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Molecular composition of aged secondary organic aerosol generated from a mixture of biogenic volatile compounds using ultrahigh resolution mass spectrometry

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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 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 radical-initiated α -pinene oxidation 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.

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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. 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 (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. Another explanation for the difference is that typical smog chamber exoxidant (e.g., O₃ or OH radicals).

have been performed with α -pinene, its oxidation products (Donahue et al., 2012; Müller et al., 2012; Denjean 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 age-

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periments are performed with only one or two SOA precursors and are limited to one 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 ing 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 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 resolution mass spectrometry (UHRMS) often identify hundreds of oligomeric compounds (Kalberer et al., 2004; Reinhardt et al., 2007; 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 aerosol ageing conditions on the molecular composition of biogenic SOA. SOA formed from dark ozonolysis of a BVOC mixture was exposed to (i) OH radicals and UV light (ii) 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 LC and direct infusion UHRMS that allows detection of thousands of individual SOA constituents at once providing their elemental formulae from accurate mass measurements (Nizkorodov et al., 2011).

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Experiments were performed in two different atmospheric simulation chambers: the CESAM chamber in Paris and 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 m³ stainless steel vessel, operated at 296 ± 2 K using synthetic air at 1 bar atmospheric pressure. The experimental conditions are outlined in Table 1. The experiments were performed at RH (2-9%). Neutral seed particles of ammonium sulfate were generated from 3 mM (NH₄)₂SO₄ (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 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 10-15s from an electric discharge generator. For the OH radical initiated ageing reactions, OH radicals were produced by photolysis of H₂O₂ (60 % w/v, Fisher Scientific) using xenon arc lamps (4kW, 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). For these experiments, the corresponding

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 NO_2 photolysis frequency was $J_{NO_2} = (2.5 \pm 0.2) \times 10^{-3} \, \mathrm{s}^{-1}$. H_2O_2 was continuously injected into the smog chamber approximately 1 h after reaching the maximum SOA concentration (mean maximum concentration $122 \pm 21 \,\mu\text{g}\,\text{m}^{-3}$, n = 6) produced from the dark ozonolysis reaction. SOA samples were collected in three stages: (a) after 5 reaching the maximum particle concentration (as measured by SMPS) produced from the dark ozonolysis reaction of the VOC mixture (b) after 3 h of exposure of the SOA particles to OH radicals and/or UV radiation and (c) after 8-9 h 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 Lmin⁻¹ sample flow and 2.0 Lmin⁻¹ sheath flow. For the SOA mass concentration, the density of the organic material was assumed to be $1.0 \, \mathrm{g \, cm^{-3}}$.

Infrared absorbing species such as SOA precursors and their oxidation products were measured using multi-path in-situ Fourier-transform infrared (FTIR) spectrometry (Bruker GmbH, Ettlingen, Germany) with an optical pathlength of 192 m.

CRAC experiments

 α -pinene ozonlysis and OH radical initiated experiments 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 m3. 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 m³ min⁻¹. Aerosol seed particles produced from atom**ACPD**

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ising $(NH_4)_2SO_4$ were neutralised by a Krypton-85 (Kr-85) charge neutraliser before introduction to the chamber. 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 ($\sim 40-50\,^{\circ}C$) solution of $50\,^{\circ}M_2O_2$. After the introduction of all reactants, the mixture was allowed to mix for $10\,$ min before turning on 12 Philips TL12 ($40\,$ W) lamps with $\lambda_{max} = 310\,$ nm to initiate photolysis of the OH radical precursor. For the ozonolysis-only experiments, ozone was introduced into the chamber over a period of $1-2\,$ min from an electric discharge generator. Cyclohexane ($\sim 40\,$ ppm, Sigma, $> 99\,^{\circ}$ purity) was used as an OH scavenger in the ozonolysis-only experiments.

2.3 Aerosol sample collection

Total aerosol mass was collected on prebaked (at 650 $^{\circ}$ C) quartz fibre filter (47 mm diameter, Tissuquartz 2500 QAT-UP, Pall) using a filter pack. The gas phase species were removed using a denuder packed with activated charcoal. The sampling was performed at flow rate of 18–30 L min⁻¹ for 1–2 h 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, a part of the quartz fibre filter $(5-20\,\text{cm}^2)$ 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 $(0.2\,\mu\text{m}, \text{ISO-DiscTM Supelco})$, and reduced

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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 LC/MS portion was further evaporated to 20 µL and diluted by 0.1 % aqueous solution of formic acid to 100 μL. The final extracts were analysed as described in Kourtchev et al. (2013) using 5 an ultrahigh 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 μ L⁻¹), glutaric acid (30 ng μ L⁻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: spray voltage and back pressure were set at -1.4 kV and 0.8 psi, respectively. 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).

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 60 %. 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 mm × 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 100000 and the mass ranges of m/z 100–650 and m/z 150–900. On the basis of prescan information from the

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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 dimers were quantified using *cis*-pinonic acid as surrogate. Six-point calibration curves were constructed over two concentration ranges 0.2–50 and 50–200 ng µL⁻¹.

2.5 Ultrahigh MS resolution data analysis

The direct infusion data analysis was performed using procedures described in detail in Kourtchev et al. (2013). Briefly, for each sample analysis, 60–90 mass spectral scans were averaged into one mass spectrum. Molecular assignments were done using *Xcalibur 2.1* software applying the following constraints $^{12}\text{C} \le 100$, $^{13}\text{C} \le 1$, $^{1}\text{H} \le 200$, $^{16}\text{O} \le 50$, $^{14}\text{N} \le 5$, $^{32}\text{S} \le 2$, $^{34}\text{S} \le 1$. 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 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 O₃, 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

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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 previous laboratory studies with biogenic SOA (e.g., 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 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. Moreover, several of the oligomers were not affected by the 8-9 h 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 ozonolysis conditions. indicating their stability once they are formed in the atmosphere. In all experiments, the mass spectra were dominated by the ions at m/z 185 and m/z 357 in the monomeric and dimeric regions, respectively. As confirmed by LC/MS analysis (discussed below), the ion at m/z185 corresponds to at least three different oxidation products with the same molecular formula ($C_0H_{14}O_4$) 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 357 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

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Considering, a very large mass spectral dataset obtained from the UHRMS analysis, the data was visualised using carbon oxidation state (OS_C) plots (Kroll et al., 2011). The OS_C is shown to be strongly linked to aerosol volatility and is thus a useful parameter to classify SOA. Carbon oxidation state was calculated for each molecular formula identified in the mass spectra using the following equation:

$$OS_{C} = -\sum_{i} OS_{i} \frac{n_{i}}{n_{C}}$$
 (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 aerosols (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

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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 $_{5}$ 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.

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 O₃ 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 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 photolysis reaction indicates that this oxidation regime also results in a significant degree of oligomerisation. 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 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), SOA from the photolysis reaction had substantially higher O/C ratios compared to those 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).

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In the UV-only ageing experiments (without addition of H₂O₂) 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 ₅ 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 change in the O/C ratio, 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.

LC/MS results 3.2

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. 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 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 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.,

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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 5 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 observed using the LC/MS method in all samples, irrespective of the ageing conditions. These dimers include isomers with m/z 337, m/z 343, m/z 357, m/z 367, m/z 387 and m/z 369, 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), pinyl-diaterebyl dimer MW 344 (m/z 343), pinonyl-pinyl dimer MW 368 (m/z 367) and MW 388 dimer ester (m/z 387) 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 was observed in the SOA from the OH radical initiated oxidation of α -pinene (Kristensen et al., 2014). 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. 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, does not necessarily mean that oligomers are not formed in the latter

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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 (Figs. S1 and S2) reveals the presence 5 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 (Fig. 7a), 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. 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 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

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no statistical difference (Table S2) indicating that none of the studied conditions have an effect on dimer decomposition or formation.

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. SOA formed from ozonolysis of a BVOC mixture was aged for 8-9 h in dark conditions in the presence of ozone, under UV irradiation, and by OH radicals formed from the continuous photolysis of H₂O₂. 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-radical initiated α pinene oxidation 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 h) 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

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5 Acknowledgements. Research at the University of Cambridge was supported by a M. Curie Intra-European fellowship (project no. 254319), the European Research Council (ERC starting grant 279 405). The work at Universités Paris-Est-Créteil et Paris Diderot and University College Cork was funded by the European Commission (project EUROCHAMP-2, contract no. 228 335). Researchers in Cork acknowledge funding from Science Foundation Ireland (11/RFP/GEO3200). Authors would like to thank Olalekan Popoola at University of Cambridge for helping to improve Mathematica code for mass spectral data evaluation. Aline Gratien, Manuela Cirtog and Ricardo Suarez-Bertoa are gratefully acknowledged for carrying overnight ageing experiments at CESAM in the preparatory phase of this work.

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 Table 1. Experimental conditions at CESAM chamber.

SOA Exposure type	Experiment	O ₃ conc., ppb	RH, %	SOA exposure time, hours
5 5	Replicate 1	450	3–6	9
	Replicate 2	450	2.7-4.9	9
	Replicate 1	300	4.9-8.2	8
	Replicate 2	300	4-7.2	8
•	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). (NH₄)₂SO₄ aerosol seed concentration was about 5 μ g m⁻³ in all experiments.

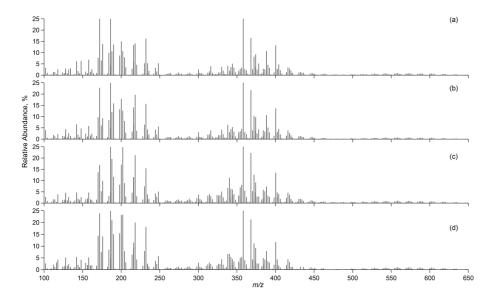


Figure 1. Direct infusion (–) nanoESI UHRMS of SOA from dark ozonolysis of BVOC mixture: **(a)** fresh aerosol, **(b)** aged for 9 h in dark (with residual ozone), **(c)** aged for 8 h in the presence of O_3 , O_2 and UV light and **(d)** aged for 9 h in the presence of O_3 and UV light.

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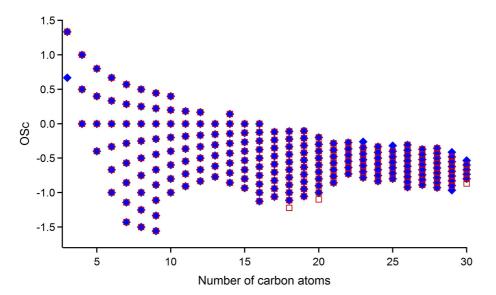


Figure 2. Carbon oxidation state of SOA from BVOC mixture from dark ageing experiments with O₃. Blue diamonds correspond to molecules in "fresh SOA", red squares to "aged SOA" for 9 h.

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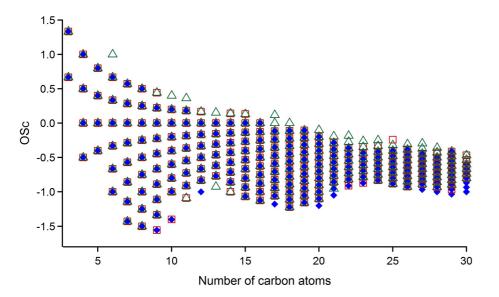


Figure 3. Carbon oxidation state of SOA from OH radical-initiated ageing of aerosol from ozonolysis of BVOC mixture. Blue diamonds correspond to molecules in "fresh SOA", red squares to "aged SOA" for 3 h and green triangles to "aged SOA" for 9 h.

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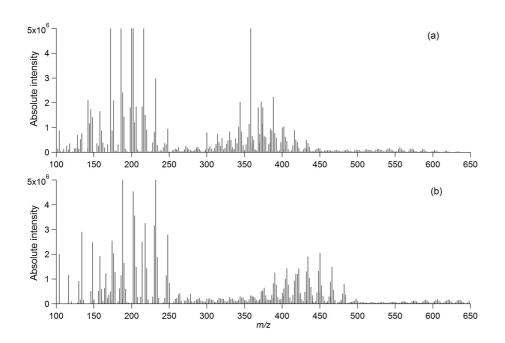


Figure 4. Direct infusion (-) nanoESI-UHR mass spectra of the SOA from (a) dark ozonolysis and **(b)** OH radical-initiated reaction with α -pinene.

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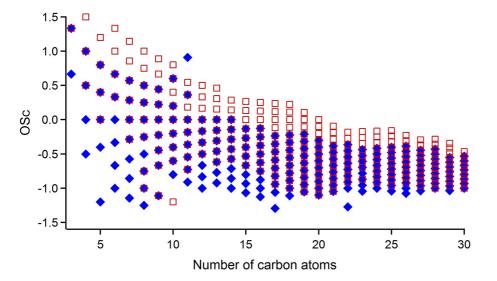


Figure 5. Carbon oxidation state of the molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α -pinene.

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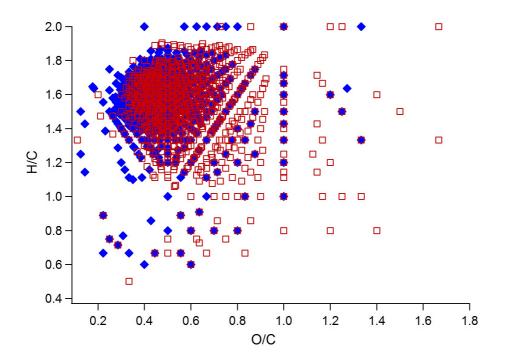


Figure 6. Van Krevelen diagram for molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α -pinene.

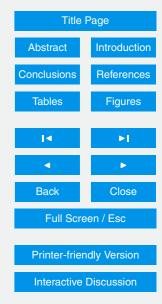


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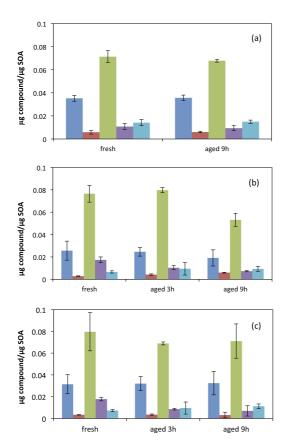


Figure 7. Normalised concentrations (μg μg⁻¹ SOA) of pinic acid (light green), pinonic acid (violet), terpenylic acid (dark blue), MBTCA (red) and a dimer MW 358 (light blue) at three ageing conditions: (a) dark ageing, (b) OH radical-initiated ageing and (c) UV-only ageing experiments.