

Author Response for “Aqueous SOA formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate” by Mabato et al.

We thank the reviewers for the thorough review and many constructive comments that helped improve the manuscript. The major issues identified during the review are as follows: (1) focus of the study, (2) uncertainties for the normalized abundance of products, and (3) speculative discussions due to the lack of detailed reaction mechanisms and kinetic model analysis. Below are our overall responses to these, followed by our point-by-point responses to the reviewers' comments (changes to the second version of the manuscript and supporting information are in red, moved content in double-line strikethrough, and removed content in strikethrough). Please note that the line numbers in the responses refer to our revised manuscript with tracked changes.

(1) First, we have revised the title to ‘Aqueous SOA formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate’ to reflect the focus of this study. We have also removed the guaiacol + nitrate experiments to avoid distracting the readers from the main objectives of the paper. The novelty of the paper includes the (a) evaluation of aqSOA formation from the direct photosensitized oxidation of a triplet precursor (vanillin, VL, a phenolic aromatic carbonyl) alone (VL\*) and in the presence of ammonium nitrate (VL+AN) based on VL decay kinetics, detected products, and light absorbance changes, (b) investigation of the effects of different reaction conditions (air- vs. N<sub>2</sub>-saturated experiments, solution pH, and reactants concentration and molar ratios) on aqSOA formation, and (c) assessment of aqSOA formation from the oxidation of guaiacol, a non-carbonyl phenol, via photosensitized reactions of VL.

(2) Moreover, the rationale and purpose of using the normalized abundance of products were already stated in the previous version of the manuscript. The comparisons of peak abundance in mass spectrometry have been used in many recent studies (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 (Wang et al., 2021). Also, the assumption of equal ionization efficiency for calculating the normalized abundance of products is commonly used to estimate O:C ratios of SOA (e.g., Bateman et al., 2012; Lin et al., 2012; Laskin et al., 2014; De Haan et al., 2019). In the revised version, we emphasize the uncertainties associated with the normalized abundance of products due to the variability in ionization efficiencies for various compounds. Despite the intrinsic uncertainties, the normalized abundance of products enables a semi-quantitative analysis that gives an overview of how the signal intensities (extracted ion chromatogram peak areas from UHPLC-qToF-MS) changed under different experimental conditions. In addition, the use of the more common ‘relative abundance’ (product peaks are normalized to the highest peak) (e.g., Lee et al., 2014; Romonosky et al., 2017; Fleming et al., 2018; Klodt et al., 2019) would yield the same major products determined using the normalized abundance of products and maintain the conclusions of this work. This demonstrates the usefulness of the normalized abundance of products for comparisons among different experimental conditions.

(3) Lastly, there are not enough experimental results on the reactive intermediates in this study to provide detailed mechanisms without being speculative and to build a kinetic model. Further work is needed to exclude all other possibilities, and hence we are on the conservative side. Regardless, the discussions in this study were supported by our results and compared with previous studies.

## References

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

De Haan, D.O., Pajunoja, A., Hawkins, L. N., Welsh, H.G., Jimenez, N. G., De Loera, A., Zauscher, M., Andretta, A. D., Joyce, B. W., De Haan, A. C., Riva, M., Cui, T., Surratt, J. D., Cazaunau, M., Formenti, P., Gratien, A., Pangui, E., and Doussin, J-F.: Methylamine's effects on methylglyoxal-containing aerosol: chemical, physical, and optical changes, *ACS Earth Space Chem.*, 3, 1706–1716, <https://doi.org/10.1021/acsearthspacechem.9b00103>, 2019.

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

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

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

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

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

Ning, C., Gao, Y., Zhang, H., Yu, H., Wang, L., Geng, N., Cao, R., and Chen, J.: Molecular characterization of dissolved organic matters in winter atmospheric fine particulate matters (PM<sub>2.5</sub>) from a coastal city of northeast China, *Sci. Total Environ.*, 689, 312–321, <https://doi.org/10.1016/j.scitotenv.2019.06.418>, 2019.

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

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

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

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

### Reviewer 3

The authors have addressed some of the major comments and questions and the paper has improved upon revision. However, I think this manuscript still fails to address the following important issues. Though the topic is very interesting, this manuscript doesn't tell a very clear and nice story that meets the requirements of ACP.

1. The novelty of this study is that it characterized the product compositions and light absorbance changes. However, it failed to show a link between the observed changes in the chemical composition among different experiments (e.g. more oligomers, functionalized monomers, nitration) and the changes in light absorbance. The authors replied in the final response "However, it is possible that the products detected using UHPLC-qToF-MS in positive ESI mode might not have contributed significantly to all products formed and hence may not be the primary contributors to the absorbance enhancement.", but meanwhile they got the conclusion that "The majority of the most abundant products from both VL photo-oxidation pathways were potential Brown carbon (BrC) chromophores.". In Fig. S11, they showed the major compounds from pH 4 experiments under air-saturated conditions are potential BrC compounds, including both monomers and oligomers, compounds with and without N. However, this doesn't help to explain the differences in light absorption under different experimental conditions (Fig. 3).

Response: Thank you for your comment. The main novelty of this study is the investigation of aqSOA formation from the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate. The reactions were characterized based on VL decay kinetics, detected products, and light absorbance changes. As mentioned in lines 189-190, 'the major products detected in this study are probably those with high concentration or high ionization efficiency in the positive ESI mode.' Based on this, the products detected using UHPLC-qToF-MS in positive ESI mode might not have contributed significantly to the total products formed and hence may not be the primary contributors to the absorbance enhancement. In other words, the absorbance enhancement may not necessarily correlate directly with the products detected.

Correlating speciated chromophores with absorbance changes may be useful in demonstrating how aqSOA influence the Earth's radiative balance and identifying chemical reactions that can affect the overall light absorption by aqSOA. This can be accomplished by using liquid chromatography coupled with photodiode array (PDA) detector and high-resolution mass spectrometry (LC/PDA/HRMS platform) (e.g., Lin et al., 2017; Jiang et al., 2021; Misovich et al., 2021). In our experiments, VL (and GUA) concentration measurements, product characterization, and absorbance measurements were performed using UHPLC-PDA, UHPLC-qToF-MS, and UV-Vis spectrophotometry, respectively. A similar approach is then possible using the current methods in this work by matching the retention time (RT) of the products detected using UHPLC-qToF-MS with that in the PDA. However, the concentration of the chromophores in this study is below the detection limit of the PDA based on the lack of distinct PDA signals from the products. Nonetheless, the overall light absorbance changes

were characterized by integrating the area of absorbance from 350 to 550 nm to incorporate all light-absorbing compounds. Fig. S11 was used to show that majority of the detected products (50 most abundant products) from pH 4 experiments were potential BrC chromophores. The differences in the light absorbance changes under different experimental conditions (Fig. 3) were discussed in lines 321-360 for VL photo-oxidation under N<sub>2</sub> and air-saturated conditions, lines 411-418 for VL photo-oxidation under varying pH conditions, and lines 540-543 for oxidation of guaiacol by photosensitized reactions of VL, next to the discussions for detected products and their normalized abundance. Overall, we agree with the reviewer that it would be interesting and valuable to examine and identify the specific BrC chromophores responsible for the changes in the optical properties, unfortunately, this is an experimental limitation for the current work. Changes in the text and clarifications regarding these are as follows:

Lines 325-344: For both VL\* and VL+AN, evident absorbance enhancement was observed under air-saturated conditions, while the absorbance changes under N<sub>2</sub>-saturated conditions were minimal, consistent with the VL decay trends. **Dimers and functionalized products have been shown to contribute to chromophore formation for the aqueous photo-oxidation of guaiacyl acetone (another aromatic phenolic carbonyl) by <sup>3</sup>DMB\* (Jiang et al., 2021). Based on this, the higher normalized abundance of** ~~This absorbance enhancement can be explained by the formation of oligomers, which~~ **have large, conjugated  $\pi$ -electron systems (Chang and Thompson, 2010), and hydroxylated products (Li et al., 2014; Zhao et al., 2015), in agreement with the observed reaction products** ~~observed under air-saturated conditions have contributed to the absorbance enhancement. However, it is worth noting that the products detected may not have contributed significantly to the total products formed and hence may not be the primary contributors to the absorbance enhancement. As mentioned earlier, the major products detected in this study are probably those with high concentration or high ionization efficiency in the positive ESI mode. In other words, the absorbance enhancement may not necessarily correlate directly with the products detected.~~

Correlating speciated chromophores with absorbance changes may be useful in demonstrating how aqSOA influence the Earth's radiative balance and identifying chemical reactions that can affect the overall light absorption by aqSOA. This can be accomplished by using liquid chromatography coupled with photodiode array (PDA) detector and high-resolution mass spectrometry (LC/PDA/HRMS platform) (e.g., Lin et al., 2017; Jiang et al., 2021; Misovich et al., 2021). In our experiments, VL (and GUA) concentration measurements, product characterization, and absorbance measurements were performed using UHPLC-PDA, UHPLC-qToF-MS, and UV-Vis spectrophotometry, respectively. A similar approach is then possible using the current methods in this work by matching the retention time (RT) of the products detected using UHPLC-ToF-MS with that in the PDA. However, the concentration of the chromophores in this study is below the detection limit of the PDA based on the lack of distinct PDA signals from the products.

2. The addition of guaiacol (as another non-carbonyl phenol) oxidation experiments doesn't help a lot with the topic of this manuscript. The major conclusion from this part (as written in the abstract) is "guaiacol oxidation by photosensitized reaction of VL is less efficient relative to nitrate-mediated photo-oxidation." As claimed by the authors in the final response:

“However, we did not intend to compare  $^3\text{VL}^*$  and nitrated-mediated pathways either”, why did they compare the efficiency of photosensitized reaction of VL with nitrated-mediated photo-oxidation of guaiacol?

Response: Thank you for pointing this out. We apologize for the confusion. As stated in lines 495-498: ‘The oxidation of phenols by  $^3\text{C}^*$  has been mainly studied using non-phenolic aromatic carbonyls (Anastasio et al., 1997; Smith et al., 2014, 2015; Yu et al., 2014; Chen et al., 2020) and aromatic ketones (Canonica et al., 2000) as triplet precursors. Recently,  $^3\text{VL}^*$  has also been shown to oxidize syringol (Smith et al., 2016), a non-carbonyl phenol, although the reaction products remain unknown.’ The guaiacol experiments were added to examine the formation of aqSOA from guaiacol oxidation via VL photosensitized reactions. Indeed, we did not intend to compare  $^3\text{VL}^*$  and nitrated-mediated pathways in this study. The primary objective of this study is to investigate aqSOA formation from the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate. To reflect the focus of the paper, we have revised the title to ‘Aqueous SOA formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate’. Also, to avoid distracting the readers from the main objectives of the paper, guaiacol + nitrate experiments have been removed from the manuscript. Changes in the text are as follows:

Abstract: Vanillin (VL), a phenolic aromatic carbonyl abundant in biomass burning emissions, forms triplet excited states ( $^3\text{VL}^*$ ) under simulated sunlight leading to aqueous secondary organic aerosol (aqSOA) formation. Nitrate and ammonium are among the main components of biomass burning aerosols and cloud/fog water. Under atmospherically relevant cloud and fog conditions, solutions composed of either VL only or VL with ammonium nitrate were subjected to simulated sunlight irradiation to compare aqSOA formation via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate. The reactions were characterized. This direct photosensitized oxidation of VL was compared with nitrate-mediated VL photo-oxidation under atmospherically relevant cloud and fog conditions through by examining the VL decay kinetics, product compositions, and light absorbance changes. The majority of the most abundant products from both VL photo-oxidation pathways were potential Brown carbon (BrC) chromophores. In addition, both pathways conditions generated oligomers, functionalized monomers, and oxygenated ring-opening products, and ammonium but nitrate promoted functionalization and nitration, which can be ascribed likely due to its photolysis products ( $^{\bullet}\text{OH}$ ,  $^{\bullet}\text{NO}_2$ , and  $\text{N(III)-NO}_2^-$  or HONO). Moreover, a potential imidazole derivative observed from nitrate-mediated VL photo-oxidation in the presence of ammonium nitrate suggested that ammonium may be involved participated in the reactions. The majority of the most abundant products from both conditions were potential Brown carbon (BrC) chromophores. The effects of oxygen ( $\text{O}_2$ ), pH, and reactants concentration and molar ratios on VL photo-oxidation the reactions were also explored. Our findings show that  $\text{O}_2$  plays an essential role in VL photo-oxidation the reactions and oligomer formation was enhanced at  $\text{pH} < 4$ . Also, functionalization was dominant at low VL concentration, whereas oligomerization was favored at high VL concentration. Furthermore, oligomers and hydroxylated products were detected from the oxidation of comparisons of the apparent quantum efficiency of guaiacol (a non-carbonyl phenol) via VL photosensitized

reactions photodegradation indicate that in this study, guaiacol oxidation by photosensitized reactions of VL is less efficient relative to nitrate-mediated photo-oxidation. Lastly, potential aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate VL photo-oxidation were proposed. This study indicates that the direct photosensitized oxidation of VL and nitrate-mediated VL photo-oxidation may be an important aqSOA sources in areas influenced by biomass burning emissions and underscores the importance of nitrate in the aqueous-phase processing of aromatic carbonyls.

Lines 89-122: Nitrate and ammonium are also among the main biomass burning aerosol components (Xiao et al., 2020; Zielinski et al., 2020). As BB aerosols are typically internally mixed with other aerosol components (Zielinski et al., 2020), VL may coexist with ammonium nitrate in BB aerosols. The aqueous-phase photo-oxidation direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate may then reveal insights into the atmospheric processing of BB aerosols. Moreover, the  $^3C^*$  of non-phenolic aromatic carbonyls (e.g., 3,4-dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the reaction products from the latter are unknown.

Previous works aqSOA formation via triplet-mediated oxidation are mostly based on reactions between phenols and a non-phenolic aromatic carbonyl as triplet precursor (e.g., Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021). Also, studies examining the effects of inorganic nitrate on aqSOA formation and properties remain limited. The present study aimed to evaluate aqSOA formation via the direct photosensitized oxidation of a triplet precursor (VL) alone. Furthermore, aqSOA formation via the direct photosensitized oxidation of VL in the presence of ammonium nitrate was also examined. Accordingly, the main goals of this study are (1) to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate, (2) to evaluate the influences of  $O_2$ , solution pH, and reactants concentration and molar ratios on the reactions, (3) to investigate the participation of ammonium in the direct photosensitized oxidation of VL in the presence of ammonium nitrate, and (4) to examine aqSOA formation from the oxidation of guaiacol, a non-carbonyl phenol, via photosensitized reactions of VL. To achieve these goals, solutions composed of either VL only or VL in the presence of ammonium nitrate were subjected to simulated sunlight irradiation under atmospherically relevant cloud and fog conditions. Solutions composed of VL in the presence of sodium nitrate were also examined for comparison with the presence of ammonium nitrate. To evaluate the potential significance of VL and its reactions with nitrate in aqSOA formation in cloud/fog water, we studied the direct photosensitized oxidation of VL and nitrate-mediated VL photo-oxidation under atmospherically relevant conditions. In this work, The reactions were characterized based on VL decay kinetics, detected products, and light absorbance changes, and. The influences of  $O_2$ , solution pH, and reactants concentration and molar ratios on these two photo-oxidation pathways were also assessed. The  $^3C^*$  of non-phenolic aromatic carbonyls (e.g., 3,4-dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the reaction products from the latter are unknown. We then examined the photo-oxidation of guaiacol, another

~~non-carbonyl phenol~~, in the presence of VL and compared it with nitrate-mediated photo-oxidation. Finally, we proposed aqSOA formation pathways via **the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate** ~~VL photo-oxidation~~. This work presents a comprehensive comparison of aqSOA formation from the **direct photosensitized oxidation of VL** ~~photo-oxidation in the absence and presence of ammonium nitrate~~ **by VL photosensitization and in the presence of inorganic nitrate**.

Lines 145-146: Moreover, ~~comparisons were made between~~ the photo-oxidation of guaiacol (GUA) (0.1 mM), a non-carbonyl phenol, in the presence of VL (0.1 mM) **was studied** ~~or AN (1 mM)~~.

Lines 211-213: In this work, the direct photosensitized oxidation of VL **in the absence** (VL only experiments) and ~~nitrate-mediated VL photo-oxidation~~ **presence of ammonium nitrate** are referred to as VL\* and VL+AN, respectively.

Lines 554-556: ~~In this study, shows that the photo-oxidation of VL via its~~ **the direct photosensitized reactions oxidation of VL in the absence and in the presence of ammonium nitrate under atmospherically relevant cloud and fog conditions have been shown to can** generate aqSOA composed of oligomers, functionalized monomers, oxygenated ring-opening products, and nitrated compounds (~~for nitrate-mediated reactions~~ **from VL+AN**).

#### **Minor comments:**

1. The updated explanation of pH-dependency of light absorbance is not clear to me. The pH range tested in this study was 2.5 – 4. In Fig. S10, the UV-Vis absorption spectra of VL\*-derived aqSOA didn't change between the pH range of 1.5 – 4, though the intensity of absorption at longer wavelengths significantly increased when the pH was higher than 5.5

Response: In Fig. S10, we showed the changes in the UV-Vis absorption spectra of the aqSOA formed from VL\* at pH 4 and 2.5 measured over a range of pH conditions from 1.5 to 10.5 to determine whether the observed pH dependence is due to the acid-base chemistry of the products or of the reactions. If the changes in the UV-Vis absorption spectra for the two solutions of varying pH are different, the pH dependence is due to different products formed from VL\* at pH 4 compared to pH 2.5. However, the comparable changes in the UV-Vis absorption spectra for the two solutions indicate that the observed pH dependence (Fig. 3b) may be attributed to the acid-base chemistry of the reactions, which may involve <sup>3</sup>VL\* or the excimer of VL (Smith et al., 2016). Changes in the text are as follows:

Lines 411-418: Higher absorbance enhancement for both VL\* and VL+AN (Fig. 3b) was observed as pH increased. To determine whether the pH dependence is due to the acid-base chemistry of the products or of the reactions, ~~we measured~~ **the changes in the UV-Vis absorption spectra** ~~pH-dependence of the aqSOA formed from VL\* at pH 4 and 2.5~~ **were measured** over a range of pH conditions from 1.5 to 10.5 (Fig. S10). For both cases, the intensity of absorption at longer wavelengths significantly increased as the pH of the solutions was raised. Moreover, the ~~comparable pH-dependence of~~ **changes in the UV-Vis absorption**



spectra for the two solutions of varying pH are comparable, suggesting that the observed pH dependence may be attributed to the is rooted in acid-base chemistry of the reactions involving, which may involve  $^3\text{VL}^*$  or the excimer of VL (Smith et al., 2016), as discussed earlier.

## References

Anastasio, C., Faust, B. C., and Rao, C. J.: Aromatic carbonyl compounds as aqueous-phase photochemical sources of hydrogen peroxide in acidic sulfate aerosols, fogs, and clouds. 1. Non-phenolic methoxybenzaldehydes and methoxyacetophenones with reductants (phenols), *Environ. Sci. Technol.*, 31, 218–232, <https://doi.org/10.1021/es960359g>, 1997.

Canonica, S., Hellrung, B., and Wirz, J.: Oxidation of phenols by triplet aromatic ketones in aqueous solution, *J. Phys. Chem*, 104, 1226–1232, <https://doi.org/10.1021/jp9930550>, 2000.

Chang, J. L. and Thompson, J. E.: Characterization of colored products formed during irradiation of aqueous solutions containing  $\text{H}_2\text{O}_2$  and phenolic compounds, *Atmos. Environ.*, 44, 541–551, <https://doi.org/10.1016/j.atmosenv.2009.10.042>, 2010.

Chen, Y., Li, N., Li, X., Tao, Y., Luo, S., Zhao, Z., Ma, S., Huang, H., Chen, Y., Ye, Z., and Ge, X.: Secondary organic aerosol formation from  $^3\text{C}^*$ -initiated oxidation of 4-ethylguaiacol in atmospheric aqueous-phase, *Sci. Total Environ.*, 723, 137953, <https://doi.org/10.1016/j.scitotenv.2020.137953>, 2020.

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

Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y., and Chan, C. K.: Aqueous-phase photochemical oxidation and direct photolysis of vanillin - a model compound of methoxy phenols from biomass burning, *Atmos. Chem. Phys.*, 14, 2871–2885, <https://doi.org/10.5194/acp-14-2871-2014>, 2014.

Lin, P., Bluvshstein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular chemistry of atmospheric brown carbon inferred from a nationwide biomass burning event, *Environ. Sci. Tech.*, 51, 11561–11570, <https://doi.org/10.1021/acs.est.7b02276>, 2017.

Misovich, M. V., Hettiyadura, A. P. S., Jiang, W., Zhang, Q., and Laskin, A.: Molecular-level study of the photo-oxidation of aqueous-phase guaiacyl acetone in the presence of  $^3\text{C}^*$ : formation of brown carbon products, *ACS Earth Space Chem.*, 5, 1983–1996, <https://doi.org/10.1021/acsearthspacechem.1c00103>, 2021.

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

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

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

Xiao, H.-W., Wu, J.-F., Luo, L., Liu, C., Xie, Y.-J., and Xiao, H.-Y.: Enhanced biomass burning as a source of aerosol ammonium over cities in Central China in autumn, *Environ. Pollut.*, **266**, art. no. 115278, <https://doi.org/10.1016/j.envpol.2020.115278>, 2020.

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

Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F., and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric brown carbon, *Atmos. Chem. Phys.*, **15**, 6087–6100, <https://doi.org/10.5194/acp-15-6087-2015>, 2015.

Zielinski, T., Bolzacchini, E., Cataldi, M., Ferrero, L., Graßl, S., Hansen, G., Mateos, D., Mazzola, M., Neuber, R., Pakszys, P., Posyniak, M., Ritter, C., Severi, M., Sobolewski, P., Traversi, R., and Velasco-Merino, C.: Study of chemical and optical properties of biomass burning aerosols during long-range transport events toward the Arctic in summer 2017, *Atmosphere*, **11**, 84, <https://doi.org/10.3390/atmos11010084>, 2020.

#### Reviewer 4

Mabato et al., studied the aqueous-phase photochemistry of vanillin (VN) in cloud/fog relevant conditions leading to aqSOA. They conducted two types of photochemistry, photolysis of VN and nitrate-mediated VN (irradiation of VN + Ammonium Nitrate mixture) and analyzed VN decay, product mass spectra, O<sub>2</sub>/pH/ammonium effects, and UV spectra for light absorbance of products. They indeed conducted full analyses of aqSOA chemistry. However, novel findings with compelling experimental evidence in this manuscript are not well written. Instead, their arguments are mostly speculative:

1. (a) The purpose of conducting two types of photochemistry is not clear. Didn't you compare the photolysis and OH-radical reactions of VN? Then, it is not clear how much of OH radical was generated in their condition. (b) According to Fig. S3 and also the main text, photochemistry by OH radical is negligible. Then, why not set the concentration of OH radical relevant to cloud/fog condition adjusting nitrate concentration, which can be obtained by a kinetic model based on decay rate of VN and table 1? (c) If the purpose is to study the nitration, then why was ammonium nitrate (AN) used? Ammonium clearly complicates the system. Since authors used sodium nitrate (SN), why did not authors conduct explicit comparison between AN and SN that could lead to chemical insights in the aqueous phase?

#### Response:

(a) In this work, we aimed to compare aqSOA formation in cloud/fog water via direct photosensitized oxidation of VL in the absence (VL\*) and presence of ammonium nitrate (VL+AN). The motivations for this are already stated in the introduction. From lines 83-89: 'Photodegradation kinetics and aqSOA yields have been reported for direct VL photodegradation under simulated sunlight (Smith et al., 2016), with oxygenated aliphatic-like compounds (high H:C,  $\geq 1.5$  and low O:C,  $\leq 0.5$  ratios) noted as the most likely products (Loisel et al., 2021). Additionally, aqueous-phase reactions of phenols with reactive nitrogen species have been proposed to be a significant source of nitrophenols and SOA (Grosjean, 1985; Kitanovski et al., 2014; Kroflič et al., 2015, 2021; Pang et al., 2019a; Yang et al., 2021). For instance, nitrite-mediated VL photo-oxidation can generate nitrophenols, and the reactions are influenced by nitrite/VL molar ratios, pH, and the presence of  $\cdot\text{OH}$  scavengers (Pang et al., 2019a).' The major group of products from the direct irradiation of VL (0.1 mM) (Loisel et al., 2021) has been reported to be mainly oxygenated aliphatic-like compounds, probably due to the use of ESI in the negative ion mode, which has higher sensitivity for detecting compounds such as carboxylic acids (Holčapek et al., 2010; Liigand et al., 2017), and solid-phase extraction (SPE) procedure causing the loss of some oligomers (LeClair et al., 2012; Zhao et al., 2013; Bianco et al., 2019). Moreover, nitrate and ammonium are also among the main biomass burning aerosol components (Xiao et al., 2020; Zielinski et al., 2020). As BB aerosols are typically internally mixed with other aerosol components (Zielinski et al., 2020), VL may coexist with ammonium nitrate in BB aerosols. The direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate may then reveal insights into the atmospheric processing of BB aerosols. These reactions were characterized based on VL decay kinetics, light absorbance changes, and detected products. Aside from reporting the most

abundant products, we also compared different reaction conditions using the normalized abundance of products. The addition of ammonium nitrate was not specifically to initiate  $\cdot\text{OH}$ -driven reactions, but rather to examine its effect on aqSOA formation from the direct photosensitized oxidation of VL. As mentioned in lines 244-246, 'Furthermore, while the irradiation of other phenolic compounds can produce  $\text{H}_2\text{O}_2$ , a precursor for  $\cdot\text{OH}$  (Anastasio et al., 1997), the amount of  $\text{H}_2\text{O}_2$  is small. Based on this, only trace amounts of  $\text{H}_2\text{O}_2$  were likely generated from VL\* (Li et al., 2014) under-air saturated conditions, suggesting that contribution from  $\cdot\text{OH}$  was minor.' Changes in the text are as follows:

Lines 76-122: Biomass burning (BB) is a significant atmospheric source of both phenolic and non-phenolic aromatic carbonyls (Rogge et al., 1998; Nolte et al., 2001; Schauer et al., 2001; Bond et al., 2004). Upon exposure to sunlight, aromatic carbonyls are excited to their triplet excited states, which can initiate oxidation leading to aqSOA formation (e.g., Smith et al., 2014; 2015, 2016). For An example is, vanillin (VL) (Henry's law constant of  $4.56 \times 10^5 \text{ M atm}^{-1}$ ; Yaws, 1994), a phenolic aromatic carbonyl that has been used as a model compound for methoxyphenols, which are abundant in BB emissions (Li et al., 2014; Pang et al., 2019a). The aqueous  $\cdot\text{OH}$  oxidation and direct photodegradation of VL, has have been shown to yield low-volatility products, although these findings were based on 254-nm irradiation (Li et al., 2014) via aqueous  $\cdot\text{OH}$  oxidation and direct photodegradation. Photodegradation kinetics and aqSOA yields have been reported for direct VL photodegradation under simulated sunlight (Smith et al., 2016), with oxygenated aliphatic-like compounds (high H:C,  $\geq 1.5$  and low O:C,  $\leq 0.5$  ratios) reported noted as the most likely products (Loisel et al., 2021). Additionally, aqueous-phase reactions of phenols with reactive nitrogen species have been proposed to be a significant source of nitrophenols and SOA (Grosjean, 1985; Kitanovski et al., 2014; Kroflič et al., 2015, 2021; Pang et al., 2019a; Kroflic et al., 2021; Yang et al., 2021). For instance, nitrite-mediated VL photo-oxidation can generate nitrophenols, and the reactions are influenced by nitrite/VL molar ratios, pH, and the presence of  $\cdot\text{OH}$  scavengers (Pang et al., 2019a). Nitrate and ammonium are also among the main biomass burning aerosol components (Xiao et al., 2020; Zielinski et al., 2020). As BB aerosols are typically internally mixed with other aerosol components (Zielinski et al., 2020), VL may coexist with ammonium nitrate in BB aerosols. The aqueous-phase photo-oxidation direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate may then reveal insights into the atmospheric processing of BB aerosols. Moreover, the  $^{13}\text{C}^*$  of non-phenolic aromatic carbonyls (e.g., 3-,4-dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the reaction products from the latter are unknown.

Previous works aqSOA formation via triplet-mediated oxidation are mostly based on reactions between phenols and a non-phenolic aromatic carbonyl as triplet precursor (e.g., Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021). Also, studies examining the effects of inorganic nitrate on aqSOA formation and properties remain limited. The present study aimed to evaluate aqSOA formation via the direct photosensitized oxidation of a triplet precursor (VL) alone. Furthermore, aqSOA formation via the direct photosensitized oxidation of VL in in

the presence of ammonium nitrate was also examined. Accordingly, the main goals of this study are (1) to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate, (2) to evaluate the influences of O<sub>2</sub>, solution pH, and reactants concentration and molar ratios on the reactions, (3) to investigate the participation of ammonium in the direct photosensitized oxidation of VL in the presence of ammonium nitrate, and (4) to examine aqSOA formation from the oxidation of guaiacol, a non-carbonyl phenol, via photosensitized reactions of VL. To achieve these goals, solutions composed of either VL only or VL in the presence of ammonium nitrate were subjected to simulated sunlight irradiation under atmospherically relevant cloud and fog conditions. Solutions composed of VL in the presence of sodium nitrate were also examined for comparison with the presence of ammonium nitrate. ~~To evaluate the potential significance of VL and its reactions with nitrate in aqSOA formation in cloud/fog water, we studied the direct photosensitized oxidation of VL and nitrate-mediated VL photo-oxidation under atmospherically relevant conditions. In this work, The reactions were characterized based on VL decay kinetics, detected products, and light absorbance changes, and. The influences of O<sub>2</sub>, solution pH, and reactants concentration and molar ratios on these two photo-oxidation pathways were also assessed. The <sup>3</sup>C\* of non-phenolic aromatic carbonyls (e.g., 3-4 dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the reaction products from the latter are unknown. We then examined the photo-oxidation of guaiacol, another non-carbonyl phenol, in the presence of VL and compared it with nitrate-mediated photo-oxidation. Finally, we proposed aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate-VL photo-oxidation. This work presents a comprehensive comparison of aqSOA formation from the direct photosensitized oxidation of VL photo-oxidation in the absence and presence of ammonium nitrate by VL photosensitization and in the presence of inorganic nitrate.~~

(b) In this study, we aimed to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate under atmospherically relevant cloud and fog conditions. The addition of ammonium nitrate was not specifically to initiate •OH-driven reactions but rather to examine its effect on aqSOA formation from the direct photosensitized oxidation of VL. Experiments using sodium nitrate were also performed for comparison with the presence of ammonium nitrate and confirm the participation of ammonium in the reactions. As mentioned in lines 139–144, ‘Although the concentration of VL in cloud/fog water has been estimated to be < 0.01 mM (Anastasio et al., 1996, 1997), a higher VL concentration (0.1 mM) was used in this study to guarantee sufficient signals for product identification (Vione et al., 2019). The chosen ammonium nitrate (AN) or sodium nitrate (SN) concentration (1 mM) was based on values observed in cloud and fog water (Munger et al., 1983; Collett et al., 1998; Zhang and Anastasio, 2003; Li et al., 2011; Giulianelli et al., 2014; Bianco et al., 2020). It should be noted that this study is not intended to identify the concentrations of ammonium nitrate that would affect the kinetics.’ Additional text are as follows:

Lines 143-145: It should be noted that this study is not intended to identify the concentrations of ammonium nitrate that would affect the kinetics but to examine the effect of ammonium nitrate on aqSOA formation from the direct photosensitized oxidation of VL.

(c) Thank you for pointing this out. The main objective of this study is to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate under atmospherically relevant cloud and fog conditions. Inorganic salts such as ammonium nitrate are major components of aerosols and cloud/fog water. Based on these, we chose AN as the nitrate source in our experiments. We aimed to investigate aqSOA formation from these reactions in general, and not being necessarily focused on nitration. For instance, ammonium ( $\text{NH}_4^+$ ) can react with carbonyls producing light-absorbing compounds and highly oxygenated oligomers, as well as catalyze different reactions (De Haan et al., 2009, 2011; Nozière et al., 2009, 2010, 2018; Shapiro et al., 2009; Yu et al., 2011; Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabato et al., 2019). Our findings indicate the participation of ammonium in the reactions based on the detection of a potential imidazole derivative from VL+AN experiment at pH 4. In addition to N-containing compounds, the addition of nitrate also resulted in the formation of more functionalized monomers, as well as  $\text{C}_8\text{H}_9\text{NO}_3$  which is likely an aminophenol (VL\* vs. VL+AN under  $\text{N}_2$ -saturated conditions). We also did parallel experiments with SN (VL+SN at pH 4 under air-saturated conditions) to confirm the participation of ammonium in the photosensitized oxidation of VL in the presence of ammonium nitrate. We have performed kinetics and absorbance measurements for VL+SN as well, and the results were similar with those for VL+AN. We have now added this in the discussion. Comparisons between VL+AN and VL+SN at pH 4 in terms of reaction products and oxidative characteristics were already provided in section 3.1.3. Changes in the text as follows:

Lines 419-438: ~~3.3 Participation of ammonium in the aqueous photo-oxidation of vanillin~~  
**3.1.3 Participation of ammonium in the direct photosensitized oxidation of VL in the presence of AN**

Ammonium salts are an important constituent of atmospheric aerosols particles (Jimenez et al., 2009), and reactions between dicarbonyls (e.g., glyoxal) and ammonia or primary amines have been demonstrated to form BrC (De Haan et al., 2009, 2011; Nozière et al., 2009; Shapiro et al., 2009; Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabato et al., 2019). Imidazole and imidazole derivatives ~~are~~ have been reported to be the major products of glyoxal and ammonium sulfate reactions at pH 4 (Galloway et al., 2009; Yu et al., 2011; Sedehi et al., 2013; Gen et al., 2018; Mabato et al., 2019). Here, we compared VL+AN and VL+SN at pH 4 ~~under air-saturated conditions in terms of reaction products and oxidative characteristics~~ to confirm the participation of ammonium in the ~~aqueous photo-oxidation~~ photosensitized oxidation of VL. ~~The presence of ammonium did not appear to influence the kinetics of VL decay and light absorbance changes based on VL+AN and VL+SN having no statistically significant difference ( $p > 0.05$ ) with respect to VL decay rate constants (Table 2) and yielding comparable absorbance enhancement (Fig. 3a), respectively. However, it is important to note that this may not be the case for lower concentrations of VL. As previously~~

stated, the reactions in this study were dominated by  $^3\text{VL}^*$  chemistry, likely due to the higher molar absorptivity of VL than that of nitrate and the high VL concentration used. Similarly, the normalized abundance of the products was comparable in both experiments (A7 and A9; Table 2), with  $\text{C}_{10}\text{H}_{10}\text{O}_5$  (No. 54, Table S2) as the most abundant product (Figs. 1d and S6a), but in VL+SN, there was a significant amount of a VL dimer ( $\text{C}_{15}\text{H}_{12}\text{O}_8$ ; No. 108, Table S2). The normalized abundance of N-containing compounds was also similar for VL+AN and VL+SN but the ~~Moreover, the detected nitrogen~~ N-containing compounds were distinct. Aside from the potential imidazole derivative ( $\text{C}_5\text{H}_5\text{N}_3\text{O}_2$ ; No. 65, Table S2),  $\text{C}_8\text{H}_9\text{NO}_3$  (No. 32, Table S2), possibly an aminophenol, was also observed from VL+AN but only under  $\text{N}_2$ -saturated conditions (Fig. 1b), probably due to further oxidation by  $^3\text{VL}^*$ . Relative to VL+AN, the products from VL+SN had higher O:C ratios (e.g.,  $\text{C}_7\text{H}_4\text{N}_2\text{O}_7$ ; No. 119, Table S2),  $\text{OS}_c$ , and  $\langle\text{OS}_c\rangle$  values (Table 2). In summary, while the VL decay kinetics and absorbance enhancement for VL+AN and VL+SN were similar, the product analysis supports suggests the participation of ammonium in the aqueous-phase reactions. ~~Ammonium salts are an important constituent of atmospheric aerosols particles (Jimenez et al., 2009), and reactions between dicarbonyls (e.g., glyoxal) and ammonia or primary amines have been demonstrated to form BrC (De Haan et al., 2009, 2011; Nozière et al., 2009; Shapiro et al., 2009; Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabate et al., 2019). Relative to VL+AN, the products from VL+SN had higher O:C ratios (e.g.,  $\text{C}_7\text{H}_4\text{N}_2\text{O}_7$ ; No. 9, Table S2),  $\text{OS}_c$ , and  $\langle\text{OS}_c\rangle$  values (Table 2).~~

2. The explicit mechanisms that could support their arguments are lacking. Fig. 2 is oversimplified. Their arguments about explaining chemistry were heavily based on chemical mechanisms, but the arguments were not convincing because authors did not propose explicit mechanisms—radical-based full mechanisms containing steps in details.

Response: In this work, we did not intend to develop full mechanisms of these complex reactions. Mechanistic speculations have been greatly reduced from the initial version of the manuscript based on the suggestions of Reviewer 1. Further experiments on the reactive intermediates in this study are required to propose explicit mechanisms without being speculative. Instead, we proposed major pathways for aqSOA formation based on the detected products. Fig. 2 and its discussions have been revised to show more potential aqSOA formation pathways consistent with previous studies. Changes in the text are as follows:

Lines 282-296: The potential aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate ~~photo-oxidation~~ in this study are summarized in Fig. 2. At pH 4,  $^3\text{VL}^*$ -initiated reactions yielded oligomeric species such as  $\text{C}_{16}\text{H}_{12}\text{O}_6$  and  $\text{C}_{22}\text{H}_{22}\text{O}_6$ . Earlier works on phenolic aqSOA formation have reported that oligomers can form via the coupling of phenoxy radicals or phenoxy and cyclohexadienyl radicals (Sun et al., 2010; Yu et al., 2014; Vione et al., 2019). In this work, phenoxy radicals (in resonance with a carbon-centered cyclohexadienyl radical) can be generated from several processes such as the oxidation of ground-state VL by  $^3\text{VL}^*$  via H-atom abstraction or electron transfer coupled with proton transfer from the phenoxyl radical cation or from solvent water (Neumann et al., 1986a, 1986b; Anastasio et al., 19961997) and photoinduced O-H bond-breaking (Berto et al., 2016). Also, similar reactions can be initiated by  $\cdot\text{OH}$  (Gelencsér et al.,

2003; Hoffer et al., 2004; Chang and Thompson, 2010; Sun et al., 2010), which in this study can be generated from the reaction between  $^3\text{VL}^*$  and  $\text{O}_2$ , as well as nitrate photolysis. Trace amounts of  $\text{H}_2\text{O}_2$  could be ~~were~~ likely formed during VL photodegradation (Li et al., 2014), similar to the case of other phenolic compounds (Anastasio et al., ~~1996~~1997). In addition, ring-opening products (Fig. S5) from fragmentation in both  $\text{VL}^*$  and  $\text{VL}+\text{AN}$  may have reacted with VL or dissolved ammonia to generate  $\text{C}_{10}\text{H}_{10}\text{O}_5$  (No. 54, Table S2) (Pang et al., 2019b) or a potential imidazole derivative ( $\text{C}_5\text{H}_5\text{N}_3\text{O}_2$ ; No. 65, Table S2), respectively. Moreover, nitrate photolysis products promoted functionalization and nitration (e.g.,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_9$ ; No. 43, Table S2).

Lines 391-401: At  $\text{pH} < 4$ ,  $^3\text{VL}^*$  likely have higher reactivity as suggested by the increased normalized abundance of oligomers (e.g.,  $\text{C}_{16}\text{H}_{14}\text{O}_6$ ; No. 76, Table S2 and  $\text{C}_{31}\text{H}_{24}\text{O}_{11}$ ) and N-containing compounds (e.g.,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_9$ ; No. 43, Table S2 and  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_{10}$ ) (Fig. 2). The most abundant product at  $\text{pH} < 4$ ,  $\text{C}_{16}\text{H}_{14}\text{O}_6$  (No. 7, Table S2), is likely a C–O coupled dimer. In previous studies on phenolic aqSOA formation, the generation of phenolic dimers has been proposed to occur via C–C or C–O coupling of phenoxy radicals (Sun et al., 2010; Yu et al., 2014; Huang et al., 2018; Chen et al., 2020; Misovich et al., 2021). Similarly, functionalized monomers such as  $\text{C}_7\text{H}_6\text{O}_3$  (demethylated VL; No. 8, Table S2) and hydroxylated products (e.g.,  $\text{C}_8\text{H}_8\text{O}_4$ ; No. 9, Table S2) also had increased normalized abundance for both  $\text{VL}^*$  and  $\text{VL}+\text{AN}$ . The formation of  $\text{C}_7\text{H}_6\text{O}_3$  (No. 8, Table S2), which varies from the structure of VL by  $\text{CH}_2$ , can be explained by  $^{\bullet}\text{OH}$  addition at the carbon containing the methoxy group, succeeded by the elimination of a methoxy radical ( $^{\bullet}\text{OCH}_3$ ) (Yee et al., 2013). This reaction has also been postulated for the  $^{\bullet}\text{OH}$  oxidation of syringol (2,6-dimethoxyphenol) (Yee et al., 2013) and transformation of DMB in a system composed of guaiacyl acetone and  $^3\text{DMB}^*$  (Misovich et al., 2021).

3. Most of the discussions sound speculative (words like “may, probably” were used often). Experimental data and analyses do not seem to support their arguments. Although they attempt to show their results to be consistent with others previous studies, it is difficult to find the novelty of this manuscript.

Response: Thank you for pointing this out. Words such as ‘may, probably’ were used to indicate more than one possible explanation for certain cases or further work is needed to give a more detailed explanation. We have not conducted experiments to exclude all other possibilities, and hence we are on the conservative side. Nonetheless, the discussions in this study were supported by our results and compared with previous studies.

The novelty of this study are as follows: (a) Previous works on aqSOA formation via triplet-mediated oxidation are mostly based on reactions between phenols and a non-phenolic aromatic carbonyl as triplet precursor. Also, studies examining the effects of inorganic nitrate on aqSOA formation and properties remain limited. In this work, we evaluated aqSOA formation from direct photosensitized oxidation of a triplet precursor (VL, a phenolic aromatic carbonyl) alone and in the presence of ammonium nitrate (VL+AN) based on VL decay kinetics, detected products, and light absorbance changes. The photo-oxidation of VL has been studied



previously (Li et al., 2014, Smith et al., 2016, and Loisel et al., 2021,)) but the discussions were mainly on aqSOA yields, kinetics, ionic strength effects, and major group of compounds (oxygenated aliphatic-like compounds). (b) The effects of different reaction conditions (air- vs. N<sub>2</sub>-saturated experiments, solution pH, and reactants concentration and molar ratios) on aqSOA formation were further explored. (c) Moreover, triplets of non-phenolic aromatic carbonyls (e.g., 3,4-dimethoxybenzaldehyde, DMB) and phenolic aromatic carbonyls (including VL) have been shown to oxidize phenols, but the reaction products from the latter are unknown. In this work, we showed that aqSOA formation from the oxidation of guaiacol, a non-carbonyl phenol, via photosensitized reactions of VL yield oligomers and hydroxylated compounds as major products. These are now reflected in the revised objectives:

Lines 98-122: Previous works aqSOA formation via triplet-mediated oxidation are mostly based on reactions between phenols and a non-phenolic aromatic carbonyl as triplet precursor (e.g., Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021). Also, studies examining the effects of inorganic nitrate on aqSOA formation and properties remain limited. The present study aimed to evaluate aqSOA formation via the direct photosensitized oxidation of a triplet precursor (VL) alone. Furthermore, aqSOA formation via the direct photosensitized oxidation of VL in the presence of ammonium nitrate was also examined. Accordingly, the main goals of this study are (1) to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate, (2) to evaluate the influences of O<sub>2</sub>, solution pH, and reactants concentration and molar ratios on the reactions, (3) to investigate the participation of ammonium in the direct photosensitized oxidation of VL in the presence of ammonium nitrate, and (4) to examine aqSOA formation from the oxidation of guaiacol, a non-carbonyl phenol, via photosensitized reactions of VL. To achieve these goals, solutions composed of either VL only or VL in the presence of ammonium nitrate were subjected to simulated sunlight irradiation under atmospherically relevant cloud and fog conditions. Solutions composed of VL in the presence of sodium nitrate were also examined for comparison with the presence of ammonium nitrate. ~~To evaluate the potential significance of VL and its reactions with nitrate in aqSOA formation in cloud/fog water, we studied the direct photosensitized oxidation of VL and nitrate mediated VL photo-oxidation under atmospherically relevant conditions. In this work, The reactions were characterized based on VL decay kinetics, detected products, and light absorbance changes, and. The influences of O<sub>2</sub>, solution pH, and reactants concentration and molar ratios on these two photo-oxidation pathways were also assessed. The <sup>13</sup>C\* of non-phenolic aromatic carbonyls (e.g., 3-4 dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the reaction products from the latter are unknown. We then examined the photo-oxidation of guaiacol, another non-carbonyl phenol, in the presence of VL and compared it with nitrate mediated photo-oxidation. Finally, we proposed aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate VL photo-oxidation. This work presents a comprehensive comparison of aqSOA formation from the direct photosensitized oxidation of VL photo-oxidation in the absence and presence of ammonium nitrate by VL photosensitization and in the presence of inorganic nitrate.~~

4. Therefore, substantial revisions and restructure are recommended for publication.

Response: The manuscript has been revised and restructured to clarify the objectives and discussions. Changes are shown throughout the author's response.

### Minor comments

1. Line 55: There needs to be a reason why NO<sub>3</sub><sup>-</sup> in the aqueous phase is the source of nitration in this work. In most of cases, nitration (organonitrate formation) occurs in the gas phase. Why your aqueous phase study is suitable instead of multiphase experiments.

Response: The nitration of aromatic compounds can occur in both the aqueous and gas phases (Harrison et al., 2005). In this study, we demonstrated that such reactions can take place in the aqueous phase. Upon photolysis (Vione et al., 2006; Herrmann, 2007; Scharko et al., 2014), inorganic nitrate in cloud and fog water can contribute to BrC (Minero et al., 2007) and aqSOA formation (Huang et al., 2018; Klodt et al., 2019; Zhang et al., 2021) by generating <sup>•</sup>OH and nitrating agents (e.g., <sup>•</sup>NO<sub>2</sub>). As stated in the introduction, aqueous reactions can be an important source of SOA (Blando and Turpin, 2000; Volkamer et al., 2009; Lim et al., 2010; Ervens et al., 2011; Huang et al., 2011; Lee et al., 2011; Smith et al., 2014) such as highly-oxygenated and low-volatility organics (Hoffmann et al., 2018; Liu et al., 2019) which may affect aerosol optical properties due to contributions to Brown Carbon (BrC) (Gilardoni et al., 2016). Moreover, the atmospheric processing of phenols can occur in both the aqueous and gas phases (e.g., Yee et al., 2013; Smith et al., 2014; Yu et al., 2014), and aqueous-phase chemistry has been reported to be likely as important as gas-phase chemistry for phenolic carbonyls (Huang et al., 2018). Recent works have demonstrated that phenols and phenolic carbonyls can undergo reactions in atmospheric aqueous phases to form aqSOA with high mass yields (Smith et al., 2014; Yu et al., 2014; Huang et al., 2018).

Aqueous photodegradation has been reported to be the dominant loss pathway for certain phenolic aromatic carbonyls (including VL) (Smith et al., 2016). The opposite has been reported for almost all the aliphatic carbonyls that Epstein et al. (2013) considered, in which gas-phase photolysis and <sup>•</sup>OH oxidation were the major pathways, while aqueous reactions (photodegradation and <sup>•</sup>OH oxidation) were insignificant. This is due to the much higher Henry's law constants (10<sup>5</sup> to 10<sup>8</sup> M atm<sup>-1</sup>) of these phenolic aromatic carbonyls compared to those of aliphatic carbonyls. Based on these, the current work is intended to simulate the formation of aqSOA via the direct photosensitized oxidation of VL in atmospheric cloud and fog water. For a more atmospherically relevant approach, the presence of nitrate and the effects of reaction conditions such as solution pH and reactants concentrations were also considered.

2. Line 100-101: I don't understand this statement. Shouldn't you want nitrates to affect the kinetics of VN photolysis by generating sufficient OH radicals? The purpose of adding ammonium nitrate should be clearly stated.

Response: In this study, the addition of ammonium nitrate was not specifically to affect the VL decay kinetics but rather to examine the effect of ammonium nitrate on aqSOA formation

from the direct photosensitized oxidation of VL in general. The concentration of ammonium nitrate (1 mM) used was based on values observed in cloud and fog water (Munger et al., 1983; Collett et al., 1998; Zhang and Anastasio, 2003; Li et al., 2011; Giulianelli et al., 2014; Bianco et al., 2020). Thank you for this suggestion. The introduction and objectives have been revised to clarify this as follows:

Line 60: Inorganic salts such as ammonium nitrate are a major components of aerosols and cloud/fog water.

Lines 65-67: For example, the aqSOA yields from the photo-oxidation of phenolic carbonyls in ammonium nitrate are twice as high as that in ammonium sulfate solution (Huang et al., 2018).

Lines 68-75: Moreover, nitrate photolysis has been proposed to be a potentially important process for SO<sub>2</sub> oxidation and SOA formation via the generation of <sup>•</sup>OH, <sup>•</sup>NO<sub>2</sub>, and N(III) within particles (Gen et al., 2019a, 2019b; Zhang et al., 2020, 2021), and it can also potentially change the morphology of atmospheric viscous particles (Liang et al., 2021). Furthermore, ammonium (NH<sub>4</sub><sup>+</sup>) can react with carbonyls producing light-absorbing compounds and highly oxygenated oligomers, as well as catalyze different reactions (De Haan et al., 2009, 2011; Nozière et al., 2009, 2010, 2018; Shapiro et al., 2009; Yu et al., 2011; Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabato et al., 2019). Accordingly, therefore, both <sup>3</sup>C\* and inorganic nitrate can contribute to aqSOA and BrC formation.

Lines 89-93: Nitrate and ammonium are also among the main biomass burning aerosol components (Xiao et al., 2020; Zielinski et al., 2020). As BB aerosols are typically internally mixed with other aerosol components (Zielinski et al., 2020), VL may coexist with ammonium nitrate in BB aerosols. The aqueous-phase photo-oxidation direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate may then reveal insights into the atmospheric processing of BB aerosols.

Lines 98-122: Previous works aqSOA formation via triplet-mediated oxidation are mostly based on reactions between phenols and a non-phenolic aromatic carbonyl as triplet precursor (e.g., Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021). Also, studies examining the effects of inorganic nitrate on aqSOA formation and properties remain limited. The present study aimed to evaluate aqSOA formation via the direct photosensitized oxidation of a triplet precursor (VL) alone. Furthermore, aqSOA formation via the direct photosensitized oxidation of VL in the presence of ammonium nitrate was also examined. Accordingly, the main goals of this study are (1) to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate, (2) to evaluate the influences of O<sub>2</sub>, solution pH, and reactants concentration and molar ratios on the reactions, (3) to investigate the participation of ammonium in the direct photosensitized oxidation of VL in the presence of ammonium nitrate, and (4) to examine aqSOA formation from the oxidation of guaiacol, a non-carbonyl phenol, via photosensitized reactions of VL. To achieve these goals, solutions composed of either VL only or VL in the presence of ammonium nitrate were subjected to simulated sunlight irradiation under atmospherically relevant cloud

and fog conditions. Solutions composed of VL in the presence of sodium nitrate were also examined for comparison with the presence of ammonium nitrate. To evaluate the potential significance of VL and its reactions with nitrate in aqSOA formation in cloud/fog water, we studied the direct photosensitized oxidation of VL and nitrate-mediated VL photo-oxidation under atmospherically relevant conditions. In this work, the reactions were characterized based on VL decay kinetics, detected products, and light absorbance changes, and the influences of O<sub>2</sub>, solution pH, and reactants concentration and molar ratios on these two photo-oxidation pathways were also assessed. The <sup>3</sup>C\* of non-phenolic aromatic carbonyls (e.g., 3,4-dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the reaction products from the latter are unknown. We then examined the photo-oxidation of guaiacol, another non-carbonyl phenol, in the presence of VL and compared it with nitrate-mediated photo-oxidation. Finally, we proposed aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate-VL photo-oxidation. This work presents a comprehensive comparison of aqSOA formation from the direct photosensitized oxidation of VL photo-oxidation in the absence and presence of ammonium nitrate by VL photosensitization and in the presence of inorganic nitrate.

3. Line 126-127: I disagree the equal ionization efficiency for different compounds. This cannot be true.

Response: The reviewer is correct that ionization efficiency varies among different compounds. As stated in lines 172-178, 'Comparisons of peak abundance in mass spectrometry have been used in many recent studies (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 (Wang et al., 2021). However, ionization efficiency may greatly vary for different classes of compounds (Kebarle, 2000; Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Krueve et al., 2014), and so uncertainties may arise from comparisons of peak areas among compounds. In this work, we assumed equal ionization efficiency of different compounds, which is commonly used to estimate O:C ratios of SOA (e.g., Bateman et al., 2012; Lin et al., 2012; Laskin et al., 2014; De Haan et al., 2019), to calculate their normalized abundance.' We understand that it can be a weak assumption, but it is also in line with many similar studies in the literature on related analysis.

The normalized abundance of products in this study is a semi-quantitative analysis intended to provide an overview of how the signal intensities (as normalized in Eq. 2) changed under different experimental conditions, but not to quantify the absolute concentration of products. Even if relative abundance (product peaks are normalized to the highest peak), which has been widely utilized (e.g., Lee et al., 2014, <https://pubs.acs.org/doi/10.1021/es502515r>; Romonosky et al., 2017, <https://pubs.acs.org/doi/10.1021/acs.jpca.6b10900>; Fleming et al., 2018, <https://doi.org/10.5194/acp-18-2461-2018>; Klodt et al., 2019, <https://pubs.acs.org/doi/pdf/10.1021/acsearthspacechem.9b00222>) in the literature is used instead of normalized abundance in our analysis, the major products detected as well as the

conclusions of this study will remain the same. While ESI ionization is not ideal for product quantification, Nguyen et al. (2013) (<https://doi.org/10.1039/C2AY25682G>) found a positive correlation between ESI signal and “adjusted mass” (= molecular mass  $\times$  H: C). Based on 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 disregarded. However, what we compared is not the absolute concentrations (or contributions) of the products observed. The comparison was based on how the signal intensities (as normalized in Eq. 2) changed under different experimental conditions. We compared the responses of the same products (or at least the same class of products) as conditions varied, and their ionization efficiency might not be very different within the same class, according to the “adjusted mass” concept by Nguyen et al. (2013). Moreover, given the same instrumental settings, the variations caused by the instrumental fluctuations would be smaller than the effects caused by the difference in ionization efficiency among different species. If there is any, it would be taken into account by the normalization in Eq. 2, which is why the normalized signal intensities were used instead of absolute signal intensities. For reference, relative uncertainties for MS signal peak areas of VL at the same concentration measured from different experiments range from 0.14 to 0.25. The propagated uncertainties from the MS signal intensities and [VL] are shown in Table 2.

4. Line 133-138: The term, “normalized abundance of products” is scientifically meaningless, unless ionization efficiencies for each product were taken into account.

Response: Please see our response to minor comment #3 for the use of normalized abundance of products in this study.

5. Line 149-156: A schematic containing radical-based full mechanisms is required. This should be Fig. 2, which is currently oversimplified.

Response: Thank you for the suggestion. Please see our response to major comment #2 for the modifications involving Fig. 2.

6. Line 179-181: Building a kinetic model based on Table 1 is recommended. You can verify it by simulating a kinetic model.

Response: Thank you for the suggestion. Further experiments on the reactive intermediates in this study are needed to build a kinetic model, unfortunately, this is beyond the scope of the current work. Nonetheless, these statements are based on the findings of Anastasio et al. (1997) and Li et al. (2014).

7. Line 192-194: I do not understand the purpose of conducting N<sub>2</sub> experiments in the first place. Clearly, O<sub>2</sub> is the oxidant that required for the oxidation. Therefore, you expect better oxidation with O<sub>2</sub>. There always exists O<sub>2</sub> in cloud/fog droplets. This is not a novel finding.

Response: We are not aiming to show that there is oxidation under air-saturated conditions. The purpose of the air- and N<sub>2</sub>-saturated experiments are provided in lines 130-133: ‘The aim

of the air-saturated experiments was to enable the generation of secondary oxidants ( $^1\text{O}_2$ ,  $\text{O}_2^{\bullet-}/\text{HO}_2$ ,  $^{\bullet}\text{OH}$ ) from  $^3\text{VL}^*$  as  $\text{O}_2$  is present. Conversely, the  $\text{N}_2$ -saturated experiments would inhibit the formation of these secondary oxidants, which can lead to  $^3\text{VL}^*$ -driven reactions (Chen et al., 2020).<sup>7</sup> In this study, we found that the direct photosensitized oxidation of VL is likely governed by  $^3\text{VL}^*$  and that these secondary oxidants have minor participation (line 237). Nonetheless, further study on the impact of  $\text{O}_2$  on the reactive intermediates involved is required to understand the exact mechanisms occurring under air-saturated conditions (line 262). Revisions in the text are as follows:

Lines 133-134: Comparison of results of air and  $\text{N}_2$ -saturated experiments can yield information on the reaction pathways that require  $\text{O}_2$  involved in the direct photosensitized oxidation of VL.

8. Line 225-227: Negative-mode analysis sounds more suitable for oxidized products. The reason for conducting positive-mode analysis that would bring a benefit and unique results in this work needs to be addressed.

Response: The selectivity and sensitivity of ESI in the positive and negative ion modes can vary towards specific biomass burning organic aerosols (Lin et al., 2016). However, in this study, the negative ion mode signals were too low for our analyses (as mentioned in line 153), hence only positive ion mode data were useful for our analyses.

9. Line 234-237: This statement is weak. You need to make a strong statement based on your compelling evidence.

Response: These statements summarize the findings for the comparisons of detected products and their normalized abundance from the  $\text{N}_2$  and air-saturated experiments. For both  $\text{VL}^*$  and  $\text{VL}+\text{AN}$  under air-saturated conditions ( $\text{O}_2$  is present), the products had higher normalized abundance, and the higher  $\text{OS}_c$  indicates the formation of more oxidized aqSOA. For  $\text{VL}+\text{AN}$ , the N-containing products also had higher normalized abundance under air-saturated condition, suggesting a potential enhancement of VL nitration in the presence of  $\text{O}_2$ .

10. Line 244-246: It is difficult to conclude that products are mainly conjugated pi system based on your ESI analysis (even MS-MS analysis).

Response: Obvious absorbance enhancement was noted under air-saturated conditions, while the absorbance changes under  $\text{N}_2$ -saturated conditions were minimal. Also, the normalized abundance of oligomers was observed to be higher under air-saturated conditions compared to  $\text{N}_2$ -saturated conditions for both  $\text{VL}^*$  and  $\text{VL}+\text{AN}$ . Dimers and functionalized products have been shown to contribute to chromophore formation for the aqueous photo-oxidation of guaiacyl acetone (another aromatic phenolic carbonyl) by  $^3\text{DMB}^*$  (Jiang et al., 2021). Based on this, the higher normalized abundance of oligomers, which have large, conjugated  $\pi$ -electron systems (Chang and Thompson, 2010), and hydroxylated products (Li

et al., 2014; Zhao et al., 2015) observed in the presence of O<sub>2</sub> have contributed to the absorbance enhancement. Moreover, the shaded area in Fig. S11 indicates compounds with double-bond equivalency that form conjugated systems and hence are potential BrC chromophores. Based on Fig. S11, majority of the 50 most abundant products from all pH 4 experiments in this work were potential BrC chromophores. Revisions in the text are as follows:

Lines 325-332: For both VL\* and VL+AN, evident absorbance enhancement was observed under air-saturated conditions, while the absorbance changes under N<sub>2</sub>-saturated conditions were minimal, consistent with the VL decay trends. **Dimers and functionalized products have been shown to contribute to chromophore formation for the aqueous photo-oxidation of guaiacyl acetone (another aromatic phenolic carbonyl) by <sup>3</sup>DMB\* (Jiang et al., 2021). Based on this, the higher normalized abundance of** ~~This absorbance enhancement can be explained by the formation of oligomers, which~~ **have** large, conjugated π-electron systems (Chang and Thompson, 2010), and hydroxylated products (Li et al., 2014; Zhao et al., 2015), ~~in agreement with the observed reaction products~~ **observed under air-saturated conditions have contributed to the absorbance enhancement.**

11. Line 266: The range of pH 2.5 and pH 4 seems too narrow to study a pH effect.

Response: Typical cloud pH values have been reported to range from 2 to 7, and the upper limit (pH 4) of the pH range considered in this study is representative of moderately acidic aerosol and cloud pH values (Pye et al., 2020). As discussed in section 3.1.2, our results showed a clear pH effect indicated by marked differences within the pH range studied in terms of VL decay kinetics, products characterization, and light absorbance changes. Nonetheless, future studies evaluating a wider range of pH values for similar reactions systems would be interesting and may provide additional insights into these reactions.

12. Line 270-271: This is speculative, again. You need to make a strong statement based on your novel analysis.

Response: As discussed in section 3.1.1, the direct photosensitized oxidation of VL in this study is likely governed by <sup>3</sup>VL\* and that the secondary oxidants have only minor participation. In this work, the observed pH dependence was attributed to two possibilities based on observed differences between pH 4 and pH < 4 and previous studies (Anastasio et al., 1997; Smith et al., 2014; Smith et al., 2016): <sup>3</sup>VL\* being more reactive in its protonated form and the excimer of VL being sensitive to acid-base chemistry. Again, we are cautious that we cannot exclude all other possibilities from these experiments.

13. (a) Line 296-300 & (b) 305-306: Speculative

Response:

(a) As mentioned in minor comment #12, the direct photosensitized oxidation of VL in this study is likely governed by <sup>3</sup>VL\* and that the secondary oxidants have only minor

participation. Moreover, as discussed in section 3.1.2 (VL photo-oxidation under varying pH conditions), the VL decay kinetics, products characterization, and the observed pH dependence of the absorbance enhancement indicate that the pH effect can be due to  $^3\text{VL}^*$  being more reactive in its protonated form or the excimer of VL being sensitive to acid-base chemistry (Anastasio et al., 1997; Smith et al., 2014; Smith et al., 2016). Furthermore, the higher normalized abundance of N-containing compounds at lower pH could be explained by the dependence of N(III) ( $\text{NO}_2^- + \text{HONO}$ ) speciation on solution acidity.

(b) In Fig. S10, we showed the changes in the UV-Vis absorption spectra of the aqSOA formed from  $\text{VL}^*$  at pH 4 and 2.5 measured over a range of pH conditions from 1.5 to 10.5 to determine whether the observed pH dependence is due to the acid-base chemistry of the products or of the reactions. If the changes in the UV-Vis absorption spectra for the two solutions of varying pH are different, the pH dependence is due to different products formed from  $\text{VL}^*$  at pH 4 compared to pH 2.5. However, the comparable changes in the UV-Vis absorption spectra for the two solutions indicate that the observed pH dependence (Fig. 3b) may be attributed to the acid-base chemistry of the reactions, which may involve  $^3\text{VL}^*$  or the excimer of VL (Smith et al., 2016). Changes in the text are as follows:

Lines 411-418: Higher absorbance enhancement for both  $\text{VL}^*$  and  $\text{VL}+\text{AN}$  (Fig. 3b) was observed as pH increased. To determine whether the pH dependence is due to the acid-base chemistry of the products or of the reactions, ~~we measured the~~ **changes in the UV-Vis absorption spectra** ~~pH dependence of the aqSOA formed from  $\text{VL}^*$  at pH 4 and 2.5 were measured~~ over a range of pH conditions from 1.5 to 10.5 (Fig. S10). For both cases, the intensity of absorption at longer wavelengths significantly increased as the pH of the solutions was raised. Moreover, the ~~comparable pH dependence of~~ **changes in the UV-Vis absorption spectra for** the two solutions ~~of varying pH are comparable,~~ **is rooted in** acid-base chemistry of the reactions ~~involving,~~ **is rooted in** ~~which may involve~~  $^3\text{VL}^*$  or the excimer of VL (Smith et al., 2016), as discussed earlier.

14. Line 315: The term, “the 50 most abundant products” provides no scientific meaning. You cannot tell the abundance of products by ESI signal. Besides, why did you choose 50?

Response: We agree with the reviewer that ESI ionization is not ideal for product quantification. Please see our response to minor comment #3 for the use of normalized abundance of products in this study. As mentioned in lines 200-201, ‘In general, the 50 most abundant products contributed more than half of the total normalized abundance of products.’ These were then used as representative products for discussions of reaction pathways and calculation of the average carbon oxidation state ( $\langle \text{OS}_c \rangle$ ). They are useful for internal comparison among experiments under different conditions. Changes in the text are as follows:



Lines 200-202: In general, the 50 most abundant products contributed more than half of the total normalized abundance of products and can serve as representative products for discussions of reaction pathways and calculation of the  $\langle OS_c \rangle$ .

15. Line 330-332: Speculative. Propose an explicit mechanism to support your argument.

Response: Thank you for this suggestion. More experiments on the reactive intermediates in this study are needed to propose explicit mechanisms, unfortunately, this is beyond the scope of this work. As the formation mechanism of dimers and higher oligomers during aqueous-phase reactions of phenolic compounds involves the coupling of phenoxy radicals (Kobayashi and Higashimura, 2003; Sun et al., 2010), the enhanced oligomerization at high [VL] can be attributed to an increased concentration of phenoxy radicals (in resonance with a carbon-centered cyclohexadienyl radical) at high [VL], promoting radical-radical polymerization (Sun et al., 2010; Li et al., 2014). This is consistent with more oligomers reported from high phenols concentration (e.g., 0.1 to 3 mM) (Li et al., 2014; Slikboer et al., 2015; Ye et al., 2019). Revisions in the text are as follows:

Lines 459-467: For both VL\* and VL+AN, the contribution of  $< 200$  m/z to the normalized abundance of products was higher at low [VL] than at high [VL], while the opposite was observed for  $> 300$  m/z (Fig. S12d). This indicates that functionalization was favored at low [VL], as supported by the higher  $\langle OS_c \rangle$ , while oligomerization was the dominant pathway at high [VL], consistent with more oligomers or polymeric products reported from high phenols concentration (e.g., 0.1 to 3 mM) (Li et al., 2014; Slikboer et al., 2015; Ye et al., 2019). **As the formation mechanism of dimers and higher oligomers during aqueous-phase reactions of phenolic compounds involves the coupling of phenoxy radicals (Kobayashi and Higashimura, 2003; Sun et al., 2010), the enhanced oligomerization at high [VL] can be attributed** ~~This is probably due~~ to an increased concentration of phenoxy radicals (in resonance with a carbon-centered cyclohexadienyl radical) at high [VL], promoting radical-radical polymerization (Sun et al., 2010; Li et al., 2014).

16. Line 350-352: How can you prove this based on your experiments?

Response: Imidazole formation requires the nucleophilic attack of ammonia on the carbonyl group (Yu et al., 2011). The potential imidazole derivative ( $C_5H_5N_3O_2$ ) observed from VL+AN was not detected in VL+SN. Aside from this potential imidazole derivative,  $C_8H_9NO_3$  (No. 3, Table S2), possibly an aminophenol, was also observed from VL+AN but only under  $N_2$ -saturated conditions, probably due to further oxidation by  $^3VL^*$ . The detection of these products in VL+AN but not in VL+SN supports the participation of ammonium in the reactions.

17. Line 352-354: (a) What are the anticipated product based on  $NH_4^+$  chemistry? What are the corresponding products you have found? (b) How does that related to BrC absorbance or conjugate bond?

Response:

(a) The products reported from the reactions between dicarbonyls (e.g., glyoxal) and ammonia or primary amines include imidazole and imidazole derivatives, oligomeric species, and N-containing compounds (De Haan et al., 2009, 2011; Galloway et al., 2009; Nozière et al., 2009; Shapiro et al., 2009; Yu et al., 2011; Lee et al., 2013; Sedehi et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabato et al., 2019). For VL+AN at pH 4, the products observed were oligomers, functionalized monomers, N-containing compounds, ring-opening products (e.g., formic, oxalic acid), and a potential imidazole derivative ( $C_5H_5N_3O_2$ ) that was not detected in VL+SN. In addition,  $C_8H_9NO_3$  (No. 3, Table S2), possibly an aminophenol, was also observed from VL+AN but only under  $N_2$ -saturated conditions, probably due to further oxidation by  $^3VL^*$ .

(b) Comparable absorbance enhancement was noted among  $VL^*$ , VL+AN, and VL+SN (Fig. 3), likely due to  $^3VL^*$  chemistry dominating the reactions even at 1:10 molar ratio of VL/AN, probably due to the much higher molar absorptivity of VL compared to that of nitrate (Fig. S1) and the high VL concentration (0.1 mM) used in this study. As mentioned in minor comment #10, the shaded area in Fig. S11 indicates compounds with double-bond equivalency that form conjugated systems and hence are potential BrC chromophores. Based on Fig. S11, majority of the 50 most abundant products from  $VL^*$ , VL+AN, and VL+SN were potential BrC chromophores.

#### 18. Line 366: speculative

Response: As stated in lines 511-514: 'The decay rate constant of VL in GUA+VL (A14; Table 2) was 3 times slower than that of  $VL^*$  (A5; Table 2), which may be due to competition between ground-state VL and GUA for reactions with  $^3VL^*$  or increased conversion of  $^3VL^*$  back to the ground state through the oxidation of GUA (Anastasio et al., 1996, 1997; Smith et al., 2014).' These suggest that in this study, GUA was oxidized by  $^3VL^*$ , similar to the findings of Smith et al. (2016) in which the addition of syringol decreased the loss rate of VL. We have revised this in the text as follows:

Line 501-514: Accordingly, ~~the direct GUA photodegradation resulted in minimal decay, which plateaued after ~3 hours. However, in the presence of VL or nitrate, the GUA decay rate constant was 2.2 times higher by 2.2 (GUA+VL) and 1.3 (GUA+AN) times, respectively, than for direct GUA photodegradation. The enhancement of GUA decay rate constant in the presence of VL is statistically significant ( $p < 0.05$ ), while that in the presence of AN is not ( $p > 0.05$ ). This enhanced GUA decay rate constant may be due to the oxidation of GUA by  $^3VL^*$ . As mentioned earlier,  $^3VL^*$  chemistry appears to be more important than that of nitrate photolysis even at 1:10 molar ratio of VL/nitrate on account of the much higher molar absorptivity of VL compared to that of nitrate (Fig. S1) and the high VL concentration (0.1 mM) used in this study. However, the apparent quantum efficiency of GUA photodegradation ( $\Phi_{GUA}$ ) in the presence of nitrate ( $1.3 \times 10^{-2} \pm 2.9 \times 10^{-3}$ ) is ~14 times larger than that in the presence of VL ( $9.0 \times 10^{-4} \pm 4.0 \times 10^{-4}$ ), suggesting that nitrate-mediated photo-oxidation of GUA is more efficient than that by photosensitized reactions of VL (see Text S7 for more details).~~ The decay rate constant of VL in GUA+VL (A14; Table 2) was 3 times slower than that

of VL\* (A5; Table 2), which may be due to competition between ground-state VL and GUA for reactions with <sup>3</sup>VL\* or increased conversion of <sup>3</sup>VL\* back to the ground state through the oxidation of GUA (Anastasio et al., 1996, 1997; Smith et al., 2014).

## References:

Anastasio, C., Faust, B. C., and Rao, C. J.: Aromatic carbonyl compounds as aqueous-phase photochemical sources of hydrogen peroxide in acidic sulfate aerosols, fogs, and clouds. 1. Non-phenolic methoxybenzaldehydes and methoxyacetophenones with reductants (phenols), *Environ. Sci. Technol.*, 31, 218–232, <https://doi.org/10.1021/es960359g>, 1997.

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

Berto, S., De Laurentiis, E., Tota, T., Chiavazza, E., Daniele, P.G., Minella, M., Isaia, M., Brigante, M., and Vione, D.: Properties of the humic-like material arising from the photo-transformation of L-tyrosine, *Sci. Total Environ.*, 434–444, <https://doi.org/10.1016/j.scitotenv.2015.12.047>, 2016.

Bianco, A., Riva, M., Baray, J.-L., Ribeiro, M., Chaumerliac, N., George, C., Bridoux, M., and Deguillaume, L.: Chemical characterization of cloud water collected at Puy de Dôme by FT-ICR MS reveals the presence of SOA components, *ACS Earth Space Chem.*, 3, 2076–2087, <https://doi.org/10.1021/acsearthspacechem.9b00153>, 2019.

Bianco, A., Passananti, M., Brigante, M., and Mailhot, G.: Photochemistry of the cloud aqueous phase: a review, *Molecules*, 25, 423, <https://doi.org/10.3390/molecules25020423>, 2020.

Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623–1632, [https://doi.org/10.1016/S1352-2310\(99\)00392-1](https://doi.org/10.1016/S1352-2310(99)00392-1), 2000.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J.-H., and Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion, *J. Geophys. Res.*, 109, <https://doi.org/10.1029/2003JD003697>, 2004.

Chang, J. L. and Thompson, J. E.: Characterization of colored products formed during irradiation of aqueous solutions containing H<sub>2</sub>O<sub>2</sub> and phenolic compounds, *Atmos. Environ.*, 44, 541–551, <https://doi.org/10.1016/j.atmosenv.2009.10.042>, 2010.

Chen, Y., Li, N., Li, X., Tao, Y., Luo, S., Zhao, Z., Ma, S., Huang, H., Chen, Y., Ye, Z., and Ge, X.: Secondary organic aerosol formation from <sup>3</sup>C\*-initiated oxidation of 4-ethylguaiacol in atmospheric aqueous-phase, *Sci. Total Environ.*, 723, 137953, <https://doi.org/10.1016/j.scitotenv.2020.137953>, 2020.

Collett, J. L. Jr., Hoag, K. J., Sherman, D. E., Bator, A., and Richards, L. W.: Spatial and temporal variations in San Joaquin Valley fog chemistry, *Atmos. Environ.*, **33**, 129–140, [https://doi.org/10.1016/S1352-2310\(98\)00136-8](https://doi.org/10.1016/S1352-2310(98)00136-8), 1998.

De Haan, D. O., Corrigan, A. L., Tolbert, M. A., Jimenez, J. L., Wood, S. E., and Turley, J. J.: Secondary organic aerosol formation by self-reactions of methylglyoxal and glyoxal in evaporating droplets, *Environ. Sci. Technol.*, **43**, 8184–8190, <https://doi.org/10.1021/es902152t>, 2009.

De Haan, D. O., Hawkins, L. N., Kononenko, J. A., Turley, J. J., Corrigan, A. L., Tolbert, M. A., and Jimenez, J. L.: Formation of nitrogen-containing oligomers by methylglyoxal and amines in simulated evaporating cloud droplets, *Environ. Sci. Technol.*, **45**, 984–991, <https://doi.org/10.1021/es102933x>, 2011.

De Haan, D.O., Pajunoja, A., Hawkins, L. N., Welsh, H.G., Jimenez, N. G., De Loera, A., Zauscher, M., Andretta, A. D., Joyce, B. W., De Haan, A. C., Riva, M., Cui, T., Surratt, J. D., Cazaunau, M., Formenti, P., Gratien, A., Pangui, E., and Doussin, J-F.: Methylamine's effects on methylglyoxal-containing aerosol: chemical, physical, and optical changes, *ACS Earth Space Chem.*, **3**, 1706–1716, <https://doi.org/10.1021/acsearthspacechem.9b00103>, 2019.

Epstein, S. A., Tapavicza, E., Furche, F., and Nizkorodov, S. A.: Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets, *Atmos. Chem. Phys.*, **13**, 9461–9477, <https://doi.org/10.5194/acp-13-9461-2013>, 2013.

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, **11**, 11069–11102, <https://doi.org/10.5194/acp-11-11069-2011>, 2011.

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

Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, *Atmos. Chem. Phys.*, **9**, 3331–3345, <https://doi.org/10.5194/acp-9-3331-2009>, 2009.

Gelencsér, A., Hoffer, A., Kiss, G., Tombácz, E., Kurdi, R., and Bencze, L.: In-situ formation of light-absorbing organic matter in cloud water, *J. Atmos. Chem.*, **45**, 25–33, <https://doi.org/10.1023/A:1024060428172>, 2003.

Gen, M., Huang, D. D., and Chan, C. K.: Reactive uptake of glyoxal by ammonium-containing salt particles as a function of relative humidity, *Environ. Sci. Technol.*, **52**, 6903–6911, <https://doi.org/10.1021/acs.est.8b00606>, 2018.

Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous SO<sub>2</sub> oxidation in sulfate formation by photolysis of particulate nitrate, *Environ. Sci. Technol. Lett.*, **6**, 86–91, <https://doi.org/10.1021/acs.estlett.8b00681>, 2019a.

Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous oxidation of SO<sub>2</sub> in sulfate production during nitrate photolysis at 300 nm: effect of pH, relative humidity, irradiation intensity, and the presence of organic compounds, *Environ. Sci. Technol.*, **53**, 8757–8766, <https://doi.org/10.1021/acs.est.9b01623>, 2019b.

Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F., Gobbi, G.P., Pietrogrande, M.C., Visentin, M., Scotto, F., Fuzzi, S., and Facchini, M.C.: Direct observation of aqueous secondary organic aerosol from biomass-burning emissions, *PNAS.*, **113**, 10013–10018, <https://doi.org/10.1073/pnas.1602212113>, 2016.

Giulianelli, L., Gilardoni, S., Tarozzi, L., Rinaldi, M., Decesari, S., Carbone, C., Facchini, M. C., and Fuzzi, S.: Fog occurrence and chemical composition in the Po valley over the last twenty years, *Atmos. Environ.*, **98**, 394–401, <https://doi.org/10.1016/j.atmosenv.2014.08.080>, 2014.

Grosjean, D.: Reactions of o-cresol and nitrocresol with nitrogen oxides (NO<sub>x</sub>) in sunlight and with ozone–nitrogen dioxide mixtures in the dark, *Environ. Sci. Technol.*, **19**, 968–974, <https://doi.org/10.1021/es00140a014>, 1985.

Harrison, M. A. J., Barra, S., Borghesi, D., Vione, D., Arsene, C., and Iulian Olariu, R.: Nitrated phenols in the atmosphere: a review, *Atmos. Environ.*, **39**, 231–248, <https://doi.org/10.1016/j.atmosenv.2004.09.044>, 2005.

Herrmann, H.: On the photolysis of simple anions and neutral molecules as sources of O<sup>-</sup>/OH, SO<sub>x</sub><sup>-</sup> and Cl in aqueous solution, *Phys. Chem. Chem. Phys.*, **9**, 3935–3964, <https://doi.org/10.1039/B618565G>, 2007.

Hoffer, A., Kiss, G., Blazsó, M., and Gelencsér, A.: Chemical characterization of humic-like substances (HULIS) formed from a lignin-type precursor in model cloud water, *Geophys. Res. Lett.*, **31**, <https://doi.org/10.1029/2003GL018962>, 2004.

Hoffmann, E. H., Tilgner, A., Wolke, R., Böge, O., Walter, A., and Herrmann, H.: Oxidation of substituted aromatic hydrocarbons in the tropospheric aqueous phase: kinetic mechanism development and modelling, *Phys. Chem. Chem. Phys.*, **20**, 10960–10977, <https://doi.org/10.1039/C7CP08576A>, 2018.

Holčapek, M., Jirásko, R., and Lída, M.: Basic rules for the interpretation of atmospheric pressure ionization mass spectra of small molecules, *J. Chromatogr. A*, **1217**, 3908–3921, <https://doi.org/10.1016/j.chroma.2010.02.049>, 2010.

Huang, D. D., Zhang, Q., Cheung, H. H. Y., Yu, L., Zhou, S., Anastasio, C., Smith, J. D., and Chan, C. K.: Formation and evolution of aqSOA from aqueous-phase reactions of phenolic carbonyls:

comparison between ammonium sulfate and ammonium nitrate solutions, *Environ. Sci. Technol.*, 52, 9215–9224, <https://doi.org/10.1021/acs.est.8b03441>, 2018.

Huang, X. H. H., Ip, H. S. S., and Yu, J. Z.: Secondary organic aerosol formation from ethylene in the urban atmosphere of Hong Kong: a multiphase chemical modeling study, *J. Geophys. Res.*, 116, D03206, <https://doi.org/10.1029/2010JD014121>, 2011.

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

Kebarle, P.: A brief overview of the present status of the mechanisms involved in electrospray mass spectrometry, *J. Mass Spectrom.*, 35, 804–817, [https://doi.org/10.1002/1096-9888\(200007\)35:7<804::AID-JMS22>3.0.CO;2-Q](https://doi.org/10.1002/1096-9888(200007)35:7<804::AID-JMS22>3.0.CO;2-Q), 2000.

Kitanovski, Z., Čusak, A., Grgić, I., and Claeys, M.: Chemical characterization of the main products formed through aqueous-phase photolysis of guaiacol, *Atmos. Meas. Tech.*, 7, 2457–2470, <https://doi.org/10.5194/amt-7-2457-2014>, 2014.

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

Kroflíč, A., Anders, J., Drventić, I., Mettke, P., Böge, O., Mutzel, A., Kleffmann, J., and Herrmann, H.: Guaiacol nitration in a simulated atmospheric aerosol with an emphasis on atmospheric nitrophenol formation mechanisms, *ACS Earth Space Chem.*, 5, 1083–1093, <https://doi.org/10.1021/acsearthspacechem.1c00014>, 2021.

Kroflíč, A., Grilc, M., and Grgić, I.: Unraveling pathways of guaiacol nitration in atmospheric waters: nitrite, a source of reactive nitronium ion in the atmosphere, *Environ. Sci. Technol.*, 49, 9150–9158, <https://doi.org/10.1021/acs.est.5b01811>, 2015.

Kobayashi, S. and Higashimura, H.: Oxidative polymerization of phenols revisited, *Prog. Polym. Sci.*, 28, 1015–1048, [https://doi.org/10.1016/S0079-6700\(03\)00014-5](https://doi.org/10.1016/S0079-6700(03)00014-5), 2003.

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

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

LeClair, J. P., Collett, J. L., and Mazzolen, L. R.: Fragmentation analysis of water-soluble atmospheric organic matter using ultrahigh-resolution FT-ICR mass spectrometry, *Environ. Sci. Technol.*, **46**, 4312–4322, <https://doi.org/10.1021/es203509b>, 2012.

Lee, A. K. Y., Herckes, P., Leitch, W. R., Macdonald, A. M., and Abbatt, J. P. D.: Aqueous OH oxidation of ambient organic aerosol and cloud water organics: Formation of highly oxidized products, *Geophys. Res. Lett.*, **38**, L11805, <https://doi.org/10.1029/2011GL047439>, 2011.

Lee, A. K. Y., Zhao, R., Li, R., Liggio, J., Li, S.-M., and Abbatt, J. P. D.: Formation of light absorbing organo-nitrogen species from evaporation of droplets containing glyoxal and ammonium sulfate, *Environ. Sci. Technol.*, **47**, 12819–12826, <https://doi.org/10.1021/es402687w>, 2013.

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

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

Li, P., Li, X., Yang, C., Wang, X., Chen, J., and Collett, J. L. Jr.: Fog water chemistry in Shanghai, *Atmos. Environ.*, **45**, 4034–4041, <https://doi.org/10.1016/j.atmosenv.2011.04.036>, 2011.

Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y., and Chan, C. K.: Aqueous-phase photochemical oxidation and direct photolysis of vanillin - a model compound of methoxy phenols from biomass burning, *Atmos. Chem. Phys.*, **14**, 2871–2885, <https://doi.org/10.5194/acp-14-2871-2014>, 2014.

Liang, Z., Zhang, R., Gen, M., Chu, Y., and Chan, C. K.: Nitrate photolysis in mixed sucrose–nitrate–sulfate particles at different relative humidities, *J. Phys. Chem. A*, **125**, 3739–3747, <https://doi.org/10.1021/acs.jpca.1c00669>, 2021.

Liigand, P., Kaupmees, K., Haav, K., Liigand, J., Leito, I., Girod, M., Antoine, R., and Krueve, A.: Think negative: finding the best electrospray ionization/MS mode for your analyte, *Anal. Chem.*, **89**, 5665–5668, <https://doi.org/10.1021/acs.analchem.7b00096>, 2017.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, **10**, 10521–10539, <https://doi.org/10.5194/acp-10-10521-2010>, 2010.

Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A., and Laskin, A.: Molecular characterization of brown carbon in biomass burning aerosol particles, *Environ. Sci. Technol.*, **50**, 11815–11824, <https://doi.org/10.1021/acs.est.6b03024>, 2016.

Lin, P., Bluvshstein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular chemistry of atmospheric brown carbon inferred from a nationwide biomass burning event, *Environ. Sci. Tech.*, 51, 11561–11570, <https://doi.org/10.1021/acs.est.7b02276>, 2017.

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

Liu, C., Liu, J., Liu, Y., Chen, T., and He, H.: Secondary organic aerosol formation from the OH-initiated oxidation of guaiacol under different experimental conditions, *Atmos. Environ.*, 207, 30–37, <https://doi.org/10.1016/j.atmosenv.2019.03.021>, 2019.

Loisel, G., Mekic, M., Liu, S., Song, W., Jiang, B., Wang, Y., Deng, H., and Gligorovski, S.: Ionic strength effect on the formation of organonitrate compounds through photochemical degradation of vanillin in liquid water of aerosols, *Atmos. Environ.*, 246, 118140, <https://doi.org/10.1016/j.atmosenv.2020.118140>, 2021.

Mabato, B. R. G., Gen, M., Chu, Y., and Chan, C. K.: Reactive uptake of glyoxal by methylammonium-containing salts as a function of relative humidity, *ACS Earth Space Chem.*, 3, 150–157, <https://doi.org/10.1021/acsearthspacechem.8b00154>, 2019.

Minero, C., Bono, F., Rubertelli, F., Pavino, D., Maurino, V., Pelizzetti, E., and Vione, D.: On the effect of pH in aromatic photolysis upon nitrate photolysis, *Chemosphere*, 66, 650–656, <https://doi.org/10.1016/j.chemosphere.2006.07.082>, 2007.

Misovich, M. V., Hettiyadura, A. P. S., Jiang, W., Zhang, Q., and Laskin, A.: Molecular-level study of the photo-oxidation of aqueous-phase guaiacyl acetone in the presence of  $^3\text{C}^*$ : formation of brown carbon products, *ACS Earth Space Chem.*, 5, 1983–1996, <https://doi.org/10.1021/acsearthspacechem.1c00103>, 2021.

Munger, J. W., Jacob, D. J., Waldman, J. M., and Hoffmann, M. R.: Fogwater chemistry in an urban atmosphere, *J. Geophys. Res. Oceans*, 88, 5109–5121, <https://doi.org/10.1029/JC088iC09p05109>, 1983.

Neumann, M. G., De Groote, R. A. M. C., and Machado, A. E. H.: Flash photolysis of lignin: Part 1. Deaerated solutions of dioxane-lignin, *Polym. Photochem.*, 7, 401–407, [https://doi.org/10.1016/0144-2880\(86\)90007-2](https://doi.org/10.1016/0144-2880(86)90007-2), 1986a.

Neumann, M. G., De Groote, R. A. M. C., and Machado, A. E. H.: Flash photolysis of lignin: II. Oxidative photodegradation of dioxane-lignin, *Polym. Photochem.*, 7, 461–468, [https://doi.org/10.1016/0144-2880\(86\)90015-1](https://doi.org/10.1016/0144-2880(86)90015-1), 1986b.

Nguyen, T. B., Nizkorodov, S. A., Laskin, A., and Laskin, J.: An approach toward quantification of organic compounds in complex environmental samples using high-resolution electrospray ionization mass spectrometry, *Anal. Methods*, 5, 72–80, <https://doi.org/10.1039/C2AY25682G>, 2013.



Ning, C., Gao, Y., Zhang, H., Yu, H., Wang, L., Geng, N., Cao, R., and Chen, J.: Molecular characterization of dissolved organic matters in winter atmospheric fine particulate matters (PM<sub>2.5</sub>) from a coastal city of northeast China, *Sci. Total Environ.*, 689, 312–321, <https://doi.org/10.1016/j.scitotenv.2019.06.418>, 2019.

Nolte, C. G., Schauer, J. J., Cass, G. R., and Simoneit, B. R. T.: Highly polar organic compounds present in wood smoke and in the ambient atmosphere, *Environ. Sci. Technol.*, 35, 1912–1919, <https://doi.org/10.1021/es001420r>, 2001.

Nozière, B., Dziedzic, P., and Córdova, A.: Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by ammonium ions (NH<sub>4</sub><sup>+</sup>), *J. Phys. Chem. A*, 113, 231–237, <https://doi.org/10.1021/jp8078293>, 2009.

Nozière, B., Dziedzic, P., and Córdova, A.: Inorganic ammonium salts and carbonate salts are efficient catalysts for aldol condensation in atmospheric aerosols, *Phys. Chem. Chem. Phys.*, 12, 3864–3872, <https://doi.org/10.1039/B924443C>, 2010.

Nozière, B., Fache, F., Maxut, A., Fenet, B., Baudouin, A., Fine, L., and Ferronato, C.: The hydrolysis of epoxides catalyzed by inorganic ammonium salts in water: kinetic evidence for hydrogen bond catalysis, *Phys. Chem. Chem. Phys.*, 20, 1583–1590, <https://doi.org/10.1039/C7CP06790A>, 2018.

Pang, H., Zhang, Q., Lu, X. H., Li, K., Chen, H., Chen, J., Yang, X., Ma, Y., Ma, J., and Huang, C.: Nitrite-mediated photooxidation of vanillin in the atmospheric aqueous phase, *Environ. Sci. Technol.*, 53, 14253–14263, <https://doi.org/10.1021/acs.est.9b03649>, 2019a.

Pang, H., Zhang, Q., Wang, H., Cai, D., Ma, Y., Li, L., Li, K., Lu, X., Chen, H., Yang, X., and Chen, J.: Photochemical aging of guaiacol by Fe(III)-oxalate complexes in atmospheric aqueous phase, *Environ. Sci. Technol.*, 53, 127–136, <https://doi.org/10.1021/acs.est.8b04507>, 2019b.

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

Powelson, M. H., Espelien, B. M., Hawkins, L. N., Galloway, M. M., and De Haan, D. O.: Brown carbon formation by aqueous-phase carbonyl compound reactions with amines and ammonium sulfate, *Environ. Sci. Technol.*, 48, 985–993, <https://doi.org/10.1021/es4038325>, 2014.

Pye, H., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett, J. L. Jr., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I-T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, *Atmos. Chem. Phys.*, 20, 4809–4888, <https://doi.org/10.5194/acp-20-4809-2020>, 2020.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., and Cass, G. R.: Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces, *Environ. Sci. Technol.*, 32, 13–22, <https://doi.org/10.1021/es960930b>, 1998.

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

Scharko, N. K., Berke, A. E., and Raff, J. D.: Release of nitrous acid and nitrogen dioxide from nitrate photolysis in acidic aqueous solutions, *Environ. Sci. Technol.*, 48, 20, 11991–1200, <https://doi.org/10.1021/es503088x>, 2014.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 3. C<sub>1</sub>–C<sub>29</sub> organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.*, 35, 1716–1728, <https://doi.org/10.1021/es001331e>, 2001.

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

Sedehi, N., Takano, H., Blasic, V. A., Sullivan, K. A., and De Haan, D. O.: Temperature- and pH-dependent aqueous-phase kinetics of the reactions of glyoxal and methylglyoxal with atmospheric amines and ammonium sulfate, *Atmos. Environ.*, 77, 656–663, <https://doi.org/10.1016/j.atmosenv.2013.05.070>, 2013.

Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R., and McNeill, V. F.: Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics, *Atmos. Chem. Phys.*, 9, 2289–2300, <https://doi.org/10.5194/acp-9-2289-2009>, 2009.

Slikboer, S., Grandy, L., Blair, S. L., Nizkorodov, S. A., Smith, R. W., and Al-Abadleh, H. A.: Formation of light absorbing soluble secondary organics and insoluble polymeric particles from the dark reaction of catechol and guaiacol with Fe(III), *Environ. Sci. Technol.*, 49, 7793–7801, <https://doi.org/10.1021/acs.est.5b01032>, 2015.

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

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

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

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

Sun, Y. L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry, *Atmos. Chem. Phys.*, 10, 4809–4822, <https://doi.org/10.5194/acp-10-4809-2010>, 2010.

Vione, D., Albinet, A., Barsotti, F., Mekic, M., Jiang, B., Minero, C., Brigante, M., and Gligorovski, S.: Formation of substances with humic-like fluorescence properties, upon photoinduced oligomerization of typical phenolic compounds emitted by biomass burning, *Atmos. Environ.*, 206, 197–207, <https://doi.org/10.1016/j.atmosenv.2019.03.005>, 2019.

Vione, D., Maurino, V., Minero, C., Pelizzetti, E., Harrison, M. A. J., Olariu, R., and Arsene, C.: Photochemical reactions in the tropospheric aqueous phase and on particulate matter, *Chem. Soc. Rev.*, 35, 441–453, <https://doi.org/10.1039/B510796M>, 2006.

Volkamer, R., Ziemann, P. J., and Molina, M. J.: Secondary organic aerosol formation from acetylene (C<sub>2</sub>H<sub>2</sub>): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, *Atmos. Chem. Phys.*, 9, 1907–1928, <https://doi.org/10.5194/acp-9-1907-2009>, 2009.

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

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

Xiao, H.-W., Wu, J.-F., Luo, L., Liu, C., Xie, Y.-J., and Xiao, H.-Y.: Enhanced biomass burning as a source of aerosol ammonium over cities in Central China in autumn, *Environ. Pollut.*, 266, art. no. 115278, <https://doi.org/10.1016/j.envpol.2020.115278>, 2020.

Yang, J., Au, W. C., Law, H., Lam, C. H., and Nah, T.: Formation and evolution of brown carbon during aqueous-phase nitrate-mediated photooxidation of guaiacol and 5-nitroguaiacol, *Atmos. Environ.*, 254, 118401, <https://doi.org/10.1016/j.atmosenv.2021.118401>, 2021.

Yaws, C. L.: Handbook of vapor pressure: Volume 3: Organic compounds C<sub>8</sub> to C<sub>28</sub>, Gulf Professional Publishing, USA, 1994.

Ye, Z., Qu, Z., Ma, S., Luo, S., Chen, Y., Chen, H., Chen, Y., Zhao, Z., Chen, M., and Ge, X.: A comprehensive investigation of aqueous-phase photochemical oxidation of 4-ethylphenol, *Sci. Total Environ.*, 685, 976–985, <https://doi.org/10.1016/j.scitotenv.2019.06.276>, 2019.

Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crouse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, *Atmos. Chem. Phys.*, 13, 8019–8043, <https://doi.org/10.5194/acp-13-8019-2013>, 2013.

Yu, G., Bayer, A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., and Keutsch, F. N.: Glyoxal in aqueous ammonium sulfate solutions: products, kinetics and hydration effects, *Environ. Sci. Technol.*, 45, 6336–6342, <https://doi.org/10.1021/es200989n>, 2011.

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

Zhang, Q. and Anastasio, C.: Conversion of fogwater and aerosol organic nitrogen to ammonium, nitrate, and NO<sub>x</sub> during exposure to simulated sunlight and ozone, *Environ. Sci. Technol.*, 37, 3522–3530, <https://doi.org/10.1021/es034114x>, 2003.

Zhang, R., Gen, M., Fu, T-M., and Chan, C. K.: Production of formate via oxidation of glyoxal promoted by particulate nitrate photolysis, *Environ. Sci. Technol.*, 55, 5711–5720, <https://doi.org/10.1021/acs.est.0c08199>, 2021.

Zhang, R., Gen, M., Huang, D. D., Li, Y., and Chan, C. K.: Enhanced sulfate production by nitrate photolysis in the presence of halide ions in atmospheric particles, *Environ. Sci. Technol.*, 54, 3831–3839, <https://dx.doi.org/10.1021/acs.est.9b06445>, 2020.

Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F., and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric brown carbon, *Atmos. Chem. Phys.*, 15, 6087–6100, <https://doi.org/10.5194/acp-15-6087-2015>, 2015.

Zhao, Y., Hallar, A.G., and Mazzoleni, L.R.: Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry, *Atmos. Chem. Phys.* 13, 12343–12362, <https://doi.org/10.5194/acp-13-12343-2013>, 2013.

Zielinski, T., Bolzacchini, E., Cataldi, M., Ferrero, L., Graßl, S., Hansen, G., Mateos, D., Mazzola, M., Neuber, R., Pakszys, P., Posyniak, M., Ritter, C., Severi, M., Sobolewski, P., Traversi, R., and Velasco-Merino, C.: Study of chemical and optical properties of biomass burning aerosols during long-range transport events toward the Arctic in summer 2017, *Atmosphere*, 11, 84, <https://doi.org/10.3390/atmos11010084>, 2020.

1 **Aqueous SOA formation from the direct photosensitized -oxidation of**  
2 **vanillin in the absence and presence of ammonium nitrate: Direct**  
3 **photosensitized reactions and nitrate-mediated reactions**

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14 **Abstract.** Vanillin (VL), a phenolic aromatic carbonyl abundant in biomass burning emissions, forms triplet excited states  
15 (<sup>3</sup>VL\*) under simulated sunlight leading to aqueous secondary organic aerosol (aqSOA) formation. Nitrate and ammonium  
16 are among the main components of biomass burning aerosols and cloud/fog water. Under atmospherically relevant cloud and  
17 fog conditions, solutions composed of either VL only or VL with ammonium nitrate were subjected to simulated sunlight  
18 irradiation to compare aqSOA formation via the direct photosensitized oxidation of VL in the absence and presence of  
19 ammonium nitrate. The reactions were characterized. This direct photosensitized oxidation of VL was compared with nitrate-  
20 mediated VL photo-oxidation under atmospherically relevant cloud and fog conditions throughby examining the VL decay  
21 kinetics, product compositions, and light absorbance changes. The majority of the most abundant products from both VL  
22 photo-oxidation pathways were potential Brown carbon (BrC) chromophores. In addition, Both pathways conditions  
23 generated oligomers, functionalized monomers, and oxygenated ring-opening products, and ammonium but nitrate promoted  
24 functionalization and nitration, which can be ascribed likely due to its photolysis products (\*OH, \*NO<sub>2</sub>, and N(III)-NO<sub>2</sub> or  
25 HONO). Moreover, a potential imidazole derivative observed from nitrate-mediated VL photo-oxidation in the presence of  
26 ammonium nitrate suggested that ammonium may be involved participated in the reactions. The majority of the most abundant  
27 products from both conditions were potential Brown carbon (BrC) chromophores. The effects of oxygen (O<sub>2</sub>), pH, and reactants  
28 concentration and molar ratios on VL photo-oxidation the reactions were also explored. Our findings show that O<sub>2</sub> plays an  
29 essential role in VL photo-oxidation the reactions, and oligomer formation was enhanced at pH < 4. Also, functionalization  
30 was dominant at low VL concentration, whereas oligomerization was favored at high VL concentration. Furthermore,  
31 oligomers and hydroxylated products were detected from the oxidation of comparisons of the apparent quantum efficiency of  
32 guaiacol (a non-carbonyl phenol) via VL photosensitized reactions photodegradation indicate that in this study, guaiacol

33 ~~oxidation by photosensitized reactions of VL is less efficient relative to nitrate-mediated photo-oxidation.~~ Lastly, potential  
34 aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium nitrate  
35 ~~VL photo-oxidation~~ were proposed. This study indicates that the direct photosensitized oxidation of VL ~~and nitrate-mediated~~  
36 ~~VL photo-oxidation~~ may be an important aqSOA sources in areas influenced by biomass burning ~~emissions and underscores~~  
37 the importance of nitrate in the aqueous-phase processing of aromatic carbonyls.  
38  
39  
40

## 41 **1 Introduction**

42 Aqueous reactions can be an important source of secondary organic aerosols (SOA) (Blando and Turpin, 2000; Volkamer et  
43 al., 2009; Lim et al., 2010; Ervens et al., 2011; Huang et al., 2011; Lee et al., 2011; Smith et al., 2014) such as highly-  
44 oxygenated and low-volatility organics (Hoffmann et al., 2018; Liu et al., 2019) which may affect aerosol optical properties  
45 due to contributions to Brown Carbon (BrC) (Gilardoni et al., 2016). BrC refers to organic aerosols that absorb radiation  
46 efficiently in the near-ultraviolet (UV) and visible regions (Laskin et al., 2015). The formation of aqueous SOA (aqSOA) via  
47 photochemical reactions involves oxidation, with hydroxyl radical ( $\cdot\text{OH}$ ) usually considered as the primary oxidant (Herrmann  
48 et al., 2010; Smith et al., 2014). The significance of photosensitized chemistry in atmospheric aerosols has recently been  
49 reviewed (George et al., 2015). For instance, triplet excited states of organic compounds ( $^3\text{C}^*$ ) from the irradiation of light-  
50 absorbing organics such as non-phenolic aromatic carbonyls (Canonica et al., 1995; Anastasio et al., ~~1996~~1997; Vione et al.,  
51 2006; Smith et al., 2014) have been reported to oxidize phenols at higher faster-rates and with greaterhigher aqSOA yields  
52 compared to  $\cdot\text{OH}$  (Sun et al., 2010; Smith et al., 2014; Yu et al., 2014; Smith et al., 2016). Aside from being an oxidant,  $^3\text{C}^*$   
53 can also be a precursor of singlet oxygen ( $^1\text{O}_2$ ), superoxide ( $\text{O}_2^-$ ) or hydroperoxyl ( $\cdot\text{HO}_2$ ) radical, and  $\cdot\text{OH}$  (via  $\text{HO}_2/\text{O}_2^-$   
54 formation) upon reactions with  $\text{O}_2$  and substrates (e.g., phenols) (George et al., 2018). The  $^3\text{C}^*$  concentration in typical fog  
55 water has been estimated to be  $> 25$  times than that of  $\cdot\text{OH}$ , making  $^3\text{C}^*$  the primary photo-oxidant for biomass burning phenolic  
56 compounds (Kaur and Anastasio, 2018; Kaur et al., 2019). Recent works on triplet-driven oxidation of phenols have mainly  
57 focused on changes of physicochemical properties (e.g., light absorption) and aqSOA yield (e.g., Smith et al., 2014, 2015,  
58 2016), with few reports on reaction ~~pathways mechanisms and characterization of reaction~~-products (e.g., Yu et al., 2014; Chen  
59 et al., 2020; Jiang et al., 2021).

60 Inorganic salts such as ammonium nitrate ~~are is a~~ major components of aerosols and cloud/fog water. In cloud and fog  
61 water, the concentrations of inorganic nitrate can vary from  $50\ \mu\text{M}$  to  $> 1000\ \mu\text{M}$ , with higher levels typically noted under  
62 polluted conditions (Munger et al., 1983; Collett et al., 1998; Zhang and Anastasio, 2003; Li et al., 2011; Giulianelli et al.,  
63 2014; Bianco et al., 2020). Upon photolysis (Vione et al., 2006; Herrmann, 2007; Scharko et al., 2014), inorganic nitrate in  
64 cloud and fog water can contribute to BrC (Minero et al., 2007) and aqSOA formation (Huang et al., 2018; Klodt et al., 2019;

65 Zhang et al., 2021) by generating  $\cdot\text{OH}$  and nitrating agents (e.g.,  $\cdot\text{NO}_2$ ). For example, the aqSOA yields from the photo-  
66 oxidation of phenolic carbonyls in ammonium nitrate are twice as high as that in ammonium sulfate solution (Huang et al.,  
67 2018). Nitration is a significant process in the formation of light-absorbing organics or BrC in the atmosphere (Jacobson, 1999;  
68 Kahnt et al., 2013; Mohr et al., 2013; Laskin et al., 2015; Teich et al., 2017; Li et al., 2020). ~~Moreover~~Furthermore, nitrate  
69 photolysis has been proposed to be a potentially important process for  $\text{SO}_2$  oxidation and SOA formation via the generation of  
70  $\cdot\text{OH}$ ,  $\cdot\text{NO}_2$ , and N(III) within particles (Gen et al., 2019a, 2019b; Zhang et al., 2020, 2021), and it can also potentially change  
71 the morphology of atmospheric viscous particles (Liang et al., 2021). Furthermore, ammonium ( $\text{NH}_4^+$ ) can react with carbonyls  
72 producing light-absorbing compounds and highly oxygenated oligomers, as well as catalyze different reactions (De Haan et  
73 al., 2009, 2011; Nozière et al., 2009, 2010, 2018; Shapiro et al., 2009; Yu et al., 2011; Lee et al., 2013; Powelson et al., 2014;  
74 Gen et al., 2018; Mabato et al., 2019). ~~Accordingly~~Therefore, both  $\cdot^3\text{C}^*$  and inorganic nitrate can contribute to aqSOA and BrC  
75 formation.

76 Biomass burning (BB) is a significant atmospheric source of both phenolic and non-phenolic aromatic carbonyls  
77 (Rogge et al., 1998; Nolte et al., 2001; Schauer et al., 2001; Bond et al., 2004). Upon exposure to sunlight, aromatic carbonyls  
78 are excited to their triplet excited states, which can initiate oxidation leading to aqSOA formation (e.g., Smith et al., 2014;  
79 2015, 2016). ~~For~~An example is: vanillin (VL) (Henry's law constant of  $4.56 \times 10^5 \text{ M atm}^{-1}$ ; Yaws, 1994), a phenolic aromatic  
80 carbonyl that has been used as a model compound for methoxyphenols, which are abundant in BB emissions (Li et al., 2014;  
81 Pang et al., 2019a). The aqueous  $\cdot\text{OH}$  oxidation and direct photodegradation of VL, ~~has~~have been shown to yield low-volatility  
82 products, although these findings were based on 254-nm irradiation (Li et al., 2014) ~~via aqueous  $\cdot\text{OH}$  oxidation and direct~~  
83 photodegradation. Photodegradation kinetics and aqSOA yields have been reported for direct VL photodegradation under  
84 simulated sunlight (Smith et al., 2016), with oxygenated aliphatic-like compounds (high H:C,  $\geq 1.5$  and low O:C,  $\leq 0.5$  ratios)  
85 ~~reported~~noted as the most likely products (Loisel et al., 2021). Additionally, aqueous-phase reactions of phenols with reactive  
86 nitrogen species have been proposed to be a significant source of nitrophenols and SOA (Grosjean, 1985; Kitanovski et al.,  
87 2014; Kroflič et al., 2015, 2021; Pang et al., 2019a; ~~Kroflič et al., 2021~~; Yang et al., 2021). For instance, nitrite-mediated VL  
88 photo-oxidation can generate nitrophenols, and the reactions are influenced by nitrite/VL molar ratios, pH, and the presence  
89 of  $\cdot\text{OH}$  scavengers (Pang et al., 2019a). Nitrate and ammonium are also among the main biomass burning aerosol components  
90 (Xiao et al., 2020; Zielinski et al., 2020). As BB aerosols are typically internally mixed with other aerosol components  
91 (Zielinski et al., 2020), VL may coexist with ammonium nitrate in BB aerosols. The ~~aqueous-phase photo-oxidation-direct~~  
92 photosensitized oxidation of VL in the absence and presence of ammonium nitrate may then reveal insights into the  
93 atmospheric processing of BB aerosols. Moreover, the  $\cdot^3\text{C}^*$  of non-phenolic aromatic carbonyls (e.g., 3,4-  
94 dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021) and  
95 phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to oxidize phenols, but the  
96 reaction products from the latter are unknown.

97

98 Previous works on aqSOA formation via triplet-mediated oxidation are mostly based on reactions between phenols  
99 and a non-phenolic aromatic carbonyl as triplet precursor (e.g., Smith et al., 2014; Yu et al., 2014; Jiang et al., 2021). Also,  
100 studies examining the effects of inorganic nitrate on aqSOA formation and properties remain limited. The present study aimed  
101 to evaluate aqSOA formation via the direct photosensitized oxidation of a triplet precursor (VL) alone. Furthermore, aqSOA  
102 formation via the direct photosensitized oxidation of VL in the presence of ammonium nitrate was also examined. Accordingly,  
103 the main goals of this study are (1) to compare aqSOA formation in cloud/fog water via the direct photosensitized oxidation  
104 of VL in the absence and presence of ammonium nitrate, (2) to evaluate the influences of O<sub>2</sub>, solution pH, and reactants  
105 concentration and molar ratios on the reactions, (3) to investigate the participation of ammonium in the direct photosensitized  
106 oxidation of VL in the presence of ammonium nitrate, and (4) to examine aqSOA formation from the oxidation of guaiacol, a  
107 non-carbonyl phenol, via photosensitized reactions of VL. To achieve these goals, solutions composed of either VL only or  
108 VL in the presence of ammonium nitrate were subjected to simulated sunlight irradiation under atmospherically relevant cloud  
109 and fog conditions. Solutions composed of VL in the presence of sodium nitrate were also examined for comparison with the  
110 presence of ammonium nitrate. To evaluate the potential significance of VL and its reactions with nitrate in aqSOA formation  
111 in cloud/fog water, we studied the direct photosensitized oxidation of VL and nitrate-mediated VL photo-oxidation under  
112 atmospherically relevant conditions. In this work, the reactions were characterized based on VL decay kinetics, light  
113 absorbance changes, and detected products, and light absorbance changes. The influences of O<sub>2</sub>, solution pH, and reactants  
114 concentration and molar ratios on these two photo-oxidation pathways were also assessed. The <sup>13</sup>C\* of non-phenolic aromatic  
115 carbonyls (e.g., 3,4-dimethoxybenzaldehyde, DMB; a non-phenolic aromatic carbonyl) (Smith et al., 2014; Yu et al., 2014;  
116 Jiang et al., 2021) and phenolic aromatic carbonyls (e.g., acetosyringone, vanillin) (Smith et al., 2016) have been shown to  
117 oxidize phenols, but the reaction products from the latter are unknown. We then examined the photo-oxidation of guaiacol,  
118 another non-carbonyl phenol, in the presence of VL and compared it with nitrate-mediated photo-oxidation. Finally, we  
119 proposed aqSOA formation pathways via the direct photosensitized oxidation of VL in the absence and presence of ammonium  
120 nitrate VL-photo-oxidation. This work presents a comprehensive comparison of aqSOA formation from the direct  
121 photosensitized oxidation of VL photo-oxidation in the absence and presence of ammonium nitrate by VL photosensitization  
122 and in the presence of inorganic nitrate.

## 125 2 Methods

### 126 2.1 Aqueous-phase photo-oxidation experiments

127 Photo-oxidation experiments were performed in a custom-built quartz photoreactor. The solutions (initial volume of 500 mL)  
128 were continuously mixed throughout the experiments using a magnetic stirrer. The solutions were bubbled with synthetic air  
129 or nitrogen (N<sub>2</sub>) (> 99.995%) (0.5 dm<sup>3</sup>/min) for 30 min before irradiation to achieve air- or N<sub>2</sub>-saturated conditions,  
130 respectively, and the bubbling was continued throughout the reactions (Du et al., 2011; Chen et al., 2020). The aim of the air-



131 saturated experiments was to enable the generation of secondary oxidants ( $^1\text{O}_2$ ,  $\text{O}_2^{\cdot-}$ / $\text{HO}_2$ ,  $\cdot\text{OH}$ ) from  $^3\text{VL}^*$  as  $\text{O}_2$  is present.  
132 Conversely, the  $\text{N}_2$ -saturated experiments would inhibit the formation of these secondary oxidants, which can lead to  $^3\text{VL}^*$ -  
133 driven reactions (Chen et al., 2020). [Comparison of results of air and  \$\text{N}\_2\$ -saturated experiments can yield information on the](#)  
134 [reaction pathways that require  \$\text{O}\_2\$  involved in the direct photosensitized oxidation of VL](#). Solutions were irradiated through  
135 the quartz window of the reactor using a xenon lamp (model 6258, Ozone free xenon lamp, 300 W, Newport) equipped with  
136 a longpass filter (20CGA-305 nm cut-on filter, Newport) to eliminate light below 300 nm. Cooling fans positioned around the  
137 photoreactor and lamp housing maintained reaction temperatures at  $27 \pm 2$  °C. The averaged initial photon flux in the reactor  
138 from 300 to 380 nm measured using a chemical actinometer (2-nitrobenzaldehyde) was  $2.6 \times 10^{15}$  photons  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$  (Fig.  
139 S1). Although the concentration of VL in cloud/fog water has been estimated to be  $< 0.01$  mM (Anastasio et al., [1996](#)[1997](#)), a  
140 higher VL concentration (0.1 mM) was used in this study to guarantee sufficient signals for product identification (Vione et  
141 al., 2019). The chosen ammonium nitrate (AN) [or sodium nitrate \(SN\)](#) concentration (1 mM) was based on values observed in  
142 cloud and fog water (Munger et al., 1983; Collett et al., 1998; Zhang and Anastasio, 2003; Li et al., 2011; Giulianelli et al.,  
143 2014; Bianco et al., 2020). It should be noted that this study is not intended to identify the concentrations of [ammonium](#) nitrate  
144 that would affect the kinetics [but to examine the effect of ammonium nitrate on aqSOA formation from the direct](#)  
145 [photosensitized oxidation of VL](#). Moreover, ~~comparisons were made between~~ the photo-oxidation of guaiacol ([GUA](#)) (0.1  
146 mM), a non-carbonyl phenol, in the presence of VL (0.1 mM) ~~was studied~~ [AN \(1 mM\)](#). [The GUA experiments allowed us](#)  
147 [to examine aqSOA formation from the oxidation of phenols by  \$^3\text{VL}^\*\$](#) . Samples (10 mL) were collected hourly for a total of 6  
148 h for offline ~~optical and chemical~~ [and optical](#) analyses. ~~Absorbance measurements,~~ VL (and GUA) decay kinetics  
149 ~~measurements~~ (calibration curves for VL and GUA standard solutions; Fig. S2), ~~small organic acids measurements, and~~  
150 product characterization, ~~small organic acids measurements, and a~~ [Absorbance measurements,](#) were conducted using [ultra-](#)  
151 [high-performance liquid chromatography with photodiode array detector \(UHPLC-PDA\), UHPLC coupled with quadrupole](#)  
152 [time-of-flight mass spectrometry \(UHPLC-qToF-MS\) equipped with an electrospray ionization \(ESI\) source and operated in](#)  
153 [the positive ion mode \(the negative ion mode signals were too low for our analyses\), ion chromatography \(IC\), and UV-Vis](#)  
154 [spectrophotometry,](#) ~~ultra-high-performance liquid chromatography with photodiode array detector (UHPLC-PDA), ion~~  
155 ~~chromatography (IC), and UHPLC coupled with quadrupole time of flight mass spectrometry (UHPLC-qToF-MS) equipped~~  
156 ~~with an electrospray ionization (ESI) source and operated in the positive ion mode (the negative ion mode signals were too~~  
157 ~~low for our analyses),~~ respectively. Each experiment was repeated independently at least three times and measurements were  
158 done in triplicate. The reported decay rate constants and absorbance enhancement are the average of results from triplicate  
159 experiments, and the corresponding errors represent one standard deviation. The mass spectra are based on the average of  
160 results from duplicate experiments. The Supporting Information (Text S1 to [S67](#)) provides details on the materials and  
161 analytical procedures. The pseudo-first-order rate constant ( $k'$ ) for VL decay was determined using the following equation  
162 (Huang et al., 2018):

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

165

166

167 where  $[VL]_t$  and  $[VL]_0$  are the concentrations of VL at time  $t$  and 0, respectively. Replacing VL with GUA in Eq. 1 enabled  
168 the calculation of GUA decay rate constant. The decay rate constants were normalized to the photon flux measured for each  
169 experiment through dividing  $k'$  by the measured 2-nitrobenzaldehyde (2NB) decay rate constant,  $j(2NB)$  (see Text S6 for more  
170 details).

## 171 2.2 Calculation of normalized abundance of products

172 Comparisons of peak abundance in mass spectrometry have been used in many recent studies (e.g., Lee et al., 2014;  
173 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  
174 show the relative importance of different types of compounds (Wang et al., 2021). However, ionization efficiency may greatly  
175 vary for different classes of compounds (Kebarle, 2000; Schmidt et al., 2006; Leito et al., 2008; Perry et al., 2008; Krueve et  
176 al., 2014), and so uncertainties may arise from comparisons of peak areas among compounds. In this work, we assumed equal  
177 ionization efficiency of different compounds, which is commonly used to estimate O:C ratios of SOA (e.g., Bateman et al.,  
178 2012; Lin et al., 2012; Laskin et al., 2014; De Haan et al., 2019), to calculate their normalized abundance. The normalized  
179 abundance of a product, [P] (unitless), was calculated as follows:

180

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

181

182 where  $A_{P,t}$  and  $A_{VL,t}$  are the extracted ion chromatogram (EIC) peak areas of the product P and VL from UHPLC-qToF-MS  
183 analyses at time  $t$ , respectively;  $[VL]_t$  and  $[VL]_0$  are the VL concentrations ( $\mu\text{M}$ ) determined using UHPLC-PDA at time  $t$  and  
184 0, respectively. Here, we relied on the direct quantification of [VL] using UHPLC-PDA (see Fig. S2 for VL calibration curve).  
185 ~~It should be noted~~We emphasize that the normalized abundance of products in this study is a semi-quantitative analysis  
186 intended to provide an overview of how the signal intensities changed under different experimental conditions but not to  
187 quantify the absolute concentration of products. Also, as it is based on comparisons of peak abundance from UHPLC-qToF-  
188 MS analyses, the normalized abundance of products in this study is associated with intrinsic uncertainties due to the variability  
189 in ionization efficiencies for various compounds. Moreover, the major products detected in this study are probably those with  
190 high concentration or high ionization efficiency in the positive ESI mode. The use of relative abundance (product peaks are  
191 normalized to the highest peak) (e.g., Lee et al., 2014; Romonosky et al., 2017; Fleming et al., 2018; Klodt et al., 2019) would  
192 yield the same major products reported. Typical fragmentation behavior observed in MS/MS spectra for individual functional  
193 groups from Holčapek et al. (2010) are outlined in Table S1.

194

### 195 3 Results and Discussion

#### 196 3.1 Kinetics, mass spectrometric, and absorbance changes analyses during the direct photosensitized oxidation of VL 197 in the aqueous phase photo-oxidation of vanillin

198 For clarity purposes, the reactions involving reactive species referred to in the following discussions are provided in Table 1.  
199 Table 2 summarizes the reaction conditions, initial VL (and GUA) decay rate constants, normalized abundance of products,  
200 and average carbon oxidation state ( $\langle OS_c \rangle$ ) (of the 50 most abundant products). In general, the 50 most abundant products  
201 contributed more than half of the total normalized abundance of products and can serve as representative products for  
202 discussions of reaction pathways and calculation of the  $\langle OS_c \rangle$ .

203 As shown in Figure S3, VL underwent oxidation both directly and in the presence of ammonium (and sodium) nitrate  
204 upon simulated sunlight illumination. VL absorbs light and is promoted to its excited singlet state ( $^1VL^*$ ), then undergoes  
205 intersystem crossing (ISC) to the excited triplet state,  $^3VL^*$ . In principle,  $^3VL^*$  can oxidize ground-state VL (Type I  
206 photosensitized reactions) via H-atom abstraction/electron transfer and form  $O_2^{\cdot-}$  or  $HO_2^{\cdot}$  in the presence of  $O_2$  (George et al.,  
207 2018), or react with  $O_2$  (Type II photosensitized reactions) to yield  $^1O_2$  via energy transfer or  $O_2^{\cdot-}$  via electron transfer (Lee et  
208 al., 1987; Foote et al., 1991). The disproportionation of  $HO_2^{\cdot}/O_2^{\cdot-}$  (Anastasio et al., 19961997) form hydrogen peroxide ( $H_2O_2$ ),  
209 which is a photolytic source of  $\cdot OH$ . Overall, air-saturated conditions, in which  $O_2$  is present, enable the generation of  
210 secondary oxidants ( $^1O_2, O_2^{\cdot-}/HO_2^{\cdot}, \cdot OH$ ) from  $^3VL^*$  ( $^1O_2, O_2^{\cdot-}/HO_2^{\cdot}, \cdot OH$ ). Moreover,  $\cdot OH$ ,  $\cdot NO_2$ , and  $NO_2^{\cdot}/HNO_2$ , i.e., N(III),  
211 generated via nitrate photolysis (Reactions 1–3; Table 1), can also oxidize or nitrate VL. In this work, the direct photosensitized  
212 oxidation of VL in the absence (VL only experiments) and nitrate-mediated VL photo-oxidation presence of ammonium  
213 nitrate are referred to as VL\* and VL+AN, respectively.

214

#### 215 3.1.1 VL photo-oxidation under $N_2$ and air-saturated conditions

216 As previously stated, the  $N_2$ -saturated experiments would inhibit the formation of secondary oxidants ( $^1O_2, O_2^{\cdot-}/HO_2^{\cdot}, \cdot OH$ )  
217 from  $^3VL^*$ , facilitating  $^3VL^*$ -driven reactions (Chen et al., 2020). In contrast, the air-saturated experiments can enable the  
218 generation of these secondary oxidants from  $^3VL^*$  as  $O_2$  is present. Moreover, for experiments conducted under three saturated  
219 gases (air,  $O_2$ , and  $N_2$ ), the rate constant for 4-ethylguaiacol (a non-carbonyl phenol) loss by  $^3DMB^*$  decreased in the order of  
220 air >  $N_2$  >  $O_2$ . This was attributed to the presence of  $O_2$  resulting in a synergistic effect of  $^1O_2$  and  $^3C^*$  under air-saturated  
221 conditions (Chen et al., 2020). The differences in air and  $N_2$ -saturated experiments can then be used to infer the role of reaction  
222 pathways that require  $O_2$  in the direct photosensitized oxidation of VL. -The photosensitized-oxidation of VL under both  $N_2$ -  
223 and air-saturated conditions (Fig. S3a) were carried out at pH 4, which is representative of moderately acidic aerosol and cloud  
224 pH values (Pye et al., 2020). No significant VL loss was observed for dark experiments. The oxidation of ground-state VL by  
225  $^3VL^*$  via H-atom abstraction or electron transfer can form phenoxy (which is in resonance with a carbon-centered

226 cyclohexadienyl radical that has a longer lifetime) and ketyl radicals (Neumann et al., 1986a, 1986b; Anastasio et al.,  
227 ~~1996~~1997). The coupling of phenoxy radicals or phenoxy and cyclohexadienyl radicals can form oligomers as observed for  
228 both N<sub>2</sub>- and air-saturated experiments (see discussions later). However, the ~~minimal~~ decay of VL under N<sub>2</sub>-saturated  
229 condition indicates that these radicals probably ~~predominantly~~ decayed via back-hydrogen transfer to regenerate VL (Lathioor  
230 et al., 1999). A possible explanation for this is the involvement of O<sub>2</sub> in the secondary steps of VL decay. For instance, a major  
231 fate of the ketyl radical is reaction with O<sub>2</sub> (Anastasio et al., ~~1996~~1997). In the absence of O<sub>2</sub>, radical formation occurs, but the  
232 forward reaction of ketyl radical and O<sub>2</sub> is blocked, leading to the regeneration of VL as suggested by the minimal VL decay.  
233 Aside from potential inhibition of secondary oxidants generation (Chen et al., 2020), N<sub>2</sub> purging may have also hindered the  
234 secondary steps for VL decay.

235 Contrastingly, the VL\* decay rate constant ~~for VL\*~~ under air-saturated conditions was 4 times higher ~~than under~~  
236 ~~N<sub>2</sub>-saturated conditions~~ (Table 2). As mentioned earlier, secondary oxidants (<sup>1</sup>O<sub>2</sub>, O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub>, •OH) can be generated from <sup>3</sup>VL\*  
237 when O<sub>2</sub> is present (~~e.g.~~ under air-saturated conditions). However, the ~~direct photosensitized~~ oxidation of VL in this study is  
238 likely ~~mainly~~ governed by <sup>3</sup>VL\* and that these secondary oxidants have only minor participation. <sup>1</sup>O<sub>2</sub> is also a potential oxidant  
239 for phenols (Herrmann et al., 2010; Minella et al., 2011; Smith et al., 2014), but <sup>1</sup>O<sub>2</sub> reacts much faster (by ~60 times) with  
240 phenolate ions ~~compared to~~ ~~than~~ neutral phenols (Tratnyek and Hoigne, 1991; Canonica et al., 1995; McNally et al., 2005).  
241 Under the pH values (pH 2.5 to 4) considered in this study, the amount of phenolate ion is negligible (~~pK<sub>a</sub> of VL = 7.9~~), so the  
242 reaction between VL and <sup>1</sup>O<sub>2</sub> should be slow. Interestingly, however, ~~both <sup>3</sup>C\* and <sup>1</sup>O<sub>2</sub>~~ ~~have~~ been shown to be important in  
243 the photo-oxidation of 4-ethylguaicol (~~pK<sub>a</sub> = 10.3~~) by ~~<sup>3</sup>DMBC\* of 3,4 dimethoxybenzaldehyde~~ (solution with pH of ~3)  
244 (Chen et al., 2020). Furthermore, while the irradiation of other phenolic compounds can produce H<sub>2</sub>O<sub>2</sub>, a precursor for •OH  
245 (Anastasio et al., ~~1996~~1997), the amount of H<sub>2</sub>O<sub>2</sub> is small. Based on this, only trace amounts of H<sub>2</sub>O<sub>2</sub> were likely generated  
246 from VL\* (Li et al., 2014) under-air saturated conditions, suggesting that contribution from •OH was minor. Overall, these  
247 suggest that the direct photosensitized oxidation of VL in this study is ~~mainly~~ driven by <sup>3</sup>VL\*. ~~Further study on the impact of~~  
248 ~~O<sub>2</sub> on the reactive intermediates involved is required to understand the exact mechanisms occurring under air saturated~~  
249 ~~conditions. Nonetheless, the VL\* decay trends clearly indicate that O<sub>2</sub> is important for efficient VL photo-oxidation.~~

250 The VL decay rate constant for VL+AN under air-saturated conditions was also higher (6.6 times) than ~~under~~ N<sub>2</sub>-  
251 saturated conditions, ~~which may be possibly~~ due to reactions facilitated by nitrate photolysis products that may have been  
252 enhanced in the presence of O<sub>2</sub> (Vione et al., 2005; Kim et al., 2014; Pang et al., 2019a). As shown later, more ~~nitrogen-~~  
253 ~~containing~~ ~~N-containing~~ species were observed ~~for VL+AN~~ under air-saturated conditions ~~than under N<sub>2</sub>-saturated conditions~~.  
254 An example is enhanced VL nitration likely from increased •NO<sub>2</sub> formation such as from the reaction of •OH and O<sub>2</sub><sup>•-</sup> with  
255 NO<sub>2</sub> (Reactions 4 and 5, respectively; Table 1) or the autoxidation of •NO from NO<sub>2</sub><sup>-</sup> photolysis (Reactions 6–9; Table 1) in  
256 aqueous solutions (Pang et al., 2019a). Nevertheless, the comparable decay rate constants for VL\* and VL+AN imply that  
257 <sup>3</sup>VL\* chemistry still dominates even at 1:10 molar ratio of VL/AN ~~nitrate. This can be attributed~~ ~~probably due~~ to the much  
258 higher molar absorptivity of VL compared to that of nitrate (Fig. S1) and the high VL concentration (0.1 mM) used in this

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259 study. ~~Although we have no-~~The quantification of the oxidants in our reaction systems ~~is not explored here and require~~  
260 ~~additional work as it is outside the scope of this study,~~ these observations clearly substantiate that photosensitized oxidation  
261 ~~of VL and nitrate-mediated VL photo-oxidation are more efficient in the presence of O<sub>2</sub>.~~ In essence, the N<sub>2</sub>-saturated  
262 ~~experiments suggest that the secondary steps for VL decay via <sup>3</sup>VL\* may require to O<sub>2</sub> proceed. Nonetheless, ~~Further study~~  
263 ~~on the impact of O<sub>2</sub> on the reactive intermediates involved is required to understand the exact mechanisms occurring under air-~~  
264 ~~saturated conditions.~~~~

265 The products from VL\* under N<sub>2</sub>-saturated conditions were mainly oligomers (e.g., C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>) (Fig. 1a), consistent  
266 with triplet-mediated oxidation forming higher molecular weight products, ~~probably~~ with less fragmentation relative to  
267 oxidation by <sup>•</sup>OH (Yu et al., 2014; Chen et al., 2020). A threefold increase in the normalized abundance of products was noted  
268 upon addition of ~~AN~~nitrate (VL+AN under N<sub>2</sub>-saturated conditions; Fig. 1b), and in addition to oligomers, functionalized  
269 monomers (e.g., C<sub>8</sub>H<sub>6</sub>O<sub>5</sub>) and ~~nitrogen-containing~~N-containing compounds (e.g., C<sub>8</sub>H<sub>9</sub>NO<sub>3</sub>; No. 32, Table S2) were also  
270 observed, in agreement with <sup>•</sup>OH-initiated oxidation yielding more functionalized/oxygenated products compared to triplet-  
271 mediated oxidation (Yu et al., 2014; Chen et al., 2020). Oligomers, functionalized monomers (e.g., demethylated VL; Fig. S4),  
272 and ~~nitrogen-containing~~N-containing compounds (e.g., C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>9</sub>; No. 43, Table S2) (for VL+AN) had higher normalized  
273 abundance under air-saturated conditions (Figs. 1c-d), ~~attributable likely due~~ to efficient <sup>3</sup>VL\*-initiated oxidation and enhanced  
274 VL nitration in the presence of O<sub>2</sub>. For both VL\* and VL+AN under air-saturated conditions, the most abundant product was  
275 C<sub>10</sub>H<sub>10</sub>O<sub>5</sub> (No. 54, Table S2), a substituted VL. Irradiation of VL by 254-nm lamp has also been reported to lead to VL  
276 dimerization and functionalization via ring-retaining pathways, as well as small oxygenates ~~formation~~ but only when <sup>•</sup>OH from  
277 H<sub>2</sub>O<sub>2</sub> were involved (Li et al., 2014). In this work, small organic acids (e.g., formic acid) were observed from both VL\* and  
278 VL+AN under air-saturated conditions (Fig. S5) due to simulated sunlight that could access the 308-nm VL band (Smith et al.,  
279 2016). Interestingly, we observed a potential imidazole derivative (C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>; No. 65, Table S2) from VL+AN under air-  
280 saturated conditions (Fig. 1d), which may have formed from reactions induced by ammonium. This compound was not  
281 observed in a parallel experiment in which AN was replaced with ~~sodium nitrate~~(SN) (Fig. S6a; see Sect. 3.1.3 for discussion).

282 -The potential aqSOA formation pathways via ~~the direct photosensitized oxidation of VL in the absence and presence~~  
283 ~~of AN photo-oxidation~~ in this study are summarized in Fig. 2.- At pH 4, ~~<sup>3</sup>VL\*-initiated reactions yielded oligomeric species~~  
284 ~~such as- C<sub>16</sub>H<sub>12</sub>O<sub>6</sub> and C<sub>27</sub>H<sub>22</sub>O<sub>6</sub>. Earlier works on phenolic aqSOA formation have reported that oligomers can form via the~~  
285 ~~coupling of phenoxy radicals or phenoxy and cyclohexadienyl radicals (Sun et al., 2010; Yu et al., 2014; Vione et al., 2019).~~  
286 ~~In this work, phenoxy radicals (in resonance with a carbon-centered cyclohexadienyl radical) can be generated from several~~  
287 ~~processes such as the oxidation of ground-state VL by <sup>3</sup>VL\* via H-atom abstraction or electron transfer coupled with proton~~  
288 ~~transfer from the phenoxy radical cation or from solvent water (Neumann et al., 1986a, 1986b; Anastasio et al., 19961997)~~  
289 ~~and photoinduced O-H bond-breaking (Berto et al., 2016). Also, similar reactions can be initiated by <sup>•</sup>OH (Gelencsér et al.,~~  
290 ~~2003; Hoffer et al., 2004; Chang and Thompson, 2010; Sun et al., 2010), which in this study can be generated from the reaction~~  
291 ~~between <sup>3</sup>VL\* and O<sub>2</sub>, as well as nitrate photolysis. Trace amounts of H<sub>2</sub>O<sub>2</sub> could be were likely formed during VL~~  
292 ~~photodegradation (Li et al., 2014), similar to the case of other phenolic compounds (Anastasio et al., 19961997). In addition,~~

293 ring-opening products (Fig. S5) from fragmentation in both VL\* and VL+AN may have reacted with VL or dissolved ammonia  
294 to generate C<sub>10</sub>H<sub>10</sub>O<sub>5</sub> (No. 54, Table S2) (Pang et al., 2019b) or a potential imidazole derivative (C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>; No. 65, Table  
295 S2), respectively. Moreover, nitrate photolysis products promoted functionalization and nitration (e.g., C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>9</sub>; No. 43,  
296 Table S2).

297 The molecular transformation of VL upon photosensitized-oxidation was examined using the van Krevelen diagrams  
298 (Fig. S7). For all experiments (A1-145; Table 2) in this study, the O:C and H:C ratios of the products were mainly similar to  
299 those observed from the aging of other phenolic compounds (Yu et al., 2014) and BB aerosols (Qi et al., 2019). Under N<sub>2</sub>-  
300 saturated conditions, oligomers with O:C ratios ≤ 0.6 were dominant in VL\*, while smaller molecules (n<sub>c</sub> ≤ 8) with higher O:C  
301 ratios (up to 0.8) were also observed for VL+AN. In contrast, more products with higher O:C ratios (≥ 0.6) were noted under  
302 air-saturated conditions for both VL\* and VL+AN. For experiments A5 to A8, H:C ratios were mostly around 1.0 and double  
303 bond equivalent (DBE) values were typically (58% of the 50 most abundant products) > 7, indicating that the products were  
304 mainly oxidized aromatic- compounds (Xie et al., 2020). Compounds with H:C ≤ 1.0 and O:C ≤ 0.5 are common for aromatic  
305 species, while compounds with H:C ≥ 1.5 and O:C ≤ 0.5 are typical for more aliphatic species (Mazzoleni et al., 2012;  
306 Kourtchev et al., 2014; Jiang et al., 2021). In contrast, Loisel et al. (2021) reported mainly oxygenated aliphatic-like compounds  
307 from the direct irradiation of VL (0.1 mM), ~~attributable probably due~~ to their use of ESI in the negative ion mode, which has  
308 higher sensitivity for detecting compounds such as carboxylic acids (Holčapek et al., 2010; Liigand et al., 2017), and solid-  
309 phase extraction (SPE) procedure causing the loss of some oligomers (LeClair et al., 2012; Zhao et al., 2013; Bianco et al.,  
310 20198). Among experiments A5 to A8, VL+AN under air-saturated conditions (A7) had the highest normalized abundance of  
311 products and <OS<sub>c</sub>>, probably due to the combined influence of <sup>3</sup>VL\* and enhanced VL nitration in the presence of O<sub>2</sub>. Our  
312 measured <OS<sub>c</sub>> for all experiments range from -0.28 to +0.12, while other studies on phenolic aqSOA formation reported  
313 <OS<sub>c</sub>> ranging from -0.14 to +0.47 (Sun et al., 2010) and 0.04 to 0.74 (Yu et al., 2014). ~~The <OS<sub>c</sub>> in this study likely were~~  
314 ~~lower estimates since This is likely because~~ we excluded contributions from ring-opening products, which may have higher  
315 OS<sub>c</sub> values as these products are not detectable in the positive ion mode. ~~Thus, the <OS<sub>c</sub>> in this study likely were lower~~  
316 ~~estimates. In brief, more oxidized aqSOA and higher the presence—O<sub>2</sub> increased the—~~normalized abundance of products ~~such~~  
317 ~~as oligomers and functionalized monomers were noted under air-saturated conditions due to efficient VL oxidation by <sup>3</sup>VL\*~~  
318 ~~in and promoted the formation of more oxidized aqSOA the presence of O<sub>2</sub>.~~ Compared to N<sub>2</sub>-saturated condition, the higher  
319 normalized abundance of ~~nitrogen-containingN-containing~~ products under air-saturated condition for VL+AN (at pH 4)  
320 suggests a potential enhancement of VL nitration in the presence of O<sub>2</sub>.

321 Illumination of phenolic aromatic carbonyls with high molar absorptivities (ε<sub>λmax</sub>) (~8 to 22 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) leads to  
322 an overall loss of light absorption but increased absorbance at longer wavelengths (> 350 nm), where the carbonyls did not  
323 initially absorb light (Smith et al., 2016). Fig. 3a illustrates the changes in total absorbance from 350 to 550 nm of VL\* and  
324 VL+AN under N<sub>2</sub>- and air-saturated conditions. The absorption spectra of VL\* under air- and N<sub>2</sub>- saturated conditions (pH 4)  
325 at different time intervals are shown in Fig. S8. For both VL\* and VL+AN, evident absorbance enhancement was observed  
326 under air-saturated conditions, while the absorbance changes under N<sub>2</sub>-saturated conditions were minimal, consistent with the

327 VL decay trends. Dimers and functionalized products have been shown to contribute to chromophore formation for the aqueous  
328 photo-oxidation of guaiacyl acetone (another aromatic phenolic carbonyl) by  $^3\text{DMB}^*$  (Jiang et al., 2021). Based on this, the  
329 higher normalized abundance of This absorbance enhancement can be explained by the formation of oligomers, which have  
330 large, conjugated  $\pi$ -electron systems (Chang and Thompson, 2010), and hydroxylated products (Li et al., 2014; Zhao et al.,  
331 2015), in agreement with the observed reaction products observed under air-saturated conditions have contributed to the  
332 absorbance enhancement. However, it is worth noting that the products detected may not have contributed significantly to the  
333 total products formed and hence may not be the primary contributors to the absorbance enhancement. As mentioned earlier,  
334 the major products detected in this study are probably those with high concentration or high ionization efficiency in the positive  
335 ESI mode. In other words, the absorbance enhancement may not necessarily correlate directly with the products detected.

336 Correlating speciated chromophores with absorbance changes may be useful in demonstrating how aqSOA influence  
337 the Earth's radiative balance and identifying chemical reactions that can affect the overall light absorption by aqSOA. This  
338 can be accomplished by using liquid chromatography coupled with photodiode array (PDA) detector and high-resolution mass  
339 spectrometry (LC/PDA/HRMS platform) (e.g., Lin et al., 2017; Jiang et al., 2021; Misovich et al., 2021). In our experiments,  
340 VL (and GUA) concentration measurements, product characterization, and absorbance measurements were performed using  
341 UHPLC-PDA, UHPLC-qToF-MS, and UV-Vis spectrophotometry, respectively. A similar approach is then possible using the  
342 current methods in this work by matching the retention time (RT) of the products detected using UHPLC-ToF-MS with that  
343 in the PDA. However, the concentration of the chromophores in this study is below the detection limit of the PDA based on  
344 the lack of distinct PDA signals from the products. In this work, phenoxy radicals (in resonance with a carbon-centered  
345 cyclohexadienyl radical) can be generated from several processes such as the oxidation of ground-state VL by  $^2\text{VL}^*$  via H-  
346 atom abstraction or electron transfer coupled with proton transfer from the phenoxy radical cation or from solvent water  
347 (Neumann et al., 1986a, 1986b; Anastasio et al., 1996) and photoinduced O-H bond-breaking (Berto et al., 2016). Also, similar  
348 reactions can be initiated by  $^{\bullet}\text{OH}$  (Gelenesér et al., 2003; Hoffer et al., 2004; Chang and Thompson, 2010; Sun et al., 2010),  
349 which in this study can be generated from the reaction between  $^2\text{VL}^*$  and  $\text{O}_2$ , as well as nitrate photolysis. Trace amounts of  
350  $\text{H}_2\text{O}_2$  were likely formed during VL photodegradation (Li et al., 2014), similar to the case of other phenolic compounds  
351 (Anastasio et al., 1996). Oligomers can then form via the coupling of phenoxy radicals or phenoxy and cyclohexadienyl radicals  
352 (Sun et al., 2010; Yu et al., 2014; Vione et al., 2019). Absorbance increase at  $> 350$  nm has also been reported for the  
353 photosensitized oxidation of phenol and 4-phenoxyphenol (De Laurentiis et al., 2013a, 2013b) and direct photolysis of tyrosine  
354 and 4-phenoxyphenol (Bianco et al., 2014) in which dimers have been identified as initial substrates. The continuous  
355 absorbance enhancement throughout 6 h of irradiation correlated with the observation of oligomers and nitrated compounds  
356 after irradiation. However, the increasing concentration of small organic acids (Fig. S5) throughout the experiments suggests  
357 that fragmentation, which results in the decomposition of initially formed oligomers and formation of smaller oxygenated  
358 products (Huang et al., 2018), is important at longer irradiation times. Overall, these trends establish that compared to  $\text{N}_2$ -  
359 saturated conditions, VL oxidation by  $^3\text{VL}^*$  under air-saturated conditions ( $\text{O}_2$  is present) enabled  $-\text{O}_2$  is necessary for the  
360 efficient formation of light-absorbing compounds from both  $\text{VL}^*$  and  $\text{VL}+\text{AN}$ .

### 3.1.2 VL photo-oxidation under varying Effect of pH conditions

The reactivity of  $^3\text{C}^*$  (Smith et al., 2014, 2015, 2016), aromatic photolysis by nitrate (Machado and Boule, 1995; Dzengel et al., 1999; Vione et al., 2005; Minero et al., 2007), and N(III)-mediated VL photo-oxidation (Pang et al., 2019a) have been demonstrated to be pH-dependent. In this study, the effect of pH on the direct photosensitized oxidation of VL photo-oxidation was investigated over within the pH range of 2.5 to 4, which is within corresponding to typical cloud pH values (2-7) (Pye et al., 2020). The decay rate constants for both VL\* and VL+AN increased by 1.6 and 1.4 times, respectively, as pH decreased from 4 to 2.5 (VL\* and VL+AN at pH 2.5: 1.6 and 1.4 times faster than at pH 4, respectively) (Fig. S3b Table 2). These differences in decay rate constants are small but statistically significant ( $p < 0.05$ ). The  $pK_a$  for the  $^3\text{VL}^*$  triplet has been reported to be 4.0 (Smith et al., 2016). As there are is a greater fraction of  $^3\text{VL}^*$  triplets that are protonated at pH 2.5 (0.96) than at pH 4 (0.50), it is possible that the pH dependence of the VL decay rate constants observed in this study is due to  $^3\text{VL}^*$  being more reactive in its protonated form. Smith et al. (2016) also observed a pH dependence for the direct photodegradation of VL (0.005 mM) (rate constants at  $\text{pH} \leq 3$  are ~two times lower than at  $\text{pH} \geq 5$ ) which they has been attributed to the sensitivity of the excimer of VL (i.e., the charge-transfer complex formed between an excited state VL molecule and a separate ground state VL molecule; Birks, 1973; Turro et al., 2010) to acid-base chemistry. The opposite trend observed in this study for 0.1 mM VL may be due to the reactivities of the protonated and neutral forms of the  $^3\text{VL}^*$  being dependent on the VL concentration (Smith et al., 2016). It has been reported that the quantum yield for direct VL photodegradation is higher at pH 5 than at pH 2 for 0.005 mM VL, but they are not statistically different for 0.03 mM VL (Smith et al., 2016). As pH decreases, the higher reactivity of  $^3\text{VL}^*$  and sensitivity of the excimer of VL to acid-base chemistry may have led to faster VL photo-oxidation. Similar to pH 4 experiments, comparable decay rate constants between VL\* and VL+AN were also noted at  $\text{pH} < 4$ , again suggesting the predominant role of  $^3\text{VL}^*$  chemistry compared to nitrate, likely due to the high VL concentration (0.1 mM) used in this study.

As pH decreased, the normalized abundance of products, particularly oligomers and functionalized monomers, was higher for both VL\* and VL+AN, consistent with further indicating that  $^3\text{VL}^*$  potentially being may be more reactive in their its protonated form. The most abundant products observed were a substituted VL ( $\text{C}_{10}\text{H}_{10}\text{O}_5$ ; No. 54, Table S2) and VL dimer ( $\text{C}_{16}\text{H}_{14}\text{O}_6$ ; No. 76, Table S2) at pH 4 and  $\text{pH} < 4$ , respectively (Figs. 1c-h). Furthermore, a tetramer ( $\text{C}_{31}\text{H}_{24}\text{O}_{11}$ ) was observed only in VL\* at pH 2.5. For VL+AN, the normalized abundance of nitrogen-containing compounds was also higher at lower pH (Table 2), likely due to increased  $^{\bullet}\text{OH}$  and  $^{\bullet}\text{NO}_2$  formation, which may be caused by the dependence of N(III) ( $\text{NO}_2^- + \text{HONO}$ ) speciation on solution acidity (Pang et al., 2019a). At pH 3.3, half of N(III) exists as HONO (Fischer and Warneck, 1996; Pang et al., 2019a), which has a higher quantum yield for  $^{\bullet}\text{OH}$  formation than that of  $\text{NO}_2^-$  in the near-UV region (Arakaki et al., 1999; Kim et al., 2014). Also,  $\text{NO}_2^-/\text{HONO}$  can generate  $^{\bullet}\text{NO}_2$  via oxidation by  $^{\bullet}\text{OH}$  (Reactions 4 and 10; Table 1) (Pang et al., 2019a). At  $\text{pH} < 4$ ,  $^3\text{VL}^*$  likely have higher reactivity as suggested by the increased normalized abundance of oligomers (e.g.,  $\text{C}_{16}\text{H}_{14}\text{O}_6$ ; No. 76, Table S2 and  $\text{C}_{31}\text{H}_{24}\text{O}_{11}$ ) and N-containing compounds (e.g.,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_9$ ; No. 43, Table S2 and  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_{10}$ ) (Fig. 2). The most abundant product at  $\text{pH} < 4$ ,  $\text{C}_{16}\text{H}_{14}\text{O}_6$  (No. 7, Table S2), is likely a C-

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394 O coupled dimer. In previous studies on phenolic aqSOA formation, the generation of phenolic dimers has been proposed to  
395 occur via C–C or C–O coupling of phenoxy radicals (Sun et al., 2010; Yu et al., 2014; Huang et al., 2018; Chen et al., 2020;  
396 Misovich et al., 2021). Similarly, functionalized monomers such as C<sub>7</sub>H<sub>6</sub>O<sub>3</sub> (demethylated VL; No. 8, Table S2) and  
397 hydroxylated products (e.g., C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>; No. 9, Table S2) also had increased normalized abundance for both VL\* and VL+AN.  
398 The formation of C<sub>7</sub>H<sub>6</sub>O<sub>3</sub> (No. 8, Table S2), which varies from the structure of VL by CH<sub>2</sub>, can be explained by <sup>•</sup>OH addition  
399 at the carbon containing the methoxy group, succeeded by the elimination of a methoxy radical (<sup>•</sup>OCH<sub>3</sub>) (Yee et al., 2013).  
400 This reaction has also been postulated for the <sup>•</sup>OH oxidation of syringol (2,6-dimethoxyphenol) (Yee et al., 2013) and  
401 transformation of DMB in a system composed of guaiacyl acetone and <sup>3</sup>DMB\* (Misovich et al., 2021). The potential imidazole  
402 derivative (C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>; No. 65, Table S2) was observed only at pH 4, following possibly due to the pH dependence of  
403 ammonium speciation (pK<sub>a</sub> = 9.25). Imidazole formation requires the nucleophilic attack of ammonia on the carbonyl group  
404 (Yu et al., 2011), and at pH 4, the concentration of dissolved ammonia in VL+AN was about 10 or 30 times higher than that  
405 at pH 3 or pH 2.5, respectively. At different pH For the pH values considered in this study, the O:C and H:C ratios in VL\* and  
406 VL+AN had no significant differences (Figs. S7c–d and S9), but molecules with higher O:C ratios (> 0.6) were more abundant  
407 at pH < 4. Accordingly In addition, the <OS> at pH < 4 for both VL\* and VL+AN were higher than that at pH 4, consistent  
408 with higher <OS> observed at pH 5 compared to pH 7 for the <sup>•</sup>OH-mediated photo-oxidation of syringol (Sun et al., 2010).  
409 Essentially, the higher reactivity of <sup>3</sup>VL\* and predominance of HONO over nitrite at lower pH may have resulted in increased  
410 formation higher normalized abundance of products mainly composed of oligomers and functionalized monomers.

411 Higher absorbance enhancement for both VL\* and VL+AN (Fig. 3b) was observed as pH increased. To determine  
412 whether the pH dependence is due to the acid-base chemistry of the products or of the reactions, ~~we measured the changes in~~  
413 ~~the UV-Vis absorption spectra pH dependence~~ of the aqSOA formed from VL\* at pH 4 and 2.5 ~~were measured~~ over a range  
414 of pH conditions from 1.5 to 10.5 (Fig. S10). For both cases, the intensity of absorption at longer wavelengths significantly  
415 increased as the pH of the solutions was raised. Moreover, the ~~comparable pH dependence of changes in the UV-Vis absorption~~  
416 ~~spectra for~~ the two solutions ~~of varying pH are comparable~~, suggesting that the observed pH dependence ~~may be attributed~~  
417 ~~to the is rooted in~~ acid-base chemistry of the reactions ~~involving, which may involve~~ <sup>3</sup>VL\* or the excimer of VL (Smith et al.,  
418 2016), as discussed earlier.

### 419 **3.1.3 Participation of ammonium in the direct photosensitized oxidation of VL in the presence of AN**

420 Ammonium salts are an important constituent of atmospheric aerosols particles (Jimenez et al., 2009), and reactions between  
421 dicarbonyls (e.g., glyoxal) and ammonia or primary amines form BrC (De Haan et al., 2009, 2011; Nozière et al., 2009; Shapiro  
422 et al., 2009; Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabato et al., 2019). Imidazole and imidazole derivatives  
423 are the major products of glyoxal and ammonium sulfate reactions at pH 4 (Galloway et al., 2009; Yu et al., 2011; Sedehi et  
424 al., 2013; Gen et al., 2018; Mabato et al., 2019). Here, we compared VL+AN and VL+SN at pH 4 under air-saturated conditions  
425 to confirm the participation of ammonium in the photosensitized oxidation of VL. The presence of ammonium did not appear  
426 to influence the kinetics of VL decay and light absorbance changes based on VL+AN and VL+SN having no statistically

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427 significant difference ( $p > 0.05$ ) with respect to VL decay rate constants (Table 2) and yielding comparable absorbance  
428 enhancement (Fig. 3a), respectively. However, it is important to note that this may not be the case for lower concentrations of  
429 VL. As previously stated, the reactions in this study were dominated by  $^3\text{VL}^*$  chemistry, likely due to the higher molar  
430 absorptivity of VL than that of nitrate and the high VL concentration used. Similarly, the normalized abundance of products  
431 was comparable in both experiments (A7 and A9; Table 2) with  $\text{C}_{10}\text{H}_{10}\text{O}_5$  (No. 5, Table S2) as the most abundant product  
432 (Figs. 1d and S6a), but in VL+SN, there was a significant amount of a VL dimer ( $\text{C}_{15}\text{H}_{12}\text{O}_8$ ; No. 10, Table S2). The normalized  
433 abundance of N-containing compounds was also similar for VL+AN and VL+SN but the detected N-containing compounds  
434 were distinct. Aside from the potential imidazole derivative ( $\text{C}_5\text{H}_5\text{N}_3\text{O}_2$ ; No. 6, Table S2),  $\text{C}_8\text{H}_9\text{NO}_3$  (No. 3, Table S2), possibly  
435 an aminophenol, was also observed from VL+AN but only under  $\text{N}_2$ -saturated conditions (Fig. 1b), probably due to further  
436 oxidation by  $^3\text{VL}^*$ . Relative to VL+AN, the products from VL+SN had higher O:C ratios (e.g.,  $\text{C}_7\text{H}_4\text{N}_2\text{O}_7$ ; No. 11, Table S2),  
437  $\text{OS}_c$ , and  $\langle\text{OS}_c\rangle$  values (Table 2). In summary, while the VL decay kinetics and absorbance enhancement for VL+AN and  
438 VL+SN were similar, the product analysis supports the participation of ammonium in the aqueous-phase reactions.

### 439 **3.1.43 Distribution of potential BrC compounds**

440 Figure S11 plots the DBE values vs. number of carbons ( $n_c$ ) (Lin et al., 2018) for the 50 most abundant products from pH 4  
441 experiments under air-saturated conditions, along with reference to DBE values corresponding to fullerene-like hydrocarbons  
442 (Lobodin et al., 2012), cata-condensed polycyclic aromatic hydrocarbons (PAHs) (Siegmann and Sattler, 2000), and linear  
443 conjugated polyenes with a general formula  $\text{C}_x\text{H}_{x+2}$ . As light absorption by BrC requires uninterrupted conjugation across a  
444 significant part of the molecular structure, compounds with DBE/ $n_c$  ratios (shaded area in Fig. S11) greater than that of linear  
445 conjugated polyenes are potential BrC compounds (Lin et al., 2018). Based on this criterion and the observed absorbance  
446 enhancement at  $> 350$  nm (Fig. 3), the majority of the 50 most abundant products from pH 4 experiments under air-saturated  
447 conditions were potential BrC chromophores composed of monomers and oligomers up to tetramers. However, as ESI-detected  
448 compounds in BB organic aerosols has been reported to be mainly molecules with  $n_c < 25$  (Lin et al., 2018), there may be  
449 higher oligomers that were not detected in our reaction systems.

450

### 451 **3.2 Effect of reactants concentration and molar ratios on the direct photosensitized oxidation of VL in the aqueous** 452 **phaseaqueous photo-oxidation of vanillin**

453 To examine the influence of VL and AN-nitrate concentration and their molar ratios on the direct photosensitized oxidation of  
454 VL-VL-photo-oxidation, we also characterized the reaction products from lower [VL] (0.01 mM VL\*; A10; Table 2), lower  
455 [VL] and equal molar ratio of VL/AN-nitrate (0.01 mM VL + 0.01 mM AN; A11; Table 2), and lower [VL] and 1:100 molar  
456 ratio of VL/AN-nitrate (0.01 mM VL + 1 mM AN; A12; Table 2) at pH 4. The normalized abundance of products from low  
457 [VL] experiments (A10-A12; Table 2) were up to 1.4 times higher than that of high [VL] experiments (A5 and A7; Table 2).

458 Nevertheless, the major products for both low and high [VL] experiments were functionalized monomers (Figs. 1c-d and S12a-  
459 c) such as  $C_8H_6O_4$  (No. 127, Table S2) and  $C_{10}H_{10}O_5$  (No. 54, Table S2). For both VL\* and VL+AN, the contribution of < 200  
460 m/z to the normalized abundance of products was higher at low [VL] than at high [VL], while the opposite was observed for  
461 > 300 m/z (Fig. S12d). This indicates that functionalization was favored at low [VL], as supported by the higher <OS<sub>c</sub>>, while  
462 oligomerization was the dominant pathway at high [VL], consistent with more oligomers or polymeric products reported from  
463 high phenols concentration (e.g., 0.1 to 3 mM) (Li et al., 2014; Slikboer et al., 2015; Ye et al., 2019). As the formation  
464 mechanism of dimers and higher oligomers during aqueous-phase reactions of phenolic compounds involves the coupling of  
465 phenoxy radicals (Kobayashi and Higashimura, 2003; Sun et al., 2010), the enhanced oligomerization at high [VL] can be  
466 attributed. This is probably due to an increased concentration of phenoxy radicals (in resonance with a carbon-centered  
467 cyclohexadienyl radical) at high [VL], promoting radical-radical polymerization (Sun et al., 2010; Li et al., 2014). At low  
468 [VL], the contribution of < 200 m/z to the normalized abundance of products was higher for 1:1 than 1:100 VL/ANnitrate  
469 molar ratio, suggesting the prevalence of functionalization for the former. In addition, 1:1 VL/ANnitrate (A11; Table 2) had  
470 higher <OS<sub>c</sub>> than 1:100 VL/ANnitrate (A12; Table 2), indicating the formation of more oxidized products, but had fewer N-  
471 containing compounds compared to the latter. A possible explanation is that at 1:1 VL/ANnitrate, VL may compete with NO<sub>2</sub><sup>-</sup>  
472 for 'OH (from nitrate or nitrite photolysis, Reaction 4; Table 1) and indirectly reduce 'NO<sub>2</sub>. Similarly, hydroxylation has been  
473 suggested to be a more important pathway for 1:1 VL/nitrite than in 1:10 VL/nitrite (Pang et al., 2019a). Fragmentation, which  
474 leads to the decomposition of previously formed oligomers and generation of small, oxygenated products such as organic acids  
475 (Huang et al., 2018), may also occur for the low [VL] experiments. However, its importance would likely be observed at longer  
476 irradiation times, similar to the high [VL] experiments.

### 477 3.3 Participation of ammonium in the aqueous photo-oxidation of vanillin

478 ~~Imidazole and imidazole derivatives have been reported to be the major products of glyoxal and ammonium sulfate reactions~~  
479 ~~at pH 4 (Galloway et al., 2009; Yu et al., 2011; Sedehi et al., 2013; Gen et al., 2018; Mabato et al., 2019). Here, we compared~~  
480 ~~VL+AN and VL+SN at pH 4 in terms of reaction products and oxidative characteristics to confirm the participation of~~  
481 ~~ammonium in the aqueous photo-oxidation of VL. The normalized abundance of the products was comparable in both~~  
482 ~~experiments (A7 and A9; Table 2), with  $C_{10}H_{10}O_5$  (No. 4, Table S2) as the most abundant product (Figs. 1d and S6a), but in~~  
483 ~~VL+SN, there was a significant amount of a VL dimer ( $C_{18}H_{12}O_8$ ; No. 8, Table S2). Moreover, the nitrogen containing~~  
484 ~~compounds were distinct. Aside from the potential imidazole derivative ( $C_5H_5N_2O_2$ ; No.5, Table S2),  $C_8H_5NO_3$  (No. 2, Table~~  
485 ~~S2) was also observed from VL+AN but only under N<sub>2</sub>-saturated conditions (Fig. 1b), probably due to further oxidation by~~  
486 ~~<sup>3</sup>VL\*. Relative to VL+AN, the products from VL+SN had higher O:C ratios (e.g.,  $C_5H_5N_2O_2$ ; No. 9, Table S2), OS<sub>c</sub>, and~~  
487 ~~<OS<sub>c</sub>> values (Table 2). The product analysis suggests the participation of ammonium in the aqueous phase reactions.~~  
488 ~~Ammonium salts are an important constituent of atmospheric aerosols particles (Jimenez et al., 2009), and reactions between~~  
489 ~~dicarbonyls (e.g., glyoxal) and ammonia or primary amines have been demonstrated to form BrC (De Haan et al., 2009, 2011;~~  
490 ~~Nozière et al., 2009; Shapiro et al., 2009; Lee et al., 2013; Powelson et al., 2014; Gen et al., 2018; Mabato et al., 2019).~~

491 Relative to VL+AN, the products from VL+SN had higher O:C ratios (e.g., C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>; No. 9, Table S2), OS<sub>n</sub>, and <OS>  
492 values (Table 2).  
493

### 494 3.34 Oxidation of guaiacol by photosensitized reactions of vanillin VL and photolysis of nitrate

495 The oxidation of phenols by <sup>3</sup>C\* has been mainly studied using non-phenolic aromatic carbonyls (Anastasio et al., 1996, 1997;  
496 Smith et al., 2014, 2015; Yu et al., 2014; Chen et al., 2020) and aromatic ketones (Canonica et al., 2000) as triplet precursors.  
497 Recently, <sup>3</sup>VL\* have also been shown to oxidize syringol (Smith et al., 2016), a non-carbonyl phenol, although the reaction  
498 products remain unknown. In this section, we discussed the photo-oxidation of guaiacol (GUA), a non-carbonyl phenol that is  
499 also a lignocellulosic BB pollutant (Kroflič et al., 2015) that is also a non-carbonyl phenol, in the presence of VL (GUA+VL)  
500 or nitrate (GUA+AN). The dark experiments did not show any substantial loss of VL or GUA (Fig. S3c). Due to its poor light  
501 absorption in the solar range, GUA is not an effective photosensitizer (Smith et al., 2014; Yu et al., 2014). Accordingly, the  
502 direct GUA photodegradation resulted in minimal decay, which plateaued after ~3 hours. However, in the presence of VL or  
503 nitrate, the GUA decay rate constant was 2.2 times higher by 2.2 (GUA+VL) and 1.3 (GUA+AN) times, respectively, than for  
504 direct GUA photodegradation. The enhancement of GUA decay rate constant in the presence of VL is statistically significant  
505 ( $p < 0.05$ ), while that in the presence of AN is not ( $p > 0.05$ ). This enhanced GUA decay rate constant may be due to the  
506 oxidation of GUA by <sup>3</sup>VL\*. As mentioned earlier, <sup>3</sup>VL\* chemistry appears to be more important than that of nitrate photolysis  
507 even at 1:10 molar ratio of VL/nitrate on account of the much higher molar absorptivity of VL compared to that of nitrate (Fig.  
508 S1) and the high VL concentration (0.1 mM) used in this study. However, the apparent quantum efficiency of GUA  
509 photodegradation ( $\phi_{\text{GUA}}$ ) in the presence of nitrate ( $1.3 \times 10^{-3} \pm 2.9 \times 10^{-3}$ ) is ~14 times larger than that in the presence of VL  
510 ( $9.0 \times 10^{-4} \pm 4.0 \times 10^{-4}$ ), suggesting that nitrate-mediated photo-oxidation of GUA is more efficient than that by photosensitized  
511 reactions of VL (see Text S7 for more details). The decay rate constant of VL in GUA+VL (A14; Table 2) was 3 times slower  
512 than that of VL\* (A5; Table 2), which may be due to competition between ground-state VL and GUA for reactions with <sup>3</sup>VL\*  
513 or increased conversion of <sup>3</sup>VL\* back to the ground state through the oxidation of GUA (Anastasio et al., 1996, 1997; Smith et  
514 al., 2014). The corresponding absorbance changes for the GUA experiments (Fig. 3c) were consistent with the observed decay  
515 trends. The minimal absorbance changes for the direct GUA photodegradation also plateaued after ~3 hours. Moreover, the  
516 difference between GUA photo-oxidation in the presence of VL or nitrate was more evident, with the former showing much  
517 higher absorbance enhancement. Yang et al. (2021) also observed greater light absorption during nitrate-mediated photo-  
518 oxidation relative to direct GUA photodegradation.

519 For GUA experiments, the direct GUA photodegradation, GUA+VL, and GUA+AN, the normalized abundance of  
520 products was calculated only for GUA+VL (2.2; Table 2); as the GUA signal from the UHPLC-qToF-MS in the positive ion  
521 mode was weak, which may introduce large uncertainties during normalization. Nonetheless, the number of products detected  
522 from these experiments (178, 266, and 844 for the direct GUA photodegradation, GUA+AN, and GUA+VL, respectively)  
523 corroborates the kinetics and absorbance results. The major products (Fig. 4a) from the direct GUA photodegradation of GUA

524 were  $C_{14}H_{14}O_4$  (No. 130, Table S2), a typical GUA dimer, and  $C_{21}H_{20}O_6$  (No. 14, Table S2), a trimer ( $C_{21}H_{20}O_6$ ; No. 11, Table  
525 S2) which likely originated from photoinduced O-H bond-breaking (Berto et al., 2016). In general, higher absolute signal  
526 intensities were noted for oligomers (e.g.,  $C_{14}H_{14}O_4$ , No. 130 and  $C_{21}H_{20}O_6$ , No. 14, Table S2) and hydroxylated products  
527 (e.g.,  $C_7H_8O_4$ ) in both GUA+VL and GUA+AN, similar to those observed from GUA oxidation by triplets of 3,4-  
528 dimethoxybenzaldehyde (DMB; a non-phenolic aromatic carbonyl)DMB\* or \*OH (from  $H_2O_2$  photolysis) (Yu et al., 2014;  
529 Jiang et al., 2021). In contrast to the GUA aqSOA reported by Yu et al. (2014), the photo-oxidation of GUA in this study  
530 yielded nitrated compounds (e.g.,  $C_9H_{14}N_2O_6$ ,  $C_{11}H_{14}N_2O_8$ ) from GUA+AN and VL dimers (e.g.,  $C_{16}H_{12}O_8$ ) from GUA+VL.  
531 However, based on a recent work on the aqueous photo-oxidation of guaiacyl acetone (another aromatic phenolic carbonyl)  
532 by DMB triplets, the hydroxylation and dimerization of DMB can also contribute to aqSOA (Jiang et al., 2021). The  
533 contributions from DMB-participated reactions were only minor due to the low initial DMB concentration (0.005 mM).  
534 Relative to GUA+AN, higher signals for dimers such as  $C_{14}H_{14}O_4$  (No. 10, Table S2) and  $C_{16}H_{12}O_8$  were noted in GUA+VL,  
535 possibly due to both GUA and ground-state VL being available as oxidizable substrates for  $^3VL^*$ . Also, a potential GUA  
536 tetramer ( $C_{28}H_{26}O_8$ , No. 152, Table S2) was observed only in GUA+VL, consistent with more efficient higher-oligomer  
537 formation from the triplet-mediated photo-oxidation of phenols relative to direct photodegradation\*OH-assisted photo-  
538 oxidation (Yu et al., 2014). In general, the products from the direct GUA photodegradation and GUA+VL, and GUA+AN  
539 had mostly similar  $OS_c$  values (-0.5 to 0.5) (Figs. 4b-cd), falling into the criterion of biomass burning organic aerosol (BBOA)  
540 and semivolatile oxygenated organic aerosol (SV-OOA) (Kroll et al., 2011). The corresponding absorbance changes for the  
541 GUA experiments (Fig. 3c) were consistent with the observed VL and GUA decay trends and detected products. While minimal  
542 absorbance changes, which also plateaued after ~3 hours, were observed for direct GUA photodegradation, significant and  
543 continuous absorbance enhancement was noted for GUA+VL. In this work, GUA photo-oxidation was observed in the  
544 presence of VL or AN, forming aqSOA composed of oligomers, hydroxylated products, and nitrated compounds (for  
545 GUA+AN). The higher product signals from GUA+VL compared to GUA+AN is likely due to the availability of both GUA  
546 and ground-state VL as aqSOA precursors. Compared to direct GUA photodegradation, GUA oxidation by photosensitized  
547 reactions of VL occurred rapidly and yielded higher absolute signal intensities for oligomers and hydroxylated products, which  
548 likely contributed to the pronounced absorbance enhancement. These findings indicate that phenol oxidation by  $^3VL^*$  can also  
549 contribute to aqSOA formation.

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#### 553 4 Conclusions and atmospheric implications

554 In this study, the direct photosensitized oxidation of VL in the absence and presence of AN under atmospherically relevant  
555 cloud and fog conditions have been shown to generate aqSOA composed of oligomers, functionalized monomers, oxygenated  
556 ring-opening products, and nitrated compounds (from VL+AN). The oligomers from these reaction systems may be rather  
557 recalcitrant to fragmentation based on their high normalized abundance, even at the longest irradiation time used in this study.

558 Nonetheless, the increasing concentration of small organic acids over time implies that fragmentation becomes important at  
559 extended irradiation times. The reactions were observed to be influenced by O<sub>2</sub>, pH, and reactants concentration and molar  
560 ratios. Our results suggest that O<sub>2</sub> could be required for the secondary steps in VL decay (e.g., the reaction of ketyl radical and  
561 O<sub>2</sub>) via <sup>3</sup>VL\* to proceed. Compared to N<sub>2</sub>-saturated conditions, <sup>3</sup>VL\*-initiated reactions under air-saturated conditions (O<sub>2</sub> is  
562 present) proceeded rapidly, promoted the formation of more oxidized aqSOA, and generated products (e.g., oligomers,  
563 functionalized monomers, and N-containing compounds) with higher normalized abundance which exhibited stronger light  
564 absorption. For pH 4 experiments, the presence of both O<sub>2</sub> and nitrate resulted in the highest normalized abundance of products  
565 (including N-containing compounds) and <OS>, which is attributed to O<sub>2</sub> promoting VL nitration. Nevertheless, further work  
566 on the effect of O<sub>2</sub> on the reactive intermediates involved in the reactions is necessary to elucidate the mechanisms of direct  
567 photosensitized oxidation of VL under air-saturated conditions. Additionally, the formation of oligomers from the direct  
568 photosensitized oxidation of VL was promoted at low pH (< 4). Low VL concentration favored functionalization, while  
569 oligomerization prevailed at high VL concentration, consistent with past works (Li et al., 2014; Slikboer et al., 2015; Ye et al.,  
570 2019). Hydroxylation was observed to be important at equal molar ratios of VL and nitrate, likely due to VL competing with  
571 nitrite for \*OH. Furthermore, the oxidation of guaiacol, a non-carbonyl phenol, via VL photosensitized reactions was shown to  
572 form oligomers and hydroxylated products. Aromatic carbonyls and nitrophenols have been reported to be the most significant  
573 classes of BrC in cloud water heavily affected by biomass burning in the North China Plain (Desyaterik et al., 2013).  
574 Correspondingly, the most abundant products from our reaction systems (pH 4, air-saturated solutions) are mainly potential  
575 BrC chromophores. These suggest that aqSOA generated in cloud/fog water from the oxidation of biomass burning aerosols  
576 via direct photosensitized reactions and nitrate photolysis products can impact aerosol optical properties and radiative forcing,  
577 particularly for areas where biomass burning is intensive.

578 This study shows that the photo-oxidation of VL via its direct photosensitized reactions and in the presence of nitrate  
579 can generate aqSOA composed of oligomers, functionalized monomers, oxygenated ring-opening products, and nitrated  
580 compounds (for nitrate-mediated reactions). The characterization of products presented in this work complements earlier  
581 studies (e.g., Smith et al. 2014, 2015, 2016) that mainly discussed the kinetics and aqSOA yield of triplet-driven oxidation of  
582 phenols. Although Ammonium (and sodium) nitrate was not found to ~~did not~~ substantially affect the VL decay rate constants,  
583 likely due to the much higher molar absorptivity of VL than nitrate and high VL concentration used in this work, However,  
584 the presence of ammonium (and sodium) nitrate promoted functionalization and nitration, indicating the significance of nitrate  
585 photolysis ~~in the~~ for aqSOA formation ~~from biomass burning-derived compounds pathway.~~ This work demonstrates that  
586 nitration, which is an important process for producing light-absorbing organics or BrC (Jacobson, 1999; Kahnt et al., 2013;  
587 Mohr et al., 2013; Laskin et al., 2015; Teich et al., 2017; Li et al., 2020), can also affect the aqueous-phase processing of  
588 triplet-generating aromatics. In addition, a potential imidazole derivative observed from VL+AN at pH 4 reveals that  
589 ammonium participates in aqSOA formation from the photo-oxidation of phenolic aromatic carbonyls. This observation also  
590 suggests that the photosensitized oxidation of phenolic aromatic carbonyls in the presence of AN could be a source of

591 ~~imidazoles in the aqueous phase. It is important to understand the source of imidazoles due to their possible effects on human~~  
592 ~~health, their photosensitizing potential, and their effect on aerosol optical properties as BrC compounds (Teich et al., 2016).~~

593 ~~A On a related note, a recent work (Ma et al., 2021) mimicking phenol oxidation by <sup>3</sup>DMB\* (a non-phenolic aromatic~~  
594 ~~carbonyl) triplets in more concentrated conditions of aerosol particles containing high her AN concentration (0.5 M) increased~~  
595 ~~the photodegradation rate constant for guaiacyl acetone (an aromatic phenolic carbonyl with high Henry's law constant,  $1.2 \times$~~   
596  ~~$10^6$  M atm<sup>-1</sup>; McFall et al., 2020) by > 20 times which was ascribed to <sup>•</sup>OH formation from nitrate photolysis (Brezonik and~~  
597 ~~Fulkerson-Brekken, 1998; Chu and Anastasio, 2003). The same study also estimated that reactions of phenols with high~~  
598 ~~Henry's law constants ( $10^6$  to  $10^9$  M atm<sup>-1</sup>) can be important for SOA formation in- aerosol particles-ALW, with mechanisms~~  
599 ~~mainly governed by <sup>3</sup>C\* and <sup>1</sup>O<sub>2</sub> (Ma et al., 2021). Likewise, Zhou et al. (2019) reported that the direct photodegradation of~~  
600 ~~acetosyringone was faster by about 6 times in the presence of 2 M NaClO<sub>4</sub>. However, the opposite was noted for the~~  
601 ~~photodegradation of VL in sodium sulfate or sodium nitrate, which would occur slower (~2 times slower in 0.5 M sodium~~  
602 ~~sulfate and ~10 times slower in 0.124 M sodium nitrate) in ALW-aerosol particles relative to dilute aqueous phase in clouds~~  
603 ~~(Loisel et al., 2021), implying that ~~These suggest that~~ the nature of inorganic ions may have an essential role in the~~  
604 ~~photodegradation of organic compounds in the aqueous phase (Loisel et al., 2021).~~

605 ~~Furthermore, a potential imidazole derivative observed from the VL+AN (A7; Table 2) experiment suggests that~~  
606 ~~ammonium may participate in aqSOA formation from the photo-oxidation of phenolic aromatic carbonyls. Also, the oligomers~~  
607 ~~from these reaction systems may be rather recalcitrant to fragmentation based on their high abundance, even at the~~  
608 ~~longest irradiation time used in this study. Nonetheless, the increasing concentration of small organic acids over time implies~~  
609 ~~that fragmentation becomes important at extended irradiation times. Aromatic carbonyls and nitrophenols have been reported~~  
610 ~~to be the most important classes of BrC in cloud water heavily affected by biomass burning in the North China Plain~~  
611 ~~(Desyaterik et al., 2013). Correspondingly, the most abundant products from our reaction systems (pH 4, air-saturated~~  
612 ~~solutions) are mainly potential BrC chromophores. These suggest that aqSOA generated in cloud/fog water from the oxidation~~  
613 ~~of biomass burning aerosols via direct photosensitized reactions and nitrate photolysis products can impact aerosol optical~~  
614 ~~properties and radiative forcing, particularly for areas where biomass burning is intensive.~~

615 ~~Our results indicate that the photo-oxidation of VL is influenced by O<sub>2</sub>, pH, and reactants concentration and molar~~  
616 ~~ratios. Under N<sub>2</sub> saturated conditions, the absence of O<sub>2</sub> likely hindered the secondary steps in VL decay (e.g., reaction of~~  
617 ~~ketyl radical and O<sub>2</sub>), regenerating VL as suggested by the minimal VL decay. In contrast, <sup>3</sup>VL\* initiated reactions proceeded~~  
618 ~~rapidly under air-saturated conditions (O<sub>2</sub> is present) as indicated by higher VL decay rate constant and increased normalized~~  
619 ~~abundance of products. For pH 4 experiments, the presence of both O<sub>2</sub> and nitrate resulted in the highest normalized abundance~~  
620 ~~of products (including N-containing compounds) and <OS<sub>c</sub>>, which may be due to O<sub>2</sub>-promoting VL nitration. Nevertheless,~~  
621 ~~further work is necessary to assess the effect of O<sub>2</sub> on the reactive intermediates involved in <sup>3</sup>VL\* driven photo-oxidation and~~  
622 ~~elucidate the mechanisms of VL photo-oxidation under air-saturated conditions. Additionally, the formation of oligomers from~~  
623 ~~VL photo-oxidation was promoted at low pH (< 4). Moreover, low VL concentration favored functionalization, while~~  
624 ~~oligomerization prevailed at high VL concentration, consistent with past works (Li et al., 2014; Slikboer et al., 2015; Ye et al.,~~

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625 2019). Hydroxylation was observed to be important for equal molar ratios of VL and nitrate, likely due to VL competing with  
626 nitrite for  $\cdot\text{OH}$ . The oxidation of guaiacol, a non-carbonyl phenol, by photosensitized reactions of vanillin was also shown to  
627 be less efficient than that by nitrate photolysis products based on its lower apparent quantum efficiency.

628 ~~In this study, we investigated reactions of VL and nitrate at concentrations in cloud/fog water.~~ The concentrations of  
629 VL and nitrate can be significantly higher in aqueous aerosol particles than what we have used to mimic cloud/fog water. As  
630 a major component of aerosols, ~~the concentration of~~ nitrate can have concentrations be as high as sulfate (Huang et al., 2014).  
631 More studies should then explore the direct photosensitized oxidation ~~and nitrate-mediated photo-oxidation~~ of other biomass  
632 burning-derived phenolic aromatic carbonyls, particularly those with high molar absorption coefficients ~~and can generate  $\cdot\text{C}^\bullet$ .~~  
633 Based on our findings, the presence of nitrate should be considered for examining aqSOA formation from these reactions.  
634 The influences of reaction conditions should also be investigated to better understand the oxidation pathways. As aerosols  
635 comprise more complex mixtures of organic and inorganic compounds, it is worthwhile to explore the impacts of other  
636 potential aerosol constituents on aqSOA formation and photo-oxidation studies. This can also be beneficial in understanding  
637 the interplay among different reaction ~~mechanisms~~ during photo-oxidation. Considering that biomass burning emissions are  
638 expected to increase continuously, further studies on these aqSOA formation pathways are strongly suggested.

639

640 *Data availability.*

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

642 *Author contributions.*

643 BRGM designed and conducted the experiments; YL provided assistance in measurements and helped to analyze experimental  
644 data; YJ provided assistance in measurements; BRGM, YL, and CKC wrote the paper. All co-authors contributed to the  
645 discussion of the manuscript.

646 *Competing interests.*

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

648 *Acknowledgments.*

649 This work was financially supported by the National Natural Science Foundation of China (41875142 and 42075100). Y.J.L.  
650 acknowledges support from the Science and Technology Development Fund, Macau SAR (File no. 0019/2020/A1), the Multi-  
651 Year Research grant (No. MYRG2018-00006-FST) from the University of Macau. D.D.H. acknowledges support from the  
652 National Natural Science Foundation of China (21806108). X.L. acknowledges support from the Local Innovative and  
653 Research Teams Project of Guangdong Pearl River Talents Program (2019BT02Z546). T.N. acknowledges support from the  
654 Hong Kong Research Grants Council (21304919) and City University of Hong Kong (9610409). C.H.L. acknowledges support  
655 from the City University of Hong Kong (9610458 and 7005576).



656 **References**

- 657 Anastasio, C., Faust, B. C., and Rao, C. J.: Aromatic carbonyl compounds as aqueous-phase photochemical sources of  
658 hydrogen peroxide in acidic sulfate aerosols, fogs, and clouds. 1. Non-phenolic methoxybenzaldehydes and  
659 methoxyacetophenones with reductants (phenols), *Environ. Sci. Technol.*, 31, 218–232, <https://doi.org/10.1021/es960359g>,  
660 ~~1996~~1997.
- 661
- 662 Arakaki, T., Miyake, T., Hirakawa, T., and Sakugawa, H.: pH dependent photoformation of hydroxyl radical and absorbance  
663 of aqueous-phase N(III) (HNO<sub>2</sub> and NO<sub>2</sub><sup>-</sup>), *Environ. Sci. Technol.*, 33, 2561–2565, <https://doi.org/10.1021/es980762i>, 1999.
- 664
- 665 Bateman, A. P., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Applications of high-resolution electrospray ionization mass  
666 spectrometry to measurements of average oxygen to carbon ratios in secondary organic aerosols, *Environ. Sci. Technol.*, 46,  
667 8315–8324, <https://doi.org/10.1021/es3017254>, 2012.
- 668
- 669 Benedict, K. B., McFall, A. S., and Anastasio, C.: Quantum yield of nitrite from the photolysis of aqueous nitrate above 300  
670 nm, *Environ. Sci. Technol.*, 51, 4387–4395, <https://doi.org/10.1021/acs.est.6b06370>, 2017.
- 671
- 672 Berto, S., De Laurentiis, E., Tota, T., Chiavazza, E., Daniele, P.G., Minella, M., Isaia, M., Brigante, M., and Vione, D.:  
673 Properties of the humic-like material arising from the photo-transformation of L-tyrosine, *Sci. Total Environ.*, 434–444,  
674 <https://doi.org/10.1016/j.scitotenv.2015.12.047>, 2016.
- 675
- 676 Bianco, A., Minella, M., De Laurentiis, E., Maurino, V., Minero, C., and Vione, D.: Photochemical generation of photoactive  
677 compounds with fulvic-like and humic-like fluorescence in aqueous solution, *Chemosphere*, 111, 529–536,  
678 <https://doi.org/10.1016/j.chemosphere.2014.04.035>, 2014.
- 679
- 680 Bianco, A., Riva, M., Baray, J.-L., Ribeiro, M., Chaumerliac, N., George, C., Bridoux, M., and Deguillaume, L.: Chemical  
681 characterization of cloud water collected at Puy de Dôme by FT-ICR MS reveals the presence of SOA components, *ACS Earth  
682 Space Chem.*, 3, 2076–2087, <https://doi.org/10.1021/acsearthspacechem.9b00153>, 2019.
- 683
- 684 Bianco, A., Passananti, M., Brigante, M., and Mailhot, G.: Photochemistry of the cloud aqueous phase: a review, *Molecules*,  
685 25, 423, <https://doi.org/10.3390/molecules25020423>, 2020.
- 686
- 687 Birks, J.B.: *Organic Molecular Photophysics*, John Wiley & Sons, 1973.
- 688
- 689 Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of  
690 plausibility, *Atmos. Environ.*, 34, 1623–1632, [https://doi.org/10.1016/S1352-2310\(99\)00392-1](https://doi.org/10.1016/S1352-2310(99)00392-1), 2000.
- 691
- 692 Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J.-H., and Klimont, Z.: A technology-based global inventory of  
693 black and organic carbon emissions from combustion, *J. Geophys. Res.*, 109, <https://doi.org/10.1029/2003JD003697>, 2004.
- 694
- 695 Brezonik, P. L. and Fulkerson-Brekken, J.: Nitrate-induced photolysis in natural waters: controls on concentrations of hydroxyl  
696 radical photo-intermediates by natural scavenging agents, *Environ. Sci. Technol.*, 32, 3004–3010,  
697 <https://doi.org/10.1021/es9802908>, 1998.
- 698
- 699 Canonica, S., Hellrung, B., and Wirz, J.: Oxidation of phenols by triplet aromatic ketones in aqueous solution. *J. Phys. Chem.*  
700 104, 1226–1232. <https://doi.org/10.1021/jp9930550>, 2000.  
701  
702

703 Canonica, S., Jans, U., Stemmler, K., and Hoigne, J.: Transformation kinetics of phenols in water: photosensitization by  
704 dissolved natural organic material and aromatic ketones, *Environ. Sci. Technol.*, 29, 1822–1831,  
705 <https://doi.org/10.1021/es00007a020>, 1995.

706 Canonica, S., Hellrung, B., and Wirz, J.: Oxidation of phenols by triplet aromatic ketones in aqueous solution, *J. Phys. Chem.*  
707 *104*, 1226–1232, <https://doi.org/10.1021/jp9930550>, 2000.

708  
709

710 Chang, J. L. and Thompson, J. E.: Characterization of colored products formed during irradiation of aqueous solutions  
711 containing H<sub>2</sub>O<sub>2</sub> and phenolic compounds, *Atmos. Environ.*, 44, 541–551, <https://doi.org/10.1016/j.atmosenv.2009.10.042>,  
712 2010.

713  
714

715 Chen, Y., Li, N., Li, X., Tao, Y., Luo, S., Zhao, Z., Ma, S., Huang, H., Chen, Y., Ye, Z., and Ge, X.: Secondary organic aerosol  
716 formation from <sup>3</sup>C-initiated oxidation of 4-ethylguaicol in atmospheric aqueous-phase, *Sci. Total Environ.*, 723, 137953,  
717 <https://doi.org/10.1016/j.scitotenv.2020.137953>, 2020.

718  
719

720 Chu, L. and Anastasio, C.: Quantum yields of hydroxyl radical and nitrogen dioxide from the photolysis of nitrate on ice, *J.*  
721 *Phys. Chem. A*, 107, 9594–9602, <https://doi.org/10.1021/jp0349132>, 2003.

722  
723

724 Collett, J. L. Jr., Hoag, K. J., Sherman, D. E., Bator, A., and Richards, L. W.: Spatial and temporal variations in San Joaquin  
725 Valley fog chemistry, *Atmos. Environ.*, 33, 129–140, [https://doi.org/10.1016/S1352-2310\(98\)00136-8](https://doi.org/10.1016/S1352-2310(98)00136-8), 1998.

726  
727

728 De Haan, D. O., Corrigan, A. L., Tolbert, M. A., Jimenez, J. L., Wood, S. E., and Turley, J. J.: Secondary organic aerosol  
729 formation by self-reactions of methylglyoxal and glyoxal in evaporating droplets, *Environ. Sci. Technol.*, 43, 8184–8190,  
730 <https://doi.org/10.1021/es902152t>, 2009.

731  
732

733 De Haan, D. O., Hawkins, L. N., Kononenko, J. A., Turley, J. J., Corrigan, A. L., Tolbert, M. A., and Jimenez, J. L.: Formation  
734 of nitrogen-containing oligomers by methylglyoxal and amines in simulated evaporating cloud droplets, *Environ. Sci. Technol.*,  
735 45, 984–991, <https://doi.org/10.1021/es102933x>, 2011.

736  
737

738 De Haan, D. O., Pajunoja, A., Hawkins, L. N., Welsh, H. G., Jimenez, N. G., De Loera, A., Zauscher, M., Andretta, A. D.,  
739 Joyce, B. W., De Haan, A. C., Riva, M., Cui, T., Surratt, J. D., Cazaunau, M., Formenti, P., Gratien, A., Pangui, E., and  
740 Doussin, J.-F.: Methylamine’s effects on methylglyoxal-containing aerosol: chemical, physical, and optical changes, *ACS*  
741 *Earth Space Chem.*, 3, 1706–1716, <https://doi.org/10.1021/acsearthspacechem.9b00103>, 2019.

742  
743

744 De Laurentiis, E., Socorro, J., Vione, D., Quivet, E., Brigante, M., Mailhot, G., Wortham, H., and Gligorovski, S.:  
745 Phototransformation of 4-phenoxyphenol sensitised by 4-carboxybenzophenone: Evidence of new photochemical pathways in  
746 the bulk aqueous phase and on the surface of aerosol deliquescent particles, *Atmos. Environ.*, 81, 569–578,  
747 <https://doi.org/10.1016/j.atmosenv.2013.09.036>, 2013a.

748  
749

750 De Laurentiis, E., Sur, B., Pazzi, M., Maurino, V., Minero, C., Mailhot, G., Brigante, M., and Vione, D.: Phenol transformation  
751 and dimerisation, photosensitised by the triplet state of 1-nitronaphthalene: a possible pathway to humic-like substances  
752 (HULIS) in atmospheric waters, *Atmos. Environ.*, 70, 318–327, <https://doi.org/10.1016/j.atmosenv.2013.01.014>, 2013b.

753  
754

755 Desyaterik, Y., Sun, Y., Shen, X., Lee, T., Wang, X., Wang, T., and Collett, J. L. Jr.: Speciation of “brown” carbon in cloud  
756 water impacted by agricultural biomass burning in eastern China, *J. Geophys. Res. Atmos.*, 118, 7389–7399,  
757 <https://doi.org/10.1002/jgrd.50561>, 2013.

758  
759

760 Du, Y., Fu, Q. S., Li, Y., and Su, Y.: Photodecomposition of 4-chlorophenol by reactive oxygen species in UV/air system, *J.*  
761 *Hazard. Mater.*, 186, 491–496, <https://doi.org/10.1016/j.jhazmat.2010.11.023>, 2011.

753  
754 Dzengel, J., Theurich, J., and Bahnemann, D. W.: Formation of nitroaromatic compounds in advanced oxidation processes:  
755 photolysis versus photocatalysis, *Environ. Sci. Technol.*, 33, 294–300, <https://doi.org/10.1021/es980358j>, 1999.  
756  
757 Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles  
758 (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069–11102, [https://doi.org/10.5194/acp-](https://doi.org/10.5194/acp-11-11069-2011)  
759 [11-11069-2011](https://doi.org/10.5194/acp-11-11069-2011), 2011.  
760  
761 Fischer, M. and Warneck, P.: Photodecomposition of nitrite and undissociated nitrous acid in aqueous solution, *J. Phys. Chem.*,  
762 100, 18749–18756, <https://doi.org/10.1021/jp961692+>, 1996.  
763  
764 Fleming, L. T., Lin, P., Laskin, A., Laskin, J., Weltman, R., Edwards, R. D., Arora, N. K., Yadav, A., Meinardi, S., Blake, D.  
765 R., Pillarisetti, A., Smith, K. R., and Nizkorodov, S. A.: Molecular composition of particulate matter emissions from dung and  
766 brushwood burning household cookstoves in Haryana, India, *Atmos. Chem. Phys.*, 18, 2461–2480,  
767 <https://doi.org/10.5194/acp-18-2461-2018>, 2018.  
768  
769 Foote, C.S.: Definition of type I and type II photosensitized oxidation, *Photochem. Photobiol.*, 54, 659,  
770 <https://doi.org/10.1111/j.1751-1097.1991.tb02071.x>, 1991.  
771  
772 Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal  
773 uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions,  
774 *Atmos. Chem. Phys.*, 9, 3331–3345, <https://doi.org/10.5194/acp-9-3331-2009>, 2009.  
775  
776 Gelencsér, A., Hoffer, A., Kiss, G., Tombácz, E., Kurdi, R., and Bencze, L.: In-situ formation of light-absorbing organic matter  
777 in cloud water, *J. Atmos. Chem.*, 45, 25–33, <https://doi.org/10.1023/A:1024060428172>, 2003.  
778  
779 Gen, M., Huang, D. D., and Chan, C. K.: Reactive uptake of glyoxal by ammonium-containing salt particles as a function of  
780 relative humidity, *Environ. Sci. Technol.*, 52, 6903–6911, <https://doi.org/10.1021/acs.est.8b00606>, 2018.  
781  
782 Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous SO<sub>2</sub> oxidation in sulfate formation by photolysis  
783 of particulate nitrate, *Environ. Sci. Technol. Lett.*, 6, 86–91, <https://doi.org/10.1021/acs.estlett.8b00681>, 2019a.  
784  
785 Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous oxidation of SO<sub>2</sub> in sulfate production during nitrate  
786 photolysis at 300 nm: Effect of pH, relative humidity, irradiation intensity, and the presence of organic compounds, *Environ.*  
787 *Sci. Technol.*, 53, 8757–8766, <https://doi.org/10.1021/acs.est.9b01623>, 2019b.  
788  
789 George, C., Ammann, M., D'Anna, B., Donaldson, D. J., and Nizkorodov, S.A.: Heterogeneous photochemistry in the  
790 atmosphere, *Chem. Rev.*, 115, 4218–4258, <https://doi.org/10.1021/cr500648z>, 2015.  
791  
792 George, C., Brüggemann, M., Hayeck, N., Tinel, L., and Donaldson, D. J.: Interfacial photochemistry: physical chemistry of  
793 gas-liquid interfaces, in: *Developments in Physical & Theoretical Chemistry*, edited by: Faust, J. A. and House, J. E., Elsevier,  
794 435–457, <https://doi.org/10.1016/B978-0-12-813641-6.00014-5>, 2018.  
795  
796 Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F.,  
797 Gobbi, G.P., Pietrogrande, M.C., Visentin, M., Scotto, F., Fuzzi, S., and Facchini, M.C.: Direct observation of aqueous  
798 secondary organic aerosol from biomass-burning emissions, *PNAS.*, 113, 10013–10018,  
799 <https://doi.org/10.1073/pnas.1602212113>, 2016.  
800

801 Giulianielli, L., Gilardoni, S., Tarozzi, L., Rinaldi, M., Decesari, S., Carbone, C., Facchini, M. C., and Fuzzi, S.: Fog occurrence  
802 and chemical composition in the Po valley over the last twenty years, *Atmos. Environ.*, 98, 394–401,  
803 <https://doi.org/10.1016/j.atmosenv.2014.08.080>, 2014.  
804

805 Goldstein, S. and Czapski, G.: Kinetics of nitric oxide autoxidation in aqueous solution in the absence and presence of various  
806 reductants. The nature of the oxidizing intermediates, *J. Am. Chem. Soc.*, 117, 12078–12084,  
807 <https://doi.org/10.1021/ja00154a007>, 1995.  
808

809 Grosjean, D.: Reactions of o-cresol and nitrocresol with nitrogen oxides (NO<sub>x</sub>) in sunlight and with ozone–nitrogen dioxide  
810 mixtures in the dark, *Environ. Sci. Technol.*, 19, 968–974, <https://doi.org/10.1021/es00140a014>, 1985.  
811

812 Herrmann, H.: On the photolysis of simple anions and neutral molecules as sources of O<sup>•</sup>/OH, SO<sub>x</sub><sup>-</sup> and Cl in aqueous solution,  
813 *Phys. Chem. Chem. Phys.*, 9, 3935–3964, <https://doi.org/10.1039/B618565G>, 2007.  
814

815

816 Herrmann, H., Hoffmann, D., Schaefer, T., Brüner, P., and Tilgner, A.: Tropospheric aqueous-phase free-radical chemistry:  
817 **r**Radical sources, spectra, reaction kinetics and prediction tools, *Chem Phys Chem.*, 11, 3796–3822,  
818 <https://doi.org/10.1002/cphc.201000533>, 2010.  
819

820 Hoffer, A., Kiss, G., Blazsó, M., and Gelencsér, A.: Chemical characterization of humic-like substances (HULIS) formed from  
821 a lignin-type precursor in model cloud water, *Geophys. Res. Lett.*, 31, <https://doi.org/10.1029/2003GL018962>, 2004.  
822

823 Hoffmann, E. H., Tilgner, A., Wolke, R., Böge, O., Walter, A., and Herrmann, H.: Oxidation of substituted aromatic  
824 hydrocarbons in the tropospheric aqueous phase: kinetic mechanism development and modelling, *Phys. Chem. Chem. Phys.*,  
825 20, 10960–10977, <https://doi.org/10.1039/C7CP08576A>, 2018.  
826

827 Holčapek, M., Jirásko, R., and Lisa, M.: Basic rules for the interpretation of atmospheric pressure ionization mass spectra of  
828 small molecules, *J. Chromatogr. A*, 1217, 3908–3921, <https://doi.org/10.1016/j.chroma.2010.02.049>, 2010.  
829

830 Huang, D. D., Zhang, Q., Cheung, H. H. Y., Yu, L., Zhou, S., Anastasio, C., Smith, J. D., and Chan, C. K.: Formation and  
831 evolution of aqSOA from aqueous-phase reactions of phenolic carbonyls: comparison between ammonium sulfate and  
832 ammonium nitrate solutions, *Environ. Sci. Technol.*, 52, 9215–9224, <https://doi.org/10.1021/acs.est.8b03441>, 2018.  
833

834 Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco,  
835 F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade,  
836 G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prévôt, A. S. H.: High  
837 secondary aerosol contribution to particulate pollution during haze events in China, *Nature*, 514, 218–222,  
838 <https://doi.org/10.1038/nature13774>, 2014.  
839

840 Huang, X. H. H., Ip, H. S. S., and Yu, J. Z.: Secondary organic aerosol formation from ethylene in the urban atmosphere of  
841 Hong Kong: **a**A multiphase chemical modeling study, *J. Geophys. Res.*, 116, D03206, <https://doi.org/10.1029/2010JD014121>,  
842 2011.  
843

844 Jacobson, M. Z.: Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption,  
845 *J. Geophys. Res.*, 104, 3527–3542, <https://doi.org/10.1029/1998JD100054>, 1999.  
846

847 Jiang, W., Misovich, M. V., Hettiyadura, A. P. S., Laskin, A., McFall, A. S., Anastasio, C., and Zhang, Q.: Photosensitized  
848 reactions of a phenolic carbonyl from wood combustion in the aqueous phase—chemical evolution and light absorption  
849 properties of aqSOA, *Environ. Sci. Technol.*, 55, 5199–5211, <https://doi.org/10.1021/acs.est.0c07581>, 2021.  
850

851 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe,  
852 H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson,  
853 K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M.,  
854 Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R.,  
855 Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D.,  
856 Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel,  
857 J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C.  
858 E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, *Science*, 326, 1525–1529,  
859 <https://doi.org/10.1126/science.1180353>, 2009.

860

861 Kahnt, A., Behrouzi, S., Vermeylen, R., Shalamzari, M. S., Vercauteren, J., Roekens, E., Claeys, M., and Maenhaut, W.: One-  
862 year study of nitro-organic compounds and their relation to wood burning in PM<sub>10</sub> aerosol from a rural site in Belgium, *Atmos.*  
863 *Environ.*, 81, 561–568, <https://doi.org/10.1016/j.atmosenv.2013.09.041>, 2013.

864

865 Kaur, R. and Anastasio, C.: First measurements of organic triplet excited states in atmospheric waters, *Environ. Sci. Technol.*,  
866 52, 5218–5226, <https://doi.org/10.1021/acs.est.7b06699>, 2018.

867

868 Kaur, R., Labins, J. R., Helbock, S. S., Jiang, W., Bein, K. J., Zhang, Q., and Anastasio, C.: Photooxidants from brown carbon  
869 and other chromophores in illuminated particle extracts, *Atmos. Chem. Phys.*, 19, 6579–6594, [https://doi.org/10.5194/acp-19-](https://doi.org/10.5194/acp-19-6579-2019)  
870 [6579-2019](https://doi.org/10.5194/acp-19-6579-2019), 2019.

871

872 Kebarle, P.-A.: A brief overview of the present status of the mechanisms involved in electrospray mass spectrometry, *J. Mass*  
873 *Spectrom.*, 35, 804–817, [https://doi.org/10.1002/1096-9888\(200007\)35:7<804::AID-JMS22>3.0.CO;2-](https://doi.org/10.1002/1096-9888(200007)35:7<804::AID-JMS22>3.0.CO;2-Q)  
874 [Qhttps://doi.org/10.1002/9783527628728.ch1](https://doi.org/10.1002/9783527628728.ch1), 2000.

875

876 Kim, D.-h., Lee, J., Ryu, J., Kim, K., and Choi, W.: Arsenite oxidation initiated by the UV photolysis of nitrite and nitrate,  
877 *Environ. Sci. Technol.*, 48, 4030–4037, <https://doi.org/10.1021/es500001q>, 2014.

878

879 Kitanovski, Z., Čusak, A., Grgić, I., and Claeys, M.: Chemical characterization of the main products formed through aqueous-  
880 phase photolysis of guaiacol, *Atmos. Meas. Tech.*, 7, 2457–2470, <https://doi.org/10.5194/amt-7-2457-2014>, 2014.

881

882

883 Klodt, A. L., Romonosky, D. E., Lin, P., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Aqueous photochemistry of secondary  
884 organic aerosol of  $\alpha$ -pinene and  $\alpha$ -humulene in the presence of hydrogen peroxide or inorganic salts, *ACS Earth Space Chem.*,  
885 3, 12, 2736–2746, <https://doi.org/10.1021/acsearthspacechem.9b00222>, 2019.

886

887 [Kobayashi, S. and Higashimura, H.: Oxidative polymerization of phenols revisited, \*Prog. Polym. Sci.\*, 28, 1015–1048,](https://doi.org/10.1016/S0079-6700(03)00014-5)  
888 [https://doi.org/10.1016/S0079-6700\(03\)00014-5, 2003.](https://doi.org/10.1016/S0079-6700(03)00014-5)

889

890 Kourtchev, I., Fuller, S. J., Giorio, C., Healy, R. M., Wilson, E., O'Connor, I., Wenger, J. C., McLeod, M., Aalto, J.,  
891 Ruuskanen, T. M., Maenhaut, W., Jones, R., Venables, D. S., Sodeau, J. R., Kulmala, M., and Kalberer, M.: Molecular  
892 composition of biogenic secondary organic aerosols using ultrahigh-resolution mass spectrometry: comparing laboratory and  
893 field studies, *Atmos. Chem. Phys.*, 14, 2155–2167, <https://doi.org/10.5194/acp-14-2155-2014>, 2014.

894

895 [Kroflić, A., Anders, J., Drvenčić, I., Mettke, P., Böge, O., Mutzel, A., Kleffmann, J., and Herrmann, H.: Guaiacol nitration in](https://doi.org/10.1021/acsearthspacechem.1c00014)  
896 [a simulated atmospheric aerosol with an emphasis on atmospheric nitrophenol formation mechanisms, \*ACS Earth Space Chem.\*,](https://doi.org/10.1021/acsearthspacechem.1c00014)  
897 [5, 1083–1093, https://doi.org/10.1021/acsearthspacechem.1c00014, 2021.](https://doi.org/10.1021/acsearthspacechem.1c00014)

898

899

900

901 Kroflič, A., Grilc, M., and Grgič, I.: Unraveling pathways of guaiacol nitration in atmospheric waters: nitrite, a source of  
902 reactive nitronium ion in the atmosphere, *Environ. Sci. Technol.*, 49, 9150–9158, <https://doi.org/10.1021/acs.est.5b01811>,  
903 2015.

904

905 [Kroflič, A., Anders, J., Drventić, I., Mettke, P., Böge, O., Mutzel, A., Kleffmann, J., and Herrmann, H.: Guaiacol nitration in  
906 a simulated atmospheric aerosol with an emphasis on atmospheric nitrophenol formation mechanisms, \*ACS Earth Space Chem.\*,  
907 <https://doi.org/10.1021/acsearthspacechem.1c00014>, 2021.](https://doi.org/10.1021/acsearthspacechem.1c00014)

908

909 Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L.  
910 R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric  
911 for describing the chemistry of atmospheric organic aerosol, *Nat. Chem.*, 3, 133–139, <https://doi.org/10.1038/nchem.948>, 2011.

912

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

915

916 Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of atmospheric brown carbon, *Chem. Rev.*, 115, 4335–4382,  
917 <https://doi.org/10.1021/cr5006167>, 2015.

918

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

921

922 Lathioor, E. C., Leigh, W. J., and St. Pierre, M. J.: Geometrical effects on intramolecular quenching of aromatic ketone ( $\pi,\pi^*$ )  
923 triplets by remote phenolic hydrogen abstraction, *J. Am. Chem. Soc.*, 121, 11984–11992,  
924 <https://pubs.acs.org/doi/abs/10.1021/ja991207z>, 1999.

925

926 LeClair, J. P., Collett, J. L., and Mazzoleni, L. R.: Fragmentation analysis of water-soluble atmospheric organic matter using  
927 ultrahigh-resolution FT-ICR mass spectrometry, *Environ. Sci. Technol.*, 46, 4312–4322, <https://doi.org/10.1021/es203509b>,  
928 2012.

929

930 Lee, A. K. Y., Herckes, P., Leitch, W. R., Macdonald, A. M., and Abbatt, J. P. D.: Aqueous OH oxidation of ambient organic  
931 aerosol and cloud water organics: Formation of highly oxidized products, *Geophys. Res. Lett.*, 38, L11805,  
932 <https://doi.org/10.1029/2011GL047439>, 2011.

933

934 Lee, A. K. Y., Zhao, R., Li, R., Liggio, J., Li, S.-M., and Abbatt, J. P. D.: Formation of light absorbing organo-nitrogen species  
935 from evaporation of droplets containing glyoxal and ammonium sulfate, *Environ. Sci. Technol.*, 47, 12819–12826,  
936 <https://doi.org/10.1021/es402687w>, 2013.

937

938 Lee, H. J., Aiona, P. K., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Effect of solar radiation on the optical properties and  
939 molecular composition of laboratory proxies of atmospheric brown carbon, *Environ. Sci. Technol.*, 48, 10217–  
940 10226, <https://doi.org/10.1021/es502515r>, 2014.

941

942 Lee, P. C. C. and Rodgers, M. A. J.: Laser flash photokinetic studies of Rose Bengal sensitized photodynamic interactions of  
943 nucleotides and DNA, *Photochem. Photobiol.*, 45, 79–86, <https://doi.org/10.1111/j.1751-1097.1987.tb08407.x>, 1987.

944

945 Leito, I., Herodes, K., Huopola, M., Virro, K., Künnapas, A., Kruve, A., and Tanner, R.: Towards the electrospray  
946 ionization mass spectrometry ionization efficiency scale of organic compounds, *Rapid Commun. Mass Sp.*, 22, 379–  
947 384, <https://doi.org/10.1002/rcm.3371>, 2008.

948

949 Li, F., Tang, S., Tsona, N. T., and Du, L.: Kinetics and mechanism of OH-induced  $\alpha$ -terpineol oxidation in the atmospheric  
950 aqueous phase, *Atmos. Environ.*, 237, 117650, <https://doi.org/10.1016/j.atmosenv.2020.117650>, 2020.

951  
952 Li, P., Li, X., Yang, C., Wang, X., Chen, J., and Collett, J. L. Jr.: Fog water chemistry in Shanghai, *Atmos. Environ.*, 45,  
953 4034–4041, <https://doi.org/10.1016/j.atmosenv.2011.04.036>, 2011.

954  
955 Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y., and Chan, C. K.: Aqueous-phase photochemical oxidation and direct  
956 photolysis of vanillin - a model compound of methoxy phenols from biomass burning, *Atmos. Chem. Phys.*, 14, 2871–2885,  
957 <https://doi.org/10.5194/acp-14-2871-2014>, 2014.

958  
959 Liang, Z., Zhang, R., Gen, M., Chu, Y., and Chan, C. K.: Nitrate photolysis in mixed sucrose–nitrate–sulfate particles at  
960 different relative humidities, *J. Phys. Chem. A*, 125, 3739–3747, <https://doi.org/10.1021/acs.jpca.1c00669>, 2021.

961  
962 Liigand, P., Kaupmees, K., Haav, K., Liigand, J., Leito, I., Girod, M., Antoine, R., and Kruve, A.: Think negative: finding the  
963 best electrospray ionization/MS mode for your analyte, *Anal. Chem.*, 89, 5665–5668,  
964 <https://doi.org/10.1021/acs.analchem.7b00096> ~~<https://doi.org/10.1021/acs.analchem.7>~~, 2017.

965  
966 Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic  
967 aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10, 10521–10539, <https://doi.org/10.5194/acp-10-10521-2010>, 2010.

968  
969 [Lin, P., Bluvshstein, N., Rudich, Y., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular chemistry of atmospheric brown](https://doi.org/10.1021/acs.est.7b02276)  
970 [carbon inferred from a nationwide biomass burning event, \*Environ. Sci. Technol.\*, 51, 11561–](https://doi.org/10.1021/acs.est.7b02276)  
971 [11570, <https://doi.org/10.1021/acs.est.7b02276>, 2017.](https://doi.org/10.1021/acs.est.7b02276)

972  
973  
974 Lin, P., Fleming, L. T., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Comprehensive molecular characterization of  
975 atmospheric brown carbon by high resolution mass spectrometry with electrospray and atmospheric pressure photoionization,  
976 *Anal. Chem.*, 90, 12493–12502, <https://doi.org/10.1021/acs.analchem.8b02177>, 2018.

977  
978 Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in humic-like substance fraction isolated from aerosols at  
979 seven locations in East Asia: a study by ultra-high-resolution mass spectrometry, *Environ. Sci. Technol.*, 46, 13118–13127,  
980 <https://doi.org/10.1021/es303570v>, 2012.

981  
982 Liu, C., Liu, J., Liu, Y., Chen, T., and He, H.: Secondary organic aerosol formation from the OH-initiated oxidation of guaiacol  
983 under different experimental conditions, *Atmos. Environ.*, 207, 30–37, <https://doi.org/10.1016/j.atmosenv.2019.03.021>, 2019.

984  
985 Lobodin, V. V., Marshall, A. G., and Hsu, C. S.: Compositional space boundaries for organic compounds, *Anal. Chem.*, 84,  
986 3410–3416, <https://doi.org/10.1021/ac300244f>, 2012.

987  
988 Loisel, G., Mekic, M., Liu, S., Song, W., Jiang, B., Wang, Y., Deng, H., and Gligorovski, S.: Ionic strength effect on the  
989 formation of organonitrate compounds through photochemical degradation of vanillin in liquid water of aerosols, *Atmos.*  
990 *Environ.*, 246, 118140, <https://doi.org/10.1016/j.atmosenv.2020.118140>, 2021.

991  
992 Ma, L., Guzman, C., Niedek, C., Tran, T., Zhang, Q., and Anastasio, C.: Kinetics and mass yields of aqueous secondary organic  
993 aerosol from highly substituted phenols reacting with a triplet excited state, *Environ. Sci. Technol.*, 55, 5772–5781,  
994 <https://doi.org/10.1021/acs.est.1c00575>, 2021.

995  
996 Mabato, B. R. G., Gen, M., Chu, Y., and Chan, C. K.: Reactive uptake of glyoxal by methylammonium-containing salts as a  
997 function of relative humidity, *ACS Earth Space Chem.*, 3, 150–157, <https://doi.org/10.1021/acsearthspacechem.8b00154>, 2019.

998  
999

999 Machado, F. and Boule, P.: Photonitration and photonitrosation of phenolic derivatives induced in aqueous solution by  
1000 excitation of nitrite and nitrate ions, *J. Photochem. Photobiol. A: Chem.*, 86, 73–80, [https://doi.org/10.1016/1010-](https://doi.org/10.1016/1010-6030(94)03946-R)  
1001 [6030\(94\)03946-R](https://doi.org/10.1016/1010-6030(94)03946-R), 1995.

1002

1003 Mack, J. and Bolton, J. R.: Photochemistry of nitrite and nitrate in aqueous solution: a review, *J. Photochem. Photobiol. A: Chem.*,  
1004 [128, 1–13, https://doi.org/10.1016/S1010-6030\(99\)00155-0](https://doi.org/10.1016/S1010-6030(99)00155-0), 1999.

1005

1006 Mazzoleni, L. R., Saranjampour, P., Dalbec, M. M., Samburova, V., Hallar, A. G., Zielinska, B., Lowenthal, D. H., and Kohl,  
1007 S.: Identification of water-soluble organic carbon in non-urban aerosols using ultrahigh-resolution FT-ICR mass spectrometry:  
1008 organic anions, *Environ. Chem.*, 9, 285–297, <https://doi.org/10.1071/EN11167>, 2012.

1009

1010 McFall, A. S., Johnson, A. W., and Anastasio, C.: Air–water partitioning of biomass-burning phenols and the effects of  
1011 temperature and salinity, *Environ. Sci. Technol.*, 54, 3823–3830, <https://doi.org/10.1021/acs.est.9b06443>, 2020.

1012

1013 McNally, A. M., Moody, E. C., and McNeill, K.: Kinetics and mechanism of the sensitized photodegradation of lignin model  
1014 compounds, *Photochem. Photobiol. Sci.*, 4, 268–274, <https://doi.org/10.1039/B416956E>, 2005.

1015

1016 Minella, M., Romeo, F., Vione, D., Maurino, V., and Minero, C.: Low to negligible photoactivity of lake-water matter in the  
1017 size range from 0.1 to 5  $\mu\text{m}$ , *Chemosphere*, 83, 1480–1485, <https://doi.org/10.1016/j.chemosphere.2011.02.093>, 2011.

1018

1019 Minero, C., Bono, F., Rubertelli, F., Pavino, D., Maurino, V., Pelizzetti, E., and Vione, D.: On the effect of pH in aromatic  
1020 photonitration upon nitrate photolysis, *Chemosphere*, 66, 650–656, <https://doi.org/10.1016/j.chemosphere.2006.07.082>, 2007.

1021

1022 [Misovich, M. V., Hettiyadura, A. P. S., Jiang, W., Zhang, Q., and Laskin, A.: Molecular-level study of the photo-oxidation of](https://doi.org/10.1021/acsearthspacechem.1c00103)  
1023 [aqueous-phase guaiacyl acetone in the presence of  \$^3\text{C}^\*\$ : formation of brown carbon products, \*ACS Earth Space Chem.\*, 5,](https://doi.org/10.1021/acsearthspacechem.1c00103)  
1024 [1983–1996, https://doi.org/10.1021/acsearthspacechem.1c00103, 2021.](https://doi.org/10.1021/acsearthspacechem.1c00103)

1025

1026 Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prévôt, A. S. H., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J.  
1027 P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton,  
1028 J. A.: Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during  
1029 winter time, *Environ. Sci. Technol.*, 47, 6316–6324, <https://doi.org/10.1021/es400683v>, 2013.

1030

1031 Munger, J. W., Jacob, D. J., Waldman, J. M., and Hoffmann, M. R.: Fogwater chemistry in an urban atmosphere, *J. Geophys.*  
1032 *Res. Oceans*, 88, 5109–5121, <https://doi.org/10.1029/JC088iC09p05109>, 1983.

1033

1034 Neumann, M. G., De Groot, R. A. M. C., and Machado, A. E. H.: Flash photolysis of lignin: Part I. Deaerated solutions of  
1035 dioxane-lignin, *Polym. Photochem.*, 7, 401–407, [https://doi.org/10.1016/0144-2880\(86\)90007-2](https://doi.org/10.1016/0144-2880(86)90007-2), 1986a.

1036

1037 Neumann, M. G., De Groot, R. A. M. C., and Machado, A. E. H.: Flash photolysis of lignin: II. Oxidative photodegradation  
1038 of dioxane-lignin, *Polym. Photochem.*, 7, 461–468, [https://doi.org/10.1016/0144-2880\(86\)90015-1](https://doi.org/10.1016/0144-2880(86)90015-1), 1986b.

1039

1040 Ning, C., Gao, Y., Zhang, H., Yu, H., Wang, L., Geng, N., Cao, R., and Chen, J.: Molecular characterization of dissolved  
1041 organic matters in winter atmospheric fine particulate matters ( $\text{PM}_{2.5}$ ) from a coastal city of northeast China, *Sci. Total*  
1042 *Environ.*, 689, 312–321, <https://doi.org/10.1016/j.scitotenv.2019.06.418>, 2019.

1043

1044 Nolte, C. G., Schauer, J. J., Cass, G. R., and Simoneit, B. R. T.: Highly polar organic compounds present in wood smoke and  
1045 in the ambient atmosphere, *Environ. Sci. Technol.*, 35, [1912–1919, https://doi.org/10.1021/es001420r](https://doi.org/10.1021/es001420r), ~~1912–1919~~, 2001.

1046

1047 Nozière, B., Dziedzic, P., and Córdova, A.: Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by  
1048 ammonium ions ( $\text{NH}_4^+$ ), *J. Phys. Chem. A*, 113, 231–237, <https://doi.org/10.1021/jp8078293>, 2009.



1049  
1050 [Nozière, B., Dziedzic, P., and Córdoba, A.: Inorganic ammonium salts and carbonate salts are efficient catalysts for aldol](#)  
1051 [condensation in atmospheric aerosols, \*Phys. Chem. Chem. Phys.\*, 12, 3864–3872, <https://doi.org/10.1039/B924443C>, 2010.](#)  
1052  
1053 [Nozière, B., Fache, F., Maxut, A., Fenet, B., Baudouin, A., Fine, L., and Ferronato, C.: The hydrolysis of epoxides catalyzed](#)  
1054 [by inorganic ammonium salts in water: kinetic evidence for hydrogen bond catalysis, \*Phys. Chem. Chem. Phys.\*, 20,](#)  
1055 [1583–1590, <https://doi.org/10.1039/C7CP06790A>, 2018.](#)  
1056  
1057  
1058 Pang, H., Zhang, Q., Lu, X. H., Li, K., Chen, H., Chen, J., Yang, X., Ma, Y., Ma, J., and Huang, C.: Nitrite-mediated  
1059 photooxidation of vanillin in the atmospheric aqueous phase, *Environ. Sci. Technol.*, 53, 14253–14263,  
1060 <https://doi.org/10.1021/acs.est.9b03649>, 2019a.  
1061  
1062 Pang, H., Zhang, Q., Wang, H., Cai, D., Ma, Y., Li, L., Li, K., Lu, X., Chen, H., Yang, X., and Chen, J.: Photochemical aging  
1063 of guaiaicol by Fe(III)-oxalate complexes in atmospheric aqueous phase, *Environ. Sci. Technol.*, 53, 127–136,  
1064 <https://doi.org/10.1021/acs.est.8b04507>, 2019b.  
1065  
1066 Perry, R. H., Cooks, R. G., and Noll, R. J.: Orbitrap mass spectrometry: instrumentation, ion motion and applications, *Mass*  
1067 *Spectrom. Rev.*, 27, 661–699, <https://doi.org/10.1002/mas.20186>, 2008.  
1068  
1069 Powelson, M. H., Espelien, B. M., Hawkins, L. N., Galloway, M. M., and De Haan, D. O.: Brown carbon formation by  
1070 aqueous-phase carbonyl compound reactions with amines and ammonium sulfate, *Environ. Sci. Technol.*, 48, 985–993,  
1071 <https://doi.org/10.1021/es4038325>, 2014.  
1072  
1073 Pye, H., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett, J. L. Jr., Fahey, K. M., Hennigan, C. J.,  
1074 Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I.-T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker,  
1075 J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, *Atmos.*  
1076 *Chem. Phys.*, 20, 4809–4888, <https://doi.org/10.5194/acp-20-4809-2020>, 2020.  
1077  
1078 Qi, L., Chen, M., Stefenelli, G., Pospisilova, V., Tong, Y., Bertrand, A., Hueglin, C., Ge, X., Baltensperger, U., Prévôt, A. S.  
1079 H., and Slowik, J. G.: Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight  
1080 mass spectrometer (EESI-TOF-MS) — Part 2: Biomass burning influences in winter, *Atmos. Chem. Phys.*, 19, 8037–8062,  
1081 <https://doi.org/10.5194/acp-19-8037-2019>, 2019.  
1082  
1083 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., ~~and~~ Cass, G. R., ~~and~~ Simoneit, B. R. T.: Sources of fine organic aerosol. 9.  
1084 Pine, oak, and synthetic log combustion in residential fireplaces, *Environ. Sci. Technol.*, 32, 13–22,  
1085 <https://doi.org/10.1021/es960930b>, 1998.  
1086  
1087 Romonosky, D. E., Li, Y., Shiraiwa, M., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Aqueous photochemistry of secondary  
1088 organic aerosol of  $\alpha$ -Pinene and  $\alpha$ -Humulene oxidized with ozone, hydroxyl radical, and nitrate radical, *J. Phys. Chem. A*, 121,  
1089 1298–1309, <https://doi.org/10.1021/acs.jpca.6b10900>, 2017.  
1090  
1091 Scharko, N. K., Berke, A. E., and Raff, J. D.: Release of nitrous acid and nitrogen dioxide from nitrate photolysis in acidic  
1092 aqueous solutions, *Environ. Sci. Technol.*, 48, 20, 11991–1200, <https://doi.org/10.1021/es503088x>, 2014.  
1093  
1094 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 3.  
1095 C<sub>1</sub>–C<sub>29</sub> organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.*, 35, 1716–1728,  
1096 <https://doi.org/10.1021/es001331e>, 2001.  
1097

1098 Schmidt, A-C., Herzs Schuh, R., Matysik, F-M., and Engewald, W.: Investigation of the ionisation and fragmentation behaviour  
1099 of different nitroaromatic compounds occurring as polar metabolites of explosives using electrospray ionising tandem mass  
1100 spectrometry, *Rapid Commun. Mass Sp.*, 20, 2293–2302, <https://doi.org/10.1002/rcm.2591>, 2006.

1101  
1102 Sedehi, N., Takano, H., Blasic, V. A., Sullivan, K. A., and De Haan, D. O.: Temperature- and pH-dependent aqueous-phase  
1103 kinetics of the reactions of glyoxal and methylglyoxal with atmospheric amines and ammonium sulfate, *Atmos. Environ.*, 77,  
1104 656–663, <https://doi.org/10.1016/j.atmosenv.2013.05.070>, 2013.

1105  
1106 Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R., and McNeill, V. F.: Light-absorbing secondary organic  
1107 material formed by glyoxal in aqueous aerosol mimics, *Atmos. Chem. Phys.*, 9, 2289–2300, [https://doi.org/10.5194/acp-9-](https://doi.org/10.5194/acp-9-2289-2009)  
1108 2289-2009, 2009.

1109  
1110 Siegmann, K. and Sattler, K.-D.: Formation mechanism for polycyclic aromatic hydrocarbons in methane flames, *J. Chem.*  
1111 *Phys.*, 112, 698–709, <https://doi.org/10.1063/1.480648>, 2000.

1112  
1113 Slikboer, S., Grandy, L., Blair, S. L., Nizkorodov, S. A., Smith, R. W., and Al-Abadleh, H. A.: Formation of light absorbing  
1114 soluble secondary organics and insoluble polymeric particles from the dark reaction of catechol and guaiacol with Fe(III),  
1115 *Environ. Sci. Technol.*, 49, 7793–7801, <https://doi.org/10.1021/acs.est.5b01032>, 2015.

1116  
1117 ~~Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of~~  
1118 ~~atmospheric phenols with an organic triplet excited state, *Environ. Sci. Technol.*, 48, 1049–1057,~~  
1119 ~~<https://doi.org/10.1021/es4045715>, 2014.~~

1120  
1121 Smith, J. D., Kinney, H., and Anastasio, C.: Aqueous benzene-diols react with an organic triplet excited state and hydroxyl  
1122 radical to form secondary organic aerosol, *Phys. Chem. Chem. Phys.*, 17, 10227–10237, <https://doi.org/10.1039/C4CP06095D>,  
1123 2015.

1124  
1125 Smith, J. D., Kinney, H., and Anastasio, C.: Phenolic carbonyls undergo rapid aqueous photodegradation to form low-volatility,  
1126 light-absorbing products, *Atmos. Environ.*, 126, 36–44, <https://doi.org/10.1016/j.atmosenv.2015.11.035>, 2016.

1127  
1128 ~~Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of~~  
1129 ~~atmospheric phenols with an organic triplet excited state, *Environ. Sci. Technol.*, 48, 1049–1057,~~  
1130 ~~<https://doi.org/10.1021/es4045715>, 2014.~~

1131  
1132 Song, J., Li, M., Jiang, B., Wei, S., Fan, X., and Peng, P.: Molecular characterization of water-soluble humic like substances  
1133 in smoke particles emitted from combustion of biomass materials and coal using ultrahigh-resolution electrospray ionization  
1134 Fourier transform ion cyclotron resonance mass spectrometry, *Environ. Sci. Technol.*, 52, 2575–2585,  
1135 <https://doi.org/10.1021/acs.est.7b06126>, 2018.

1136  
1137 Sun, Y. L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions  
1138 of phenolic compounds based on high resolution mass spectrometry, *Atmos. Chem. Phys.*, 10, 4809–4822,  
1139 <https://doi.org/10.5194/acp-10-4809-2010>, 2010.

1140  
1141 ~~Teich, M., van Pinxteren, D., Kecorius, S., Wang, Z., and Herrmann, H.: First quantification of imidazoles in ambient aerosol~~  
1142 ~~particles: potential photosensitizers, brown carbon constituents, and hazardous components, *Environ. Sci. Technol.*, 50, 1166–~~  
1143 ~~1173, <https://doi.org/10.1021/acs.est.5b05474>, 2016.~~

1144  
1145 Teich, M., van Pinxteren, D., Wang, M., Kecorius, S., Wang, Z., Müller, T., Močnik, G., and Herrmann, H.: Contributions of  
1146 nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric  
1147 environments in Germany and China, *Atmos. Chem. Phys.*, 17, 1653–1672, <https://doi.org/10.5194/acp-17-1653-2017>, 2017.

1148  
1149 Tratnyek, P. G. and Hoigne, J.: Oxidation of substituted phenols in the environment: a QSAR analysis of rate constants for  
1150 reaction with singlet oxygen, *Environ. Sci. Technol.*, 25, 1596–1604, <https://doi.org/10.1021/es00021a011>, 1991.  
1151  
1152 Turro, N., Ramamurthy, V., and Scaiano, J.C.: *Modern Molecular Photochemistry*, University Science Books, 2010.  
1153  
1154 Vione, D., Albinet, A., Barsotti, F., Mekic, M., Jiang, B., Minero, C., Brigante, M., and Gligorovski, S.: Formation of  
1155 substances with humic-like fluorescence properties, upon photoinduced oligomerization of typical phenolic compounds  
1156 emitted by biomass burning. *Atmos. Environ.*, 206, 197–207, <https://doi.org/10.1016/j.atmosenv.2019.03.005>, 2019.  
1157  
1158 Vione, D., Maurino, V., Minero, C., and Pelizzetti, E.: Phenol photonitration upon UV irradiation of nitrite in aqueous solution  
1159 I: effects of oxygen and 2-propanol, *Chemosphere*, 45, 893–902, [https://doi.org/10.1016/S0045-6535\(01\)00035-2](https://doi.org/10.1016/S0045-6535(01)00035-2), 2001.  
1160  
1161 Vione, D., Maurino, V., Minero, C., and Pelizzetti, E.: Reactions induced in natural waters by irradiation of nitrate and nitrite  
1162 ions, in: *The Handbook of Environmental Chemistry Vol. 2M - Environmental Photochemistry Part II*, Springer, Berlin,  
1163 Heidelberg, Germany, 221–253, <https://doi.org/10.1007/b138185>, 2005.  
1164  
1165 Vione, D., Maurino, V., Minero, C., Pelizzetti, E., Harrison, M. A. J., Olariu, R., and Arsene, C.: Photochemical reactions in  
1166 the tropospheric aqueous phase and on particulate matter, *Chem. Soc. Rev.*, 35, 441–453, <https://doi.org/10.1039/B510796M>,  
1167 2006.  
1168  
1169 ~~Vione, D., Albinet, A., Barsotti, F., Mekic, M., Jiang, B., Minero, C., Brigante, M., and Gligorovski, S.: Formation of~~  
1170 ~~substances with humic-like fluorescence properties, upon photoinduced oligomerization of typical phenolic compounds~~  
1171 ~~emitted by biomass burning. *Atmos. Environ.*, 206, 197–207, <https://doi.org/10.1016/j.atmosenv.2019.03.005>, 2019.~~  
1172  
1173 Volkamer, R., Ziemann, P. J., and Molina, and M. J.: Secondary organic aerosol formation from acetylene (C<sub>2</sub>H<sub>2</sub>): seed effect  
1174 on SOA yields due to organic photochemistry in the aerosol aqueous phase, *Atmos. Chem. Phys.*, 9, 1907–1928,  
1175 <https://doi.org/10.5194/acp-9-1907-2009>, 2009.  
1176  
1177 Wang, K., Huang, R.-J., Brüggemann, M., Zhang, Y., Yang, L., Ni, H., Guo, J., Wang, M., Han, J., Bilde, M., Glasius, M., and  
1178 Hoffmann, T.: Urban organic aerosol composition in eastern China differs from north to south: molecular insight from a liquid  
1179 chromatography–mass spectrometry (Orbitrap) study, *Atmos. Chem. Phys.*, 21, 9089–9104, [https://doi.org/10.5194/acp-21-](https://doi.org/10.5194/acp-21-9089-2021)  
1180 [9089-2021](https://doi.org/10.5194/acp-21-9089-2021), 2021.  
1181  
1182 Wang, X., Hayeck, N., Brüggemann, M., Yao, L., Chen, H., Zhang, C., Emmelin, C., Chen, J., George, C., and Wang, L.:  
1183 Chemical characteristics of organic aerosols in Shanghai: a study by ultrahigh-performance liquid chromatography  
1184 coupled with orbitrap mass spectrometry, *J. Geophys. Res. Atmos.*, 122, 11703–11722,  
1185 <https://doi.org/10.1002/2017JD026930>, 2017.  
1186  
1187 Xiao, H.-W., Wu, J.-F., Luo, L., Liu, C., Xie, Y.-J., and Xiao, H.-Y.: Enhanced biomass burning as a source of aerosol  
1188 ammonium over cities in Central China in autumn, *Environ. Pollut.*, 266, art. no. 115278,  
1189 <https://doi.org/10.1016/j.envpol.2020.115278>, 2020.  
1190  
1191 Xie, Q., Su, S., Chen, S., Xu, Y., Cao, D., Chen, J., Ren, L., Yue, S., Zhao, W., Sun, Y., Wang, Z., Tong, H., Su, H., Cheng,  
1192 Y., Kawamura, K., Jiang, G., Liu, C.-Q., and Fu, P.: Molecular characterization of firework-related urban aerosols using Fourier  
1193 transform ion cyclotron resonance mass spectrometry, *Atmos. Chem. Phys.*, 20, 6803–6820, [10.5194/acp-2019-1180](https://doi.org/10.5194/acp-2019-1180),  
1194 <https://doi.org/10.5194/acp-20-6803-2020>, 2020.  
1195

1196 Yang, J., Au, W. C., Law, H., Lam, C. H., and Nah, T.: Formation and evolution of brown carbon during aqueous-phase nitrate-  
1197 mediated photooxidation of guaiacol and 5-nitroguaiacol, *Atmos. Environ.*, 254, 118401,  
1198 <https://doi.org/10.1016/j.atmosenv.2021.118401> <https://doi.org/10.1016/j.atmosenv.2020.118440>, 2021.  
1199

1200 Yaws, C. L.: Handbook of vapor pressure: Volume 3: Organic compounds C<sub>8</sub> to C<sub>28</sub>, Gulf Professional Publishing, USA, 1994.  
1201

1202 Ye, Z., Qu, Z., Ma, S., Luo, S., Chen, Y., Chen, H., Chen, Y., Zhao, Z., Chen, M., and Ge, X.: A comprehensive investigation  
1203 of aqueous-phase photochemical oxidation of 4-ethylphenol, *Sci. Total Environ.*, 685, 976–985,  
1204 <https://doi.org/10.1016/j.scitotenv.2019.06.276>, 2019.  
1205

1206 [Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H.,  
1207 Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from  
1208 biomass burning intermediates: phenol and methoxyphenols, \*Atmos. Chem. Phys.\*, 13, 8019–8043,  
1209 <https://doi.org/10.5194/acp-13-8019-2013>, 2013.  
1210](https://doi.org/10.5194/acp-13-8019-2013)

1211 Yu, G., Bayer, A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., and Keutsch, F. N.: Glyoxal in aqueous ammonium sulfate  
1212 solutions: products, kinetics and hydration effects, *Environ. Sci. Technol.*, 45, 6336–6342, <https://doi.org/10.1021/es200989n>,  
1213 2011.  
1214

1215 Yu, L., Smith, J., Laskin, A., Anastasio, C., Laskin, J., and Zhang, Q.: Chemical characterization of SOA formed from aqueous-  
1216 phase reactions of phenols with the triplet excited state of carbonyl and hydroxyl radical, *Atmos. Chem. Phys.*, 14,  
1217 13801–13816, <https://doi.org/10.5194/acp-14-13801-2014>, 2014.  
1218

1219 Zhang, Q. and Anastasio, C.: Conversion of fogwater and aerosol organic nitrogen to ammonium, nitrate, and NO<sub>x</sub> during  
1220 exposure to simulated sunlight and ozone, *Environ. Sci. Technol.*, 37, 3522–3530, <https://doi.org/10.1021/es034114x>, 2003.  
1221  
1222

1223 Zhang, R., Gen, M., Fu, T.-M., and Chan, C. K.: Production of formate via oxidation of glyoxal promoted by particulate nitrate  
1224 photolysis, *Environ. Sci. Technol.*, 55, 5711–5720, <https://doi.org/10.1021/acs.est.0c08199>, 2021.  
1225

1226 [Zhang, R., Gen, M., Huang, D. D., Li, Y., and Chan, C. K.: Enhanced sulfate production by nitrate photolysis in the presence  
1227 of halide ions in atmospheric particles, \*Environ. Sci. Technol.\*, 54, 3831–3839, <https://dx.doi.org/10.1021/acs.est.9b06445>,  
1228 2020.  
1229  
1230](https://doi.org/10.1021/acs.est.9b06445)

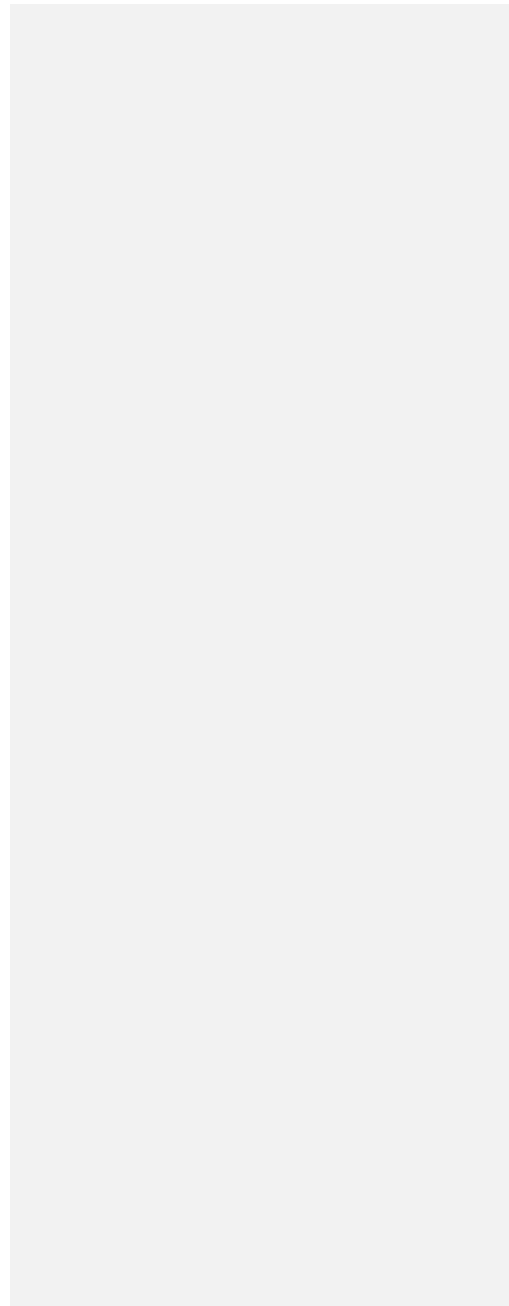
1231 Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F., and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric  
1232 brown carbon, *Atmos. Chem. Phys.*, 15, 6087–6100, <https://doi.org/10.5194/acp-15-6087-2015>, 2015.  
1233

1234 Zhao, Y., Hallar, A. G., and Mazzoleni, L. R.: Atmospheric organic matter in clouds: exact masses and molecular formula  
1235 identification using ultrahigh-resolution FT-ICR mass spectrometry, *Atmos. Chem. Phys.*, 13, 12343–12362,  
1236 <https://doi.org/10.5194/acp-13-12343-2013>, 2013.  
1237

1238 Zhou, W., Mekić, M., Liu, J., Loisel, G., Jin, B., Vione, D., and Gligorovski, S.: Ionic strength effects on the photochemical  
1239 degradation of acetosyringone in atmospheric deliquescent aerosol particles, *Atmos. Environ.*, 198, 83–88,  
1240 <https://doi.org/10.1016/j.atmosenv.2018.10.047>, 2019.  
1241

1242 Zielinski, T., Bolzacchini, E., Cataldi, M., Ferrero, L., Graßl, S., Hansen, G., Mateos, D., Mazzola, M., Neuber, R., Pakszys,  
1243 P., Posyniak, M., Ritter, C., Severi, M., Sobolewski, P., Traversi, R., and Velasco-Merino, C.: Study of chemical and optical  
1244 properties of biomass burning aerosols during long-range transport events toward the Arctic in summer 2017, *Atmosphere*, 11,  
1245 84, <https://doi.org/10.3390/atmos11010084>, 2020.

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1248 **Table 1.** List of reactions involving reactive species relevant to this study.

No.	Reactions	References
1	$\text{NO}_3^- + h\nu \rightarrow \cdot\text{NO}_2 + \text{O}^-; \phi = 0.01$	Vione et al., 2006; Benedict et al., 2017
2	$\text{O}^- + \text{H}_3\text{O}^+ \leftrightarrow \cdot\text{OH} + \text{H}_2\text{O}$	
3	$\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + \text{O}({}^3\text{P}); \phi = 0.011$	
4	$\text{NO}_2^- + \cdot\text{OH} \rightarrow \cdot\text{NO}_2 + \text{OH}^- (k = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$	Mack and Bolton, 1999; Pang et al., 2019a
5	$\text{O}_2^{\cdot-} + \text{NO}_2^- + 2\text{H}^+ \rightarrow \cdot\text{NO}_2 + \text{H}_2\text{O}_2$	Vione et al., 2001; Pang et al., 2019a
6	$\text{NO}_2^- + h\nu \rightarrow \cdot\text{NO} + \text{O}^-; \phi_{\text{OH},300} = 6.7 (\pm 0.9)\%$	Fischer and Warneck, 1996; Mack and Bolton, 1999; Pang et al., 2019a
7	$\cdot\text{NO} + \text{O}_2 \leftrightarrow \cdot\text{ONOO}$	Goldstein and Czapski, 1995; Pang et al., 2019a
8	$\cdot\text{ONOO} + \cdot\text{NO} \rightarrow \text{ONOONO}$	
9	$\text{ONOONO} \rightarrow 2\cdot\text{NO}_2$	
10	$\text{HNO}_2 + \cdot\text{OH} \rightarrow \cdot\text{NO}_2 + \text{H}_2\text{O} (k = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$	Kim et al., 2014; Pang et al., 2019a

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1286 **Table 2.** Reaction conditions, initial VL (and GUA) decay rate constants, normalized abundance of products, and average  
1287 carbon oxidation state (<OS<sub>c</sub>>) in each experiment. Except where noted, the reaction systems consisted of VL (0.1 mM); GUA  
1288 (0.1 mM), AN (1 mM); ~~sodium nitrate~~-(SN)<sub>2</sub> (1 mM) under air-saturated conditions after 6 h of simulated sunlight irradiation.  
1289 Analyses were performed using UHPLC-qToF-MS equipped with an ESI source and operated in the positive ion mode.

Exp no.	pH	Reaction conditions	Initial VL (and GUA) decay rate constants (min <sup>-1</sup> ) <sup>b</sup>	Ratio of 50 most abundant products to total products <sup>c</sup>	Normalized abundance of products <sup>d</sup>	Normalized abundance of N-containing compounds <sup>d</sup>	<OS <sub>c</sub> > <sup>e</sup> (OS <sub>c</sub> of VL: <del>-0.25</del> ; OS <sub>c</sub> of GUA: <del>-0.57</del> )
A1	2.5	VL*	$2.0 \times 10^{-2} \pm 5.8 \times 10^{-5}$	0.59	$1.7 \pm 0.16$	N/A	-0.05
A2		VL+AN	$1.7 \times 10^{-2} \pm 7.3 \times 10^{-4}$	0.63	$1.4 \pm 0.19$	$5.3 \times 10^{-2}$	-0.04
A3		VL*	$1.5 \times 10^{-2} \pm 4.2 \times 10^{-4}$	0.53	$1.9 \pm 0.33$	N/A	-0.04
A4	3	VL+AN	$1.5 \times 10^{-2} \pm 2.3 \times 10^{-4}$	0.56	$1.9 \pm 0.30$	$3.6 \times 10^{-2}$	-0.05
A5		VL*	$1.2 \times 10^{-2} \pm 5.9 \times 10^{-4}$	0.58	$0.26 \pm 0.42$	N/A	-0.16
A6	4	VL* (N <sub>2</sub> -saturated)	$3.2 \times 10^{-3} \pm 1.1 \times 10^{-3}$	0.96	$4.7 \times 10^{-2} \pm 0.0027$	N/A	-0.24
A7		VL+AN	$1.2 \times 10^{-2} \pm 8.8 \times 10^{-4}$	0.53	$0.37 \pm 0.38$	$1.7 \times 10^{-2}$	-0.13
A8		VL+AN (N <sub>2</sub> -saturated)	$1.9 \times 10^{-3} \pm 9.2 \times 10^{-5}$	0.89	$0.12 \pm 0.0095$	$6.3 \times 10^{-3}$	-0.21
A9		VL+SN	<del><math>1.3 \times 10^{-2} \pm 3.5 \times 10^{-4}</math></del> N/A	0.51	$0.42 \pm 0.33$	$1.7 \times 10^{-2}$	-0.07
A10		VL* (0.01 mM) <sup>a</sup>	N/A	0.90	$0.37 \pm 0.018$	N/A	-0.07
A11		VL (0.01 mM) + AN (0.01 mM)	N/A	0.77	$0.40 \pm 0.074$	$8.6 \times 10^{-3}$	0.12
A12		VL (0.01 mM) + AN	N/A	0.42	$0.45 \pm 0.025$	$1.2 \times 10^{-2}$	-0.06
A13		GUA only	$6.2 \times 10^{-3} \pm 2.5 \times 10^{-4}$	0.77	N/A	N/A	-0.28
A14		GUA+VL	GUA: $1.4 \times 10^{-2} \pm 4.0 \times 10^{-4}$ VL: $4.3 \times 10^{-3} \pm 2.2 \times 10^{-4}$	0.60	$2.2 \pm 0.47$	N/A	-0.27
A15		GUA+AN	<del><math>8.0 \times 10^{-2} \pm 2.9 \times 10^{-3}</math></del>	<del>0.77</del>	<del>N/A</del>	<del>N/A</del>	<del>-0.26</del>

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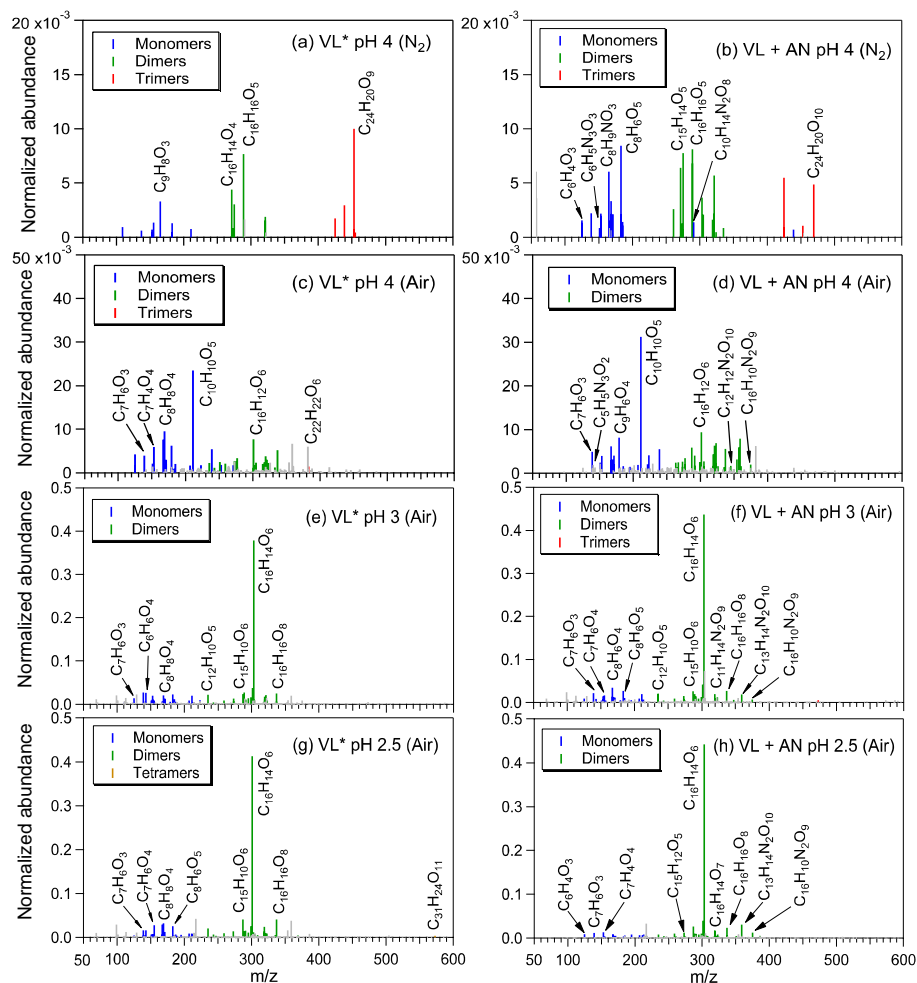
1292 <sup>a</sup>Irradiation time for VL\* (0.01 mM, A10) was 3 h. <sup>b</sup>The data fitting was performed in the initial linear region. Each value is  
1293 the average of results from triplicate experiments. Errors represent one standard deviation. Kinetic measurements were not  
1294 performed for experiments marked with N/A. <sup>c</sup>Ratio of the normalized abundance of the 50 most abundant products to that of  
1295 total products, except for direct GUA photodegradation ~~and~~ GUA+VL ~~and~~ GUA+AN (A13–145) whose ratios are based on  
1296 the absolute signals of products. <sup>d</sup>The normalized abundance of products was calculated using Eq. 2. The samples for  
1297 experiments without nitrate (marked with N/A) were not analyzed for N-containing compounds. For the GUA experiments,  
1298 the normalized abundance of products was calculated only for GUA+VL as the GUA signal from the UHPLC-qToF-MS in

1299 the positive ion mode was weak, which may introduce large uncertainties during normalization.  $\langle OS_c \rangle$  of the 50 most  
1300 abundant products.

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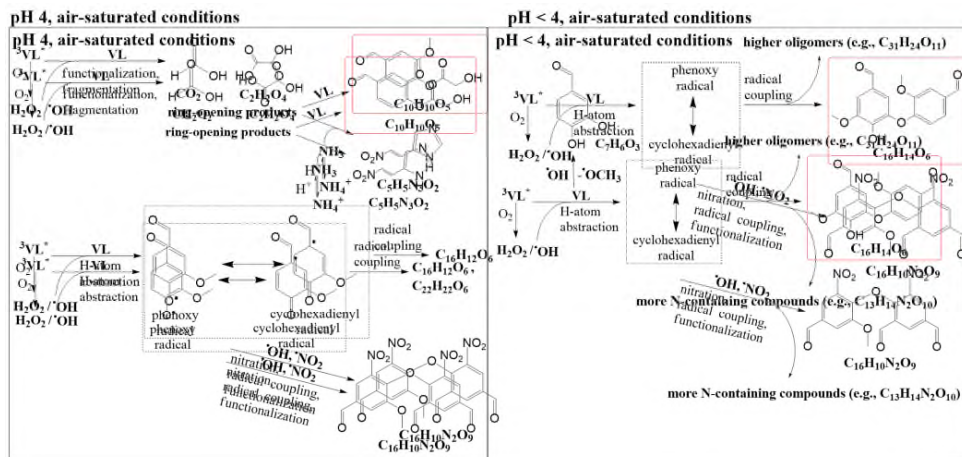




1307 sunlight irradiation. The normalized abundance of products was calculated ~~using from the ratio of the peak area of the product~~  
1308 ~~to that of VL~~ (Eq. 2). The 50 most abundant products contributed more than half of the total normalized abundance of products,  
1309 and they were identified as monomers (blue), dimers (green), trimers (red), and tetramers (orange). Grey peaks denote peaks  
1310 with low abundance or unassigned formula. Examples of high-intensity peaks were labeled with the corresponding neutral  
1311 formulas. Note the different scales on the y-axes.

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1334 **Figure 2.** Potential aqSOA formation pathways via [the direct photosensitized oxidation of VL in the absence \(VL\\*\) and](#)  
 1335 [presence of and ammonium nitrate \(VL+AN\)-mediated VL-photo-oxidation](#) at pH 4 and pH < 4 under air-saturated conditions.  
 1336 Product structures were proposed based on the molecular formulas, DBE values, and MS/MS fragmentation patterns. The  
 1337 [molecular formulas/structures](#) presented were the major products detected using UHPLC-qToF-MS in positive ESI mode. The  
 1338 highlighted structures are the most abundant product for each condition.

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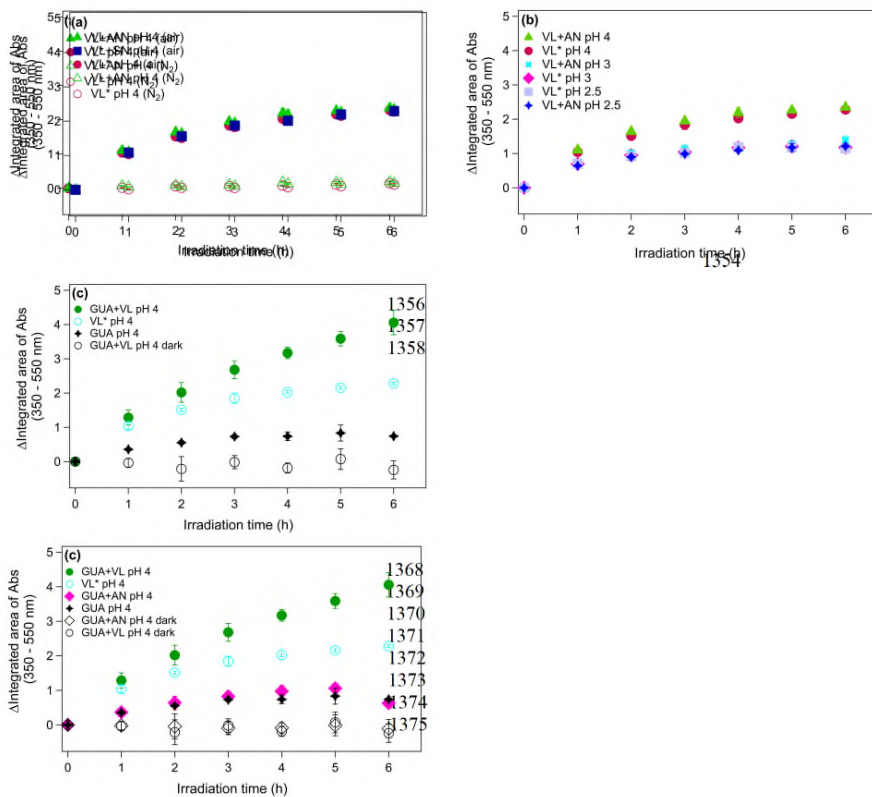
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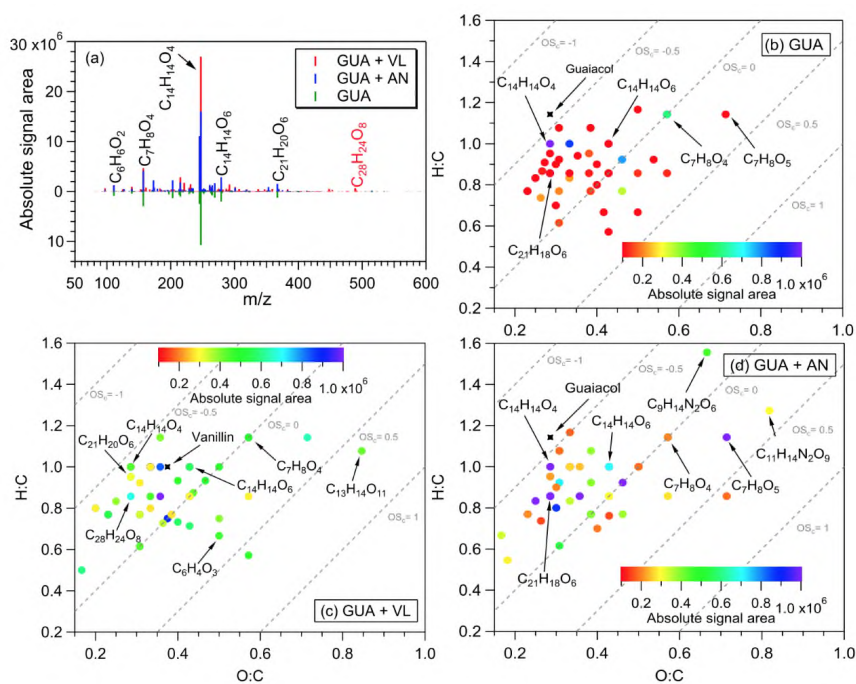
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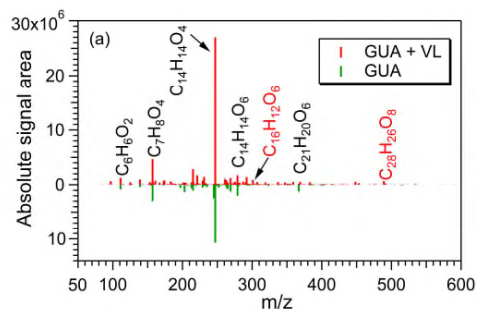
1380 **Figure 3.** (a-c) Increase in light absorption under different experimental conditions for direct photosensitized oxidation of VL  
1381 in the absence (VL\*) and nitrate-mediated VL-photo-oxidation presence of ammonium nitrate (VL+AN): (a) VL\* and VL+AN  
1382 at pH 4 under N<sub>2</sub>- (A6, A8) and air-saturated (A5, A7) conditions. Direct photosensitized oxidation of VL in the presence of  
1383 sodium nitrate (VL+SN) at pH 4 under air-saturated condition (A9). (b) Effect of pH on VL\* and VL+AN at pH 2.5 (A1, A2),  
1384 3 (A3, A4), and 4 (A5, A7) under air-saturated conditions. (c) Increase in light absorption during direct GUA

1385 photodegradation (A13) and photo-oxidation of GUA in the presence of VL via photosensitized reactions of VL (GUA+VL;  
 1386 A14) or nitrate (GUA+AN; A15) at pH 4 under air-saturated conditions after 6 h of simulated sunlight irradiation. Error bars  
 1387 represent one standard deviation; most error bars are smaller than the markers.

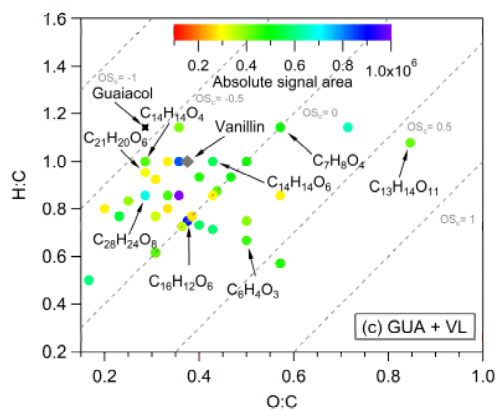
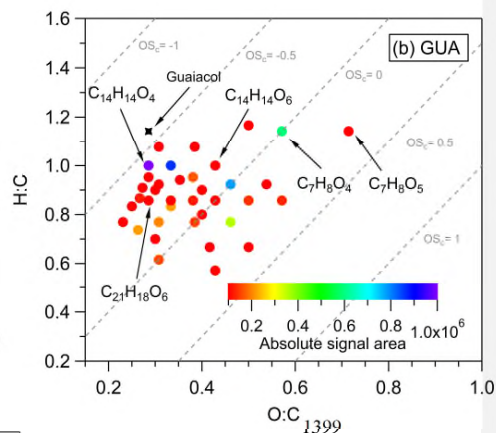


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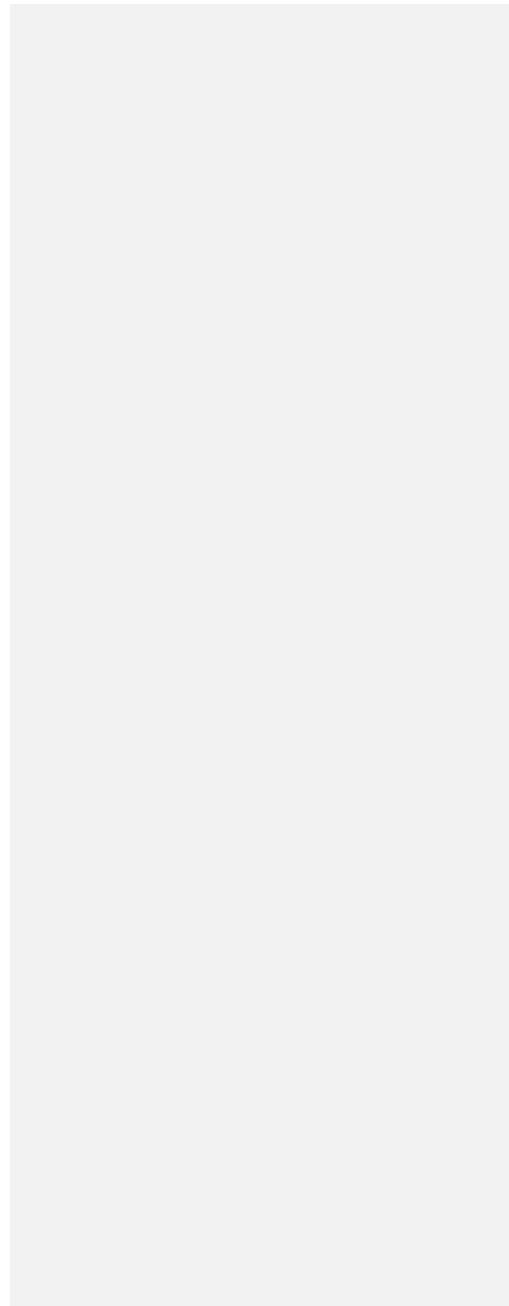
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413 **Figure 4.** (a) Reconstructed mass spectra of assigned peaks from the direct GUA photodegradation (A13) and **photo**-oxidation  
414 of GUA **via photosensitized reactions in the presence** of VL (GUA+VL; A14) **or nitrate** (GUA+AN; A15) at pH 4 under air-  
415 saturated conditions after 6 h of simulated sunlight irradiation. The y-axis is the absolute signal area of the products. Examples  
416 of high-intensity peaks were labeled with the corresponding neutral formulas. **The formulas in red text correspond to products**  
417 **observed only from GUA+VL.** (b-c) van Krevelen diagrams of the 50 most abundant products from the (b) direct  
418 photodegradation of GUA (A13) **and** (c) GUA+VL (A14) **and** (d) GUA+AN (A15) at pH 4 under air-saturated conditions

1419 after 6 h of simulated sunlight irradiation. The color bar denotes the absolute signal area. The grey dashed lines indicate the  
1420 carbon oxidation state values (e.g.,  $OS_c = -1, 0, \text{ and } 1$ ).



1 **Supplementary material**

2  
3 **Aqueous SOA formation from the direct photosensitized -**  
4 **oxidation of vanillin in the absence and presence of ammonium**  
5 **nitrate: ~~Direct photosensitized reactions and nitrate-mediated~~**  
6 **reactions**

7  
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26 **Text S1. Materials.**

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28 Initial solutions of 0.1 mM vanillin (VL, Acros Organics, 99%, pure), 0.1 mM guaiacol (GUA,

29 Sigma Aldrich,  $\geq 98.0\%$ ), 1 mM ammonium nitrate (AN, Acros Organics, 99+%, for analysis),

30 and 1 mM sodium nitrate (SN, Sigma-Aldrich,  $\geq 99.5\%$ ) were prepared in Milli-Q water. The pH

31 values of the samples were adjusted using sulfuric acid ( $\text{H}_2\text{SO}_4$ ; Acros Organics, ACS reagent, 95%

32 solution in water).

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34 **Text S2. UV-Vis spectrophotometric analyses.**

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36 The absorbance changes for all samples were characterized using a UV-Vis

37 spectrophotometer (UV-3600, Shimadzu Corp., Japan). The absorbance values from 200 to 700

38 nm were recorded instantly after sample collection, and measurements were done in triplicate.

39 Absorbance enhancements were calculated as the change in the integrated area of absorbance from

40 350 to 550 nm. The increase of light absorption at this wavelength range, where VL and GUA did

41 not initially absorb light, suggests the formation of light-absorbing compounds (Zhou et al., 2019).

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43 **Text S3. UHPLC-PDA analyses.**

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45 An ultra-high performance liquid chromatography system (UHPLC, Waters Acquity H-

46 Class, Waters, Milford, USA) coupled to a photodiode array (PDA) detector (Waters, Milford,

47 USA) was used for the quantification of VL and GUA concentrations. The drawn solutions were

48 first filtered through a 0.2  $\mu\text{m}$  Chromafil<sup>®</sup>Xtra PTFE filter (Macherey-Nagel GmbH & Co. KG,

49 Germany). Briefly, the separation of products was performed using an Acquity HSS T3 column

50 (1.8  $\mu\text{m}$ , 2.1 mm  $\times$  100 mm; Waters Corp.). The column oven was held at 30  $^\circ\text{C}$ , and the

51 autosampler was cooled at 4  $^\circ\text{C}$ . The injection volume was set to 5  $\mu\text{L}$ . The binary mobile phase

52 consisted of A (water) and B (acetonitrile). The gradient elution was performed at a flow rate of  
53 0.2 mL/min: 0–1 min, 10% eluent B; 1–25 min, linear increase to 90% eluent B; 25–29.9 min,  
54 hold 90% eluent B; 29.9–30 min, decrease to 10% eluent B; 30–35 min, re-equilibrate at 10%  
55 eluent B for 5 min. Standard solutions of VL and GUA ranging from 10 to 130  $\mu\text{M}$  were analyzed  
56 along with samples and blanks using the channels with UV absorption at 300 and 274 nm,  
57 respectively. The calibration curves for VL and GUA standard solutions are shown in Figure S2.

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59 **Text S4.** IC analyses of small organic acids.

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61 The small organic acids were analyzed using an ion chromatography system (IC, Dionex  
62 ICS-1100, Sunnyvale, CA) equipped with a Dionex AS-DV autosampler (Sunnyvale, CA). The  
63 separation was achieved using an IonPac<sup>TM</sup> AS15 column (4  $\times$  250 mm) with an AG15 guard  
64 column (4  $\times$  50 mm). The isocratic gradient was applied at a flow rate of 1.2 mL/min with 38 mM  
65 sodium hydroxide (NaOH) as the eluent. The total run time was set at 20 min. The standard  
66 solutions (1–50  $\mu\text{M}$ ) of formic, succinic, and oxalic acid were analyzed three times along with the  
67 samples and water blank. Formic, succinic, and oxalic acid had retention times of 3.6 min, 8.3 min,  
68 and 11.9 min, respectively.

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70 **Text S5.** UHPLC-qToF-MS analyses.

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72 The characterization of reaction products was performed using a UHPLC system  
73 (ExionLC<sup>TM</sup> AD, ABSciex, Concord, Canada) coupled to a quadrupole time-of-flight mass  
74 spectrometer (qToF-MS) (TripleTOF 6600+, ABSciex). The settings (e.g., column, mobile phase,  
75 gradient, oven temperature) in the UHPLC system were the same as those used in UHPLC-PDA  
76 (Text S3). The mass spectrometer was equipped with an electrospray ionization (ESI) source and  
77 operated in the positive ion mode (the negative ion mode signals were too low for our analyses) at

78 a resolving power (full width at half-maximum (fwhm) at  $m/z$  300) of 30000 in MS and 30000 in  
79 MS/MS (high-resolution mode). Information-dependent acquisition (IDA) scanning was adapted  
80 for product identification. The acquisition using IDA consisted of a ToF-MS scan and information-  
81 dependent trigger events. The ToF-MS scan had an accumulation time of 250 ms and covered a  
82 mass range of  $m/z$  30–700 with a declustering potential (DP) of 40 and collision energy (CE) of  
83 10 eV. The accumulation time for the IDA experiment was 100 ms, and the MS/MS scan range  
84 was set from  $m/z$  30–700 in high-resolution mode. The IDA criteria were as follows: 5 most intense  
85 ions (number of IDA experiments) with an intensity threshold above 50 cps, isotope exclusion was  
86 switched off, and dynamic background subtraction was switched on. The automated calibration  
87 device system (CDS) was set to perform an external calibration every four samples. The ESI source  
88 conditions were as follows: temperature, 500 °C; curtain gas (CUR), 25 psi; ion source gas 1 at 50  
89 psi; ion source gas 2 at 50 psi; and ion-spray voltage floating (ISVF) at 4.5 kV.

90 All parameters in the liquid chromatography system and mass spectrometer were controlled  
91 using Analyst TF Software 1.8 (ABSciex). The high-resolution LC-MS data were processed with  
92 PeakView and Analyst in the SCIEX OS software 1.5 (ABSciex). Peaks from the blank sample  
93 were subtracted from the sample signals. In addition to a minimum signal-to-noise ratio of 30, a  
94 peak was determined as a product if the difference in peak area between the samples before and  
95 after irradiation is  $\geq 10$  times. The formula assignments were carried out using the MIDAS  
96 molecular formula calculator (<http://magnet.fsu.edu/~midas/>) with the following constraints:  $C \leq$   
97 35,  $H \leq 70$ ,  $N \leq 5$ ,  $O \leq 20$ ,  $Na \leq 1$ , and the mass error was initially set at 10 ppm. The nitrogen  
98 atom was removed in the constraints for the experiments without AN or SN. The detected adducts  
99 in ESI positive ion mode have several types (e.g.,  $[M+H]^+$ ,  $[M+Na]^+$ ), and their formation can be  
100 influenced by the sample matrix (Erngren et al., 2019). For simplification purposes, we mainly

101 considered  $[M+H]^+$  adducts for formula assignments, except for specific experiments with AN or  
102 SN in which  $[M+NH_4]^+$  adducts and  $[M+Na]^+$  adducts were observed. The final assigned formulas  
103 were constrained by a mass error of mostly  $< 5$  ppm, which is a requirement for product  
104 identification using positive ion mode (Roemmelt et al., 2015). The double bond equivalent (DBE)  
105 values and carbon oxidation state ( $OS_c$ ) of the neutral formulas were calculated using the following  
106 equations (Koch and Dittmar, 2006):

$$107 \quad DBE = C - H/2 + N/2 + 1 \quad \text{(Eq. S1)}$$

$$108 \quad OS_c = 2 \times O/C - H/C$$

109 (Eq. S2)

110

111

112

113 where C, H, O, and N correspond to the number of carbon, hydrogen, oxygen, and nitrogen atoms  
114 in the neutral formula, respectively. Based on the identified products, the average oxygen to carbon  
115 (O:C) ratios,  $\langle O:C \rangle$ : ( $\langle O:C \rangle = \sum_i(\text{abundance}_i)O_i / \sum_i(\text{abundance}_i)C_i$ ) and average hydrogen  
116 to carbon (H:C) ratios,  $\langle H:C \rangle$ : ( $\langle H:C \rangle = \sum_i(\text{abundance}_i)H_i / \sum_i(\text{abundance}_i)C_i$ ) after the  
117 reactions were further estimated using the signal-weighted method (Bateman et al., 2012). The  
118 average  $OS_c$  ( $\langle OS_c \rangle$ ) was calculated as follows:

$$119 \quad \langle OS_c \rangle = 2 \times \langle O:C \rangle - \langle H:C \rangle \quad \text{(Eq. S3)}$$

120

121 Based on the typical MS/MS fragmentation behavior for individual functional groups (Table S1)  
122 and DBE values, examples of structures for products ~~detected~~identified from VL (and GUA)  
123 photo-oxidation experiments were proposed (Table S2).

124

125 **Text S6.** Photon flux measurements.

126

127 In this work, 2-nitrobenzaldehyde (2NB), a chemical actinometer, was used to determine  
128 the photon flux in the aqueous photoreactor. Briefly, the photolysis of 50  $\mu\text{M}$  2NB in the reactor  
129 was monitored by determining its concentration every 5 min for a total of 35 min, during which  
130 2NB was almost completely decayed. The concentration of 2NB was measured using UHPLC-  
131 PDA, and the settings (e.g., column, mobile phase, gradient, oven temperature) were the same as  
132 those for VL decay analysis (Text S3). The channel with UV absorption at 254 nm was used for  
133 the quantification of 2NB. The concentration of 2NB in the reactor followed exponential decay,  
134 and its decay rate constant was determined using the following equation:

135 
$$\ln\left(\frac{[2\text{NB}]_t}{[2\text{NB}]_0}\right) = -j(2\text{NB}) \times t \quad (\text{Eq. S4})$$

136

137 where  $[2\text{NB}]_t$  and  $[2\text{NB}]_0$  are the 2NB concentrations at time  $t$  and 0, respectively. The calculated  
138 2NB decay rate constant,  $j(2\text{NB})$ , was  $0.0026 \text{ s}^{-1}$ . The following equation can also be used to  
139 calculate  $j(2\text{NB})$ :

140 
$$j(2\text{NB}) = 2.303 \times (10^3 \text{ cm}^3 \text{ L}^{-1} \times 1 \text{ mol}/N_A \text{ mlc}) \times \sum(I'_\lambda \times \Delta\lambda \times \varepsilon_{2\text{NB},\lambda} \times \Phi_{2\text{NB}}) \quad (\text{Eq. S5})$$

141 where  $N_A$  is Avogadro's number,  $I'_\lambda$  is the actinic flux ( $\text{photons cm}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ ),  $\Delta\lambda$  is the  
142 wavelength interval between actinic flux data points (nm), and  $\varepsilon_{2\text{NB},\lambda}$  and  $\Phi_{2\text{NB},\lambda}$  are the base-10  
143 molar absorptivity ( $\text{M}^{-1} \text{ cm}^{-1}$ ) and quantum yield ( $\text{molecule photon}^{-1}$ ) for 2NB, respectively.

144 Values of  $\varepsilon_{2\text{NB},\lambda}$  (in water) at each wavelength under 298 K and a wavelength-independent  $\Phi_{2\text{NB}}$   
145 value of 0.41 were adapted from Galbavy et al. (2010). Similar to Smith et al. (2014, 2016), we  
146 measured the spectral shape of the photon output of our illumination system (i.e., the relative flux  
147 at each wavelength) using a high-sensitivity spectrophotometer (Brolight Technology Co. Ltd,

148 Hangzhou, China). Using a scaling factor (SF), this measured relative photon output,  $I_{\lambda}^{\text{relative}}$ , is  
 149 related to  $I'_{\lambda}$  as follows (Hullar et al., 2020):

$$150 \quad I'_{\lambda} = I_{\lambda}^{\text{relative}} \times \text{SF} \quad (\text{Eq. S6})$$

151  
 152  
 153 Substitution of Eq. S6 into Eq. S5 and rearrangement yields:

$$154 \quad \text{SF} = \frac{j(2\text{NB})}{2.303 \times (10^3 \text{ cm}^3 \text{ L}^{-1} \times 1 \text{ mol}/N_{\text{A}} \text{ mlc}) \times \sum(I_{\lambda}^{\text{relative}} \times \Delta\lambda \times \varepsilon_{2\text{NB},\lambda} \times \Phi_{2\text{NB}})} \quad (\text{Eq. S7})$$

155  
 156  
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 159  
 160 and substitution of Eq. S6 into Eq. S7 yields:

$$161 \quad I'_{\lambda} = I_{\lambda}^{\text{relative}} \frac{j(2\text{NB})}{2.303 \times (10^3 \text{ cm}^3 \text{ L}^{-1} \times 1 \text{ mol}/N_{\text{A}} \text{ mlc}) \times \sum(I_{\lambda}^{\text{relative}} \times \Delta\lambda \times \varepsilon_{2\text{NB},\lambda} \times \Phi_{2\text{NB}})} \quad (\text{Eq. S8})$$

162  
 163  
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 167 Finally,  $I'_{\lambda}$  was estimated through Eq. S8. The estimated photon flux in the aqueous reactor is shown  
 168 in Fig. S1. The actinic flux during a haze event over Beijing (40° N, 116° E) on January 12,  
 169 2013, at 12:00 pm (GMT+8) (Che et al., 2014) estimated using the National Center for  
 170 Atmospheric Research—Tropospheric Ultraviolet-Visible (TUV) Radiation Model  
 171 ([http://cprm.acom.ucar.edu/Models/TUV/Interactive\\_TUV/](http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/)) is also shown in Figure S2. The  
 172 parameters used for the Quick TUV calculator were: Overhead Ozone Column: 300 du; Surface  
 173 Albedo: 0.1; Ground Elevation: 0 km asl; Measured Altitude: 0 km asl; Clouds optical depth: 0,  
 174 base: 4, top: 5; Aerosols optical depth: 2.5, single scattering albedo: 0.9, Angstrom exponent: 1;  
 175 Sunlight direct beam, diffuse down, diffuse up: 1; 4 streams transfer model. For clear days, the  
 176 actinic flux was estimated over Beijing (at the same date and time) using the default parameters.

177

178 **Text S7.** Estimation of the apparent quantum efficiency of guaiacol photodegradation.

179  
180 The apparent quantum efficiency of GUA photodegradation ( $\Phi_{\text{GUA}}$ ) in the presence of  
181 either VL or nitrate during simulated sunlight illumination can be defined as (Anastasio et al., 1996;  
182 Smith et al., 2014, 2016):

$$183 \Phi_{\text{GUA}} = \frac{\text{mol GUA destroyed}}{\text{mol photons absorbed}} \quad (\text{Eq. S9})$$

184  $\Phi_{\text{GUA}}$  was calculated using the measured rate of GUA decay and rate of light absorption by either  
185 VL or nitrate through the following equation:

$$187 \Phi_{\text{GUA}} = \frac{\text{rate of GUA decay}}{\text{rate of light absorption by VL or nitrate}} = \frac{k'_{\text{GUA}} \times [\text{GUA}]}{\sum_i \left( (1 - 10^{-\epsilon_i [\text{C}] l}) \times I'_{\lambda} \right)} \quad (\text{Eq. S10})$$

188  
189 where  $k'_{\text{GUA}}$  is the pseudo first order rate constant for GUA decay, [GUA] is the concentration of  
190 GUA (M),  $\epsilon_i$  is the base-10 molar absorptivity ( $\text{M}^{-1} \text{cm}^{-1}$ ) of VL or nitrate at wavelength  $\lambda$ , [C] is  
191 the concentration of VL or nitrate (M),  $l$  is the pathlength of the illumination cell (cm), and  $I'_{\lambda}$  is  
192 the volume averaged photon flux ( $\text{mol photons L}^{-1} \text{s}^{-1} \text{nm}^{-1}$ ) determined from 2NB actinometry:

$$194 j(2\text{NB}) = 2.303 \times \Phi_{2\text{NB}} \times l \times \int_{300 \text{ nm}}^{350 \text{ nm}} (\epsilon_{2\text{NB},\lambda} \times I'_{\lambda} \times \Delta\lambda) \quad (\text{Eq. S11})$$

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**Table S1.** Typical fragmentation behavior observed in MS/MS spectra for individual functional groups from Holčapek et al. (2010).

Functional group	Fragment ions	MS/MS loss
Nitro (RNO <sub>2</sub> )	[M+H-OH] <sup>+</sup> *	-OH
	[M+H-H <sub>2</sub> O] <sup>+</sup>	-H <sub>2</sub> O
	[M+H-NO] <sup>+</sup> *	-NO
	[M+H-NO <sub>2</sub> ] <sup>+</sup> *	-NO <sub>2</sub>
Nitroso (RNO)	[M+H-NO] <sup>+</sup>	-NO
Carboxylic acid (ROOH)	[M+H-H <sub>2</sub> O] <sup>+</sup>	-H <sub>2</sub> O
	[M+H-CO <sub>2</sub> ] <sup>+</sup>	-CO <sub>2</sub>
	[M+H-H <sub>2</sub> O-CO] <sup>+</sup>	-H <sub>2</sub> O-CO
Phenol (ROH)	[M+H-H <sub>2</sub> O] <sup>+</sup>	-H <sub>2</sub> O
	[M+H-CO] <sup>+</sup>	-CO
Methoxy (ROCH <sub>3</sub> )	[M+H-CH <sub>3</sub> ] <sup>+</sup> *	-CH <sub>3</sub>
	[M+H-CH <sub>3</sub> O] <sup>+</sup> *	-CH <sub>3</sub> O
	[M+H-CH <sub>3</sub> OH] <sup>+</sup>	-CH <sub>3</sub> OH
	[M+H-HCOH] <sup>+</sup>	-HCOH
Ester (R <sup>1</sup> COOR <sup>2</sup> )	[M+H-R <sup>2</sup> OH] <sup>+</sup>	-R <sup>2</sup> OH
	[M+H-R <sup>2</sup> OH-CO] <sup>+</sup>	-R <sup>2</sup> OH-CO
Amine	[M+H-NH <sub>3</sub> ] <sup>+</sup>	-NH <sub>3</sub>
Aldehyde (RCHO)	[M+H-CO] <sup>+</sup>	-CO

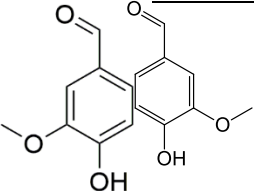
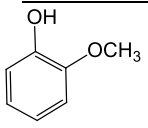
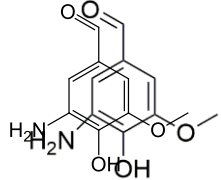
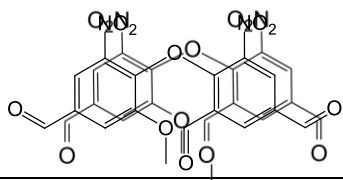
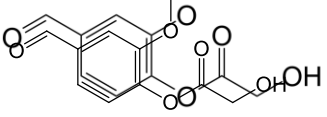
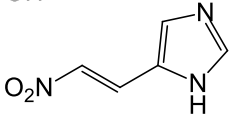
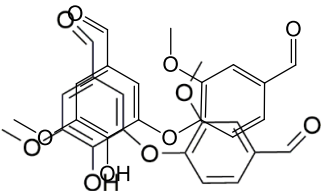


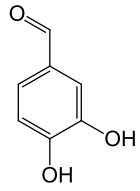
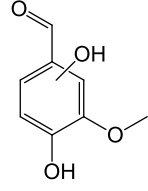
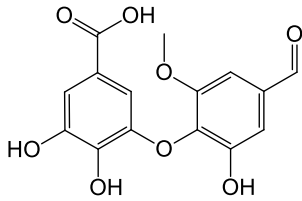
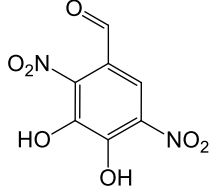
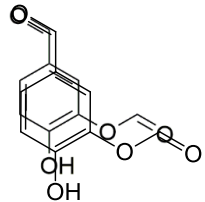
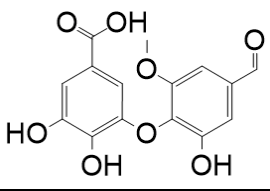
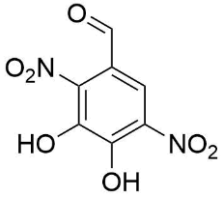
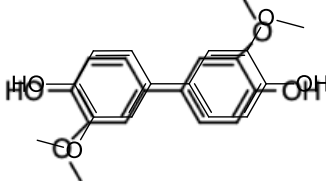
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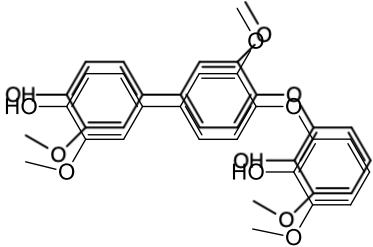
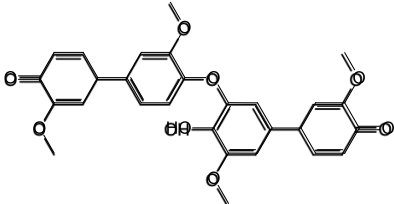
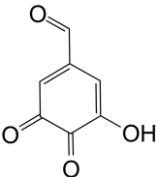
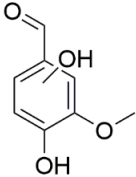
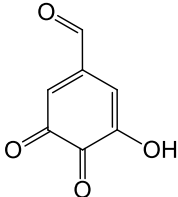
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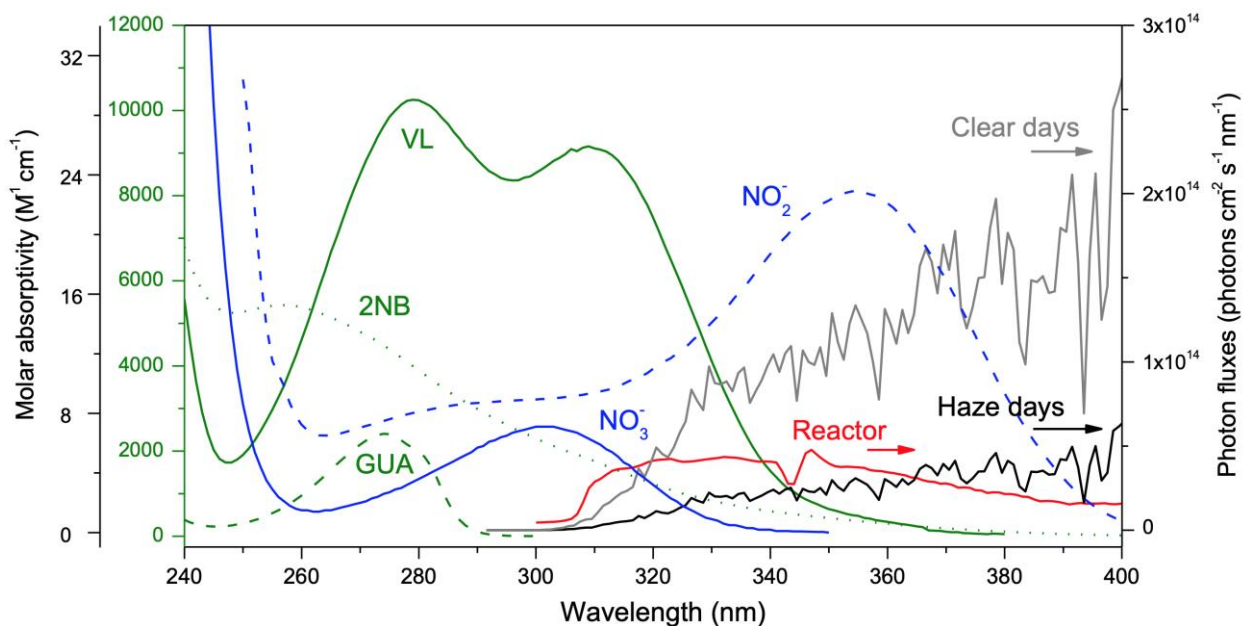
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234 **Table S2.** Examples of proposed ~~molecular~~ structures for products ~~detected~~ identified from  
 235 vanillin (and guaiacol)-photo-oxidation experiments in this study.  
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No.	Formula	DBE	Proposed structure	MS/MS fragment ions		
1	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> (VL; <u>triplet</u> <u>and</u> <u>aqSOA</u> precursor)	5		-CO-CH <sub>3</sub> OH	-CO	-CO- CH <sub>3</sub> OH-CO
<u>2</u>	<u>C<sub>7</sub>H<sub>8</sub>O<sub>2</sub></u> ( <u>GUA</u> ; <u>aqSOA</u> precursor)	<u>4</u>				
<u>32</u>	C <sub>8</sub> H <sub>9</sub> NO <sub>3</sub>	5		-CO-CH <sub>3</sub>	-NH <sub>3</sub>	
<u>43</u>	C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> O <sub>9</sub>	13		-NO <sub>2</sub>		
<u>54</u>	C <sub>10</sub> H <sub>10</sub> O <sub>5</sub>	6		-CH <sub>3</sub> OH	-CH <sub>3</sub> OH- CO	
6	C <sub>5</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>	5		-NH		
<u>76</u>	C <sub>16</sub> H <sub>14</sub> O <sub>6</sub>	10		-CO-CH <sub>3</sub> OH- CO	-CO- CH <sub>3</sub> OH- CO-CH <sub>3</sub> OH	-CO- CH <sub>3</sub> OH- CO-CO

<u>8</u>	<u>C<sub>7</sub>H<sub>6</sub>O<sub>3</sub></u>	<u>5</u>				
<u>9</u>	<u>C<sub>8</sub>H<sub>8</sub>O<sub>4</sub></u>	<u>5</u>		<u>-CO-CH<sub>3</sub>OH</u>	<u>-CO</u>	<u>-H<sub>2</sub>O</u>
<u>10</u>	<u>C<sub>15</sub>H<sub>12</sub>O<sub>8</sub></u>	<u>10</u>		<u>-COOH</u>		
<u>11</u>	<u>C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>7</sub></u>	<u>7</u>				
<u>127</u>	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	6		-CO	-CO-CO	
<u>8</u>	<u>C<sub>15</sub>H<sub>12</sub>O<sub>8</sub></u>	<u>10</u>		<u>-COOH</u>		
<u>9</u>	<u>C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>7</sub></u>	<u>7</u>				
<u>130</u>	C <sub>14</sub> H <sub>14</sub> O <sub>4</sub>	8				

<del>141</del>	$C_{21}H_{20}O_6$	12				
<del>152</del>	$C_{28}H_{26}O_8$	<del>167</del>				
<del>13</del>	$C_7H_4O_4$	6		<del>-CO</del>	<del>-CO-CO</del>	
14	$C_8H_8O_4$	5		<del>-CO-CH_3OH</del>	<del>-CO</del>	<del>-H_2O</del>
<u>16</u>	<u><math>C_7H_4O_4</math></u>	<u>6</u>		<u>-CO</u>	<u>-CO-CO</u>	

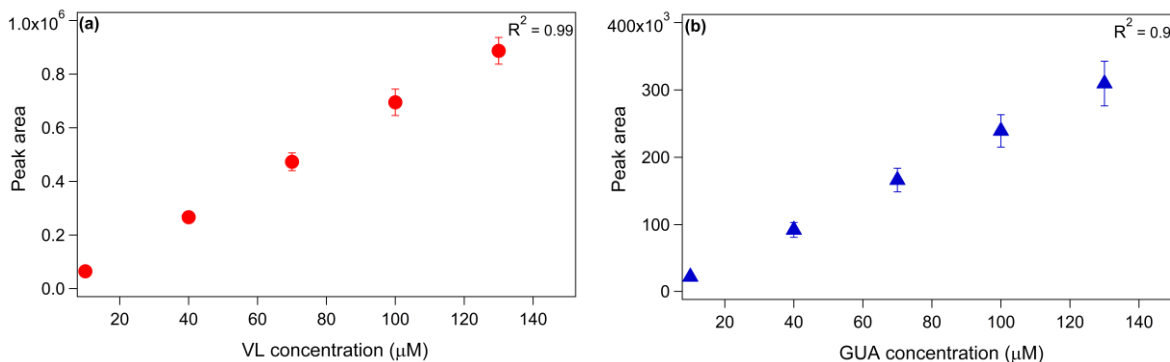


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242 **Figure S1.** The base-10 molar absorptivities ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ) of vanillin (VL, green solid line), 2-  
243 nitrobenzaldehyde (2NB, green dotted line), guaiacol (GUA, green dashed line),  $NO_2^-$  (blue  
244 dashed line),  $NO_3^-$  (blue solid line), and photon flux in the aqueous reactor (red line) during typical  
245 haze days (black line) or clear days (grey line) in Beijing, China. The  $\epsilon$  values for 2NB and  $NO_2^-$   
246 were adapted from Galbavy et al. (2010) and Chu and Anastasio (2007), respectively.

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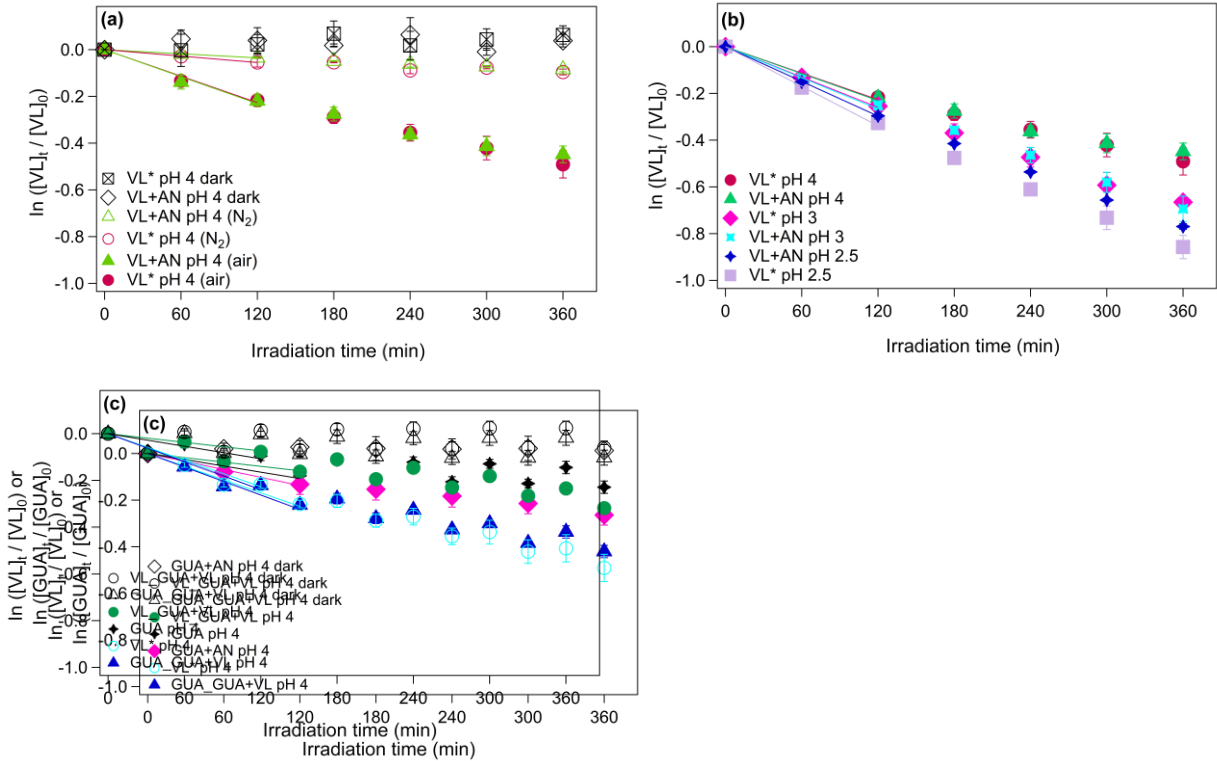
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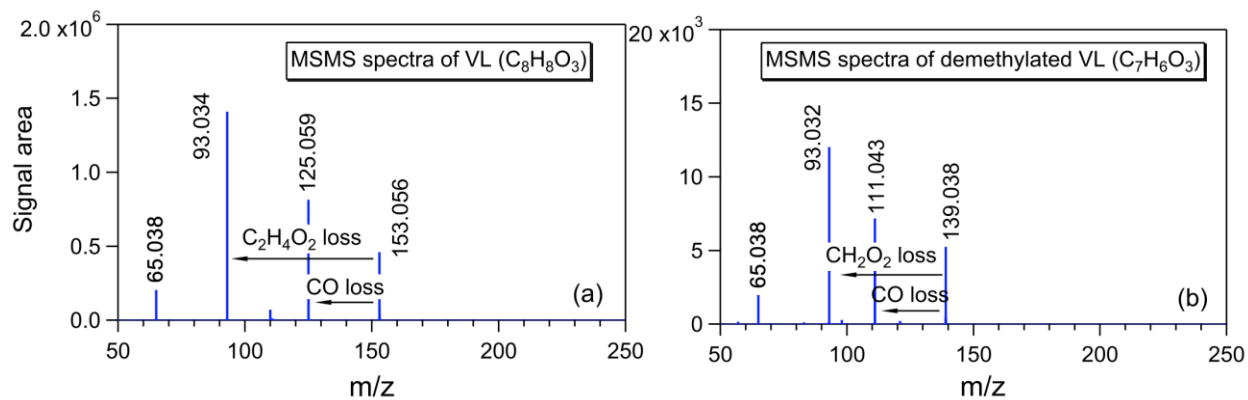
253 **Figure S2.** Calibration curves for (a) VL and (b) GUA standard solutions (10–130  $\mu M$ ). Error  
254 bars represent one standard deviation.

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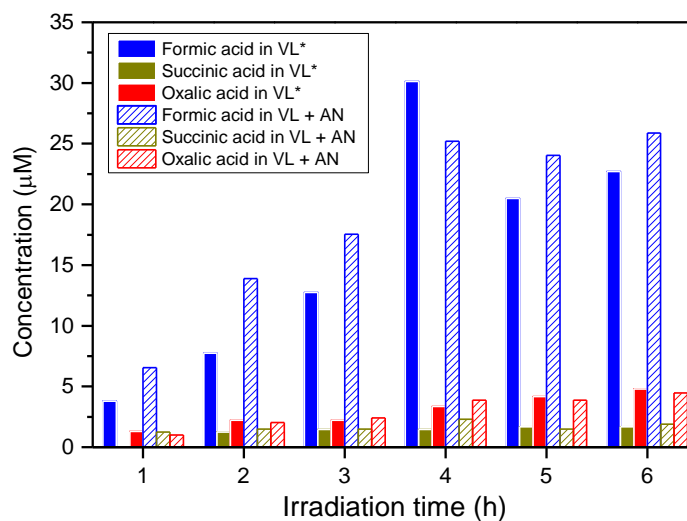


**Figure S3.** (a–c) The decay of VL under different experimental conditions for direct photosensitized oxidation of VL in the absence (VL\*) and presence of ammonium nitrate-mediated VL photo-oxidation (VL+AN): (a) VL\* and VL+AN at pH 4 under N<sub>2</sub>- (A6, A8) and air-saturated (A5, A7) conditions. No statistically significant difference ( $p > 0.05$ ) was noted between VL+AN (A7) and VL+SN (A9; not shown here). (b) Effect of pH on VL\* and VL+AN at pH 2.5 (A1, A2), 3 (A3, A4), and 4 (A5, A7) under air-saturated conditions. (c) The decay of VL (and GUA) during direct GUA photodegradation (A13) and photo-oxidation of GUA in the presence via photosensitized reactions of VL (GUA+VL; A14) or nitrate (GUA+AN; A15) at pH 4 under air-saturated conditions after 6 h of simulated sunlight irradiation. Error bars represent one standard deviation; most error bars are smaller than the markers.



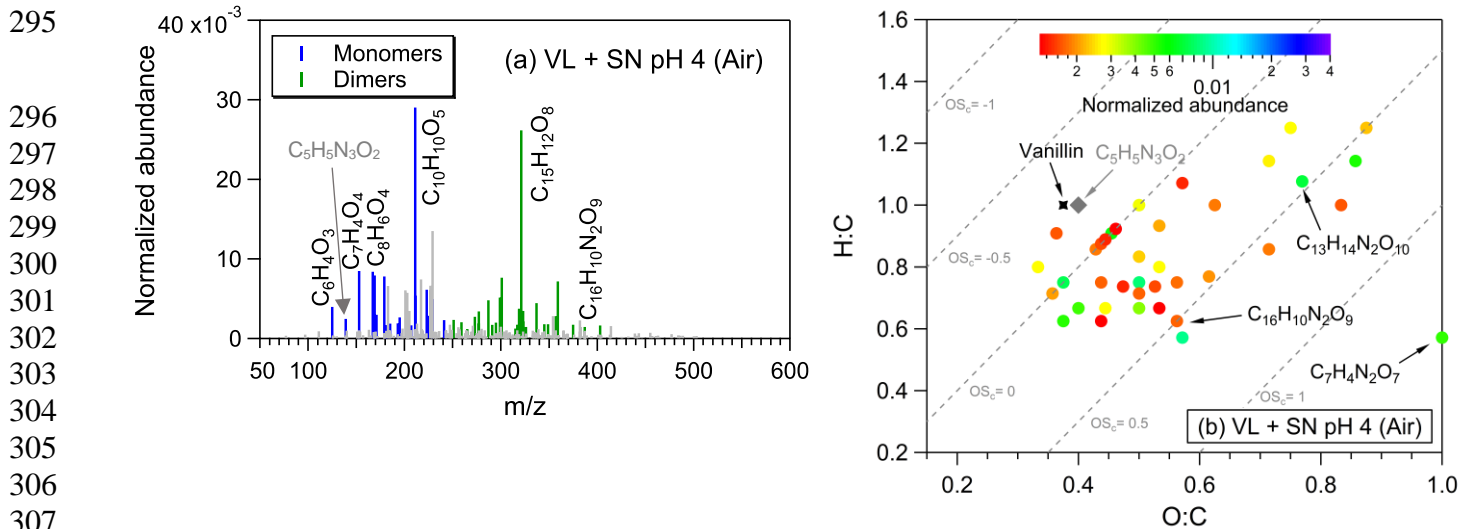
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 285 **Figure S4.** MS/MS spectra of (a) VL and (b) demethylated VL. The arrows indicate possible  
 286 fragmentation pathways of VL and demethylated VL.

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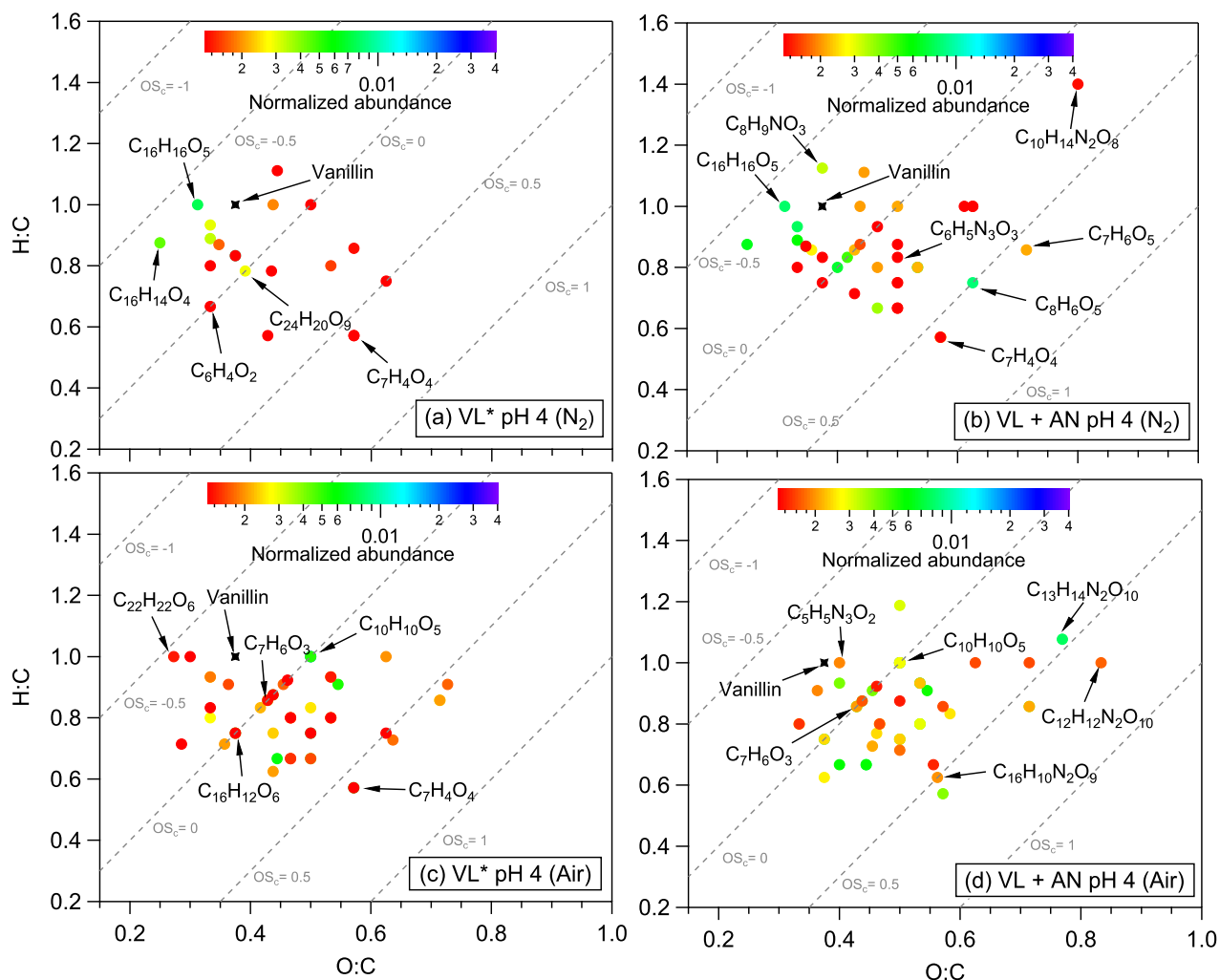


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 290 **Figure S5.** The concentration of formic, oxalic, and succinic acid at different reaction times for  
 291 VL\* (A5) and VL+AN (A7) at pH 4 under air-saturated conditions.

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 310 **Figure S6.** (a) Reconstructed mass spectra of assigned peaks and (b) van Krevelen diagram of the  
 311 50 most abundant products from VL+SN (A9) at pH 4 under air-saturated conditions after 6 h of  
 312 simulated sunlight irradiation. The normalized abundance of products was calculated ~~from the~~  
 313 ~~ratio of the peak area of the product to that of VL using~~ (Eq. 2). The 50 most abundant products  
 314 contributed more than half of the total normalized abundance of products, and they were identified  
 315 as monomers (blue) and dimers (green). Grey peaks denote peaks with low abundance or  
 316 unassigned formula. The grey arrows show where the potential imidazole derivative (C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>)  
 317 from VL+AN (A7) was observed. Examples of high-intensity peaks were labeled with the  
 318 corresponding neutral formulas. The color bar denotes the normalized abundance of products. The  
 319 grey dashed lines indicate the carbon oxidation state values (e.g., OS<sub>c</sub> = -1, 0, and 1). ~~The grey~~  
 320 ~~arrows show where the potential imidazole derivative (C<sub>5</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>) from VL+AN was observed.~~



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322 **Figure S7.** van Krevelen diagrams of the 50 most abundant products from (a) VL\* (N<sub>2</sub>-saturated;  
 323 A6), (b) VL+AN (N<sub>2</sub>-saturated; A8), (c) VL\* (air-saturated; A5), and (d) VL+AN (air-saturated;  
 324 A7) at pH 4 after 6 h of simulated sunlight irradiation. The color bar denotes the normalized  
 325 abundance of products. The grey dashed lines indicate the carbon oxidation state values (e.g., OS<sub>c</sub>  
 326 = -1, 0, and 1).

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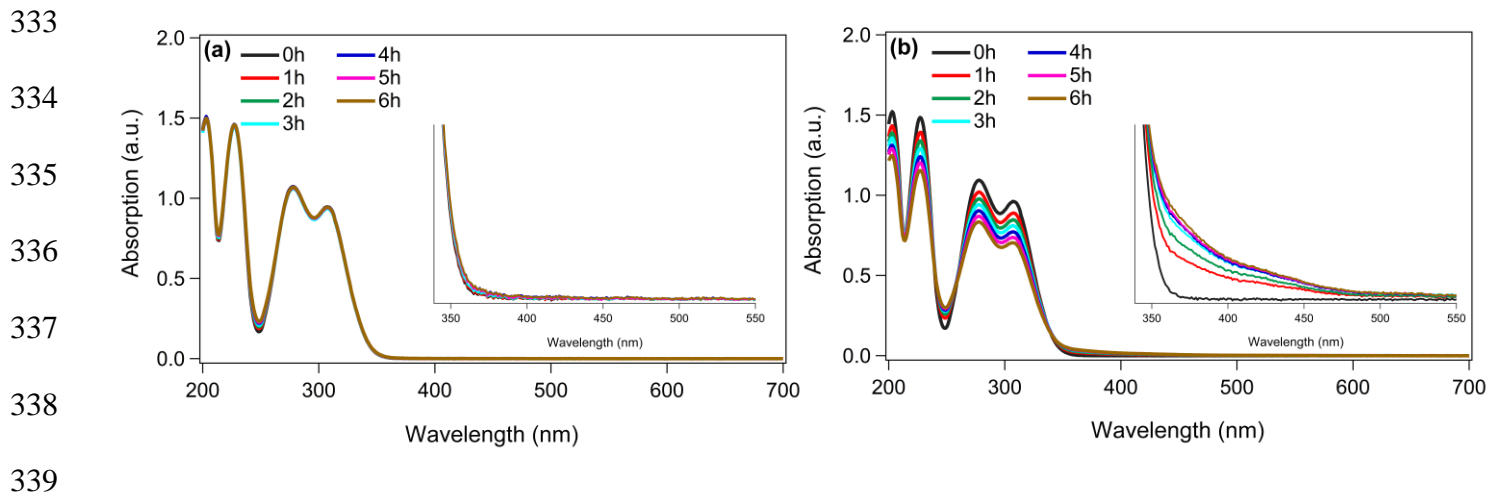
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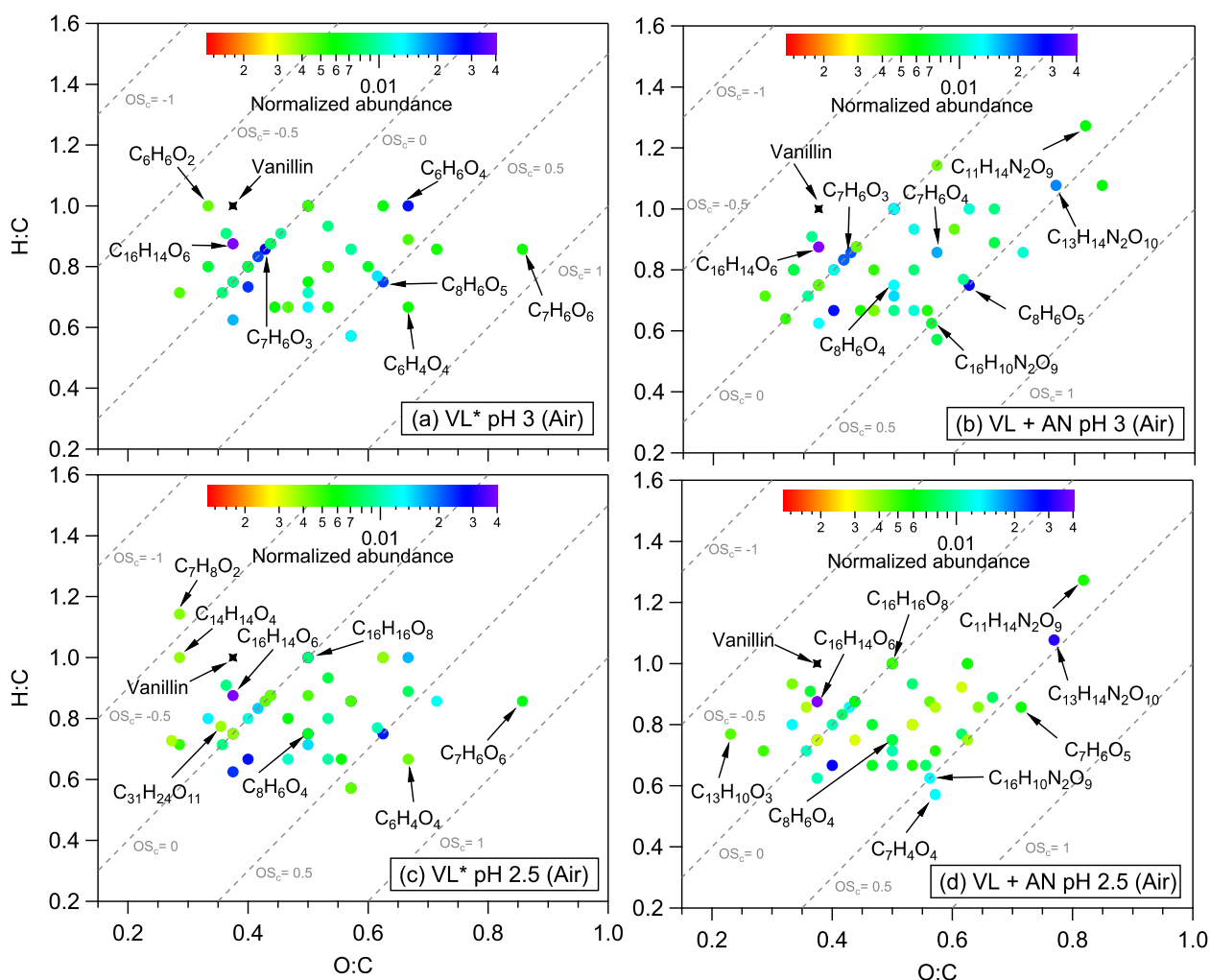
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340 **Figure S8.** UV-Vis absorption spectra of VL\* (A6, A5; pH 4) under (a) N<sub>2</sub>- and (b) air-saturated  
 341 conditions at different time intervals. The insets show the absorbance enhancement from 350 to  
 342 550 nm.  
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346 **Figure S9.** van Krevelen diagrams of the 50 most abundant products from (a) VL\* pH 3 (A3), (b)  
 347 VL+AN pH 3 (A4), (c) VL\* pH 2.5 (A1), and (d) VL+AN pH 2.5 (A2) under air-saturated  
 348 conditions after 6 h of simulated sunlight irradiation. The color bar denotes the normalized  
 349 abundance of products. The grey dashed lines indicate the carbon oxidation state values (e.g., OS<sub>c</sub>  
 350 =-1, 0, and 1).

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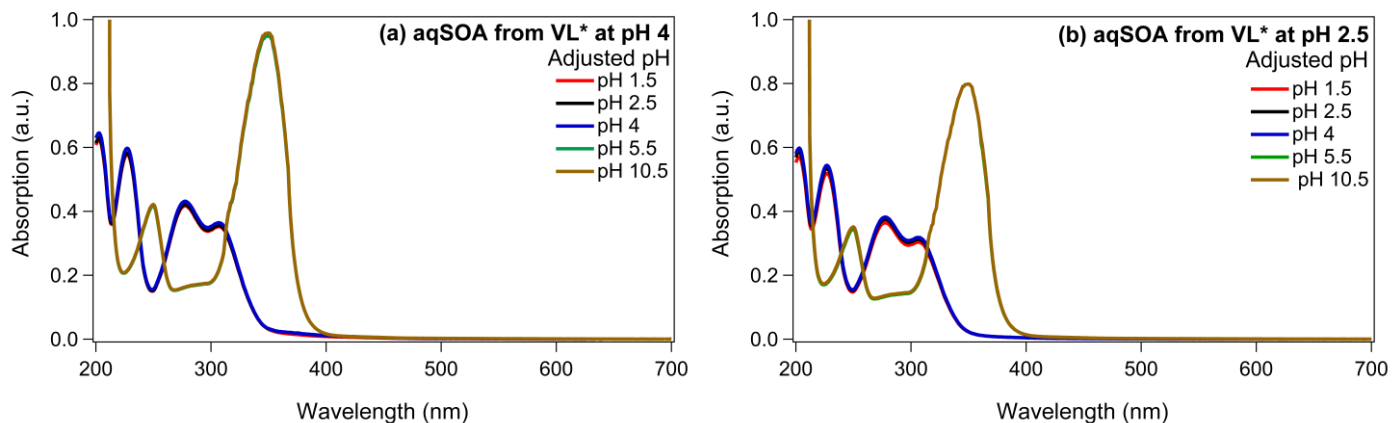
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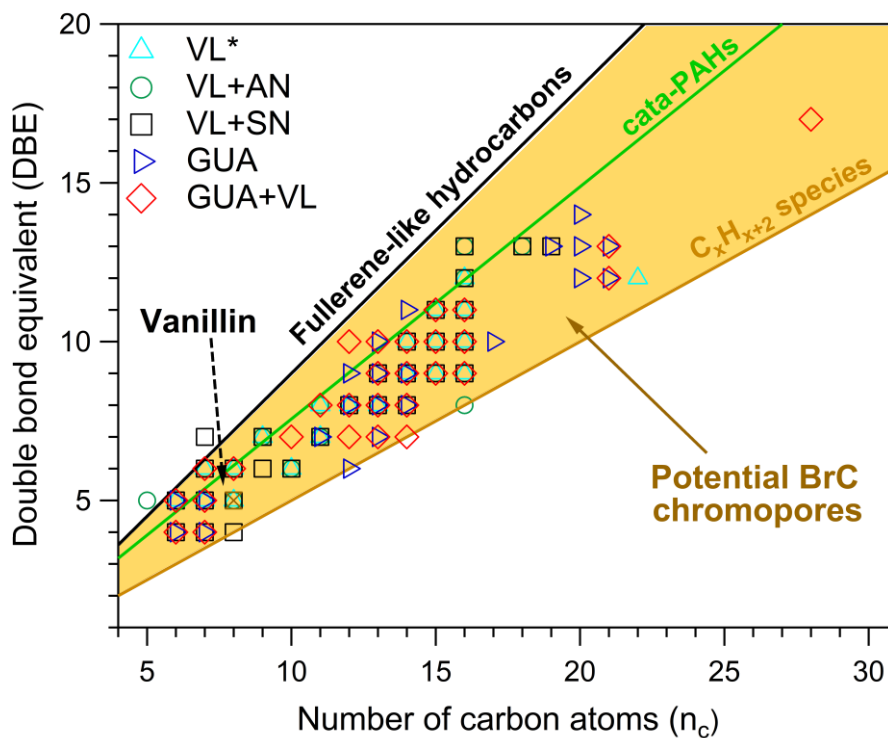
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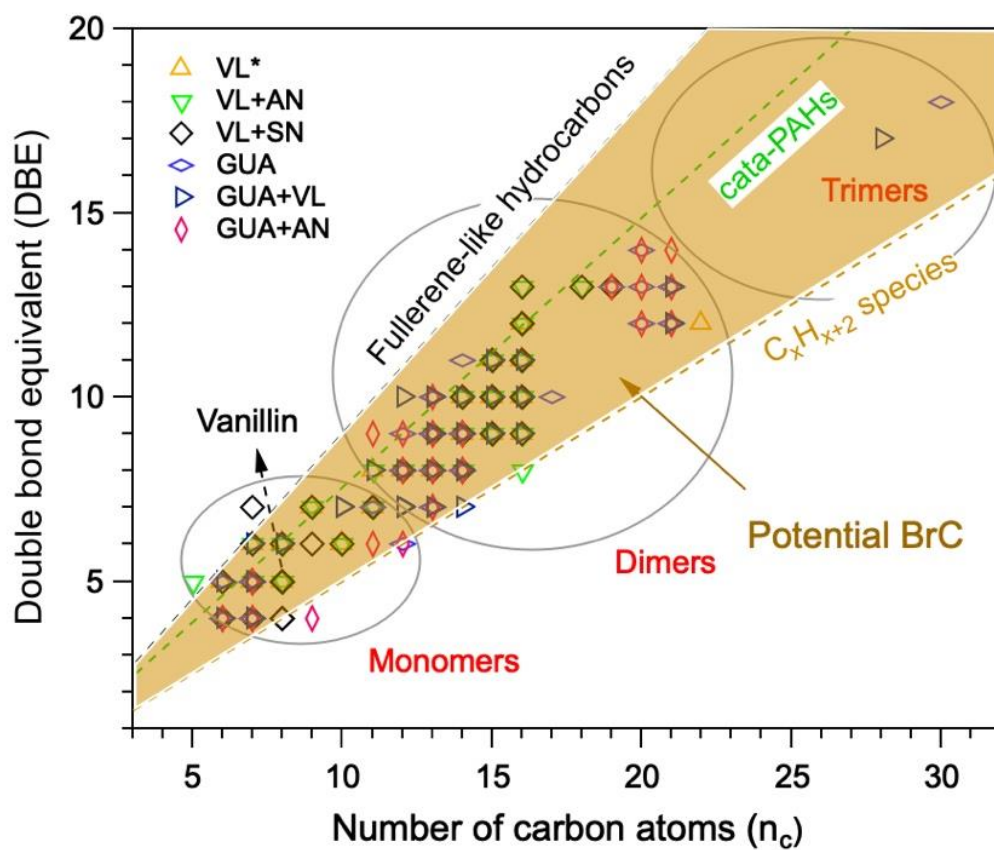
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 358 **Figure S10.** UV–Vis absorption spectra of VL\*-derived aqSOA formed at (a) pH 4 and (b) pH 2.5  
 359 over a range of pH conditions from 1.5 to 10.5.

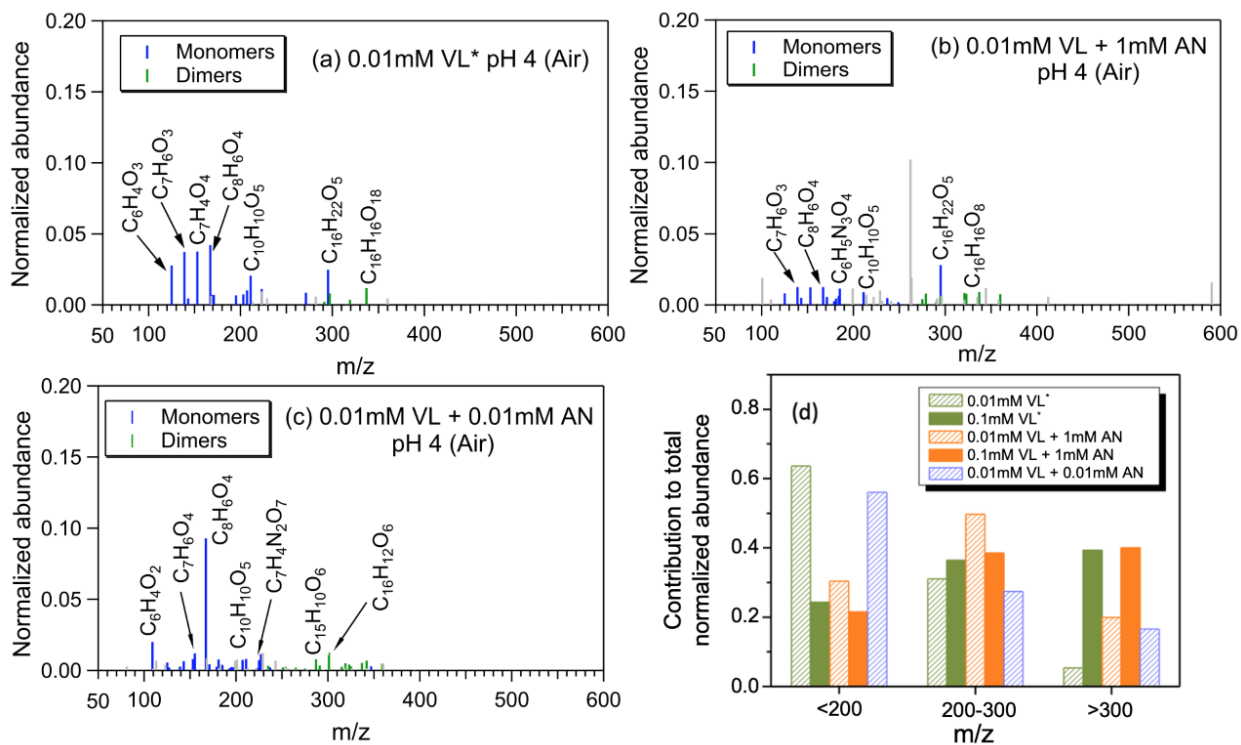
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396 **Figure S11.** The plot of the double bond equivalent (DBE) values vs. number of carbon atoms ( $n_c$ )  
 397 (Lin et al., 2018) for the 50 most abundant products from pH 4 experiments under air-saturated

398 conditions. Dashed lines indicate DBE reference values of fullerene-like hydrocarbons (black solid  
 399 line; Lobodin et al., 2012) (black dashed line), cata-condensed polycyclic aromatic hydrocarbons  
 400 (PAHs) (green solid line; Siegmann and Sattler, 2000) (green dashed line), and linear conjugated  
 401 polyenes (general formula  $C_xH_{x+2}$ ) (brown dashed-solid line). Data points within the shaded area  
 402 are potential BrC chromophores. Light grey circles show the classification of the data points as  
 403 monomers, dimers, trimers, or tetramers.



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 406 **Figure S12.** Reconstructed mass spectra of assigned peaks from (a) 0.01 mM VL\* (A10), (b) 0.01  
 407 mM VL + 1 mM AN (A12+), and (c) 0.01 mM VL + 0.01 mM AN (A112) at pH 4 under air-  
 408 saturated conditions after 6 h of simulated sunlight irradiation. The normalized abundance of  
 409 products was calculated from the ratio of the peak area of the product to that of VL using (Eq. 2).  
 410 The 50 most abundant products contributed more than half of the total normalized abundance of  
 411 products, and they were identified as monomers (blue) and dimers (green). Grey peaks denote  
 412 peaks with low abundance or unassigned formula. Examples of high-intensity peaks were labeled  
 413 with the corresponding neutral formulas. (d) Contributions of different m/z ranges to the  
 414 normalized abundance of products from experiments with low [VL] = 0.01 mM (A10–A12) and  
 415 high [VL] = 0.1 mM (A5 and A7) at pH 4 under air-saturated conditions after 6 h of simulated  
 416 sunlight irradiation.

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## References

~~Anastasio, C., Faust, B. C., and Rao, C. J.: Aromatic carbonyl compounds as aqueous phase photochemical sources of hydrogen peroxide in acidic sulfate aerosols, fogs, and clouds. 1. Non-phenolic methoxybenzaldehydes and methoxyacetophenones with reductants (phenols), Environ. Sci. Technol., 31, 218–232, <https://doi.org/10.1021/es960359g>, 1996.~~

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

Che, H., Xia, X., Zhu, J., Li, Z., Dubovik, O., Holben, B., Goloub, P., Chen, H., Estelles, V., Cuevas-Agulló, E., Blarel, L., Wang, H., Zhao, H., Zhang, X., Wang, Y., Sun, J., Tao, R., Zhang, X., and Shi, G.: Column aerosol optical properties and aerosol radiative forcing during a serious haze-fog month over North China Plain in 2013 based on ground-based sunphotometer measurements, Atmos. Chem. Phys., 14, 2125–2138, <https://doi.org/10.5194/acp-14-2125-2014>, 2014.

Chu, L. and Anastasio, C.: Temperature and wavelength dependence of nitrite photolysis in frozen and aqueous solutions, Environ. Sci. Technol., 41, 3626–3632, <https://doi.org/10.1021/es062731q>, 2007.

Erngren, I., Haglöf, J., Engskog, M. K. R., Nestor, M., Hedeland, M., Arvidsson, T., and Pettersson, C.: Adduct formation in electrospray ionisation-mass spectrometry with hydrophilic interaction liquid chromatography is strongly affected by the inorganic ion concentration of the samples, J. Chromatogr. A, 1600, 174–182, <https://doi.org/10.1016/j.chroma.2019.04.049>, 2019.

467 Galbavy, E. S., Ram, K., and Anastasio, C.: 2-Nitrobenzaldehyde as a chemical actinometer for  
468 solution and ice photochemistry, *J. Photochem. Photobiol. A*, 209, 186–192,  
469 <https://doi.org/10.1016/j.jphotochem.2009.11.013>, 2010.

470  
471 Holčápek, M., Jirásko, R., and Lísa, M.: Basic rules for the interpretation of atmospheric pressure  
472 ionization mass spectra of small molecules, *J. Chromatogr. A*, 1217, 3908–3921,  
473 <https://doi.org/10.1016/j.chroma.2010.02.049>, 2010.

474  
475 [Hullar, T., Bononi, F. C., Chen, Z., Magadia, D., Palmer, O., Tran, T., Rocca, D., Andreussi, O.,](https://doi.org/10.1039/d0em00242a)  
476 [Donadio, D., and Anastasio, C.: Photodecay of guaiacol is faster in ice, and even more rapid on](https://doi.org/10.1039/d0em00242a)  
477 [ice, than in aqueous solution, \*Environ. Sci.: Processes Impacts\*, 22, 1666–](https://doi.org/10.1039/d0em00242a)  
478 [1677, <https://doi.org/10.1039/d0em00242a>, 2020.](https://doi.org/10.1039/d0em00242a)

479  
480 Koch, B. P. and Dittmar, T.: From mass to structure: an aromaticity index for high-resolution mass  
481 data of natural organic matter, *Rapid Commun. Mass Spectrom.*, 20, 926–932,  
482 <https://doi.org/10.1002/rcm.2386>~~<https://doi.org/10.1002/rem.7433>~~, 2006.

483  
484 Lin, P., Fleming, L. T., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Comprehensive molecular  
485 characterization of atmospheric brown carbon by high resolution mass spectrometry with  
486 electrospray and atmospheric pressure photoionization, *Anal. Chem.*, 90, 12493–12502,  
487 <https://doi.org/10.1021/acs.analchem.8b02177>, 2018.

488  
489 Lobodin, V. V., Marshall, A. G., and Hsu, C. S.: Compositional space boundaries for organic  
490 compounds, *Anal. Chem.*, 84, 3410–3416, <https://doi.org/10.1021/ac300244f>, 2012.

491  
492 Roemmelt, A. T., Steuer, A. E., and Kraemer, T.: Liquid chromatography, in combination with a  
493 quadrupole time-of-flight instrument, with sequential window acquisition of all theoretical  
494 fragment-ion spectra acquisition: validated quantification of 39 antidepressants in whole blood as  
495 part of a simultaneous screening and quantification procedure, *Anal. Chem.*, 87, 9294–9301,  
496 <https://doi.org/10.1021/acs.analchem.5b02031>, 2015.

497  
498 Siegmann, K. and Sattler, K.-D.: Formation mechanism for polycyclic aromatic hydrocarbons in  
499 methane flames, *J. Chem. Phys.*, 112, 698–709, <https://doi.org/10.1063/1.480648>, 2000.

500  
501 [Smith, J. D., Kinney, H., and Anastasio, C.: Phenolic carbonyls undergo rapid aqueous](https://doi.org/10.1016/j.atmosenv.2015.11.035)  
502 [photodegradation to form low-volatility, light-absorbing products, \*Atmos. Environ.\*, 126, 36–44,](https://doi.org/10.1016/j.atmosenv.2015.11.035)  
503 <https://doi.org/10.1016/j.atmosenv.2015.11.035>, 2016.

504  
505  
506 Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production  
507 from aqueous reactions of 973 atmospheric phenols with an organic triplet excited state, *Environ.*  
508 *Sci. Technol.*, 48, 1049–1057, <https://doi.org/10.1021/es4045715>, 2014.

509  
510 ~~[Smith, J. D., Kinney, H., and Anastasio, C.: Phenolic carbonyls undergo rapid aqueous](https://doi.org/10.1016/j.atmosenv.2015.11.035)~~  
511 ~~[photodegradation to form low-volatility, light-absorbing products, \*Atmos. Environ.\*, 126, 36–44,](https://doi.org/10.1016/j.atmosenv.2015.11.035)~~  
512 ~~<https://doi.org/10.1016/j.atmosenv.2015.11.035>, 2016.~~

513  
514 Zhou, W., Mekic, M., Liu, J., Loisel, G., Jin, B., Vione, D., and Gligorovski, S.: Ionic strength  
515 effects on the photochemical degradation of acetosyringone in atmospheric deliquescent aerosol  
516 particles, *Atmos. Environ.*, 198, 83–88, <https://doi.org/10.1016/j.atmosenv.2018.10.047>, 2019.