

1 Comparison of aqueous SOA product distributions from guaiacol 2 oxidation by non-phenolic and phenolic methoxybenzaldehydes as 3 photosensitizers in the absence and presence of ammonium nitrate

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12 **Abstract.** Aromatic carbonyls (e.g., methoxybenzaldehydes), an important class of photosensitizers, are abundant in the
13 atmosphere. Photosensitization and nitrate-mediated photo-oxidation can occur simultaneously, yet studies about their
14 interactions, particularly for aqueous secondary organic aerosol (aqSOA) formation, remain limited. This study compared
15 non-phenolic (3,4-dimethoxybenzaldehyde, DMB) and phenolic (vanillin, VL) methoxybenzaldehydes as photosensitizers
16 for aqSOA formation via guaiacol (GUA) oxidation in the absence and presence of ammonium nitrate (AN) under
17 atmospherically relevant cloud and fog conditions. GUA oxidation by triplet excited states of DMB (³DMB*) (GUA+DMB)
18 was ~4 times faster and exhibited greater light absorption than oxidation by ³VL* (GUA+VL). Both GUA+DMB and
19 GUA+VL formed aqSOA composed of oligomers, functionalized monomers, oxygenated ring-opening species, and N-
20 containing products in the presence of AN. The observation of N-heterocycles such as imidazoles indicates the participation
21 of ammonium in the reactions. The majority of generated aqSOA are potential brown carbon (BrC) chromophores.
22 Oligomerization and functionalization dominated in GUA+DMB and GUA+VL, but functionalization appeared to be more
23 important in GUA+VL due to contributions from VL itself. AN did not significantly affect the oxidation kinetics, but it had
24 distinct effects on the product distributions, likely due to differences in the photosensitizing abilities and structural features
25 of DMB and VL. In particular, the more extensive fragmentation in GUA+DMB than in GUA+VL likely generated more N-
26 containing products in GUA+DMB+AN. In GUA+VL+AN, the increased oligomers may be due to VL-derived phenoxy
27 radicals induced by [•]OH or [•]NO₂ from nitrate photolysis. Furthermore, increased nitrated products observed in the presence
28 of both DMB or VL and AN than in AN alone implies that photosensitized reactions may promote nitration. This work
29 demonstrates how the structural features of photosensitizers affect aqSOA formation via non-carbonyl phenol oxidation.
30 Potential interactions between photosensitization and AN photolysis were also elucidated. These findings facilitate a better
31 understanding of photosensitized aqSOA formation and highlight the importance of AN photolysis in these reactions.

32 **1 Introduction**

33 Photosensitized reactions involving triplet excited states of organic compounds ($^3\text{C}^*$) are efficient pathways for the
34 formation of secondary organic aerosol in the aqueous phase (aqSOA; Smith et al., 2014, 2015, 2016; Yu et al., 2014, 2016;
35 Chen et al., 2018; Lu et al., 2019; Ye et al., 2019; Chen et al., 2020; Liu et al., 2020; Jiang et al., 2021; Ma et al., 2021;
36 Misovich et al., 2021; Ou et al., 2021; F. Li et al., 2022; X. Li et al., 2022; Aregahegn et al., 2022; Mabato et al., 2022;
37 Wang et al., 2022). Upon irradiation by solar radiation, photosensitizers form an excited triplet state that directly reacts with
38 substrates (e.g., phenols), and can generate singlet oxygen ($^1\text{O}_2$), superoxide ($\text{O}_2^{\cdot-}$) or hydroperoxyl ($^{\cdot}\text{HO}_2$) radicals, and
39 hydroxyl radicals ($^{\cdot}\text{OH}$) upon reactions with O_2 and substrates (George et al., 2018; Chen et al., 2020), thereby facilitating
40 the oxidation of rather volatile species and contributing to aqSOA formation. An important class of photosensitizers is
41 aromatic carbonyls (e.g., methoxybenzaldehydes) which are abundant in aerosol particles, cloud waters, and fog waters
42 (Anastasio et al., 1997; Felber et al., 2021). Aromatic carbonyls can be emitted from anthropogenic sources and biomass
43 burning (BB; Lipari et al., 1984; Edye and Richards, 1991; Hawthorne et al., 1992; Simoneit et al., 1993, 1999; Anastasio et
44 al., 1997; Felber et al., 2021), or formed via atmospheric oxidation of aromatic hydrocarbons (Hoshino et al., 1978; Calvert
45 and Madronich, 1987; Anastasio et al., 1997; Felber et al., 2021). BB is also a significant source of phenols through lignin
46 pyrolysis (Simpson et al., 2005). Phenolic carbonyls have a hydroxyl ($-\text{OH}$) group on the aromatic ring, whereas non-
47 phenolic carbonyls do not. BB smoke has been reported to have comparable concentrations of phenolic and non-phenolic
48 carbonyls (Simoneit et al., 1993; Anastasio et al., 1997).

49 Most previous studies on aqSOA formation via photosensitized non-carbonyl phenol oxidation have examined 3,4-
50 dimethoxybenzaldehyde (DMB), a non-phenolic methoxybenzaldehyde, as the photosensitizer (Smith et al., 2014, 2015; Yu
51 et al., 2014, 2016; Ye et al., 2019; Chen et al., 2020; Jiang et al., 2021; Ma et al., 2021; Misovich et al., 2021; Ou et al.,
52 2021; X. Li et al., 2022). By contrast, phenolic carbonyls have been mainly studied as aqSOA precursors via $^{\cdot}\text{OH}$ -, nitrate-,
53 nitrite-, and $^3\text{DMB}^*$ -mediated oxidation (Li et al., 2014; Huang et al., 2018; Pang et al., 2019; Jiang et al., 2021; Misovich et
54 al., 2021). However, strongly light-absorbing phenolic carbonyls (e.g., molar absorptivity above 300 nm $\geq 7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)
55 can also serve as photosensitizers to promote aqSOA formation (Smith et al., 2016; Mabato et al., 2022). For instance, the
56 direct photosensitized oxidation of phenolic carbonyls (i.e., oxidation of phenolic carbonyls by their $^3\text{C}^*$ or $^3\text{C}^*$ -derived
57 oxidants) such as vanillin (VL; another methoxybenzaldehyde) efficiently form low-volatility products, with aqSOA mass
58 yields of up to 140% (Smith et al., 2016). Moreover, the aqSOA mass yields from the oxidation of syringol by $^3\text{DMB}^*$ and
59 $^3\text{VL}^*$ are similar (111% and 114%, respectively; Smith et al., 2014, 2016). In addition, we recently reported that the direct
60 photosensitized oxidation of VL and guaiacol oxidation by $^3\text{VL}^*$ yield similar products (oligomers, functionalized
61 monomers, and oxygenated ring-opening products) as observed with $^3\text{DMB}^*$ (Yu et al., 2014; Mabato et al., 2022). Guaiacol
62 is a non-carbonyl BB methoxyphenol with an emission rate from fireplace wood combustion in the range of 172 to 279
63 mg/kg (Schauer et al., 2001; Simoneit, 2002). The atmospheric reactivity of methoxyphenols has recently been reviewed
64 (Liu et al., 2022). However, our previous experiments (Mabato et al., 2022) were performed at a concentration (0.1 mM VL)

65 higher than what was typically used for DMB (0.005 to 0.01 mM; Smith et al., 2014, 2015; Yu et al., 2014, 2016). Therefore,
66 direct comparisons between photosensitization by ³DMB* and ³VL* cannot be made. Despite the above findings, much is
67 still unknown about how aqSOA formation proceeds in systems using phenolic carbonyls as photosensitizers.

68 BB aerosols are typically internally mixed with other aerosol components, such as ammonium nitrate (AN;
69 Zielinski et al., 2020). Hence, aromatic carbonyls and phenols may coexist with AN in BB aerosols. Nitrate and ammonium
70 facilitate the formation of aqSOA and brown carbon (BrC) via a number of pathways. Nitrate photolysis can produce [•]OH
71 and nitrating agents (e.g., [•]NO₂; Minero et al., 2007; Huang et al., 2018; Mabato et al., 2022; Wang et al., 2022; Yang et al.,
72 2022), and ammonium reacts with carbonyls to yield N-containing heterocycles (e.g., imidazoles) and oligomers capable of
73 UV-Vis light absorption (De Haan et al., 2009, 2011; Nozière et al., 2009, 2010, 2018; Shapiro et al., 2009; Yu et al., 2011;
74 Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Grace et al., 2019; Mabato et al., 2019). Furthermore, nitrate
75 photolysis may be an important process for SO₂ oxidation and SOA formation in the particle phase (Gen et al., 2019a,
76 2019b, 2022; Zhang et al., 2020, 2021, 2022), and it can potentially modify the morphology of atmospheric viscous particles
77 (Liang et al., 2021). Yet, understanding of the effects of inorganic nitrate on aqSOA formation remains limited. In addition,
78 aqSOA formation studies involving aromatic carbonyls and phenols have probed either photosensitization or nitrate-
79 mediated photo-oxidation, but these reactions can occur simultaneously. For instance, we previously reported nitrated
80 compounds, including a potential imidazole derivative from the direct photosensitized oxidation of VL in the presence of AN
81 (Mabato et al., 2022). Accordingly, investigations on reaction systems including both photosensitizers and AN may provide
82 further insights into the aqueous-phase processing of BB aerosols.

83 In this work, we compared aqSOA formation from photosensitized guaiacol (GUA) oxidation by ³C* of non-
84 phenolic and phenolic methoxybenzaldehydes under identical conditions (simulated sunlight and reactants concentration)
85 relevant to cloud and fog waters. The effects of AN on photosensitized aqSOA formation were also examined. In this study,
86 the dominant aqSOA precursor is GUA (Henry's law constant of $9.2 \times 10^2 \text{ M atm}^{-1}$; Sagebiel et al., 1992), and DMB and VL
87 were used as photosensitizers to oxidize GUA. DMB and VL (Henry's law constants of $7.3 \times 10^3 \text{ M atm}^{-1}$ and $4.7 \times 10^5 \text{ M}$
88 atm^{-1} , respectively; Yaws, 1994; EPI Suite version 4.1, 2012; Felber et al., 2021), which are also abundant in BB emissions
89 (Schauer et al., 2001; Li et al., 2014; Chen et al., 2017; Pang et al., 2019; Mabato et al., 2022) and whose structures differ
90 only by one functional group (–OCH₃ for the former and –OH for the latter, Fig. 1), represented non-phenolic and phenolic
91 methoxybenzaldehydes, respectively. The structures of GUA, DMB, and VL are provided in Figure 1. Based on their
92 quantum yield of ³C* formation, DMB and VL have been classified as moderate and poor photosensitizers, respectively
93 (Felber et al., 2021). The photosensitized oxidation of GUA by ³DMB* or ³VL* in the absence (and presence) of AN are
94 referred to as GUA+DMB(+AN) and GUA+VL(+AN), respectively. GUA photo-oxidation by AN alone (GUA+AN) was
95 also explored for comparison with GUA+DMB+AN and GUA+VL+AN. The molar absorptivities of GUA, DMB, VL, and
96 nitrate are shown in Figure 1. The precursor and photosensitizer decay kinetics, detected products, and absorbance
97 enhancement were used to characterize the reactions. However, it should be noted that we mainly focused on the analyses of
98 the reaction products and product distribution.

99 While several studies on photo-oxidation of BB emissions are available, this work focuses on the comparison
100 between non-phenolic and phenolic methoxybenzaldehydes as photosensitizers in the absence and presence of AN for
101 aqSOA formation. We found that GUA oxidation by $^3\text{DMB}^*$ was faster and exhibited greater light absorption relative to
102 GUA+VL. These are likely attributed to the stronger photosensitizing ability of DMB and the $-\text{OH}$ group of VL, making it
103 more prone to oxidation and more reactive towards electrophilic aromatic substitution. Oligomerization and functionalization
104 dominated in GUA+DMB and GUA+VL, but functionalization appeared to be more significant in GUA+VL due to VL
105 transformation products. Although AN did not significantly influence the oxidation kinetics due to the predominant role of
106 photosensitizer chemistry compared to nitrate, AN promoted the formation of N-containing products. These include N-
107 heterocycles (e.g., imidazoles), suggesting the participation of ammonium in the reactions. Moreover, the product
108 distributions indicate distinct interactions between photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$ and AN photolysis. In particular,
109 AN generated more N-containing products in GUA+DMB+AN than in GUA+VL+AN, and increased the oligomers in
110 GUA+VL+AN. Furthermore, increased nitrated compounds in GUA+DMB+AN and GUA+VL+AN compared to GUA+AN
111 suggest that photosensitized reactions may promote reactions by nitrate photolysis.

112 **2 Methods**

113 **2.1 Aqueous phase photo-oxidation experiments**

114 Procedures for the photo-oxidation experiments are presented in detail in our previous study (Mabato et al., 2022).
115 Experimental solutions were prepared using 0.1 mM guaiacol (GUA, Sigma Aldrich, $\geq 98.0\%$) and 0.01 mM 3,4-
116 dimethoxybenzaldehyde (DMB, Acros Organics, 99+%) or 0.01 mM vanillin (VL, Acros Organics, 99%, pure), in the
117 absence and presence of ammonium nitrate (1 mM; AN, Acros Organics, 99+%, for analysis). These GUA and
118 methoxybenzaldehydes concentrations are within the values expected in cloud or fog drops in areas with significant wood
119 combustion (Anastasio et al., 1997; Rogge et al., 1998; Nolte et al., 2001). The AN concentration represents values usually
120 observed in cloud and fog waters (Munger et al., 1983; Collett et al., 1998; Zhang and Anastasio, 2003; Li et al., 2011;
121 Giulianelli et al., 2014; Bianco et al., 2020). It must be noted that this study did not intend to identify the AN concentrations
122 that would affect the kinetics but attempted to analyze the effects of AN on photosensitized aqSOA formation. A solution
123 composed of 0.1 mM GUA and 1 mM AN (GUA+AN) was also examined for comparison with GUA+DMB+AN and
124 GUA+VL+AN. Sulfuric acid (H_2SO_4 ; Acros Organics, ACS reagent, 95% solution in water) was used to adjust the pH of the
125 solutions to 4, which is within typical cloud pH values (2–7; Pye et al., 2020) and pH values observed in wood burning-
126 impacted cloud and fog waters (Collett et al., 1998; Raja et al., 2008). The solutions (initial volume of 500 mL) were
127 bubbled with synthetic air (0.5 dm^3/min) for 30 min before irradiation and throughout the reactions to achieve air-saturated
128 conditions (Du et al., 2011; Chen et al., 2020) and were continuously magnetically stirred. In this study, the reactions can
129 generate $^3\text{DMB}^*/^3\text{VL}^*$ and secondary oxidants ($^1\text{O}_2$, $\text{O}_2^{\cdot-}/\text{HO}_2$, $\cdot\text{OH}$) but not ozone. Solutions contained in a quartz
130 photoreactor were irradiated using a xenon lamp (model 6258, Ozone free xenon lamp, 300 W, Newport) equipped with a

131 longpass filter (20CGA-305 nm cut-on filter, Newport) to eliminate light below 300 nm. The reaction temperatures were
132 maintained at 27 ± 2 °C using cooling fans positioned around the photoreactor and lamp housing. The averaged initial
133 photon flux in the reactor measured from 300 to 380 nm was $\sim 3 \times 10^{15}$ photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ (Fig. 1), similar to our previous
134 work (Mabato et al., 2022). Samples were collected every 30 min for 180 min for offline analyses of (1) GUA, DMB, and
135 VL concentrations using ultra-high-performance liquid chromatography with photodiode array detector (UHPLC-PDA) and
136 (2) absorbance measurements using UV-Vis spectrophotometry. Moreover, the samples collected before and after irradiation
137 (180 min) were analyzed for (3) reaction products using UHPLC coupled with heated electrospray ionization Orbitrap mass
138 spectrometry (UHPLC-HESI-Orbitrap-MS) operated in positive and negative ion modes and (4) concentrations of small
139 organic acids using ion chromatography (IC). Each experiment was repeated independently at least three times. The reported
140 decay rate constants, small organic acids concentration, and absorbance enhancement were averaged from triplicate
141 experiments, and the corresponding errors represent one standard deviation. The pseudo-first-order rate constant (k') for
142 GUA decay was determined using the following equation (Huang et al., 2018):

$$143 \quad \ln ([\text{GUA}]_t / [\text{GUA}]_0) = -k't \quad (\text{Eq. 1})$$

144 where $[\text{GUA}]_t$ and $[\text{GUA}]_0$ are GUA concentrations at time t and 0, respectively. DMB or VL decay rate constants were
145 calculated by replacing GUA with DMB or VL in Eq. 1. The decay rate constants were normalized to the photon flux
146 measured for each experiment through dividing k' by the measured 2-nitrobenzaldehyde (2NB; a chemical actinometer)
147 decay rate constant, $j(2\text{NB})$ (Mabato et al., 2022). In addition, the decay rate constants were corrected for the internal light
148 screening due to DMB, VL, and AN (Leifer, 1988; Zhang and Anastasio, 2003; Smith et al., 2014, 2015, 2016). The values
149 of the internal light screening factor (S_i) determined around the peak in the light absorption action spectrum (DMB: 310-335
150 nm, VL: 304-364 nm, nitrate: 300-331 nm) (Smith et al., 2014, 2015, 2016) for an 8.5 cm cell were 0.95 for GUA+AN, 0.51
151 for GUA+DMB, 0.54 for GUA+DMB+AN, 0.57 for GUA+VL, and 0.59 for GUA+VL+AN. Moreover, two independently
152 prepared samples for each reaction condition were analyzed using UHPLC-HESI-Orbitrap-MS. Only peaks that were
153 reproducibly detected in both sets of samples were considered. For clarity, the formulas discussed in this work correspond to
154 neutral analytes (e.g., with H^+ or NH_4^+ removed from the ion formula). The details of the analytical procedures are provided
155 in the Supplement (Sects. S1 to S4).

156 2.2 Calculation of normalized abundance of products

157 Several recent studies have used comparisons of relative abundance of products based on peak areas from mass spectrometry
158 (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
159 et al., 2019; Ning et al., 2019) to show the relative importance of different types of compounds (K. Wang et al., 2021).
160 However, comparisons of relative abundance among different compounds can be subject to uncertainties as ionization
161 efficiencies in soft ionization, such as ESI, may significantly vary between different compounds (Kearle, 2000; Schmidt et
162 al., 2006; Leito et al., 2008; Perry et al., 2008; Krueve et al., 2014). In our previous work (Mabato et al., 2022), we introduced
163 the normalized abundance of products ($[\text{P}]$, unitless) (Eq. 2) as a semi-quantitative analysis that gives an overview of how

164 the signal intensities changed under different experimental conditions but not the quantification of the absolute product
165 concentration. The calculation assumes equal ionization efficiencies of different compounds, which is commonly used to
166 estimate O:C ratios of SOA (Bateman et al., 2012; Lin et al., 2012; Laskin et al., 2014; De Haan et al., 2019):

167

$$168 \quad [P] = \frac{A_{P,t}}{A_{GUA,t}} \cdot \frac{[GUA]_t}{[GUA]_0} \quad (\text{Eq. 2})$$

169 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-
170 Orbitrap-MS analyses at time t , respectively; $[GUA]_t$ and $[GUA]_0$ are the GUA concentrations (μM) determined using
171 UHPLC-PDA at time t and 0, respectively. Note that the normalized abundance of products has intrinsic uncertainties due to
172 the variability in ionization efficiencies for various compounds. Moreover, it should be noted that the normalized abundance
173 of products was calculated using only the positive ion mode data as the GUA signal from the negative ion mode was weak
174 and thus may present large uncertainties during normalization. Therefore, products that may not give signals or may have
175 weak signals in the positive ion mode were possibly underestimated in the normalized product abundance. Nevertheless, it
176 enables the comparison of MS results among different experiments. As demonstrated in our previous work (Mabato et al.,
177 2022) and the current study, a higher normalized abundance of products generally correlates with higher efficiency of
178 oxidation. The reported uncertainties were propagated from the changes in $[GUA]$ measured using UHPLC-PDA and the MS
179 signal intensities.

180

181 **3 Results and Discussion**

182 Using kinetics data, MS analyses, and absorbance enhancement data, we first examined the differences between GUA+DMB
183 and GUA+VL (Sect. 3.1). Then, we analyzed GUA+DMB+AN, GUA+VL+AN, and GUA+AN (Sect. 3.2) to explore the
184 effects of nitrate photolysis and ammonium on photosensitized aqSOA formation.

185 **3.1 Comparison of photosensitized GUA oxidation by non-phenolic ($^3\text{DMB}^*$) and phenolic ($^3\text{VL}^*$)** 186 **methoxybenzaldehydes**

187 Prior studies have reported that photosensitized non-carbonyl phenol oxidation in the presence of 3,4-
188 dimethoxybenzaldehyde (DMB) and vanillin (VL) (separately) was mainly driven by $^3\text{DMB}^*$ and $^3\text{VL}^*$, respectively (Smith
189 et al., 2014; Mabato et al., 2022), while contributions from secondary oxidants such as $^1\text{O}_2$ and $^{\bullet}\text{OH}$ were likely minor.
190 However, both $^3\text{DMB}^*$ and $^3\text{VL}^*$ are efficiently quenched by O_2 , suggesting that energy transfer should be considered in
191 evaluating photosensitized processes involving these methoxybenzaldehydes (Felber et al., 2021). Moreover, it was found
192 that $^3\text{DMB}^*$, $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$ were the major contributors to the photosensitized oxidation of 4-ethylguaiaicol (Chen et al., 2020).
193 Recently, the oxidation of guaiacyl acetone (a non-conjugated phenolic carbonyl) in the presence of DMB has been reported

194 to be initiated by $^3\text{DMB}^*$, $^1\text{O}_2$, $^{\bullet}\text{OH}$, or methoxy radical ($^{\bullet}\text{OCH}_3$) (Misovich et al., 2021). Further studies are thus required to
195 identify the specific oxidants in these reaction systems. In this study, reactions initiated in the presence of DMB or VL are
196 collectively referred to as photosensitized reactions. The reaction conditions, initial guaiacol (GUA) and DMB or VL decay
197 rate constants, normalized product abundance, and the chemical characteristics of aqSOA formed in this work are
198 summarized in Table 1.

199 **3.1.1 Kinetic analysis of photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$**

200 No significant loss of GUA or photosensitizers was observed for dark experiments ($p > 0.05$). Figure S1 shows the decay of
201 GUA, DMB, and VL under different experimental conditions. Upon irradiation, the GUA decay rate constant in GUA+DMB
202 was ~ 4 times higher than in GUA+VL. In GUA+DMB, the decay rate constant of GUA was ~ 8 times higher than that of
203 DMB, consistent with a previous study (Smith et al., 2014). Contrastingly, the decay rate constant of VL was 2.4 times
204 higher than that of GUA in GUA+VL. This VL consumption was also observed in our earlier work using 0.1 mM GUA +
205 0.1 mM VL (Mabato et al., 2022). These trends could be explained by the following reasons. First, DMB has a stronger
206 photosensitizing ability than VL based on its higher quantum yield of $^3\text{C}^*$ formation and longer lifetime of $^3\text{DMB}^*$
207 compared to $^3\text{VL}^*$ (Felber et al., 2021). Second, VL is also a phenolic compound similar to GUA, and is therefore highly
208 reactive towards oxidation. For instance, its $-\text{OH}$ group can be oxidized by $^3\text{VL}^*$ via H-atom abstraction to form phenoxy
209 radicals which can undergo coupling to form oligomers (Kobayashi and Higashimura, 2003; Sun et al., 2010; Mabato et al.,
210 2022). The faster consumption of VL than GUA suggests a competition between ground-state VL and GUA for reaction with
211 $^3\text{VL}^*$. Moreover, compared to a $-\text{OCH}_3$ group (in DMB), an $-\text{OH}$ group (in VL) has a stronger electron-donating ability and
212 is thus more activating towards electrophilic aromatic substitution. It should be noted that the differences in the GUA decay
213 rate constants among different reaction systems are not quantitatively equivalent to photosensitizing efficiencies, and a
214 detailed quantitative analysis of which is beyond the scope of this study. Nonetheless, these results suggested that GUA
215 oxidation in GUA+DMB was overall more efficient than in GUA+VL. Our kinetic analysis focused on the decay rate
216 constants of the aqSOA precursor (GUA) and the photosensitizers (DMB and VL) during photosensitization under the same
217 experimental conditions (same aqSOA precursor and concentration, same photosensitizer concentration, and same lamp
218 photon flux). The effects of other factors (e.g., intersystem crossing efficiency) on the rate constants were not examined.
219 Explicit kinetic studies (e.g., Smith et al., 2014, 2015) that measure second-order rate constants should be conducted in the
220 future to extend the applicability of the kinetic parameters to other conditions.

221 **3.1.2 Product distributions and chemical characteristics of aqSOA from photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$**

222 The products detected using UHPLC-HESI-Orbitrap-MS were used to characterize the aqSOA formed in this work. The
223 signal-weighted distributions of aqSOA calculated from combined positive (POS) and negative (NEG) ion modes MS results
224 are summarized in Figure 2. The signal-weighted distributions calculated separately from POS and NEG ion modes MS
225 results are available in Figures S2 and S3. It should be noted that in this work, the product distributions for all experiments

226 were based on the same irradiation time of 180 min. An irradiation time of 180 min was chosen as it was sufficient to show
227 the differences in the extent of reaction of GUA among the reaction systems studied. For reaction systems with precursors of
228 different reactivities, chemical analysis at a fixed reaction time may be looking at different generations of products of each
229 precursor, as Yu et al. (2014) reported. Measuring the product distribution at a fixed time might have missed the information
230 on what/how many products are formed at the similar amounts of precursors reacted. The situation could be even more
231 complicated if different precursors had major differences in pathways and dominant intermediates. However, comparing the
232 product distributions after a certain time of light exposure, as is the case for this study, is useful to evaluate what products
233 would form after a certain time of photosensitization. Oligomers and derivatives of GUA dominated both GUA+DMB and
234 GUA+VL, in agreement with pronounced oligomerization from triplet-mediated oxidation of relatively high phenol
235 concentration (e.g., 0.1 to 3 mM; Li et al., 2014; Yu et al., 2014, 2016; Slikboer et al., 2015; Ye et al., 2019; Mabato et al.,
236 2022). Figure 3 schematically depicts the main differences between photosensitized GUA oxidation by $^3\text{DMB}^*$ and $^3\text{VL}^*$ in
237 the absence and presence of AN. As shown in Fig. 3, $^3\text{DMB}^*$ and $^3\text{VL}^*$ can oxidize GUA via H-atom abstraction to form
238 phenoxy radicals which undergo coupling to form oligomers (Kobayashi and Higashimura, 2003; Sun et al., 2010; Mabato et
239 al., 2022). The higher oligomer contribution in GUA+DMB is likely due to the better photosensitizing ability of DMB than
240 VL and partly the lower abundance of $^3\text{VL}^*$ due to fast VL consumption. VL was consumed faster than DMB during GUA
241 oxidation ascribable to the -OH group of VL, making it more susceptible to oxidation and more reactive towards
242 electrophilic aromatic substitution. In addition, the normalized product abundance for GUA+DMB was ~4 times higher than
243 that for GUA+VL (Table 1), further suggesting more efficient photosensitized GUA oxidation by $^3\text{DMB}^*$ than by $^3\text{VL}^*$. The
244 oxidation of GUA or transient organic intermediates by secondary oxidants (e.g., $^1\text{O}_2$ and $\cdot\text{OH}$) from $^3\text{DMB}^*$ or $^3\text{VL}^*$ and the
245 fragmentation of larger compounds generate highly oxidized ring-opening products (Yu et al., 2014; Huang et al., 2018;
246 Chen et al., 2020). GUA+DMB had a higher contribution of ring-opening products than GUA+VL, likely due to the greater
247 availability of secondary oxidants in the former and fast VL consumption lowering the production of these species in
248 GUA+VL. The IC analyses also indicate the formation of small organic acids (e.g., formic acid), which appeared to have
249 higher concentrations in the presence of DMB than in VL (Fig. S4). Although no data is available for the concentration
250 changes (every 30 min) of small organic acids during the reaction, it is likely that an increasing trend would be observed as
251 fragmentation, which leads to the decomposition of initially formed oligomers and the generation of smaller oxygenated
252 products, becomes important at longer irradiation times (Huang et al., 2018). This trend has also been observed in our
253 previous work on the direct photosensitized oxidation of VL (Mabato et al., 2022), as well as other studies on
254 photosensitized oxidation of non-carbonyl phenols and phenolic carbonyls (e.g., Yu et al., 2016; Jiang et al., 2021). The
255 reactions of secondary oxidants or ring-opening products with GUA can form functionalized products. Notably, the
256 contribution of monomers in GUA+VL was almost twice as high as in GUA+DMB, ascribable to VL transformation
257 products. We previously showed that for the direct photosensitized oxidation of VL, functionalization prevails over
258 oligomerization at 0.01 mM VL, the [VL] used in this work, while oligomerization dominates at higher [VL] (0.1 mM;
259 Mabato et al., 2022).

260 It has been reported that oligomerization could occur during the electrospray ionization process (Yasmeen et al.,
261 2010). In this work, it was confirmed that the oligomers observed were generated in the solutions via aqueous reactions
262 instead of being artefacts of HESI-MS. This is based on the absence of dimers and higher oligomers in the HESI mass
263 spectra of dark control solutions acquired by direct infusion (Yu et al., 2016).

264 The major GUA+DMB and GUA+VL products (Tables S1-S2) are mostly oligomers which can be formed through
265 the coupling of phenoxy radicals (Kobayashi and Higashimura, 2003; Sun et al., 2010; Mabato et al., 2022). GUA+DMB
266 products matched those reported in previous works on $^3\text{DMB}^*$ - and/or $^{\bullet}\text{OH}$ -mediated phenol oxidation (Yu et al., 2014,
267 2016). These include GUA dimers and trimers (e.g., $\text{C}_{14}\text{H}_{14}\text{O}_4$ and $\text{C}_{21}\text{H}_{18}\text{O}_8$, #1 and 19; Table S1), aldehydes ($\text{C}_7\text{H}_6\text{O}_4$, #13;
268 Table S1), and esters ($\text{C}_{16}\text{H}_{18}\text{O}_6$, #14; Table S1). Functionalized products include $\text{C}_{11}\text{H}_{12}\text{O}_5$ and $\text{C}_{10}\text{H}_{12}\text{O}_3$ (#8 and 12; Table
269 S1). More than half of the major GUA+VL products are the same oligomers detected from GUA+DMB (e.g., $\text{C}_{13}\text{H}_{10}\text{O}_4$ and
270 $\text{C}_{20}\text{H}_{18}\text{O}_6$, #4 and 21; Table S1). The rest are mainly functionalized species such as $\text{C}_7\text{H}_8\text{O}_4$ and $\text{C}_8\text{H}_8\text{O}_5$ (#28 and 35; Table
271 S2), corresponding to a hydroxylated GUA and hydroxylated VL, respectively.

272 The average elemental ratios and elemental distribution of the products (Fig. S5a–d) were consistent with those in
273 previous studies on similar reaction systems (Yu et al., 2014, 2016; Mabato et al., 2022). The majority of the GUA+DMB
274 and GUA+VL products had $\text{H}:\text{C} \leq 1.0$ and $\text{O}:\text{C} \leq 0.5$, typical for aromatic species (Mazzoleni et al., 2012; Kourtchev et al.,
275 2014; Jiang et al., 2021). GUA+DMB had more compounds with higher $\text{O}:\text{C}$ (≥ 0.6), in agreement with higher contributions
276 of ring-opening products than in GUA+VL (Fig. 2). The higher $\langle \text{OS}_\text{C} \rangle$ for GUA+VL than in GUA+DMB (Table 1) was
277 probably due to the significant functionalization in the former. Moreover, the distributions of OS_C and carbon number (Fig.
278 S6a–d) show that these aqSOA products have similar elemental composition to those of low-volatility oxygenated organic
279 aerosols (LV-OOA), semi-volatile oxygenated organic aerosols (SV-OOA), and slightly with biomass burning organic
280 aerosols (BBOA) (Kroll et al., 2011). Further discussions on van Krevelen diagrams (Fig. S5a–d) and OS_C vs. carbon
281 number plots (Fig. S6a–d) for GUA+DMB and GUA+VL aqSOA are available in the Supplement (Sect. S5). In brief,
282 $^3\text{DMB}^*$ -initiated GUA oxidation was faster and yielded higher normalized product abundance than oxidation by $^3\text{VL}^*$. This
283 is likely due to the stronger photosensitizing ability of DMB than VL and the $-\text{OH}$ group of VL facilitating its rapid
284 consumption. In addition, oligomerization and functionalization dominated in both GUA+DMB and GUA+VL, as reported
285 in similar studies (Yu et al., 2014, 2016; Chen et al., 2020; Jiang et al., 2021; Misovich et al., 2021; Mabato et al., 2022).
286 However, functionalization was more prominent in the latter, attributable to the transformation of VL. Nonetheless, it must
287 be noted that for phenolic aqSOA, fragmentation will ultimately be more predominant at longer irradiation times (Huang et
288 al., 2018; Yu et al., 2016; Mabato et al., 2022).

289 3.1.3 Light absorption of aqSOA from photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$

290 The absorbance enhancement of phenolic aqSOA generated via reactions with $^3\text{C}^*$ has been linked to the formation of
291 conjugated structures due to oligomerization and functionalization (e.g., additions of hydroxyl and carbonyl groups; Yu et
292 al., 2014, 2016; Smith et al., 2016; Ye et al., 2019; Chen et al., 2020; Jiang et al., 2021; Misovich et al., 2021; Ou et al.,

293 2021; F. Li et al., 2022; X. Li et al., 2022; Mabato et al., 2022; Wang et al., 2022). Moreover, the aqueous-phase photo-
294 oxidation of BB emissions can enhance BrC absorbance via the formation of aromatic dimers and functionalized products
295 (Hems et al., 2020). The increase in light absorption throughout 180 min of irradiation and the change in the rate of sunlight
296 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
297 all the reaction systems studied are provided in Figure 4. Figure S7 shows the absorption spectra after 180 min of irradiation
298 for each reaction system studied. In this work, the absorbance enhancement of GUA+DMB and GUA+VL (Fig. 4a) could be
299 due to oligomers and functionalized monomers, which are the highest contributors to the product signals. Identifying the
300 chromophores responsible for the absorbance enhancement may be beneficial in understanding the impact of aqSOA on the
301 Earth's radiative balance and determining the reactions that affect light absorption by aqSOA (Mabato et al., 2022).
302 However, the detected products did not exhibit distinct peaks in the UHPLC-PDA chromatograms, likely due to the
303 concentration of the chromophores being below the detection limit of PDA. Nevertheless, the higher absorbance
304 enhancement and ΔR_{abs} for GUA+DMB than GUA+VL was probably due to the higher contribution and normalized
305 abundance (by ~6 times) of oligomers in the former.

306 Additional information about aqSOA light absorption can be deduced from the plots of the double bond equivalent
307 (DBE) values vs. carbon number (n_{C}) (Lin et al., 2018). Figure S8 shows these plots along with the DBE reference values of
308 fullerene-like hydrocarbons (Lobodin et al., 2012), cata-condensed polycyclic aromatic hydrocarbons (PAHs; Siegmund and
309 Sattler, 2000), and linear conjugated polyenes with a general formula C_xH_{x+2} . The shaded area indicates a sufficient level of
310 conjugation for visible light absorption, and species within this region are potential BrC chromophores. GUA+DMB and
311 GUA+VL aqSOA exhibited a significant overlap in the DBE vs. n_{C} space; nearly all products from both systems, including
312 the high-relative-abundance species, are potential BrC chromophores. GUA+DMB had more oligomeric products with high
313 relative abundance ($n_{\text{C}} \geq 12$ and $\text{DBE} \geq 8$). For GUA+VL, high-relative-abundance products also include monomeric species
314 ($n_{\text{C}} = 7-8$ and 4-5 DBE) corresponding to hydroxylated products (e.g., $\text{C}_7\text{H}_8\text{O}_4$ and $\text{C}_8\text{H}_8\text{O}_5$; 28 and 35; Table S2). These
315 observations further indicate the importance of oligomerization and functionalization for the absorbance enhancement of
316 aqSOA generated via photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$. In summary, $^3\text{DMB}^*$ and $^3\text{VL}^*$ can oxidize GUA resulting in
317 aqSOA and BrC formation, but GUA+DMB products exhibited stronger light absorption. In GUA+VL, the extent of GUA
318 oxidation was limited by significant VL consumption.

319 **3.2 Comparison of photosensitized GUA oxidation by non-phenolic ($^3\text{DMB}^*$) and phenolic ($^3\text{VL}^*$)** 320 **methoxybenzaldehydes in the presence of AN**

321 **3.2.1 Kinetic analysis of photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$ in the presence of AN**

322 Ammonium nitrate (AN) did not significantly affect ($p > 0.05$) the decay rate constants of GUA, DMB, and VL for both
323 GUA+DMB+AN and GUA+VL+AN (Table 1), likely due to the higher molar absorptivities of the photosensitizers
324 compared to that of nitrate. This implies that the chemistry of $^3\text{DMB}^*$ and $^3\text{VL}^*$ dominated that of nitrate. In this work, the
325 GUA decay rate constants decreased in the order of GUA+DMB/GUA+DMB+AN > GUA+VL/GUA+VL+AN > GUA+AN

326 (Table 1). Note that as the molar absorptivities of the photosensitizers are higher than that of nitrate, the kinetics data were
327 also analyzed on a per-photon-absorbed basis for a more appropriate comparison of reaction efficiency (Sect. S6). The
328 apparent quantum efficiency of GUA photodegradation (ϕ_{GUA}) in the presence of nitrate (GUA+AN: $0.17 \pm 3.8 \times 10^{-2}$) was
329 ~ 2 and ~ 7 times higher than that in the presence of DMB ($0.10 \pm 2.9 \times 10^{-3}$) or VL ($0.026 \pm 7.2 \times 10^{-3}$), respectively. This
330 suggests that nitrate-mediated GUA photo-oxidation is more efficient than photosensitization by $^3\text{DMB}^*$ or $^3\text{VL}^*$ on a per-
331 photon-absorbed basis.

332 **3.2.2 Product distributions and chemical characteristics of aqSOA from photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$ in** 333 **the presence of AN**

334 For both GUA+DMB+AN and GUA+VL+AN, AN had no significant effect on the normalized product abundance (Table 1),
335 but it induced the formation of N-containing products composed of N-heterocycles (e.g., imidazoles and pyridines) and
336 oligomers, as well as nitrated species. Similarly, we previously reported a potential imidazole derivative from the direct
337 photosensitized oxidation of VL in the presence of AN, which was attributed to the reaction of ring-opening products with
338 dissolved ammonia (Mabato et al., 2022). Oligomers remained the highest signal contributors in the presence of AN (Fig. 2),
339 but interactions between photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$ and AN photolysis were distinct. First, nitrated species had
340 similar contributions in both cases, but the contribution and normalized abundance of all N-containing products in
341 GUA+DMB+AN were 2 and ~ 14 times higher, respectively, than in GUA+VL+AN. This difference can be attributed to the
342 higher contribution of N-heterocycles and N-containing oligomers in GUA+DMB+AN. Compared to GUA+VL,
343 GUA+DMB had a higher contribution of ring-opening products which can react with ammonia, as discussed earlier (Figs. 2
344 and 3). Second, the decrease in oligomers in GUA+DMB+AN may be due to their fragmentation induced by $\cdot\text{OH}$ from
345 nitrate photolysis, then conversion to N-containing products. Correspondingly, the contribution of possibly ring-retaining N-
346 containing products in GUA+DMB+AN (18.6%) was ~ 3 times higher than that in GUA+VL+AN (6.5%). While
347 fragmentation of oligomers likely occurred in GUA+VL+AN as well, the increase in oligomers suggests that other reactions
348 have taken place. For GUA+VL+AN, $\cdot\text{OH}$ or $\cdot\text{NO}_2$ from nitrate photolysis may have initiated H-atom abstraction from the –
349 OH group of VL, generating phenoxy radicals which can undergo coupling to form more oligomers (Kobayashi and
350 Higashimura, 2003; Sun et al., 2010; Mabato et al., 2022). This may also explain the more significant decrease of monomers
351 in GUA+VL+AN (~ 3 times) compared to GUA+DMB+AN (~ 2 times). Similarly, we previously observed an increase in
352 oligomers during the direct photosensitized oxidation of 0.01 mM VL (Mabato et al., 2022), the [VL] used in this work,
353 upon adding 1 mM AN. These findings indicate that photosensitization by non-phenolic and phenolic
354 methoxybenzaldehydes may interact differently with AN photolysis.

355 GUA+AN mainly formed oligomers analogous to $\cdot\text{OH}$ -mediated phenol oxidation (Yu et al., 2014, 2016), followed
356 by N-containing products. The normalized product abundance of GUA+AN was the lowest among all experiments, likely
357 due to the lower GUA decay constant relative to photosensitized oxidation. Moreover, the normalized abundance of N-
358 containing products in GUA+AN was ~ 12 times lower than that in GUA+DMB+AN but comparable to that in

359 GUA+VL+AN. This discrepancy for GUA+VL+AN might be due to the weaker signals of its N-containing products in the
360 positive compared to the negative ion mode. As previously mentioned, the normalized product abundance was calculated
361 using only the positive ion mode data as the GUA signal from the negative ion mode was weak and thus may present large
362 uncertainties during normalization. Interestingly, the contributions from nitrated species in GUA+DMB+AN and
363 GUA+VL+AN were higher than in GUA+AN, suggesting possible enhancement of nitration reactions. This is likely due to
364 the increased formation of $\cdot\text{NO}_2$, for instance, via the reactions of $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ (from $^3\text{DMB}^*$ or $^3\text{VL}^*$) with NO_2^- (Pang et
365 al., 2019; Mabato et al., 2022). Similarly, we previously reported enhanced nitration via the direct photosensitized oxidation
366 of VL in the presence of AN under air-saturated conditions (O_2 is present) relative to nitrogen-saturated conditions (Mabato
367 et al., 2022). These imply that photosensitization may promote reactions induced by nitrate photolysis.

368 The major products from GUA+DMB+AN, GUA+VL+AN, and GUA+AN (Tables S3–S5) include oligomers and
369 functionalized monomers detected in GUA+DMB and GUA+VL (Tables S1–S2). The N-heterocycles from
370 GUA+DMB+AN include $\text{C}_6\text{H}_6\text{N}_4$ (#41; Table S3), which may be 2,2'-biimidazole (BI), a reaction product from glyoxal +
371 reduced nitrogenous compounds (e.g., ammonium salts) (De Haan et al., 2009; Galloway et al., 2009; Nozière et al., 2009;
372 Shapiro et al., 2009; Yu et al., 2011; Kampf et al., 2012; Gen et al., 2018; Mabato et al., 2019). The nitrated products include
373 $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3$ and $\text{C}_{15}\text{H}_{10}\text{N}_4\text{O}_3$ (#42 and 49; Table S3), which possibly have a nitrated imidazole moiety and a nitrophenol
374 moiety, respectively. For GUA+VL+AN, oligomers ($\text{C}_{14}\text{H}_{12}\text{O}_6$ and $\text{C}_{20}\text{H}_{16}\text{O}_7$; #55 and 59, Table S4) which were not among
375 the major products in GUA+VL were noted. $\text{C}_{10}\text{H}_8\text{O}_2$ likely has a furanone group (#50; Table S4); furanones are the primary
376 products of the reaction of $\cdot\text{OH}$ with toluene and other aromatic hydrocarbons (Smith et al., 1999). Moreover, $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_3$
377 (#57; Table S4) has a nitrated imidazole moiety. Among the N-containing compounds in GUA+AN is $\text{C}_4\text{H}_3\text{N}_3\text{O}_3$ (#69; Table
378 S5), which may be a nitrated imidazole-2-carboxaldehyde. Imidazole-2-carboxaldehyde is also a reaction product from
379 glyoxal + reduced nitrogenous compounds (e.g., ammonium salts) (De Haan et al., 2009; Galloway et al., 2009; Nozière et
380 al., 2009; Shapiro et al., 2009; Yu et al., 2011; Kampf et al., 2012; Gen et al., 2018; Mabato et al., 2019).

381 The $\langle\text{O:C}\rangle$ for GUA+DMB+AN and GUA+VL+AN were lower than those in the absence of AN (Table 1), possibly
382 due to the formation of N-heterocycles, altering the elemental ratios. The $\langle\text{O:C}\rangle$ and $\langle\text{H:C}\rangle$ were comparable in
383 GUA+DMB+AN and GUA+VL+AN, but the $\langle\text{N:C}\rangle$ for the former was higher, implying a greater extent of reactions
384 involving AN. Relative to GUA+DMB+AN and GUA+VL+AN, GUA+AN had a higher $\langle\text{N:C}\rangle$, as can be expected given
385 that AN was the only oxidant source. The lower $\langle\text{OS}_c\rangle$ of GUA+DMB+AN and GUA+VL+AN compared to GUA+AN may
386 be attributed to triplet-initiated oxidation generating higher-molecular-weight products with less fragmentation compared to
387 $\cdot\text{OH}$ -mediated oxidation (Yu et al., 2014; Chen et al., 2020). Nonetheless, AN generally increased the $\langle\text{OS}_c\rangle$ for both
388 GUA+DMB and GUA+VL, with a more noticeable increase for the former, suggesting more oxidized products. Similarly, in
389 a previous work, the more oxygenated and oxidized aqSOA from the photo-oxidation of phenolic carbonyls in AN solutions
390 than in ammonium sulfate solutions has been ascribed to nitrate photolytic products promoting the reactions (Huang et al.,
391 2018). Furthermore, GUA+DMB+AN and GUA+VL+AN aqSOA had mainly similar features in the OS_c vs. n_c plots as
392 those observed in the absence of AN (Fig. S6). More information on van Krevelen diagrams (Figs. S5e–h and S9) and OS_c

393 vs. n_c plots (Figs. S6e–h and S10) for GUA+DMB+AN, GUA+VL+AN, and GUA+AN aqSOA are provided in the
394 Supplement (Sect. S7). In essence, AN had no significant effect on the decay kinetics ascribable to photosensitizer chemistry
395 prevailing over nitrate, but it induced the formation of N-containing products. Moreover, AN modified the product
396 distributions, albeit in different ways (Figs. 2 and 3). In particular, N-containing products were more abundant in
397 GUA+DMB+AN, probably due to more extensive fragmentation in GUA+DMB than in GUA+VL. In GUA+VL+AN, AN
398 promoted oligomer formation likely via the -OH group of VL. Furthermore, GUA+DMB+AN and GUA+VL+AN had more
399 nitrated products than GUA+AN, suggesting that photosensitized reactions may promote nitrate photolysis-initiated
400 reactions.

401 3.2.3 Light absorption of aqSOA from photosensitization by $^3\text{DMB}^*$ and $^3\text{VL}^*$ in the presence of AN

402 The presence of AN also did not appreciably affect the absorbance enhancement and ΔR_{abs} for both GUA+DMB+AN and
403 GUA+VL+AN (Fig. 4). For GUA+DMB+AN, the N-containing products may have offset the decrease in oligomers to
404 maintain the absorbance enhancement observed from GUA+DMB. Wang et al. (2022) reported that nitration might
405 contribute significantly to absorbance enhancement for methoxyphenols in sodium nitrate. In GUA+VL+AN, the decrease in
406 monomers may have counteracted the increased oligomers and the generated N-containing products. Compared to
407 GUA+DMB+AN, the N-containing products from GUA+VL+AN probably had less impact on the absorbance enhancement
408 based on their smaller signal contribution.

409 Similar to experiments without AN, CHO species from GUA+DMB+AN and GUA+VL+AN were mainly
410 overlapped in the DBE vs. n_c space (Fig. S8c,d) and were mostly potential BrC chromophores. In both systems, GUA dimers
411 were the products with the highest relative abundance. For GUA+DMB+AN, products with high relative abundance also
412 include a CHN species, while two CHON species had high n_c (18,20) and DBE (16,14) values. In GUA+VL+AN, products
413 with high relative abundance include a CHON species ($n_c = 11$ and 9 DBE). Approximately 30% and 43% of the N-
414 containing products for GUA+DMB+AN and GUA+VL+AN, respectively, were among the potential BrC chromophores.
415 This suggests the possible significance of N-containing products for light absorption of aqSOA from photosensitization by
416 methoxybenzaldehydes and AN photolysis. Correspondingly, nitroaromatic compounds and N-heterocycles are frequently
417 noted in BBOA (Iinuma et al., 2010; Kitanovski et al., 2012; Kourtchev et al., 2016) and have been proposed to be potential
418 contributors to BrC light absorption (Laskin et al., 2015). Relative to GUA+DMB+AN and GUA+VL+AN, only 19% of the
419 N-containing products in GUA+AN were potential BrC chromophores (Fig. S8e,f), and these did not include CHN species.
420 These indicate that the N-containing products formed in the presence of both photosensitizers and AN may be more
421 significant contributors to the light absorption of phenolic aqSOA than those formed in AN only.

422 4 Conclusions and atmospheric implications

423 The photosensitized oxidation of guaiacol (GUA) by triplet excited states of 3,4-dimethoxybenzaldehyde ($^3\text{DMB}^*$) and
424 vanillin ($^3\text{VL}^*$) (separately) in the absence and presence of ammonium nitrate (AN) were compared under identical
425 conditions (simulated sunlight and reactants concentration) relevant to atmospheric cloud and fog waters. Compared to
426 GUA+VL, faster GUA oxidation and stronger light absorption by the products were observed in GUA+DMB. Moreover, VL
427 was consumed faster relative to DMB, limiting the extent of GUA oxidation in GUA+VL. These differences are rooted in
428 DMB having a better photosensitizing ability than VL and the $-\text{OH}$ group of VL, making it more susceptible to oxidation
429 and more reactive towards electrophilic aromatic substitution. Both GUA+DMB and GUA+VL generated aqSOA (including
430 potential BrC chromophores) composed of oligomers, functionalized monomers, oxygenated ring-opening products, and N-
431 containing products in the presence of AN. The major aqSOA formation processes for GUA+DMB and GUA+VL were
432 oligomerization and functionalization, but functionalization appeared to be more significant in GUA+VL due to VL
433 transformation products. The photochemical evolution of aqSOA from GUA+DMB has been reported by Yu et al. (2016).
434 Similar experiments for aqSOA from GUA+VL should be conducted in the future to better understand photosensitized
435 reactions involving phenolic carbonyl photosensitizers.

436 AN did not significantly affect the decay kinetics due to the predominant effect of $^3\text{DMB}^*$ and $^3\text{VL}^*$ chemistry
437 compared to nitrate, but it promoted the formation of N-containing products; these are composed of N-heterocycles (e.g.,
438 imidazoles) and oligomers and nitrated species. The observation of N-heterocycles agrees with our previous findings that
439 ammonium participates in photosensitized oxidation of phenolic compounds in the presence of AN (Mabato et al., 2022).
440 These results also suggest that photosensitized oxidation of phenolic compounds in the presence of AN might be an
441 important source of N-heterocycles and nitrated products. Identifying the sources of N-heterocycles and nitrated compounds
442 is important due to their environmental and health impacts (Laskin et al., 2009). Moreover, photosensitized reactions by non-
443 phenolic and phenolic methoxybenzaldehydes may be differently influenced by AN photolysis. For instance, the more
444 extensive fragmentation in GUA+DMB than in GUA+VL possibly resulted in more N-containing products in
445 GUA+DMB+AN. Furthermore, the increased oligomers in GUA+VL+AN may be due to VL-derived phenoxy radicals
446 induced by $\cdot\text{OH}$ or $\cdot\text{NO}_2$ from nitrate photolysis. In addition, more nitrated compounds observed in GUA+DMB+AN and
447 GUA+VL+AN than in GUA+AN imply that photosensitized reactions may promote nitrate-mediated photolytic reactions.
448 On a related note, the significance of photosensitization by BrC (via formation of solvated electrons; Y. Wang et al., 2021)
449 and marine dissolved organic matter (via $\text{O}_2^{\cdot-}$ formation; Garcia et al., 2021) in enhanced nitrite production from nitrate
450 photolysis have been reported. A recent study from our group has shown that glyoxal photo-oxidation mediated by both
451 nitrate photolysis and photosensitization can significantly enhance the atmospheric sink of glyoxal (Zhang et al., 2022).
452 Further studies are needed to improve our understanding of the interplay between photosensitized reactions and nitrate
453 photolysis.

454 This study demonstrates that the structural features of photosensitizers affect aqSOA formation via non-carbonyl
455 phenol oxidation. The VL results are broadly relevant to other phenolic carbonyls, but the effects of different functional
456 groups should still be considered. For instance, the aldehyde/ketone pair of syringaldehyde and acetosyringone, both
457 phenolic carbonyls, have been reported to have equal reactivity towards direct photosensitized oxidation. This is due to the
458 greater light absorption by the aldehyde form but higher quantum efficiency for loss for the ketone form (Smith et al. 2016).
459 However, more aqSOA was observed from syringaldehyde than acetosyringone (in either AN or ammonium sulfate; Huang
460 et al., 2018). Our findings also imply that while the contributions of photosensitization by ³VL* (and other phenolic
461 carbonyls with similar photosensitizing abilities) to aqSOA formation would be relatively less compared to that of ³DMB*
462 (and other non-phenolic carbonyls with similar photosensitizing abilities), these are not negligible. As both non-phenolic and
463 phenolic carbonyls such as the methoxybenzaldehydes examined in this work are emitted in large amounts from biomass
464 burning, future experiments should probe the aqSOA contribution of a wider variety of photosensitizers. Moreover, further
465 experiments on photosensitized reactions in authentic particulate matter (PM) samples should be conducted in the future.
466 Multicomponent reactions such as GUA+DMB+AN and GUA+VL+AN should also be explored for a more accurate
467 simulation of ambient conditions. These would be useful in assessing the overall impact of photosensitized reactions and AN
468 photolysis on aqSOA formation in areas impacted by biomass burning and high AN concentrations, and for their better
469 representation in aqSOA models.

470

471 *Data availability.*

472 The data used in this publication are available to the community and can be accessed by request to the corresponding author.

473 *Author contributions.*

474 BRGM designed and conducted the experiments; BRGM and CKC wrote the paper. All co-authors contributed to the
475 discussion of the manuscript.

476 *Competing interests.*

477 The authors declare that they have no conflict of interest.

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922 **Table 1.** Reaction conditions, initial GUA (and DMB or VL) decay rate constants, normalized abundance of products,
 923 average elemental ratios, and average carbon oxidation state ($\langle \text{OS}_C \rangle$) in each experiment. The reaction systems consisted of
 924 GUA (0.1 mM), DMB (0.01 mM), VL (0.01 mM), and AN (1 mM) under air-saturated conditions after 180 min of simulated
 925 sunlight irradiation. The UHPLC-HESI-Orbitrap-MS data were obtained in both positive (POS) and negative (NEG) ion
 926 modes.
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Exp no.	Reaction conditions	Initial GUA (and DMB or VL) decay rate constants ($\text{min}^{-1}/\text{s}^{-1}$) ^a	Normalized abundance of products ^b	Normalized abundance of N-containing compounds ^b	$\langle \text{O:C} \rangle^c$	$\langle \text{H:C} \rangle^c$	$\langle \text{N:C} \rangle^c$	$\langle \text{OS}_C \rangle^c$
1	GUA+DMB	GUA: 6.3 ± 0.25 DMB: 0.78 ± 0.10	376 \pm 22	NA	POS: 0.34	0.91	NA	-0.22
					NEG: 0.40	0.94	NA	-0.15
2	GUA+DMB+AN	GUA: 5.3 ± 0.50 DMB: 0.69 ± 0.052	310 \pm 4	114	POS: 0.28	0.94	0.12	-0.03
					NEG: 0.37	0.91	0.04	-0.05
3	GUA+VL	GUA: 1.5 ± 0.14 VL: 3.6 ± 0.55	94 \pm 5	NA	POS: 0.41	0.91	NA	-0.10
					NEG: 0.40	0.94	NA	-0.14
4	GUA+VL+AN	GUA: 1.6 ± 0.12 VL: 2.9 ± 0.032	100 \pm 2	8	POS: 0.31	1.02	0.02	-0.34
					NEG: 0.39	0.91	0.03	-0.02
5	GUA+AN	0.57 ± 0.036	23 \pm 1	9	POS: 0.35	0.99	0.16	0.19
					NEG: 0.38	1.01	0.05	-0.08

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929 ^aThe data fitting was performed in the initial linear region. Each value is the average of results from triplicate experiments,
 930 corrected for internal light screening due to DMB, VL, and AN, and normalized to the experimental photon flux. Errors
 931 represent one standard deviation. ^bThe normalized product abundance was calculated using the data from UHPLC-HESI-
 932 Orbitrap-MS in the positive (POS) ion mode as the GUA signal from the negative (NEG) ion mode was weak, which may
 933 introduce significant uncertainties during normalization. The uncertainties were propagated from the changes in [GUA]
 934 measured using UHPLC-PDA and the MS signal intensities. The samples for experiments without AN (marked with NA)
 935 were not analyzed for N-containing compounds. ^cThe average elemental ratios ($\langle \text{O:C} \rangle$, $\langle \text{H:C} \rangle$, and $\langle \text{N:C} \rangle$) and $\langle \text{OS}_C \rangle$ were
 936 based on the UHPLC-HESI-Orbitrap-MS results and estimated using the signal-weighted method (Bateman et al., 2012).
 937 The OS_C of GUA, DMB, and VL are -0.57, -0.44, and -0.25, respectively.

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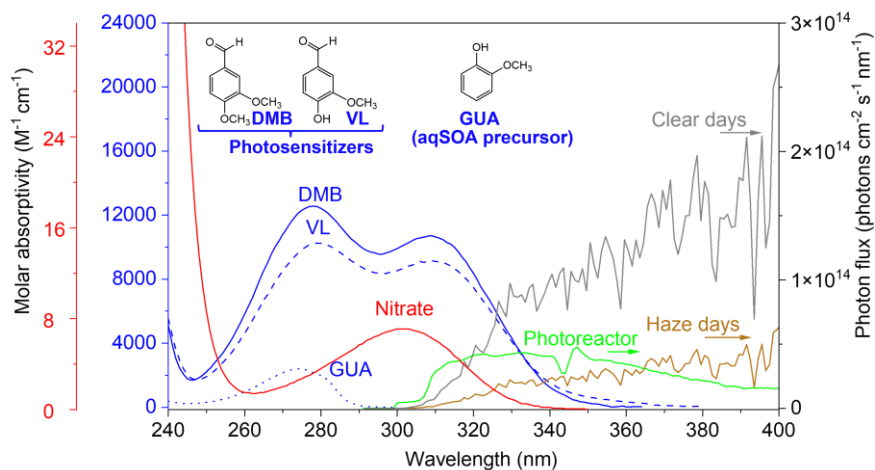
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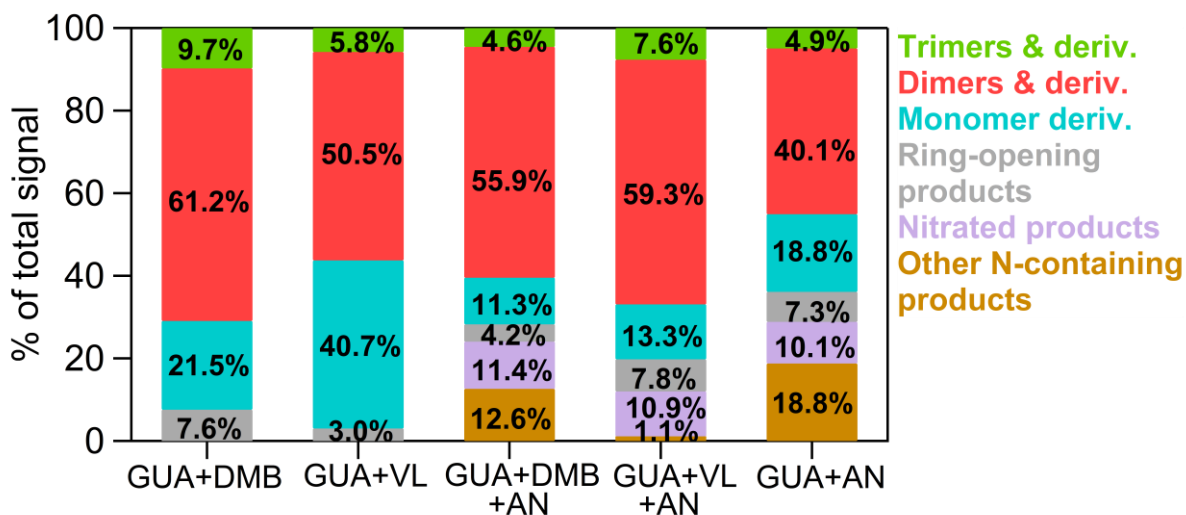
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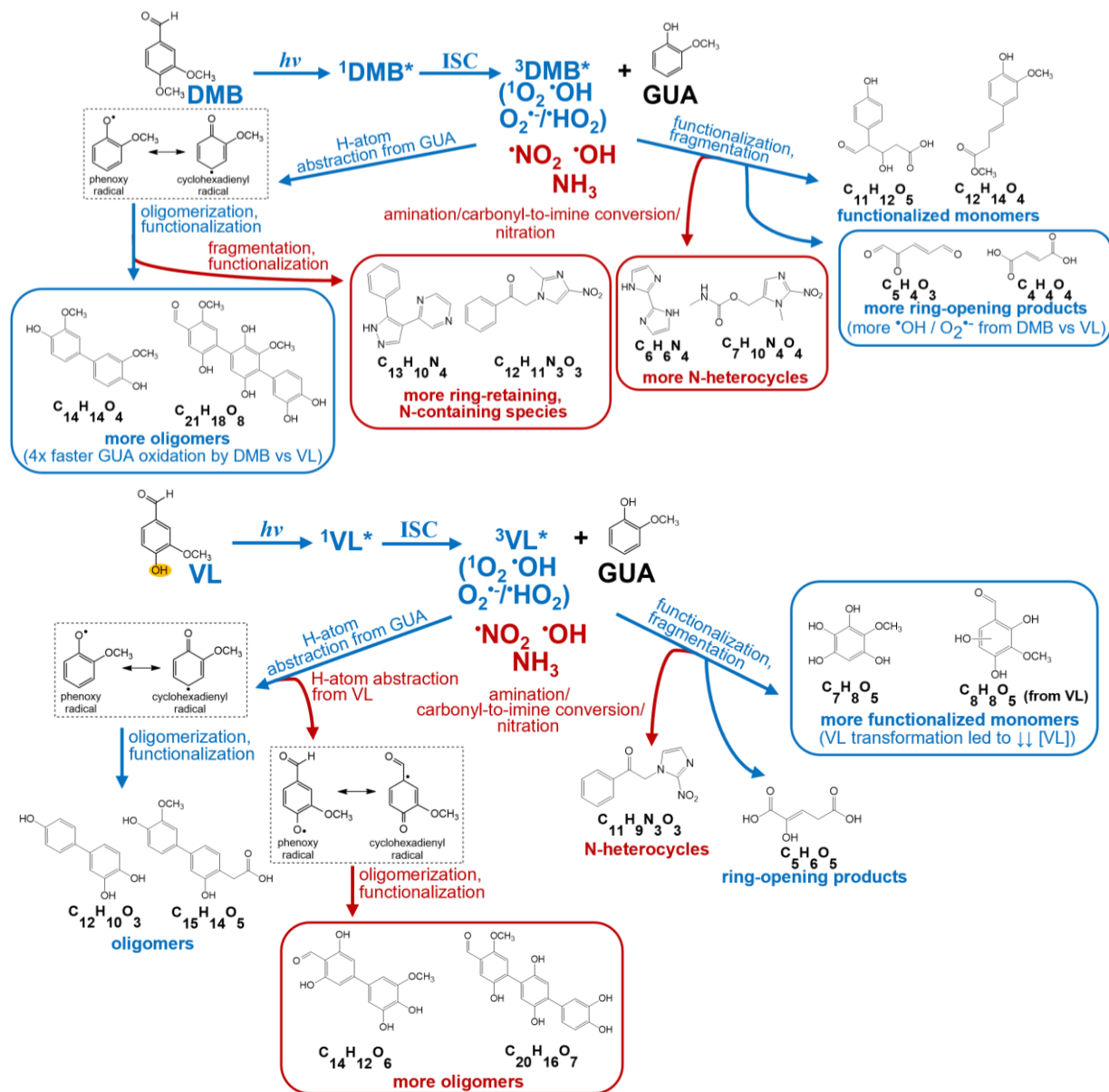
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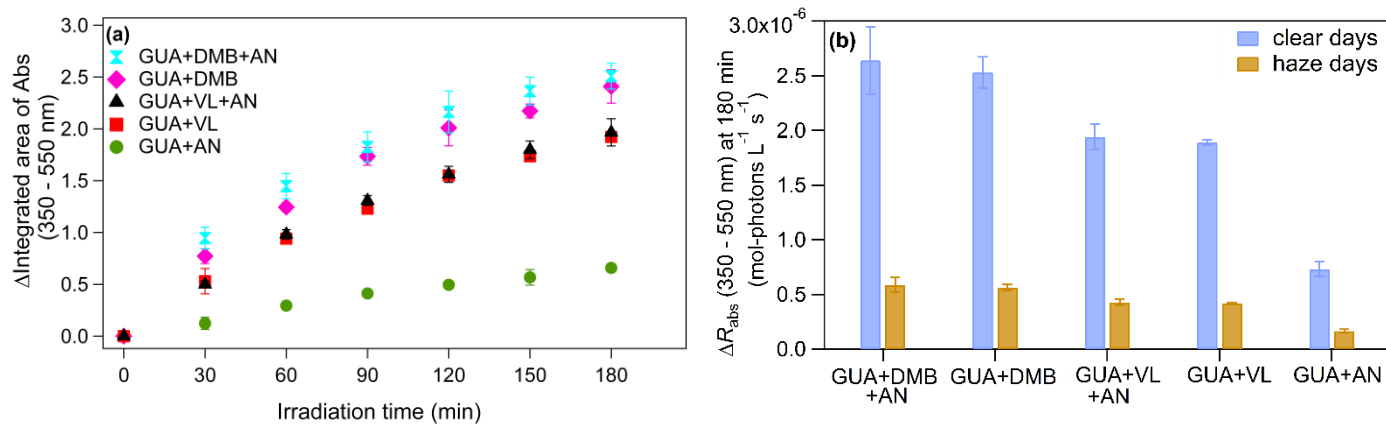
956 **Figure 1.** The base-10 molar absorptivities ($M^{-1} \text{ cm}^{-1}$) of 3,4-dimethoxybenzaldehyde (DMB, blue solid line), vanillin (VL, 957 blue dashed line), guaiacol (GUA, blue dotted line), and nitrate (red solid line). The green line is the photon flux in the 958 aqueous photoreactor. The gray and brown lines are the photon fluxes on typical clear and haze days, respectively, in 959 Beijing, China (Mabato et al., 2022). The top of the figure also shows the structures of DMB, VL, and GUA.



960 **Figure 2.** Signal-weighted distributions of aqSOA from GUA+DMB, GUA+VL, GUA+DMB+AN, GUA+VL+AN, and 961 GUA+AN. These product distributions were calculated from combined UHPLC-HESI-Orbitrap-MS data obtained in positive 962 (POS) and negative (NEG) ion modes. The values indicate the contribution of different product classifications to the total 963 signals for each reaction condition.



964 **Figure 3.** Summary of the main differences between photosensitized GUA oxidation by $^3\text{DMB}^*$ (top) and $^3\text{VL}^*$ (bottom) in
 965 the absence (blue labels and boxes) and presence (red labels and boxes) of ammonium nitrate at pH 4 under air-saturated
 966 conditions. Boxed structures indicate product classifications with notable differences. DMB and VL absorb light and are
 967 promoted to their singlet excited states ($^1\text{DMB}^*$ and $^1\text{VL}^*$), which then undergo intersystem crossing (ISC) to form $^3\text{DMB}^*$
 968 and $^3\text{VL}^*$. Secondary oxidants ($^1\text{O}_2$, $\text{O}_2^{\cdot-}/\text{HO}_2$, $\cdot\text{OH}$) can be formed from $^3\text{DMB}^*$ and $^3\text{VL}^*$ upon reactions with O_2 and GUA
 969 (George et al., 2018; Chen et al., 2020; Misovich et al., 2021; Mabato et al., 2022). The structures shown are examples of the
 970 major products (Tables S1 to S4) for different product classifications.



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