Response to comments

Dear Editor

Thank you very much again for your comments regarding our manuscript! According to your guidance, we do realize that some implications drawn from our findings are overstated and may not be appropriate, they were either deleted or modified. In addition, other comments were also addressed point-by-point (as shown below) with your comments repeating in *italics*. All relevant data is now deposited on a website that is specified in the Data availability section. The manuscript was also checked carefully again with all your technical corrections incorporated, please check the manuscript with tracked changes.

I. Major comments

1) Atmospheric implications

The stated implications exceed the conclusions that can be drawn on the current study

Reply: Agree. We have either deleted or modified some statements, please see below.

l. 42/43: "as well as its impacts on particulate matter concentration and toxicity, radiative balance and climate change" – Since these aspects are not discussed in the paper, it seems that these conclusions are too far reaching. – I suggest deleting.

Reply: Agree. The sentence is deleted.

l. 765 – 767: The paper by Ma et al., 2021 does not quantify the amount of phenols into the aqueous phase. I do not think that your statement is correct; there are several issues:

1) Syringol and eugenol are equally substituted phenols, as they have both three functional groups on the aromatic ring.

2) How can such different partitioning behavior be explained? The Henry's law constants for eugenol and syringol are 729 M/atm (Sander, 2015; doi:10.5194/acp-15-4399-2015) and 2.6e4 M/atm (www.atmos-chem-phys-discuss.net/10/C2298/2010/). Thus, one would expect syringol to partition ~30 times more efficiently into water.

3) The Henry's law constants allow an estimate of the partitioned fraction into an aqueous phase by appropriate unit conversion of the concentration ratio as given by Henry's law, e.g:

$$CR\,[dimensionless] = K_H \left[\frac{mol}{L(aq)\ atm}\right] \underbrace{LWC \left[\frac{L(aq)}{cm^3(gas)}\right] \frac{N_A \left[\frac{molecules}{mol}\right]}{2.5e19 \left[\frac{molecules}{cm^3(g)\ atm}\right]}}_{Conversion\ factor\ 'X'}$$

For a typical cloud water content of 0.3 g/m3 (=3e-10 L(aq)/cm3(gas)): X = 7.22e-6; for typical aerosol water contents of 50 ug/m3, X = 1.2e-10

The fraction in the aqueous phase can then be calculated as

$$\varepsilon_{aq} = \frac{CR}{CR+1}$$

As indicated in this interactive comment (https://acp.copernicus.org/preprints/10/C2298/2010/acpd-10-C2298-2010-print.pdf -

citing a reference that is not open access) , aqueous phase concentrations of methoxy phenols may be higher by a factor of 3-4 than predicted by Henry's law. Even such enhancement would not lead to a significant partitioning of eugenol or other methoxy phenols into aerosol water (<<1%). Reasons why reactions in aerosol water may be more important than in cloud water might include different reaction pathways due to concentration effects such as oligomerization and/or enhanced solubility due to ionic strength effects ('salting-in'). However, phenols show generally a salting-out effect (Wang et al., Envoron Sci. Technol., 2014 https://doi.org/10.1021/es5035602) Unless you can argue that such effects occur for eugenol in aerosol water as compared to cloud water, your discussion on the relevance in aerosol water is not convincing.

Reply: Thanks very much for your clarification and reminder! We read it carefully and agree with your viewpoint. Ma et al. (2021) does state that "The low liquid water content (LWC) of ALW leads to very limited partitioning of simple phenols to particle water; e.g., less than 0.001% of syringol will partition into the water phase for an ALW content of 100 µg $m^{-3,}$", and they argued that for the six phenols they studied, the aqueous fractions can be 2-58%, therefore highlighted the importance of their precursors in aerosol water reactions. However, this may not be applicable to eugenol we used here, as its Henry's law coefficient is not high and eugenol is not a highly substituted phenol as ones in that paper. We are sorry that we just blindly cited their reference without considering the difference between the henry's law constant of eugenol and those in Ma et al. (2021); eugenol indeed is unable to partition into aqueous water as your calculations have verified, and the importance of aerosol water reactions of eugenol is small. Even though the reactions of some other high substituted phenols might be important in aerosol water but this is not a convincing statement that can be drawn base on our current study on eugenol. Therefore such statement is now deleted.

l. 780 - 784: The liquid water content of aerosol water is about 10000 times smaller than that of cloud (~50 ug m-3 vs 0.5 g m-3). Even if the reaction rates in aerosol water were 10 times higher than those in cloud water due to higher oxidant concentration, the overall importance of the aerosol phase would be still 100 times smaller than that of chemical reactions in cloud water. Such values should be taken into account in the discussion.

Reply: Agree. This point is now added, our intention is to state that $^3C*$ may be important than OH in aerosol water (or in cloud water), but not to state that role of $^3C*$ (or OH) in aerosol water is more important that it in cloud water. This is now made clear.

l. 813 – 816: '…our findings here underscore the potential of aqueous processing on 813 the enhancement of particle toxicity. Considering high PM concentration is often accompanied with cold and humid weather conditions, the additional adverse health effects caused by aqueous oxidation may amplify the health hazards of PM pollution.'

These conclusions are quite far-fetched. 1) If you do not compare the OP from gas-phase reactions, you cannot state that aqueous phase reactions cause a higher oxidation potential'. 2) Toxicity is not only defined by OP.

Reply: Agree. This is indeed over-interpreted. Without evidence that proves OP of aq-SOA is higher than that of gasSOA, this argument is incorrect, and toxicity is not only indicated by OP. This sentence is now deleted.

l. 821: You only investigated one aspect of potential adverse health effects, i.e. the oxidation potential. This is by no means a 'systematic investigation of toxicity'.

Reply: Agree. "systamatically" is now deleted.

l. 851: '...our findings highlight the importance of aqueous oxidation of BB emissions to SOA formation, its potentially important role in affecting radiative balance and climate through formation of BrC, as well as possible additional adverse health effects. Such effects should be considered in air quality or climate models to better assess the influence of BB emissions.' Again, these conclusions are way overstating your findings. You neither reported absorption coefficients, nor any radiation calculation, nor the yields of brown carbon nor an estimate of the amount of SOA that can be formed from such precursors.

Reply: Agree. This is indeed over-interpreted, and is now deleted.

2) Wrong terminology

l. 121, l. 196, l. 574, l. 819: 3C is not a radical. Write '...and oxidation by OH radicals and 3C* triplet states' – please check the remainder of the manuscript for other instances of its wrong terminology*

Reply: Thanks for pointing out this. Wrong use of "radical" for $^3C*$ is now all corrected throughout the manuscript.

Sections 3.4 and 3.5: I am still confused by your use of 'reaction products' and 'HULIS'. In Section 3.4, you describe HULIS properties, whereas in Section 3.5 you talk about Reaction products. Are the HULIS you are referring to the same or just a subset of the total products? – I realized that you do mention it briefly in l. 725 – but this assumption should be added earlier in the text.

Reply: Yes, HULISs is just a subset of the total products, this is now made clear in the beginning of Section 3.5 as you suggested, "HULIS is only a subset of the products from aqueous oxidation, and here we used AMS to further quantify the total reaction products". Section 3.4 investigated HULIS as EEM measurement suggests the presence of HULIS. Section 3.5 is separated from Section 3.4, and we investigated the total reaction products by using AMS. To avoid confusion, we also deleted the first two sentences referring to HULIS in Section 3.7, as this section investigated OPs of total products not only HULIS.

l. 459/460: 'which can be explained by the transfer of electrons from 3C to O2 to form 1O2' – this is chemically wrong. Both O2 and 1O2 have the same number of electrons. Please clarify what you mean here.*

Reply: This sentence is now corrected,"The maximum consumed DO was found in $^3C*$-initiated oxidation, which might be explained by the consumption of O_2 that reacts with $^3C*$ form $^1O_2$ (R5)."

l. 826: 'Photolysis rate constants' only refers to the direct photolysis, not to the oxidation by OH. Please correct.

Reply: Thanks. Wrong use of this terminology is now corrected throughout the paper.

3) Methodology

l. 316 - 320: 'The optimum molar ratio of eugenol to quencher was chosen when the inhibition degree of eugenol degradation unchanged with the increase of added quencher' does not read well. I do not understand what you mean by 'inhibition degree' or 'inhibitory degree' in this context – they usually refer to enzyme reactions. Do you mean 'The optimum molar ratio of eugenol to quencher was selected such that the eugenol degradation did not change with the increase of added quencher'?

Reply: The use of "inhibition degree" or "inhibitory degree" is probably not accurate. The sentence should be read as you suggested, it is now changed.

l. 335 - 342: I do not understand this text. What contribution is calculated by Equation 5? Does it only refer to the reactions of 3C? What units does k and kROS have? It is not clear how the various contributions can add up to more than 100%. I understand it as follows: In the course of the reaction of the triplet state, other reactive species such as OH, O2- and 1O2 are formed. They all react with eugenol and thus contribute to its degradation. Thus, there are four contributions (3C*, OH, 1O2 and O2-) that cause the concentration of eugenol to decrease. If the full decrease were normalized to 100%, the sum of the four contributions should add up to these 100% - not more. Can you express your results in this sense? Or did I misunderstand Equation 5? If so, please clarify.*

Reply: Thanks for your comment. We have explained but not well why the sum of contributions might be larger than 100%. After a careful consideration, it is indeed not proper to call it "contribution" of ROS through equation (5). The calculation is only a reflection of the relative importance of that ROS, not an absolute contribution. The quenching test works as follows: We first determined the original rate constant with $^3C*$ (or OH) as k, then we added a quencher to completely scavenge a certain ROS, and determined a new k as k_{quencher}; the reduction of k (equal to (k-k_{quencher})) reflects the impact of that ROS on k; then (k-k_{quencher})/k can be used as an indicator of the relative importance of that ROS to oxidation. However, as we explained, addition of a specific quencher will remove the oxidation by a certain ROS, but on the other hand, the reactions via other ROS may be enhanced if compared to the one without that quencher; in this regard, the sum of calculated reductions (no longer called as "contributions") from all four ROS might not add up to 100%. To answer your question, the equation also refers to quenching experiments for OH-oxidation, and the units of k and k_{quencher} (k_{ROS} is no longer used) are both s^{-1} (the first-order rate constant). This is now made clear in the manuscript.

Figure quality:

Figure 3: I do not see much difference in this figure compared to the previous version. The insets still look blurry and are hard to read. I suggest moving them outside of the figures and making separate panels, the same size as the three panels a, b, c.

Reply: As suggested, the insets are moved outside and named separately as (d-f)

Figure 5: Please make the legend in panel a) larger or even move it out of the panels so that you can use a readable font size.

Reply: The legend in (a) is now enlarged so it can be clearly seen.

Captions of Figures 7 and 8: Please give more details in this figure caption. The legend of the figures shows 'direct', OH, and 3C - which are not conditions but refer to reaction pathways. The reader has to be able to understand what 'conditions' refers to.*
Reply: Thanks. The three conditions are now specified as "under direct photolysis, OH-initiated oxidation, and 3C*-initiated oxidation" in captions of Figure 7 and 8 (as well as Figure 1 and Figure 4, and relevant texts in the manuscript)

Figure 9: I do not understand the figure caption and the legend. The caption states (a) direct photolysis, (b) OH-initiated reaction, (c) 3C initiated oxidation. However, the legend in panel a) implies that all three processes are shown in panels a-c . Please also add a caption for panels d-f.*
Reply: Sorry for the mistake. (a),(b) and (c) before direct photolysis, OH-initiated oxidation and 3C*-initiated oxidation should be (d), (e) and (f), which refer to the f44 vs f43 plots for the three sets of oxidation experiments.

Scheme 1: I see only one text in red here: MW 164 Eugenol; all other text looks pink to me. It might be clearer to just say: "The compounds labeled by Product 1-9 are those identified by GC-MS (Table 2)."
Reply: The caption is changed to "The red text represents the precursor, and the compounds labeled by Product 1-9 are those identified by GC-MS (Table 2). "

II. Technical comments
l. 1: add 'and' – 'Optical and chemical properties ...'
l. 16: remove 'etc' – it is very vague and not very powerful as a first sentence of an abstract.
Reply: Done.

l. 21 – 23: Quenching experiments verified that ^{3}C indeed played a dominant role in 3C*-initiated oxidation, while O2•- generated was important for OH- initiated oxidation.*
*This sentence does not read well. It seems obvious that *C3 plays a dominant role in *C3 reactions. What do you mean by the second part of the sentence? - Do you imply that O2- is a main reactant with eugenol? Please clarify.*
Reply: Here is what we want to state, "During ^{3}C*-initiated oxidation, there are different reactive oxygen species (ROS) including ^{3}C*, OH, $^1O_2$ and $O_2^{\bullet-}$ that can participate in oxidation of eugenol, quenching experiments verified ^{3}C* was the most important one; while during OH-initiated oxidation, $O_2^{\bullet-}$ was a more important ROS than OH to oxidize eugenol."

l. 81: remove 'as'
l. 96: add 'which' : '..which had some similarities'
l. 120: remove 'too'
Reply: Done.

l. 125: Which ROS do you refer here to? You only compare OH and 3C reactions – OH is an ROS, 3C* is not.*
Reply: This sentence is deleted, as the content was in fact included in the previous sentence.

l. 149: add 'the' : '...at the bottom'
l. 153: add 'the': '...at the surface'
l. 165: remove 'the' before 'aluminum foil'
l. 209: replace 'blew' by 'blown'
l. 238: replace 'Products' by 'Product'
Reply: Done.

l. 258: Are there any other major factors beyond atomization efficiency and carrier gas flow? If so, list them, if not, remove 'etc'.
Reply: "etc" is removed.

l. 282: 'The lowest BDE was found for the O-H bond and C=C bond.' Is this a finding from your study or just repeating the information of the previous sentence? If the latter, it can be removed.
Reply: It is information from previous literature, and is now removed as suggested.

l. 290: in lines 280-282, you state that all BDEs are in the range of 340 – 403 kJ/mol. Thus, the photon energy of 412 kJ/mol should be sufficient to break any of these bonds. Please clarify.
Reply: Here what we want to state is that since the energies of 300 nm and 350 nm lights are 412 kJ/mol and 353 kJ/mol, both of these energies are higher than that of the weakest BDE of 340 kJ/mol, therefore both lights can lead to breakage of eugenol. It is changed to, "The energy of photon of 300 nm is 412 kJ/mol therefore is able to break all major bonds in eugenol, and the energy of 350 nm is 352 kJ/mol, being able to break some bonds in eugenol as well. Thus, eugenol can be easily decomposed after absorbing the photons. "

l. 301: 'Regressed' is not an English word to be used in this context. Change to 'first-order rate constants obtained based on Equation 1'
l. 331: What other oxidants are you referring to here? If none, remove 'etc'
l. 332: remove 'it
l. 353: do you mean 'quenching effect' rather than 'inhibitive effect'?
l. 443: Replace 'dramatically' by 'quickly' or 'significantly'
l. 447: replace 'likely ascribing' by 'which can be likely ascribed'
l. 447-449: 'Note a small amount of acids can change solution pH significantly when original pH is high, but cannot change pH remarkably when the original solution pH was low.'
This sentence does not seem necessary. Instead, I suggest starting the next sentence as 'Since the solution was acidic (pH = 3), we cannot rule out ...'
l. 465: replace 'dissolve' by 'dissolved'
Reply: Done.

l. 498: What does the addition of 'possibly linking with HULIS or oligomers' add to the content here?
Reply: It is now deleted.

l. 526: Please add a reference for the statement that HULIS are highly oxygenated.
Reply: "highly oxygenated" should not be used here.

l. 536: replace 'caveats' by 'caution'
l. 537: what do you mean by 'complicated'? I suggest removing.
l. 544- 546: ' EEM fluorescence spectra of HULIS from fog water are reported to have peaks

at shorter excitation and emission wavelengths than those of terrestrial fulvic acids (Graber and Rudich, 2006).' – This sentence seems out of place here. What does it contribute to the discussion here?
Reply: Done.

l. 549: Can you quantify 'a few' in this context?
Reply: It refers to small organic acids, and it was changed to "organic acids with a few carbon atoms" according to your suggestion in last time. Since we did not perform measurements of organic acids here, it is difficult to know their structures. But traditionally, they may refers to C1-C6 organic acids.

l. 579: This still adds to the confusion I had pointed out in the last round of reviews: Are you implying that HULIS cannot be high MW oligomers?
Reply: Very sorry if it is still not clear to you. What we want to say is that since high MW oligomers can be formed in the initial stage of oxidation, while HULIS concentration also quickly increase in the initial stage of oxidation as we observed here, so we imply that HULIS can be (*not cannot be*) some of the high MW oligomers. This is made clear in the text.

l. 610: 'simulated lights' is not correct. Do you mean 'light intensity' or 'wavelength' – or both?
Reply: should be both.

l. 641/2: 'As a result, all data points located outside the f44 vs. f43 space established by Ng et al. (2010) for ambient aerosols, owing to the relatively low f43 values.'
This sentence seems grammatically wrong; it is also not clear what you try to say.
Reply: It is now changed to, "As a result, all data points located outside the established f_{44} vs. f_{43} region (bounded by the two dash lines in Figs. 9d-f) by Ng et al. (2010) for ambient aerosols."

l. 725: Can you quantify the fraction of HULIS to total reaction products?
Reply: It is practically difficult to do so in this work.

l. 750: 'This finding further indicates the effectiveness of DTT method to represent OP.' Which finding do you refer to here? Isn't this a circular and redundant statement? – The DTT method was developed to quantify OP – thus, it seems obvious that it can used to do this.
Reply: This sentence is deleted.

l. 791: replace 'photolyze itself' by 'undergo direct photolysis'
l. 800: replace 'foil' by 'fuel'
Reply: Done

l. 801 – 803: 'Aqueous oxidation of 4-nitrophenol with OH can lead to a photobleaching effect too.' Nitrophenols are not comparable at all to the compounds you studied. There, the nitro group causes light absorption – thus this comparison seems out pf place and not relevant.
Reply: Agree. This sentence is deleted.

Data availability: Please deposit your data in a suitable repository according to the journal data policy https://www.atmospheric-chemistry-and-physics.net/policies/data_policy.html
Reply: As suggested, we have deposit the data at : http://nuistairquality.com/eugenol_data_and_figure