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# The role of VOC oxidation products in continental new particle formation

A. Laaksonen<sup>1,4</sup>, M. Kulmala<sup>2</sup>, C. D. O'Dowd<sup>3</sup>, J. Joutsensaari<sup>1,\*</sup>, P. Vaattovaara<sup>1</sup>, S. Mikkonen<sup>1</sup>, K. E. J. Lehtinen<sup>1,4</sup>, L. Sogacheva<sup>2</sup>, M. Dal Maso<sup>2</sup>, P. Aalto<sup>2</sup>, T. Petäjä<sup>2</sup>, A. Sogachev<sup>2</sup>, Y. Jun Yoon<sup>3,\*\*</sup>, H. Lihavainen<sup>4</sup>, D. Nilsson<sup>5</sup>, M. Cristina Facchini<sup>6</sup>, F. Cavalli<sup>6,\*\*\*</sup>, S. Fuzzi<sup>6</sup>, T. Hoffmann<sup>7</sup>, F. Arnold<sup>8</sup>, M. Hanke<sup>8</sup>, K. Sellegri<sup>8,\*\*\*\*</sup>, B. Umann<sup>8</sup>, W. Junkermann<sup>9</sup>, H. Coe<sup>10</sup>, J. D. Allan<sup>10</sup>, M. Rami Alfarra<sup>10,\*\*\*\*\*</sup>, D. R. Worsnop<sup>11</sup>, M.-L. Riekkola<sup>12</sup>, T. Hyötyläinen<sup>12</sup>, and Y. Viisanen<sup>4</sup>

<sup>1</sup>University of Kuopio, Department of Physics, P.O. Box 1627, 70211 Kuopio, Finland

<sup>2</sup>University of Helsinki, Department of Physical Sciences, Helsinki, Finland

<sup>3</sup>National University of Ireland, Galway, Department of Physics

<sup>4</sup>Finnish Meteorological Institute, P.O. Box 503, 00101 Helsinki, Finland

<sup>5</sup>Stockholm University, Department of Applied Environmental Science (ITM), Atmospheric Science Unit, 10691, Stockholm, Sweden

<sup>6</sup>Istituto di Scienze dell'Atmosfera e del Clima – CNR, Italy Via Gobetti 101, 40 129 Bologna, Italy

<sup>7</sup>Johannes Gutenberg-University of Mainz, 55128, Mainz, Germany

<sup>8</sup>Max-Planck-Institute for Nuclear Physics, Heidelberg, Germany

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<sup>9</sup>Forschungszentrum Karlsruhe, Institute for Meteorology and Climate Research, IMK-IFU, Garmisch-Partenkirchen, Germany

<sup>10</sup>School of Atmospheric and Environmental Science, University of Manchester, P.O. Box 88, Manchester, M60 1QD, UK

<sup>11</sup>Aerodyne Research Inc., 45 Manning Road, Billerica, Ma 01821-3976, USA

<sup>12</sup>University of Helsinki, Department of Chemistry, Helsinki, Finland

\*now at: University of Kuopio, Department of Environmental Sciences, P.O. Box 1627, 70211 Kuopio, Finland

\*\*now at: Korea Polar Research Institute, SongDo Techno Park, 7–50, Songdo-dong, Yeonsu-Gu, Incheon City 406-840, Korea

\*\*\*now at: Joint Research Centre, Via E. Fermi, 1, 21020 Ispra, Italy

\*\*\*\*now at: Laboratoire de Météorologie Physique (LaMP), Observatoire de Physique du Globe de Clermont-Ferrand (OPGC), UMR 6016 CNRS, France

\*\*\*\*\*now at: Paul Scherrer Institut, 5232 Villigen, Switzerland

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Correspondence to: A. Laaksonen (ari.laaksonen@uku.fi)

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## Abstract

Aerosol physical and chemical properties and trace gas concentrations were measured during the QUEST field campaign in March–April, 2003, in Hyytiälä, Finland. Our aim was to understand the role of oxidation products of VOC's such as mono- and sesquiterpenes in atmospheric nucleation events. Particle chemical compositions were measured using the Aerodyne Aerosol Mass Spectrometer, and chemical compositions of aerosol samples collected with low-pressure impactors and a high volume sampler were analysed using a number of techniques. The results indicate that during and after new particle formation, all particles larger than 50 nm in diameter contained similar organic substances that are likely to be mono- and sesquiterpene oxidation products. The oxidation products identified in the high volume samples were shown to be mostly aldehydes. In order to study the composition of particles in the 10–50 nm range, we made use of Tandem Differential Mobility Analyzer results. We found that during nucleation events, both 10 and 50 nm particle growth factors due to uptake of ethanol vapour correlate strongly with gas-phase monoterpene oxidation product (MTOX) concentrations, indicating that the organic constituents of particles smaller than 50 nm in diameter are at least partly similar to those of larger particles. We furthermore showed that particle growth rates during the nucleation events are correlated with the gas-phase MTOX concentrations. This indicates that VOC oxidation products may have a key role in determining the spatial and temporal features of the nucleation events. This conclusion was supported by our aircraft measurements of new 3–10 nm particle concentrations, which showed that the nucleation event on 28 March 2003, started at the ground layer, i.e. near the VOC source, and evolved together with the mixed layer. Furthermore, no new particle formation was detected upwind away from the forest, above the frozen Gulf of Bothnia.

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## 1 Introduction

Atmospheric nucleation of new aerosol particles has in the recent years received considerable attention (Kulmala, 2003) as it has become evident that, given favourable circumstances, nucleation takes place almost everywhere in the atmosphere (Kulmala et al., 2004), and is potentially an important source of cloud condensation nuclei (Laaksonen et al., 2005; Komppula et al., 2005) . Despite extensive research efforts, both experimental and theoretical, many aspects of atmospheric new particle formation remain elusive. Perhaps the most widely accepted theory (Kulmala et al., 2000) postulates that ternary nucleation of sulfuric acid, ammonia and water explains the appearance of thermodynamically stable clusters (TSC) in the 1–2 nm size range. However, the concentrations of sulfuric acid are generally too low to allow the clusters to grow beyond the 3 nm detection limit of modern aerosol instruments before they are scavenged during collisions with large aerosol particles.

It is suspected that the vapors causing the condensational growth of the clusters to observable sizes are low vapor pressure organic species whose exact chemical natures are unknown. So far, the experimental evidence of this is scarce: O'Dowd et al. (2002) showed, based on particle growth inside a pulse-height analyzing condensation particle counter, that fresh 3–4 nm particles are likely to contain organics, and recently the particle growth rates were shown to correlate with the product of monoterpene concentration and global radiation (Kulmala et al., 2004), a quantity that is expected to be proportional to the concentration of the condensable organics.

Notwithstanding the challenging questions to resolve in terms of micro-scale or nano-scale processes, there also exist many questions regarding the role of macro-scale features of the events. Some key questions arise: what are the spatial scales and degree of homogeneity of continental nucleation events? Does nucleation and growth occur in the free troposphere or in the boundary layer? Is nucleation primarily driven by the mixing of different air parcels? These questions need to be answered before the relevance of homogeneous nucleation as a source of climatically active aerosol

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particles and cloud condensation nuclei can be assessed and quantified.

Here, we report results from an intensive field measurement campaign that took place in March–April 2003 in Hyytiälä, Finland. Our results shed light on many of the open questions associated with continental boundary layer nucleation. The campaign, featuring two aircraft and an array of state-of-the-art instrumentation, was a part of the EU-funded project QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer), in which experimental and computational tools were used in a comprehensive and focused manner to elucidate key processes and scales associated with atmospheric nucleation events and to better quantify their contribution to the European aerosol population. The measurement site is situated inside a Scots Pine canopy in a rural area in Southern Finland. More than eleven years of continuous aerosol particle size distribution data in the 3–500 nm size range is available from the site, where on average 50–100 nucleation events takes place annually with the frequency of the events peaking in springtime. Below, we present new findings on the nature of the chemical species participating in growth of new particles, and link these findings to the spatial and temporal variability of the nucleation events observed during aircraft measurements.

## 2 Experimental

### 2.1 Meteorological and gas phase measurements

Several meteorological and gas phase parameters are being measured continuously at the Hyytiälä station, including temperature, pressure, relative humidity, wind speed and direction, and SO<sub>2</sub>, NO, NO<sub>x</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S and O<sub>3</sub> concentrations. Several radiation parameters (UVA, UVB, global radiation, PAR) are also being measured continuously. Wind and radiation parameters are also being measured at different heights from a 75 m high mast. Detailed information of these measurements is provided in Kulmala et al. (2001).

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During the 2003 QUEST campaign, a Chemical Ionization Mass Spectrometer (Sellegri et al., 2005a) was operated between 17–29 March to measure volatile organic compounds. As described by Sellegri et al. (2005b), these compounds included acetone, di- and trimethylamine, monoterpenes, isoprene, methyl vinyl ketone and methacrolein, and monoterpene oxidation products (MTOp).

## 2.2 Aerosol measurements

Aerosol size distributions between 3–500 nm have been recorded at the Hyytiälä station continuously from the beginning of 1996 (e.g. Kulmala et al., 2001). These measurements are taken from 2 m height inside the canopy using a twin Differential Mobility Particle Sizer (DMPS) system. The size distribution is recorded in 10 min intervals. The size distribution of particles larger than 500 nm is currently measured using an aerodynamic particle sizer (APS).

In order to understand the chemical composition of aerosol particles during events of new particle nucleation and growth, we employed during the 2003 QUEST campaign an array of different techniques capable of resolving different chemical features of particles in varying size ranges. Size resolved impactor samples of particles with sizes between 50 nm and 10  $\mu\text{m}$  were collected during nucleation event days (see Cavalli et al., 2006, for details), and these samples were subsequently analysed for inorganic ions concentrations by ion chromatography and for water-soluble organic carbon (WSOC) content by TOC liquid analyser. Furthermore a functional group analysis of the water-soluble organic compounds was performed by Proton Nuclear Magnetic Resonance, HNMR (Cavalli et al., 2006).

To keep the sampling time short, high volume sampler was employed for the collection of aerosol samples for the subsequent analysis of organic compounds, including MTOp. Sampling conditions and analytical procedures for the determination of organics by LC-MS, GC-MS and GC\*GC-FID are described elsewhere (Rissanen et al., 2006; Anttila et al., 2005; Kallio et al., 2006)

A quadrupole type Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000;

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Jimenez et al., 2003) was used to measure the size and composition of particles between 50 and 700 nm. This instrument used thermal desorption and 70 eV electron ionisation and the data analysis techniques described by Allan et al. (2003, 2004) were employed. Using this configuration, it was possible to quantify the nonrefractory component of the particles, which in practice meant the mass concentrations of organics, sulphate, nitrate and ammonium. The instrument was also able to derive composite mass spectra for the organic fraction. More information on this deployment and the results gained can be found in Allan et al. (2006).

In order to obtain chemical information about smaller particles, we used an Ultrafine Organic Tandem Differential Mobility Analyzer (UFO-TDMA) (Joutsensaari et al., 2001; Vaattovaara et al., 2005) to measure ethanol uptake efficiencies of 10 and 50 nm sized particles. In this instrument, nearly monodisperse particles of desired size are selected from a dried (at RH of about 3%) polydisperse ambient aerosol using the first DMA of the TDMA system. These particles are then introduced into air mixed with ethanol vapor (saturation ratio 83%), and their size change is measured using the second DMA. The growth factor (GF, ratio of wet and dry sizes) depends on the solubility of the particle material in ethanol and on the relative difference of the molecular sizes of the aerosol compounds and of ethanol (i.e. smaller molecules taking up the same mole fraction of ethanol have higher GF's than larger molecules). Particles consisting of inorganic salts such as ammonium sulfate and sodium chloride do not grow (GF=1) whereas many organic substances show GF's up to 1.4–1.5 at 50–100 nm dry sizes (Joutsensaari et al., 2001; Vaattovaara et al., 2005) and up to 1.2 at 10 nm dry sizes (Vaattovaara et al., 2005). Ammonium bisulfate shows modest growth at 50–100 nm (Vaattovaara et al., 2005; Joutsensaari et al., 2004) but does not grow at 10 nm (Vaattovaara et al., 2005). Similarly, mixed particles of ammonium bisulfate and sulfuric acid (sulfuric acid mass fractions up to 0.50) have GF's of unity at 10 nm dry size (Vaattovaara et al., 2005). The decrease of the GF as a function of particle dry size for a given substance is mainly due to the Kelvin effect, increasing the vapor pressure of ethanol in the solution droplets as droplet curvature increases. Information concern-

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ing the UFO-TDMA measurements during the 2003 QUEST campaign is available in Petäjä et al. (2005).

## 2.3 Aircraft measurements

A Twin Otter (DHC-6/300 operated by the Geological Survey of Finland) aircraft (O'Dowd et al., manuscript in preparation) and the IMK-IFU microlight, a motorized hangglider (Junkermann, 2001, 2005), were deployed during this campaign in order to obtain information about the regional-scale spatial and temporal features of nucleation events. Both of these carried aerosol, gas and meteorological instrumentation to elucidate the spatial extent of these nucleation events and to try to locate the region of the atmosphere where nucleation first occurred.

One of the strongest nucleation events during the campaign occurred on the 28 March 2003. This coincided with the most extensive aircraft missions, with two Twin Otter flights and a microlight flight in between. The flights were designed to capture boundary layer meteorological structure and existing aerosol concentrations prior to the onset of nucleation and to try to locate the region where nucleation occurred first, and then to follow the evolution of boundary layer and aerosol properties throughout the event.

## 3 Results and discussion

### 3.1 Overall aerosol chemistry during the campaign

When the air originated from the more southerly sector, the composition tended to contain organics, ammonium, nitrate, elemental carbon and anthropogenic tracers such as PAHs. The particles were often pH neutral (based on the measured ions), and submicron aerosol mass concentrations typically reached several  $\mu\text{g m}^{-3}$ . Additionally, the mass spectra of the organic fraction measured by the AMS during continental out-breaks exhibited a signature typical of heavily oxidised organic material, previously

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measured in other background sites subjected to regional pollution (Topping et al., 2004). The sources of these particulate materials are likely to be processed emissions from within continental Europe. The presence of monoterpene oxidation products such as pinic and cis-norpinonic acids (at around  $10 \text{ ng m}^{-3}$ ) in these samples indicates that there are biogenic sources in addition to those of anthropogenic origin.

During the arctic air outbreaks, the pre-existing aerosol were often acidic, mainly composed of sulfate with little ammonium. While being the dominant species, the mass concentrations of sulfate were low, typically less than  $0.5 \mu \text{ g m}^{-3}$ . Organic matter was always present, but this was not accompanied with elemental carbon, indicating that it was probably not of anthropogenic origin.

### 3.2 Aerosol chemistry following nucleation events

By the late evening of most nucleation days the particles were large enough ( $>30 \text{ nm}$  (13, 14)) to be analyzed by the AMS and possessed enough mass to be distinguishable in the size-resolved data produced by the AMS (Allan et al., 2006). On each nucleation event recorded, the majority of the mass of growing particles was organic in nature. The growing particles only gave a response in AMS  $m/z$  (mass number/electric charge) channels associated with organic species (e.g.  $m$  equal to 43, 55, 57), confirming that the majority of the mass of the growing particles is organic in nature. The base mass peak was invariably  $m/z=43$ , which can be produced by both aliphatic chains or oxidized functional groups (Allan et al., 2006). Several mass peaks were present at a relative intensity that had not previously been observed with an AMS (Allan et al., 2006), demonstrating that the nature of the organic matter was significantly different from that observed in either anthropogenic emission dominated or remote environments. The overall mass spectral fingerprint was identical in each case for small ( $<200 \text{ nm}$  in diameter) and large ( $300\text{--}700 \text{ nm}$ ) particles, implying that similar secondary organic species were condensing onto all particles. Further to this, it supports the assumption that the analyses of impactor and filter samples should be generally representative of the condensing organic species, regardless of the sizes of the particles sampled.

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A comparison between the H-NMR spectra of the impactor-collected nucleation event aerosols and those of secondary organic aerosol (SOA) generated from  $\alpha$ -pinene in smog chamber experiments, indicates that, in samples collected during nucleation days when anthropogenic pollution levels were low, the oxidation products of  $\alpha$ -pinene accounted for 72% of the total H-NMR signal (Cavalli et al., 2006), corresponding to 51% of water-soluble organic compounds, on average. This finding allows us to postulate that,  $\alpha$ -pinene oxidation products (and probably also oxidation products from other monoterpenes) are the most likely species to contribute to the growth of nanometer-sized particles. The AMS mass spectra (Allan et al., 2006) are consistent with the identification of these oxidation products.

Previously it has been shown that interaction of organic acids, for example, pinonic acid, produced by photo-oxidation of terpenes with other organic or inorganic species present in the atmosphere most probably causes observed growth of new particles over forest (Kavouras et al., 1998). However, results of our investigation indicate that aldehydes, such as pinonaldehyde, are responsible for the aerosol growth at least as much as acids. Previously, Boy et al. (2004) found pinonaldehyde in Hyytiälä aerosol samples. Concentrations of  $\alpha$ -pinene oxidation products obtained from our samples are presented in Table 1. As can be seen, the concentration of pinonaldehyde is considerably higher than the concentrations of corresponding acids. If the emissions of different terpene compounds is taken in account, the significance of sesquiterpene oxidation products for aerosol growth can be expected to be high. The relative contribution of  $\alpha$ -pinene oxidation products to SOA formation has been predicted to be 23.5% (Andersson-Sköld et al., 2001). The significance of aldehydes in oxidation of sesquiterpenes, and especially their stability and presence in aerosol samples are confirmed by our most recent results (Parshintsev et al., 2007<sup>1</sup>).

Evidence that freshly nucleated 10 nm particles contain similar organic substances

<sup>1</sup>Parshintsev, J., Nurmi J., Lespine, A., Vestenius M., Hartonen, K., Kilpeläinen I., Kulmala M., and Riekkola, M.-L.: Preparation and analysis of beta-caryophyllene oxidation products and their determination in ambient aerosol samples, in preparation, 2007.

as the larger particles comes from an examination of the ethanol vapor uptake efficiencies of 10 nm and 50 nm particles. Figures 1 and 2 show how the 50 and 10 nm GF's measured during nucleation events (i.e. during times when there clearly are freshly formed particles of these sizes present) correlate with gas-phase MTOP whose concentration can be used as a marker for the simultaneous formation of less volatile monoterpene oxidation products. The correlations are very clear, but they vanish when data measured during non-event periods are included.

Figure 3 shows a positive correlation between particle growth rates (*GR*) during different nucleation events, and gas-phase MTOP concentrations averaged over the events. In stark contrast to observations made in Pittsburgh (Zhang et al., 2004) no such correlation can be seen between the *GR* and gas phase sulfuric acid concentration. We therefore conclude that oxidation products of  $\alpha$ -pinene and other monoterpenes are not only present in the freshly nucleated particles at all detectable sizes, but also determine their growth rates and thus their survival probability into a size range where they become optically active and relevant as CCN.

### 3.3 Evolution of nucleation event

The spatial and temporal evolution of the nucleation events depends on two quite different gas phase species: sulphur dioxide, the precursor of  $\text{H}_2\text{SO}_4$  which is likely to be the controlling factor in the nucleation of the smallest stable clusters, and VOC oxidation products which, as shown above, dominate particle growth.  $\text{SO}_2$  at the Hyttiälä station is mostly long range transported, its residence time is on the order of days, and it has quite uniform concentrations in the mixed layer air. Mono- and sesquiterpenes, on the other hand, have shorter lifetime, and they are locally released by trees. As MTOP determine particle growth rates, it is conceivable that observable particle formation is limited to areas close to the mono- and sesquiterpene sources. Demonstrations of this were obtained from aircraft measurements carried out during the measurement campaign.

The descent into the aircraft operation area on 28 March 2003, indicated a decoupled

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boundary layer structure following a night of significant nocturnal cooling. The boundary layer comprised a mixed layer inversion up to 250 m, a first decoupled mixed layer or residual layer at 300–900 m and a second residual layer between 900 and 1400 m where the free troposphere inversion was located. Total particle concentrations in the free troposphere and upper residual layer was of the order of (70–100 cm<sup>-3</sup>), increasing to 2500–3000 cm<sup>-3</sup> at about 600 m (through the lower residual layer and mixed layer). No nucleation mode particles were encountered during the descent. Following the descent, a series of 10-min horizontal runs (corresponding to a spatial scale of 60 km) were conducted at heights between 30 m and 300 m above ground level and over fixed ground positions. On the return to the starting ground position, an ascent from the end-ground position to 1000 m was conducted, followed by a descent to the start ground position. The first evidence of particle formation was encountered at approximately 09:00 a.m. on the 30 m horizontal where particle concentrations briefly increased from 3000 to 8000 cm<sup>-3</sup>. For the next hour, during these runs, more small parcels of air containing nucleation mode particles were encountered and gradually, the whole boundary layer become laden with nucleation mode particles and by 10:50 a.m., peak particle concentrations exceeded 30 000 cm<sup>-3</sup>.

In order to characterise the boundary layer evolution during the morning of 28 March, the mixed layer height was modelled using radiation and wind recorded at different heights from the 75 m high mast at the Hyytiälä measurement station. Figure 4 shows potential temperature evolution as a function of altitude during the day. The red line is mixed layer height, which is determined by threshold of the turbulent kinetic energy equal to 0.01 m<sup>2</sup> s<sup>-2</sup>. The dashed magenta line is height at which in reality the growth of the mixed layer may start.

A total of 24 aircraft profiles were conducted to characterise the evolution of the boundary layer aerosol during the nucleation event and to identify where the particles are most likely to be formed. An interpolated composite of particle concentration and evolution through the duration of the three flights is shown in Fig. 5. The data shows that new particles are first formed close to the surface, and that the layer of 3–10 nm

particles then evolves together with the growth of the mixed layer (Fig. 4). This demonstrates that mono- and sesquiterpenes, rather than  $\text{SO}_2$ , regulate the evolution of the fresh particle concentrations.

A further demonstration of the canopy influence was obtained from a horizontal flight from the Hyytiälä area to the coast and out over the Gulf of Bothnia (thus moving upwind of the forest canopy). No nucleation was observed over the frozen sea once out of the forest canopy region, showing that production of particles with diameters larger than 3 nm is confined to regions influenced by the canopy.

## 4 Conclusions

Our aim during the 2003 QUEST campaign was to obtain extensive chemical information of the composition of particles in the widest possible size range, and to use aircraft in characterising the spatial and temporal evolution of nucleation events. In order to study aerosol chemistry, we used an array of techniques including aerosol mass spectrometry, several analytical techniques for aerosol samples, and tandem differential mobility analysis. In this way we were able to obtain information of similarities in the chemical features of particles in the 10 nm–10  $\mu\text{m}$  size range during and after nucleation events.

During nucleation events, the aerosol chemical characteristics as determined from impactor and filter samples were seen to be consistent with AMS mass spectra. Ethanol growth factors of 10 and 50 nm particles recorded during nucleation events correlated with gas phase MTOP concentrations, indicating that their organic compositions had similar features. Our results indicate that following nucleation, oxidation products of monoterpenes and possibly also sesquiterpenes are condensing on particles of all sizes in measurable quantities. Particularly, the relatively high concentrations of aldehydes in particle phase indicate that these compounds have an important role in particle growth beside the acids. Further, the correlation between gas-phase MTOP and particle growth rates indicates that the VOC oxidation products dominate particle

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growth. This is reflected in our aircraft results, which show that the first observable particles in the start of the nucleation event emerge close to the VOC source, in this case the forest canopy. As SOA has been very widely observed in other non-boreal environments, the growth of freshly formed particles to CCN active sizes may well be governed by the availability and composition of the SOA material available in that environment.

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**Table 1.** Concentrations of oxidation products of  $\alpha$ -pinene and in aerosol samples ( $\text{ng}/\text{m}^3$ ).

Sample	pinon-aldehyde	pinic acid	pinonic acid
22 March 2003 10:00–12:00	73.58	0.48	1.16
22 March 2003 12:00–14:00	61.39	1.38	1.15
24 March 2003 08:00–12:00	130.17	0.32	1.69
24 March 2003 12:00–16:00	139.71	1.26	1.87
10 April 2003 09:00–13:00	41.22	0.20	3.69
10 April 2003 13:00–17:00	90.07	0.71	3.03

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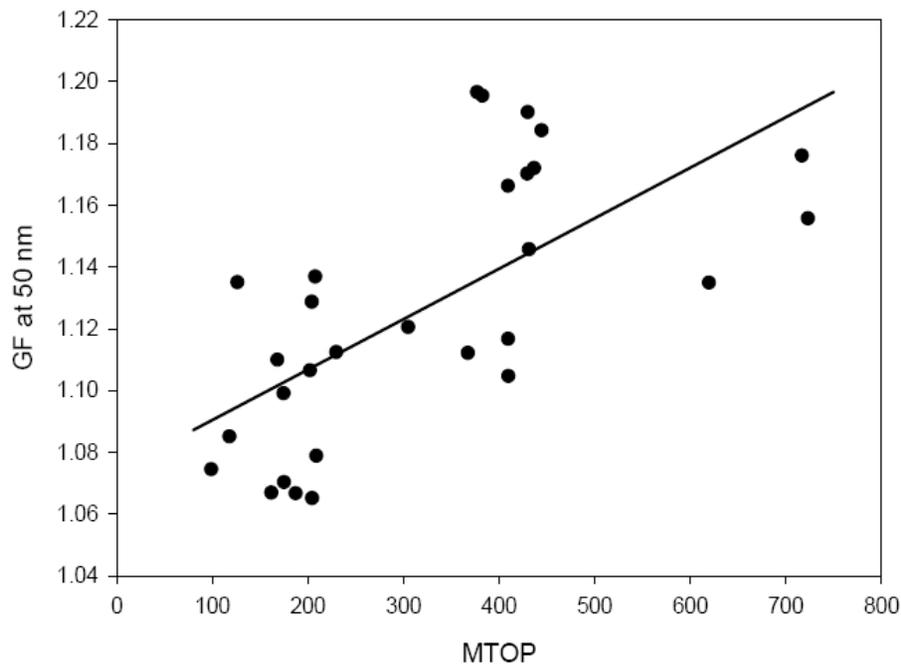
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**Fig. 1.** MTOP concentration (ppt) vs. particle growth factor (wet diameter/dry diameter) of 50 nm dry particles due to uptake of ethanol. The linear fit is given by  $GF=1.074+1.634e-4 \times MTOP$ ,  $R^2=0.44$ .

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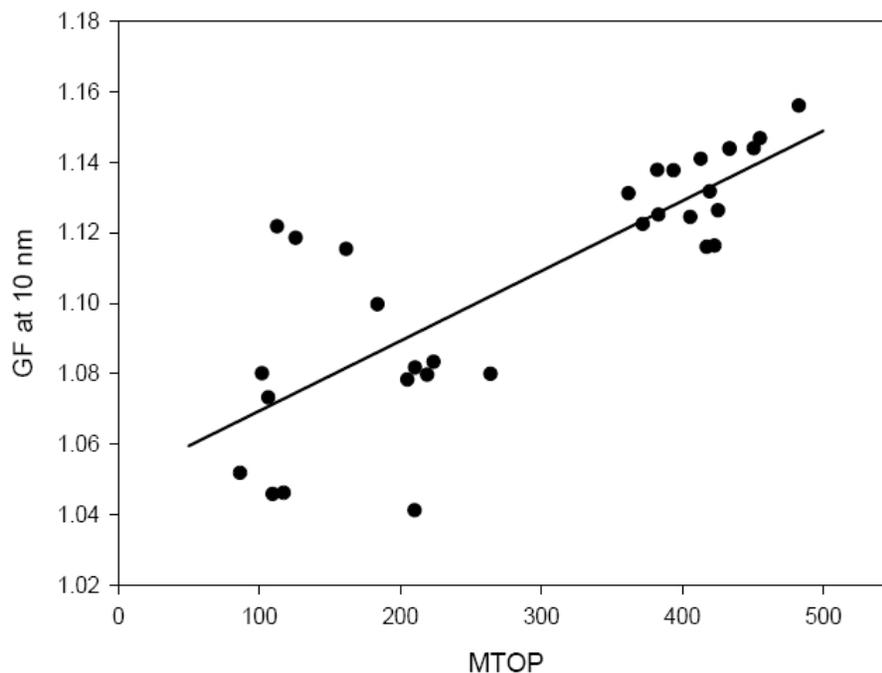
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**Fig. 2.** MTOP concentration (ppt) vs. particle growth factor (wet diameter/dry diameter) of 10 nm dry particles due to uptake of ethanol. The linear fit is given by  $G=1.050+1.988e-4\times\text{MTOP}$ ,  $R^2=0.64$ .

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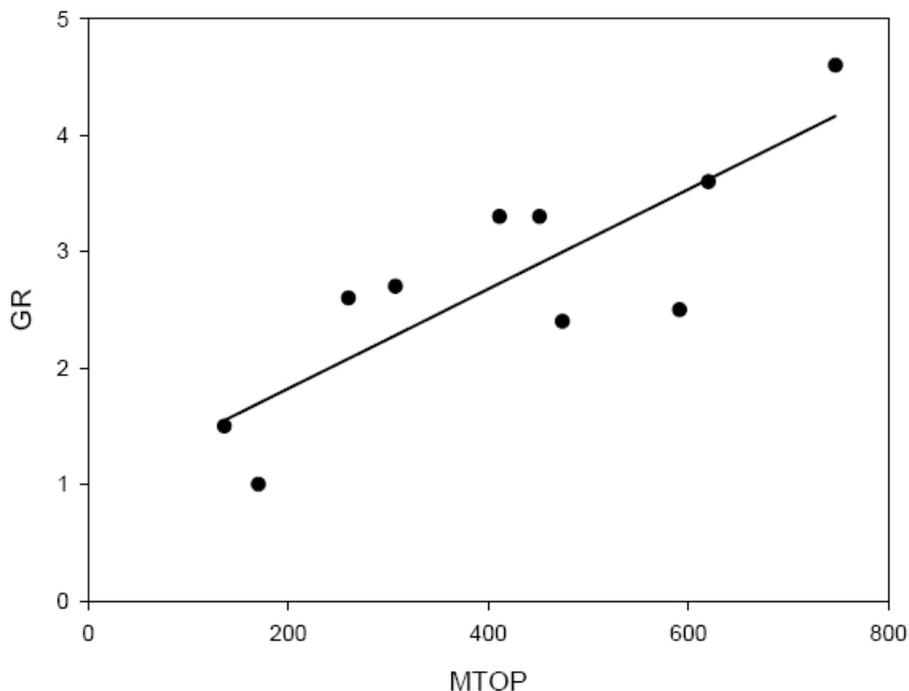
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**Fig. 3.** Particle diameter growth rates (GR,  $\text{nmh}^{-1}$ ) during ten different nucleation events vs. gas-phase MTOP concentration (ppt). MTOP values have been averaged over the time interval from which the growth rate was determined. The linear fit is given by  $\text{GR} = 0.97 + 0.0043 \times \text{MTOP}$ ,  $R^2 = 0.965$ .

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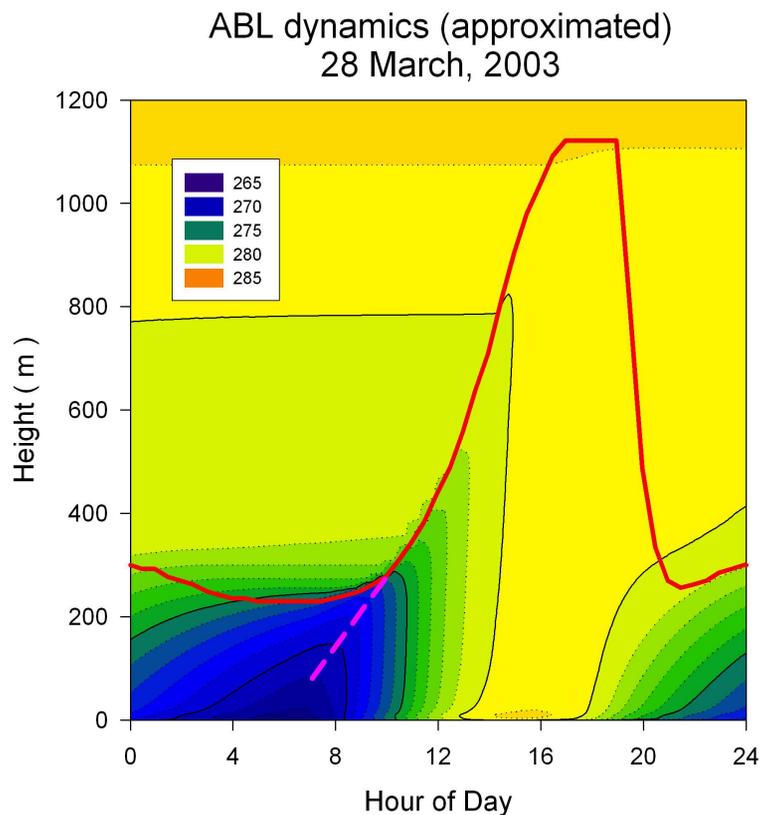
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**Fig. 4.** Evolution of height of mixed layer during 28 March 2003. Color indicates potential temperature. See text for details.

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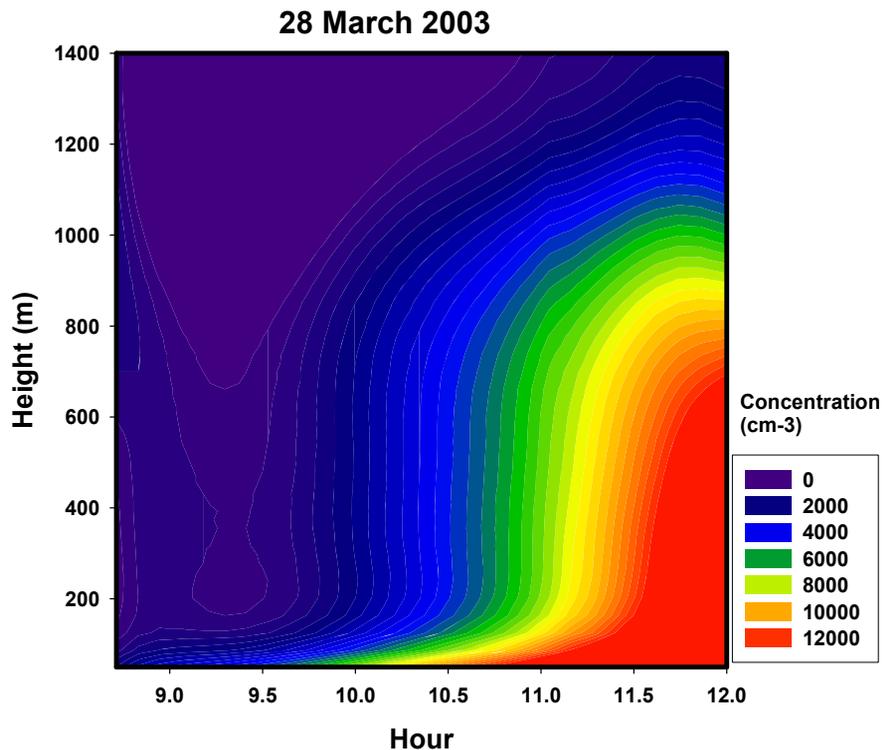
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**Fig. 5.** Interpolated contour plot of total particle concentration variation with height and time of day. The first occurrence of particle production is seen at the lowest levels after which they gradually fill the whole mixed layer.

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