Line 126. What was the flow rate of air through the solutions during illumination. Is it fast enough to be a significant loss mechanism for volatile compounds (e.g., NO_x, small organics, etc.)?

Response: The flow rate used in this work was 0.5 dm³/min. We have added the flow rate used as well as the initial volume of the solutions in the text as follows:

Line 125: The solutions (initial volume of 500 mL) were bubbled with synthetic air (0.5 dm³/min) for 30 min before irradiation and throughout the reactions to achieve air-saturated conditions (Du et al., 2011; Chen et al., 2020) and were continuously magnetically stirred.

Our control experiment of bubbling air through 0.01 mM formic acid for 6 hours did not result in a significant change ($p > 0.05$) in concentration. Based on this, we believe that the flow rate used in this work is not fast enough to be a significant loss mechanism for volatile compounds (e.g., NO_x, small organics, etc.).

3. Line 129. (a) What was the pathlength of the photoreactor? (b) What were the corresponding light screening factors for each solution? (c) Are corrections for light screening required to correct the rate constants?

Response: (a) The path length of the photoreactor is 8.5 cm.

(b) Following Smith et al. (2014, 2016), the values of the internal light screening factor (S_λ) determined around the peak in the light absorption action spectrum (DMB: 310-335 nm, VL: 304-364 nm, and nitrate: 300-331 nm) for an 8.5 cm cell were as follows:

Reaction conditions	Internal light screening factor (S_λ)
GUA+AN	0.95
GUA+DMB	0.51
GUA+DMB+AN	0.54
GUA+VL	0.57
GUA+VL+AN	0.59

(c) Thank you for pointing this out. The decay rate constants were initially not corrected for light screening as the same concentration was used for DMB and VL. However, given the significant difference between the S_λ of GUA+AN and those of other reaction conditions, we corrected the decay rate constants for S_λ in Table 1. The following information has been added to the text to reflect these changes:

Line 143: The decay rate constants were normalized to the photon flux measured for each experiment through dividing k' by the measured 2-nitrobenzaldehyde (2NB; a chemical actinometer) decay rate constant, $j(2NB)$ (Mabato et al., 2022). In addition, the decay rate constants were corrected for the internal light screening due to DMB, VL, and AN (Leifer, 1988; Zhang and Anastasio, 2003; Smith et al., 2014, 2016). The values of the internal light screening factor (S_λ) determined around the peak in the light absorption action spectrum (DMB: 310-335 nm, VL: 304-364 nm, nitrate: 300-331 nm) (Smith et al., 2014, 2016) for an 8.5 cm cell were 0.95 for GUA+AN, 0.51 for GUA+DMB, 0.54 for GUA+DMB+AN, 0.57 for GUA+VL, and 0.59 for GUA+VL+AN.

Footnote of Table 1: ^aThe data fitting was performed in the initial linear region. Each value is the average of results from triplicate experiments, corrected for internal light screening due to DMB, VL, and AN, and normalized to the experimental photon flux. Errors represent one standard deviation.

4. Line 141. Were the decays of GUA, VL, and DMB always first-order? It seems unlikely given that the reactions proceeded for many half-lives of some of the compounds (e.g., VL). It would be helpful to show both examples of good (first-order) and not so good kinetics in the supplement.

Response: In this work, the decay of GUA, DMB, and VL were treated as pseudo-first-order, and the reported decay rate constants were obtained by performing the data fitting in the initial linear region, as noted in the original text (line 176) and Table 1. This is based on the consideration that the exact composition of the solutions during the reactions is unknown (e.g., due to the generation of intermediates).

The plots of the GUA, DMB, and VL decay (shown below) have now been added to Figure S1. The corresponding changes in the text are as follows:

Line 180: Figure S1 shows the decay of GUA, DMB, and VL under different experimental conditions.

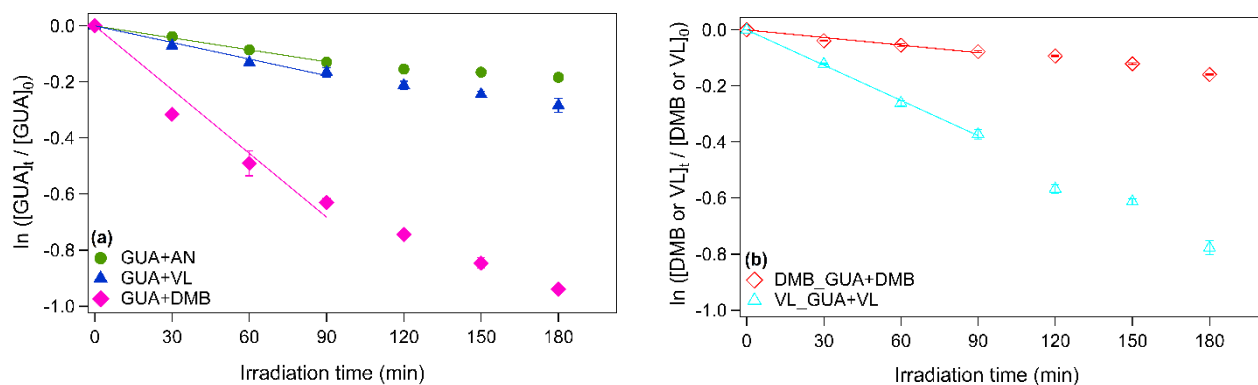


Figure S1. (a) The decay of GUA during (ammonium) nitrate-mediated photo-oxidation (GUA+AN) and photosensitized oxidation by $^3VL^*$ (GUA+VL) or $^3DMB^*$ (GUA+DMB). (b) The decay of DMB or VL during GUA photo-oxidation in GUA+DMB and GUA+VL, respectively. No statistically significant difference ($p > 0.05$) was noted between GUA+DMB and GUA+DMB+AN and between GUA+VL and GUA+VL+AN. Error bars represent 1 standard deviation; most error bars are smaller than the markers.

5. Line 234. These two sentences seem contradictory: GUA+DMB had more compounds with higher O:C, but GUA+VL had a higher average OS(C). How to reconcile this apparent discrepancy?

Response: We apologize that we may have misled the Reviewer. They are not inconsistent. The statement on GUA+DMB indicates having more compounds in terms of quantity or number with higher O:C than in GUA+VL. However, overall, the average O:C and OS_C calculated using the signal-weighted method (Bateman et al., 2012) were higher for GUA+VL than for GUA+DMB. This is probably due to the more significant functionalization in GUA+VL (as mentioned in line 236).

6. Line 254. Is this statement based only on the higher amounts of oligomers and functionalized monomers in the GUA+DMB case compared to the GUA+VL case? If so, this is weak evidence and really not a "correlation".

Response: Line 254 does not compare the absorbance enhancement for GUA+DMB vs. GUA+VL. Rather, it is about attributing the absorbance enhancement for both GUA+DMB and GUA+VL to oligomers and functionalized monomers which are the highest signal contributors. Regardless, we revised the text as follows:

Line 254: 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.

7. Table 1. (a) Are these rate constants normalized to a specific $j(2NB)$ value? Line 144 indicates that rate constants were normalized by dividing by $j(2NB)$, but this does not appear to have been done to the Table 1 rate constants based on their units. If the authors aren't going to normalize the rate constants, they should discuss the variation in $j(2NB)$ across their samples and give average $j(2NB)$ values for each reaction condition. (b) In the presence of AN, GUA has a rate constant of $8.1E-3 \text{ min}^{-1}$, which is appreciable. But the addition of AN to the DMB or VL solutions has no apparent impact on the rate constant for GUA loss, with a difference much less than the addition increment expected of $8E-3 \text{ min}^{-1}$. How to explain this discrepancy in the kinetics? Is light screening an issue? (c) Experiment #4 is labeled as a second #3.

Response: (a) Thank you for pointing this out. Yes, these rate constants were normalized to the photon flux measured for each experiment, but we inadvertently used the wrong unit for 2-nitrobenzaldehyde (2NB) decay rate constants during normalization. Table 1 now shows the correct photon flux-normalized rate constants, which were also corrected for internal light screening due to DMB, VL, and AN, based on the Reviewer's other comment #3. We apologize for the confusion.

(b) The addition of AN to GUA+DMB and GUA+VL had no significant effect on the decay rate constants, likely due to the higher molar absorptivities of DMB and VL compared to that of nitrate. This indicates that the chemistry of $^3\text{DMB}^*$ and $^3\text{VL}^*$ dominated that of nitrate photolysis. This information was already provided in lines 277-279. The estimated light-absorbing fraction (molar absorptivities from 300 to $\sim 360 \text{ nm} \times \text{concentration}$) of DMB, VL, and nitrate in these multicomponent systems were: 95.50% DMB and 4.50% nitrate for GUA+DMB+AN; and 95.12% VL and 4.88% nitrate for GUA+VL+AN. Similarly, in our previous work, we estimated comparable VL decay constants for the direct photosensitized oxidation of VL in the absence and presence of AN (Mabato et al., 2022). We do not think that this is a light screening issue as S_λ for GUA+DMB (0.51) and GUA+DMB+AN (0.54) (also for GUA+VL, 0.57, and GUA+VL+AN, 0.59) were comparable. However, although AN did not significantly affect the oxidation kinetics, it had distinct effects on the product distributions.

(c) Thank you for catching this error. The labeling has been corrected in Table 1.

Minor Comments

1. Line 87. The Henry's law constant listed for DMB ($5.4E1 \text{ M/atm}$) is far too low. This is either a typo or a problem in the source reference.

Response: The initially provided Henry's law constant for DMB ($5.4 \times 10^1 \text{ M atm}^{-1}$) is based on the group method estimate from EPI Suite. We have updated the listed Henry's law constant based on vapor pressure/water solubility estimate, which is more accurate compared to the group and bond methods:

Line 87: DMB and VL (Henry's law constants of ~~5.4×10^1~~ $7.3 \times 10^3 \text{ M atm}^{-1}$ and $4.7 \times 10^5 \text{ M}.$

2. Line 108. "...AN generated more N-containing products..." More than what condition?

Response: We apologize for the confusion. AN generated more N-containing products in GUA+DMB+AN than in GUA+VL+AN. This has been corrected in the text as follows:

Line 107: In particular, AN generated more N-containing products in GUA+DMB+AN than in GUA+VL+AN, and increased the oligomers in GUA+VL+AN.

3. Line 129. To better simulate sunlight, I recommend the authors add an airmass filter to their illumination system for future work.

Response: Thank you for the suggestion. We will keep this in mind for our future work.

4. Line 191. The authors posit that the OH + VL rate constant is larger than the OH + DMB rate constant, but it seems unlikely that the difference is large given that they are probably both very fast. Have the authors looked for these rate constants?

Response: This statement is based on the -OH group (in VL) being more activating than the -OCH₃ group (in DMB). The second-order rate constant for the reaction between [•]OH and VL has been reported to be $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Li et al., 2014), while we are unaware of any data for [•]OH + DMB. To avoid confusion, we omitted this phrase in the text.

5. Line 377. Should clarify that this is referring to stronger light absorption by the products.

Response: Thank you for the suggestion. This has been clarified in the text as follows:

Line 377: Compared to GUA+VL, faster GUA oxidation and stronger light absorption by the products were observed in GUA+DMB.

Line 271: In summary, ³DMB* and ³VL* can oxidize GUA resulting in aqSOA and BrC formation, but GUA+DMB products exhibited stronger light absorption.

Recommendation

This is a difficult manuscript to rate, as it has a few interesting points but some major issues. However, given that there is not a lot that is novel about the work, I am sorry to recommend that it be rejected.

References for responses to Reviewer 4:

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