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.

<u>Main comments:</u>
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.

<u>Author response:</u> In this study, AMS was working with a 1 min time resolution and sampling at each temperature for 15 to 20 min. The results given in this paper correspond to the average of the AMS measurements at each temperature. Error bars correspond to the standard deviation of the data during the sampling time. When a ratio was determined from the data, the error bars were estimated according to the classical propagation error calculation:

$$\frac{d(m/z44/org)}{m/z44/org} = \frac{\mathrm{d\ m/z44}}{\mathrm{m/z\ 44}} + \frac{\mathrm{d\ org}}{\mathrm{org}}$$

We added in the text: “Data were then averaged for each experimental condition. In the following, error bars represent the experimental uncertainties estimated for each condition by the standard deviation and according to the classical propagation error calculations for ratios”.

Ozonolysis of α-pinene lead to formation of C10 and C9 compounds with one or more aldehydes and organic acids functions (pinonaldehyde, norpinonaldehyde, pinonic acid, pinic acid, norpinoninc acid …) as well as smaller organic compounds. Induced modifications of the SOA chemical composition by the presence of water during the ozonolysis procedure correspond to changes between different oxidation pathways which will directly contribute to the changes on the volatility and hygroscopic properties of the particles. With the setup used during this work, we can not determine the exact chemical composition of the generated SOA; AMS provided information of the bulk of the SOA. Moreover, the ionization source of the AMS induced a high fragmentation level of the organic compounds. For this reason, modification of the molecular weight of the molecule by example can not be measured.

However, modification of the bulk composition can easily be measured using the oxidation level of the SOA as we did using ratio CO_2^+/CH and ratio CHO/CH. For this reason, we can say that we have modification of the ratios when it is in agreement with the measurement uncertainties.

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.

Author response: We changed non-volatile to less volatile in the text.

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.

Author response: It is true that Takegawa et al. (2007) reported the contribution of selected dicarboxyilic and ω-Oxocarboxylic acids to the AMS mass fragment m/z 44. However, they also reported that their selected organic acids can not explain the whole m/z 44 measured during field campaign and suggested that: "the rest of the signal of m/z 44 may have originated from mono-/poly- carboxylic acids and perhaps from peroxides because these compounds could produce CO_2^+ in the vaporization and ionization processes of the AMS". Nevertheless, we changed in the text "mono- and polycarboxylic acids" to "different kinds organic acids".

Page 16687, line13-16: the scope and objectives of the paper should be expressed in a bit more detail.

Author response: The text was changed to "In our previous papers (Petters et al., 2009; Wex et al., 2009), we were focused on the determination of the hygroscopic properties of the generated SOA, particularly on solving the issue regarding the generally observed low hygroscopic growth but rather high cloud droplet activation potential for SOA. In this third paper, we will focus on the induced modification of the SOA chemical composition by water vapour and how this variation on the chemical composition can be correlated with the observed deviation of the SOA volatility and hygroscopic properties".

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.

Author response: As we also answer to the reviewer 1, a detail description of the experimental setup can be found in our previous paper (Wex et al., 2009). "The α-pinene vapor was generated by injecting a liquid flow of α-pinene, controlled by a microliter peristaltic pump into a stainless Swagelok tube, fitting reducer (SS-200-R-2) where it evaporated into 5-10L min-1 of dry hydrocarbon free synthetic air. (…) In the absence of chemical reactions, α-pinene concentrations were in excess of that of ozone, i.e. < 1 ppmv. So the amount of VOC that reacted was controlled with the ozone concentration". Therefore, the SOA only depended on the ozone concentration, which was measured during all experiments. This was added in the text.

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.

Author response: As suggested by the reviewer we reduced the AMS description as "briefly the AMS allow two alternative detection modes to generate the particle size distribution (PTOF mode) and the chemical composition of the particle (MS-mode). Before detection by the time of flight mass spectrometer, the particles are flash vaporized by impaction on a heated surface (600°C) and the vapors are ionizated by an electron impact ionization source at 70eV."
During our experiment the AMS vaporizer was working at 600°C (the most common temperature used) as It was noted in the AMS description during these experiments (p16690 line 4: "the particles are vaporized by impaction on a heated surface (600°C)".

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.

Author response: The AMS is not able to provide real chemical composition of particles and chemical information obtained is more correlated to the aerosol bulk composition, as we explained previously. Moreover, water induce changed in the oxidation mechanism modified the ratio between the different reaction products which contribute to observed change on the physical properties. However, using our setup it is difficult to correlate these modifications with variation on the SOA density. As wrote in the text, error in the density estimation method is around 10 % (Bahreini et al., 2005) which corresponding for an effective density of 1.40 an error of +/- 0.14. Then, obtained effective density in dry condition are included on the error range of the wet conditions. For these reason, it is not easy to observe a clear water dependent of the generated α-pinene SOA effective density.

Text was changed by: "If the presence of water during the α-pinene ozonolysis can induce modification of the physical properties of the generated SOA (Petters et al., 2009; Wex et al., 2009); changed in effective density are too small to be detected in our experimental conditions."

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).

Author response: Figure 3 is only an example of the obtained thermogram. We have chosen to not include result of the experiment 10 in Fig. 3 in order to avoid showing redundant results. Indeed, the result of the MFR at 100°C for the experiment 10 can be found in the Fig. 4.

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

Author response: We thank a lot the reviewer to point out this error. The exp 9-b was missing in the list of data marker when we plotted the figure.

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?

Author response: Results presented in Fig. 5 correspond to a series of preliminary tests with different water vapor and SOA concentration. They were used to calibrate our system and to test to what extent the presence of water vapor during the particle generation could modify the ratio m/z 44 to organic as explained in the text.
To improve the understanding of the Fig. 5, we labeled all the experiments that were used further in this study, according to the labels given in the other plots. Also the caption of Fig. 5 was changed.

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

Author response: Corrected in the text.

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!

Author response: We thank a lot the reviewer to point out this important error on the figure 9. We corrected the figures

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

Author response: The reviewer is absolutely right. We corrected this misprint.

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"

Author response: All of these corrections are included in the final version of the manuscript.

Page 16710: Re-write the captions for Fig 5. It is not clear.

Author response: Fig. 5 is now entitled: Influence of the presence of water vapor during SOA generation to the oxidation level of the generated particles during preliminary test. Numbers in the plot refer to those experiments that are used in the following examinations presented in this study.

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?

Author response: From the AMS point of view, I don't think that such ozone concentrations disturb the AMS. This is mainly due to the fact that the instrument is working under vacuum, so the gas phase is removed by the aerodynamic lenses. For example, (Zhang et al., 2006) measured with an AMS with same order of ozone concentration during Limonene ozonolysis experiments. Also, size segregated particles were used in all experiments. Therefore the ozone concentration in the aerosol has been greatly reduced in the DMA before the particles reached the instruments. No problems were noticed.

References

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