Author Response for “Aqueous SOA formation from the photo-oxidation of vanillin: Direct photosensitized reactions and nitrate-mediated reactions” by Mabato et al.

We thank the reviewer for the thorough review and many constructive comments that helped improve the manuscript. Our point-by-point responses are below (changes to the original manuscript text 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. Also, please note that because we restructured the manuscript, the numbering of some figures and tables in the revised manuscript is different from those in the original manuscript.

Reviewer 2

The manuscript describes very well-designed studies of vanillin photooxidation in bulk liquid solutions where pH, concentrations, reactant ratios, dissolved gases (N2 or O2), ions (nitrate, bicarbonate) and other species (isopropanol) were varied in many combinations. The work is technically sound, with the loss of reactants, the identification and quantification of products, and the absorbance changes in solution all monitored hourly. The authors exhaustively discuss the differences between each experimental variation, pulling out as much detail as possible. This paper will be of interest to those interested in biomass burning aerosol and brown carbon formation, and is publishable after major revision to address the following points.

1. In places the discussion veers off into speculation, or suggests theories that aren’t adequately explained enough to be convincing to the reader, as noted below. Generally the discussion is convincing and well-connected to the literature, but the discussion section reads like it has a thousand detailed conclusions, leaving the reader often feeling “lost in the weeds” and blunting the impact of the work. In general, the focus of the paper could be improved by moving Table 1 to the SI, removing a lot of speculative discussion, and bringing Tables S2 and maybe S3 from the SI to the main paper. These tables are more vital to the discussion at many points, in my opinion.

Response: Thank you for the suggestion. Speculative discussions have been removed from the revised text. First, Section 3.1.1 has been amended to emphasize the importance of VL triplets:

Line 187: ~~Effect of secondary oxidants from VL~~ VL photo-oxidation under N_2 and air-saturated conditions

Lines 188–240: ~~As mentioned earlier, secondary oxidants ($^1O_2$, $O_2^{\bullet-}$/$^{\bullet}HO_2$, $^{\bullet}OH$) can be generated from $^3VL^*$ when O_2 is present (e.g., under air-saturated conditions), while $^3VL^*$ is the only oxidant expected under N_2-saturated conditions.~~ The photo-oxidation of VL ~~To examine the contributions of $^3VL^*$-derived secondary oxidants and $^3VL^*$ only on VL photo-oxidation, experiments~~ under both N_2- ~~air-~~ and air- ~~N_2-~~saturated conditions (Fig. S3a) were carried out at pH 4, which is representative of moderately acidic aerosol and cloud pH values (Pye et al., 2020). No significant VL loss was observed for dark experiments. The oxidation of ground-state VL by $^3VL^*$ via H-atom abstraction or electron transfer can form phenoxy (which is in resonance with a carbon-centered cyclohexadienyl radical that has a longer lifetime) and ketyl radicals (Neumann et al., 1986a, 1986b; Anastasio et al., 1996). The coupling of phenoxy radicals or phenoxy and cyclohexadienyl radicals can form oligomers as observed for both N_2- and air-saturated experiments (see discussions later). However, the little decay of VL under N_2-saturated condition indicates that these radicals probably predominantly decayed via back-hydrogen transfer to regenerate VL (Lathioor et al., 1999). A possible explanation for this is the involvement of O_2 in the secondary steps of VL decay. For instance, a major fate of the ketyl radical is reaction with O_2 (Anastasio et al., 1996). In the absence of O_2, radical formation occurs, but the forward reaction of ketyl radical and O_2 is blocked, leading to the regeneration of VL as suggested by the minimal VL decay. Aside from potential inhibition of secondary oxidants generation (Chen et al., 2020), N_2 purging may have also hindered the secondary steps for VL decay.

~~The low decay rate for VL* under N_2-saturated conditions suggests a minimal role for ^{3}VL* in VL photo-oxidation.~~ Contrastingly, the VL* decay rate constant under air-saturated conditions was 4 times higher~~, revealing the importance of ^{3}VL*-derived secondary oxidants for photosensitized oxidation of VL~~. As mentioned earlier, secondary oxidants ($^1O_2$, $O_2^{\bullet-}$/$^{\bullet}HO_2$, $^{\bullet}OH$) can be generated from ^{3}VL* when O_2 is present (e.g., under air-saturated conditions). However, the photo-oxidation of VL in this study is likely mainly governed by ^{3}VL* and that these secondary oxidants have only minor participation. ~~Aside from $^{\bullet}OH$, $O_2^{\bullet-}$/$^{\bullet}HO_2$ and $^1O_2$ can also promote VL photo-oxidation (Kaur and Anastasio, 2018; Chen et al., 2020).~~ $^1O_2$ is also a potential oxidant for phenols (Herrmann et al., 2010; Minella et al., 2011; Smith et al., 2014), but $^1O_2$ reacts much faster (by ~60 times) with phenolate ions compared to neutral phenols (Tratnyek and Hoigne, 1991; Canonica et al., 1995; McNally et al., 2005). Under the pH values (pH 2.5 to 4) considered in this study, the amount of phenolate ion is negligible, so the reaction between VL and $^1O_2$ should be slow. Interestingly, however, $^1O_2$ has been shown to be important in the photo-oxidation of 4-ethylguaiacol ($pK_a = 10.3$) by ^{3}C* of 3,4-dimethoxybenzaldehyde (solution with pH of ~3) (Chen et al., 2020). Furthermore, while the irradiation of other phenolic compounds can produce H_2O_2, a precursor for $^{\bullet}OH$ (Anastasio et al., 1996), the amount of H_2O_2 is small. Based on this, only trace amounts of H_2O_2 were likely generated from VL* (Li et al., 2014) under-air saturated conditions, suggesting that contribution from $^{\bullet}OH$ was minor. Overall, these suggest that VL photo-oxidation in this study is driven by ^{3}VL*. Further study on the impact of O_2 on the reactive intermediates involved is required to understand the exact mechanisms occurring under air-saturated conditions. Nonetheless, the VL* decay trends clearly indicate that O_2 is important for efficient VL photo-oxidation ~~an efficient oxidant for unsaturated organic compounds and has a lifetime that is much longer than ^{3}C* (Chen et al., 2020)~~. ~~Similar to VL*, t~~The decay rate constant for VL+AN under air-saturated conditions was also higher ~~faster~~ (6.6 times) than N_2-saturated conditions~~,~~ which may ~~can~~ be due to ~~several~~ reactions facilitated by nitrate photolysis products ~~and the enhancement of N(III)-mediated photo-oxidation~~ that may have been enhanced in the presence of O_2 ~~as reported in early works~~ (Vione et al., 2005; Kim et al., 2014; Pang et al., 2019a). As shown later, more nitrogen-containing species were observed under air-saturated conditions. An example is enhanced VL nitration likely from increased $^{\bullet}NO_2$ formation such as from the reaction of $^{\bullet}OH$ and $O_2^{\bullet-}$ with NO_2^- (Reactions 4 and 5, respectively; Table 1) or the autoxidation of $^{\bullet}NO$ from NO_2^- photolysis (Reactions 6–9; Table 1) in aqueous solutions (Pang et al., 2019a).

~~Reactions involving ${}^{\bullet}HO_2/O_2^{\bullet-}$ which may originate from the photolysis of nitrate alone, likely from the production and subsequent photolysis of peroxynitrous acid (HOONO) (Reaction 10; Table 1) (Jung et al., 2017; Wang et al., 2021), or the reactions of ${}^{3}VL^{*}$ in the presence of O_2, may have contributed as well. For instance, Wang et al. (2021) recently demonstrated that nitrate photolysis generates ${}^{\bullet}HO_2/O_2^{\bullet-}{}_{(aq)}$ and $HONO_{(g)}$ in the presence of dissolved aliphatic organic matter (e.g., nonanoic acid, ethanol), with the enhanced $HONO_{(g)}$ production caused by secondary photochemistry between ${}^{\bullet}HO_2/O_2^{\bullet-}{}_{(aq)}$ and photoproduced $NO_{x(aq)}$ (Reactions 11 and 12; Table 1), in agreement with Scharko et al. (2014). The significance of this increased HONO production is enhanced ${}^{\bullet}OH$ formation (Reaction 13; Table 1). In addition, ${}^{\bullet}HO_2$ can react with ${}^{\bullet}NO$ (Reaction 10; Table 1) from NO_2^{-} photolysis (Reaction 6; Table 1) to form HOONO, and eventually ${}^{\bullet}NO_2$ and ${}^{\bullet}OH$ (Reaction 14; Table 1) (Pang et al., 2019a)~~. Nevertheless, the comparable decay rate~~s~~ constants for VL* and VL+AN imply that ${}^{3}VL^{*}$ chemistry still dominates even at 1:10 molar ratio of VL/nitrate, 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. Although we have no quantification of the oxidants in our reaction systems as it is outside the scope of this study, these observations clearly substantiate that~~secondary oxidants from ${}^{3}VL^{*}$, which are formed when O_2 is present, are required for efficient~~ photosensitized oxidation of VL and nitrate-mediated VL photo-oxidation are more efficient in the presence of O_2.

Moreover, Section 3.1.3 (Effect of VOCs and inorganic anions) and related sentences have also been deleted based on the likely minor contribution of ${}^{\bullet}OH$ to VL photo-oxidation in this study as pointed out by Reviewer 1 and suggested by other published literature (Anastasio et al., 1996; Li et al., 2014). Also, Section 3.5 has been deleted and Fig. 4, now 2, has been shown for the first time when potential aqSOA formation pathways were discussed, then referred to throughout the text. Table 1, which was reduced to half, was maintained in the revised version, while Table S2 (now 2) was moved to the main text, as suggested by the reviewer.

2. I do not trust using results for IPA to make generalizations about the effect of all VOCs on vanillin photooxidation. The authors repeat this questionable generalization several times throughout the manuscript, including twice in the abstract. Especially because the authors' explanation for the effect of IPA on their results relies on alcohol / water microstructure arguments, generalization to all VOCs seems unwarranted. Plus, IPA would be present only at very low concentrations in aqueous aerosol or cloud droplets due to its high volatility. It would be more appropriate if the authors remove (or heavily qualify) all statements about VOCs.

Response: We concur with the reviewer that the initial generalization for the effect of all VOCs on VL photo-oxidation based on IPA results is unsubstantiated. Moreover, the contribution of ${}^{\bullet}OH$ to VL photo-oxidation in this study is likely minimal, as pointed out by Reviewer 1 and suggested by other published literature (Anastasio et al., 1996; Li et al., 2014). Section 3.1.3 (Effect of VOCs and inorganic anions) and related sentences have been deleted altogether. Nonetheless, we maintain that it would be worthwhile to explore the effects of other potential aerosol constituents on aqSOA formation and photo-oxidation studies (lines 627–631).

3. At several points, the authors discuss rather small differences between experiments (factors of 1.2 to 1.5) as significant, but the uncertainties in the parameter values being compared are never quantified. This raises doubts in readers' minds about which differences are actually statistically significant. Some discussion of uncertainties and random error is needed.

Response: Thank you for pointing this out. We have added relevant statements to discuss these uncertainties as follows:

Line 132: Each experiment was repeated independently at least three times and measurements were done in triplicate. The reported decay rate constants and absorbance enhancement are the average of results from triplicate experiments, and the corresponding errors represent one standard deviation.

The footnote of Table S2, now 2, has been revised as follows:

Table 2: ^{b}The data fitting was performed in the initial linear region. Each value is the average of results from triplicate experiments. Errors represent one standard deviation.

The revised text also now indicates whether a difference of less than a factor of 2 is statistically significant or not:

Line 331: The decay rate~~s~~ constants for both VL* and VL+AN increased as pH decreased (VL* and VL+AN at pH 2.5: 1.6~~5~~ and 1.4~~3~~ times faster than at pH 4, respectively) (Fig. S3b). These differences in decay rate constants are small but statistically significant ($p < 0.05$).

Line 510: 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 ($p > 0.05$).

4. The argument that ^{3}VL* is more reactive in its protonated form as an explanation for the observed pH effects does not make sense to me. The pKa of VL is 7.4, which means that more than 99.9% of it is protonated in all experiments, negating the possibility of any detectable acceleration at low pH by this mechanism. Furthermore, the authors describe reasonable alternative explanations for their observed pH effects, such as the more efficient photolysis of HONO vs NO2- producing more OH radicals at low pH. However, the questionable claim that 3VL* is more reactive in its protonated form is repeated several times throughout the manuscript (for example, lines 267, 270, 280, 449 and 500). This claim needs to be convincingly justified or removed from the manuscript.

Response: The pK_a (7.4) mentioned by the reviewer is for ground state VL, while the pK_a for the VL triplet has been reported to be 4.0 (Smith et al., 2016). As there are a greater fraction of VL triplets that are protonated at pH 2.5 (0.96) than at pH 4 (0.5), it is possible that the pH dependence observed in this study is due to ^{3}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 pH ≤ 3 are ~two times lower than at pH ≥ 5) which they 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}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). We have added a statement to include the sensitivity of the excimer of VL to acid-base chemistry as another possibility for the observed pH dependence. In addition, we have removed the discussion of N(III) photolysis as an alternative explanation for the effects of pH on VL decay kinetics as there is no significant difference between the decay rate constants of VL* and VL+AN. Changes in the text are as follows:

Lines 331–352: The decay rate~~s~~ constants for both VL* and VL+AN increased as pH decreased (VL* and VL+AN at pH 2.5: 1.6~~5~~ and 1.4~~3~~ times faster than at pH 4, respectively) (Fig. S3b). These differences in decay rate constants are small but statistically significant ($p < 0.05$). The pK_a for the VL triplet has been reported to be 4.0 (Smith et al., 2016). As there are a greater fraction of VL triplets that are protonated at pH 2.5 (0.96) than at pH 4 (0.5), it is possible that the pH dependence of the decay rate constants observed in this study is due to ^{3}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 pH ≤ 3 are ~two times lower than at pH ≥ 5) which they 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}VL* being dependent on the VL concentration (Smith et al., 2016). ~~For VL*, this pH trend indicates that ^{3}VL* are more reactive in their protonated form, which is opposite to that reported for 0.005 mM VL (Smith et al., 2016), likely due to the concentration dependence of the relative reactivities of protonated and neutral forms of ^{3}VL*.~~ 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). ~~Also, increases in hydrogen ion concentration can enhance the formation of $HO_2^•$ and H_2O_2 and in turn, $^•OH$ formation (Du et al., 2011). In addition to these pH influences on VL*, the dependence of N(III) (NO_2^- + HONO) speciation on solution acidity (Pang et al., 2019a) also contributed to the observed pH effects for VL+AN. 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 $^•OH$ formation than that of NO_2^- in the near-UV region (Arakaki et al., 1999; Kim et al., 2014). The increased $^•OH$ formation rates as pH decreases can lead to faster VL decay (Pang et al., 2019a). Also, NO_2^-/HONO can generate $^•NO_2$ via oxidation by $^•OH$ (Reactions 4 and 15; Table 1) (Pang et al., 2019a).~~ As pH decreases, the higher reactivity of ^{3}VL* and sensitivity of the excimer of VL to acid-base chemistry ~~HONO being the dominant N(III) species can lead to faster VL photo-oxidation~~ may have led to faster VL photo-oxidation.

Line 356: further indicating that ^{3}VL* ~~are~~ may be more reactive in their protonated form.

Line 372: Essentially, the higher reactivity of ^{3}VL* and predominance of HONO over nitrite at lower pH may have resulted in increased formation of products mainly composed of oligomers and functionalized monomers.

Specific comments:

1. Line 25: The authors conclude that photosensitized reactions of VL were "more efficient" relative to nitrate-mediated photo-oxidation. However, as pointed out by the authors, VL is much more light-absorbing that nitrate. Can the authors make a comparative statement after taking this difference into account? Which is more efficient on a per-photon-absorbed basis? This would be a more appropriate comparison of reaction efficiency.

Response: Thank you for this suggestion. The apparent quantum efficiency of GUA photodegradation (ϕ_{GUA}) in the presence of either VL or nitrate during simulated sunlight illumination can be defined as (Anastasio et al., 1996; Smith et al., 2014, 2016):

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

Φ_{GUA} was calculated using the measured rate of GUA decay and rate of light absorption by either VL or nitrate through the following equation:

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

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

$$j(2\mathrm{NB}) = 2.303 \times \Phi_{2\mathrm{NB}} \times l \times \Sigma_{300\,nm}^{350\,nm} (\varepsilon_{2\mathrm{NB},\lambda} \times I'_{\lambda} \times \Delta\lambda) \qquad \text{(Eq. S11)}$$

The ϕ_{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. We have revised this in the text as follows and added the information shown above in the supporting information: **Text S7**. Estimation of the apparent quantum efficiency of guaiacol photodegradation.

Line 29: Furthermore, comparisons of the apparent quantum efficiency of guaiacol photodegradation indicate that in this study, guaiacol oxidation by photosensitized reactions of VL ~~was observed to be more~~ is less efficient relative to nitrate-mediated photo-oxidation.

Other relevant revisions in the text are as follows:

Line 514: As mentioned earlier, ~~the~~ ^{3}VL* 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 (ϕ_{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 the more details).

Line 619: The oxidation of guaiacol, a non-carbonyl phenol, by photosensitized reactions of vanillin was also shown to be ~~more~~ less efficient than that by nitrate photolysis products based on its lower apparent quantum efficiency.

2. Line 226: The authors at several points claim that VL triplet states and nitrate photolysis products have a "synergistic effect," but evidence in support of this claim is lacking, or at best the evidence supporting it is not adequately explained. The inadequately supported claim is repeated in line 497.

Response: Thank you for this point. The trends in line 297 (formerly 226) pertain to nitrate enhancing the increased normalized abundance of products and formation of more oxidized aqSOA from VL photo-oxidation in the presence of O_2 (VL* and VL+AN under air-saturated conditions) at pH 4, suggesting a potential enhancement of VL nitration in the presence of O_2. This has been revised as follows:

Lines 295–300: In brief, the presence of ~~secondary oxidants from ^{3}VL* and~~ O_2 increased the normalized abundance of products and promoted the formation of more oxidized aqSOA. ~~These trends were reinforced in the presence of nitrate, indicating synergistic effects between secondary oxidants from VL triplets and nitrate photolysis products.~~ Compared to N_2-saturated condition, the higher normalized abundance of nitrogen-containing products under air-saturated condition for VL+AN (at pH 4) suggests a potential enhancement of VL nitration in the presence of O_2.

Line 606–611: ~~Further enhancement of VL photo-oxidation under air-saturated conditions in the presence of nitrate indicates synergistic effects between secondary oxidants from VL triplets and nitrate photolysis products.~~ In contrast, ^{3}VL*-initiated reactions proceeded rapidly under air-saturated conditions (O_2 is present) as indicated by higher VL decay rate constant and increased normalized abundance of products. For pH 4 experiments, the presence of both O_2 and nitrate resulted in the highest normalized abundance of products (including N-containing compounds) and $\langle OS_c \rangle$, which may be due to the presence of O_2 promoting VL nitration.

3. Line 258: This explanation of opposite pH trends at 0.1 and 0.005 mM VL is extremely speculative.

Response: Smith et al. (2016) reported that the relative reactivities of the protonated and neutral forms of VL triplets depend on the VL concentration. Specifically, they found 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). The opposite trend observed in our study may then be due to this concentration dependence of the reactivities of the protonated and neutral forms of $^3VL^*$. Moreover, as mentioned in our response to major comment #6 by Reviewer 1, the comparable pH dependence of the aqSOA formed from VL* at pH 4 and 2.5 over a range of pH conditions from 1.5 to 10.5 suggests that the pH dependence observed is likely due to the acid-base chemistry of the reactions which may involve $^3VL^*$ or the excimer of VL (Smith et al., 2016). Please see our response to your major comment #4 for relevant changes made in the text.

4. Line 272: For greater clarity, it would be helpful if the manuscript would always match product formulas mentioned in the text to the structures shown in Table S3. Is this product structure #21 in Table S3?

Response: We thank the reviewer for this suggestion. We have added the product structures (if applicable) to the formulas mentioned in the text. No, product structure #21, now #12, refers to a GUA tetramer that was observed only in the GUA+VL experiment (Line 544). Unfortunately, we do not have a product structure for the tetramer mentioned in Line 358 (formerly 272), although we have now added the proposed formula for this tetramer as follows:

Line 358: Furthermore, a tetramer ($C_{31}H_{24}O_{11}$) was observed only in VL* at pH 2.5.

5. Line 297: is this dimer product structure #5 in Table S3?

Response: Sentences related to $^•OH$ scavengers have been deleted from the original manuscript.

6. Line 334: The solvent cage effect explanation seems questionable. Why would two negatively charged ions share a solvent cage, given their electrostatic repulsion? Furthermore, in line 339 the authors state that “NaBC did not cause any substantial change in the decay of VL,” thus making this whole solvent cage discussion irrelevant to the data at hand.

Response: Sentences related to $^•OH$ scavengers have been deleted from the original manuscript.

7. Line 341 – 346: the authors state that “no tetramers were observed in VL*+NaBC” and “VL+AN+IPA had more oligomers,” and then go on to suggest that the formation of oligomers can be promoted by inorganic ions, likely via the generation of radicals such as .CO3. No evidence has been provided, as far as I can tell, that NaBC promotes oligomer formation, so I was confused by the authors’ claim here that bicarbonate does in fact promote oligomer formation via .CO3 radicals.

Response: Sentences related to $^•OH$ scavengers have been deleted from the original manuscript.

8. Line 363: ESI-MS is routinely used to detect macromolecules in biochemistry. This suggestion that the method cannot detect molecules with more than 25 carbons is an erroneous conclusion to draw from Lin et al. (2018).

Response: Lin et al. (2018) also studied BrC from BBOA, similar to our experiments. As they reported that majority of ESI-detected compounds in their study are smaller molecules with fewer than 25 carbon atoms, we raise the possibility that this may also be the case for our study.

9. Line 379: The logic needs to be better spelled out here. Why is the formation of more oxidized products suggested by a larger fraction of small-mass products observed for 1:1 VL/nitrate mixtures compared to 1:100? Do small product masses imply fragmentation, or is there a competition with oligomerization?

Response: We apologize for the confusion. The larger fraction of small product masses (< 200 m/z) observed for 1:1 compared to 1:100 VL/nitrate suggests the prevalence of functionalization for the former. In addition, the higher <OS_C> for 1:1 VL/nitrate indicates the formation of more oxidized products compared to 1:100 VL/nitrate. The small product masses (< 200 m/z) imply functionalization, while the contribution of > 300 m/z suggests oligomerization. Fragmentation was indicated by the observed small organic acids (analyzed using IC), but not the mass spectrometric analyses as the small organic acids are not detectable in the positive ion mode. Fragmentation, which leads to the decomposition of previously formed oligomers and generation of small, oxygenated products such as organic acids (Huang et al., 2018), may also occur for the low [VL] experiments. However, its importance would likely be observed at longer irradiation times, similar to the high [VL] experiments. Oligomerization probably occurred for both 1:1 and 1:100 VL/nitrate as suggested by the observed contribution of > 300 m/z, although to a lesser extent than functionalization based on the higher contribution of < 200 m/z. Lines 466–485 have been revised as follows:

Lines 466–485: 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. S12~~3~~d). This indicates that functionalization was favored at low [VL], as supported by the higher <OS_C>, 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). 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). ~~Moreover~~ At low [VL], the contribution of < 200 m/z to the normalized abundance of products was higher for 1:1 than 1:100 VL/nitrate molar ratio, ~~further~~ suggesting the prevalence of functionalization for the former ~~formation of more oxidized products~~. ~~This may also be the reason why~~ In addition, 1:1 VL/nitrate (A11~~5~~; Table ~~S~~2) had higher <OS_C> than 1:100 VL/nitrate (A12~~6~~; Table ~~S~~2), indicating the formation of more oxidized products, but had fewer N-containing compounds compared to the latter. A possible explanation is that at 1:1 VL/nitrate, VL may ~~efficiently~~ compete~~s~~ with NO_2^- for $^{\bullet}OH$ (from nitrate or nitrite photolysis, Reaction 4; Table 1) and indirectly reduce~~s~~ $^{\bullet}NO_2$. Similarly, hydroxylation has been suggested to be a~~n~~ more important pathway for 1:1 VL/nitrite than in 1:10 VL/nitrite (Pang et al., 2019a). ~~This may also be the reason why 1:1 VL/nitrate (A15; Table S2) had higher $\langle OS_C \rangle$ than 1:100 (A16; Table S2) VL/nitrate but had fewer N-containing compounds compared to the latter.Moreover, the contribution of <200 m/z to the normalized abundance of products was higher for 1:1 than 1:100 VL/nitrate molar ratio, further suggesting the formation of more oxidized products.~~ Fragmentation, which leads to the decomposition of previously formed oligomers and generation of small, oxygenated products such as organic acids (Huang et al., 2018), may also occur for the low [VL] experiments. However, its importance would likely be observed at longer irradiation times, similar to the high [VL] experiments.

10. Line 389: $C_8H_9NO_3$ should be identified as product structure #2 (an amine) on Table S3.

Response: Thank you for this suggestion. We have now added the structure number to $C_8H_9NO_3$ in line 494 (formerly 389) as follows:

Line 494: … $C_8H_9NO_3$ (No. 2, Table S2) was also…

11. Line 408: The nitrate photolysis explanations may not be needed, given that the observed enhancement of nitrate on guaiacol decay rates was only a factor of 1.2. Is this a statistically significant change?

Response: Thank you for pointing this out. The reviewer is correct that the nitrate photolysis explanation is not needed in this case, given that the observed enhancement for GUA+AN is not statistically significant. Changes in the text are as follows:

Line 510: 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 ($p > 0.05$).

12. Line 418: The word "Similarly" is being used to relate two seemingly dissimilar observations, causing needless confusion. In the previous sentence, VL shows much higher absorbance enhancement than nitrate, but in this sentence nitrate is being compared to an experiment without nitrate.

Response: The reviewer is correct. The word 'similarly' has been removed in Line 525 (formerly 418) to avoid confusion.

Line 525: ~~Similarly,~~ Yang et al. (2021) also observed greater light absorption during nitrate-mediated photo-oxidation relative to direct GUA photodegradation.

13. Line 471: This sentence is confusing. Doesn't this work address (among other things) the effects of nitration on triplet-generating aromatics?

Response: Thank you for catching this. We have clarified this sentence as follows:

Line 574: Although nitrate did not substantially affect the VL decay rate~~s~~ constants~~,~~ likely due to much higher molar absorptivity of VL than nitrate and high VL concentration used in this work, the presence of nitrate promoted functionalization and nitration, indicating the significance of nitrate photolysis in this aqSOA formation pathway. ~~While~~ This work demonstrates that nitration, which is ~~can be~~ an important process for producing light-absorbing organics or BrC (Jacobson, 1999; Kahnt et al., 2013; Mohr et al., 2013; Laskin et al., 2015; Teich et al., 2017; Li et al., 2020), ~~its effect on~~ can also affect the aqueous-phase processing of triplet-generating aromatics ~~has not yet been examined in detail~~.

14. Line 481: Why would VL photodegrade 10 times slower in ALW relative to dilute cloudwater? This effect is important for applying this work to the atmosphere. Could the authors provide some theory or explanation here?

Response: There is no generalization yet for these increased or decreased photodegradation of methoxyphenols and by far, only VL has been observed to exhibit decreased photodegradation in ALW. The study for VL in ALW (Loisel et al., 2021) stated that the nature of inorganic ions would affect the photodegradation of organic compounds. Further work on the effects of inorganic ions on photodegradation of VL in ALW is warranted.

15. (a) On Table S2, experiments without nitrate are listed as "—" in the column of normalized abundances of N-containing compounds. Is this because no N-containing compounds were detected in the top 50, or because these samples were not analyzed for N-containing compounds? (b) It would be helpful to map the reactant molecule onto the Figure S12 graph.

Response: (a) The reviewer is right. The samples for experiments without nitrate were not analyzed for N-containing compounds. This information has been added to the footnote of Table S2 as follows:

…[d]The normalized abundance of products was calculated using Eq. 2. The samples for experiments without nitrate (marked with N/A ~~‘-‘~~) were not analyzed for N-containing compounds.

(b) VL has now been added to Fig. S12, now S11.

Technical Corrections:

1. Line 349: "increased" should be "increase"

Response: Sentences related to $^{\bullet}$OH scavengers have been deleted from the original manuscript.

2. Line 377: "an important" should be "a more important"

Response: Thank you for pointing this out. Line 478 (formerly 377) has been revised accordingly:

Line 478: Similarly, hydroxylation has been suggested to be a~~n~~ more important pathway for 1:1 VL/nitrite than in 1:10 VL/nitrite (Pang et al., 2019a).

3. Line 459: "decompose" should be "decomposes"

Response: Sentences related to •OH scavengers have been deleted from the original manuscript.

4. Sodium nitrate in my opinion would be better abbreviated "NaN" to be more consistent with other abbreviations such as "NaBC."

Response: Sentences related to •OH scavengers have been deleted from the original manuscript.

5. Table S3: Compound number 4, the most abundant product in some studies, is missing an oxygen atom. It should be clarified that structure #1 is the reactant molecule vanillin rather than a product.

Response: Thank you for the correction and suggestion. We have corrected these on Table S2, formerly S3.

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