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 3**

This study investigated the aqueous photo-oxidation of vanillin (VL) via both direct photosensitized reaction and nitrate-mediated photo-oxidation and discussed the influence of secondary oxidants from triplet excited states ($^3$VL*), solution pH, VOCs, and inorganic anions, etc. in detail. The experiments and data analysis are well done, and the mechanisms that are proposed are plausible. This study provides valuable information about the chemical composition, optical properties, and possible reaction mechanisms for SOA formed from the VL photo-oxidation under different conditions. However, there are a few major and minor comments I would like the authors to address before it is considered for publication in ACP.

**Major comments**

(1) With the experiment design, it is difficult to directly compare $^3$VL* pathway and nitrated-mediated pathway, as also mentioned by the authors that the VL concentration was very high, and $^3$VL* chemistry dominated in all the VL + ammonium nitrate (AN) experiments. Maybe more precisely, what was compared was photo-oxidation of VL via $^3$VL* chemistry with and without nitrate. However, both the title and some places in the manuscript are misleading.

Response: We agree with the reviewer that $^3$VL* chemistry dominated in VL+AN experiments, as mentioned throughout the manuscript. However, we did not intend to compare $^3$VL* and nitrated-mediated pathways either. It is our opinion that the current title does not have such connotation. Despite the high VL concentration, the VL+AN experiments showed some differences in the aqSOA formed. Hence, we would like to keep the current title. With the revised abstract, we hope it will not confuse readers into expecting a comparison.

(2) I suggest the authors restructure the manuscript: on the one hand, to move part of the figures and tables from the SI to the manuscript, e.g. Table S2 and Figure S12, to make it easier to follow. On the other hand, to simplify the article by cutting some “maybe interesting” but not that important/related findings/discussions to make the main storyline clearer.

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 $^3VL^*$ in VL photo-oxidation.~~ Contrastingly, the VL* decay rate constant under air-saturated conditions was 4 times higher~~, revealing the importance of $^3VL^*$-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 $^3VL^*$ 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 $^3VL^*$ 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 $^3C^*$ 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.

(3) (a) It is very interesting to see the changes in optical properties, and their relation to the changes in chemical composition. However, I only see very general discussions about it (e.g. line 234-238 and line 282-289). It will be nice to discuss the specific compounds, possible chromophores, and to explain the changes in the optical properties.

(b) To explain the pH-dependency, the authors cited Pang et al. 2019a, which reported the pH-dependent light absorbance of nitrophenols. However, the dominating products in this study were those without N, different from those in Pang et al. 2019a. In addition, the chemical composition of SOA with pH 4 and pH < 4 are quite different, which could also lead to different functional group/chromophores, and changes in optical properties.

Response:

(a) Thank you for this suggestion. We agree that identifying the BrC chromophores would enrich the discussion for the changes in the optical properties. However, it is possible that the products detected using UHPLC-qToF-MS in positive ESI mode might not have contributed significantly to all products formed and hence may not be the primary contributors to the absorbance enhancement. In other words, the absorbance enhancement may not necessarily correlate directly with the products detected. Detailed characterization of specific chromophores is indeed interesting, but it is outside of the scope of this study. Instead, the changes in the optical properties for this study are based on the integrated area of the absorption spectra from 350 to 550 nm in order to consider the contributions of all potentially light-absorbing products.

(b) The reviewer is correct that the dominant products in this study do not contain nitrogen. We have revised this explanation based on the comparable pH dependence of the aqSOA formed from VL* at pH 2.5 and 4 over a range of pH conditions from 1.5 to 10.5. This suggests that the observed pH dependence is due to the acid-base chemistry of the reactions, which may involve $^3$VL* or the excimer of VL (Smith et al., 2016). Changes in the text are as follows:

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 p$K_a$ 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.

(4) Adding the experiments of guaiacol (GUA) is a little bit confusing, as the title is the photo-oxidation of VL. I understand it is a good addition to the manuscript, and these experiments nicely compared the photo-oxidation of GUV via the two pathways. However, the conclusion (line 25-26) "guaiacol oxidation by photosensitized reactions of VL was observed to be more efficient relative to nitrate-mediated photo-oxidation" is still problematic, as the concentration of VL in GUA + VL experiment was still 10 times higher than the observed value in the cloud and fog but the concentration of AN in GUA + AN experiments was similar to the observed concentration.

Response: Thank you for this suggestion. The apparent quantum efficiency of GUA photodegradation ($\phi_{GUA}$) 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):

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

$\Phi_{\mathrm{GUA}}$ 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 $k'_{\mathrm{GUA}}$ is the pseudo-first-order rate constant for GUA decay, [GUA] is the concentration of GUA (M), $\varepsilon_\lambda$ 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 $I'_\lambda$ 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 $\phi_{\mathrm{GUA}}$ 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 ($\phi_{\mathrm{GUA}}$) 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.

**Minor comments**

1. Line 27-28 In the abstract, the sentence "which nitrate photolysis products can further enhance" sounds not clear to me.

Response: We apologize for the confusion. This sentence was supposed to convey two things: a) the direct photosensitized oxidation of VL may be an important aqSOA source and b) the addition of nitrate photolysis products to (a) can initiate further reactions that can enhance aqSOA formation. We have revised this sentence as follows:

Line 32: This study indicates that the direct photosensitized oxidation of VL~~,~~ and nitrate-mediated photo-oxidation of VL ~~which nitrate photolysis products can further enhance,~~ may be ~~an~~ important aqSOA sources in areas influenced by biomass burning emissions.

2. Line 121 Did you average these replicates for mass spectra and/or decay rates? Please clarify it.

Response: Yes, the reported mass spectra are based on the average of results from duplicate experiments, while the decay rate constants and absorbance enhancement are average of results from triplicate experiments. We have added the following sentence in the methods 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.

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.

3. Line 168-169 It would be nice to explain it together with the chemical composition shown in Figure 1.

Response: This paragraph discusses the VL decay trends. Line 249 (formerly 196) already includes an example for this ($C_{16}H_{10}N_2O_9$; No. 3, Table S2). Changes in the text are as follows:

Lines 220: ~~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).

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.

4. Line 181 "VL*" should be "$^3$VL*"?

Response: Thank you for catching this error. This has been corrected as follows:

Line 235: Nevertheless, the comparable decay rate~~s~~ constants for VL* and VL+AN imply that $^3$VL* chemistry

5. Line 187 In both VL* and VL + AN under N2-saturated conditions (Fig. 1(a) and (b)), trimer signals are very high. Any explanations?

Response: $N_2$-saturated experiments would inhibit the formation of secondary oxidants, which can lead to $^3$VL*-driven reactions (Chen et al., 2020) (line 107). Compared to $^{\bullet}$OH-mediated oxidation which yields more functionalized/oxygenated products, triplet-driven oxidation has been suggested to produce higher molecular weight products, probably with less fragmentation (Yu et al., 2014; Chen et al., 2020), as mentioned in lines 241–243. This likely explains the prevalence of dimers and trimers for the $N_2$-saturated experiments.

6. Line 212 Could you give some numbers to show "majority"?

Response: It is 58% of the 50 most abundant products for experiments A5 to A8. This has been added to the text as follows:

Lines 277–279: 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).

7. Line 255 Should it be pH 4?

Response: Thank you for catching this error. The text has now been corrected as follows:

Line 331: the range of 2.5 to 4~~5~~

## References

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