We would like to thank Referee #3 for his/her comments and suggestions. All of the comments and suggestions have been considered. Point by point responses to these comments are listed below.

Referee #3 comments:

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 highresolution mass spectrometry provides an opportunity to distinguish molecular-level differences in the chemical composition of SOA aged under different conditions. However, 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 (a-pinene, b-pinene, g-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.

Authors' response: As suggested by the reviewer, the introduction and discussion sections have been updated with the following text:

*"The influence of aqueous photochemical processing on the average molecular composition of SOA produced from several biogenic and anthropogenic precursors has also been recently investigated (Romonosky et al., 2015). A reduction of the average number of atoms in the SOA molecular formulae was observed after photolysis; however, without a significant effect on the overall O/C and H/C ratios. In another study, condensed-phase photochemistry in the near-ultraviolet (λ>300 nm) was shown to induce significant changes in SOA particle size and composition (Epstein et al., 2014)."* Lines 81-88, page 3.

*"This is in contrast to results reported for the aqueous photochemical processing of SOA from various biogenic (α- pinene, β-pinene, D-limonene, α-humulene) and anthropogenic (1,3,5-trimethylbenzene and guaiacol) precursors, (Romonosky et al., 2015). In this latter study, areduction of the average number of atoms in the SOA molecular formulae was observed after photolysis suggesting that the presence of water plays an important role in the ageing processes of SOA. It has also been shown that relative humidity can affect the viscosity of SOA particles and potentially affect heterogeneous oxidation kinetics (e.g. Zhou et al., 2013)."* Lines 325-332, page 11.

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 O3 and OH oxidation of a-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.

Authors' response: This is misunderstanding; the separate OH-initiated experiments with α-pinene were not used for direct comparison with the VOC mixture ageing experiments. These experiments, however, were used to investigate whether separate oxidation regimes (i.e., ozonolysis and OH initiated reactions) would lead to the formation of SOA with a different molecular composition and the effect of different oxidant on the oligomer formation. A sentence clarifying the differences in the RH conditions between the experiments performed at CRAC and CESAM chambers has been added: "*It must be noted that the later experiments were performed at the different smog chamber (CRAC) and high RH (~55%)".* Lines 390-391, page 13.

A recent paper by Nizkorodov et al. is relevant to the discussion of the chemical composition of a-pinene SOA produced using O3 and OH oxidation chemistry (J. Phys. Chem. A, 2015, 119, 2594).

Authors' response: We assume the reviewer refers to the publication of Romonosky et al. (2015). The reference has been added to the text.

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

Authors' response: We disagree with this remark. A number of identified species using current chromatographic technique agrees with those published by the other groups (e.g. Yasmeen et al., 2010; 2012; Kristensen at al., 2013; 2014). The purpose of the LC/MS analysis was not to separate the entire organic fraction (which would be impossible to achieve) but to support the direct infusion results with semi-quantitative data.

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.

Authors' response: The following explanation has been added to the text: *"The identification was performed by comparing MS fragmentation and chromatographic elution times reported in the literature (Yasmeen et al., 2010; Kristensen et al., 2014)".* Lines 281-284, page 9

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.

Authors' response: As suggested by the reviewer the citation list has been extended.

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

Authors' response: The suggested corrections have been made.

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

Authors' response: The suggested reference does not fit to the current discussion.

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.

Authors' response: Several additional references have been added.

p. 5364 line 16. "concentrations exceeded those observed at the Finnish site" – please, be more specific. How much higher concentrations were used?

Authors' response: The information on the rough differences between the VOC mix concentration in the smog chamber and the Finnish sites are added to the text. *"While the total concentrations of the BVOC mixture used in these chamber experiments exceeded (up to 10 times depending on the season) those observed at the Finnish site, their molar ratios were kept very close to the reported values (i.e. α-pinene (0.4), $\Delta_3$-carene (0.3), β -pinene (0.2) and isoprene (0.1))".* Lines 133-137, page 5.

What is the potential effect of VOC concentration on SOA composition?.

Authors' response: It is well known that changes in SOA precursor concentration affect the composition of SOA especially of semi-volatile components. We find this information irrelevant for the current discussion and thus we did not include it.

p. 5364 Please, specify the RH.

Authors' response: The RH information was already provided on this page (see line 10)

p. 5365 line 1. Why is it important to mention the photolysis frequency of NO2?

Authors' response: J(NO2) is widely used as a standard parameter to describe the light intensity in atmospheric simulation chambers. It is especially relevant to report this information for the CESAM chamber where photochemical ageing of the aerosol was performed. We therefore prefer to keep this information in the text.

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

Authors' response: Please see our response to similar question above and below.

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

Authors' response: The aerosol mass has been provided: *"…., which varied between 50-150 ug per filter".*

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.

Authors' response: For direct infusion analysis, which suffers from competitive ionisation, it is important that compared aerosol extracts have very similar organic concentration. Therefore, as stated in the text concentration of the SOA in the extract was adjusted by extracting different portion of the filter and adjusting the final volume of the extracts. The concentration of SOA extracts for all samples was adjusted to the same level of approximately 0.25µg organic carbon µL$^{-1}$.

The following statement has been added to the text: "*The concentration of SOA extracts for direct infusion analysis was adjusted to the same level of approximately 0.25 µg organic carbon µL$^{-1}$"* Lines 230-232, page 8*.*

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?

Authors' response: For the direct infusion analysis the purity of organic solvent is very crucial. We tested a large number of high grade solvents (more than 15) and Optima grade methanol showed significantly smaller number of impurity peaks compared to the same grade acetonitrile, which contained a large number of sulphur and nitrogen containing peaks. We are aware of potential methylation reactions. To minimise methyl ester formation, which is a time and temperature dependant process, the samples were extracted in ice slurry and kept in the freezer and analysed within 24-hours. The comparison of mass spectra of both methanol and acetonitrile extracts of several ambient and laboratory generated samples did not show any major differences that could be attributed to methylesters of carboxylic acids. We already discussed this issue in our preceding paper (Kourtchev et al., 2013).

The following statement has been added to the text: *"Literature data (e.g., Bateman et al., 2008) suggests that compounds containing carboxylic acid groups may react with methanol resulting in the formation of esters and therefore acetonitrile was the preferred solvent for SOA extraction. Although the detailed evaluation of the differences between the two solvents was not performed in this study, a preliminary comparison of the mass spectra for both methanol and acetonitrile extracts of several boreal forest samples did not show any major differences that could be attributed to methylesters of carboxylic acids."* Lines 234-240, page 8.

p. 5367. How were blank samples collected?

Authors' response: The blank collection is described in the paper. See lines 18-22, p5366: *"A series of chamber blanks were collected by drawing 'clean' air containing aerosol seed that was exposed to ozone, $H_2O_2$ and UV irradiation from the smog chamber"*.

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

Authors' response: The LC-MS-HESI parameters were initially listed: "*spray voltage −3.6 kV; capillary temperature 300°C; sheath gas flow 10 arbitrary units, auxiliary gas flow 10; sweep gas flow rate 5; S-lens RF level 55%. The sample extracts were injected at a flow rate of 200 µL min$^{-1}$.*"(lines 18-20, P5367 of the ACPD discussion paper).

The voltage and pressure for the direct infusion nanoESI were provided: "-1.4 kV and 0.8 psi respectively" (lines 14-15, P5367). The sample flow rate for nanoESI is not set and varies with applied voltage, pressure and sample viscosity. Generally it is in the range of a few hundred nL min$^{-1}$. The inlet temperature was 200°C.

The following information was added to the text: *"The inlet temperature was 200°C. The sample flow rate was approximately 200-300 nL min$^{-1}$."* Lines 252-253, page 8.

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

Authors' response: The blank mass spectra were acquired in the same way as those of the real samples. As mentioned in the text the data treatment (including blank subtraction step) procedure is described in details in our preceding work (Kourtchev et al., 2013). The background spectra obtained from the procedural blanks were also processed using the rules described in Kourtchev et al., 2013. The formulas lists of the background spectra were subtracted from those of the ambient samples and only formulas with a sample to background ratio ≥10 were retained.

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).

Authors' response: The figure has been modified as suggested. An example of replicate spectra for both analytical and smog chamber replicates has been added to the SI (Figures S1 and S2). A text referring to these figures and a comment on the reproducibility between analytical and smog chamber replicates has been added:
"*Examples of the spectra obtained for both analytical and smog chamber replicates are shown in Figures S1 and S2 (Supplementary Information). The average percentage of common peaks between analytical replicates was 78% (range of 70−87%), which strongly agrees with literature reports for similar data analysis (Sleighter et al., 2012). The percentage of common peaks between smog chamber replicates varied between 82 and 90%. A largest fraction of the 'uncommon' ions in the replicates had RI<0.05%."* Lines 257-263, pages 9-10.

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.

Authors' response: The information suggested by the reviewer would fill more than 100 pages and is not usually provided in publications using mass spectrometry. We therefore do not add this information to this paper. We are happy to provide this data to anyone interested on request.

The y-axis in Figure 1 corresponds to the relative abundance of of individual peaks in the spectrum. The most abundant peak in the spectrum 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%.

Authors' response: The axis has been changed to 100%.

p. 5369 line 8. Unbalanced citations.

Authors' response: The reference list has been extended.

p. 5370 line 1. This statement is not supported by the data. An alternative explanation is that reactions with O3 and OH generate different products with different reactivity.

Authors' response: This statement is not our interpretation but the one of Kristensen et al (2014) as indicated in the text.

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

Authors' response: The statement was removed as a part of the corrections requested by the first reviewer.

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.

Authors' response: The requested information has been added to the text: "*The $OS_C$ was introduced in aerosol science by Kroll et al. (2011) to describe the composition of a complex mixture of organics undergoing dynamic oxidation processes. It is strongly linked to aerosol volatility and thus is a useful parameter to classify SOA. While highly oxidised organics in organic aerosol have $OS_C \geq +1$; the reduced molecules have $OS_C \leq 0$. The maximum in chemical complexity is located at $OS_C = 0$ (Kroll et al., 2011).*" Lines 347-352, page 11.

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

Authors' response: The additional experiments with α-pinene at CRAC chamber were used to determine how separate oxidation regimes (O3 and OH-initiated oxidation) may influence composition of SOA. Moreover they were used to support the hypothesis that OH-oxidation causes more highly oxidised SOA and to support interpretation derived from comparing Fig 2 and 3. In the experiments performed at CESAM chamber, SOA was formed from the ozonolysis reaction and we expect that after 1 hour the majority of the VOC is already reacted away. Therefore, it is anticipated that observed changes during the subsequent OH initiated ageing will occur due to the OH radical reaction with the SOA formed from the ozonolysis rather than reaction with the VOCs present in the system.

In the previous study (Kourtchev et al., 2014) we compared molecular composition of SOA from a single VOC (α-pinene) with that from the VOC mixture (α-pinene, β-pinene, Δ3-carene and isoprene) and we showed that molecular composition of α-pinene SOA was very similar to that from the BVOC mixture. Therefore, we believe that a comparison of α-pinene-SOA with that of the BVOC mixture is adequate.

The following clarifying statements have been added to the text:

*"In a previous study (Kourtchev et al., 2014) we compared molecular composition of SOA from ozonolysis of a single VOC (α-pinene) with that from the VOC mixture (α-pinene, β-pinene, Δ3-carene and isoprene) and showed that the molecular composition of α-pinene SOA was very similar to that from the BVOC mixture." Lines 386-390, pages 12-13.*

To difference in the RH between experiments performed in CRAC and CESAM chamber has been additionally emphasised in the text: *"It must be noted that the later experiments were performed at the different smog chamber (CRAC) and high RH (~55%)." Lines 390-391, page 13.*

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.

Authors' response: We agree that the observed differences are very interesting. However, considering absence of the authentic standards (as mentioned in the text) for the detected dimers a mechanistic explanation would be highly speculative and is not in the scope of the current paper.

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

Authors' response: The missing reference has been added.

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

Authors' response: The following explanation has been added to the text: "*The identification was performed by comparing MS fragmentation patterns and chromatographic elution times reported in the literature (Yasmeen et al., 2010; Kristensen et al., 2014)"* Lines 281-284, page 9.

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

Authors' response: The sentence has been changed. "*Most of the detected compounds* …" has been changed to "*Most of the tentatively identified compounds* …"

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.

Authors' response: This is misunderstanding. Dynamic range describes the quantitative reliable performance of a method and we do not discuss any quantitative aspects of the direct infusion analysis. As it can be seen from the Figures S1 and S2 (S3 and S4 in the revised manuscript, respectively) very large number of oligomers is observed by the LC; however, they are not readily separated.

Authors' response: To clarify this, the word *"observed"* was replaced by "*separated*". Line 15 P5373.

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

Authors' response: The clarifying sentence and the exact masses were added to the text: *"It must be noted that these dimers were also observed during the direct infusion analysis."*

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.

Authors’ response: The scale was adjusted to 100%.

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