We would like to thank the referees 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. A marked-up manuscript version and a version with line numbers are shown below the responses to the referees' comments .

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±0.4)×10^{-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.

Referee #2 comments:

The title should be clarified to emphasize the unique aspects of this study – perhaps "Molecular composition of biogenic secondary organic aerosol following additional aging" or something that better describes the study?

Authors' response: As suggested, the title has been clarified. A new title is *"Molecular composition of fresh and aged secondary organic aerosol from a mixture of biogenic volatile compounds: a high resolution mass spectrometry study".*

Also, the authors use the term "ultrahigh resolution" mass spectrometry; however, they use an Orbitrap with a resolution of 100,000 at m/z 400, which is typically not considered to be "ultrahigh", rather just "high resolution". This phrasing should be fixed throughout the manuscript so that it is not misleading.

Authors' response: Corrected

Otherwise, the manuscript is well-written.

I agree with many of the comments of referee #1. Here are additional comments:

Introduction: The intro is well-written and provides great justification for the study. In discussing oligomer content of a-pinene SOA, however, the authors should consider the work of Hall and Johnston (2011, Aerosol Sci. Technol.).

Authors' response: The suggested reference has been added to the text.

Page 5369, Lines 6-7: What fraction of peaks was shared between the spectra?

Authors' response: In this sentence we are not comparing elemental composition but emphasising that all spectra contained distinct groups of oligomers. To clarify this, the sentence (lines 6-7) has been rephrased: *"Irrespectively of the applied atmospheric oxidation conditions, the mass spectra from all SOA samples contained distinct groups of monomers, dimers and trimers in the mass range 100-650."*

Page 5370, Lines 3-4: Odd phrasing.

Authors' response: The sentence has been changed to: *"In addition, the data was visualised using carbon oxidation state (OS_C) plots."*

Page 5371, Lines 5-7: What study is this result from? This is not clear.

Authors' response: The sentence was a continuation of the previous statement. To clarify this, the reference was added to the statement.

Additional list of molecular formulae for fresh SOA: It would be useful to add an additional column to this to note if this peak has been observed previously in lab studies, and if so, what precursor(s) it is attributed to.

Authors’ response: Direct infusion analysis does not allow structural identification. For example, in our preceding study (Kourtchev et al., 2014) we demonstrated that the mass spectra from chamber experiments and ambient OA from Hyytiälä, Finland were dominated by an ion at *m/z* 185.0818. While in α-pinene experiments this ion corresponded to *cis*-pinic acid, in the BVOC mixture experiments and Hyytiälä ambient samples this ion was related to three (i.e. *cis*-pinic acid, homoterpenylic acid, and *cis*-caric acid) and five (*i.e.* cis-pinic acid, homoterpenylic acid, limonic acid, ketolimononic acid and *cis*-caric acid) different compounds, respectively. Therefore, we feel that providing source information for more than 600 molecular formulae and comparing it with the previous studies would be highly speculative.

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), Δ_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^{o}C.

The following information was added to the text: *"The inlet temperature was 200^{o}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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Molecular composition of fresh and aged secondary organic aerosol ~~generated~~ from a mixture of biogenic volatile compounds~~ using ultrahigh~~: a high resolution mass spectrometry study

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Abstract

Field observations over the past decade indicate that a significant fraction of organic aerosol in remote areas may contain highly oxidised molecules. Aerosol processing or further oxidation (ageing) of organic aerosol has been suggested to be responsible for their formation through heterogeneous uptake of oxidants and multigenerational oxidation of vapours by OH radicals. In this study we investigated the influence of several ageing processes on the molecular composition of secondary organic aerosols (SOA) using direct infusion and liquid chromatography ~~ultrahigh~~high resolution mass spectrometry. SOA was formed in simulation chamber experiments from ozonolysis of a mixture of four biogenic volatile organic compounds (BVOC): *α*-pinene, *β*-pinene, Δ_3-carene and isoprene. The SOA was subsequently aged under three different sets of conditions: in the dark in the presence of residual ozone, with UV irradiation and OH radicals, and using UV light only. Among all studied conditions, only OH radical-initiated ageing was found to

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influence the molecular composition of the aerosol and showed an increase in carbon oxidation state ($\mathrm{OS_C}$) and elemental O/C ratios of the SOA components. None of the ageing processes produced an observable effect on the oligomers formed from ozonolysis of the BVOC mixture, which were found to be equally abundant in both ‘fresh’ and ‘aged’ SOA. Additional experiments using *α*-pinene as the sole precursor demonstrated that oligomers are an important group of compounds in SOA produced from both ozonolysis and OH radical-initiated oxidation processes; however, a completely different set of oligomers is formed under these two oxidation regimes. SOA from the OH ~~radical~~-initiated ~~*α*-pinene~~ oxidation of *α*-pinene had a significantly higher overall $\mathrm{OS_C}$ and O/C compared to that from pure ozonolysis experiments confirming that the OH radical reaction is more likely to be responsible for the occurrence of highly oxidised species in ambient biogenic SOA.

1. Introduction

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric chemistry and give rise to secondary organic aerosols (SOA) that affect climate and air quality (Kanakidou et al., 2005; Hallquist et al., 2009). Although a substantial fraction (20−90%) of atmospheric fine particulate matter is comprised of organic compounds (Jimenez et al., 2009), its molecular composition remains ~~largely unknown.~~poorly understood. The limited knowledge of aerosol composition ultimately restricts our understanding of the most relevant particle sources.

Laboratory chamber experiments have been performed for decades in an attempt to mimic atmospheric SOA formation. However, it is still unclear how close the aerosol particles generated in laboratory experiments resemble atmospheric SOA with respect to their detailed chemical composition. Field observations over the past decade indicate that a significant fraction of organic aerosol in remote areas may contain highly oxidised molecules (Chen et al., 2009; Kroll et al., 2011). In contrast, laboratory-generated SOA is oxidised to a much lesser extent, suggesting that the conditions in smog chamber experiments are not optimal for mimicking ageing in the atmosphere (Donahue et al., 2012). One likely reason for this difference in composition is that the reaction times in chamber experiments are significantly shorter than the lifetime of organic aerosol in the real atmosphere~~.~~ (e.g., Shilling et al., 2009). Another explanation for the difference is that typical smog chamber

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experiments are performed with only one or two SOA precursors and are limited to one oxidant (e.g., O_3 or OH radicals).

It has been suggested that aerosol processing or further oxidation (ageing) of OA could be responsible for formation of highly oxidised OA components through heterogeneous uptake of oxidants and multigenerational oxidation of vapours by OH radicals (Henry and Donahue, 2012). Several OH radical initiated ageing experiments have been performed with α-pinene, its oxidation products (Donahue et al., 2012; Müller et al., 2012; Denjean et al., 2015; Romonosky et al., 2015) and a mixture with limonene and *p*-xylene (Emanuelsson et al., 2013; Flores et al., 2014). It was found that hydroxyl radical ageing significantly increases the concentration of first generation BSOA components as determined from both O/C elemental ratios and individual marker compounds. In addition, atmospheric ageing was proposed to have a role in the formation of high molecular weight compounds or oligomers (Kalberer et al., 2004) through condensed (Rudich et al., 2007) or aqueous (Renard et al., 2014) phase chemistry.

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).

The influence of ageing on oligomer formation is generally inferred from analysis of the elemental O/C and H/C ratios. However, other chemical processes such as carboxylation and carbonylisation are also known to affect the elemental ratios. Additionally, the effects of ageing on oligomerisation have been assessed by monitoring the concentration of 2-5 dimers that could be identified by liquid chromatography mass spectrometry (LC/MS) (Emanuelsson et al., 2013). Other techniques such as ~~ultrahigh~~high resolution mass spectrometry (~~UHRMS~~HRMS) often identify hundreds of oligomeric compounds (Tolocka et al., 2004; Kalberer et al., 2004; Reinhardt et al., 2007; Hall and Johnston, 2011; Putman et al., 2012;

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Kundu et al., 2012; Kourtchev et al., 2014), which raises the question of whether the small number of dimers that can be quantified with LC/MS reliably represent the entire oligomer content of the SOA.

The objectives of this work were to examine the influence of several ~~aerosol~~ ageing conditions on the molecular composition of biogenic SOA. SOA formed from ~~dark~~ ozonolysis of a BVOC mixture was exposed to; (i) residual ozone in the dark, (ii) OH radicals and UV light (~~ii~~iii) UV light only~~ and (iii) ozone~~. The BVOC mixture contained the four most abundant compounds (i.e., *α* and *β*-pinene, Δ_3-carene, and isoprene) detected at a remote boreal forest site Hyytiälä, Finland (Hakola et al., 2003; Aaltonen et al., 2011; Bäck et al., 2012, Kourtchev et al., 2014). The aged SOA was characterised using direct infusion and LC ~~UHR~~HR-MS that allows detection of thousands of individual SOA constituents at once providing their elemental formulae from accurate mass measurements (Nizkorodov et al., 2011).

2. Methods

~~Experiments~~All aerosol ageing experiments were performed in ~~two different atmospheric simulation chambers:~~ 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.

2.1. CESAM experiments

Aerosol ageing experiments were carried out in the CESAM chamber (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber). A detailed description of the chamber is provided elsewhere (Wang et al., 2011). Briefly, the chamber is a 4.2 m^3 stainless steel vessel, operated at 296±2 K using synthetic air at 1 bar atmospheric pressure. The solar irradiation is mimicked using xenon arc lamps (4 kW, XPO 4000 W/HS, OSRAM) fitted with 8 mm Pyrex filters that provide an emission spectrum closely resembling that at the Earth's surface near the Equator over the wavelength range 290-700 nm (Wang et al., 2011). For these experiments, the corresponding NO_2 photolysis frequency was $J_{NO2}=(2.5\pm0.2)\times10^{-3}$ s^{-1}. The experimental conditions are outlined in Table 1. The experiments were performed at a relative humidity (RH~~ (~~) of 2-9~~ %).~~%. Neutral seed particles of ammonium sulfate were generated from 3 mM $(NH_4)_2SO_4$ (Sigma-Aldrich, 99.99 %) solution using an

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atomiser (TSI® model 3075) and dried using a diffusion dryer (TSI®, model 3062) before introduction into the chamber. BVOCs (i.e. α-pinene, β-pinene, Δ_3-carene and isoprene) were introduced into the chamber by flowing purified air over known amounts of the compounds in a gently heated Pyrex impinger. 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), Δ_3-carene (0.3), β~~—~~-pinene (0.2) and isoprene (0.1)). The total VOC mixture concentration was about 150 ppb for all CESAM experiments. The precursor hydrocarbons concentrations and their decay were measured using *in-situ* FTIR spectroscopy. After injecting the BVOC mixture and allowing it to stabilise for 5-10 min, ozone was introduced into the chamber over a period of 10-15 s from an electric discharge generator. ~~For the OH radical initiated ageing reactions, OH radicals were produced by photolysis of H_2O_2 (60% w/v, Fisher Scientific) using xenon arc lamps (4 kW, XPO 4000 W/HS, OSRAM) fitted with 8 mm Pyrex filters that provide an emission spectrum closely resembling that at the Earth's surface near the Equator over the wavelength range 290-700 nm (Denjean et al., 2015).~~Infrared absorbing species such as SOA precursors and their oxidation products were measured during the reactions using multi-path in-situ Fourier-transform infrared (FTIR) spectrometry (Bruker GmbH, Ettlingen, Germany) with an optical pathlength of 192 metres. The concentration of NOx throughout the experiments was below the detection limit.~~ For these experiments, the corresponding NO_2 photolysis frequency was J_{NO2}=(2.5±0.2)×10^{-3} s^{-1}. H_2O_2 was continuously injected into the smog chamber approximately 1 hour after reaching the maximum SOA concentration (mean maximum concentration 122±21 µg m^{-3}, n=6) produced from the dark ozonolysis reaction. SOA samples were collected in three stages: (a) after reaching the maximum particle concentration (as measured by SMPS) produced from the dark ozonolysis reaction of the VOC mixture (b) after 3 hours of exposure of the SOA particles to OH radicals and/or UV radiation and (c) after 8-9 hours of exposure of the SOA particles to OH radicals and/or UV radiation.~~

Particle size distributions (from 19 to 980 nm in diameter) were measured with a TSI® 3080 scanning mobility particle sizer (SMPS) and a TSI® 3010 condensation particle counter operating with 0.2 L.min^{-1} sample flow and 2.0 L.min^{-1} sheath flow. For the SOA mass concentration, the density of the organic material was assumed to be 1.0 g.cm^{-3}.

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SOA samples were collected in three stages: (a) after reaching the maximum particle concentration (as measured by SMPS) during the dark ozonolysis reaction of the VOC mixture; (b) after 3 hours of exposure of the SOA particles to OH radicals and/or UV radiation and (c) after 8-9 hours of exposure of the SOA particles to OH radicals and/or UV radiation.

OH radicals for the ageing experiments were produced by photolysis of H_2O_2 (60% w/v, Fisher Scientific). H_2O_2 was continuously injected into the smog chamber approximately 1 hour after reaching the maximum SOA concentration (mean maximum concentration 122±21 µg m^{-3}, n=6) produced from the dark ozonolysis reaction.~~Infrared absorbing species such as SOA precursors and their oxidation products and were measured using multi-path in-situ Fourier-transform infrared (FTIR) spectrometry (Bruker GmbH, Ettlingen, Germany) with an optical pathlength of 192 metres.~~

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 d3-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)

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2.2 CRAC experiments

~~*α*-pinene ozonlysis~~Supplementary experiments on the ozonolysis and OH~~-radical-~~ initiated ~~experiments~~oxidation of *α*-pinene were performed at the Centre for Research into Atmospheric Chemistry (CRAC) simulation chamber in Cork (Thüner et al., 2004, Kourtchev et al., 2014). The chamber is a cylinder made of fluorine–ethene–propene (FEP) Teflon® foil with a volume of 3.91 m^3. It was operated at 296±2 K using purified air at 0.1–1 mbar above atmospheric pressure. The experiments were performed at 55±2% relative humidity produced from bubbling purified air through heated water. The humidity and temperature were measured using a dew point meter (DRYCAP®DM70 Vaisala). Between experiments the chamber was cleaned by introducing about 1 ppm of ozone into the chamber and flushing with purified air at a flow rate of 0.15 m^3 min^{-1}. Aerosol seed particles produced from atomising $(NH_4)_2SO_4$ were neutralised by a Krypton-85 (Kr-85) charge neutraliser before introduction to the chamber~~.~~ with a concentration of approximately 5 µg m^{-3}. *α*-pinene was introduced into the chamber in the similar manner as described above for the CESAM experiments. OH radicals were generated from the photolysis of hydrogen peroxide (H_2O_2), which was added to the chamber by bubbling purified air into a slightly heated (~40-50 °C) solution of 50% H_2O_2. After the introduction of all reactants, the mixture was allowed to mix for 10 min before turning on 12 Philips TL12 (40W) lamps with λ_{max} = 310 nm to initiate photolysis of the OH radical precursor. 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}. For the ozonolysis-only experiments, ~ 2 ppm of ozone was introduced into the chamber over a period of 1-2 min from an electric discharge generator. Cyclohexane (~40 ppm, Sigma, >99% purity) was used as an OH scavenger in the ozonolysis-only experiments. 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).

2.2 Aerosol sample collection

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Total aerosol mass was collected on prebaked (at 650 °C) quartz fibre ~~filter~~filters (47 mm diameter, Tissuquartz 2500 QAT-UP, Pall Life Sciences) using a ~~filter pack.~~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. The sampling was performed at flow rate of 18-30 L min^{-1} for 1-2 hours depending on the SOA concentration in the chamber. To maintain constant pressure in the CESAM chamber, synthetic air was added during aerosol sample collection. 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. Aerosol samples were immediately placed into prewashed glass vials and stored in the freezer until analysis.

2.4 Aerosol analysis

Depending on the aerosol loading of the filter samples, which varied between 50 and 150 µg per filter, a part of the quartz fibre filter (5–20 cm^2) was extracted three times with 5 mL of methanol (Optima TM grade, Fisher Scientific) under ultrasonic agitation in slurry ice for 30 min. The extracts were combined, filtered through a Teflon filter (0.2 µm, ISO-DiscTM Supelco), and reduced by volume to approximately 50-200 µL under a gentle stream of nitrogen. The sample was split into two parts for direct infusion and LC/MS analyses. The concentration of SOA extracts for direct infusion analysis was adjusted to the same level of approximately 0.25 µg organic carbon µL^{-1}. The LC/MS portion was further evaporated to 20 µL and diluted by 0.1% aqueous solution of formic acid to 100 µL.

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.

The final extracts were analysed as described in Kourtchev et al. (2013) using ~~an ultrahigh~~a high resolution LTQ Orbitrap Velos mass spectrometer (Thermo Fisher,

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Bremen, Germany) equipped with electrospray ionization (ESI) and a TriVersa Nanomate robotic nanoflow chip-based ESI (Advion Biosciences, Ithaca NY, USA) source.

The Orbitrap MS was calibrated using an Ultramark 1621 solution (Sigma-Aldrich, UK). The mass accuracy of the instrument was routinely checked before the analysis and was below 1 ppm. The instrument mass resolution was 100 000 at *m*/*z* 400. A mixture of camphor sulfonic acid (20 ng μL^{-1}), glutaric acid (30 ng μL^{-1}), and *cis*-pinonic acid (30 ng μL^{-1}) in methanol and Ultramark 1621 solution were used to optimize the ion transmission settings.

The direct infusion nanoESI parameters were as follows: the ionization voltage and back pressure were set at −1.4 kV and 0.8 psi, respectively. The inlet temperature was 200 ^{o}C. The sample flow rate was approximately 200-300 nL min^{-1}. The negative ionization mass spectra were collected in three replicates at ranges *m*/*z* 100–650 and *m*/*z* 150–900 and processed using Xcalibur 2.1 software (Thermo Scientific).

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%.

LC-MS ESI parameters were as follows: 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}.

LC/(-)ESI-MS analysis was performed using an Accela system (Thermo Scientific, San Jose, USA) coupled with LTQ Orbitrap Velos MS and a T3 Atlantis C18 column (3 μm; 2.1 × 150 mm; Waters, Milford, USA). The mobile phases consisted of 0.1% formic acid (v/v) (A) and methanol (B). The applied gradient was as follows: 0–3 min 3% B, 3–25 min from 3% to 50% B (linear), 25–43 min from 50% to 90% B (linear),

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43–48 min from 90% to 3% B (linear), and kept for 12 min at 3% B (total run time 60 min). MS spectra were collected in full scan using the lock mass for the deprotonated dimer of formic acid at *m*/*z* 91.00368 with the resolution of 100 000 and the mass ranges of *m*/*z* 100–650 and *m*/*z* 150–900. On the basis of prescan information from the full scan MS, a parallel data-dependent collision induced dissociation (CID) multistage mass spectrometry (MSn) (*n* = 1, 2, 3, and 4) was performed on the most intense precursor ion in three scans at a resolution of 30 000.

For the majority of the identified organic species, authentic standards were not available; therefore, *cis*-pinonic acid, ketopinic acid and terebic acid were used as surrogates to quantify most of the acids in the samples (Kristensen et al., 2014). The identification was performed by comparing MS fragmentation patterns and chromatographic elution times reported in the literature (Yasmeen et al., 2010; 2012; Kristensen et al., 2014). The dimers were quantified using *cis*-pinonic acid as surrogate. Six-point calibration curves were constructed over two concentration ranges 0.2-50 ng µL^{-1} and 50-200 ng µL^{-1}.

~~Ultrahigh~~2.5 High MS Resolution Data Analysis

The direct infusion data analysis was performed using procedures described in detail ~~in~~by Kourtchev et al~~., ~~. (2013~~.~~). Briefly, for each sample analysis, 60-90 mass spectral scans were averaged into one mass spectrum. Molecular assignments were ~~done~~made using *Xcalibur 2.1* software applying the following constraints $^{12}C \leq 100$, $^{13}C \leq 1$, $^{1}H \leq 200$, $^{16}O \leq 50$, $^{14}N \leq 5$, $^{32}S \leq 2$, $^{34}S \leq 1$. The data filtering was performed using a *Mathematica 8.0* (Wolfram Research Inc., UK) code developed in-house that employed several conservative rules and constraints used in previous studies ~~as described in ~~(Kourtchev et al~~. (~~., 2013). In this study, only ions that appeared in all three replicates were kept for evaluation.

3. Results and discussions

3.1 Direct infusion results

Figure 1 shows direct infusion (-) nano ESI ~~UHR~~HR mass spectra for ‘fresh SOA’ collected after 1 h of dark ozonolysis reaction of the BVOC mixture and ‘aged SOA’ collected after 8-9 h of ageing under different atmospheric conditions (i.e., dark exposure of SOA in the presence of residual O_3, exposure to OH radicals and UV

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light, exposure to UV light only). It should be noted that all mass spectra are blank corrected and show only ions containing carbon, hydrogen and oxygen that appeared in three analytical replicates of two repeated chamber experiments. The ESI is a soft ionisation technique which allows very little or no fragmentation. Thus, in the negative ionisation mode it is expected that the detected ions correspond to the deprotonated molecules.

Irrespective of the applied atmospheric oxidation conditions, the mass spectra from all SOA samples ~~showed very similar ion distributions and~~ contained distinct groups of monomers, dimers and trimers in the mass range 100-650. Similar to laboratory studies with biogenic SOA from previous studies (e.g., Tolocka et al., 2004; Hall and Johnston, 2011; Putman et al., 2012; Kundu et al., 2012), the ion intensities in the oligomeric region (*m/z*>280) were very high (up to 25% relative intensities, see Fig. 1) and exhibited a bell shape distribution. This is in contrast to the ~~UHRMS~~HRMS analysis of ambient organic aerosol from various sampling locations (e.g., Wozniak et al., 2008; Kourtchev et al., 2013; 2014), where mass spectra generally have a unimodal distribution with relatively low ion intensities in the high mass range.

None of the ageing reactions studied here caused any visible influence on the ~~decrease or increase of the~~ ion intensity distributions~~.~~ except for an ion at *m/z* 357.15509 Moreover, several of the oligomers were not affected by the 8-9 hour OH radical/UV light and UV light-only exposures. This clearly shows that even prolonged exposure to OH radicals and UV light does not cause decomposition of oligomers formed under the employed ozonolysis conditions~~.~~, thus indicating their stability once they are formed in the atmosphere. 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).

In all experiments, the mass spectra were dominated by the ions at *m/z* 185.08167 and *m/z* 357.15509 in the monomeric and dimeric regions respectively.

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As confirmed by LC/MS analysis (discussed below), the ion at m/z 185.08167 corresponds to at least three different oxidation products with the same molecular formula ($C_9H_{14}O_4$) which are formed from *α-, β*-pinene, and Δ_3-carene, the major compounds in the studied BVOC mixture (Table S1). They include *cis*-pinic acid, homoterpenylic acid, and *cis*-caric acid. A dimer at *m/z* m/z 357.15509 was previously identified as pinyl-diaterpinyl ester MW 358 in the SOA from ozonolysis of *α*-pinene (Müller et al., 2008, 2009; Camredon et al., 2010; Yasmeen et al., 2010; Gao et al., 2010; Kristensen et al., 2013). Since pinyl-diaterpinyl ester MW 358 was not observed in the SOA from the OH radical initiated oxidation of α-pinene, it was suggested that high molecular weight dimers are formed through gas phase reaction of the stabilised Criegee Intermediate formed from ozonolysis of the monoterpene (Kristensen et al., 2014).

~~Considering the very large mass spectral dataset obtained from the UHRMS analysis~~In addition, the data was visualised using carbon oxidation state (OS_C) plots ~~(~~. The OS_C was introduced in aerosol science by Kroll et al~~., ~~. (2011~~). The OS_C is shown~~) to ~~be~~describe the composition of a complex mixture of organics undergoing dynamic oxidation processes. It is strongly linked to aerosol volatility and ~~is~~ 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).Carbon oxidation state was calculated for each molecular formula identified in the mass spectra using the following equation:

$$OS_C = -\sum_i OS_i \frac{n_i}{n_C} \qquad \text{(Eq. 1)}$$

where OS_i is the oxidation state associated with element *i*, n_i/n_C is the molar ratio of element *i* to carbon (Kroll et al., 2011).

Figure 2 shows two overlaid OS_C plots for the 'fresh' and 'aged' SOA from the 'dark ageing' experiments. Consistent with previous studies, the majority of molecules in the SOA had OS_C between –1 and +1 with up to 30 (nC) carbon atoms (Kroll et al., 2011 and the references therein). It has been suggested that semivolatile and low-volatility oxidised organic aerosol (SV-OOA and LV-OOA) produced by multistep oxidation reactions have OS_C between –1 and +1 with 13 or less carbon atoms (nC) (Kroll et al., 2011). It should be noted that all SOA samples contained a cluster of

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molecules with OS_C between –1 and –1.5 with nC less than 10 which could possibly be associated with OH radical oxidation products of isoprene, which was present in the BVOC mixture. The dark ozonolysis experiments were performed without an OH scavenger and thus it is likely that OH radicals produced from the ozonolysis reactions could further react with isoprene resulting in the molecules with very low OS_C state. The large cluster of molecules with 15 or more carbon atoms is likely to be associated with dimers and trimers of the BVOC oxidation products.

Figure 3 shows a carbon oxidation plot for the OH radical ageing experiments performed in the presence of UV light. In contrast to dark ageing experiments, a very small shift in the oxidation state throughout the entire mass range could be observed with ageing time. This shift is not visible in the mass spectrum shown in Fig 1c because the affected ions had very low intensities (mostly <5% relative intensity). The observed increase in the oxidation state of the SOA components is consistent with the results obtained for the OH radical ageing of SOA produced by dark ozonolysis reaction of *α*-pinene (Donahue et al., 2012). Using an aerosol mass spectrometer (AMS), an increase of the O/C ratio~~ was observed after addition of OH radicals~~, which is another metric to describe the oxidation state of the SOA components~~.~~, was observed after addition of OH radicals (Donahue et al., 2012).

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~~). Since an OH radical scavenger was used in the later~~) in the CRAC chamber. 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. It must be noted that the later experiments were performed at the different smog chamber (CRAC) and high RH (~55%). Since an OH radical scavenger was used in these ozonolysis experiments, we assume that all OH radicals were efficiently removed from the system. SOA from both ozonolysis and OH radical reaction with *α*-pinene contained distinguishable groups of monomers, dimers and trimers (Fig. 4). However, a clear shift to higher masses is observed in the mass spectra from the OH radical experiments. The presence of a large number of

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oligomers in the SOA from the OH~~ photolysis~~-initiated reaction indicates that this oxidation regime also results in a significant degree of oligomerisation. 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.

The SOA from the OH reaction clearly shows higher OS_C (Fig. 5, red squares) compared to that from the dark ozonolysis experiments (blue diamonds in Fig. 5). Moreover, it contained a very large number of LV-OOA species, which are often referred to as aged SOA (Jimenez et al., 2011). As ~~could be seen from~~indicated in the Van Krevelen diagram (Fig. 6), where H/C ratio is plotted as a function of the O/C ratio for each mass and corresponding formula identified in the sample (Nizkorodov et al., 2011), ~~that~~the SOA from the ~~photolysis~~OH-initiated reaction had substantially higher O/C ratios ~~compared~~ than those for SOA obtained from ~~the~~ ozonolysis ~~experiment~~. On the other hand, H/C ratios were very similar in SOA from both ~~ozonolysis and OH photolysis~~ reactions. This may be explained by addition of carboxylic or carbonylic groups to the backbone of the hydrocarbon structure, which generally occurs without substantial loss of hydrogen (Zhao et al., 2014).

In the UV-only ageing experiments (without addition of H_2O_2) no visible effect on the mass spectral features of the oligomers (Fig. 1d) and OS_C (not shown here) could be observed. Considering that during the UV-only experiments the RH was less than 9%, the production of OH radicals from the photolysis of unreacted ozone should be minimal (Rohrer et al., 2005), confirming that the increase in the OS_C in the OH radical initiated ageing experiments (discussed above) is not due to UV-initiated decomposition of the SOA products, but to the OH radical reaction. This is in line with a recent study ~~(Denjean et al., 2015) that observed an insignificant~~where no significant change in the O/C ratio~~,~~ was determined by a time-of-flight aerosol mass spectrometer (ToF-AMS~~),~~) when the SOA produced from dark ozonolysis of *α*-pinene was exposed to light representing the solar energy distribution at Earth's surface (Denjean et al., 2015). On the other hand, this is in contrast to findings reported by

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Wong et al (2014) who observed photolytic ageing of a-pinene SOA in the presence of ammonium sulfate that exhibited a dependence on relative humidity.

3.2 LC/MS results

Due to competitive ionisation of analytes in the ESI direct infusion analysis of the aerosol samples that are known to have a very complex matrix, the ion intensities do not directly reflect the concentration of the molecules in the sample. Therefore, the effect of ageing processes on the SOA composition was additionally investigated using LC coupled with ~~UHRMS.~~HRMS. All data described in this section (except discussion of Fig S3 and S4) correspond to experiments performed at CESAM chamber. A list of tentatively identified products formed during dark ozonolysis of the BVOC mixture is shown in Table S1. The majority of the identified compounds were attributed to *α*-, and *β*-pinene oxidation products which can be explained by the fact that both of these precursors contributed to about 60% of the total BVOC mixture concentration (ppbv) used in this study. On the other hand, none of the chromatographic peaks were associated with isoprene oxidation products which could be due to the relatively low (about 10%) contribution of isoprene to the total mixture. Moreover, isoprene is known to produce very low aerosol yields (less than 0.01) when reacted with ozone (Kleindienst et al., 2007). Most of the ~~detected~~tentatively identified compounds have been previously observed in aerosol samples from laboratory (e.g., Yu et al., 1999; Szmigielski et al., 2007; Glasius et al., 2000; Müller et al., 2008, 2009; Camredon et al., 2010; Gao et al., 2010; Yasmeen et al., 2010; Kourtchev et al., 2014) and field studies (e.g., Gómez-González et al., 2012; Kristensen et al., 2013, 2014; Kourtchev et al., 2013). Therefore, to avoid unnecessary repetition, the sources and processes leading to the formation of these compounds are not discussed here. Although the LC/MS allowed separation and identification of a considerably smaller number of molecules compared to direct infusion analysis, some of them are very useful markers for aerosol source characterisation and are good indicators of the processes involved in the formation of the SOA. 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.,

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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.

Compared to the direct infusion analysis, only a very small number of dimers were ~~observed~~separated using the LC/MS method in all samples, irrespective of the ageing conditions. These dimers include isomers with *m/z* 337.20172, *m/z* 343.13983, *m/z* 357.15509, *m/z* 367.17599, *m/z* 387.20221 and *m/z* 369.19141, consistent with previous studies that applied LC/MS for the analysis of SOA (*e.g.,* Kristensen et al., 2013; 2014). ~~-~~Four of these dimers, pinyl-diaterpenyl ester MW 358 (*m/z* 357.15509), pinyl-diaterebyl dimer MW 344 (*m/z* 343.13983) and pinonyl-pinyl dimer MW 368 (*m/z* 367.17599) and MW 388 dimer ester (*m/z* 387.20221) have been identified previously in SOA from ozonolysis of *α*-pinene (*e.g.,* Yasmeen et al., 2010; Kristensen et al., 2013, 2014), while none of them were observed in the SOA from the OH radical initiated oxidation of *α*-pinene (Kristensen et al., ~~2014).~~2014). It must be noted that these dimers were also observed during the direct infusion analysis. Interestingly, the tentative structures of the three dimers reported in the literature (Yasmeen et al., 2010; Kristensen et al., 2013; 2014) contained pinic acid, which is a less important product in the OH radical initiated oxidation ~~compared to the ozonolysis of *α*-pinene.~~than in the ozonolysis of *α*-pinene (Kristensen et al., 2014). The chromatographic peak areas for all four dimers, determined by LC/MS, showed relatively good correlation ($R^2>0.90$) suggesting these compounds are possibly formed through similar processes. It should be noted that the observed small number of dimers in the LC/MS chromatogram from *α*-pinene ozonolysis, and their absence in the SOA generated from the OH radical initiated oxidation of *α*-pinene, in previous studies and the current work, does not necessarily mean that oligomers are not formed in the latter reaction. The lack of chromatographically resolved dimers in the OH radical initiated SOA could be explained by the selectivity of the utilised LC columns. The integration of chromatographic 'humps' eluting at the end of the chromatograms from both ozonolysis and OH radical initiated reaction of *α*-pinene (Fig ~~SI1~~S3 and Fig ~~SI2~~S4) reveals the presence of a large number of dimers, trimers and tetramers that were not resolved by the LC column. The overall oligomer distribution of these unresolved LC 'humps' resembles that of the respective direct infusion mass spectra.

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Figure 7 shows concentrations of selected first and later generation oxidation products, as well as dimers in the SOA produced under different ageing conditions. Irrespective of the ageing conditions, and even during the dark ozonolysis experiments (without addition of OH radicals), all samples contained MBTCA, the OH radical initiated oxidation product of *α*-pinene. It has been estimated that the ozonolysis of *α*-pinene results in the formation of OH radicals with a yield between 0.8 and 1.0 (Atkinson et al., 1997; Presto and Donahue, 2004). Therefore, without the use of an OH radical scavenger, a substantial fraction of *α*-pinene and other terpenes present in the mixture can be oxidised by OH radicals (Henry and Donahue, 2011). During the dark ageing experiments~~ (Fig. 7a~~(with SOA exposure to residual ozone), the concentrations of the marker compounds remained unchanged even after 9 h of SOA exposure, indicating that all OH radicals produced from the BVOC ozonolysis were immediately consumed in the first hour of the reaction~~.~~(Fig. 7a). The concentrations of the first generation products and the dimers did not change during the dark ageing experiments either. In contrast, the concentration of MBTCA increased when OH radicals were introduced into the system (Fig 7b) followed by a decrease in the concentration of pinonic acid and pinic acid, confirming that pinonic acid is further oxidised into MBTCA (Müller et al., 2008).

In ~~–~~the UV-only ~~exposure~~ageing experiments the concentrations of all marker compounds in the SOA remained unaffected suggesting that the observed changes in the photolysis experiments with OH radicals (discussed above) are due to the OH-radical initiated chemistry rather than photolytic degradation of the first generation products. Irrespective of the tested conditions, the contribution of the dimers to the SOA mass showed no statistical difference (Table S2) indicating that none of the studied conditions have an effect on dimer decomposition or formation.

4. Conclusions

In this study the influence of several ageing processes on the molecular composition of organic aerosols has been investigated using direct infusion and liquid chromatography ~~UHRMS~~HRMS. SOA formed from ozonolysis of a BVOC mixture was aged for 8-9 ~~hour~~h in ~~dark conditions~~ in the ~~presence of~~dark with residual ozone, under UV irradiation, and by OH radicals formed from the continuous photolysis of H_2O_2. Dark ageing and UV ageing in the presence of ozone and UV irradiation closely resembling the solar energy distribution at Earth's surface did not

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significantly affect the molecular composition of studied SOA. In contrast, OH radical initiated ageing showed an increase in OS_C and elemental O/C ratios of the BSOA components from the studied BVOC mixture. None of the ageing processes produced an observable effect on the oligomers formed from the ozonolysis of the BVOC mixture and they were found to be equally abundant in both 'fresh' and 'aged' SOA. Additional separate dark ozonolysis and OH-initiated experiments with α-pinene (a major component of the studied mixture) showed that oligomers are an important group of compounds in both oxidation schemes. However, oligomers in the OH-initiated SOA were shifted towards higher masses and were not readily resolved by the LC techniques applied here, indicating that their importance could have been underestimated in previous similar studies. SOA from the OH-~~radical~~ initiated ~~α-pinene~~ oxidation of α-pinene had a significantly higher OS_C and O/C compared to that from pure ozonolysis experiments, confirming that the OH radical reaction is more likely to be responsible for the occurrence of highly oxidized species in ambient biogenic SOA. Considering that the timescale (8-9 hours) of the ageing reaction in our experiments was still substantially lower than the lifetime of organic aerosol in the real atmosphere (up to 12 days) (Robinson et al., 2007; Rudich et al., 2007) the observed OH ageing effects could be substantially stronger when SOA is aged over a longer period in the ambient atmosphere.

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Table 1. Experimental conditions at CESAM chamber.

SOA Exposure type	**Experiment**	**O_3 conc., ppb**	**RH, %**	**SOA exposure time, hours**
Dark ageing	Replicate 1	450	3-6	9
	Replicate 2	450	2.7-4.9	9
OH radical and UV exposure	Replicate 1	300	4.9-8.2	8
	Replicate 2	300	4-7.2	8
UV exposure	Replicate 1	300	3-9	8
	Replicate 2	300	3.5-8	8

BVOC mixture concentration in all experiments was about 150 ppb (60 ppb of *α*-pinene, 45 ppb of Δ_3-carene, 30 ppb of *β*-pinene and 15 ppb of isoprene). $(NH_4)_2SO_4$ aerosol seed concentration was about 5 µg m^{-3} in all experiments. Listed conditions are for the initial formation of the SOA and not for the subsequent ageing reaction.

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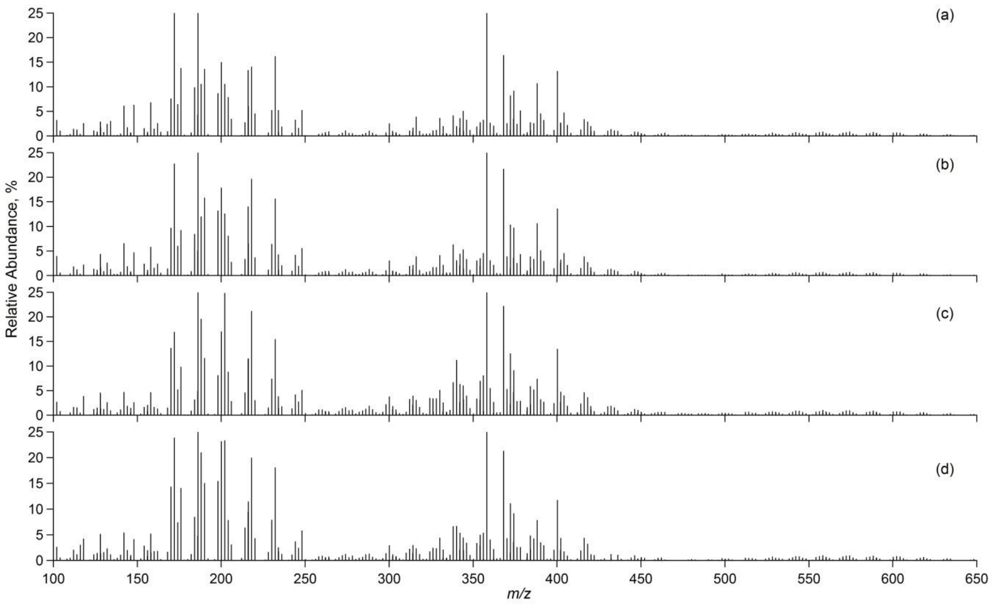

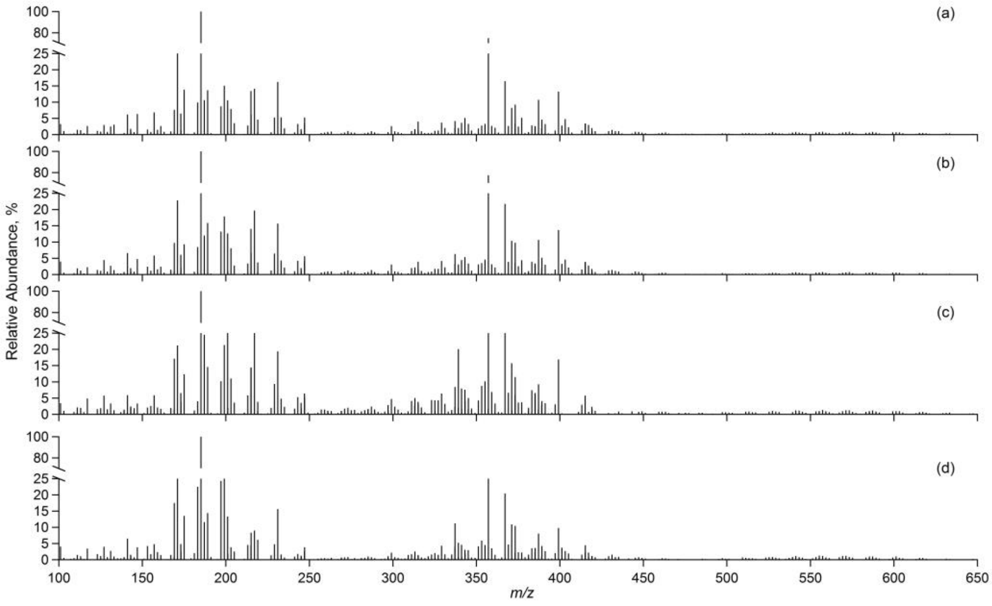

Fig. 1. Direct infusion (-) nanoESI ~~UHRMS~~HRMS of SOA from dark ozonolysis of BVOC mixture: (a) fresh aerosol, (b) aged for 9 h in dark (with residual ozone), (c) aged for 8 h in the presence of O_3, H_2O_2 and UV light and (d) aged for 9 h in the presence of O_3 and UV light.

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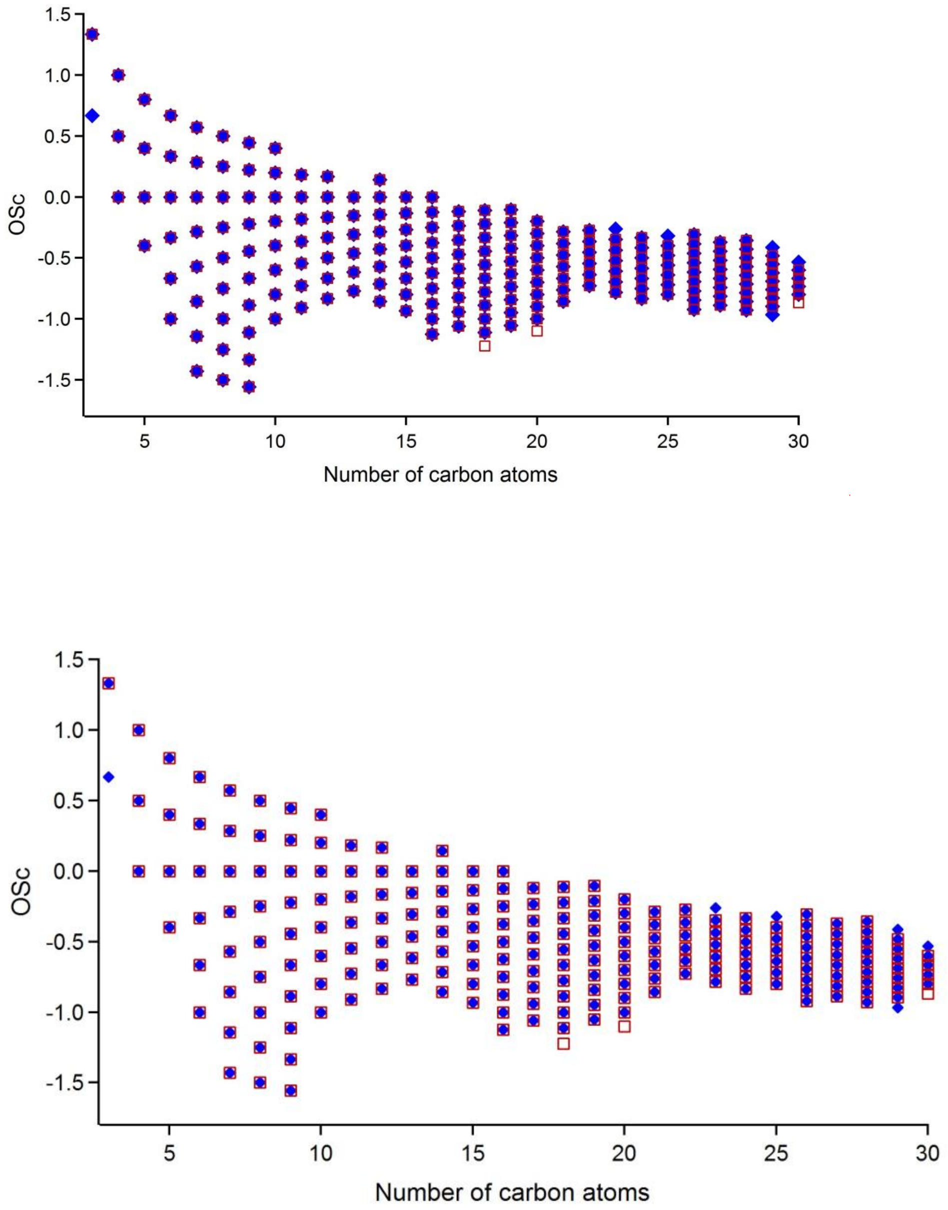

Fig. 2. Carbon oxidation state of SOA from BVOC mixture from dark ageing experiments with O_3. Blue diamonds correspond to molecules in 'fresh SOA', red squares to 'aged SOA' for 9 hours.

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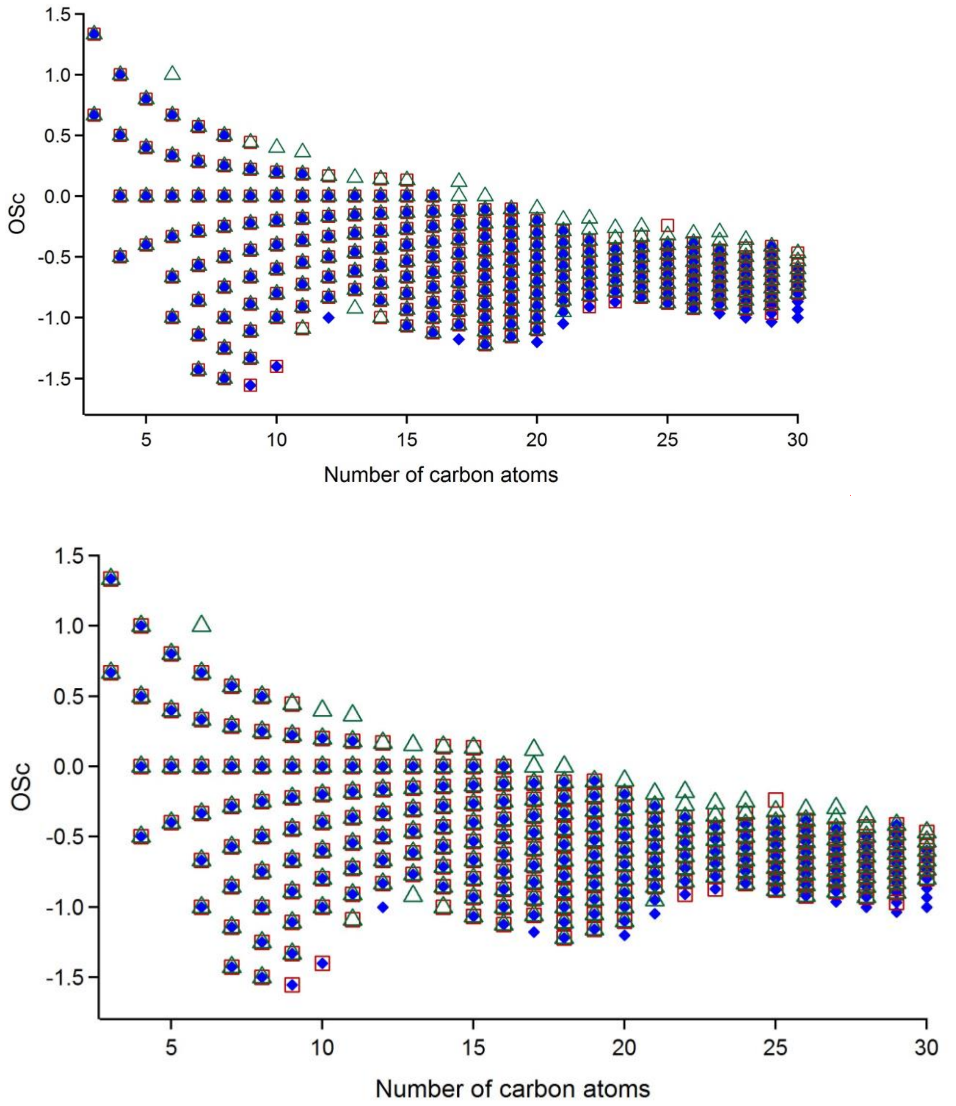

Fig. 3. Carbon oxidation state of SOA from OH-initiated ageing of aerosol from ozonolysis of BVOC mixture. Blue diamonds correspond to molecules in ‘fresh SOA’, red squares to ‘aged SOA’ for 3 hours and green triangles to ‘aged SOA’ for 9 hours.

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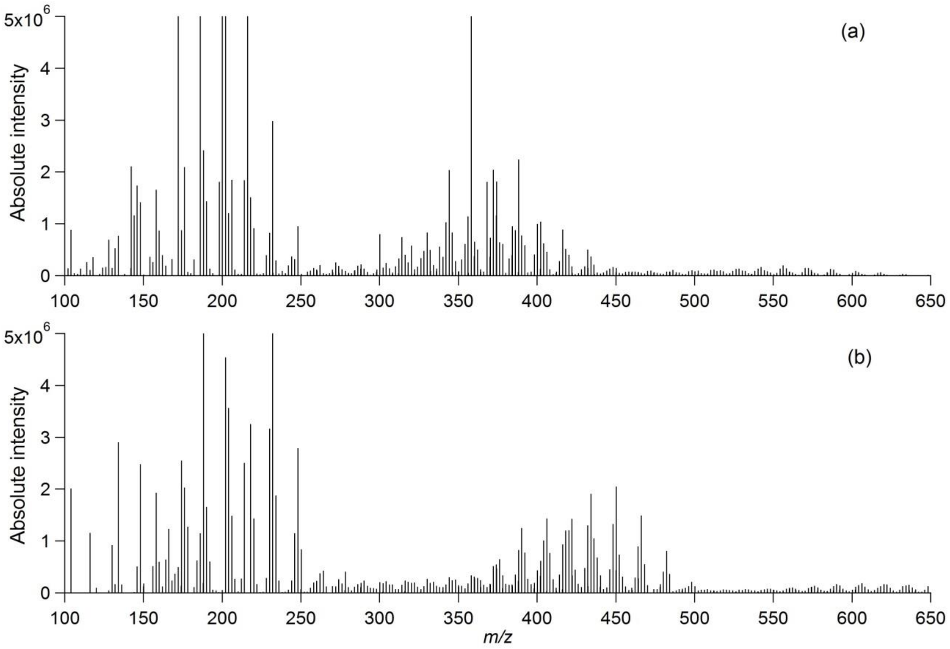

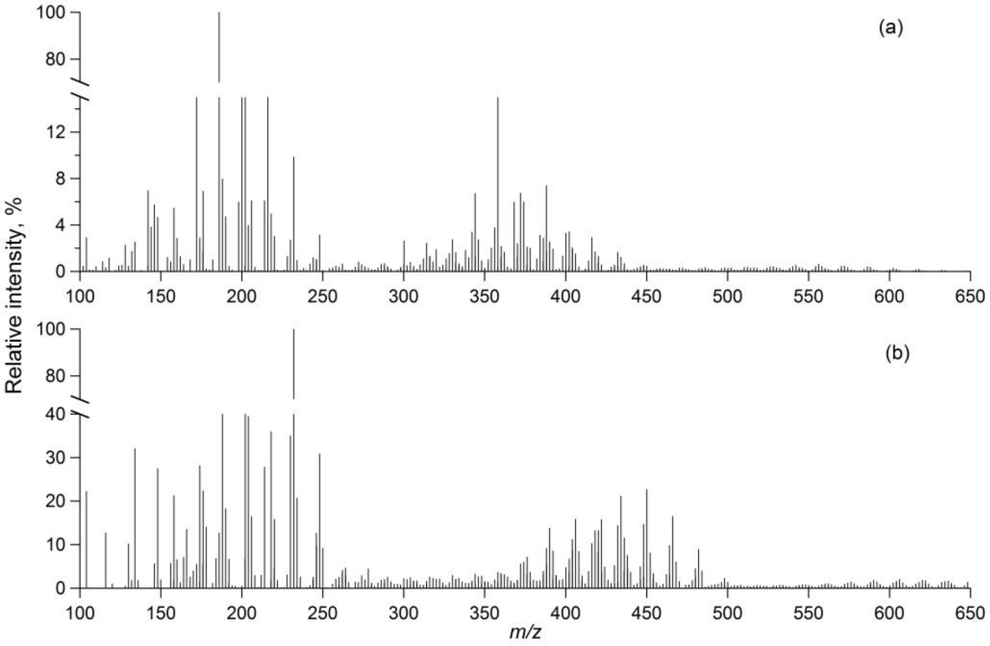

Fig. 4. Direct infusion (-) nanoESI-~~UHR~~HR mass spectra of the SOA from (a) dark ozonolysis and (b) OH-initiated reaction with α-pinene.

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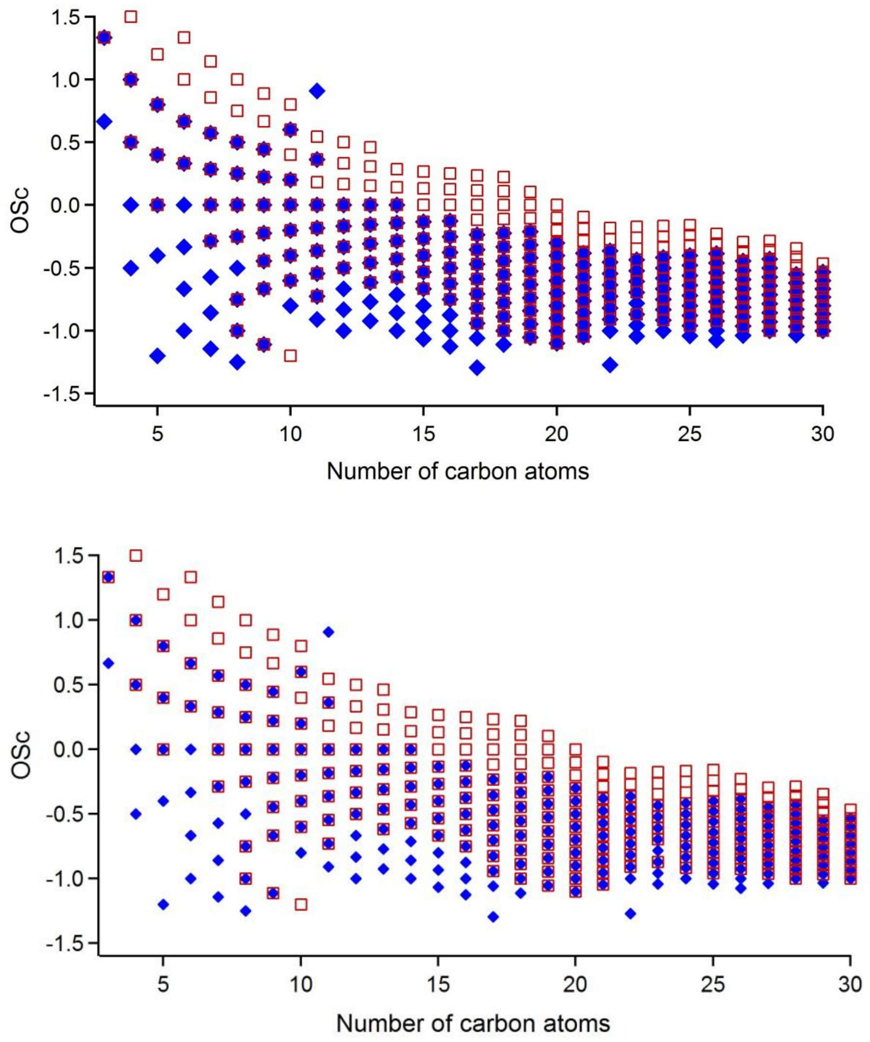

Fig. 5. Carbon oxidation state of the molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α-pinene.

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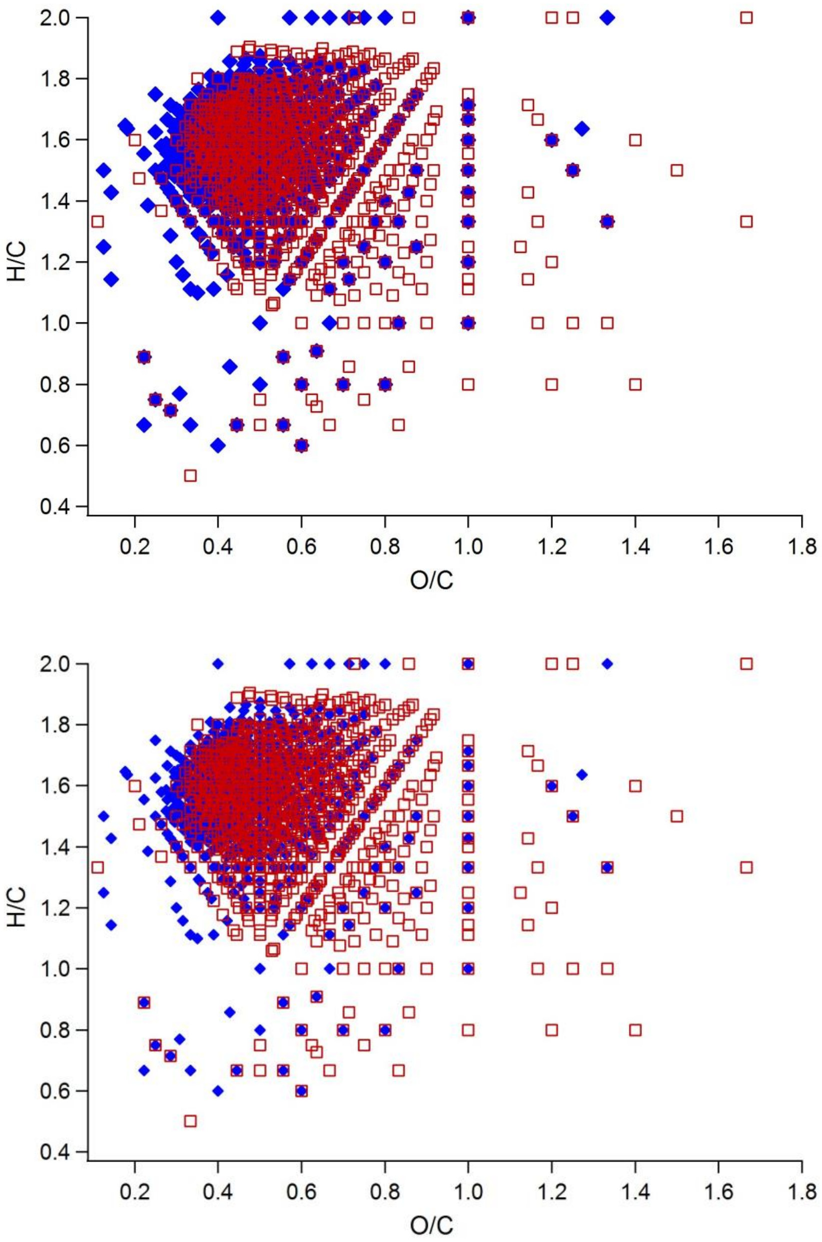

Fig. 6. Van Krevelen diagram for molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α-pinene.

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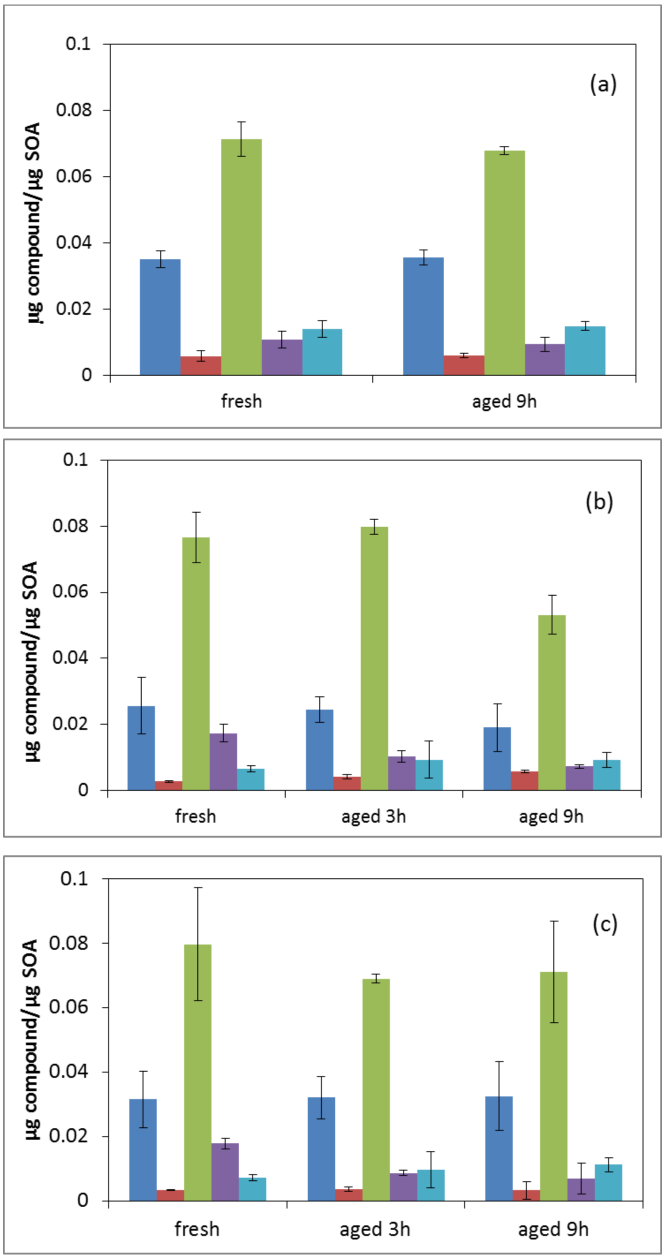

Fig. 7. Normalised concentrations (µg µg^{-1} SOA) of terpenylic acid (dark blue), MBTCA (red), pinic acid (light green), pinonic acid (violet),~~ terpenylic acid (dark blue), MBTCA (red) ~~and a dimer MW 358 (light blue) at three ageing conditions: (a) dark ageing with exposure to residual ozone, (b) OH radical initiated ageing and (c) UV-only ageing experiments. Pinic, pinonic and terpenylic acids represent organic species associated with 'fresh' SOA, whereas MBTCA is associated with 'aged' SOA. The 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.

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Molecular composition of fresh and aged secondary organic aerosol from a mixture of biogenic volatile compounds: a high resolution mass spectrometry study

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Abstract

Field observations over the past decade indicate that a significant fraction of organic aerosol in remote areas may contain highly oxidised molecules. Aerosol processing or further oxidation (ageing) of organic aerosol has been suggested to be responsible for their formation through heterogeneous uptake of oxidants and multigenerational oxidation of vapours by OH radicals. In this study we investigated the influence of several ageing processes on the molecular composition of secondary organic aerosols (SOA) using direct infusion and liquid chromatography high resolution mass spectrometry. SOA was formed in simulation chamber experiments from ozonolysis of a mixture of four biogenic volatile organic compounds (BVOC): *α*-pinene, *β*-pinene, Δ_3-carene and isoprene. The SOA was subsequently aged under three different sets of conditions: in the dark in the presence of residual ozone, with UV irradiation and OH radicals, and using UV light only. Among all studied conditions, only OH radical-initiated ageing was found to influence the molecular composition of the aerosol and showed an increase in carbon oxidation state (OS_C) and elemental O/C ratios of the SOA components. None of the ageing processes produced an observable effect on the oligomers formed from ozonolysis of the BVOC mixture, which were found to be equally abundant in both ‘fresh’ and ‘aged’ SOA. Additional experiments using *α*-pinene as the sole precursor demonstrated that oligomers are an important group of compounds in SOA produced from both ozonolysis and OH radical-initiated oxidation processes; however, a completely different set of oligomers is formed under these two oxidation regimes. SOA from the OH -initiated oxidation of *α*-pinene had a significantly higher overall OS_C and O/C compared to that from pure ozonolysis experiments confirming that the OH radical reaction is more likely to be responsible for the occurrence of highly oxidised species in ambient biogenic SOA.

1. Introduction

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric chemistry and give rise to secondary organic aerosols (SOA) that affect climate and air quality (Kanakidou et al., 2005; Hallquist et al., 2009). Although a substantial fraction (20−90%) of atmospheric fine particulate matter is comprised of organic compounds (Jimenez et al., 2009), its molecular composition remains poorly understood. The limited knowledge of aerosol composition ultimately restricts our understanding of the most relevant particle sources.

Laboratory chamber experiments have been performed for decades in an attempt to mimic atmospheric SOA formation. However, it is still unclear how close the aerosol particles generated in laboratory experiments resemble atmospheric SOA with respect to their detailed chemical composition. Field observations over the past decade indicate that a significant fraction of organic aerosol in remote areas may contain highly oxidised molecules (Chen et al., 2009; Kroll et al., 2011). In contrast, laboratory-generated SOA is oxidised to a much lesser extent, suggesting that the conditions in smog chamber experiments are not optimal for mimicking ageing in the atmosphere (Donahue et al., 2012). One likely reason for this difference in composition is that the reaction times in chamber experiments are significantly shorter than the lifetime of organic aerosol in the real atmosphere (e.g., Shilling et al. 2009). Another explanation for the difference is that typical smog chamber experiments are performed with only one or two SOA precursors and are limited to one oxidant (e.g., O_3 or OH radicals).

It has been suggested that aerosol processing or further oxidation (ageing) of OA could be responsible for formation of highly oxidised OA components through heterogeneous uptake of oxidants and multigenerational oxidation of vapours by OH radicals (Henry and Donahue, 2012). Several OH radical initiated ageing experiments have been performed with α-pinene, its oxidation products (Donahue et al., 2012; Müller et al., 2012; Denjean et al., 2015; Romonosky et al., 2015) and a mixture with limonene and *p*-xylene (Emanuelsson et al., 2013; Flores et al., 2014). It was found that hydroxyl radical ageing significantly increases the concentration of first generation BSOA components as determined from both O/C elemental ratios and individual marker compounds. In addition, atmospheric ageing was proposed to have a role in the formation of high molecular weight compounds or oligomers (Kalberer et al., 2004) through condensed (Rudich et al., 2007) or aqueous (Renard et al., 2014) phase chemistry.

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).

The influence of ageing on oligomer formation is generally inferred from analysis of the elemental O/C and H/C ratios. However, other chemical processes such as carboxylation and carbonylisation are also known to affect the elemental ratios. Additionally, the effects of ageing on oligomerisation have been assessed by monitoring the concentration of 2-5 dimers that could be identified by liquid chromatography mass spectrometry (LC/MS) (Emanuelsson et al., 2013). Other techniques such as high resolution mass spectrometry (HRMS) often identify hundreds of oligomeric compounds (Tolocka et al., 2004; Kalberer et al., 2004; Reinhardt et al., 2007; Hall and Johnston, 2011; Putman et al., 2012; Kundu et al., 2012; Kourtchev et al., 2014), which raises the question of whether the small number of dimers that can be quantified with LC/MS reliably represent the entire oligomer content of the SOA.

The objectives of this work were to examine the influence of several ageing conditions on the molecular composition of biogenic SOA. SOA formed from ozonolysis of a BVOC mixture was exposed to; (i) residual ozone in the dark, (ii) OH radicals and UV light (iii) UV light only. The BVOC mixture contained the four most abundant compounds (i.e., α and β-pinene, Δ_3-carene, and isoprene) detected at a remote boreal forest site Hyytiälä, Finland (Hakola et al., 2003; Aaltonen et al., 2011; Bäck et al., 2012, Kourtchev et al., 2014). The aged SOA was characterised using direct infusion and LC HR-MS that allows detection of thousands of individual SOA constituents at once providing their elemental formulae from accurate mass measurements (Nizkorodov et al., 2011).

2. Methods

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.

2.1. CESAM experiments

Aerosol ageing experiments were carried out in the CESAM chamber (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber). A detailed description of the chamber is provided elsewhere (Wang et al., 2011). Briefly, the chamber is a 4.2 m^3 stainless steel vessel, operated at 296±2 K using synthetic air at 1 bar atmospheric pressure. The solar irradiation is mimicked using xenon arc lamps (4 kW, XPO 4000 W/HS, OSRAM) fitted with 8 mm Pyrex filters that provide an emission spectrum closely resembling that at the Earth’s surface near the Equator over the wavelength range 290-700 nm (Wang et al., 2011). For these experiments, the corresponding NO_2 photolysis frequency was $J_{NO2}=(2.5\pm0.2)\times10^{-3}\ s^{-1}$. The experimental conditions are outlined in Table 1. The experiments were performed at a relative humidity (RH) of 2-9%. Neutral seed particles of ammonium sulfate were generated from 3 mM $(NH_4)_2SO_4$ (Sigma-Aldrich, 99.99 %) solution using an atomiser (TSI® model 3075) and dried using a diffusion dryer (TSI®, model 3062) before introduction into the chamber. BVOCs (i.e. *α*-pinene, *β*-pinene, Δ_3-carene and isoprene) were introduced into the chamber by flowing purified air over known amounts of the compounds in a gently heated Pyrex impinger. 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), Δ_3-carene (0.3), *β*-pinene (0.2) and isoprene (0.1)). The total VOC mixture concentration was about 150 ppb for all CESAM experiments. The precursor hydrocarbons concentrations and their decay were measured using *in-situ* FTIR spectroscopy. After injecting the BVOC mixture and allowing it to stabilise for 5-10 min, ozone was introduced into the chamber over a period of 10-15 s from an electric discharge generator. Infrared absorbing species such as SOA precursors and their oxidation products were measured during the reactions using multi-path in-situ Fourier-transform infrared (FTIR) spectrometry (Bruker GmbH, Ettlingen, Germany) with an optical pathlength of 192 metres. The concentration of NOx throughout the experiments was below the detection limit.

Particle size distributions (from 19 to 980 nm in diameter) were measured with a TSI® 3080 scanning mobility particle sizer (SMPS) and a TSI® 3010 condensation particle counter operating with 0.2 $L.min^{-1}$ sample flow and 2.0 $L.min^{-1}$ sheath flow. For the SOA mass concentration, the density of the organic material was assumed to be 1.0 $g.cm^{-3}$.

SOA samples were collected in three stages: (a) after reaching the maximum particle concentration (as measured by SMPS) during the dark ozonolysis reaction of the VOC mixture; (b) after 3 hours of exposure of the SOA particles to OH radicals and/or UV radiation and (c) after 8-9 hours of exposure of the SOA particles to OH radicals and/or UV radiation.

OH radicals for the ageing experiments were produced by photolysis of H_2O_2 (60% w/v, Fisher Scientific). H_2O_2 was continuously injected into the smog chamber approximately 1 hour after reaching the maximum SOA concentration (mean maximum concentration 122±21 $\mu g\ m^{-3}$, n=6) produced from the dark ozonolysis reaction.

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 d3-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)

2.2 CRAC experiments

Supplementary experiments on the ozonolysis and OH- initiated oxidation of *α*-pinene were performed at the Centre for Research into Atmospheric Chemistry (CRAC) simulation chamber in Cork (Thüner et al., 2004, Kourtchev et al., 2014). The chamber is a cylinder made of fluorine–ethene–propene (FEP) Teflon® foil with a volume of 3.91 m^3. It was operated at 296±2 K using purified air at 0.1–1 mbar above atmospheric pressure. The experiments were performed at 55±2% relative humidity produced from bubbling purified air through heated water. The humidity and temperature were measured using a dew point meter (DRYCAP®DM70 Vaisala). Between experiments the chamber was cleaned by introducing about 1 ppm of ozone into the chamber and flushing with purified air at a flow rate of 0.15 $m^3\ min^{-1}$. Aerosol seed particles produced from atomising $(NH_4)_2SO_4$ were neutralised by a Krypton-85 (Kr-85) charge neutraliser before introduction to the chamber with a concentration of approximately 5 µg m^{-3}. *α*-pinene was introduced into the chamber in the similar manner as described above for the CESAM experiments. OH radicals were generated from the photolysis of hydrogen peroxide (H_2O_2), which was added to the chamber by bubbling purified air into a slightly heated (~40-50 °C) solution of 50% H_2O_2. After the introduction of all reactants, the mixture was allowed to mix for 10 min before turning on 12 Philips TL12 (40W) lamps with λ_{max} = 310 nm to initiate photolysis of the OH radical precursor. 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}. For the ozonolysis-only experiments, ~ 2 ppm of ozone was introduced into the chamber over a period of 1-2 min from an electric discharge generator. Cyclohexane (~40 ppm, Sigma, >99% purity) was used as an OH scavenger in the ozonolysis-only experiments. 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).

2.2 Aerosol sample collection

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. The sampling was performed at flow rate of 18-30 L min^{-1} for 1-2 hours depending on the SOA concentration in the chamber. To maintain constant pressure in the CESAM chamber, synthetic air was added during aerosol sample collection. 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. Aerosol samples were immediately placed into prewashed glass vials and stored in the freezer until analysis.

2.4 Aerosol analysis

Depending on the aerosol loading of the filter samples, which varied between 50 and 150 µg per filter, a part of the quartz fibre filter (5–20 cm^2) was extracted three times with 5 mL of methanol (Optima TM grade, Fisher Scientific) under ultrasonic agitation in slurry ice for 30 min. The extracts were combined, filtered through a Teflon filter

(0.2 µm, ISO-DiscTM Supelco), and reduced by volume to approximately 50-200 µL under a gentle stream of nitrogen. The sample was split into two parts for direct infusion and LC/MS analyses. The concentration of SOA extracts for direct infusion analysis was adjusted to the same level of approximately 0.25 µg organic carbon µL^{-1}. The LC/MS portion was further evaporated to 20 µL and diluted by 0.1% aqueous solution of formic acid to 100 µL.

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.

The final extracts were analysed as described in Kourtchev et al. (2013) using a high resolution LTQ Orbitrap Velos mass spectrometer (Thermo Fisher, Bremen, Germany) equipped with electrospray ionization (ESI) and a TriVersa Nanomate robotic nanoflow chip-based ESI (Advion Biosciences, Ithaca NY, USA) source.

The Orbitrap MS was calibrated using an Ultramark 1621 solution (Sigma-Aldrich, UK). The mass accuracy of the instrument was routinely checked before the analysis and was below 1 ppm. The instrument mass resolution was 100 000 at *m*/*z* 400. A mixture of camphor sulfonic acid (20 ng µL^{-1}), glutaric acid (30 ng µL^{-1}), and *cis*-pinonic acid (30 ng µL^{-1}) in methanol and Ultramark 1621 solution were used to optimize the ion transmission settings.

The direct infusion nanoESI parameters were as follows: the ionization voltage and back pressure were set at −1.4 kV and 0.8 psi, respectively. The inlet temperature was 200 ^{o}C. The sample flow rate was approximately 200-300 nL min^{-1}. The negative ionization mass spectra were collected in three replicates at ranges *m*/*z* 100–650 and *m*/*z* 150–900 and processed using Xcalibur 2.1 software (Thermo Scientific).

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%.

LC-MS ESI parameters were as follows: 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}. LC/(-)ESI-MS analysis was performed using an Accela system (Thermo Scientific, San Jose, USA) coupled with LTQ Orbitrap Velos MS and a T3 Atlantis C18 column (3 µm; 2.1 × 150 mm; Waters, Milford, USA). The mobile phases consisted of 0.1% formic acid (v/v) (A) and methanol (B). The applied gradient was as follows: 0–3 min 3% B, 3–25 min from 3% to 50% B (linear), 25–43 min from 50% to 90% B (linear), 43–48 min from 90% to 3% B (linear), and kept for 12 min at 3% B (total run time 60 min). MS spectra were collected in full scan using the lock mass for the deprotonated dimer of formic acid at *m*/*z* 91.00368 with the resolution of 100 000 and the mass ranges of *m*/*z* 100–650 and *m*/*z* 150–900. On the basis of prescan information from the full scan MS, a parallel data-dependent collision induced dissociation (CID) multistage mass spectrometry (MSn) (*n* = 1, 2, 3, and 4) was performed on the most intense precursor ion in three scans at a resolution of 30 000.

For the majority of the identified organic species, authentic standards were not available; therefore, *cis*-pinonic acid, ketopinic acid and terebic acid were used as surrogates to quantify most of the acids in the samples (Kristensen et al., 2014). The identification was performed by comparing MS fragmentation patterns and chromatographic elution times reported in the literature (Yasmeen et al., 2010; 2012; Kristensen et al., 2014). The dimers were quantified using *cis*-pinonic acid as surrogate. Six-point calibration curves were constructed over two concentration ranges 0.2-50 ng µL^{-1} and 50-200 ng µL^{-1}.

2.5 High MS Resolution Data Analysis

The direct infusion data analysis was performed using procedures described in detail by Kourtchev et al. (2013). Briefly, for each sample analysis, 60-90 mass spectral scans were averaged into one mass spectrum. Molecular assignments were made using *Xcalibur 2.1* software applying the following constraints $^{12}C \leq 100$, $^{13}C \leq 1$, $^{1}H \leq 200$, $^{16}O \leq 50$, $^{14}N \leq 5$, $^{32}S \leq 2$, $^{34}S \leq 1$. The data filtering was performed using a *Mathematica 8.0* (Wolfram Research Inc., UK) code developed in-house that employed several conservative rules and constraints used in previous studies (Kourtchev et al., 2013). In this study, only ions that appeared in all three replicates were kept for evaluation.

3. Results and discussions

3.1 Direct infusion results

Figure 1 shows direct infusion (-) nano ESI HR mass spectra for ‘fresh SOA’ collected after 1 h of dark ozonolysis reaction of the BVOC mixture and ‘aged SOA’ collected after 8-9 h of ageing under different atmospheric conditions (i.e., dark exposure of SOA in the presence of residual O_3, exposure to OH radicals and UV light, exposure to UV light only). It should be noted that all mass spectra are blank corrected and show only ions containing carbon, hydrogen and oxygen that appeared in three analytical replicates of two repeated chamber experiments. The ESI is a soft ionisation technique which allows very little or no fragmentation. Thus, in the negative ionisation mode it is expected that the detected ions correspond to the deprotonated molecules.

Irrespective of the applied atmospheric oxidation conditions, the mass spectra from all SOA samples contained distinct groups of monomers, dimers and trimers in the mass range 100-650. Similar to laboratory studies with biogenic SOA from previous studies (e.g., Tolocka et al., 2004; Hall and Johnston, 2011; Putman et al., 2012; Kundu et al., 2012), the ion intensities in the oligomeric region (*m/z*>280) were very high (up to 25% relative intensities, see Fig. 1) and exhibited a bell shape distribution. This is in contrast to the HRMS analysis of ambient organic aerosol from various sampling locations (e.g., Wozniak et al., 2008; Kourtchev et al., 2013; 2014), where mass spectra generally have a unimodal distribution with relatively low ion intensities in the high mass range.

None of the ageing reactions studied here caused any visible influence on the ion intensity distributions except for an ion at *m/z* 357.15509 Moreover, several of the oligomers were not affected by the 8-9 hour OH radical/UV light and UV light-only exposures. This clearly shows that even prolonged exposure to OH radicals and UV light does not cause decomposition of oligomers formed under the employed ozonolysis conditions, thus indicating their stability once they are formed in the atmosphere. 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).

In all experiments, the mass spectra were dominated by the ions at *m/z* 185.08167 and *m/z* 357.15509 in the monomeric and dimeric regions respectively. As confirmed by LC/MS analysis (discussed below), the ion at *m/z* 185.08167 corresponds to at least three different oxidation products with the same molecular formula ($C_9H_{14}O_4$) which are formed from *α-, β*-pinene, and Δ_3-carene, the major compounds in the studied BVOC mixture (Table S1). They include *cis*-pinic acid, homoterpenylic acid, and *cis*-caric acid. A dimer at *m/z m/z* 357.15509 was previously identified as pinyl-diaterpinyl ester MW 358 in the SOA from ozonolysis of *α*-pinene (Müller et al., 2008, 2009; Camredon et al., 2010; Yasmeen et al., 2010; Gao et al., 2010; Kristensen et al., 2013). Since pinyl-diaterpinyl ester MW 358 was not observed in the SOA from the OH radical initiated oxidation of α-pinene, it was suggested that high molecular weight dimers are formed through gas phase reaction of the stabilised Criegee Intermediate formed from ozonolysis of the monoterpene (Kristensen et al., 2014).

In addition, the data was visualised using carbon oxidation state (OS_C) plots. 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*).*Carbon oxidation state was calculated for each molecular formula identified in the mass spectra using the following equation:

$$OS_C = -\sum_i OS_i \frac{n_i}{n_C} \qquad \text{(Eq. 1)}$$

where OS_i is the oxidation state associated with element *i*, n_i/n_C is the molar ratio of element *i* to carbon (Kroll et al., 2011).

Figure 2 shows two overlaid OS_C plots for the 'fresh' and 'aged' SOA from the 'dark ageing' experiments. Consistent with previous studies, the majority of molecules in the SOA had OS_C between –1 and +1 with up to 30 (nC) carbon atoms (Kroll et al., 2011 and the references therein). It has been suggested that semivolatile and low-volatility oxidised organic aerosol (SV-OOA and LV-OOA) produced by multistep oxidation reactions have OS_C between –1 and +1 with 13 or less carbon atoms (nC) (Kroll et al., 2011). It should be noted that all SOA samples contained a cluster of molecules with OS_C between –1 and –1.5 with nC less than 10 which could possibly be associated with OH radical oxidation products of isoprene, which was present in the BVOC mixture. The dark ozonolysis experiments were performed without an OH scavenger and thus it is likely that OH radicals produced from the ozonolysis reactions could further react with isoprene resulting in the molecules with very low OS_C state. The large cluster of molecules with 15 or more carbon atoms is likely to be associated with dimers and trimers of the BVOC oxidation products.

Figure 3 shows a carbon oxidation plot for the OH radical ageing experiments performed in the presence of UV light. In contrast to dark ageing experiments, a very small shift in the oxidation state throughout the entire mass range could be observed with ageing time. This shift is not visible in the mass spectrum shown in Fig 1c because the affected ions had very low intensities (mostly <5% relative intensity). The observed increase in the oxidation state of the SOA components is consistent with the results obtained for the OH radical ageing of SOA produced by dark ozonolysis reaction of *α*-pinene (Donahue et al., 2012). Using an aerosol mass spectrometer (AMS), an increase of the O/C ratio, which is another metric to describe the oxidation state of the SOA components, was observed after addition of OH radicals (Donahue et al., 2012).

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. 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. It must be noted that the later experiments were performed at the different smog chamber (CRAC) and high RH (~55%). Since an OH radical scavenger was used in these ozonolysis experiments, we assume that all OH radicals were efficiently removed from the system. SOA from both ozonolysis and OH radical reaction with *α*-pinene contained distinguishable groups of monomers, dimers and trimers (Fig. 4). However, a clear shift to higher masses is observed in the mass spectra from the OH radical experiments. The presence of a large number of oligomers in the SOA from the OH-initiated reaction indicates that this oxidation regime also results in a significant degree of oligomerisation. 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.

The SOA from the OH reaction clearly shows higher OS_C (Fig. 5, red squares) compared to that from the dark ozonolysis experiments (blue diamonds in Fig. 5). Moreover, it contained a very large number of LV-OOA species, which are often referred to as aged SOA (Jimenez et al., 2011). As indicated in the Van Krevelen diagram (Fig. 6), where H/C ratio is plotted as a function of the O/C ratio for each mass and corresponding formula identified in the sample (Nizkorodov et al., 2011), the SOA from the OH-initiated reaction had substantially higher O/C ratios than those for SOA obtained from ozonolysis. On the other hand, H/C ratios were very similar in SOA from both reactions. This may be explained by addition of carboxylic or carbonylic groups to the backbone of the hydrocarbon structure, which generally occurs without substantial loss of hydrogen (Zhao et al., 2014).

In the UV-only ageing experiments (without addition of H_2O_2) no visible effect on the mass spectral features of the oligomers (Fig. 1d) and OS_C (not shown here) could be observed. Considering that during the UV-only experiments the RH was less than 9%, the production of OH radicals from the photolysis of unreacted ozone should be minimal (Rohrer et al., 2005), confirming that the increase in the OS_C in the OH radical initiated ageing experiments (discussed above) is not due to UV-initiated decomposition of the SOA products, but to the OH radical reaction. This is in line with a recent study where no significant change in the O/C ratio was determined by a time-of-flight aerosol mass spectrometer (ToF-AMS) when the SOA produced from dark ozonolysis of *α*-pinene was exposed to light representing the solar energy distribution at Earth's surface (Denjean et al., 2015). On the other hand, this is in contrast to findings reported by Wong et al (2014) who observed photolytic ageing of a-pinene SOA in the presence of ammonium sulfate that exhibited a dependence on relative humidity.

3.2 LC/MS results

Due to competitive ionisation of analytes in the ESI direct infusion analysis of the aerosol samples that are known to have a very complex matrix, the ion intensities do not directly reflect the concentration of the molecules in the sample. Therefore, the effect of ageing processes on the SOA composition was additionally investigated using LC coupled with HRMS. All data described in this section (except discussion of Fig S3 and S4) correspond to experiments performed at CESAM chamber. A list of tentatively identified products formed during dark ozonolysis of the BVOC mixture is shown in Table S1. The majority of the identified compounds were attributed to *α*-, and *β*-pinene oxidation products which can be explained by the fact that both of these precursors contributed to about 60% of the total BVOC mixture concentration (ppbv) used in this study. On the other hand, none of the chromatographic peaks were associated with isoprene oxidation products which could be due to the relatively low (about 10%) contribution of isoprene to the total mixture. Moreover, isoprene is known to produce very low aerosol yields (less than 0.01) when reacted with ozone (Kleindienst et al., 2007). Most of the tentatively identified compounds have been previously observed in aerosol samples from laboratory (e.g., Yu et al., 1999; Szmigielski et al., 2007; Glasius et al., 2000; Müller et al., 2008, 2009; Camredon et al., 2010; Gao et al., 2010; Yasmeen et al., 2010; Kourtchev et al., 2014) and field studies (e.g., Gómez-González et al., 2012; Kristensen et al., 2013, 2014; Kourtchev et al., 2013). Therefore, to avoid unnecessary repetition, the sources and processes leading to the formation of these compounds are not discussed here. Although the LC/MS allowed separation and identification of a considerably smaller number of molecules compared to direct infusion analysis, some of them are very useful markers for aerosol source characterisation and are good indicators of the processes involved in the formation of the SOA. 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.

Compared to the direct infusion analysis, only a very small number of dimers were separated using the LC/MS method in all samples, irrespective of the ageing conditions. These dimers include isomers with *m/z* 337.20172, *m/z* 343.13983, *m/z* 357.15509, *m/z* 367.17599, *m/z* 387.20221 and *m/z* 369.19141, consistent with previous studies that applied LC/MS for the analysis of SOA (*e.g.,* Kristensen et al., 2013; 2014). Four of these dimers, pinyl-diaterpenyl ester MW 358 (*m/z* 357.15509), pinyl-diaterebyl dimer MW 344 (*m/z* 343.13983) and pinonyl-pinyl dimer MW 368 (*m/z* 367.17599) and MW 388 dimer ester (*m/z* 387.20221) have been identified previously in SOA from ozonolysis of *α*-pinene (*e.g.,* Yasmeen et al., 2010; Kristensen et al., 2013, 2014), while none of them were observed in the SOA from the OH radical initiated oxidation of *α*-pinene (Kristensen et al., 2014). It must be noted that these dimers were also observed during the direct infusion analysis. Interestingly, the tentative structures of the three dimers reported in the literature (Yasmeen et al., 2010; Kristensen et al., 2013; 2014) contained pinic acid, which is a less important product in the OH radical initiated oxidation than in the ozonolysis of *α*-pinene (Kristensen et al., 2014). The chromatographic peak areas for all four dimers, determined by LC/MS, showed relatively good correlation (R^2>0.90) suggesting these compounds are possibly formed through similar processes. It should be noted that the observed small number of dimers in the LC/MS chromatogram from *α*-pinene ozonolysis, and their absence in the SOA generated from the OH radical initiated oxidation of *α*-pinene, in previous studies and the current work, does not necessarily mean that oligomers are not formed in the latter reaction. The lack of chromatographically resolved dimers in the OH radical initiated

SOA could be explained by the selectivity of the utilised LC columns. The integration of chromatographic ‘humps’ eluting at the end of the chromatograms from both ozonolysis and OH radical initiated reaction of *α*-pinene (Fig S3 and Fig S4) reveals the presence of a large number of dimers, trimers and tetramers that were not resolved by the LC column. The overall oligomer distribution of these unresolved LC ‘humps’ resembles that of the respective direct infusion mass spectra.

Figure 7 shows concentrations of selected first and later generation oxidation products, as well as dimers in the SOA produced under different ageing conditions. Irrespective of the ageing conditions, and even during the dark ozonolysis experiments (without addition of OH radicals), all samples contained MBTCA, the OH radical initiated oxidation product of *α*-pinene. It has been estimated that the ozonolysis of *α*-pinene results in the formation of OH radicals with a yield between 0.8 and 1.0 (Atkinson et al., 1997; Presto and Donahue, 2004). Therefore, without the use of an OH radical scavenger, a substantial fraction of *α*-pinene and other terpenes present in the mixture can be oxidised by OH radicals (Henry and Donahue, 2011). During the dark ageing experiments(with SOA exposure to residual ozone), the concentrations of the marker compounds remained unchanged even after 9 h of SOA exposure, indicating that all OH radicals produced from the BVOC ozonolysis were immediately consumed in the first hour of the reaction(Fig. 7a). The concentrations of the first generation products and the dimers did not change during the dark ageing experiments either. In contrast, the concentration of MBTCA increased when OH radicals were introduced into the system (Fig 7b) followed by a decrease in the concentration of pinonic acid and pinic acid, confirming that pinonic acid is further oxidised into MBTCA (Müller et al., 2008).

In the UV-only ageing experiments the concentrations of all marker compounds in the SOA remained unaffected suggesting that the observed changes in the photolysis experiments with OH radicals (discussed above) are due to the OH-radical initiated chemistry rather than photolytic degradation of the first generation products. Irrespective of the tested conditions, the contribution of the dimers to the SOA mass showed no statistical difference (Table S2) indicating that none of the studied conditions have an effect on dimer decomposition or formation.

4. Conclusions

In this study the influence of several ageing processes on the molecular composition of organic aerosols has been investigated using direct infusion and liquid chromatography HRMS. SOA formed from ozonolysis of a BVOC mixture was aged for 8-9 h in in the dark with residual ozone, under UV irradiation, and by OH radicals formed from the continuous photolysis of H_2O_2. Dark ageing and UV ageing in the presence of ozone and UV irradiation closely resembling the solar energy distribution at Earth’s surface did not significantly affect the molecular composition of studied SOA. In contrast, OH radical initiated ageing showed an increase in OS_C and elemental O/C ratios of the BSOA components from the studied BVOC mixture. None of the ageing processes produced an observable effect on the oligomers formed from the ozonolysis of the BVOC mixture and they were found to be equally abundant in both ‘fresh’ and ‘aged’ SOA. Additional separate dark ozonolysis and OH-initiated experiments with α-pinene (a major component of the studied mixture) showed that oligomers are an important group of compounds in both oxidation schemes. However, oligomers in the OH-initiated SOA were shifted towards higher masses and were not readily resolved by the LC techniques applied here, indicating that their importance could have been underestimated in previous similar studies. SOA from the OH- initiated oxidation of α-pinene had a significantly higher OS_C and O/C compared to that from pure ozonolysis experiments, confirming that the OH radical reaction is more likely to be responsible for the occurrence of highly oxidized species in ambient biogenic SOA. Considering that the timescale (8-9 hours) of the ageing reaction in our experiments was still substantially lower than the lifetime of organic aerosol in the real atmosphere (up to 12 days) (Robinson et al., 2007; Rudich et al., 2007) the observed OH ageing effects could be substantially stronger when SOA is aged over a longer period in the ambient atmosphere.

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Table 1. Experimental conditions at CESAM chamber.

SOA Exposure type	Experiment	O_3 conc., ppb	RH, %	SOA exposure time, hours
Dark ageing	Replicate 1	450	3-6	9
	Replicate 2	450	2.7-4.9	9
OH radical and UV exposure	Replicate 1	300	4.9-8.2	8
	Replicate 2	300	4-7.2	8
UV exposure	Replicate 1	300	3-9	8
	Replicate 2	300	3.5-8	8

BVOC mixture concentration in all experiments was about 150 ppb (60 ppb of *α*-pinene, 45 ppb of Δ_3-carene, 30 ppb of *β*-pinene and 15 ppb of isoprene). $(NH_4)_2SO_4$ aerosol seed concentration was about 5 μg m^{-3} in all experiments. Listed conditions are for the initial formation of the SOA and not for the subsequent ageing reaction.

Figures:

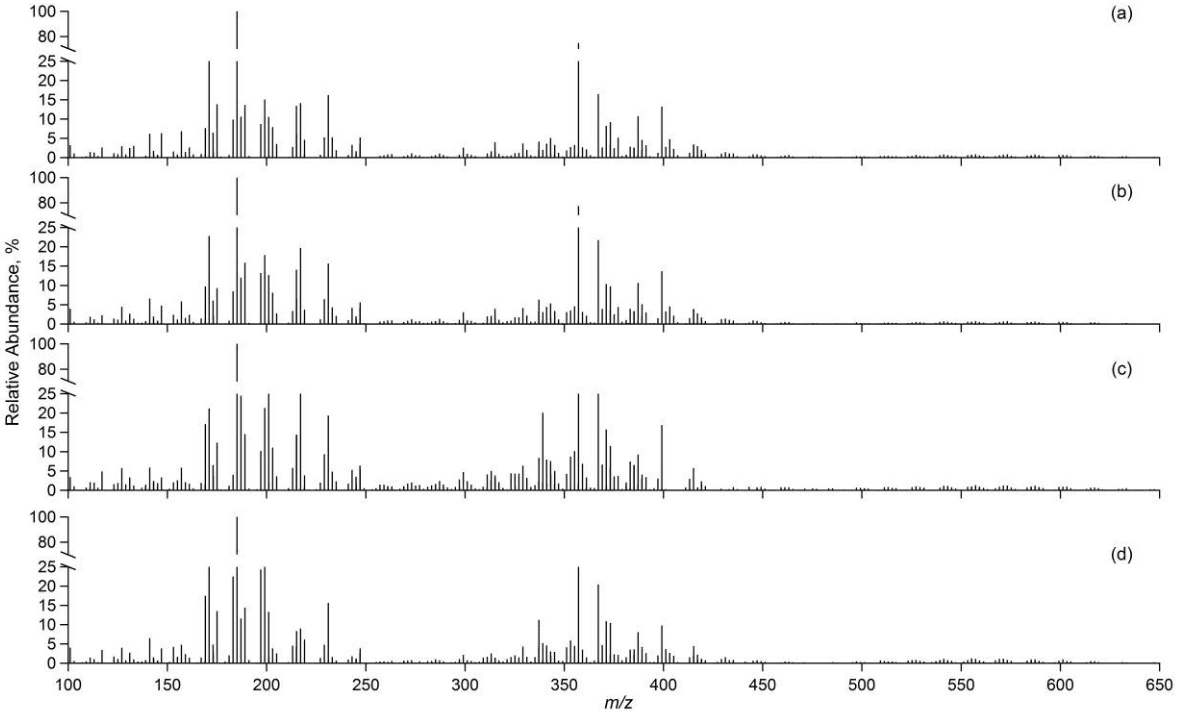

Fig. 1. Direct infusion (-) nanoESI HRMS of SOA from dark ozonolysis of BVOC mixture: (a) fresh aerosol, (b) aged for 9 h in dark (with residual ozone), (c) aged for 8 h in the presence of O_3, H_2O_2 and UV light and (d) aged for 9 h in the presence of O_3 and UV light.

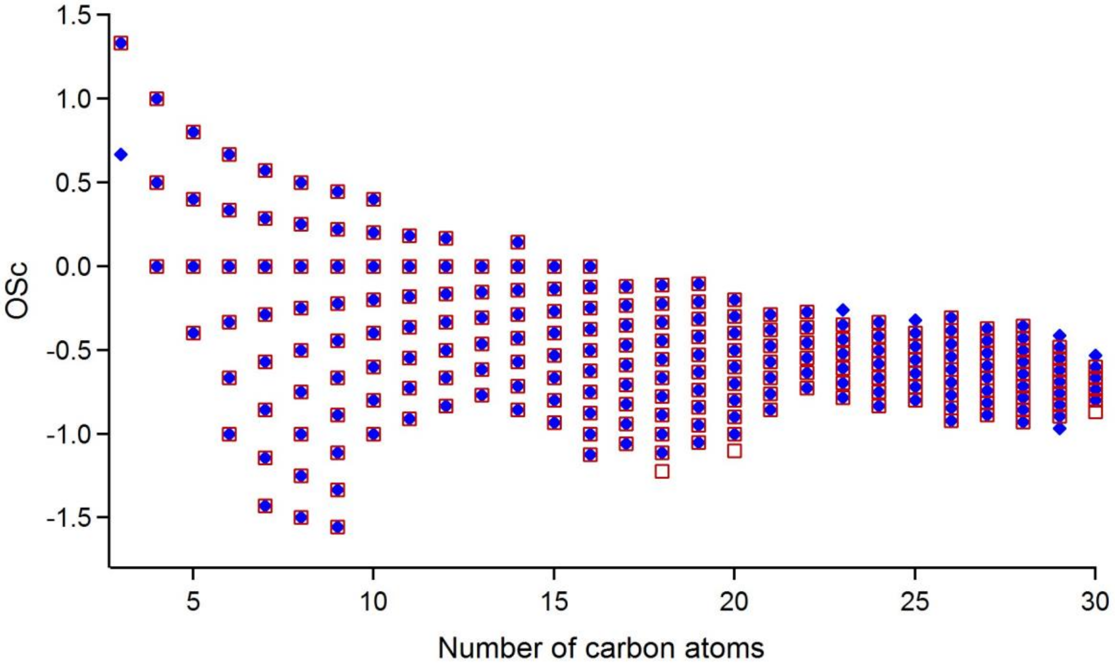

Fig. 2. Carbon oxidation state of SOA from BVOC mixture from dark ageing experiments with O_3. Blue diamonds correspond to molecules in 'fresh SOA', red squares to 'aged SOA' for 9 hours.

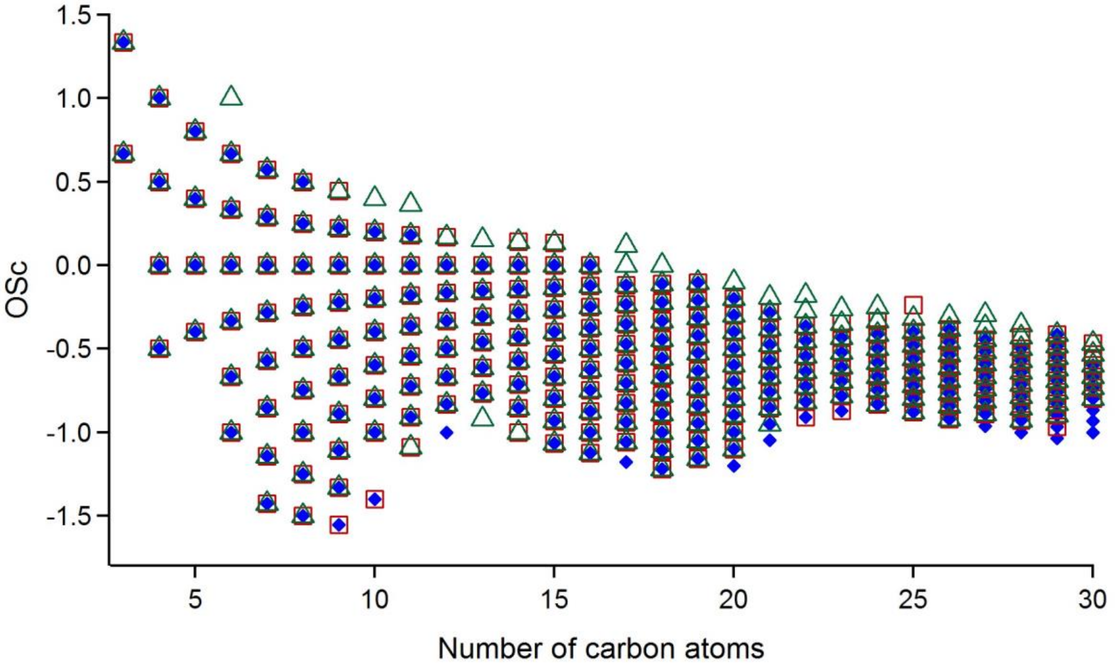

Fig. 3. Carbon oxidation state of SOA from OH-initiated ageing of aerosol from ozonolysis of BVOC mixture. Blue diamonds correspond to molecules in 'fresh SOA', red squares to 'aged SOA' for 3 hours and green triangles to 'aged SOA' for 9 hours.

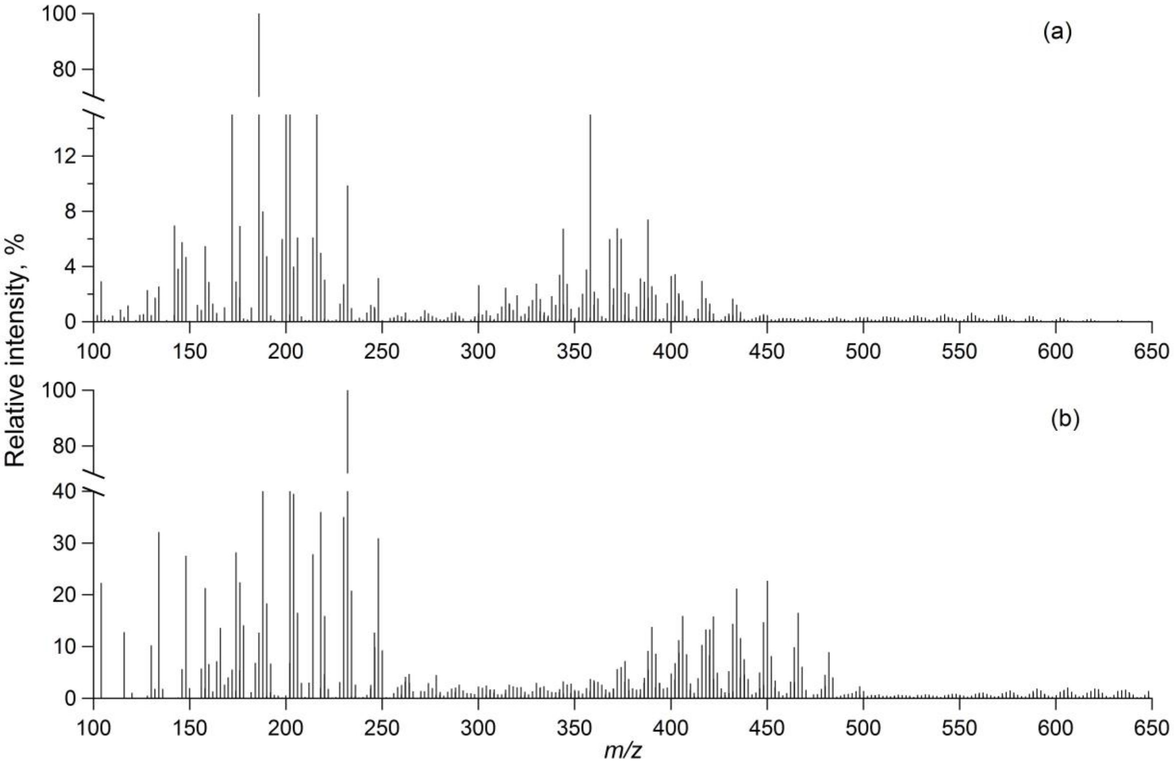

Fig. 4. Direct infusion (-) nanoESI-HR mass spectra of the SOA from (a) dark ozonolysis and (b) OH-initiated reaction with α-pinene.

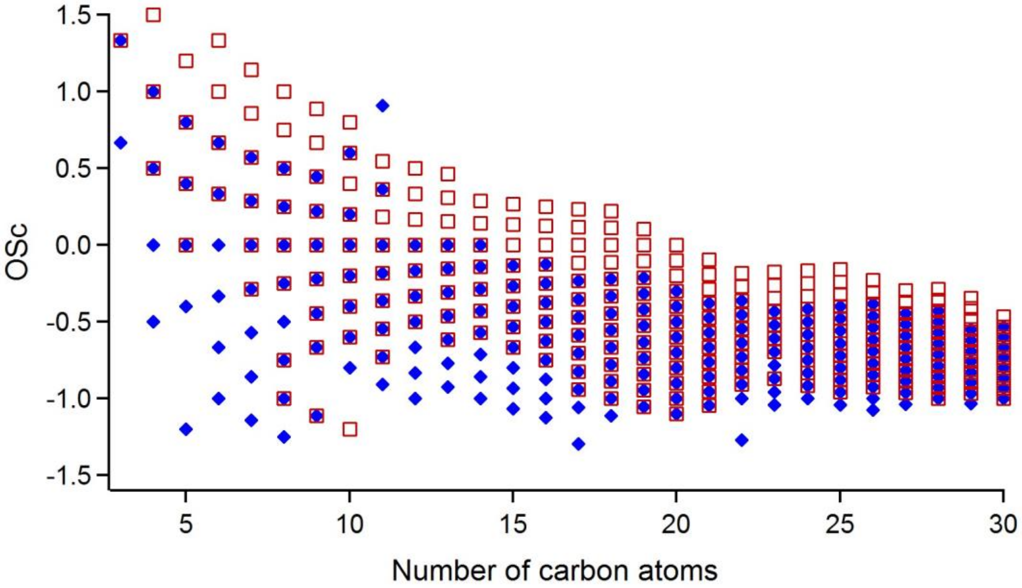

Fig. 5. Carbon oxidation state of the molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α-pinene.

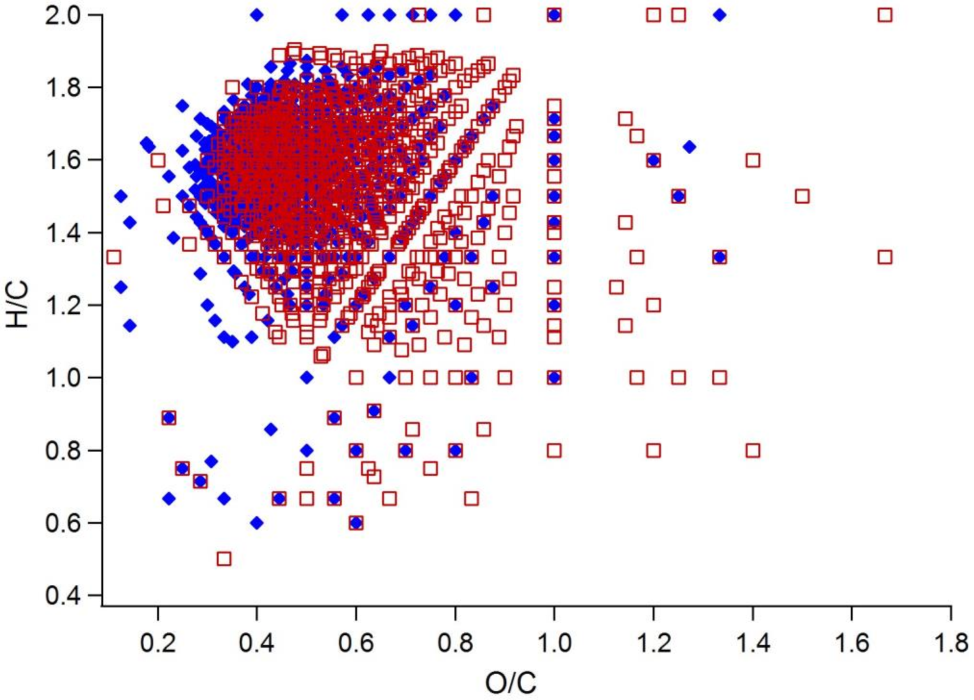

Fig. 6. Van Krevelen diagram for molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α-pinene.

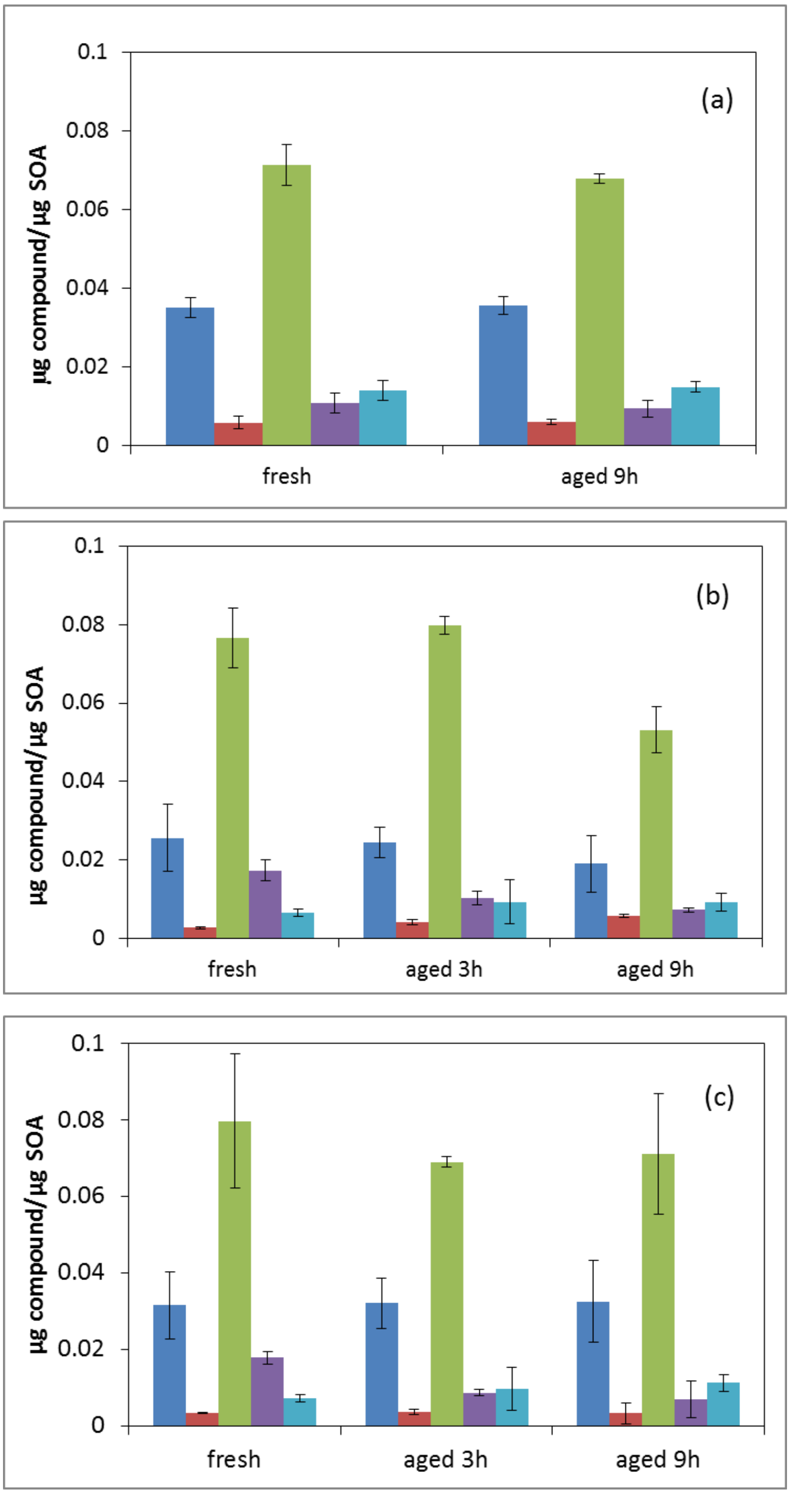

Fig. 7. Normalised concentrations (µg µg^{-1} SOA) of terpenylic acid (dark blue), MBTCA (red), pinic acid (light green), pinonic acid (violet),and a dimer MW 358 (light blue) at three ageing conditions: (a) dark ageing with exposure to residual ozone, (b) OH radical initiated ageing and (c) UV-only ageing experiments. Pinic, pinonic and terpenylic acids represent organic species associated with 'fresh' SOA, whereas MBTCA is associated with 'aged' SOA. The 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.