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Comment

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 #1

Received and published: 26 March 2015

The manuscript presents new results on the molecular composition of monoterpene SOA analysed by both direct injection ultrahigh-resolution mass spectrometry (UHRMS) and liquid chromatography coupled to UHRMS. The results should be interesting to a broad audience of atmospheric scientists and have implications to our understanding of formation and ageing of organic aerosols.

The title “Molecular composition of aged secondary organic aerosol generated from a mixture of biogenic volatile compounds using ultrahigh resolution mass spectrometry”

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does not precisely describe the work, since both fresh and aged SOA are analyzed. Furthermore, it almost says that SOA are being generated using UHRMS. I suggest changing the title to better reflect the main findings of the manuscript.

Generally it is confusing to the reader that the results from two different chambers and types of experiments are divided according to the analytical method, especially since the chamber and experiment is sometimes not clearly stated in the text. This also means that the experiments are discussed twice in different sections. The best solution would be to change the structure to be according to the type of experiment instead of analytical method. The second best solution is to more clearly state, which experiment is being presented or discussed.

The ageing experiments were conducted at very low RH (<9%). The authors must comment on the influence of low RH on the diffusion times inside particles and reactivity of the aerosol towards oxidants, citing recent findings on this important topic.

Page 5362 line 6: To say that the molecular composition of fine PM is “largely unknown” seems like a very bold statement, which I would suggest to modify or you must at least provide references.

line 12-15: This statement needs further references to be valid. Kroll et al., 2011 refers to one paper from a remote area (Amazonas).

Page 5363 line 14-15: Did these previous studies claim that the dimers observed by LC/MS represent the large number observed by direct injection?

Experimental. A number of important details are missing. These include:

- calculated or measured concentrations of OH during ageing (CESAM) and SOA formation experiments (CRAC)
- concentration of seed aerosols
- concentration of ozone in CRAC study for both ozonolysis and OH experiments

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- concentrations of NOx
- details of filter pack sampler and denuder (such as brand)

Table 1: Please specify in the caption that these conditions are for the formation of SOA, not the actual ageing experiments.

Page 5371: Line 24 and 26: Please specify what you mean by “photolysis reaction” and “OH photolysis reactions” -> probably OH reaction or oxidation.

Page 5372 line 5: The reference Rohrer et al., 2005 is missing from the list of references, which makes it difficult to check if the statement is valid.

Page 5373 Line 12-13: Please describe more clearly how “both pinonic acid and MBTCA could be used to monitor the evolution of the OH radical initiated ageing of the SOA”.

Line 25: Please provide a reference to the statement that pinic acid is a less important product from OH oxidation of alfa-pinene.

line 26-> line 2 next page: It is unclear whether you are discussing the results of the present work or speculating about previous studies.

The chromatographic conditions applied here do not seem to provide adequate separation of individual compounds (Figures S1 and S2). It is well known that the ESI technique can form dimers in the ion source. The authors must describe how they excluded this as a source to dimers and oligomers observed in the direct injection analysis as well as the LC-UHRMS analysis, where they averaged the complex mass spectrum over 12 minutes LC run time.

What were the relative levels of the previously observed dimers (MW 358, MW 344, MW 368 and MW 388) in the SOA samples from ozonolysis and OH-initiated oxidation of alfa-pinene?

Figure 7. It is not clear to the reader why these specific compounds were chosen for

the figure. Please describe the reasons for this. Why was only one dimer selected, when you observed many more?

Please change the caption in Fig. 7 to list the compounds in the same order as in the figure.

Is "dark ageing" with exposure to ozone? Please state this in the caption of Fig. 7.

The section about the results (page 5374) need some clarifications and corrections:

- line 12 OH radical initiated oxidation product of alfa-pinene -> should be pinonic acid
- line 16 and 20: During the dark ageing exposure -> do you mean ozone exposure of SOA?
- line 18: SOA exposure -> do you mean ozone exposure of SOA?

Table S2: In the caption, please describe what was tested and how.

The symbols in Figures 2, 3, 5 and 6 are too difficult to distinguish. I suggest changing one of the symbols to something smaller.

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

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