

Organic contribution to sub-micron aerosol evolution over a boreal forest—a case study

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During the spring and summer of 1998 and spring of 1999 three major international campaigns have been performed at the SMEAR II Station (Station for Measuring Forest Ecosystem–Atmosphere Relations) in Hyytiälä, Finland. The measurements have been conducted as part of the BIOFOR programme, the objectives of which were to elucidate the main factors leading to nucleation and growth of new particles over forested regions. For typical nucleation events encountered in this environment, total particle concentration and surface area reduce rapidly due to mixing processes in the late morning prior to a nucleation event. After this reduction in pre-existing aerosol, ultra-fine particles (3–10 nm) appear, and grow rapidly (over several hours) towards accumulation mode sizes (> 100 nm). Volatility measurements of new particle composition, once they have grown into accumulation mode sizes, illustrate a significant organic contribution to aerosol mass. Suggested contributors to this organic mass are pinic acid and/or *cis*-pinoic acid.

Introduction

Aerosols are assumed to have a very important influence on the climate system and could possibly negate the effect of man-made greenhouse gases on the radiative balance of the atmosphere. To understand and quantify the direct¹ and indirect² radiative impact of aerosols, one has to identify the source regions of new anthropogenic and natural aerosols and follow their growth, or evolution, into accumulation mode particles, which can efficiently scatter incoming solar radiation and, by acting as cloud condensation nuclei, modify cloud radiative properties. Before the impact of anthropogenic particles on climate forcing can be addressed correctly, the importance and contribution of natural aerosols must be quantified. In particular, important source regions of biogenic aerosols must be identified. Since natural emissions of non-methane hydrocarbons (NMHC) are believed to be an order of magnitude higher than the anthropogenic NMHC³ and are likely to contribute significantly to aerosol formation and growth, it is crucially important to understand processes leading to natural organic aerosol formation.

In the last years a few different source regions for natural aerosol formation have been investigated, like the polar marine boundary layer,^{4,5} the free troposphere,⁶ boreal forests,^{7,8} and the coastal environment.⁹ For the available data, it appears that the two most important natural sources of boundary layer aerosols are over the boreal forests, where nucleation occurs over large spatial scales,⁷ and in the coastal zone, where extraordinarily large nucleation rates are encountered.¹⁰

In acknowledgement of the importance of boreal forests as a significant source of biogenic aerosols, the forested areas of Finland have provided the focus to a dedicated nucleation field experiment, comprising a consortium of European scientists (BIOFOR homepage: see next section) aimed at eluci-

dating the factors controlling the formation and growth of biogenic aerosols in the form of the BIOFOR experiment (Biogenic Formation of Atmospheric Particles Over a Boreal Forest).

Within the framework of this dedicated nucleation experiment, two intensive field campaigns were conducted in the spring and summer of 1998, and a third experiment in the spring of 1999. The primary objectives of these experiments were to examine the role of biogenic volatile organic compound (VOC) emissions in the formation and growth of particles and the effect of these species on the hygroscopic and cloud formation properties of these biogenic aerosols. In this study, we present initial results illustrating the nature of these forest nucleation and growth events. Primary results are presented for one case study occurring during the spring of 1998.

Experimental and data analysis

The experiment measurement site is located in a boreal forest in Hyytiälä, Finland at the SMEAR II Station (Station for Measuring Forest Ecosystem–Atmosphere Relations, central southern Finland, 61°51'N, 24°17'E).¹¹ It is surrounded by a roughly homogeneous (in terms of species mix) and dense continuous forest. The nearest urban sources are the cities of Tampere located approximately 50 km to the south west and Jyväskylä approximately 100 km to the north east from the station. For a more detailed description of the forest vegetation and the site surroundings see refs. 12 and 7 and the BIOFOR homepage (<http://mist.helsinki.fi/Projects/Project.html>).

Total particle concentrations (diameters > 3 nm and > 10 nm) were measured using two pairs of condensation particle counters (a TSI CPC-3025^{13,14} and a CPC-3010^{15,16} installed at 18 and 67 m). Since these two instruments possess different

cut-off sizes, fast response measurements of ultra-fine particle (3–10 nm) concentration can be achieved, allowing calculation of the total number of particles formed immediately after nucleation and initial growth. The deployment of the two CPC pairs at 18 and 67 m allows extraction of information on the vertical distribution of the nucleation and growth, and consequently aids the elucidation of the formation region (*e.g.* if the nucleation processes occur closer to the forest canopy, nearer to the top of the boundary layer, or at all levels simultaneously). For more accurate information on the size distribution of ultra-fine, fine and accumulation modes, a series of DMPS systems (differential mobility particle system) were installed, sampling from 2, 16 and 67 m heights. The DMPS is capable of measuring the size distribution of the aerosols between 0.0015 and 0.250 μm radius (0.003 to 0.5 μm diameter) with a temporal resolution of 10 min. The DMPS installed at 2 m is an essential component of the continuous measurement programme running at Hyytiälä,¹² while the 18 and 67 m installations ran only for the duration of the campaigns. All DMPS measurements used sheath flows with no additional dryers, *etc.*, thus only de-humidification processes occurring in the sample tubes reduce the particle size and the aerosols are measured at close to ambient conditions.

Since water condensation at high humidities increases the mass of pre-existing aerosols, and consequently the condensation sink ability of the aerosol, aerosols under high humidity regimes are likely to inhibit nucleation by reducing the gas-phase precursor peak concentration. Consequently, 'wet-size' measurements of larger aerosol sizes were deployed. These 'wet' aerosol distribution measurements were achieved using two non-disturbing optical particle counters (OPCs) at a height of 18 m. The sampling air is sucked through an open optical cavity in the probe at a high volume rate. Both tubes have an isokinetic inlet tube and the residence time of the air in the probes is about a few milliseconds, so that the aerosol is not being de-humidified and no decreases in total numbers due to tube losses are expected. The two probes (CSASP-100 and ASASP-300 of particle measurement system) use the intensity distribution of the scattering function of a helium–neon laser to measure *in situ* the aerosol size distribution. They have two different size ranges, the former measuring the size range between 0.5 and 15 μm radius, the latter measuring the size range between 0.1 and 1.5 μm radius.

For the on-line characterisation of aerosol physico-chemical properties, a thermal analytic technique, comprising a coupled OPC (ASASP-X) and a fast response scanning volatility system, was deployed.⁵ Before the aerosol size distribution is sized and counted by the particle counter, the aerosol is heated in scanning cycles between 30 and 700 °C, every 15 min. From the thermal response of the aerosol number and the change in the size distribution, conclusions can be drawn about the chemical composition and the state of mixing of aerosols as a function of size. The ASASP-X measures the dry aerosol size spectrum between 0.05 and 1.5 μm radius. Several calibration experiments have been performed with laboratory generated aerosols, which were proposed to be present in the atmosphere during the campaign. For example, some of the primary inorganic aerosol species possess distinct temperature profiles, with sulfuric acid volatilising at 100 °C, ammonium sulfate at 200 °C, sea-salt at 650 °C and soot carbon at 800 °C.⁵ Particular organic aerosol species are somewhat more difficult to differentiate since there are often multiple organic species contributing to mass in an organic-rich aerosol population.

The meteorological parameters [relative humidity (RH), wind direction (WD), dry temperature (Td), wind speed (WS) and black carbon (BC)] have been observed simultaneously, too. With the combined measurements we were able to follow aerosol nucleation and growth over the nucleation mode (0.0015 to 0.01 μm radius), the Aitken mode (0.01 to 0.05 μm

radius), the accumulation mode (0.05 to 1.25 μm radius) and the coarse mode (> 1.25 μm radius).

Results

For the description of a typical nucleation event encountered, we have chosen 13th May 1998 to illustrate most of the typical features before, during and after the nucleation event. Total concentration throughout the day is shown in Fig. 1: for most of the morning, concentrations at sizes larger than 3 and 10 nm are of the order of 2000 cm^{-3} , and remain reasonably steady until mid-morning (Julian day 133.42), when a large reduction to 1000 cm^{-3} is observed. In the early afternoon (Julian day 133.56), particle number concentration at 67 m rises to a maximum of about 4000 cm^{-3} for sizes greater than 10 nm, and to about 5000 cm^{-3} for particles larger than 3 nm, indicating approximately 1000 cm^{-3} particles in the ultra-fine size range. The 18 m CPC pair (at 3 and 10 nm) do not exhibit as great an ultra-fine mode particle concentration—this may be due to a reduced counting for the TSI-3025 ($d > 3$ nm) after accidental contamination of the optics. Results of the two CPC pairs of the latest campaign during spring 1999 (with a different experimental setup of the CPCs) indeed show no clear difference in ultra-fine particle concentrations between the two levels during nucleation events, leaving no possibility for further conclusions about the location of the nucleation process. As the initial increase in particle number concentrations occurs at both levels at the same time, these results imply a rather rapid mixing of the new particles or the condensation nucleation precursor gases between the two levels. Analysis of boundary layer thermodynamic properties indicates the sudden break-up of a stable nocturnal boundary layer, followed by rapid dynamic vertical mixing, prior to the onset of nucleation.¹²

For nucleation to take place in the atmosphere, a necessary condition seems to be a very low pre-existing aerosol surface area to allow gaseous precursors to reach the necessary supersaturation to trigger nucleation. Indeed, with all of the observed nucleation events, nucleation occurred shortly after

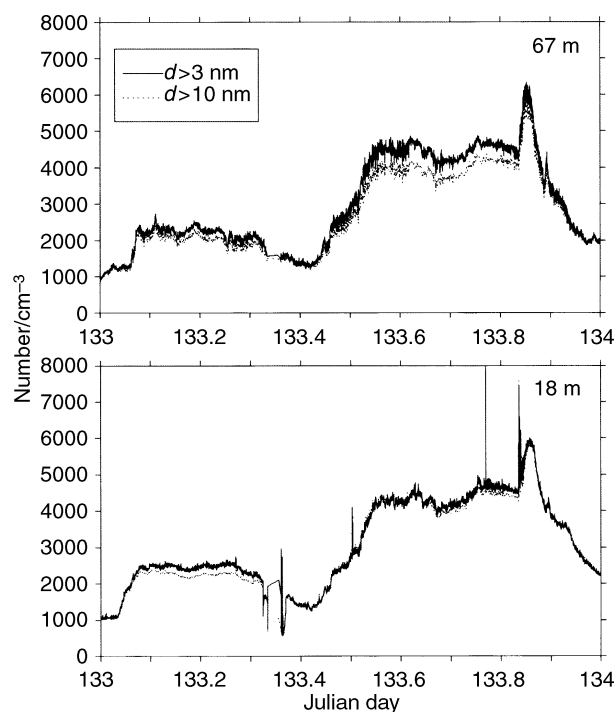


Fig. 1 Change of total number of aerosols as measured by two pairs of CPCs for 18 m (lower panel) and 67 m (upper panel) for 13th May 1998.

a sudden reduction in aerosol surface area. This change in surface area associated with this nucleation event is illustrated in Fig. 2, where a reduction in surface area, just before the onset of nucleation, is seen. An intercomparison with the DMPS data in Fig. 4 shows that the larger surface area mode between 0.05 and 0.25 μm has disappeared but that the concentration of the smaller aerosol sizes (between 0.005 and 0.05 μm) stays rather constant until the beginning of the nucleation event. The decrease in wet surface area occurs at the same time as the decrease in total numbers as measured by the twin CPC pairs and corresponds with the increasing temperature and decreasing relative humidity shown in Fig. 3. Aethalometer data indicate very low soot amounts ($< 150 \text{ ng m}^{-3}$) in the atmosphere for the entire day, indicating clean air mass conditions. Air mass back trajectories imply an Arctic maritime air mass for this case, corroborating the conclusions drawn from the soot mass concentrations. In Fig. 4 the DMPS size spectra of submicrometre particles for this case study are plotted for 2 m height. Total number concentration derived from the DMPS exhibits similar behaviour to that observed by the CPCs with a decrease in total concentration prior to nucleation. After nucleation, enhanced concentrations of particles are observed at sizes between 3 and 10 nm, shortly after which this new particle mode is observed to increase in mean size and continues to grow into accumulation mode sizes over about 11 h. The nature of the growth indicates that nucleation and growth were occurring over spatial scales of about 100 km. For this distance and considering the wind direction, we can assume that the terrain and vegetation were more or less of the same characteristics and that nucleation events occur over a very large area, as has been shown already in ref. 12.

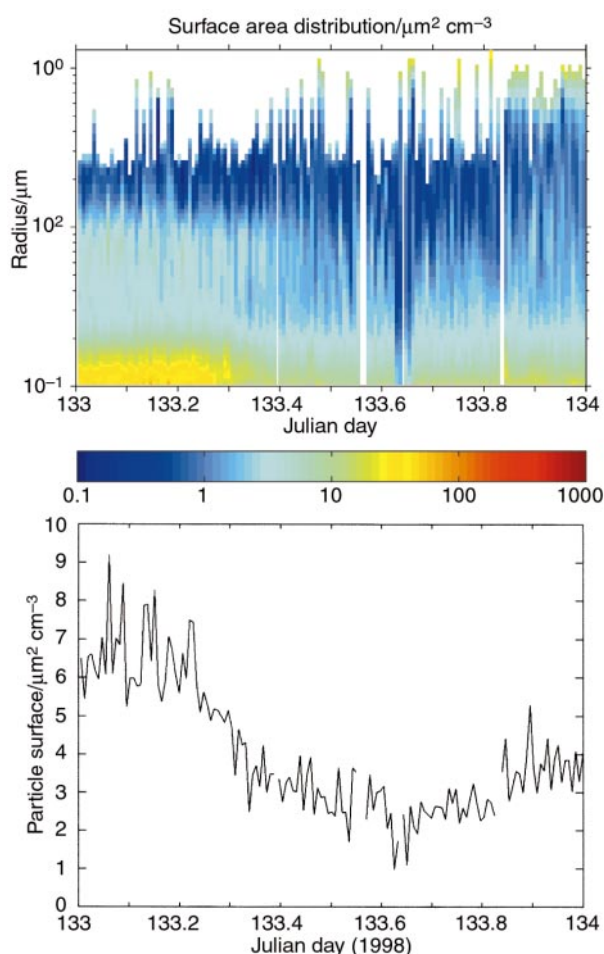


Fig. 2 Decrease of wet-surface area during the 13th May 1998 (spectral distribution and integrated surface in the 0.1 to 2.5 μm range).

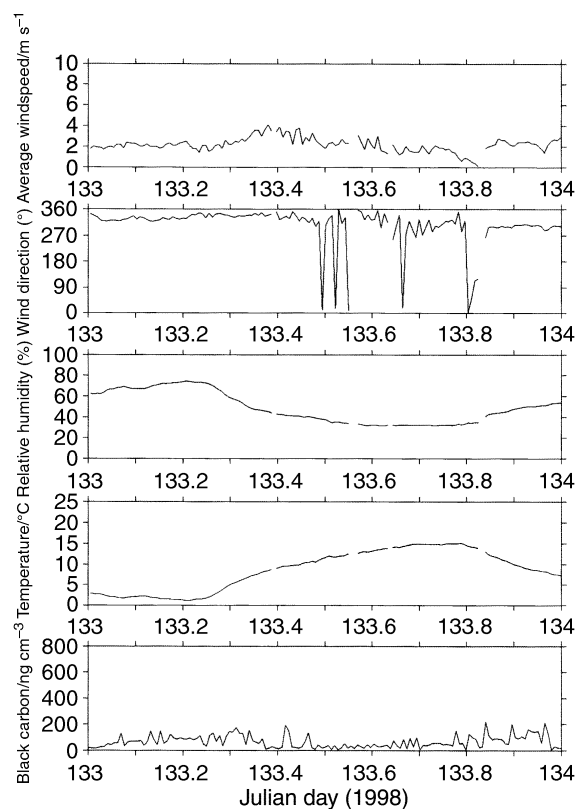


Fig. 3 Meteorological data (WS, WD, RH, Td and BC) for the 13th May 1998.

Towards the end of the growth period, an increase in the total numbers of accumulation mode particles from 140 cm^{-3} to 260 cm^{-3} is seen.

Once these recently formed particles have grown into accumulation mode sizes, their physico-chemical properties can be analysed by the volatility technique in order to elucidate their chemical composition and to identify primary condensing aerosol species. Temperature response curves and concentration for the smallest accumulation mode size (50–60 nm radius) are displayed in Fig. 5. During the night (*i.e.* JD 133.09), the thermal response clearly indicates the dominance of ammonium sulfate with a large reduction in concentration only seen at temperatures larger than 200°C .

During the start of the nucleation event (JD 133.49), concentrations have reduced due to mixing; however, the thermal response has also changed, with a significant and gradual loss of particles seen as temperature varies between 35 and 180°C . Already a big fraction of concentration loss occurs for temperatures below 100°C , and consequently this aerosol mass is not sulfuric acid (which volatilizes at 100°C). Additionally, the lack of a single step-function thermal response at these low temperatures suggests the presence of multiple species with a higher volatility than sulfuric acid. Towards the end of the growth event (JD 133.83), while the concentration of these sized particles has clearly increased by about a factor of 2, the contribution of more volatile species has also increased. While the exact chemical speciation of this more volatile mass cannot be directly identified through this technique, we can nevertheless examine temperature profiles of condensable VOC oxidation products likely to be encountered in this environment.

The thermal responses for two likely organic aerosol species¹⁷ pinic acid and *cis*-pinoic acid, are shown in Fig. 6 along with the ammonium sulfate thermal response. Pinic acid and *cis*-pinoic acid possess a similar response; however, these are sufficiently distinct from both sulfuric acid and ammonium sulfate to allow distinction between both sets of species. The organic acids start to volatilise at temperatures around 50°C ,

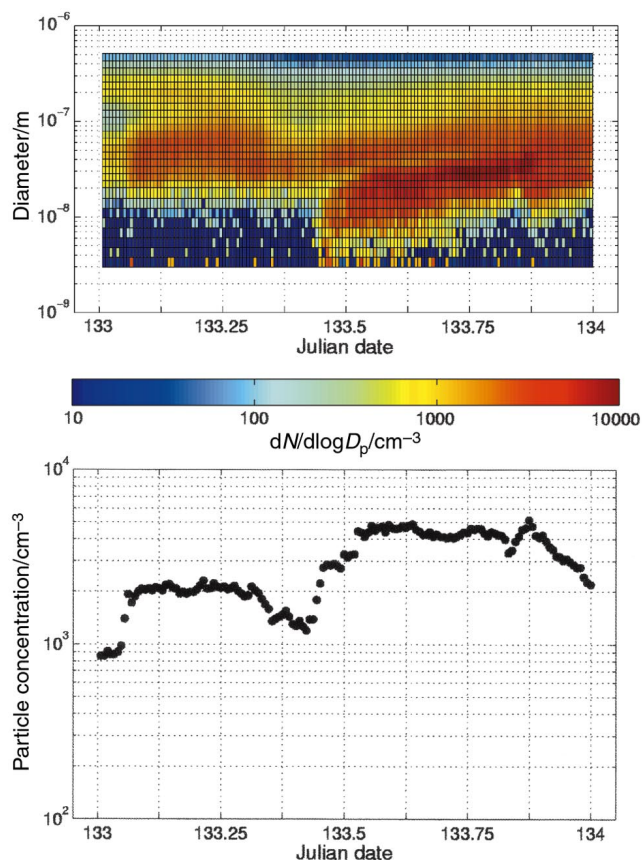


Fig. 4 DMPS data at Hyytiälä for 2 m height on 13th May 1998 (upper panel spectra as a function of time, lower panel integrated concentration from DMPS data).

although there is a secondary step-function seen at higher temperatures which is thought to correspond to their ammonium salt resulting from slight contamination by laboratory ammonia. The volatilisation curves for these acids are very similar to the response curves seen in the experimental data, suggesting that organic species with similar thermal response are likely to contribute significantly to the growth of new particles into accumulation mode sizes.

By taking size spectra at specific temperatures, we can examine where each chemical species resides in the aerosol distribution. Based on temperature response curves, spectra are extracted at temperatures of 35–180 °C to determine the

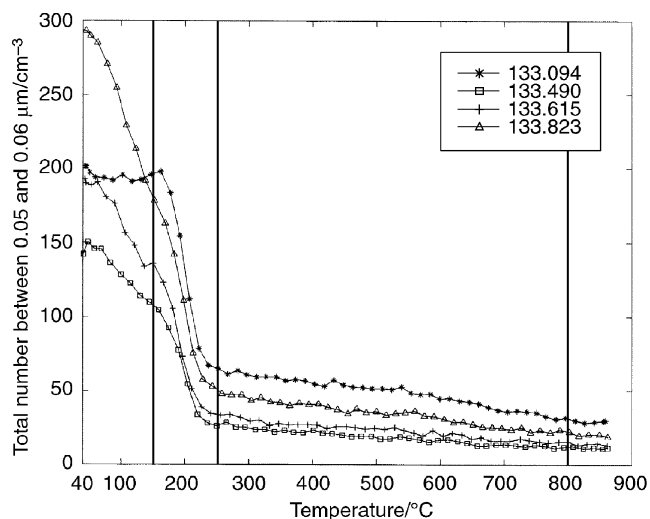


Fig. 5 Diurnal behaviour of the temperature response of the volatility system. The black lines represent the limits taken for the calculation of the composition.

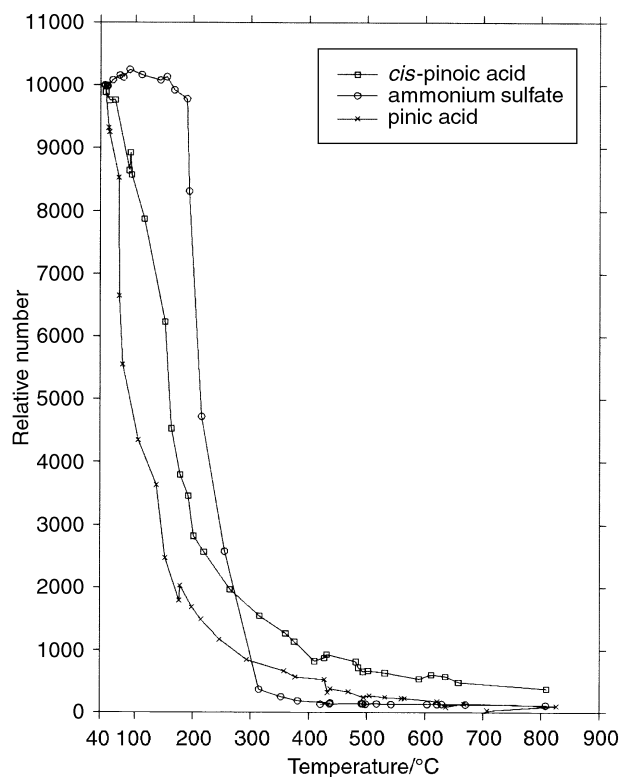


Fig. 6 Change of total numbers of laboratory aerosols upon heating. Whereas the organic aerosols are vaporised to a high amount already above 150 °C, ammonium sulfate vaporises between 200 and 250 °C. *cis*-Pinoic acid is less volatile than pinic acid, so the decrease in total number with temperature is less pronounced. Therefore even at 200 °C there are still about 40% of the original number of particles left.

organic contribution, between 180–250 °C to determine the ammonium sulfate contribution, and at 250–800 °C to determine the soot carbon contribution. The volatility spectra are shown in Fig. 7 for periods just before the onset of nucleation, and 11 h later after considerable growth has occurred. The main features observed in the spectral comparisons are the enhanced concentration at the smallest accumulation mode sizes, along with the enhanced organic contribution to these sizes.

The fractional change in relative contribution from organic and inorganic species prior to and throughout the duration of this event is illustrated in Fig. 8. During the early hours of the morning, the organic contribution is about 10%, while ammonium sulfate and soot carbon dominate the aerosol mass. Prior to the nucleation event, the organic contribution gradually increases, presumably due to condensation of biogenics before the critical supersaturation required for nucleation is achieved. By the end of the growth processes, the organic contribution to the aerosol has increased to more than 40%, while ammonium sulfate and soot reduce to <40% and <10% respectively.

Organic oxidation products from tree emissions like pinoic acid therefore appear to be very important compounds for growing freshly nucleated particles into accumulation mode sizes. The evidence for a significant contribution of organic aerosols to these recently formed particles does not, however, suggest that organic species actually nucleate to form the new particles. Recent theoretical developments in modelling ternary nucleation of new particles also suggest that the actual nucleation mechanism may be explained by the sulfuric acid–water–ammonia system.¹⁸

Conclusion

An analysis of aerosol nucleation and growth over the boreal forests indicated that these events are triggered by initial

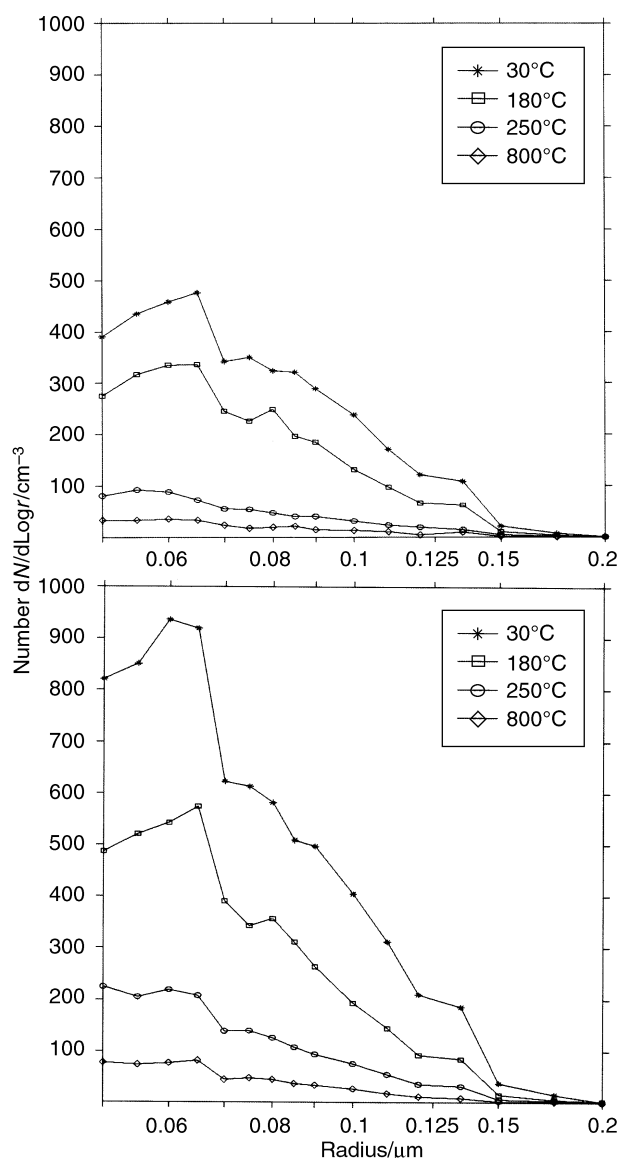


Fig. 7 Diurnal change of the spectral temperature behaviour of the volatility system during the day (top panel JD 133.469, lower panel JD 133.969). Note not only the enhancement in particle numbers at ambient temperature, but also the significant enhancement of the volatile fraction of the aerosols. Aerosol number, BIOFOR I (cm^{-3}).

dynamic mixing, leading to reduced surface area, and consequently the available condensation sink. Shortly after ultra-fine particles are observed, they are seen to grow to accumulation mode sizes over periods of up to 11 h. Volatility analysis of 'grown' accumulation mode particles indicates a significant enhancement in contribution from organic species with volatile properties similar to *cis*-pinoic acid and pinic acid. The organic contribution increases from less than 10% before the nucleation event up to more than 40% after these recently formed particles have reached accumulation mode sizes. Long-term perturbations of UV radiation flux could have an effect on biogenic volatile compound emissions and hence the concentrations and growth of new particles in the atmosphere.¹⁹

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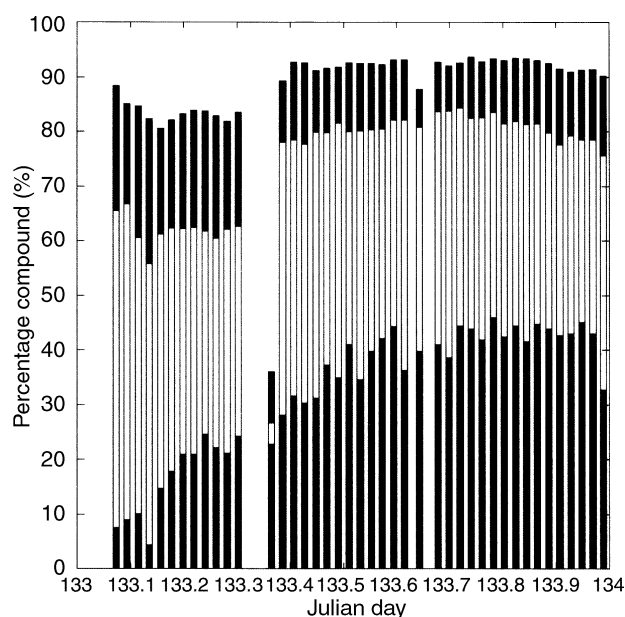


Fig. 8 Change of the chemical composition of the aerosols as determined by the analysis of the temperature response of the volatility system. Aerosol composition (%): bottom, organic; middle, NH_4SO_4 ; top, rest (soot). Size group, 0.05–0.6 μm .

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