



**Molecular
composition of aged
secondary organic
aerosol**

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

I. Kourtchev¹, J.-F. Doussin², C. Giorio^{1,3}, B. Mahon¹, E. M. Wilson⁴, N. Maurin², E. Pangui², D. S. Venables⁴, J. C. Wenger⁴, and M. Kalberer¹

¹Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK

²LISA, Universités Paris-Est-Créteil et Paris Diderot, CNRS UMR 7583, 61 Avenue du Général de Gaulle, 94010, Créteil, France

³National Centre for Atmospheric Science, School of Geography, Earth and Environmental Sciences, Division of Environmental Health and Risk Management, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

⁴Department of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland

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Correspondence to: I. Kourtchev (ink22@cam.ac.uk)

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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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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. 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 experiments are performed with only one or two SOA precursors and are limited to one oxidant (e.g., O₃ 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) 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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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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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 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 $^{12}\text{C} \leq 100$, $^{13}\text{C} \leq 1$, $^1\text{H} \leq 200$, $^{16}\text{O} \leq 50$, $^{14}\text{N} \leq 5$, $^{32}\text{S} \leq 2$, $^{34}\text{S} \leq 1$. 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 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

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weight dimers are formed through gas phase reaction of the stabilised Criegee Intermediate formed from ozonolysis of the monoterpene (Kristensen et al., 2014).

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:

$$OS_C = - \sum_i OS_i \frac{n_i}{n_C} \quad (1)$$

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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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). (NH₄)₂SO₄ aerosol seed concentration was about 5 $\mu\text{g m}^{-3}$ in all experiments.

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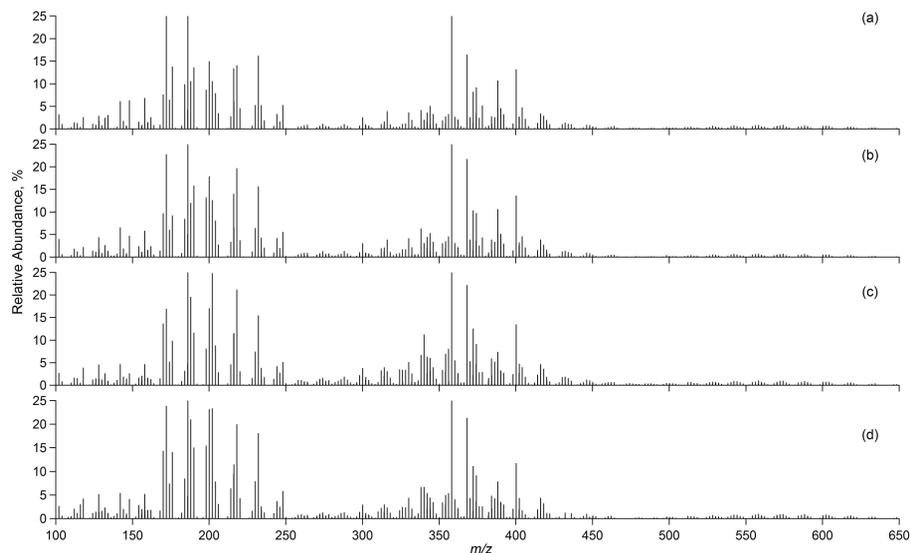


Figure 1. Direct infusion (–) nanoESI UHRMS of SOA from dark ozonolysis of BVOC mixture: **(a)** fresh aerosol, **(b)** aged for 9 h in dark (with residual ozone), **(c)** aged for 8 h in the presence of O_3 , H_2O_2 and UV light and **(d)** aged for 9 h in the presence of O_3 and UV light.

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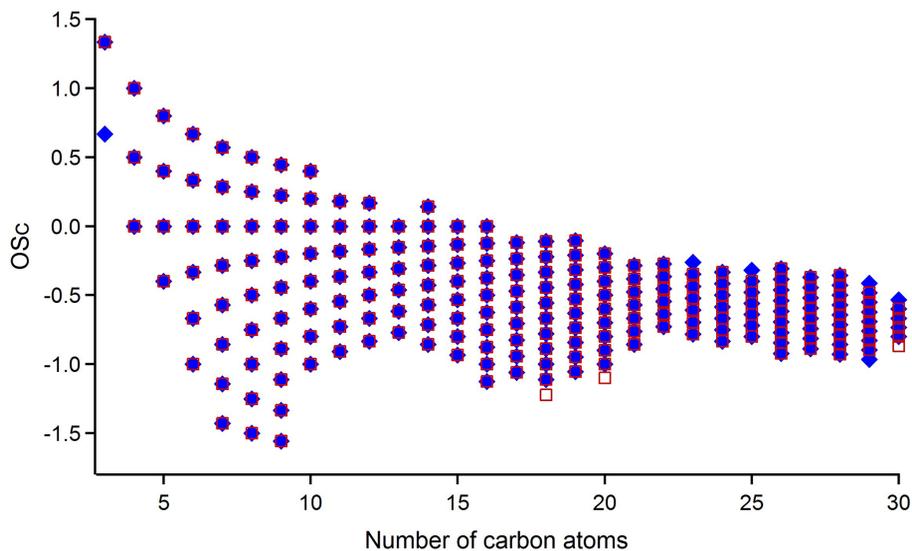


Figure 2. Carbon oxidation state of SOA from BVOC mixture from dark ageing experiments with O_3 . Blue diamonds correspond to molecules in “fresh SOA”, red squares to “aged SOA” for 9 h.

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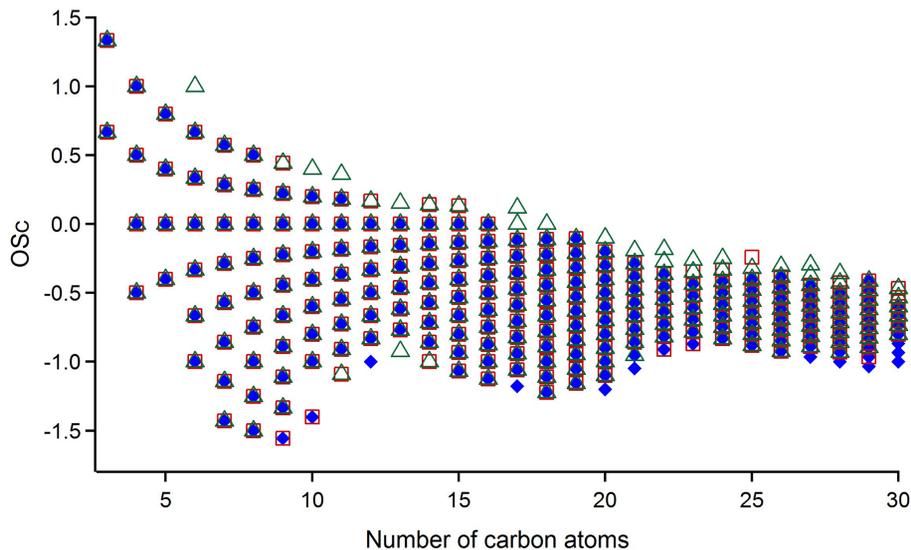


Figure 3. Carbon oxidation state of SOA from OH radical-initiated ageing of aerosol from ozonolysis of BVOC mixture. Blue diamonds correspond to molecules in “fresh SOA”, red squares to “aged SOA” for 3 h and green triangles to “aged SOA” for 9 h.

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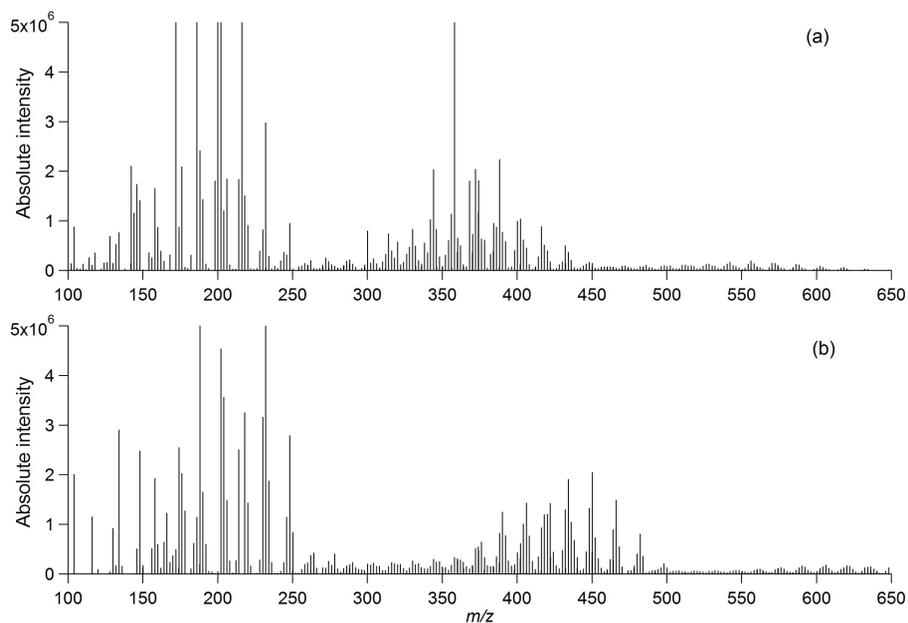


Figure 4. Direct infusion (–) nanoESI-UHR mass spectra of the SOA from **(a)** dark ozonolysis and **(b)** OH radical-initiated reaction with α -pinene.

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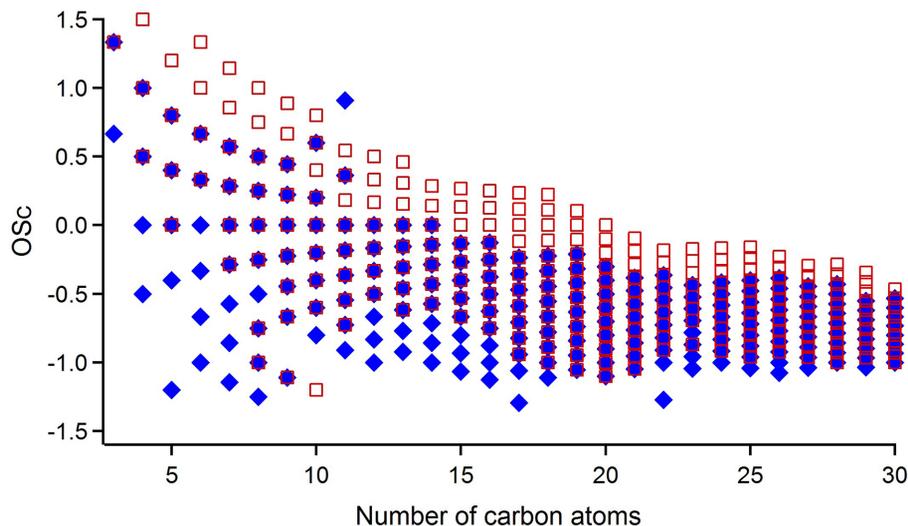


Figure 5. Carbon oxidation state of the molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α -pinene.

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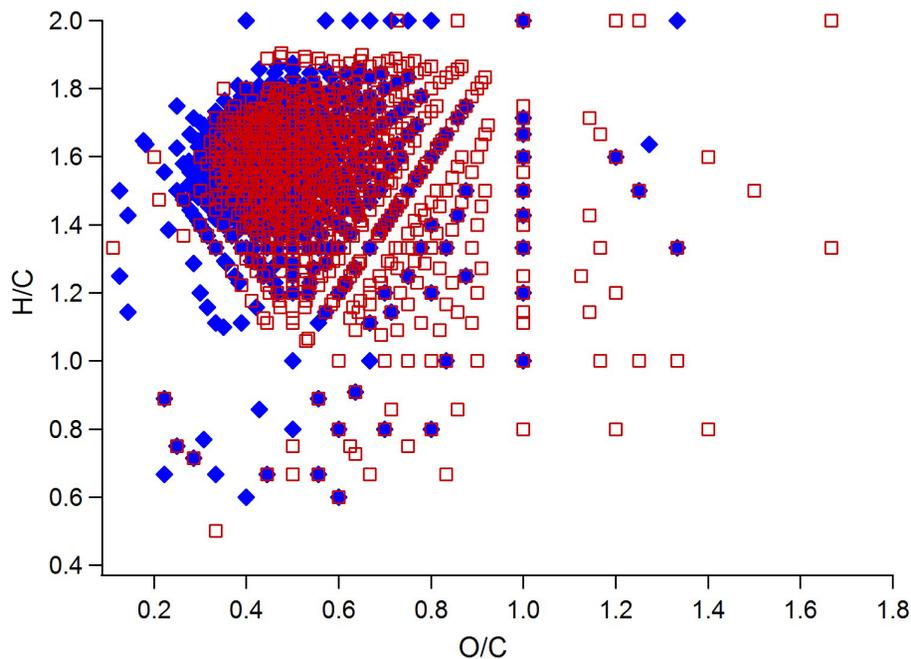


Figure 6. Van Krevelen diagram for molecules in SOA from ozonolysis (blue diamonds) and OH-initiated reaction (red squares) of α -pinene.

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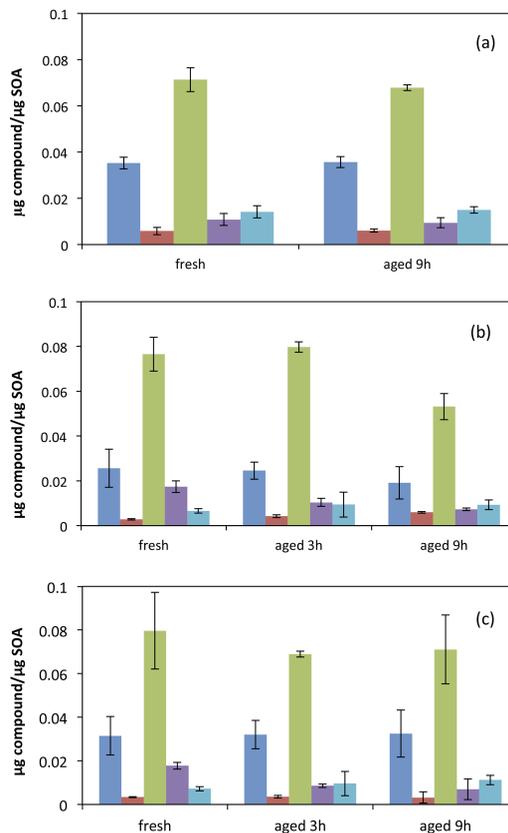


Figure 7. Normalised concentrations ($\mu\text{g}\mu\text{g}^{-1}$ SOA) of pinic acid (light green), pinonic acid (violet), terpenylic acid (dark blue), MBTCA (red) and a dimer MW 358 (light blue) at three ageing conditions: **(a)** dark ageing, **(b)** OH radical-initiated ageing and **(c)** UV-only ageing experiments.