

## **I. Major comments**

### **1) Atmospheric implications**

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

**I. 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.

**I. 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/](http://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:

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

For a typical cloud water content of 0.3 g/m<sup>3</sup> (=3e-10 L(aq)/cm<sup>3</sup>(gas)): X = 7.22e-6; for typical aerosol water contents of 50 µg/m<sup>3</sup>, X = 1.2e-10

The fraction in the aqueous phase can then be calculated as

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

Thus, the fraction partitioned into the aqueous phase ( $\varepsilon_{aq}$ ) for compounds of different Henry's law constants can be calculated for clouds and fogs

	LWC = 0.3 g/m <sup>3</sup>	LWC = 50 µg/m <sup>3</sup>
KH = 729 M/atm	$\varepsilon_{aq} = 0.005$	$8.7 \cdot 10^{-8}$
KH = 2.6e4 M/atm	$\varepsilon_{aq} = 0.158$	$3.2 \cdot 10^{-6}$

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., Environ 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.

**I. 780 - 784:** The liquid water content of aerosol water is about 10000 times smaller than that of cloud (~50  $\mu\text{g m}^{-3}$  vs 0.5 g  $\text{m}^{-3}$ ). 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.

**I. 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.

**I. 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'.

**I. 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.

## 2) Wrong terminology

I. 121, I. 196, I. 574, I. 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

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 I. 725 – but this assumption should be added earlier in the text.

I. 459/460: 'which can be explained by the transfer of electrons from 3C\* to O<sub>2</sub> to form 1O<sub>2</sub>' – this is chemically wrong. Both O<sub>2</sub> and 1O<sub>2</sub> have the same number of electrons. Please clarify what you mean here.

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

### 3) Methodology

I. 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'?

I. 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  $OH$ ,  $O_2^-$  and  $1O_2$  are formed. They all react with eugenol and thus contribute to its degradation. Thus, there are four contributions ( $3C^*$ ,  $OH$ ,  $1O_2$  and  $O_2^-$ ) 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.

### 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.

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.

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.

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.

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)."

## II. Technical comments

I. 1: add 'and' – 'Optical and chemical properties ...'

I. 16: remove 'etc' – it is very vague and not very powerful as a first sentence of an abstract.

I. 21 – 23: Quenching experiments verified that  $3C^*$  indeed played a dominant role in  $3C^*$ -initiated oxidation, while  $O_2\bullet^-$  generated was important for  $OH^-$  initiated oxidation.

This sentence does not read well. It seems obvious that  $*C_3$  plays a dominant role in  $*C_3$  reactions. What do you mean by the second part of the sentence? - Do you imply that  $O_2^-$  is a main reactant with eugenol? Please clarify.

I. 81: remove 'as'

I. 96: add 'which' : '..which had some similarities'

I. 120: remove 'too'

I. 125: Which ROS do you refer here to? You only compare OH and  $3C^*$  reactions – OH is an ROS,  $3C^*$  is not.

I. 149: add 'the' : '...at the bottom'

I. 153: add 'the': '...at the surface'

I. 165: remove 'the' before 'aluminum foil'

I. 209: replace 'blew' by 'blown'

I. 238: replace 'Products' by 'Product'

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

I. 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.

I. 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.

I. 301: 'Regressed' is not an English word to be used in this context. Change to 'first-order rate constants obtained based on Equation 1'

I. 331: What other oxidants are you referring to here? If none, remove 'etc'

I. 332: remove 'it'

I. 353: do you mean 'quenching effect' rather than 'inhibitive effect'?

I. 443: Replace 'dramatically' by 'quickly' or 'significantly'

I. 447: replace 'likely ascribing' by 'which can be likely ascribed'

I. 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 ...'

I. 465: replace 'dissolve' by 'dissolved'

I. 498: What does the addition of 'possibly linking with HULIS or oligomers' add to the content here?

I. 526: Please add a reference for the statement that HULIS are highly oxygenated.

I. 536: replace 'caveats' by 'caution'

I. 537: what do you mean by 'complicated'? I suggest removing.

I. 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?

I. 549: Can you quantify 'a few' in this context?

I. 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?

I. 610: 'simulated lights' is not correct. Do you mean 'light intensity' or 'wavelength' – or both?

I. 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.

I. 725: Can you quantify the fraction of HULIS to total reaction products?

I. 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 be used to do this.

I. 791: replace 'photolyze itself' by 'undergo direct photolysis'

I. 800: replace 'foil' by 'fuel'

I. 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 of place and not relevant.

**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](https://www.atmospheric-chemistry-and-physics.net/policies/data_policy.html)