

We would like to thank Referees #1, #2 and #3 for their very helpful comments and suggestions. All of the comments and suggestions have been considered. Point by point responses to these comments are listed below.

### **Responses to Referee #1 comments:**

1) The authors require that a peak have a signal to noise ratio of 10 to be considered for molecular formula assignment. This is a quite conservative requirement that ensures that only peaks that ionize efficiently and/or are in high concentration in the sample are detected. As a result, I have confidence that the identified molecular formulae are representative, but I wonder if how much information is lost by not including peaks at lower signal to noise ratios. Authors often report data at a much lower signal to noise.

*Authors Response:* The signal to noise ratio (10) was established experimentally. The direct infusion ESI technique is susceptible to ion suppression and competition for the charge between the components with high and low ionisation efficiencies thus resulting in a fluctuation of the ion intensities. This phenomenon is more pronounced for ions with relatively low intensities (especially in the presence of matrix compounds present in the ambient samples). We do agree that by increasing signal to noise level to 10 we might lose some molecules but at the same time we are more confident about the ions that passed the S/N threshold applied in this study.

2) Do the authors have a reason for not considering phosphorous as an elemental constituent?

*Authors Response:* We agree that phosphorous is an important element in certain environments (e.g., marine). We reanalysed a few selected samples by including phosphorous in the formulae assignment model. However, the number of chemically realistic formulae in the examined ambient samples did not change and no P-containing formulae were detected.

3) The cluster analysis technique is well explained and demonstrates differences among the samples. The authors used a binary presence/absence matrix for input which is useful. The authors correctly note that the technique used here is not quantitative and that peak intensities should be viewed with caution, but I suggest that the relative magnitude of each peak is still useful information. (See, for example, Sleighter et al. (2010).) Patterns in the relative magnitudes of peaks present across many samples may reveal differences among samples that can not be detected using a binary matrix.

*Authors Response:* As mentioned in the response to Comment 1, the direct infusion ESI method suffers from competitive ionisation of the ions especially in complex mixtures such as ambient aerosol resulting in rather high fluctuation of ion intensities. Thus, we refrained from using relative intensities for the interpretation of our results.

4) I think an important part of this study is that the authors restrict their analysis to <300 Da (the monomeric region). The authors note that the absence of dimers in ambient samples requires further study which is certainly true. Another way of interpreting these results is that the laboratory generated SOA methods used here (and in several other studies) do a fairly good job of describing what happens in nature (as indicated by the high agreement between the SOA and the boreal forest sample). But these procedures are not replicating the environment when it comes to these dimers which either don't form or have a very short half-life in nature.

*Authors Response:* We would like to thank the reviewer for this valuable remark. The following statement has been added to the text (p. 29613, line 17): *‘Thus it appears that while the laboratory experiments performed here and in other studies do a fairly good job of simulating biogenic SOA formation (as indicated by the high level of agreement between the laboratory SOA and the boreal forest samples in the monomeric mass region of the mass spectra), they do not completely replicate the processes occurring in the ambient atmosphere.’*

5) Figure 5 shows the fraction of common formulae relative to the total number of formulae in the ambient samples. Has the opposite comparison been made (relative to the SOA formulae)? And if so, are there formulae present in the SOA that just don't appear to be important in nature? This, again, could have important information for how well SOA experiments are replicating what happens in nature.

*Authors Response:* The inverse comparison of the fraction of common formulae relative to the total number of formulae in the laboratory generated samples indicated that laboratory generated SOA contained 20-25% formulae that were not observed in the boreal samples. We suggest that these molecules are first generation products that are possibly oxidised with time in the atmosphere resulting in aged oxidation products. A respective statement has been added to the text (p. 29612, line 5): *‘The inverse comparison of the fraction of common formulae relative to the total number of formulae in the laboratory generated samples in the monomeric region indicated that laboratory generated SOA contained 20-25% formulae that were not observed in the boreal samples. We suggest that these molecules are first generation products that are possibly oxidised with time in the atmosphere resulting in aged oxidation products.’*

6) I would include Figure S2 in the manuscript. I think it is useful information.

*Authors Response:* Figure S2 has been added to the manuscript as suggested.

Technical Corrections:

1) Page 29602, line 12:  $0.3 \leq H/C \leq 2.5$  is confusing to read. I suggest separating this into the two groups that are being excluded,  $0.3 \leq H/C$  and  $H/C \geq 2.5$ .

*Authors Response:* As suggested by the reviewer, the expression has been separated into the groups.

2) Page 29603, lines 1 and 3: The authors refer to "compounds" where formulae is the accurate term because the formulae could represent several isomeric compounds. In general, the authors were careful not to use compound, but the rest of the manuscript should be checked.

*Authors Response:* We agree with this statement, the word ‘compounds’ has been replaced with ‘molecules’.

3) Page 29608, line 18: "indicated" is misspelled.

*Authors Response:* The word "indicated" has been corrected.

## Responses to Referee #2 comments:

1) P29605 L1-15: Have the authors thought potential importance of OH reactions in BVOC ozonolysis? In addition to lower SOA yields of beta-pinene and isoprene ozonolysis, both the VOC might act as OH radical scavengers that influence the final SOA yields. Perhaps the authors can add a sentence or two about the importance of OH radical formation in ozonolysis and its potential impact on the SOA yields here.

*Authors Response:* We agree with the reviewer that OH reactions are very important in the BVOC ozonolysis. However, in the present study we used an OH scavenger (i.e., cyclohexane) in all our ozonolysis experiments; therefore, we expect that all OH radicals formed from the reaction of BVOCs with ozone should be efficiently removed.

2) P29607 L3 and elsewhere: I wonder why the authors present only two decimal places for SOA compounds. I presume the authors have assigned these compounds based on the  $m/z$  values with four or more decimal values. Could the authors provide  $m/z$  values used for the chemical formulae assignment instead of these 'less accurate'  $m/z$  values?

*Authors Response:* We agree with the referee's remark. The assignments were done within 1 ppm accuracy. The  $m/z$  values with two decimal units in the text were shown for simplicity. As suggested, these values have been extended to four decimal units in the text.

3) P29608 L4: I believe this dimeric compound is also reported by Müller et al., 2009 as a peroxyhemiacetal compound. L. Müller, M. C. Reinnig, H. Hayen, T. Hoffmann, Characterization of oligomeric compounds in secondary organic aerosol using liquid chromatography coupled to electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Rapid Communications in Mass Spectrometry, Vol. 23, Issue 7, 971-979, 2009

*Authors Response:* We thank the reviewer for this reference. We added the following sentence to the text and included the reference to the reference list: 'It is worth mentioning that the HMW compound at  $m/z$  357 has been previously identified in SOA produced from the ozonolysis of  $\alpha$ -pinene and attributed to a hydroxyperoxyhemiacetal (Müller et al., 2009) and pinyl-diaterpenylic ester (Kristensen et al., 2013)' (p. 29608, line 7).

4) P29610 L20-29611 L10: Such highly oxidized compounds are observed in both the laboratory generated SOA and ambient aerosols at Hyytiälä. The authors may want to add the following reference here. M. Ehn, E. Kleist, H. Junninen, T. Petäjä, G. Lönn, S. Schobesberger, M. Dal Maso, A. Trimborn, M. Kulmala, D. R. Worsnop, A. Wahner, J. Wildt, and Th. F. Mentel, Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, Atmos. Chem. Phys., 12, 5113-5127, 2012

*Authors Response:* We added the following sentence to the text and included the suggested reference to the reference list: 'It should be mentioned that highly oxidised multifunctional molecules have been previously observed in both ambient air (Hyytiälä) and chamber experiments of  $\alpha$ - and  $\beta$ -pinene ozonolysis.' (p. 29611, line 11).

### Responses to Referee #3 comments:

In this paper, the authors present a comparison of the molecular composition identified in laboratory SOA samples and ambient samples using high resolution mass spectrometry. The presented results from two different laboratory generated SOA experiments and two different ambient samples are very interesting. First of all, the SOA from the BVOC mixture containing  $\alpha$ -pinene,  $\beta$ -pinene, d3-carene and isoprene is not remarkably different than the SOA from individual  $\alpha$ -pinene. Thus, the two laboratory generated SOA samples were both very similar to the ambient OA collected in an SOA influenced region, but dissimilar to the urban sample. This may be expected, however some of the markers of monoterpene SOA may exist in the ambient urban sample since SOA is a large source of ambient OA. Interestingly, the authors did not observe ambient SOA dimers in this work.

The authors ruled out the possibility for analytical artifacts, but did not discuss ambient OA processes/implications related to this. Overall, this is a very good paper with a careful analytical approach that addresses a topic of substantial interest to the community.

1) Authors may be interested in reviewing the findings of Muller et al., *Rapid Communications in Mass Spectrometry*, 2009; Kristensen et al., *Atmospheric Chemistry and Physics*, 2013; and Zhao et al., *Atmospheric Chemistry and Physics*, 2013 for observations of monoterpene SOA “dimers”. Perhaps the lack of observation is significant with respect to condensed phase OA processes or aerosol aging.

*Authors Response:* As we stated in the text (p. 29613, line 15) the observation of dimers exclusively in the chamber experiments requires further investigations. We believe at this stage any discussion of this discrepancy would be highly speculative.

The suggested references (Müller et al., 2009 and Kristensen et al., 2013) and the following statement have been added to the manuscript (p. 29608, line 7): *‘It is worth mentioning that the HMW compound at m/z 357 has been previously identified in SOA produced from the ozonolysis of  $\alpha$ -pinene and attributed to a hydroxyperoxyhemiacetal (Müller et al., 2009) and pinyldiaterpenylic ester (Kristensen et al., 2013).’*

The work by Zhao et al. (2013) is focused on the composition of cloud water and is not deemed to be especially pertinent to the discussion of the current work; this reference is therefore not cited in the revised manuscript.

2) Authors interchange the terms BVOC mixture and VOC mixture, which I believe refer to the same experiment. For clarification, one consistent term is preferred.

*Authors Response:* The term VOC has been changed to BVOC throughout the text.

3) Please add a legend to figures 3 and 4.

*Authors Response:* Figure legends are described in the figure captions.

4) Despite the significant similarity between the  $\alpha$ -pinene ozonolysis SOA and the BVOC mixture ozonolysis SOA, the mass spectra in figure 1 appear to be different. Could the comparison of the compositions be made clearer in the discussion? This might provide hints regarding the significance of the lack of observation of the ambient SOA dimers in this work.

*Authors Response:* The mass spectra of laboratory generated samples from the BVOC mixture, a single precursor system and ambient aerosol were mainly shown to demonstrate the mass spectral differences in the dimeric region. This was explained in the text (p.29606, lines 1-7). As suggested by the reviewer we clarified the differences in the monomer regions of the mass spectra by adding the following statement (p. 29607, line 8): ‘*The mass spectral differences observed in the monomeric region of the SOA from the single precursor and BVOC mixture were mainly associated with variation of the ion intensities caused by the differences in the number of products with the same mass in the single component and BVOC mixture experiments as described above.*’

5) In the abstract, do you refer to 70% of the laboratory generated SOA compounds or the ambient compounds?

*Authors Response:* The statement in the abstract has been clarified (p. 29595, line 16): ‘*The molecular composition of SOA from both the BVOC mixture and  $\alpha$ -pinene represented the overall composition of the ambient sample from the boreal forest site reasonably well, with  $72.3 \pm 2.5\%$  ( $n=3$ ) and  $69.1 \pm 3.0\%$  ( $n=3$ ) common ions, respectively.*’

6) Please correct the reference, Hatfield and Hartz, 2011. I believe the last name is Huff Hartz. Also note, the name is misspelled on page 29597

*Authors Response:* The reference has been corrected.

7) The authors place a strong emphasis on this work being the first time SOA from BVOC mixtures is compared to the ambient OA, but didn’t emphasize the differences in the composition between the SOA from the mixture and the individual  $\alpha$ -pinene. As stated above, the differences in the composition from HRMS do not appear to be significant.

*Authors Response:* We believe we responded to this remark above in the response to Comment 4.