Response to comments

Dear Editor

Thanks very much for your comments regarding our manuscript. According to your suggestions, we have improved our manuscript by adding a separate section of "Atmospheric implications" to discuss the findings of this work, and re-wrote the whole conclusions. In addition, we have carefully read the manuscript and performed a thorough language check and made very substantial text changes to eliminate grammar mistakes and broken sentences (please see the manuscript with tracked-changes, and those you suggest in the technical comments below were marked yellow for reference). In particular, we have followed your suggestion to make the terminology consistently regarding the HULIS, aqSOA and oligomers (please also see the replies below). We sincerely hope that the new version now fits the high standards of ACP. Replies to your specific comments are listed below (with your comments repeated in *Italics*):

1) HULIS vs aqSOA vs oligomers

As I pointed out previously, not all aqSOA is HULIS and not all HULIS is aqSOA. Therefore, it cannot be used interchangeably. In addition also oligomers and brown carbon are separate products. While there might be overlaps between these compounds groups (aqSOA, HULIS, BrC, oligomers) they all different definitions and should not be used equally.

To clarify and simplify the terminology throughout the paper, I suggest using consistently 'products', 'reaction products' or 'aqueous-phase products'.

Reply： Thanks for pointing out this. We have carefully revised the paper to clarify the usage of these three terms, and followed your suggestions to use 'products', 'reaction products' or 'aqueous-phase products' instead throughout the manuscript.

l. 94: Did all three studies cited here indeed claim that the investigated reactions yield HULIS? Unfortunately, I do not have access to all of them; however, based on the abstracts, it seems to me that Smith et al., 2016 and Li et al., 2021 only refer to aqSOA or other products. Please verify the terminology in the original literature.

Reply： Yes, the HULIS and aqSOA are used inapporiately previously. We checked the literatures and Li et al. 2021 and Smith et al., 2016 did not direct refers to HULIS. The sentence is now changed to "Tang et al. (2020) reported that aqueous photooxidation of vanillic acid could be a potential source of HULIS."

l. 30 vs l. 247 vs l. 601 vs l. 633: While in the abstract you call it HULIS, in the experimental section, you call the products sometimes aqSOA, and sometimes HULIS. Please use consistently only one term (preferably 'reaction products') to avoid confusion.

Reply：We now use the term "reaction products" consistently to avoid confusion as suggested.

l. 437f: Here you refer to studies on HULIS in ambient particulate matter. The HULIS found in these samples are not (necessarily) originating from reactions as investigated in the current study. Therefore, your products (aqSOA) are not comparable to these ambient HULIS.

Reply： Agreed. This sentence and relevant literatures are now deleted.

l. 482: 'High molecular weight and conjugated structures' are also present in oligomers. Not all oligomers are HULIS. However, if these oligomers are formed by aqueous phase reactions, they can be termed aqSOA.

Reply： Agree. We have re-phrase this sentence, "The enhancement at 300-400 nm may point to products with high molecular weights and conjugated structures, likely relevant with HULIS or oligomers."

l. 550: Here you could simply delete 'of HULIS'.

Reply： Done

l. 554 – 560: This text is out of place here and would be redundant if you use 'products'. Also it incorrectly cites the review by Graber and Rudich. 'HULIS' is the acronym for 'HUmic-LIke Substances'. Therefore, the sentence 'So, we inferred most HULIS in this paper was humic-like substance rather than fulvic-like substance' does not make sense.

Graber and Rudich discuss that "HULIS relate to the water soluble fraction, which would include only the fulvic acid fraction of humic substances, and exclude the humic acid (base-soluble) and humin (insoluble) fractions of humic substances."

Reply： Agreed. The statement and interpretation with Graber and Rudich (2006) are indeed not appropriate. These text is now deleted.

l. 596: not all light-absorbing compounds are HULIS; and not all HULIS are light absorbing

Reply： Agreed. We have removed "HULIS".

l. 771: HULIS and brown carbon are not always the same.

Reply： Yes. "HULIS" is deleted.

2) Atmospheric implications

I suggest that you separate Section 4 into '4. Atmospheric implications' where you discuss more carefully the implications citing appropriate literature and 'Section 5. Summary and conclusions' where your study and the main conclusions for atmospheric implications are briefly summarized. The current, extended section 4 is too unstructured and it is not clear what it is a conclusion from your study vs previous studies.

Reply： We have added a new individual section, "4. Atmospheric implications" as you suggested. Please check the new manuscript.

The conclusions on the ranking of 3C vs OH reactions depend on the concentrations used in experiments or in the atmosphere, respectively. Therefore, please comment on the radical concentrations in your study. If you were unable to retrieve them, please add a general discussion on OH and *C3 concentration in atmospheric waters and how to relate your findings to such concentrations.*

Reply： **Yes. This is now discussed in the new section, "**Our study here used 300 μM H_2O_2 and 15 μM DMB as sources of OH and $^3C*$, and $^3C*$-mediated oxidation appeared to be faster than OH-initiated oxidation of eugenol. Of course, whether or not $^3C*$ is more important than OH in real atmosphere depends upon the concentrations of OH and $^3C*$. Herrmann et al.

(2010) estimated an average OH level of 0.35 x 10^{-14} M in urban fog water; Kaur and Anastasio (2018) measured $^3C*$ concentration to be (0.70-15) x 10^{-14} M, 10-100 times higher than OH in ambient fog waters; Kaur et al. (2019) determined both OH and $^3C*$ concentrations in PM extracts, OH steady-state concentration was 4.4(±2.3) x 10^{-16} M, similar to its level in fog, cloud and rain, while $^3C*$ concentration was 1.0(±0.4) x 10^{-13} M, a few hundred times higher than OH and nearly double its average value in fog. Therefore, together with these measurements, our findings indicate a likely more important role of $^3C*$ than OH in aqueous-phase (especially aerosol water) reactions. In addition, quenching experiments reveal that O_2 can inhibit eugenol degradation by effectively scavenging $^3C*$ radical while it can promote degradation by fostering radical chain reactions in OH-induced oxidation, which offer insights to control of reaction pathways by regulating the ROS generations; of course, such operation requires application of highly sensitive EPR method. ”

l. 296: What were the OH and 3C concentrations in the study by Yu et al. (2016)?*

Reply： The initial H_2O_2 and DMB concentrations to generate OH and $^3C*$ are 100 μM and 5 μM, respectively, which are the same ratio as those used in this work 300 μM H_2O_2 and 15 μM DMB). This information was added in the text now.

l. 328: Please report the concentrations of 3C, 1O2 and OH as used in the experiments by Laurentiis et al., 2013 and Misovich et al. 2021 to make this comparison to your study more solid.*

Reply： Thanks. We have re-wrote the sentences, “Previously, Laurentiis et al. (2013) reported that 4-carboxybenzophenone (70 μM) can act as $^3C^*$ and the photosensitized degradation was more effective than oxidants such as OH, O_3, etc. Misovich et al. (2021) investigated the aqueous DMB-photosensitized reaction (5 μM, same concentration as this study) also demonstrated that $^3C^*$ was the greatest contributor to phenol or guaiacyl acetone degradation, followed by $^1O_2$, while both OH and $^1O_2$ contributions were relatively minor.”

l. 778: How do you quantify ‘important’? How much mass of light-absorbing material is predicted to be formed from eugenol based on your experiments for atmospheric conditions?

Reply： We now deleted ”important”

l. 781 – 784: Small dicarboxylic acids are usually present to a large extent in particles and only evaporate to a small extent.

Reply： Agree. This sentence seems to be incorrect, at least for dicarboxylic acids. It is now deleted.

l. 797-806: The aqueous phase yields cannot be directly compared to gas phase yields because you have to calculate the fraction of the precursor that is present in either phase and scale the yields by them.

Reply： Agree. The arguments are now modified per your suggestion, and is incorporated into the new “Atmospheric implications” section

3) Previous work

l. 599: Huang et al., 2018 is not the only study that reported aqSOA yields from phenolic *compounds. There are several more, e.g. (Ma et al., 2021; Smith et al., 2014; Sun et al., 2010). Are the reported values similar? Please discuss.*

Reply： Yes. We have now cited more literatures, and discuss them accordingly. “The product mass yields obtained in this work overall agree with those reported previously for phenolic compounds. For examples, Huang et al. (2018) reported mass yields of 30-120% for syringaldehyde and acetosyringone; Smith et al. (2014) found that mass yields of aqSOA from three phenols with $^3C*$ were nearly 100%, and Ma et al. (2021) reported a yield ranging from 59 to 99% for six highly substituted phenols with $^3C*$; Mass yields of SOA from three benzene-diols were near 100% with both OH and $^3C*$ oxidants, as reported in Smith et al. (2015); Direct photolysis of phenolic carbonyls, and oxidation of syringol by $^3C*$, had SOA mass yields ranging from 80 to 140% (Smith et al., 2016)”

4) Technical comments

l. 113: please write it ‘eugenol (allyl guiacol)’

Reply： Done

l. 117: 1) ‘beech stove’ does not seem right here. Do you mean biomass burning of beech wood. ; 2) the study by Liu et al., 2019 does not report on new measurements of emissions; the only cite Bari et al.. Please remove Liu et al., 2019 here.

Reply： 1) Yes, we changed to “beech wood burning”; 2) Liu et al., 2019 removed.

l. 119: replace ‘compounds’ by ‘compound’

l. 123: ‘aerosol mass spectrometer’ should be ‘aerosol mass spectrometry’ to be consistent with the preceding list

l. 175: it should read ‘experiments were …’

l. 193: ‘Jenal’ should be ‘Jena’

Reply： Done

l. 221: Is ‘some time’ necessary here? Either remove ‘some time’ or quantify the time period.

Reply： We removed “some time”

l. 228: replace ‘for distinguish from At’ by ‘as blank value’.

Reply：Done

l. 279: Define BDE here

Reply： It should be “bond dissociation energies (BDEs)”

l. 286-88: This sentence does not read well. Replace by ‘When the photon energy is higher than the bond dissociation energy, chemical bonds can break, leading to 287 decomposition of compounds and possibly further mineralization.’

l. 296: remove ‘A’ at the beginning of the sentence.

Reply： Done

l. 302-4: In the headers you use ‘photooxidation’ while in the subsequent text, you use *'photodegradation'. Unless you mean two different processes here, I suggest using consistent terminology throughout the manuscript.*

Reply： Thanks. We use "photooxidation" consistently throughout the manuscript now.

l. 311: Do you mean 'Excess concentrations' instead of 'Above concentrations'?

Reply： Yes

l. 332ff: Write (k-kTMP)/k as an equation (as Equation (1) in l. 187) and define k and kTMP. Explain 'contribution' here – contribution to what?

Reply： Sorry this is not made clear previously. Now a short paragraph is added in the revised manuscript, "We propose to use the following Eq.(5) to estimate the contribution of a certain ROS (Ct_{ROS}) to eugenol degradation:

$$Ct_{ROS}=k_{ROS}/k=(k-k_{quencher})/k \qquad (5)$$

Here k_{ROS} is the rate constant contributed by the ROS, which is defined as the difference between the original rate constant in $^{3}C*$-initiated oxidation (k) and the rate constant ($k_{quencher}$) after the target ROS has been completely scavenged by its corresponding quencher. k and $k_{quencher}$ in fact refer to those reported in Fig. S1b. **"**

l. 339: either 'One should be cautious to apply' or 'It should be cautioned to apply'

l. 342: replace 'by' by 'be'

Reply： Done

l. 375-7: This sentence is not clear. Do you mean 'Since H2O2 was photolyzed at wavelength <300 nm to generate OH radicals, irradiation above 300 nm did not affect the reaction.'?

Reply： Yes, we have re-written this sentence as suggested.

l. 381: instead of 'shown later', refer to the respective section

Reply： Yes, it refers to Section 3.2.3, it is now made clear.

l. 391: Add 'conditions' (O2-saturated and N2-saturated conditions...)

Reply：Done

l. 394: Either write OH or ·OH. Both is ok but should be used consistently throughout the text.

Reply： We now use OH consistently throughout the text.

Figure 3 is of very low quality. Please provide a figure with higher resolution where the axis labels are clearer and less blurry.

Reply： Figure 3 is replaced with larger and higher resolution ones now.

l. 445: replace 'direct' by 'photolysis'

Reply： Done

l. 468: What do you mean by 'over photoreaction'? 'during the photooxidation'?

Reply： Yes

l. 468: replace 'slight' by 'light'
Reply： Done

l. 524/5: This sentence is not correct, both grammatically and scientifically. There are numerous oligomers from small organic compounds that do not have any fluorescent properties. Either delete this sentence or specify what oligomers you refer to.
Reply： This sentence is deleted now.

l. 536: What do you mean by 'small organic acid'? Small organic acids are usually referred to as acids with a few (1, 2, ..) carbon atoms. Is this what you mean?
Reply： Yes, we have now made it clear.

l. 537: Is this 'phenomenon' really 'unexpected'? It is well known that the organic content of ambient aerosol particles is composed of 1000s compounds from many different emission sources, gas phase reactions and condensed phase reactions. Thus, the fact that you do not see one particular peak in a spectrum upon the reaction of a single precursor is by no means 'unexpected'. The reference to Xie et al. 2016 seems therefore random and not appropriate in this context.
Reply： Agree. This sentence and the later sentence citing Xie et al., 2016 were both deleted.

l. 204 and l. 548: The header text is basically the same whereas the former is a method and the latter reports results. Please refine the headers such that they differ and appropriately describe the section content.
Reply： The later header text is now changed to "Characteristics of HULIS"

l. 587: replace 'yield' by 'yields', and 'value' by 'values'
l. 592: replace 'reason' by 'reasons'
l. 623: 'As we known' is grammatically wrong and seems redundant here. Replace by 'The'.
l. 632: Replace this sentence by 'The final f43 values were almost the same as compared to the initial solution'.
Reply： Done

l. 660: replace by 'based spectra from the NIST database [add reference!] and on the reactants and reaction conditions' – please check if the content is correct
Reply： It is correct. We have changed the sentence, and add a reference.

l. 662: replace 'dominate' by 'dominates' and complete the sentence. What is less important? '..functionalization dominates as compared to…'?
Reply： The sentence is re-phrased, "We also found 4-(1-hydroxypropyl)-2-methoxyphenol (product 8) was relatively abundant (Fig.S7), suggesting functionalization might be dominant as compared to oligomerization and fragmentation."

l. 671: What does this sentence refer to? Is it a footnote for the table, or where were eugenol and DMB also shown?

Reply： It is a footnote for the table, and refers to the “name” of identified compounds. We want to clarify that precursor eugenol and DMB are also listed in the table.

l. 745: ‘weaker’ than what? Why is the weaker correlation unexpected?
Reply： We changed to “weak”, and deleted “unexpected”, which is not appropriate.

l. 678: replace ‘undergo’ by ‘undergoes’
Reply： Done