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Abstract

Numerous laboratory experiments have been performed in an attempt to mimic atmospheric secondary organic aerosol (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. In this study, we generated SOA in a simulation chamber from the ozonolysis of α -pinene and a biogenic volatile organic compound (BVOC) mixture containing α - and β -pinene, Δ^3 -carene, and isoprene. The detailed molecular composition of laboratory-generated SOA was compared with that of background ambient aerosol collected at a boreal forest site (Hyytiälä, Finland) and an urban location (Cork, Ireland) using direct infusion nano-electrospray ultrahigh resolution mass spectrometry. Kendrick Mass Defect and Van Krevelen approaches were used to identify and compare compound classes and distributions of the detected species. The laboratory-generated SOA contained a distinguishable group of dimers that was not observed in the ambient samples. The presence of dimers was found to be less pronounced in the SOA from the VOC mixtures when compared to the one component precursor system. The elemental composition of the compounds identified in the monomeric region from the ozonolysis of both α -pinene and VOC mixtures represented the ambient organic composition of particles collected at the boreal forest site reasonably well, with about 70% of common molecular formulae. In contrast, large differences were found between the laboratory-generated BVOC samples and the ambient urban sample. To our knowledge this is the first direct comparison of molecular composition of laboratory-generated SOA from BVOC mixtures and ambient samples.

1 Introduction

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric chemistry and give rise to secondary organic aerosols (SOA), which have effects on climate (Hallquist et al., 2009) and human health (Pope and Dockery, 2006). SOA is

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formed within the atmosphere from gaseous precursors and gas-to-particle conversion processes. 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. One of the major challenges is the identification of the organic composition of the SOA, which is composed of thousands of organic compounds (Kanakidou et al., 2005). These compounds generally cover a wide range of polarities, volatilities and masses (Goldstein and Galbally, 2007) and therefore it is difficult to find a single analytical technique for their detailed chemical analysis at the molecular level. Conventional chromatographic methods (gas chromatography (GC) and liquid chromatography (LC)) are not capable of resolving the highly complex mixtures with a wide variety of physico-chemical properties. Moreover, commonly used mass spectrometers, which are often used as detectors following chromatographic separation, do not have sufficient mass-resolving power to distinguish and differentiate all the compounds present in the complex mixture of organic aerosol. Ultra-high resolution mass spectrometers (UHR-MS) (i.e., Fourier transform ion cyclotron resonance MS and Orbitrap MS) have a mass resolution power that is at least one order of magnitude higher ($\geq 100\,000$) than conventional MS and thus have the potential for solving this problem. Direct infusion electrospray ionisation (ESI)-UHR-MS has been successfully applied for the analysis of both ambient and laboratory-generated SOA and facilitated the characterisation of hundreds of species with individual molecular formulae (Nizkorodov et al., 2011). Despite the high analytical throughput of direct infusion MS, this method is prone to artefacts such as changes in the ionisation efficiency of an analyte due to the presence of “matrix” compounds in the complex organic mixtures (Pöschl, 2005). For instance, sulphates, nitrates and ammonium salts are important constituents of atmospheric aerosols (Pöschl, 2005) and once injected into the ESI source can cause ion suppression, adduct formation and a rapid deterioration of instrument performance (Dettmer et al., 2007). NanoESI-MS, which generally produces smaller droplet sizes and analyte flow in the electrospray (Schmidt et al., 2003), can

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corrections were calculated by considering the particle loss as a first order rate process. The background NO_x concentration measured using a NO_x analyser (Thermo Model 42i) was below 2 ppbv for all experiments. The aerosol samples were collected on quartz fibre filters (Pallflex Tissuquartz 2500QAT-UP, 47 mm diameter) 20–30 min after the maximum SOA concentration was observed. Before use, the quartz fibre filters were preheated at 650 °C for 12 h to remove any possible organic impurities. A charcoal denuder was used in front of the filter pack to remove gas phase species formed during the ozonolysis reaction. The aerosol sampling flow rate was approximately 12 L min⁻¹ and the sampling time was 40 min. In addition, “blank” chamber samples were collected by drawing “clean” air from the chamber for 40 min. The filter samples were wrapped in baked aluminium foil and stored at –20 °C prior to analysis.

2.2 Ambient samples

Biogenic ambient samples were collected at the boreal forest site SMEAR II in Hyytiälä, southern Finland (61°51' N, 24°17' E) as previously described in detail (Kourtchev et al., 2013a). The forest around the station is dominated by conifers (mainly Scots pine and Norway spruce) with some deciduous trees, such as aspen and birch, with a tree density of about 2500 ha⁻¹. Detailed descriptions of the site, instrumentation, meteorological data collection and sampling are given elsewhere (Kulmala et al., 2001; Hari and Kulmala, 2005). In total, 10 separate day and night atmospheric aerosol PM₁ samples, each representing 12 h of sampling, were collected over the period 16 to 25 August 2011.

Anthropogenic ambient samples were collected during 9–17 September 2011 at the Tivoli Industrial Estate and Docks (TIED), Cork, Ireland (51°54'5 N, 8°24'38 W). A detailed description of the TIED site is given elsewhere (Healy et al., 2009; Hellebust et al., 2010; Kourtchev et al., 2011). The site is located approximately 3 km east of Cork city centre with a population of about 120 000 inhabitants. A shipping berth is located 400–600 m to the southwest, while the main road carrying traffic east out of the city lies 200 m to the north of the site. Residential areas surround the site on all sides

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except the north and northeast. The vegetation that surrounds the site mainly consists of shrubs and some native deciduous trees, which include oak (*Quercus robur* L. and *Quercus petraea*), ash (*Fraxinus excelsior*), birch (*Betula pendula*), sycamore (*Acer pseudoplatanus*), poplar (*Populus tremula*) and beech (*Fagus sylvatica*). It should be noted that there are not many conifer species present around the sampling area and if they do exist, they are likely to be spruce (*Picea sitchensis*). PM_{2.5} aerosol samples were collected on quartz fibre filters (Pallflex Tissuquartz 2500QAT-UP, 150 mm diameter, pre-fired for 24 h at 650 °C) using a High Volume (Digitel DHA-80, Switzerland) sampler with a flow rate of 500 L min⁻¹.

2.3 Aerosol sample analysis

All ambient filters were analysed for organic carbon (OC) and elemental carbon (EC) using a thermal-optical transmission (TOT) technique (Birch and Cary, 1996). For each sample, a part of the quartz fibre filter (6–30 cm², depending on OC or total aerosol loading for ambient and laboratory samples respectively) was extracted three times with 5 mL of methanol (Optima[®] grade, Fisher Scientific) under ultrasonic agitation for 30 min. The three extracts were combined, filtered through a Teflon filter (0.2 μm) and reduced by volume to approximately 200 μL under a gentle stream of nitrogen.

The final extracts were analysed using an ultrahigh resolution LTQ Orbitrap Velos mass spectrometer (Thermo Fisher, Bremen, Germany) equipped with a TriVersa Nanomate robotic nanoflow chip-based ESI source (Advion Biosciences, Ithaca NY, USA). The Orbitrap MS instrument was calibrated using an Ultramark 1621 solution (Sigma-Aldrich, UK). The mass accuracy of the instrument was below 1.5 ppm and was routinely checked before the analysis. The instrument mass resolution was 100 000 at m/z 400. The negative ionisation mass spectra were collected in three replicates at ranges m/z 100–650 and m/z 200–900 and processed using Xcalibur 2.1 software (Thermo Scientific). A mixture of camphor, sulphonic 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 optimise the ion transmission settings. The direct infusion nanoESI pa-

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the number of compounds analysed by UHR-MS in the mass range 100–300 Da (451 molecular formulae). The X_{nm} is a binary value indicating the presence/absence of the compound m in sample n . The cluster analysis was performed using Statistica 10 (StatSoft Inc., Tulsa, OK, USA), based on the unweighted pair-group average linkage method (or average linkage method) and using the percent disagreement (Georgieva et al., 2005) distance measure. The metric used in this study is analogous to the Jaccard's dissimilarity distance measure that is commonly applied for the analyses of binary patterns (Sneath and Sokal, 1973; Anthony et al., 2002; Cordeiro et al., 2003; Kosman and Leonard, 2005). The percent disagreement or simple mismatch metric considers as a match the absence of compounds in all compared spectra. This might give misleading results because two samples could be considered close to each other just because they shared many absences of compounds (Kosman and Leonard, 2005). For this reason, results obtained using the unmodified percent disagreement or different metrics, i.e. Euclidean distance and r-Pearson correlation coefficient, which would have the same drawbacks for binary data, were not considered (Kosman and Leonard, 2005). Therefore, the percent disagreement metric was modified in order to calculate the distances on the basis of the percentage of common ions between the considered samples. The linkage distance between two samples is calculated using the following equation:

$$LD_{ij} = \frac{N - c_{ij}}{N} \times 100$$

where LD_{ij} is the linkage distance between sample i and sample j , N is the total number of ions considered in the cluster analysis (451 ions) and c_{ij} is the number of ions in common between sample i and sample j .

Robustness of the applied technique was evaluated by repeating the cluster analysis using different linkage methods, i.e. single linkage (or nearest neighbour) and complete linkage (farthest neighbour), which gave exactly the same results.

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3 Results and discussion

The VOC mixture used in the laboratory experiments contained four of the most abundant SOA-precursor monoterpenes (i.e., α -pinene, Δ^3 -carene, β -pinene and isoprene) emitted at the boreal forest site in Hyytiälä (Hakola et al., 2003; Aaltonen et al., 2011; Bäck et al., 2012). The emissions of α -pinene and Δ^3 -carene were found to be responsible for up to 97 % of the total monoterpene proportions in both plant branch emissions from Scots pine trees (a dominant species at Hyytiälä) and the ambient samples from the boreal forest site in Hyytiälä (Bäck et al., 2012). In the present study, SOA ambient samples were collected below the canopy and 5 m above the forest floor; therefore, the VOC composition is expected to be additionally influenced by emissions from ground vegetation. At the boreal ground floor the monoterpenes were also found to be the most abundant compound group with α -pinene (average $2.975 \mu\text{g m}^{-2} \text{h}^{-1}$), Δ^3 -carene (average $1.305 \mu\text{g m}^{-2} \text{h}^{-1}$), camphene (average $0.442 \mu\text{g m}^{-2} \text{h}^{-1}$) and β -pinene (average $0.191 \mu\text{g m}^{-2} \text{h}^{-1}$) accounting for 90 % of the monoterpene fluxes (Aaltonen et al., 2011). Previous studies (Kourtchev et al., 2005, 2008) indicated that SOA from Hyytiälä contained a number of oxidation products of isoprene implying that isoprene certainly plays a role in SOA formation at the boreal site. Therefore, isoprene was added to the VOC mixture in proportions estimated from the fluxes at the sampling site (Hakola et al., 2003; Aaltonen et al., 2011). Although the total concentrations of the VOC mixture used in our 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).

SOA concentrations and yields from the ozonolysis of α -pinene and VOC mixtures are shown in Table 1. The average SOA yields (corrected for wall losses) for α -pinene and VOC mixtures were 0.16 ± 0.01 ($n = 3$) and 0.11 ± 0.01 ($n = 3$), respectively. The obtained yields for the α -pinene-only experiments are in reasonable agreement with those reported in the literature for similar VOC concentration ranges (Pathak et al., 2007; Hatfield and Hartz, 2011). Surprisingly, in the present study, SOA yields for the

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average oxidation state of organic aerosol rarely exceeds this value because species with several carbonyl groups are highly unstable and will rapidly decompose to smaller molecules (Kroll et al., 2011). Considering that the studied VOC mixture mainly contained monoterpenes, which are structural isomers and the fact that highly oxidised molecules were not observed in the SOA generated from the ozonolysis of α -pinene, it is likely that species with $OS_C > +1$ were produced from the ozonolysis of isoprene. Moreover, in the VOC mixture experiments cross reactions between radicals and oxidation products of the different VOCs are expected to occur which may lead to formation of a complex range of species. These highly oxidised species are worthy of further investigation.

The majority of the species exhibited OS_C values between -1 and $+1$ with 15 or less carbon atoms, suggesting that they are semi- and low-volatile organic compounds corresponding to “fresh” and “aged” SOA produced by multistep oxidation reactions (Jimenez et al., 2009; Kroll et al., 2011). Compared to chamber samples, the Hyytiälä samples additionally contained ions with $OS_C < -1$ and more than 7 carbon atoms which is characteristic of primary biomass burning aerosol (Kourtchev et al., 2013a).

3.2 Comparison using statistical tools

Figure 5 shows the fraction of molecular formulae below 300 Da found in both the laboratory-generated SOA and the ambient samples relative to the total number of formulae in the ambient samples. Evidently, the molecular composition of SOA from both the VOC mixture and α -pinene represented the overall composition of the ambient sample from the boreal forest site reasonably well, with $72.3 \pm 2.5\%$ ($n = 3$) and $69.1 \pm 3.0\%$ ($n = 3$) common ions, respectively. Although, the VOC mixture resulted in a slightly higher number of common formulae than that from the boreal forest aerosol compared to the pure α -pinene-SOA, the difference in the mean values among the treatment groups is not large enough to exclude the possibility that the difference is due to random sampling variability; according to ANOVA test, the difference was not statistically significant ($p = 0.348$). In contrast, the molecular composition of laboratory-

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generated SOA was substantially different from that of the anthropogenically affected TIED site. The fraction of common molecular formulae from α -pinene and the VOC mixture relative to the total number of ions from the TIED sample was only $16.1 \pm 1.7\%$ and $16.9 \pm 1.2\%$, respectively, indicating the very different sources of organic compounds in these samples.

Laboratory-generated and ambient samples were also compared by hierarchical cluster analysis (HCA) that divides samples into groups (clusters) of similar molecular composition. HCA separated the samples into three clusters (Fig. 6): (1) α -pinene (replicates from three different experiments); (2) VOC mixture (three replicates) together with the common ions of the ambient samples from Hyytiälä; and (3) common ions of the ambient samples from TIED. The branches in the tree diagram (dendrogram) represent the average distance between the connected samples. It is evident from the dendrogram that all replicate samples from the α -pinene and the VOC mixture experiments cluster together, implying very good reproducibility of the applied technique (i.e., smog chamber experimental and MS analysis) to separate two experimental conditions relative to each other. Although the α -pinene data is separated from the VOC mixture and Hyytiälä cluster, the linkage distance is not large enough to conclude that their chemical composition is very different. On the other hand, the data from TIED was classified into a separate cluster confirming that its molecular composition is very different from the rest of the samples. The results from HCA clearly support the findings obtained from the statistical analysis and other visualisation methods (Van Krevelen diagrams, carbon oxidation state, DBE).

4 Conclusions

The detailed molecular composition of background ambient aerosol from a boreal forest site (Hyytiälä, Finland), an urban location (Cork, Ireland), laboratory-generated SOA from α -pinene and a mixture of four VOCs were compared using nanoESI-UHRMS. Our results demonstrate that the molecular composition of SOA in the monomeric mass

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Table 1. Summary of α -pinene and VOC mixture ozonolysis experiments.

Experiment	Total VOC conc., ppb	Ozone conc., ppb	RH, %	Seed conc., $\mu\text{g m}^{-3}$	ΔM , $\mu\text{g m}^{-3}$	SOA yield (Y) ^{a,b}
α -pinene	49.5	200	60	3.1	42.3	0.15
α -pinene	50.5	200	64	3.0	50.0	0.16
α -pinene	55.2	200	62	4.3	55.9	0.16
VOC mixture	62.9	200	63	5.2	34.8	0.11
VOC mixture	67.7	200	68	3.8	43.6	0.12
VOC mixture	62.9	200	65	3.6	41.8	0.12

^a Yields were calculated from the equation $Y = \Delta M / \Delta \text{HC}$, where ΔM ($\mu\text{g m}^{-3}$) is the particle mass loading and ΔHC ($\mu\text{g m}^{-3}$) is the reacted concentration of VOCs.

^b The data is wall loss corrected.

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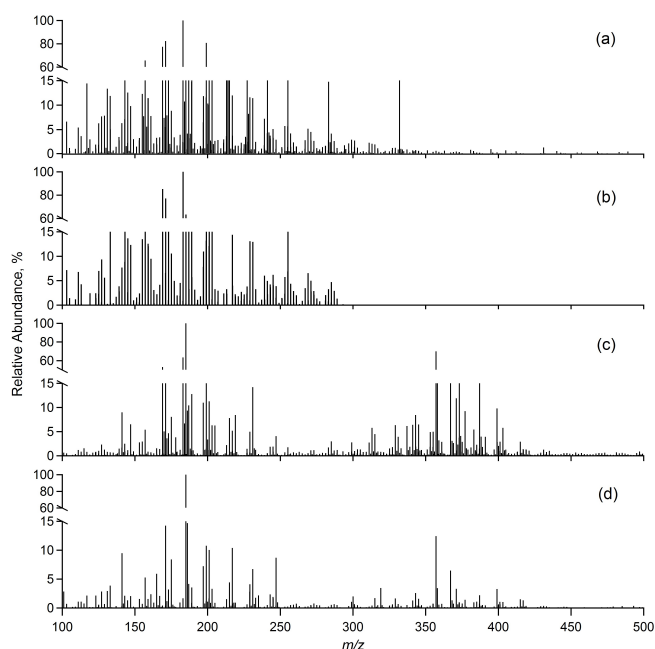


Fig. 1. Direct infusion negative-nanoESI-Orbitrap mass spectra obtained for representative OA samples from (a) boreal forest, Hyttiälä, Finland collected on 17 August (night-time), (b) boreal forest, Hyttiälä showing only “common” ions that are present in all 10 samples (see text for detailed explanation), (c) α -pinene/ O_3 experiments and (d) VOC mixture/ O_3 experiments. For clarity, the most intense peak at m/z 212 has been removed and mass spectra (a) and (b) have been normalised to the second most intense ion at m/z 185. The mass spectrum for SOA from the VOC mixture/ O_3 has been scaled up to display all ions that were suppressed by the most intense ion at m/z 185.

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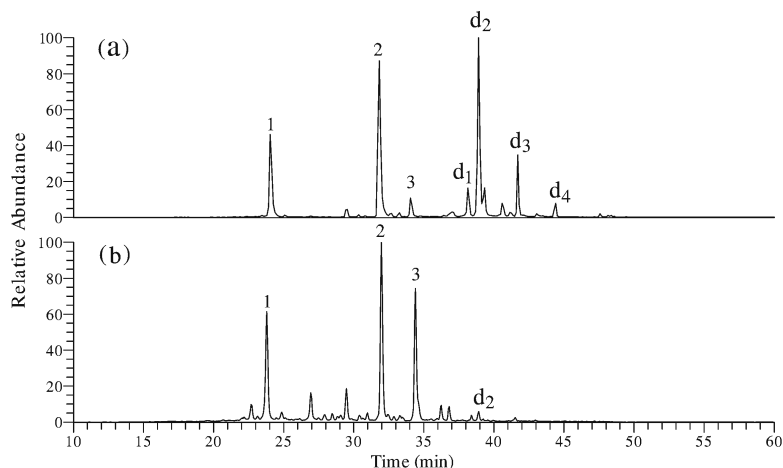


Fig. 2. LC/(-)ESI-MS extracted ion chromatogram (EIC) for **(a)** laboratory generated sample from α -pinene/ O_3 and **(b)** pooled night-time ambient summer sample from Hyytiälä, Finland collected during 16 to 25 August 2011. The chromatographic peaks correspond to (1) diaterpenylic acid with m/z 171.06, (2) *cis*-pinic acid with m/z 185.08, (3) *cis*-caric acid with m/z 185.08, (d_1) dimer with m/z 377.14, (d_2) dimer with m/z 357.15, (d_3) dimer with m/z 367.18 and (d_4) dimer with m/z 337.16. In the ambient sample **(b)** only one dimer, d_2 , was observed; the other small peaks between 36 and 42 min retention time in **(b)** do not correspond to d_1 , d_3 and d_4 .

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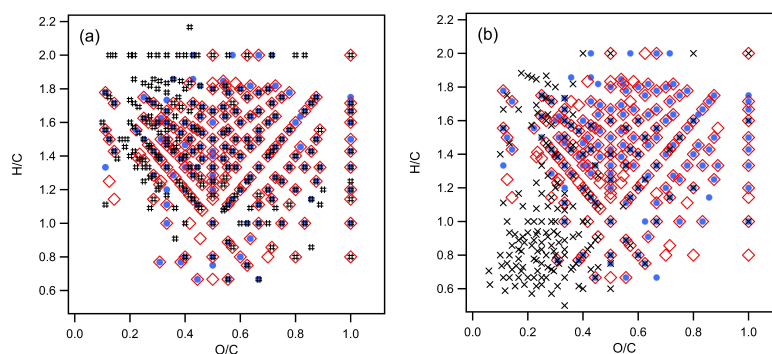


Fig. 3. Van Krevelen diagrams for compounds containing only carbon, hydrogen and oxygen in the samples from **(a)** α -pinene/ O_3 , VOC mixture/ O_3 and the boreal forest, Hyytiälä, Finland; and **(b)** α -pinene/ O_3 , VOC mixture/ O_3 and Tivoli Industrial Estate and Docks, Cork, Ireland. Filled blue circles correspond to species from α -pinene/ O_3 experiment, red diamonds to VOC mixture/ O_3 experiments, black hashes to the Hyytiälä samples and black crosses to the Tivoli Industrial Estate and Docks, Cork samples.

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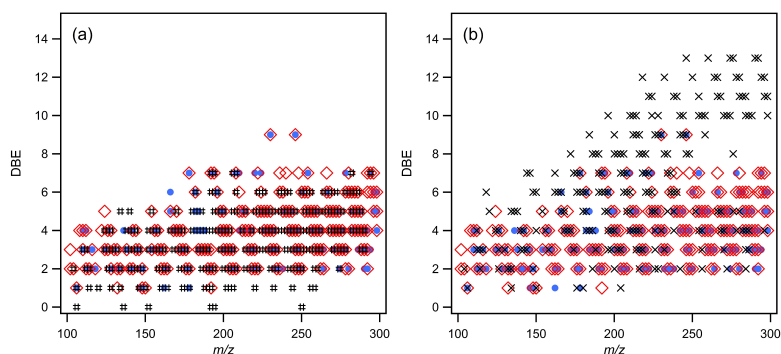


Fig. 4. Double bond equivalents (DBE) vs. mass to charge (m/z) ratios for all compounds containing only carbon, hydrogen and oxygen in the samples from **(a)** α -pinene/ O_3 , VOC mixture/ O_3 experiments and boreal forest, Hyttiälä, Finland, and **(b)** α -pinene/ O_3 , VOC mixture/ O_3 experiments and Tivoli Industrial Estate and Docks, Cork, Ireland. Filled blue circles correspond to species from α -pinene/ O_3 experiment, red diamonds to VOC mixture/ O_3 experiments, black hashes to the Hyttiälä samples and black crosses to the Tivoli Industrial Estate and Docks, Cork samples.

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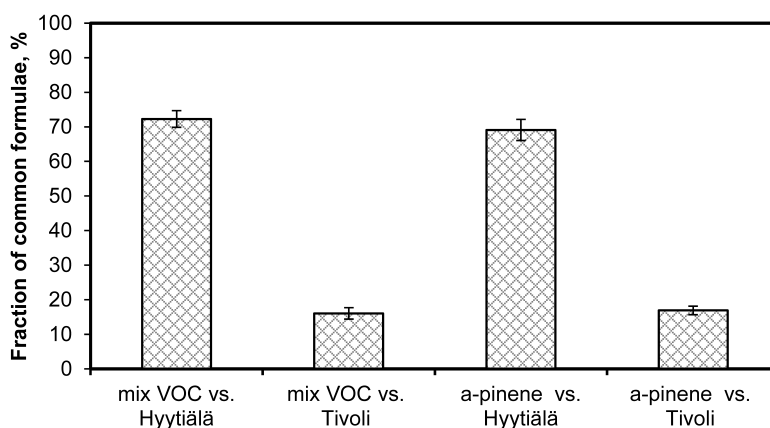


Fig. 5. Fraction of molecular formulae below 300 Da found in SOA from both laboratory-generated and ambient samples relative to the total number of formulae in the ambient samples. The error bars represent the standard deviation of three replicate chamber experiments.

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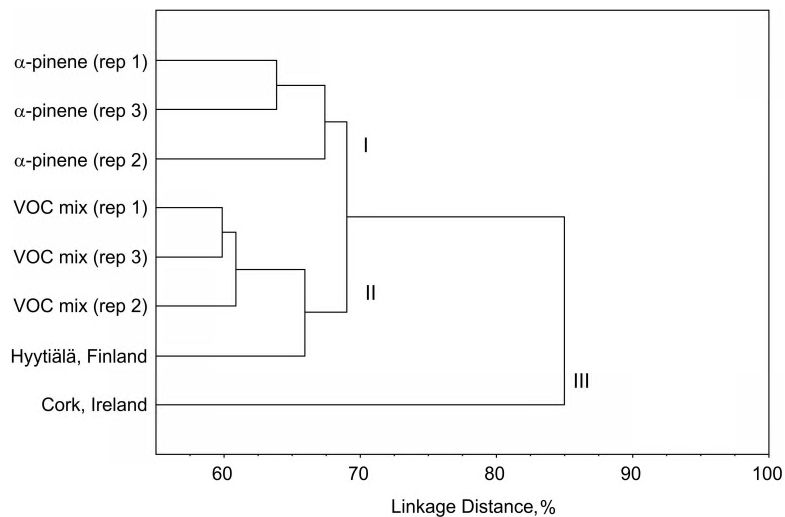


Fig. 6. Tree diagram derived from hierarchical cluster analysis (HCA) of ambient and laboratory-generated samples (unweighted pair-group average linkage method). The linkage distance between two samples, expressed in percentage, has been calculated as the difference between the total ions considered in the cluster analysis (451 ions, 100%) and the number of common ions between the samples (see text for detailed explanation). Rep 1, 2 and 3 correspond to chamber replicate experiments.