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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Towards closing the gap between hygroscopic growth and CCN activation for secondary organic aerosols – Part 3: Influence of the chemical composition on the hygroscopic properties and volatile fractions of aerosols" *by* L. Poulain et al.

Anonymous Referee #2

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I have to start by offering a sincere apology to the authors and to the editor of this manuscript for taking a shamefully long time in completing this review.

This manuscript presents results of the investigation of the influence of varying levels of water mixing ratio on hygroscopicity, volatility and chemical composition of secondary organic aerosols (SOA) generated from the dark ozonolysis of alpha-pinene in a continuous flow reaction chamber. The presented results clearly show that the parameter

k –a proxy for the hygroscopic properties of the SOA- increases with increasing levels of water vapour concentrations inside the chamber and the same is true for the volatile fraction remaining at 100 degrees C. In other words, higher water mixing ratios lead to the formation of more hygroscopic and more volatile SOA under the conditions of this study. The manuscript has potential for publication in ACP, however, not before the following issues are clarified and addressed by the authors.

Main comments:

My main issue with this manuscript is the lack of convincing evidence from the AMS data to prove that a) m/z 44: total organic ratio changed between wet and dry conditions (Fig 5) and b) varying levels of water mixing ratios lead to chemically different SOA (Figs 6 and 7). This is mainly due to the lack of proper discussion of the errors associated with the AMS measurements of m/z44: total organic. In other words: is a change from 9.2% to 10% (Fig 6) significant enough to conclude a change in the chemical composition of the SOA?. In order to establish these points, the authors should explain how they derived the error bars in Figs 5, 6 and 7 and state what change is considered significant enough to prove or disprove these conclusions.

Detailed comments:

Page 16685, line 10: the manuscript should refer to “less” and “more” volatile fractions of the SOA and avoid using the term “non-volatile” given that the measurements are performed using an aerosol mass spectrometer which is not technically capable of detecting this fraction of aerosols. This should be applied throughout the manuscript when findings are linked to AMS measurements.

Page 16685, line 19 & Page 16694, line3: the CO2+ fragment is a proxy for di- and poly-carboxylic acids and also oxygenated mono-acids (e.g. oxo- carboxylic acids). Mass fragment 44 has not been shown to arise from mono-carboxylic acids.

Page 16687, line13-16: the scope and objectives of the paper should be expressed in

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a bit more detail.

Page 16687, line 25 and page 16688, line2: The experimental procedures are not entirely clear and require more elaboration. It was first mentioned that an excess of the VOC is used with controlled levels of ozone. This was followed by the detail that the ratio of 2-butanol to alpha-pinene was set to 10:1. The concentrations of alpha-pinene and 2-butanol should be clearly stated.

Page 16689, line 22 to Page 16690 line 7: The text describing the AMS is not really required and should be omitted. I believe it is adequate to mention the type of the AMS used along with the appropriate references (as already done by the authors). The vaporiser temperature should be mentioned.

Page 16692, section 3.1.2: How can the lack of change in SOA density as a function of water mixing ratio be reconciled with the changes in hygroscopicity, volatility and chemical composition under the same conditions? Does this imply the density is independent of chemical composition? This deserves to be briefly discussed.

Page 16692, line 17 – 18: Figure 3 should include thermograms form other wet experiments (e.g. 10a and 10d given that they have similar conditions except for the water mixing ratio).

Fig 4: The data point which correspond to exp 9-b is missing from this plot. Why?

Page 16694: the procedure and conditions under which the data discussed here and shown in Fig 5 are not clear! Which experiments do they correspond to?

Page 16694, line 27 -28: should be “further increase in k did not lead to a measurable increase in this ratio”

Page 16697, line14 – 16: The figure indicates that the second CI leads to the formation of pinonic acid only not pinonaldehyde as mentioned in the text!

Page 16698, 14-16 (conclusions): The manuscript currently reads “The values of these

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ratios after heating the sample to 100 degree C showed that the most oxygenated compounds (CO+2) were more volatile at 100 degree C than were the less oxygenated ones (CHO)". The discussion of this point in the manuscript was a little confusing and should be clarified. Should it not be "less" volatile not "more"?

Minor comments:

Page 16686, line 11: replace "than" with "to" Page 16689, line 6: rearrange to ".. it simultaneously provides. . ." Page 16692, line 24 and in other places in the manuscript: "photo-oxidation" instead of "photolysis" Page 16710: Re-write the captions for Fig 5. It is not clear.

Final comment (out of personal interest): Table 1 shows that O3 levels up to 2.5ppm were used in the experiments. Did these rather high levels of O3 cause any problems to any of the instruments used for sampling?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 16683, 2009.