

## ***Interactive comment on “Molecular composition of aged secondary organic aerosol generated from a mixture of biogenic volatile compounds using ultrahigh resolution mass spectrometry” by I. Kourtchev et al.***

### **Anonymous Referee #3**

Received and published: 8 April 2015

The manuscript by Kourtchev et al. examines changes in the molecular composition of secondary organic aerosols (SOA) aged under different conditions in a simulation chamber. Chemical characterization of SOA extracted from filters into a solvent was performed using high-resolution mass spectrometry combined with soft electrospray ionization. The most interesting aspect of this study is that SOA ageing was performed in the chamber rather than in solution. Chemical characterization of SOA using high-resolution mass spectrometry provides an opportunity to distinguish molecular-level differences in the chemical composition of SOA aged under different conditions. How-

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ever, some aspects of the experimental design should be improved prior to publication. In addition, the authors should ensure that they give proper credit to other groups working in this field of research.

In this study, SOA of a ternary VOC mixture (α-pinene, β-pinene, γ-carene, and isoprene) was generated under dry (RH 9%) conditions. In a previous study, the authors described the molecular composition of SOA produced by ozonolysis of the same VOC mixture whilst under much higher RH (~60%). It would make sense to present a comparison of the effect of RH on the chemical composition of SOA. The authors find that, under dry conditions, the chemical composition of SOA does not change much upon ageing with UV irradiation and relatively minor changes are generated following ageing with OH radicals. Previous studies focused on photolysis of aqueous SOA (aqSOA) showed that UV irradiation causes significant changes in the chemical composition of aqSOA in particular in the oligomeric region. These studies not currently discussed in the manuscript should be added to discussion. The differences between the results reported in this study and previous aqSOA ageing under UV irradiation indicate that the presence of water plays an important role in the ageing processes of SOA. It is reasonable to assume that chemical ageing of SOA under higher RH of ~60% could yield very different results. It is therefore important to present experimental data for SOA ageing under higher RH conditions.

For comparison with the results presented for SOA generated from the VOC mixture, the authors examined O<sub>3</sub> and OH oxidation of α-pinene. However, these experiments were performed under substantially higher RH (~55%) conditions and hence cannot be directly compared with the results obtained for the VOC mixture. Once the authors add the data for the higher RH ageing of the VOC mixture SOA, this comparison will become much more meaningful. A recent paper by Nizkorodov et al. is relevant to the discussion of the chemical composition of α-pinene SOA produced using O<sub>3</sub> and OH oxidation chemistry (J. Phys. Chem. A, 2015, 119, 2594).

Additional characterization of SOA was performed using LC/MS. Surprisingly, only few

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compounds were separated in LC/MS while the oligomer mixture eluted as an unresolved hump, which undermines the purpose of this experiment that was designed to overcome signal suppression in direct infusion electrospray. Nevertheless, LC/MS analysis enabled quantification of 5 compounds in SOA (figure 7) and 21 compounds were tentatively identified. However, it is not clear how this identification was performed. The authors should provide a more detailed description of the quantification approach.

I found literature citations rather unbalanced and biased towards authors' own research. There is a body of related work by other groups that has been completely left out. As mentioned earlier, photolysis of aqSOA has been studied using high-resolution mass spectrometry. The molecular composition of SOA has been studied by several groups using high-resolution mass spectrometry. Oligomer formation has been discussed in numerous papers few of which are cited while several key articles have been left out. I am particularly surprised that the EST 2004 paper by Tolocka and Johnston has not been cited.

The use of the term "ultrahigh resolution" is misleading. "High-resolution mass spectrometry" is a stable term that adequately describes the experimental approach used in this study.

p. 5362 line 12. A relevant comparison of the field-collected and laboratory generated SOA was presented by O'Brien et al. JGR 2013.

p. 5362 line 18. "reaction times are significantly shorter" – and concentrations are substantially higher than in the atmosphere, which may affect the chemical composition (Shilling et al. ACP 2009).

p. 5362 line 26. Unbalanced citations: a lot more work has been done in this area.

p. 5363 line 4. Unbalanced citations.

p. 5363 line 13. Unbalanced citations.

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p. 5364 line 16. "concentrations exceeded those observed at the Finnish site" – please, be more specific. How much higher concentrations were used? What is the potential effect of VOC concentration on SOA composition?

p. 5364. Please, specify the RH.

p. 5365 line 1. Why is it important to mention the photolysis frequency of NO<sub>2</sub>?

p. 5365 line 23. Why were  $\alpha$ -pinene oxidation experiments conducted at much higher RH? How may this affect the observed molecular composition?

p. 5366, bottom. What was the mass of collected SOA?

p. 5366 line 24. Extraction into 15 mL of solvent results in significant dilution. Depending on the mass of collected SOA this may or may not be a problem.

p. 5366 line 24. Methanol is not the best solvent for SOA analysis as it reacts with carbonyl groups as shown previously by several groups. How do the authors know that their results are not affected by reactions between methanol and SOA compounds?

p. 5367. How were blank samples collected?

p. 5367 middle. Additional experimental parameters (e.g. high voltage, inlet temperature, gas flow, sample flow rate, etc.) should be specified.

p. 5368. Please, explain how blank samples/spectra were acquired and subtracted from the analyte spectra.

Figure 1 shows only species containing C, H, O. The authors should show all the observed peaks in Figure 1 and comment on the reproducibility between replicate experiments (replicate spectra should be shown in the supporting information). A table containing all the observed peaks (both assigned and unassigned), their experimentally measured m/z values, formula assignments, and OSc values should be provided in the supporting information. The y-axis in Figure 1 corresponds to the relative abundance of individual peaks in the spectrum. The most abundant peak in the spectrum

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should correspond to 100% on the y-axis. It is not clear from the figure which of the peaks is the most abundant as the y-axis is trimmed to ~25%.

p. 5369 line 8. Unbalanced citations.

p. 5370 line 1. This statement is not supported by the data. An alternative explanation is that reactions with O<sub>3</sub> and OH generate different products with different reactivity.

p. 5370 line 3. How large is the data set?

p. 5370. Please, explain the physical meaning of "carbon oxidation state". A few examples explaining low, high, and close to zero values of carbon oxidation state would be helpful.

p. 5371 line 8. It is not clear how understanding a-pinene oxidation may help explain the shift in OSc. It would be much more logical to examine the chemical composition and ageing of SOA produced from the individual VOCs and aged (a-pinene, b-pinene, g-carene, and isoprene) under the same experimental conditions used for the VOC mixture. However, the experiments with a-pinene described in this study were conducted under very different conditions and the reported results may not be directly relevant to the results described on the first part of the paper. It looks like this experiment was not very well thought through.

p. 5371 middle. The observation that OH oxidation and ozonolysis of a-pinene generate very different distribution of dimers is very interesting and requires a more detailed mechanistic explanation.

p. 5372 line 5. I could not find the paper by Rohrer et al, 2005 on the cited literature list.

p. 5372 line 17. "tentatively identified peaks" – please, explain the identification process.

p. 5372 line 25. "most of the detected compounds have been previously observed" –

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this statement requires unambiguous identification of the observed compounds. The only statement that can be made with confidence is that most of the molecular formulas have been previously observed.

p. 5373 line 4. LC/MS is usually characterized by a substantially higher dynamic range than direct infusion ESI. It is not clear why in this study LC/MS detected only a small fraction of molecules observed in direct infusion mass spectra.

p. 5373 line 16. Please, list the exact m/z values. Were these species also observed in direct infusion experiments?

Figure 4. It looks like some peak intensities are saturated in the figure. This gives a wrong impression of the overall appearance of the spectrum.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 5359, 2015.

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