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Interactive comment on “Aqueous-phase photochemical oxidation and direct photolysis of vanillin – a model compound of methoxy-phenols from biomass burning” by Y. J. Li et al.

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We thank Reviewer #1 for the suggestive comments. Below we address those comments point-by-point. Our responses are denoted by “R”. The original text to be changed is denoted by “O” and the changed text is denoted by “M”.

Reviewer #1

General impressions: This is a nice paper that will be valuable to the community and should be accepted after a few relatively minor modifications. The paper very nicely highlights the importance of particle phase chemistry on aerosol mass yields / compo-

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sition. Results suggest that a “one size fits all” approach falls short, and detailed understanding of cloud/fog water composition and photochemistry is important to predict the atmospheric fate and lifetime of molecules produced in biomass burning events. The paper could be improved by additional experiments on other model compounds within the same class, and additional efforts to oxidatively age aerosol produced under condition “B.” My suspicion is this experiment would result in a very similar pattern to “A.” In addition, the concentration of H₂O₂ in condition “A” appears to be far too high to really be interesting. The chosen conditions really represent “all” or “nothing” - that is the H₂O₂ concentration is so high that all of the organic will quickly decompose, or the concentration is so low that the other processes will be favored. In addition, the authors atomize an aqueous phase reaction mixture. While this is interesting, to a certain degree it eliminates the need for a AMS. Why not probe the chemistry of particles when they react in the aerosol phase and use the AMS to measure the particles? Heterogeneous phase chemistry may yield very different results. This is speculative, however, the authors have been provided with this fine measurement instrument to answer such questions.

R: The reviewer raised a few possibilities for further investigation. Specifically, the reviewer suggested four points for further experiments: a) to study other model compounds; b) to prolong experiments under condition (B) to see whether it results in a similar pattern as in condition (A); c) to study lower H₂O₂ concentration (although a misunderstanding may exist, see below); and d) to probe heterogeneous chemistry with suspended particles instead of aqueous solution. They are useful suggestions that are all interesting and worth exploring. For the current manuscript, we feel that it already involved a number of aspects including reactions, on-line/off-line characterizations, chemical information and hygroscopic property. We will consider these additional experiments for future studies.

Nevertheless, we will address Points a) – c), with necessary changes made to the revised manuscript, in the related specific comments later. We now address point d),

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i.e., heterogeneous chemistry, here.

Heterogeneous oxidation involves reactions between gas-phase oxidants (O₃ and OH etc.) and particle-phase organics. This is definitely an important process that would lead to changes of OA properties and even OA mass (decrease if oxidation forms more volatile products by fragmentation and increase if oxidation leads to functionalization only). To study heterogeneous oxidation of submicron organic particle and gaseous oxidants, an aerosol flow tube or a smog chamber would be needed. At the moment, we are not equipped with these facilities. On the other hand, the atomization coupled with AMS measurements in this study provided results useful in understanding cloud/fog evaporation. That is, some slightly volatile and slightly water soluble species such as vanillin can exist in aqueous droplets but would evaporate after drying. With aqueous-phase oxidation, however, the evaporative loss of this type of organics would be strongly reduced by forming less volatile products. This important feature cannot be revealed without measurements of organic in the bulk solution and real-time measurements of atomized and dried particles by the AMS.

Top of page 27646 – concentration of H₂O₂ – It lists 34.5 – 36.5 wt %. Is this correct? It seems this experiment is then somewhat dangerous, so I encourage the authors to include a section on safety measures. In addition, this is much, much higher than relevant atmospheric conditions. At such a high concentration of H₂O₂ it is not surprising most of the organic is quickly degraded - treatment with high conc. of H₂O₂ is a known wastewater treatment strategy and the literature on kinetics / mechanisms of organic degradation is very large. I feel that experiments at much lower concentration of H₂O₂ are warranted to better understand the chemistry of this system.

R: This might be a misunderstanding (related to point c) in the general expression above) due to our unclear statement. The 34.5-36.5 wt% is the concentration for the stock chemical as purchased. During the experiments, we used 11.8 mM (indicated in Table 1). We have included this concentration of H₂O₂ actually used in the experiments in the revised manuscript. Now the sentence reads as below.

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O: ... with or without H₂O₂ (Sigma-Aldrich, 34.5-36.5 wt%) ...

M: ...with or without 11.8 mM H₂O₂ (Sigma-Aldrich, 34.5-36.5 wt%)...

Page 27650, line 5-10. The authors discuss conditions A and B and draw conclusions regarding the OH mediated mechanisms vs direct photolysis of vanillin. Can the authors present a justification for this assumption? It seems the reality may be more complicated. For instance, is the 'branching ratio' H₂O₂ conc. dependent? Is OH generated during photolysis rxns? The authors later seem to allude to the fact that the conc. ratio may be important (bottom of 27659), so it seems this is important issue to clear up. Again, additional experiments in which the H₂O₂ conc. is varied could be quite valuable.

R: We respond to this comment in relation to point b) in the general impression above. For condition (B), we referred to a previous study (Anastasio et al., 1997) that a small amount of H₂O₂ might be formed during the direct photolysis of phenolic compounds. It was also our interest to see whether it is the case and attempt has been made to measure the H₂O₂ during reactions under condition (B). It was not successful, however, because the method for H₂O₂ measurement that we adopted (Allen et al., 1952) is a colorimetric method but light-absorbing materials formed under condition (B) interfered the detection. From the experiments, the H:C to O:C data in the Van Krevelen plot (Heald et al., 2010) do not show exactly the same trend for the first 60 min of (A) and the 3-hour experiments of (B), as shown in attached figure below. Without direct evidence, we do not want to go too far to speculate that condition (B) was just a slow version of condition (A) with lower concentrations of H₂O₂ (thus lower concentrations of OH).

We referred to OH oxidation under condition (A) and direct photolysis under condition (B) in a relative term. Under condition (A), photolysis of H₂O₂ and vanillin occurred simultaneously. But photolysis of H₂O₂ generated a high concentration of OH radicals, which are responsible for the fast vanillin oxidative decay (Figure 4 in the manuscript).

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Under condition (B), even if a small amount of H₂O₂ was generated and OH oxidation contributed partially, the main pathway was still photolysis. At least it was photolysis of vanillin that triggered the radical formation for further reactions. The observation that high vanillin/H₂O₂ ratio in a trial experiment also led to yellow coloration hints that a competition between polymerization (leading to highly conjugated and high-molecular-weight products) and fragmentation (leading to small oxygenates). Again, we do not want to speculate on whether there is a “branching ratio” between these two pathways based solely on results from a trial experiment.

Varying H₂O₂ concentrations for condition (A) is a topic that worth exploring but for current study, we only use one concentration to demonstrate the reactivity. Further study would be needed for more detailed study on the dependence of the reactions on H₂O₂ concentration.

General comment – it would be nice if authors could pursue measurements on other phenolic compounds produced in biomass burning. With only one model compound, it is not clear if results should serve as guidance for the entire class of materials or just vanillin.

R: This is related to point a) in the general expression above. It is definitely worthwhile to try more on methoxy phenols with similar structure and we plan to do so in future studies. As we noted in the last paragraph of the manuscript (Page 27660), the choice of vanillin is just to demonstrate reactivity of this class of compound and results may be different for other methoxy phenols.

General comment: the authors consider cases A (with H₂O₂) and B (without H₂O₂). Several times, they refer to the “final” product or the “final” condition of the experiment when comparing cases. Is it possible that data shown in figure 3B or 2 for that matter would begin to appear very similar to case “A” if sufficient oxidative aging occurred? As a general theme, it seems to be important how we define “final” condition with regards to aerosols in Earth’s atmosphere. Are the results here simply suggesting the aerosol

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of case “B” simply has not experienced the oxidative aging case “A” has? It seems to me this is the case.

R: We have modified it to correctly reflect the products (or other properties) at the highest organic mass or highest O:C ratio (60-80 min). This is because we believe that the first 40-60 min of reactions under condition (A) may be more relevant to atmospheric conditions (see discussion in Section 4). Some changes are made accordingly as follow.

Page 27651, line 23

O: ... under these two conditions indicate that the final products that retained in the particle phase formed under these two conditions were substantially different.

M: ... under these two conditions indicate that the retainable products observed were substantially different.

Page 27652, line 20

O: Therefore, the final organic products that retained in the particle phase under condition (B) are believed to be less oxygenated than those under condition (A). M: Therefore, the organic products that retained in the particle phase at the time of highest O:C ratio under condition (B) (~3 hours) are believed to be less oxygenated than those under condition (A) (~80 min).

Page 27659 line 21 – the work cited (Chang and Thompson) would clearly be of relevance to this study, however they did not report observations of brown carbon in ambient samples. Their conditions seem to be somewhere between case A and B reported here.

R: Agreed. A more relevant reference (Andreae and Gelencser, 2006) has been cited here.

Figure 2 - a major point of this paper is that differences exist between case A and B.

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Can you enlarge the mass spectra of figure 2 in an attempt to really make this point? Addition discussion in the text is also warranted.

R: Figure 2 in the manuscript has been enlarged. A more detailed discussion is provided at the end of Section 3.1 as below.

M: The differences in the evolution of mass spectral features under these two conditions indicate that the retainable products observed were substantially different within the experimental time scale of 3 hours. The disappearance of high-molecular-weight ions and emergence of ions representing small oxygenates (e.g., CO^+ and CO_2^+) under condition (A) suggested that fragmentation might dominate over functionalization. Fragmentation was very likely via ring-opening pathways, leading to the formation of carboxylic acids which generated high intensity of m/z 44 (CO_2^+) in AMS mass spectra. Under condition (B), on the other hand, the preservation of the methoxy-phenolic structure was evidenced by the presence of m/z 137 ($\text{C}_7\text{H}_5\text{O}_3^+$). Reactions might have proceeded mainly via functionalization with the ring retained. Note that even under condition (B), the intensities of high-molecular-weight ions decreased but those of m/z 18 and m/z 44 increased too, which suggested that fragmentation has occurred, albeit at a less extent than that under condition (A).

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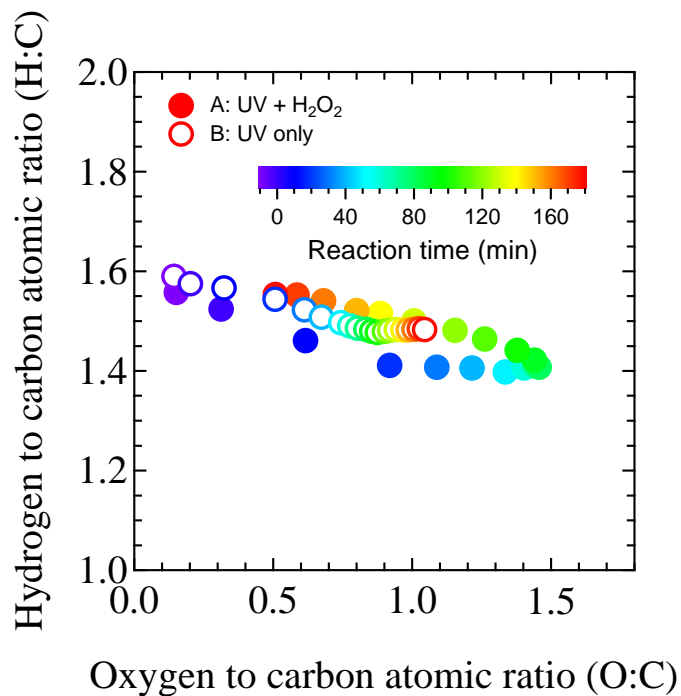
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