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Interactive comment on "Secondary organic aerosol formation and composition from the photo-oxidation of methyl chavicol (estragole)" *by* K. L. Pereira et al.

Anonymous Referee #1

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This work reported the SOA composition from the photooxidation of methyl chavicol. Experiments were performed in the European Photoreactor chamber. Two experiments with VOC:NOx ratio of about 5:1 were conducted. The gas-phase composition was monitored using PTR-MS. Aerosol samples were collected using PILS and analyzed with HPLC-ITMS, HPL-QTOFMS, and FTICR-MS. In total, 59 compounds were detected and the structures of 10 compounds were identified. The O:C of the compounds was between about 0:3-0.6, spanning a wide range of volatility (from IVOC to LVOC). A mechanism for the formation of 5 of the identified compounds was proposed.

I think the analysis were carefully conducted and the conclusions were well-supported

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by the data. My main comment is that the authors should provide more justifications/discussions in terms of the relevance of the results from this study to ambient conditions regarding 1) aerosol loading, and 2) VOC:NOx ratio (or, more precisely, the fate of RO2 radicals).

The SOA mass formed in the two experiments in this study were 126 and 430 ug/m3, respectively. These are very high mass loadings. With a higher aerosol loading, partition theory governs that more semi-volatile species will partition into the particle phase. What is the typical aerosol loading in places where there is a high emission of methyl chavicol such as the Malaysian Borneo? If the aerosol loadings at these locations are not that high, the authors need to justify how the compounds identified in this study are relevant in the atmosphere (i.e., is it possible that some compounds identified in the current study would not be present in the ambient SOA where the loadings are lower?). I understand that at times higher loadings are needed for analysis due to instrument sensitivity; nevertheless, the loadings in this study seem excessively high. The authors should address this in the revised manuscript.

The VOC: NOx ratio used in this study is about 5:1. The authors should comment on why this VOC:NOx ratio was chosen. Fundamentally, it is not the VOC:NOx ratio that governs the SOA yields and aerosol chemical composition (experiments can have the same VOC:NOx ratio but drastically different SOA yields and composition), instead, it is the fate of the RO2 radicals that matters. In the current study, it appears that most SOA is formed after [NO] approached zero, and, as the authors noted, RO2+RO2 dominated from then on. Could the authors comment more specifically on the relevance of the results from this study in terms of the fate of RO2 radicals in the chamber experiments vs. ambient conditions?

Overall, I think the manuscript is well-written. Apart from these comments, I summarized the more specific comments below. I recommend the manuscript to be published once the authors address all of the comments. Specific comments:

1. Page 33106, line 15. The authors wrote "The SOA yield was determined as 18-29% depending on initial precursor (VOC: NOx) mixing ratios". As only two experiments were performed, I think it is more appropriate to note that the yield was 18% and 29% for an initial VOC mixing ratio of 460 and 212ppb, respectively. (instead of reporting a range of SOA yields). Further, I think the "VOC:NOx" should be deleted as they did not systematically vary this ratio (the VOC:NOx ratio was about 5:1 for both experiments).

2. Page 33109, chamber experiments. What was the source of OH in these experiments? From ozonolysis of methyl chavicol? The results of this work were presented as "oxidation products from OH + methyl chavicol reaction". It appears that there was a substantial amount of ozone formed in the experiments (Figure 1). How can be authors be so sure that the oxidation products are not from ozone + methyl chavicol reaction? Based on the reaction rate constants for OH + methyl chavicol vs. ozone + methyl chavicol, can the authors show that the OH + methyl reaction dominates over the ozone + methyl chavicol reaction in their experiments? Please include this information in this revised manuscript.

3. Page 33115, line 1. A higher SOA yield for a higher initial VOC experiment (hence higher delMo) is expected from the partition theory (yield curve). Odum et al (1996) and Pankow et al (1994) would be more appropriate citations.

4. Page 33115, line 9. What are some possible reasons that the number of compounds identified in the high MC and low MC experiments is different?

5. Page 33116. The authors noted that compound 1 was detected in the first PILS sample (shortest reaction time). What reaction time did this correspond to? Can they provide more info regarding when (how long into the reaction) the other products were detected? From the proposed mechanisms, it seems compound 1 was at least a third generation oxidation product and it would be surprising if it was observed before the first or second generation oxidation products.

6. Page 33123, line 4. The difference in SOA yield between the nucleation experiments

here and those in Lee et al. is unlikely a result of the acidity effect (Czoschke et al., Gao et al., Jang et al., Zhou et al.) since only ammonium sulfate seeds were used in Lee et al. The difference might arise from the seed effect discussed in Kroll and Seinfeld (ES&T, 39, 2005).

7. Page 33123, line 10. The HC/NOx ratio for the methyl chavicol experiment in Lee et al is 0.8, not 8. (note that Lee et al used ppbC: NOx, not ppb:NOx, also see the relevant experimental info in Ng et al, 2006).

8. Page 33123, line 15. Note that Lee et al used ammonium sulfate seed, which was different from the ammonium sulfate + sulfuric acid seed used in the "acid seed" SOA literature.

9. Page 33123, line 24 onwards. The authors should include these gas-phase products in Figure 4 (and perhaps put them in a dotted box) to provide the readers a better context regarding how gas-phase oxidations lead to the formation of the proposed products in the particle phase. Currently, it is not clear how these 4 compounds fit into the mechanisms proposed in Figure 4.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 33105, 2013.