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 1

Overview

The authors examined the aqueous photodegradation of vanillin (VL), a carbonyl-containing phenol emitted from biomass burning, and accompanying formation of aqueous SOA (aqSOA). They then measured the composition of the aqSOA using high-resolution mass spectrometry and UV/Vis absorption. They also determined the impact of purging solutions with N2 (to remove dissolved oxygen) as well as the addition of ammonium nitrate (a photochemical source of hydroxyl radical, OH) and/or one of two hydroxyl radical scavengers (isopropyl alcohol or bicarbonate). They attempt to explain their results qualitatively based on a few dozen reactions, but there is little experimental attempt to text the mechanisms.

Vanillin has been studied in several past works, but this paper adds new information on the composition of the resulting aqSOA. The purging with N2 is novel, but the interpretation of the results is not clear, and I disagree that these experiments show that secondary oxidants dominate VL loss. Unfortunately, the nitrate concentration added was too low to impact kinetics (because VL direct photodegradation is so fast), but it’s interesting that it impacted the products formed. Finally, the authors seem compelled to try to mechanistically explain most of their results, but their explanations are very speculative and should be significantly cut. There are a several other major and minor issues, as described below.

Response: In this study, we aimed to investigate the photo-oxidation of VL at atmospherically relevant cloud and fog conditions. As mentioned in lines 112–116, ‘Although the concentration of VL in cloud/fog water has been estimated to be < 0.01 mM (Anastasio et al., 1996), 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) 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).’ Our study is not intended to identify the concentrations of nitrate that would affect the kinetics. This sentence has been added to the text as follows:

Line 116: It should be noted that this study is not intended to identify the concentrations of nitrate that would affect the kinetics.

Major Comments

1. The normalized abundance of products (line 131) is used throughout the paper as a key metric, but it's unclear if this is a robust endpoint, in part because its uncertainty is never discussed. (a) Based on the major products that have been identified (both via MS and IC), what is the likely range of ionization efficiencies (IEs) of the products and how much uncertainty does this introduce in the product abundance measure? (b) There is additional uncertainty in the quantification of VL, which is described on line 134 as semi-quantitative. (c) Altogether, what is the relative uncertainty in P from day to day and experiment to experiment? (d) This is an issue because there are several times when the normalized product abundance results are inconsistent with other, seemingly more quantitative metrics. For example, in section 3.1.3., the presence of OH scavengers had no significant effect upon VL decay or aqSOA light absorbance, but there were differences in the normalized abundance of products. Given the uncertainty in IE and other aspects of the product measure, I would be wary of attributing much significance to the normalized abundance of products as an endpoint when it's inconsistent with the more quantitative measures.

Response: 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. Regardless, we agree with the reviewer that we should emphasize the potential uncertainties in the normalized abundance of products. Detailed responses to the relevant sub-questions are as follows:

(a) Ionization efficiencies can indeed vary between different compounds. Unfortunately, the availability of measured relative ionization efficiencies (RIE) for different compounds is limited. We are not in a position to provide this information. The reviewer is correct that ESI ionization is not ideal for product quantification. Nevertheless, Nguyen et al. (2013) (https://doi.org/10.1039/C2AY25682G) found a positive correlation between ESI signal and "adjusted mass" (= molecular mass × 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). We have revised Sect. 2.2 to highlight the inherent uncertainties for this metric due to ionization efficiencies which can vary for different compounds as follows:

Lines 146–167: 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; Kruve 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 (Bateman et al., 2012; Lin et al., 2012; De Haan et al., 2019), to calculate their normalized abundance. The normalized abundance of a product, [P] (unitless), was calculated as follows:

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

where $\mathrm{A}_{P,t,}$ and $\mathrm{A}_{VL,t}$ are the extracted ion chromatogram (EIC) ~~signal~~ peak areas of the product P and VL from UHPLC-qToF-MS analyses at time *t*, respectively; $[\mathrm{VL}]_t$ and $[\mathrm{VL}]_0$ are the VL concentrations (μM) determined using UHPLC at time *t* and 0, respectively. Here, we relied on the direct quantification ~~more accurate measurements~~ of [VL] using UHPLC (see Fig. S2 for VL calibration curve) ~~for semi-quantification~~. ~~It should be noted that the ionization efficiency may greatly vary for different classes of compounds (Kebarle, 2000). Hence, we assumed equal ionization efficiency of different compounds to calculate their normalized abundance, which is commonly used to estimate O:C ratios of SOA (Bateman et al., 2012; Lin et al., 2012; De Haan et al., 2019).~~ It should be noted that the normalized abundance of products in this study is a semi-quantitative analysis intended to provide an overview of how the signal intensities changed under different experimental conditions but not to quantify the absolute concentration of products. Moreover, the major products detected in this study are probably those with high concentration or high ionization efficiency in the positive ESI mode. The use of 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 reported. Typical fragmentation behavior observed in MS/MS spectra for individual functional groups from Holčapek et al. (2010) are outlined in Table S1.

(b) The semi-quantification here refers to the normalized abundance of products, not the VL concentration. [VL] was directly quantified using UHPLC (see Fig. S2 for VL calibration curve). The reported [VL] are the average of results from triplicate experiments and the uncertainties from which and those from the MS signal intensities were propagated (now added in Table 2, formerly S2). This has been clarified in the text as follows:

Line 157: Here, we relied on the direct quantification ~~more accurate measurements~~ of [VL] using UHPLC (see Fig. S2 for VL calibration curve) ~~for semi-quantification~~.

(c) 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. Moreover, the propagated uncertainties from the MS signal intensities and [VL] are now shown in Table 2 (formerly S2).

(d) For $^{\bullet}$OH scavengers experiments, the insignificant changes for VL decay and absorbance enhancement might not be reflected in the products observed using UHPLC-qToF-MS in positive ESI mode. It is possible that the products observed might not have contributed significantly to all products formed and may not be the primary contributors to the absorbance enhancement. The absorbance enhancement may not necessarily correlate directly with the products detected. However, as mentioned in our response to major comment #4, we decided to omit the section for $^{\bullet}$OH scavengers based on the likely minor contribution of $^{\bullet}$OH to VL photo-oxidation in this study.

2. Throughout the manuscript, the low decay rate of VL* under N2 is taken to mean that the triplet state of VL isn't involved in VL decay and that secondary, O2-dependent, oxidants are responsible for VL decay. However, the N2-purging control experiment result is ambiguous, since secondary steps in VL decay via triplets might require oxygen to proceed. For example, a major fate of the ketyl radical formed by the 3VL* + VL reaction is to add oxygen. In the absence of oxygen, the ketyl radical will still form, but it's forward path (O2 addition) is blocked, possibly leading to eventual return to the reactants (and little apparent VL decay). So N2 purging is likely to not only remove secondary oxidants, but also to interfere with subsequent steps in the 3VL* - VL reactions. Thus the oft-stated conclusion that secondary oxidants from 3VL* are responsible for VL decay is not correct (e.g., on line 184). Without knowing the impact of O2 on the reaction intermediates in the triplet reaction, it is impossible to know what the N2-purging result means.

Another strike against the "secondary oxidants" theory is that the proposed secondary oxidants are unlikely to be important for VL decay. For example, the 1O2* + VL reaction is slow under the pH conditions here (where there is negligible phenolate). In air-saturated solutions, the 1O2* and 3VL* concentrations should be roughly equal (see the McNeil and Canonica review in ESPI), but at pH 4 (and below) the rate constants for phenols with 3C* are much faster than the 1O2* values. The bottom line is the 1O2* is unlikely to be important. Similarly, HO2/O2- was proposed as an oxidant for phenols, but these are very weak oxidants that react slowly with phenols. Finally, OH is apparently unimportant as well, based the OH scavengers having no significant impact on VL decay; however, it is possible that most of the IPA or bicarbonate was purged from the sample prior to illumination (as discussed below). Regardless, photolysis of H2O2 (formed from the 3VL* + VL reaction) will be slow, giving little OH.

Response: Thank you for this thorough and important analysis. We apologize for the confusion related to the role of VL triplets. The reviewer is correct that VL triplets are indeed important for VL decay and that the secondary oxidants generated in the presence of O_2 likely have only minor roles in the photo-oxidation of VL in this study. We also agree that without a detailed investigation of the effect of O_2 on the reactive intermediates, it is difficult to interpret the mechanism of the N_2 experiments. In principle, initial oxidation by triplets can proceed without O_2, forming 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. 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, likely concerning the fate of the ketyl radical, as the reviewer pointed out. We have amended the discussions to include these possibilities and to emphasize the importance of VL triplets as follows:

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

Lines 188–220: ~~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)~~.

Revisions made elsewhere in the text:

Line 23: The effects of oxygen (O_2) ~~secondary oxidants from ^{3}VL*~~

Line 25: Our findings show that ~~the secondary oxidants (^{1}O2, $O_2^{\bullet -}$/$^{\bullet}HO_2$, $^{\bullet}OH$) from the reactions of ^{3}VL* and~~ O_2 plays an essential role in VL photo-oxidation.

Line 91: The influences of O_2 ~~secondary oxidants from VL triplets,~~

Line 184: In this work, the direct photosensitized oxidation of VL (~~by ^{3}VL* or secondary oxidants from ^{3}VL* and O_2~~VL only experiments)

Lines 237–240: 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 oxidant 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.

Lines 247–254: ~~Compared to N_2-saturated conditions, the normalized abundance of products such as o~~Oligomers, ~~and~~ functionalized monomers (e.g., demethylated VL; Fig. S4), and nitrogen-containing compounds (e.g., $C_{16}H_{10}N_2O_9$; No. 3~~3, Table S3~~, Table S2) (for VL+AN) had higher normalized abundance ~~were also more relatively abundant~~ under air-saturated conditions ~~were significantly higher under air-saturated conditions~~ (Figs. 1c-d), likely due to efficient ~~the secondary oxidants from~~ ^{3}VL*-initiated oxidation and enhanced VL nitration in the presence of ~~and~~ O_2 ~~and their interactions with nitrate photolysis products~~. ~~The nitrogen-containing compounds (e.g., $C_{16}H_{10}N_2O_9$; No. 3, Table S3) were also more relatively abundant under air-saturated conditions.~~ For both VL* and VL+AN under air-saturated conditions, the most abundant product was $C_{10}H_{10}O_5$ (No. 4, Table S2~~3~~), a substituted VL.

Lines 287–289: Among experiments A5 to A8 ~~(Table S2)~~, VL+AN under air-saturated conditions (A7) had the highest normalized abundance of products and <OS$_c$>, ~~most~~ probably due to the combined influence of ~~the secondary oxidants from~~ ^{3}VL* and enhanced VL nitration in the presence of O_2~~, and nitrate photolysis products~~.

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.

Lines 324–326: Overall, these trends establish that ~~secondary oxidants from ^{3}VL* and~~ O_2 ~~are~~ is necessary for the efficient formation of light-absorbing compounds from both VL* and VL+AN.

Lines 493–495: Aside from the potential imidazole derivative ($C_5H_5N_3O_2$; No. 5~~10~~, Table S2~~3~~), $C_8H_9NO_3$ (No. 2, Table S2) was also observed from VL+AN but only under N_2-saturated conditions (Fig. 1b), probably due to further oxidation by ~~secondary oxidants from~~ ^{3}VL*.

Line 512: This enhanced GUA decay rate constant may be due to the ~~following main reactions:~~ oxidation of GUA by ^{3}VL* ~~(or the secondary oxidants it generates upon reaction with O_2),~~

Lines 520: which may be due to competition between ground-state VL and GUA for reactions with ^{3}VL* ~~(or the secondary oxidants it generates upon reaction with O_2)~~

Line 543: possibly due to both GUA and ground-state VL being available as oxidizable substrates for ^{3}VL* ~~and the secondary oxidants it can generate~~.

Line 601: Our results indicate that the photo-oxidation of VL is influenced by O_2 ~~secondary oxidants from VL triplets~~, pH

Lines 602–612: ~~Compared to~~ Under N_2-saturated conditions, the absence of O_2 likely hindered the secondary steps in VL decay (e.g., reaction of ketyl radical and O_2), regenerating VL as suggested by the minimal VL decay ~~more efficient VL photo-oxidation was observed under air-~~

~~saturated conditions (O_2 is present), which can be attributed to the generation of secondary oxidants (e.g., $^1O_2$, $O_2^{\bullet -}$/$^{\bullet}HO_2$, $^{\bullet}OH$) from $^3VL^*$. 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, $^3VL^*$-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 O_2 promoting VL nitration. Nevertheless, further work is necessary to assess the effect of O_2 on the reactive intermediates involved in $^3VL^*$-driven photo-oxidation and elucidate the mechanisms of VL photo-oxidation under air-saturated conditions.

3. Mechanism discussion. The authors seem compelled to try to explain all of their observations using one or more reactions, but since there is no quantitative examination of these mechanisms, they are all very speculative and mostly not useful. Worse, in some (many?) cases, the proposed mechanisms are inconsistent with some of the data. Fundamentally, without building a kinetic model of the mechanism and testing it against the observations, it is difficult to know whether the proposed reactions are important. The authors put too much emphasis on trying to mechanistically explain their observations and these explanations end up being mostly conjectures that are not grounded in data. These mechanistic speculations should be greatly reduced, especially if they are inconsistent with the kinetic or light absorption data and/or if they rely primarily upon the "normalized abundance of products" metric, which seems highly uncertain.

For example, on line 226, what trends were reinforced in the presence of nitrate? Looking at Table S2, ammonium nitrate has no effect on the kinetics, does not change the normalized product abundance at pH 2.5 or 3 (but does increase it at pH 4), and has no impact on OS(C). Later, in Fig. 2, we see that the presence of nitrate only negligibly increased the long-wavelength absorbance of the products. Overall, the bulk of the observations suggest that nitrate has a minor impact on VL decay, consistent with the fast direct photodegradation of VL.

Response: We concur with the reviewer that the current manuscript contains several speculative reaction mechanisms. As building a kinetic model of the mechanisms is beyond the scope of this study, we proposed major pathways for aqSOA formation instead (Fig. 2, formerly 4). As suggested in major comment #7, Fig. 2 has been shown for the first time when potential aqSOA formation pathways were discussed, then referred to throughout the text.

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 $^3VL^*$ 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.

4. I am concerned that the authors purged IPA and bicarbonate from solution during each experiment since solutions were bubbled continuously. Do they have any way to know if these OH scavengers were removed before or during illumination? Similarly, guaiacol shouldn't undergo direct photochemical loss under illumination above 300 nm, so the apparent decay measured in the dark could be evaporation during purging. If the purging was slow enough, each bubble would achieve Henry's law equilibrium with the solution, which would allow you to estimate the rates of IPA and bicarbonate (lost as CO2) from the rate constant for GUA loss and the ratio of Henry's law constants for GUA and OH scavenger. For GUA, which can be measured by HPLC, the authors should report the fraction of the initial concentration (0.1 mM) that was lost after the 30 min of purging in the dark and the fraction then lost in the dark control for the illumination experiment. Then for IPA and bicarbonate, some estimate of their fraction lost during purging would be helpful. At the very least, this issue needs to be raised and addressed.

Response: The reviewer has correctly pointed out that the contribution of $^{\bullet}OH$ to VL photo-oxidation in this study is likely minor, which is also suggested by other published literature (Anastasio et al., 1996; Li et al., 2014). We, therefore, decided to omit this section (and related sentences) and instead focus on the other findings of the paper.

5. Section 3.1.2. (a) Are VL (and GUA) decay rate constants normalized for photon fluxes? (b) Given the variability in kinetic decays, are the relative small differences in decay rate constants between pH 2.5 and 4 statistically different? (c) Do the authors have a good measure of the variability of the kinetics, e.g., the standard deviation of j(VL) based on triplicate experiments? Given that the decays are not first order, it is more difficult to discern differences in rate constants, so I would be cautious.

Response: (a) We thank the reviewer for pointing this out. The decay rate constants were initially not normalized for photon fluxes, although the reported values are the average of results from triplicate experiments. The values have been updated to the photon flux-normalized decay rate constants, and the following information were added to the text:

Line 142: The decay rate constants were normalized to the photon flux measured for each experiment through dividing *k′* by the measured 2-nitrobenzaldehyde (2NB) decay rate constant, *j*(2NB) (see Text S6 for more details).

(b) Yes, the differences in the decay rate constants between pH 2.5 and 4 (VL*: decay rate constant at pH 2.5 is 1.6 times higher than at pH 4; VL+AN: decay rate constant at pH 2.5 is 1.4 times higher than at pH 4) are small but statistically significant ($p < 0.05$). In addition, the variability for the decay rate constant measurements among triplicate experiments for all conditions in this study is low (the standard deviation for each condition is now added in Table 2, formerly S2). We have added this in the text as follows:

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 ($p < 0.05$).

Other relevant 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 ($p > 0.05$).

(c) Yes, the reported decay rate constants are the average of results from triplicate experiments, and the standard deviation for each condition is now added in Table 2, formerly S2. The footnote of Table 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.

6. Lines 283-289. I would be surprised if deprotonation of phenols is responsible for the higher absorbance of the aqSOA at pH 4 compared to pH 3 and 2.5. For one, the pKa values of methoxy-substituted phenols are near 10, so there's no appreciable phenolate at pH 4. Nitro-substituted phenols can have much lower pKas, but absorbance of the aqSOA formed in the presence of nitrate is nearly the same as in the absence of nitrate, so it seems nitrophenols are a minor part of the light absorption. Another possibility is that different products are made at pH 2.5 compared to pH 4. Measuring the pH dependence of the aqSOA formed at pH 2.5 and 4 would allow you to determine whether the pH dependence is rooted in acid-base chemistry of the products or of the reactions.

Response: Thank you for the suggestion. As suggested, to understand the pH effect further, we measured the pH dependence of the aqSOA formed from VL* at pH 4 and 2.5. The reviewer is correct that deprotonation of phenols does not sufficiently explain the higher absorbance enhancement observed at pH 4 compared to pH 2.5. Based on the comparable pH dependence of the aqSOA formed from VL* at pH 4 and 2.5 (see figure below), the pH dependence observed is likely due to the acid-base chemistry of the reactions, probably involving ^{3}VL* or the excimer of VL (Smith et al., 2016). Smith et al. (2016) reported that the direct photodegradation rate constants for 0.005 mM VL at pH ≤ 3 are nearly two times lower than at pH ≥ 5. The opposite trend observed in this study for 0.1 mM VL (VL* decay rate constant at pH 2.5 is 1.6 times higher than at pH 4) 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). Also, 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). Changes on the text are as follows:

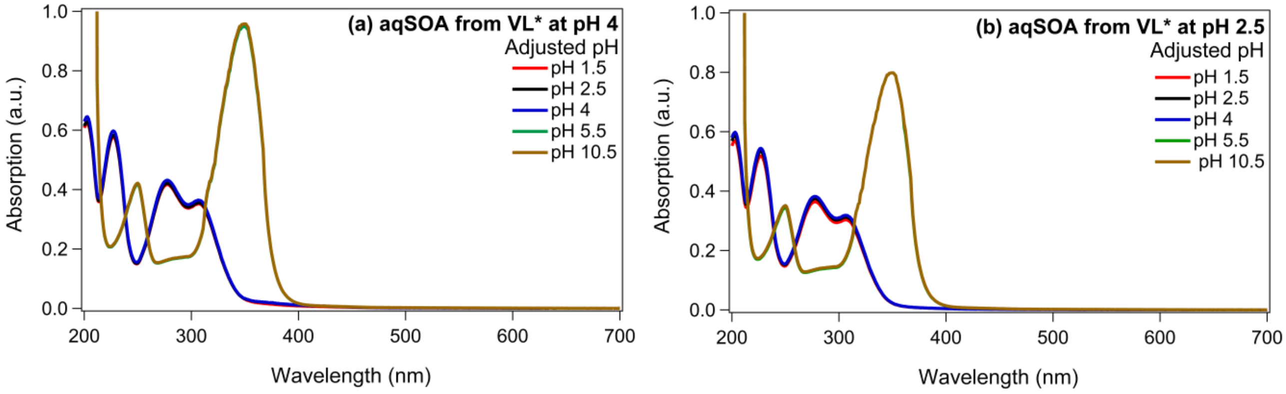

Figure S10. UV-Vis absorption spectra of VL*-derived aqSOA formed at (a) pH 4 and (b) pH 2.5 over a range of pH conditions from 1.5 to 10.5.

Lines 375–386: ~~The h~~Higher absorbance enhancement for both VL* and VL+AN (Fig. 3~~2~~b) was observed as pH increased ~~may be attributed to redshifts and increased visible light absorption of reaction products (Pang et al., 2019a~~). To determine whether the pH dependence is due to the acid-base chemistry of the products or of the reactions, we measured the 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 (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 the two solutions suggest that the observed pH dependence may be attributed to the acid-base chemistry of the reactions, which may involve ^{3}VL* or the excimer of VL (Smith et al., 2016), as discussed earlier. ~~When a phenolic molecule deprotonates at higher pH, an ortho- or para- electron-withdrawing group, such as a nitro or aldehyde group, can attract a portion of the negative charge towards its oxygen atoms through induced and conjugated effects, leading to the extension of chromophore from the electron-donating group (e.g., $-O^-$) to the electron-withdrawing group via the aromatic ring (Carey, 2000; Williams and Fleming, 2008; Pang et al., 2019a). Hence, the delocalization of the negative charge in phenolates leads to significant redshifts (Mohr et al., 2013).~~

For reference, changes in the revised text that are relevant to lines 375–386 are shown below:

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 $HO_2^{\bullet}$ and H_2O_2 and in turn, $^{\bullet}$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 $^{\bullet}$OH formation than that of NO_2^- in the near-UV region (Arakaki et al., 1999; Kim et al., 2014). The increased $^{\bullet}$OH formation rates as pH decreases can lead to faster VL decay (Pang et al., 2019a). Also, NO_2^-/HONO can generate $^{\bullet}NO_2$ via oxidation by $^{\bullet}$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.

7. Section 3.5. This section repeats what has been stated before. I would delete this section, show Figure 4 the first time discussing possible mechanisms, then refer to the Figure throughout the discussion of mechanisms (which is hopefully much shorter in the revised version).

Response: We agree with the reviewer. 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 as follows:

Line 259: This compound was not observed in a parallel experiment in which AN was replaced with sodium nitrate (SN) (Fig. S6a; see Sect. 3.3 for discussion). The potential aqSOA formation ~~most probable~~ pathways via ~~of direct photosensitized and nitrate-mediated photo-oxidation of~~ VL photo-oxidation in this study are summarized in Fig. 2~~were proposed (Fig. 4). In Scheme 1 (pH 4 and pH <4 under air-saturated conditions), ^{3}VL* and $^{\bullet}$OH (from ^{3}VL* or nitrate photolysis) can initiate H-atom abstraction to generate phenoxy or ketyl radicals (Huang et al., 2018; Vione et al., 2019).~~ At pH 4, ring-opening products (Fig. S5) from fragmentation in both VL* and VL+AN may have reacted with VL or dissolved ammonia to generate $C_{10}H_{10}O_5$ (No. 4, Table S2) (Pang et al., 2019b) or~~and~~ a potential imidazole derivative ($C_5H_5N_3O_2$; No. 5, Table S2), respectively. Moreover, nitrate photolysis products promoted functionalization and nitration (e.g., $C_{16}H_{10}N_2O_9$; No. 3, Table S2). ~~At pH<4, the reactivity of ^{3}VL* increased as suggested by the abundance of oligomers (e.g., $C_{16}H_{14}O_6$) and increased normalized abundance of N-containing compounds.~~

Line 364: At pH < 4, ^{3}VL* likely have higher reactivity as suggested by the increased normalized abundance of oligomers (e.g., $C_{16}H_{14}O_6$; No. 6, Table S2 and $C_{31}H_{24}O_{11}$) and N-containing compounds (e.g., $C_{16}H_{10}N_2O_9$; No. 3, Table S2 and $C_{13}H_{14}N_2O_{10}$) (Fig. 2).

Minor Comments

1. Line 25. This notion of "efficiency" (i.e., which reaction path is faster) depends on the concentrations of the two oxidant precursors, VL and nitrate. Thus it's not a universally true statement.

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:

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

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:

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

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~~ $^3VL^*$ 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 (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. L. 42. “respectively” doesn’t serve a purpose in this sentence.

Response: Agree, we have deleted ‘respectively’ from line 50 (formerly 42).

3. Section 2.1. What was the initial volume of solution illuminated? Were solutions stirred? What was the flow rate of gas (N2 or air) through the solution before and during the experiment?

Response: The initial volume of the illuminated solution is 500 mL. The solutions were continuously mixed throughout the experiments. A constant flow rate of 0.5 dm^3/min was used before and during the experiments. These have been added to the text as follows:

Line 102: Photo-oxidation experiments were performed in a ~~500-mL~~ custom-built quartz photoreactor. The solutions (initial volume of 500 mL) were continuously mixed throughout the experiments using ~~equipped with~~ a magnetic stirrer. The solutions were bubbled with synthetic air or nitrogen (N_2) (> 99.995%) (0.5 dm^3/min) for 30 min before irradiation to achieve air- and N_2-saturated conditions, respectively, and the bubbling was continued throughout the reactions (Du et al., 2011; Chen et al., 2020).

4. L. 100. Was there a difference in the temperature between the illuminated and dark solutions?

Response: For all experiments, the range in temperature fluctuations was 27 ± 2 °C.

5. L. 106. If the authors are going to abbreviate 2-propanol as IPA, it would be better to call it isopropyl alcohol to help readers remember the name of the abbreviation. NaBC is a poor choice for an abbreviation for sodium bicarbonate since BC stands for black carbon typically. Better to simply use its chemical formula, NaHCO3 or HCO3-, depending on the context.

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

6. L. 111. 2-propanol and bicarbonate were added in some experiments, but the description of why is odd. Their primary role will be OH scavengers, so it’s strange to call them a VOC and

inorganic anion, respectively. 2-propanol is not a common atmospheric gas, so it's a poor choice of model VOC. Similarly, calling bicarbonate an "inorganic anion" is a poor choice of words, since sulfate and nitrate are the classic inorganic ions. Better to refer to 2-propanol and bicarbonate as "OH scavengers" since that is their main role.

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

7. L. 113. What does it mean that the OH scavengers were not added "in excess"? Since they're reacting with OH (which will have a very low concentration) they are technically in excess. Better to avoid this discussion, as it's not fruitful. If you want to dive more into the OH scavengers, you could calculate the fraction of OH each intercepts in their respective solutions or the amount that they suppress the OH concentration. (But, again, this depends on if the species were purged from solution.)

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

8. L. 151. The disproportionation of HO_2/O_2^- is the same as the reaction of HO_2 with O_2^-, so this sentence repeats itself.

Response: The reviewer is right. We have corrected this sentence as follows:

Line 181: The disproportionation of $HO_2^{\bullet}/O_2^{\bullet -}$ (Anastasio et al., 1996) ~~and reaction of $HO_2^{\bullet}$ with $O_2^{\bullet -}$ (Du et al., 2011)~~ form hydrogen peroxide (H_2O_2), which is a photolytic source of $^{\bullet}$OH.

9. L. 163. It's unclear what the authors mean by "...a minimal role for $^3VL^*$ in VL photo-oxidation". Do they mean that $^3VL^*$ + VL is an unimportant reaction (but see above about this) or that the direct photodegradation of VL doesn't proceed through the triplet state?

Response: In this study, the photodegradation of VL is mainly governed by VL triplets, as explained in our response to major comment #2 (Please see this response for the revised text).

10. L. 167. It is not true that $^1O_2$ has a much longer lifetime than $^3C^*$; rather, the lifetimes are approximately the same. In cloud and fog drops, the lifetime of $^1O_2$ is controlled by water deactivation and is approximately 5 us (see Bilski et al., 1997). The lifetime of $^3C^*$is controlled by reaction with dissolved O2 and is approximately 1/((2E9 M-1 s-1)*(250uM)) ~ 2 us. Also, rather than the oxidant lifetime, it is the product of the oxidant concentration times its second-order rate constant that determines the relative importance of a given oxidant.

Response: We thank the reviewer for the correction. This sentence has been modified as part of the revision for major comment #2 (Please see this response for the revised text).

11. Page 7. This whole page is one paragraph. It should be trimmed to reduce speculative discussions of mechanisms, then broken into smaller pieces, focused on certain themes/points.

Response: We agree with the reviewer. Section 3.1.1 has been revised to reduce speculative discussions of mechanisms (Revisions for lines 188–220 are shown in response to major comment #2). Changes in the text are as follows:

Lines 220–240: ~~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 c~~an~~ 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.

Lines 241–300: The products from VL* under N_2-saturated conditions were mainly oligomers (e.g., $C_{16}H_{14}O_4$) (Fig. 1a), consistent with triplet-mediated oxidation forming higher molecular weight products, probably with less fragmentation relative to oxidation by $^{\bullet}OH$ (Yu et al., 2014; Chen et al., 2020). A threefold increase in the normalized abundance of products was noted upon addition of nitrate (VL+AN under N_2-saturated conditions; Fig. 1b), and in addition to oligomers, functionalized monomers (e.g., $C_8H_6O_5$) and nitrogen-containing compounds (e.g., $C_8H_9NO_3$; No. 2, Table S2~~3~~) were also observed, in agreement with $^{\bullet}OH$-initiated oxidation yielding more functionalized/oxygenated products compared to triplet-mediated oxidation (Yu et al., 2014; Chen et al., 2020). ~~Compared to N_2-saturated conditions, the normalized abundance of products such as o~~Oligomers, ~~and~~ functionalized monomers (e.g., demethylated VL; Fig. S4), and nitrogen-containing compounds (e.g., $C_{16}H_{10}N_2O_9$; No. 3~~3, Table S3~~,Table S2) (for VL+AN) had higher normalized abundance ~~were also more relatively abundant~~ under air-saturated conditions ~~were~~

~~significantly higher under air-saturated conditions~~ (Figs. 1c-d), likely due to efficient ~~the secondary oxidants from~~ ^{3}VL*-initiated oxidation and enhanced VL nitration in the presence of ~~and~~ O_2 ~~and their interactions with nitrate photolysis products~~. ~~The nitrogen-containing compounds (e.g., $C_{16}H_{10}N_2O_9$; No. 3, Table S3) were also more relatively abundant under air-saturated conditions.~~ For both VL* and VL+AN under air-saturated conditions, the most abundant product was $C_{10}H_{10}O_5$ (No. 4, Table S2~~3~~), a substituted VL. Irradiation of VL by 254-nm lamp has also been reported to lead to VL dimerization and functionalization via ring-retaining pathways, as well as small oxygenates but only when $^{\bullet}$OH from H_2O_2 were involved (Li et al., 2014). In this work, small organic acids (e.g., formic acid) were observed from both VL* and VL+AN under air-saturated conditions (Fig. S5) due to simulated sunlight that could access the 308-nm VL band (Smith et al., 2016). Interestingly, we observed a potential imidazole derivative ($C_5H_5N_3O_2$; ~~Fig. 1d~~No. 5, Table S2) from VL+AN under air-saturated conditions (Fig. 1d), which may have formed from reactions induced by ammonium. This compound was not observed in a parallel experiment in which AN was replaced with sodium nitrate (SN) (Fig. S6a; see Sect. 3.3 for discussion). The potential aqSOA formation~~most probable~~ pathways via ~~of direct photosensitized and nitrate-mediated photo-oxidation of~~ VL photo-oxidation in this study are summarized in Fig. 2~~were proposed (Fig. 4).~~ ~~In Scheme 1 (pH 4 and pH <4 under air-saturated conditions), ^{3}VL* and $^{\bullet}$OH (from ^{3}VL* or nitrate photolysis) can initiate H-atom abstraction to generate phenoxy or ketyl radicals (Huang et al., 2018; Vione et al., 2019).~~ At pH 4, ring-opening products (Fig. S5) from fragmentation in both VL* and VL+AN may have reacted with VL or dissolved ammonia to generate $C_{10}H_{10}O_5$ (No. 4, Table S2) (Pang et al., 2019b) or~~and~~ a potential imidazole derivative ($C_5H_5N_3O_2$; No. 5, Table S2), respectively. Moreover, nitrate photolysis products promoted functionalization and nitration (e.g., $C_{16}H_{10}N_2O_9$; No. 3, Table S2). ~~At pH<4, the reactivity of ^{3}VL* increased as suggested by the abundance of oligomers (e.g., $C_{16}H_{14}O_6$) and increased normalized abundance of N-containing compounds.~~

The molecular transformation of VL upon photo-oxidation was examined using the van Krevelen diagrams (Fig. S7). For all experiments (A1-15~~9~~; Table ~~S~~2) in this study, the O:C and H:C ratios of the products were mainly similar to those observed from the aging of other phenolics (Yu et al., 2014) and BB aerosols (Qi et al., 2019). U~~u~~nder N_2-saturated conditions, o~~O~~ligomers with O:C ratios ≤ 0.6 were dominant in VL*, ~~under N_2-saturated conditions.~~while smaller molecules ($n_c \leq 8$) with higher O:C ratios (up to 0.8) were also observed f~~F~~or VL+AN. ~~For VL+AN under air saturated conditions, smaller molecules (nc ≤8) with higher O:C ratios (up to 0.8) were also observed.~~ In contrast, ~~M~~more products with higher O:C ratios (≥ 0.6) were noted under air-saturated conditions for both VL* and VL+AN. F~~f~~or experiments A5 to A8, ~~The~~ H:C ratios were mostly around 1.0 and double bond equivalent (DBE) values were typically (58% of the 50 most abundant products) > 7, indicating that the products~~for experiments A5 to A8~~ ~~(Table S2)~~ were mainly oxidized aromatic ~~aromatic species~~ compounds (Xie et al., 2020). Compounds with H:C ≤ 1.0 and O:C ≤ 0.5 are common for aromatic species, while compounds with H:C ≥ 1.5 and O:C ≤ 0.5 are typical for more aliphatic species (Mazzoleni et al., 2012; Kourtchev et al., 2014; Jiang et al., 2021). ~~Moreover, majority of the products for experiments A5 to A8 have double bond equivalent (DBE) values >7, which corresponds to oxidized aromatic compounds (Xie et al., 2020).~~ In contrast, Loisel et al. (2021) reported mainly oxygenated aliphatic-like compounds ~~(H:C, ≥ 1.5 and O:C, ≤ 0.5 ratios)~~ from the direct irradiation of VL (0.1 mM), ~~which may be~~ probably due to their 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., 2018). Among experiments A5 to A8 ~~(Table S2)~~, VL+AN under air-saturated conditions (A7) had the highest normalized abundance of products and <OS$_c$>, ~~most~~ probably due to the combined influence of ~~the secondary oxidants from~~ ^{3}VL* and enhanced VL nitration in the presence of O$_2$~~, and nitrate photolysis products~~. ~~In our calculations, the increase in <OS$_c$> (except for VOCs and inorganic anions experiments; A9 to A12; Table S2) was lower than those in $^•$OH or triplet-mediated oxidation of phenolics (e.g., phenol, guaiacol) measured using an aerosol mass spectrometer (Sun et al., 2010; Yu et al., 2014),~~ Our measured <OS$_c$> range from -0.28 to +0.12, while other studies on phenolic aqSOA formation reported <OS$_c$> ranging from -0.14 to +0.47 (Sun et al., 2010) and 0.04 to 0.74 (Yu et al., 2014). This is likely because we excluded contributions from ring-opening products, which may have higher OS$_c$ values as these products are not detectable in the positive ion mode. Thus, the <OS$_c$> in this study likely were lower estimates. 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$_2$.

12. L. 196. The text here and elsewhere discusses the abundance of specific products (not just the normalized product abundance). The abundance of each product should be added to Table S3, along with some estimate of the relative uncertainty of these values.

Response: The abundance mentioned in line 249 (formerly 196) pertains to the normalized abundance of all nitrogen-containing products for VL* at pH 4 under air-saturated conditions, not for specific products.

13. L. 224. How much lower are OS(C) values here compared to previous work on aqSOA? Compare these values.

Response: Our measured <OS$_c$> range from -0.28 to +0.12, while other studies on phenolic aqSOA formation reported <OS$_c$> ranging from -0.14 to +0.47 (Sun et al., 2010) and 0.04 to 0.74 (Yu et al., 2014). This information has been added to the text as follows:

Line 286: Our measured <OS$_c$> range from -0.28 to +0.12, while other studies on phenolic aqSOA formation reported <OS$_c$> ranging from -0.14 to +0.47 (Sun et al., 2010) and 0.04 to 0.74 (Yu et al., 2014). This is likely because we excluded contributions from ring-opening products, which may have higher OS$_c$ values as these products are not detectable in the positive ion mode.

14. L. 240. Is there any evidence that ^{3}VL* + O$_2$ directly makes OH? This would seem energetically unfavorable and also to be minor compared to energy transfer to make ^{1}O$_2$.

Response: We do not have direct evidence of $^{\bullet}OH$ formation from $^3VL^* + O_2$, although trace amounts of H_2O_2 were likely formed during VL photodegradation (Li et al., 2014) similar to the case of other phenolic compounds (Anastasio et al., 1996). This statement has been added to line 241.

Line 316: Trace amounts of H_2O_2 were likely formed during VL photodegradation (Li et al., 2014), similar to the case of other phenolic compounds (Anastasio et al., 1996).

15. L. 242. In the presence of O_2, the ketyl radical is probably too short lived (it reacts with O2 to make an alpha-hydroxy peroxyl radical) to combine appreciably with a phenoxyl radical. But the phenoxyl radical is in resonance with a carbon-centered cyclohexadienyl radical that is longer lived; these two species can couple (Yu et al., ACP, 2014).

Response: We thank the reviewer for the additional information. We have now revised line 311 to include this as follows:

Line 317: Oligomers can then form via the coupling of phenoxy radicals or phenoxy and cyclohexadienyl ~~ketyl~~ radicals (Sun et al., 2010; Yu et al., 2014~~Berto et al., 2016~~; Vione et al., 2019).

16. L. 261. The rate constant for H_2O_2 formation is fastest near the pKa of HO_2, i.e., pH 4.8, so one wouldn't expect greater H_2O_2 formation at pH 2.5 compared to pH 4. But this also depends on the pH dependence of the HO_2/O_2^- sources and sinks.

Response: Thank you for pointing this out. This statement has been deleted.

17. L. 264. This discussion of the pH dependence of N(III) photolysis doesn't seem applicable since the addition of nitrate makes a negligible contribution to VL decay. Just because N(III) photolysis is pH dependent doesn't mean it matters here.

Response: Thank you for pointing out this error. The reviewer is correct that the pH dependence of N(III) is not relevant for the discussion of pH effects on VL decay rate constants. Some of these statements have been transferred to the next paragraph (from line 360) to provide a potential explanation for the increased normalized abundance of nitrogen-containing compounds at lower pH. Revisions for lines 333–354 are shown in our response to major comment #6. Other changes in the text are as follows:

Line 359–364: For VL+AN, the normalized abundance of nitrogen-containing compounds was also higher ~~increased~~ at lower pH (Table ~~S~~2), likely due to increased $^{\bullet}OH$ and $^{\bullet}NO_2$ formation, which may be caused by the dependence of N(III) (NO_2^- + 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 $^{\bullet}OH$ formation than that of NO_2^- in the near-UV region

(Arakaki et al., 1999; Kim et al., 2014). Also, NO_2^-/HONO can generate $^{\bullet}NO_2$ via oxidation by $^{\bullet}OH$ (Reactions 4 and 10~~5~~; Table 1) (Pang et al., 2019a).

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

18. L. 299. Why would the presence of HO2 lead to more dimer formation? HO2 (and O2-) are too weak to oxidize phenols at any significant rate.

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

19. Lines 298-301: This argument is circular: IPA cannot make more OH by scavenging OH and turning it into HOOH, which then photolyzes to make OH. Think of the associated stoichiometry. IPA will suppress [OH] because it is an OH sink, thus rendering OH an insignificant oxidant for VL. The observation that IPA has a negligible impact on VL decay (Fig. S3c) indicates that OH is not important as an oxidant for VL (with or without IPA) or that the IPA was mostly purged from the system.

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

20. L. 310. IPA makes no difference in the VL kinetics, whether nitrate is present or not. So please don't make sweeping statements such as "...the role of nitrate in VL photo-oxidation is enhanced in the presence of IPA...". And don't suggest that OH is an important intermediate in the formation of a product in the presence of IPA (e.g., line 311), since IPA will greatly suppress the OH concentration.

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

21. L. 313-322. It is hard to believe that 1 mM of IPA can significantly disrupt the structure of 55 M water. In any case, there is no increase in light absorption by the aqSOA formed in the presence of IPA (Fig. 2), so the Berke mechanism seems unimportant. Most of this should be deleted.

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

22. L. 327. It is difficult to imagine that carbonate radical is a significant oxidant in these experiments: carbonate rate constants are relatively slow (compared to triplets or OH) and VL photodegradation is very fast. If the authors want to propose carbonate radical as an important sink, they need to do some calculations of its steady-state concentration and estimate the corresponding rate of VL loss. Again, the qualitative normalized abundance of products is driving these uncertain statements, while the quantitative photodecay rates and light absorption are showing there is no significant effect of bicarbonate. Lead with the latter observations, as they are more robust.

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

23. L. 336. 1 mM IPA or bicarbonate is not high enough to reduce the cage effect from nitrate photolysis. In any case, IPA or bicarbonate are OH sinks, so they will suppress, not enhance, the OH concentration.

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

24. L. 376. If this proposed mechanism was true, then VL decay would be significantly faster in the presence of nitrate, but this is not the case. It's not clear what the authors are trying to explain here - is it the increase in oligomerization at higher [VL]? The explanation for this is probably that the concentrations of phenoxyl radicals (and the related, carbon-centered cyclohexadienyl radicals) increase with [VL], making radical-radical recombination to form oligomers a more significant fate.

Response: Thank you for pointing this out. We apologize for the confusion. There should have been an explanation here for the increased oligomerization observed at higher [VL]. We agree with the reviewer that a possible reason for this is the increased concentration of radicals with [VL] (added to the revised text). The succeeding lines are for comparing the potential pathways at 1:1 VL/nitrate and 1:100 VL/nitrate only at low [VL]. The text has been revised to clarify these 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 <OS$_c$> 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.

25. L. 405. GUA should not undergo any direct photochemistry, so its decay in the absence of VL or AN suggests either that there is an oxidant-making contaminant in the system (that is consumed within a few hours) or that GUA is evaporating during illumination. But there is no GUA loss in the dark: is this because the temperature was cooler in the dark?

Response: Vione et al. (2019) also observed the direct photodegradation of GUA (0.1 mM) upon irradiation using Xe lamp. Moreover, Sun et al. (2010) reported an intermediate rate of direct photoreaction for GUA (0.1 mM), yielding aqSOA including GUA dimers (similar to what we observed). There was no significant loss of GUA both after 30 min of purging in the dark (-0.36%) and after 360 min of dark control experiments (-1.7%). Also, the temperature fluctuations (27 ± 2 °C) were minimal.

26. L. 498. This sentence mentions "Further enhancement of VL photo-oxidation…in the presence of nitrate…", but VL photo-oxidation (i.e., photodegradation) was not enhanced in the presence of nitrate.

Response: This statement refers to the presence of both O_2 and nitrate resulting in the highest normalized abundance of products (including N-containing compounds) and $<OS_c>$ among experiments A5–A8. We have revised this as follows:

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, $^3VL^*$-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 $<OS_c>$, which may be due to the presence of O_2 promoting VL nitration.

27. L. 1004. The author order is incorrect on the Tinel et al. ref.

Response: Thank you for the correction. We have now amended the author order for this reference as follows and revised the corresponding in-text citations:

George, C., Brüggemann, M., Hayeck, N., Tinel, L., and Donaldson, D. J.: Interfacial photochemistry: physical chemistry of gas-liquid interfaces, in: Developments in Physical & Theoretical Chemistry, edited by: Faust, J. A. and House, J. E., Elsevier, 435–457, https://doi.org/10.1016/B978-0-12-813641-6.00014-5, 2018.

28. Table 1. The quantum yield for Rxn 3 is not 0.001. This is a misperception based on the O(3P) result of Warneck and Wurzinger (J Phys Chem, 1988); their paper shows a value of ~0.01 for more direct (nitrite) measurements. Benedict et al. (Env Sci Technol., 2017) confirmed this higher

value. This error doesn't affect the current work, but it would be a shame to propagate the misperception.

Response: We thank the reviewer for the careful read. We now have corrected this value in Table 1:

NO_3^- + *hv* → NO_2^- + O(^{3}P); φ = 0.~~0~~011

29. Figure 4. (a) The resolution of the figure is poor, so it's fuzzy and hard to read. (b) Scheme 1 suggests that oligomers are only formed at pH < 4, which isn't true, as past work has shown oligomer formation in similar phenol systems at pH 5. (c) Ketyl radicals formed by $^3C^*$ + phenol typically are shown as phenoxyl OH group (a result of the triplet abstracting a hydrogen) and no double bond between the C and O. As stated earlier, their lifetimes are short in the presence of O2, so they're unlikely to do the coupling as shown here.

Response:

(a) This may be a formatting issue. We ensured that this is avoided in the revised version.

(b) The reviewer is right that oligomer formation in similar phenol systems was also observed at pH 5. However, the molecular formulas initially presented in Fig. 4 were the most abundant products or products with a significant increase in normalized abundance. To avoid this confusion, Fig. 4, now 2, has been revised to show the major products for each condition, with a marker for the most abundant products.

(c) Thank you for catching this error. Ketyl radical has been deleted in Fig. 2.

Supplemental Material Notes

1. General note – it would have been helpful to have line numbers in the supplement.

Response: Line numbers have now been added to the supporting information as well.

2. Text S3. Were calibration curves only made once? Were they actually used in quantifying VL and GUA? (I don't see the need since absolute values are not needed in the kinetic plots.)

Response: No, the calibration curves were prepared weekly to account for potential changes in the detector response of UHPLC. These calibration curves were used to quantify VL and GUA as the calculated VL concentration was used for estimating the normalized abundance of products.

3. Text S6. (a) It's unclear what is meant by "Then, the average relative intensity absorbed by 2NB solution as a function of wavelength was calculated." Can you show this with an equation? (b) How much did the photon flux vary between experiments? Was this determined? If not, this variation is a source of variability in the kinetic measurements.

Response: (a) We apologize for the confusion. This statement pertains to a scaling factor (SF) that was used to determine the absolute photon flux in the reactor, I'_{λ}. Similar to Smith et al. (2014, 2016), we measured the spectral shape of the photon output of our illumination system (i.e., the relative flux at each wavelength) using a high-sensitivity spectrophotometer (Brolight Technology Co. Ltd, Hangzhou, China). Using an SF, this measured relative photon output, $I_{\lambda}^{\mathrm{relative}}$, is related to I'_{λ} as follows:

$$I'_{\lambda} = I_{\lambda}^{\mathrm{relative}} \times \mathrm{SF} \tag{Eq. S6}$$

Substitution of Eq. S6 into Eq. S5 and rearrangement yields:

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

Where *j*(2NB) is the 2NB decay rate constant, $\mathrm{N_A}$ is Avogadro's number, I'_{λ} is the actinic flux (photons $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}\ \mathrm{nm}^{-1}$), $\Delta\lambda$ is the wavelength interval between actinic flux data points (nm), and $\varepsilon_{\mathrm{2NB},\lambda}$ and $\Phi_{\mathrm{2NB},\lambda}$ are the base-10 molar absorptivity ($\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) and quantum yield (molecule photon^{-1}) for 2NB, respectively. Values of $\varepsilon_{2NB,\lambda}$ (in water) at each wavelength under 298 K and a wavelength-independent Φ_{2NB} value of 0.41 were adapted from Galbavy et al. (2010).

$$\mathrm{SF} = \frac{j(\mathrm{2NB})}{2.303 \times (10^3\ \mathrm{cm}^3\ \mathrm{L}^{-1} \times 1\ \mathrm{mol/N_A\ mlc}) \times \sum\left(I_{\lambda}^{\mathrm{relative}} \times \Delta\lambda \times \varepsilon_{\mathrm{2NB},\lambda} \times \Phi_{\mathrm{2NB}}\right)} \tag{Eq. S7}$$

and substitution of (Eq. S6) into (Eq. S7) yields:

$$I'_{\lambda} = I_{\lambda}^{\mathrm{relative}} \frac{j(\mathrm{2NB})}{2.303 \times (10^3\ \mathrm{cm}^3\ \mathrm{L}^{-1} \times 1\ \mathrm{mol/N_A\ mlc}) \times \sum\left(I_{\lambda}^{\mathrm{relative}} \times \Delta\lambda \times \varepsilon_{\mathrm{2NB},\lambda} \times \Phi_{\mathrm{2NB}}\right)} \tag{Eq. S8}$$

Finally, $I'_{\lambda}$was estimated through Eq. S8~~5~~. The estimated photon flux in the aqueous reactor is shown in Figure S1~~2~~.

We have added the above information to Text S6.

(b) The *j*(2NB) in this study varied from 0.0021 to 0.0026 s^{-1}. The decay rate constants have now been normalized to the photon flux, and the updated values are shown in Table 2, formerly S2.

4. Table S2. (a) VL (and GUA) decays are rate constants, not decay rates. (b) For reference, it would be helpful to give the OS(C) of VL. (c) What is pH of expt. A19?

Response: (a) Thank you for catching this error. This has been corrected in Table S2, now 2, as well as elsewhere in the text:

Table ~~S~~2. Reaction conditions, initial VL (and GUA) decay rate~~s~~ constants

Line 142: the calculation of GUA decay rate constant.

Line 172: initial VL (and GUA) decay rate~~s~~ constants,

Line 204: Contrastingly, the VL* decay rate constant under air-saturated conditions

Line 220: ~~Similar to VL*~~, ~~t~~The decay rate constant for VL+AN

Line 235: Nevertheless, the comparable decay rate~~s~~ constants

Line 331: The decay rate~~s~~ constants

Line 509: GUA decay rate constant was ~~faster~~ higher by 2.2 (GUA+VL)

Line 512: This enhanced GUA decay rate constant

Line 574: Although nitrate did not substantially affect the VL decay rate~~s~~ constants,

(b) Agree, we have now added the OS_c of VL (-0.25) to Table 2.

(c) The pH for exp 19, now 15, is 4, same with other experiments involving GUA. This is already listed in the second column of Table 2.

5. Figure S1. The vanillin spectrum has a problem around 305 nm - a large discontinuity that is probably caused by lamp switch. Either reacquire the spectrum or replace with a published value.

Response: Thank you for catching this. Fig. S1 has been revised to correct this.

6. Figure S3. Were the decays ever determined multiple times for the same condition? It would be helpful to show these results and derive a relative uncertainty for decay rate constants.

Response: Yes, the decays reported in Fig. S3 are the average of results from triplicate experiments, and the error bars for each data point are already shown. The photon flux-normalized decay rate constants have also been updated in Table S2, now 2, along with the standard deviation for each condition (Please see our response to major comment #5). The following sentence has been added in the methods section to clarify this:

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.

We also added this note to figure captions when applicable: most error bars are smaller than the markers.

7. Figure S6. How can we tell that the imidazole formed in the AN experiment was not formed in the SN experiment? It would be helpful to put a marker on the two plots of Fig. S6 to show where the imidazole showed up in the AN experiment.

Response: Thank you for pointing this out. Fig. S6 has been revised to show a marker for the potential imidazole compound.

Recommendation

I recommend that the manuscript be majorly revised and then reconsidered.

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