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

Referee #1 comments:

1) The title “Molecular composition of aged secondary organic aerosol generated from a mixture of biogenic volatile compounds using ultrahigh resolution mass spectrometry” does not precisely describe the work, since both fresh and aged SOA are analyzed. Furthermore, it almost says that SOA are being generated UHRMS. I suggest changing the title to better reflect the main findings of the manuscript.

Authors Response: As suggested by the reviewer the title of the paper has been changed to “Molecular composition of fresh and aged secondary organic aerosol from a mixture of biogenic volatile compounds: a high resolution mass spectrometry study”.

2) 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.

Authors Response: We accept this point, but given the comparative nature of the analysis and the detail contained within the discussion and interpretation of the results, we prefer to retain the existing structure. However, several clarifying statements have been added to the text to aid the reader:

“*All aerosol ageing experiments were performed in the CESAM chamber in Paris. Supplementary experiments on the ozonolysis and OH-initiated oxidation of α-pinene were conducted in the CRAC chamber in Cork*.” Lines 114-116, page 4

“*All data described in this section (except discussion of Fig S3 and S4) correspond to experiments performed at CESAM chamber.”* Lines 435-436, page 14.

“*To identify a possible reason for the small shift in OS_C to the higher values during the ageing reaction observed in the present study, we performed separate O_3 and OH radical initiated oxidation experiments with α-pinene (the major component of the BVOC mixture) in the CRAC chamber.* “ Line 383-386, pages 13.

“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.

3) 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.

Authors Response: We added the following new text to the manuscript:

"*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 330-332, page 11.

4) 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.

Authors Response: The phrase "*largely unknown*" has been changed to "*poorly understood*".

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

Authors Response: The reference "Chen et al. (2009)" has been added to the text.

6) 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?

Authors Response: This is a misunderstanding. We did not state that the *"previous studies claim that the dimers observed by LC/MS represent the large number observed by direct injection"*. However, these studies, including ours, extrapolated the effect of ageing on aerosol composition by monitoring a small number of dimers that could be resolved by the LC/MS. The open question is how well these dimers can represent the entire oligomer fraction.

Experimental. A number of important details are missing. These include:
- calculated or measured concentrations of OH during ageing (CESAM) and SOA formation experiments (CRAC)

Authors Response: The following information has been added to the text:

"*Based on the measured distribution of light intensity in the chamber (Healy et al., 2012), the steady-state concentration of OH radicals was estimated to be ca.* 4×10^{6} *molecule* cm^{-3}." Lines 200-202, page 7.

"*For the two OH induced ageing experiments, the OH concentration was estimated using the Master Chemical Mechanism (Jenkin et al, 1997; Saunders et al, 2003; Jenkin et al., 2015), MCM v3.3, via website: http://mcm.leeds.ac.uk/MCM. The MCM contains detailed chemical mechanisms for isoprene, α-pinene and β-pinene, but not for Δ3-carene. As a result, a module describing the chemistry of Δ3-carene was constructed using the well-characterised reactions of the structurally similar compound α-pinene as a basis. Following the work of Atkinson et al. (1986, 1990), the rate constants used for the reaction of ozone and OH with* Δ_3*-carene were 0.44 × k(*O_3 *+ α-pinene) and 0.55 × k(OH + α-pinene) respectively. The concentration of* H_2O_2*, determined from FTIR measurements, was constrained in the model, as well as the temperature, the relative humidity and the dilution flow induced by sampling. The initial concentration of VOCs and ozone used in the MCM were measured at the start of the ozonolysis reaction. A value of* $J(H_2O_2) = (3.2\pm0.4)\times10^{-6}\ s^{-1}$ *was used, based on the measured light intensity distribution in the CESAM chamber (Wang et al., 2011). Using these inputs, the overall OH exposure was determined to be* 1.7×10^{7} *and* 1.3×10^{7} *molecule* cm^{-3} *h-1 in the two experiments, which is comparable to similar studies in the literature (Eddingsaas et al., 2012; Qi et al., 2012; Henry and Donahue, 2012)*". Lines 162-179, page 6.

- concentration of seed aerosols

Authors Response: The requested information has been added: "*with a concentration of approximately 5 µg m*$^{-3}$" Lines 193-194, page 6.

- concentration of ozone in CRAC study for both ozonolysis and OH experiments

Authors Response: The ozone concentration is added to the text. Line 203, page 7.

concentrations of NOx

Authors Response: The following information about the NOx concentration has been added to the text:

"The concentration of NOx throughout the experiments was below the detection limit." Lines 145-146, page 5.

"*The concentration of NOx monitored using a standard NOx analyser (Thermo Model 42i) was found to increase gradually from 0 to around 25 ppb during the course of the reactions, due to NOx offgassing from the Teflon walls (Carter et al., 2005, Rohrer et al., 2005)."* Lines 205-209, page 7.

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

Authors Response: The requested information has been added to the text: "*Total aerosol mass was collected on prebaked (at 650 °C) quartz fibre filters (47 mm diameter, Tissuquartz 2500 QAT-UP, Pall Life Sciences) using a stainless steel 47 mm in-line filter holder (Pall Life Sciences). The gas phase species were removed using a custom-built 1 m long denuder packed with activated charcoal (NORIT®ROW 0.8 SUPRA, Sigma-Aldrich). The denuder was purged using clean air for at least 12 h prior to experiments". Linex211-217, page 7.*

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

Authors Response: The following sentence has been added: *"Listed conditions are for the initial formation of the SOA and not for the subsequent ageing reaction."*

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

Authors Response: The phrase "*photolysis reaction*" was changed to "*OH-initiated reaction*".

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.

Authors Response: The missing reference has been added.

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".

Authors Response: The justification for using pinonic acid and MBTCA was given in the text above this sentence: "*These include well known first generation oxidation products of α-pinene such as cis-pinic acid, terpenylic acid and pinonic acid, as well as later generation oxidation products of monoterpenes, i.e., 1,2,3-butanetricarboxylic acid (MBTCA). It has* *been suggested that MBTCA is a product of the hydroxyl radical initiated oxidation of pinonic acid in the gas phase (Szmigielski et al., 2007; Müller et al., 2012; Yasmeen et al., 2012). Therefore, both pinonic acid and MBTCA could be used to monitor the evolution of 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.

Authors Response: A reference "Kristensen et al., 2014" has been provided.

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

Authors Response: The text has been clarified by adding a statement: "*.. in cited above studies and current work,…*"

The chromatographic conditions applied here do not seem to provide adequate separation of individual compounds (Figures S1 and S2).

Authors Response: We agree with the statement that chromatographic conditions do not provide adequate separation of the individual dimers and therefore we initially stated this in our manuscript: *"The lack of chromatographically resolved dimers in the OH radical initiated SOA could be explained by the selectivity of the utilised LC columns."* It must be noted that Figure S1 and S2 are total ion chromatograms (TIC); therefore, they are not as 'neat' as the extracted peak (EP) or base peak (BP) chromatograms generally shown in the literature. TIC provides the raw data making unresolved 'hump' visible. An example of a base peak chromatogram corresponding to the same sample is shown in Figure S5 (SI). Nevertheless, a number of observed dimers using LC/MS in this study during the ozonolysis experiments agree with the reported literature studies that utilised similar LC columns (e.g., Yasmeen et al., 2010;2012; Kristensen et al., 2014).

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.

Authors Response: We are aware of the fact that ESI can result in the formation of noncovalent molecules. However, the in-source fragmentation experiments with a fragmentation voltage of up to 70 V showed no significant change in the number of observed oligomers in the mass spectra, thus ruling out the possibility that these oligomers are noncovalent compounds formed in the ESI source. When the fragmentation voltage was increased to 80 V, a decrease in the intensities for both monomers and dimers was observed, confirming that detected dimers are covalent species. To clarify this issue the following statement has been added to the text:
"The in-source fragmentation tests with a fragmentation voltage of up to 70 V showed no significant change in the number of observed oligomers in the mass spectra, thus ruling out the possibility that these oligomers are noncovalent compounds formed in the ESI source. When the fragmentation voltage was increased to 80 V, a decrease in the intensities for both monomers and dimers was observed, confirming that detected dimers are covalent species." Lines 398-404, page 13.

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?

Authors Response: As mentioned in the text there are no available standards for any of these dimers; therefore, such comparison is not possible.

Figure 7. It is not clear to the reader why these specific compounds were chosen for the figure. Please describe the reasons for this.

Authors Response: A clarifying sentence has been added to the legend. *"Pinic, pinonic and terpenyllic acids represent organic species associated with 'fresh' whereas MBTCA with 'aged' SOA."*

Why was only one dimer selected, when you observed many more?

Authors Response: The chromatographic peak areas for all four dimers (and their isomers) showed relatively good correlation (R^2>0.90) in all samples suggesting these compounds are possibly formed through similar processes. To avoid overloading the figure, only one, the most commonly observed dimer with MW 358 in both ambient and laboratory generated OA was shown in the figure. The following sentence was added to the text and the legend: "*The chromatographic peak areas for all four dimers, determined by LC/MS, showed relatively good correlation (R^2>0.90) suggesting these compounds are formed through similar processes." Lines 478-480, page 15.*

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

Authors Response: corrected

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

Authors Response: Added, *"dark ageing with residual exposure to ozone"*

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

Authors Response: No, in this sentence we were referring to MBTCA*: "…all samples contained MBTCA, an OH radical initiated oxidation product of α-pinene".*

- line 16 and 20: During the dark ageing exposure -> do you mean ozone exposure of SOA?

Authors Response: The sentence has been clarified: "*During dark ageing experiments (with SOA exposure to residual ozone)….."*

- line 18: SOA exposure -> do you mean ozone exposure of SOA?

Authors Response: Corrected (please see above)

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

Authors Response: As stated in the figure legend, the table presents Analysis of Variance (ANOVA) results for dimer (obtained from the LC/MS analysis) to SOA concentration ratios at different ageing conditions: "*P values derived from Analysis of Variances ANOVA test of variations in relative dimer to SOA concentrations at different ageing conditions."* A clarifying caption that the data was obtained from the LC/MS analysis has been added: *"The relative dimer concentrations were obtained from the LC/MS analysis".*

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

Authors Response: As suggested the symbols in the corresponding figures have been modified.

References:

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