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VOC measurements within a boreal forest during spring 2005: the role of monoterpenes and sulphuric acid in selected intense nucleation events

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Abstract

In this study we present measurements of selected trace gases and aerosol made in a boreal forest during the BACCI-QUEST IV intensive field campaign in Hyytiälä, Finland in April 2005. Several clear aerosol "nucleation events" were observed and characterized. One type of "event" occurred synchronously with huge increases in monoterpenes, while a second event type correlated instead with sulphuric acid. Here we elucidate the origin of these two distinct forms of aerosol production at the Hyytiälä site using the measurement data, airmass back trajectories and the optical stereoisomery of monoterpenes.

1 Introduction

Boreal coniferous forests ring much of the region immediately south of the Arctic Circle and are comparable in size (15 million km^2) to that of global rainforest (17 million km^2). They have been shown to profoundly influence regional atmospheric chemistry through the emission of reactive trace gases such as monoterpenes e.g. (Spanke et al., 2001; Bäck et al., 2005; Räisänen et al., 2009). During the atmospheric oxidation of monoterpenes, products with low vapour pressure can be produced, which can in turn condense to the aerosol phase. The role of these organics in new particle formation has been the subject of considerable research activity in recent years (e.g. Yu et al., 1999; Tunved et al., 2006; Bonn et al., 2008 and references therein), but is not fully understood. In terms of chemical composition, newly formed ultrafine atmospheric aerosols are poorly characterized and present information about organic species participating in secondary aerosol formation is far from sufficient (e.g. Shimmo et al., 2004; Hao et al., 2009). Nevertheless it has been established that the aerosol affects the radiative budget of the region (Kurten et al., 2003; Tunved et al., 2006) and the boreal forest in Finland has been reported to sustain 1000–2000 particles/cm^3 by gas to particle conversion in the climatically relevant size range 40–100 nm.

The process of atmospheric particle production through nucleation and subsequent coagulative growth has been shown to occur stochastically, in "bursts" e.g., in the free troposphere (Raes et al., 1997; Weber et al., 1999), in coastal zones (O'Dowd et al., 2002), in the continental boundary layer (Birmili et al., 2003), and in particular, over boreal forests e.g. (Mäkelä et al., 1997; Kulmala et al., 2001). These nucleation events occur on a large horizontal scale in the order of several hundreds of kilometres, and have been detected simultaneously at sites 2000 km apart (Nilsson et al., 2001). A limited number of field studies on newly formed particles (3–5 nm) e.g. (Kulmala et al., 2001) have concluded that the observed particles were primarily composed of high molecular weight oxidised organic species, such as cis-pinonic acid and pinic acid, produced by oxidation of monoterpenes (Zhang et al., 2004). However, sulphate/organic mixtures have also been implicated in such new particle formation (Marti et al., 1997). It remains an open question whether organics are only involved in the growth of stable sulphate clusters, or if they can also influence the cluster formation.

In this study we present measurements of trace gases and aerosol made in a boreal forest during the "Biosphere-Aerosol-Cloud-Climate Interactions-Quantification of Aerosol Nucleation in the European Boundary Layer" (BACCI/QUEST IV) intensive field campaign in Hyytiälä, Finland in April–May, 2005. The measurement period marked the transition from cold winter temperatures to more temperate spring temperatures. This is a particularly interesting period to examine and to compare with previous measurements, since most previous measurements have been taken in the summer e.g. (Hakola et al., 2003; Rinne et al., 2005; Haapanala et al., 2007). Several clear aerosol nucleation events were observed (Riipinen et al., 2007). Others occurred synchronously with rapid, and unexpectedly strong increases in monoterpenes, while others seemed to correlate more strongly with sulphuric acid. In this study, we examine the variations of VOC and particles during the spring campaign and identify two distinct types of aerosol production at the Hyytiälä site.

2 Site description

The data presented here were collected at the “Station for Measuring Forest Ecosystem-Atmosphere Relations” (SMEAR II) at Hyytiälä (61°51′ N, 24°17′ E), in Southern Finland (see Fig. 1). The site is 230 km north of Helsinki, 170 metres above sea level and surrounded by boreal forest (Vesala et al., 1998). The predominant tree species is Scots pine (*Pinus sylvestris*) with some spruce (*Picea abies*), aspen (*Populus* sp.) and birch (*Betula* sp.). Anthropogenic influences at the site are generally low, particularly when the wind comes from the sparsely populated northern sector. Incidental pollution from forest management activities is possible. However, the main road passing a few kilometres from the station to the southwest, and the cities of Tampere (pop. ∼205 000; 391 inh./km^2, 49 km to the south west) and Jyväskylä (pop. 84 000; 610 inh./km^2, 88 km to the north-east) can sometimes influence the site (see Fig. 1). Minor influences were expected from the few nearby settlements with low population densities (generally ∼<17 inh./km^2).

3 Experimental

At the SMEAR II station in Hyytiälä, a 74 metre high mast is used for long-term measurements of meteorological, physical, and chemical parameters as a function of height (4.2, 8.4, 16.8, 33.6, 50.4, and 67.2 m). These measurements include trace gases such as NO, NO_2, SO_2, CO, CO_2 and O_3; temperature, humidity, wind speed and direction and radiative measurements. A more detailed description of the site is given in Hari and Kulmala (2005). For the VOC measurements, a smaller mast was constructed circa 100 m from the aforementioned main SMEAR II measurement tower and circa 25 m from where the aerosol measurements were made. Gas phase sulphuric acid measurements were made from a cottage and all these measurements were conducted within an adjecent 100 m radius of the SMEAR II tower. Thus, for the interpretation of the observations all the three inlets are considered to be co-located.

VOCs were quantified using a Proton Transfer Reaction Mass Spectrometer (PTR-MS), a Thermo Desorption-Gas Chromatography Mass Spectrometer (TD-GC-MS) and a Methane and Total Non Methane Hydrocarbon (NMHC) analyser.

3.1 VOC-measurements

The VOC measurements were made at heights of 2.1, 4.6, 8.2 and 11.8 m above the forest floor. While the lowermost level was below the leaved branches, the 8.2 mm level was in the centre of the foliage and the uppermost inlet was located in the canopy crown. A single main pump was used to draw ambient air through six parallel PFA Teflon inlet lines. The length of each 6.35 mm i.d. inlets was 25 m to ensure identical residence times. Each inlet line was shrouded with black tubing to minimise any potential light induced artefacts within the lines. To prevent condensation, the lines were insulated. The flow per inlet line was restricted to a continuous 4.3 standard L min^{-1} resulting in inlet residence times of air of ∼11 s. Each of the VOC measurement techniques is described briefly in the following sections.

3.1.1 Proton Transfer Reaction Mass Spectrometer (PTR-MS)

The PTR-MS system has been described elsewhere (Eerdekens et al., 2008) and details of the technique summarized most recently in Blake et al. (2009). Measurements were performed at 2.1 mbar drift tube pressure isothermally controlled at 45°C. The PTRMS calibration factors have been corrected for humidity dependence. The time resolution for the PTR-MS was 50 s with dwell times of 1–2 s per mass. The total measurement error for α-pinene ranged from 40% (at 0.15 ppbv) to 4.3% (at 15.0 ppbv); for methanol from 50% (at 0.7 ppbv) to 14% (at 5.0 ppbv); acetone 14% (at 0.4 ppbv) to 5% (at 2.5 ppbv); acetonitrile 100% (at 0.05 ppbv) to 40% (at 0.14 ppbv), and for toluene from 50–10% for volume mixing ratios between 0.1–0.45 ppbv.

If noise at each channel is taken as the signal observed upon sampling zero air (sampling with a catalytic converter in-line), the detection limits for the unsmoothed data using a threshold of 3 signal-to-noise ratio were 60 pptv (α-pinene), 200 pptv (methanol), 42 pptv (acetone), 18 pptv (acetonitrile), and 24 pptv (toluene).

From 17 to 24 April, the PTR-MS sequentially monitored selected VOCs in 20 min intervals at all the above mentioned measuring heights, whereas the TD-GCMS and NMHC systems sampled from 8.2 m. From 24 to 29 April all 3 instruments sampled from the 8.2 m level.

3.1.2 Thermo Desorption-Gas Chromatography Mass Spectrometer (TD-GCMS/SPME)

On-line adsorption/thermal desorption was conducted using a gas chromatograph (GC 6890A) coupled to a Mass Selective Detector (MSD 5973 *inert*), both Agilent Technologies. The TD-GC-MS as used during this campaign is described elsewhere Williams et al. (2007). The MSD was operated in scan mode (20–250 amu) for the identification of compounds and in SIM mode for their quantification. Monoterpenes which differ from one another only in the way the atoms are oriented in space and consequentially are non-superimposable mirror-images of one another, better known as enantiomeric monoterpenes were separated from non-enantiomeric monoterpenes using a Cyclodex-B capillary column (30 m-long, 0.256 mm I.D., 0.25 μm film thickness) supplied by J & W Scientific (Folsom, CA, USA). The internal coating was composed of a permethylated β-cyclodextrin dissolved into a cyanopropyl-dimethyl polysiloxane liquid. The overall analysis time was 52 min with a precision error of 5–10% and accuracy against a monoterpene gas standard of 5% (Apel-Riemer Environmental, Inc., Denver, Colorado, USA). Retention time confirmation of individual chiral (being non-superposable on its mirror image) and non-chiral monoterpenes was performed by analyzing pure standards under the same conditions. The elution order of enantiomers was further confirmed by comparison with previous work Yassaa and Williams (2005) and from the literature. Subsequent experiments designed to study the enantiomeric composition of monoterpenes in the emission of natural and damaged Scots pine have been conducted with solid-phase microextraction (SPME) combined with dynamic branch enclosure cuvettes and enantioselective GC-MS (for details see Yassaa and Williams, 2007 and Bouvier-Brown et al., 2007) simultaneously with TD-GC-MS.

3.1.3 Methane and Total Non Methane Hydrocarbon Analyser (CH_4 and NMHC)

Methane and total non-methane hydrocarbons were measured using a commercial gas chromatograph flame ionization detector (Model 55C, Thermo Electron Corporation, Massachusetts, USA). Upon complete elution of methane in ~17 s, the GC column is back flushed by the carrier gas (N_2) and the non methane hydrocarbons are carried to the flame ionization detector (FID) for detection. The signal of the FID NMHC-channel is calibrated for propane and reported in propane equivalents, which can then be converted to parts per billion carbon (ppbC). The analysis time is 70 s while the accuracy and precision is ±2% of the measured value. The detection limit is 20 ppb for methane and 150 ppbC for the non-methane hydrocarbons. Methane measurements conducted with this instrument in the boreal and tropical forests have been described in Sinha et al. (2007)

3.2 Ancillary measurements

3.2.1 H_2SO_4 measurements

Gaseous sulphuric acid measurements were performed by MPIK Heidelberg (Fiedler et al., 2005) using a chemical ionization mass spectrometer (CIMS) instrument developed and built by MPIK, Heidelberg. Reagent ions of the type $NO_3^-(HNO_3)_n$ (n mostly 1) are produced in the ion source and subsequently introduced into the flow reactor. Instrumental details have been described elsewhere Hanke et al. (2002). H_2SO_4 molecules in the ambient air, are passed through the flow reactor, undergo ion-molecule reactions and the mass spectrometer measures the abundance ratio of product and reagent ions. The detection limit of H_2SO_4 was $2\times10^5\,cm^{-3}$ corresponding to an atmospheric mole fraction of 8 ppqv. The time resolution of the H_2SO_4 measurements is better than 10 s, but the H_2SO_4 concentrations presented here were integrated over 200 s to reduce statistical error. The absolute uncertainty is ±30% (Fiedler et al., 2005).

3.2.2 Aerosol measurements

Aerosols at Hyytiälä were measured by numerous instruments operated by the University of Helsinki. An aerodynamic particle sizer, (TSI3321) was used to count aerosol particles in the size range 0.7 μm to 20 μm while a Differential Mobility Particle Sizer (DMPS) instrument described by Aalto et al. (2001) measures the number of particles in the diameter range 3 nm to 850 nm. The total aerosol number concentration refers to the integrated $dN/d\log D_p$ over the DMPS-measurement range. The precision for the DMPS-measurements was calculated to be 4–10% on the total aerosol number concentration and include counting statistics, flow rate errors, detection efficiency errors, the differential mobility analyser dimension errors, and errors for temperature and pressure.

3.2.3 Other trace gas measurements

H_2O and CO_2 concentrations were measured at SMEAR II with an infrared light absorption analyser (URAS 4); O_3 concentration with ultraviolet light absorption analyser (TEI 49C) and CO with infra red absorption (Horiba APMA 360). The trace gases SO_2 and NO_x were measured by UV fluorescence (TEI 43C) and chemiluminescence (TEI 42CTL), respectively. The measurement frequency was 1 min for all analysers. Thus within 30 min each height is measured 5 times. For a detailed description see Kulmala et al. (2001) The measurement precision is expressed as standard deviation of the signal while sampling calibration gas and amount to ~0.05 g H_2O/m^3, ~0.1 ppm CO_2, ~0.5 ppb; O_3, ~0.05 ppb SO_2, ~0.05 ppb NO_x, and ~6 ppb of CO. The measurement accuracy amounts to 0.5 g/m^3 for H_2O, 5 ppm for CO_2, 1 ppb for O_3, 0.1 ppb for SO_2, 0.1 ppb for NO_x, and 10 ppb for CO. These values are based on the observed changes of the signal offsets between successive calibration checks. Relative humidity was calculated as the ratio between the measured H_2O concentration (converted to vapour pressure) and the saturation vapour pressure calculated from the measured air temperature with an accuracy of 2% (P. Keronen, personal communication, 2007).

4 General meteorology

Figure 2 shows the basic meteorological parameters measured at the SMEAR II main mast during the campaign, along with the particle number concentration (black solid line). During April the wind blew predominantly from the relatively unpopulated north (15–24 April and 29 April–2 May) and from the southeast (25–28 April). The temperature varied from +5 to +13°C by day to −5 to +5°C by night, while the humidity ranged from 25 to 100%. These conditions are typical of springtime in Finland. Lower temperatures were associated with periods of unvarying Arctic winds (higher wind speeds on all levels), whereas somewhat higher temperatures and pressures were reached during weak south-easterly winds. The precession of temperature and pressure indicate that a series of synoptic features have crossed the site in this period, only a few short-term precipitation events were observed during the campaign (19–22 April, occasionally snow, no rain). From Fig. 2, a gradual rise in temperature throughout the campaign can be ascertained, and a slow thawing of the ground and the ice covered lakes was observed in this time.

Balloon soundings of temperature and pressure made at the site between 23 and 30 April, mostly in the early morning and early evening, indicated clear nocturnal inversions. Although the development of the nocturnal boundary layer was not examined by the balloon soundings, the height of the nocturnal boundary layer was assumed to grow from ∼70 m at 20:00 to ∼160 m at ∼05:45 determined by the earliest winching.

5 Results

This study focuses on the variations of the VOCs and particles during the spring campaign in Hyytiälä. In the first section, the VOC mixing ratios and particle concentrations are characterised as a function of: time, meteorological parameters, diel cycle and height above ground. Subsequently in Sects. 5.4 and 5.5, two distinct particle burst events are selected and analysed using the VOC and gas phase H_2SO_4 measurements in order to determine the cause of each event.

5.1 General VOC variations

From Figs. 2 and 3 it can be seen that the mixing ratios of many VOCs (e.g. acetone, methanol, acetaldehyde and monoterpenes) were observed to be higher during the warmer period of this campaign (23–30 April) than during the colder period (18–23 April). During the latter period, VOCs have barely shown diel variation in their mixing ratios except monoterpenes and methanol. Monoterpenes were observed at mixing ratios between 0 and 16 ppbv with a campaign median of 0.16 ppbv. This median value is slightly lower than the observed nocturnal mixing ratios of 190 and 400 pptv of monoterpenes (25 p and 75 p) reported by Sellegri et al. (2005) at the same site in March 2003. The mixing ratios of acetone (median = 1.27 ppbv) and methanol (median = 1.62 ppbv) are in agreement with values reported from similar latitudes (Ruuskanen et al., 2009). However, while acetone values reported here (0.75–1.40 ppbv) are in good agreement with previous measurements from the same location for March 2003 (Sellegri et al., 2005), methanol values recorded in this study (0.60–2.10 ppbv) are markedly higher. However, they are comparable to those mixing ratios measured by Taipale et al. (2008) in April 2007. Table 1 summarises the mixing ratios measured during this campaign with other literature values reported for Hyytiälä.

Figure 4 shows the average 24 h cycle in the mixing ratios of monoterpenes, methanol, acetone and sulphuric acid during the warmer period. Although monoterpene emissions have been shown previously to be a function of the ambient temperature, with higher emission rates during the day (Janson, 1992; Janson and De Serves, 1999, 2001; Spanke et al., 2001), the monoterpene mixing ratios observed at Hyytiälä during spring were found to be higher at night. This is likely due to the formation of a shallow nocturnal inversion layer over the continuously emitting vegetation. Methanol, and to some extent acetone, shows a similar diel profile. Such a diel profile has not been observed previously during spring but has been reported during summertime by Ruuskanen et al. (2009). However, Taipale et al. (2008) reported occasional higher night-time mixing ratios for monoterpenes, though these increases were much weaker than observed during this campaign.

It can be seen from Fig. 3 that there were occasional extremely high nocturnal mixing ratios of monoterpenes measured at Hyytiälä. These short term peaks in the monoterpenes (Event 2) do not correlate well with the slowly changing temperature profile and will be studied in depth in the following section.

The warmer period was characterised by elevated particle background concentrations in comparison to the cold period. DMPS spectra (Fig. 6) show that the size of the particles during these periods generally varied between 20 and 110 nm, and did not occur in bursts as was the case in the nucleation events. The warmer period also exhibited comparatively more methanol relative to acetone than in the cold period. This could have been due to an influence of biomass burning, however, the absence of clear peaks and relatively low values of acetonitrile, a marker for biomass burning (Lobert et al., 1990; de Gouw et al., 2003) indicate that the regional influence from biomass burning is low at this time. Acetonitrile mixing ratios were maximum 130 pptv but generally low (25 p/median/75 p:46/59/71 pptv) and (25 p/median/75 p:25/34/44 pptv), respectively for the warm and the cold periods and thereby slightly lower than reported for March 2003. Ruuskanen et al. (2009) listed monthly mixing ratios below 130 pptv over the years 2006–2007. Levels of the anthropogenic tracers benzene and toluene are similarly low (medians 96 pptv and 69 pptv, respectively) but show occasionally short term increases. Benzene mixing ratios are generally low in this region during spring, summer and autumn but higher during wintertime (Taipale et al., 2008; Ruuskanen et al., 2009).

The results for acetone and acetaldehyde presented here are in good agreement with 24 h cartridge samples for March and April taken in 2003 (Hellén et al., 2004) which reported acetone mixing ratios between ~0.25 and ~0.85 ppbv with an average of ~0.5 ppbv and acetaldehyde between 0.09 and 0.28 ppbv with a mean of ~0.18 ppbv. Ruuskanen et al. (2009) shows that the boreal forest is only a weak emitter of isoprene in springtime, approximately 10 times less than levels typically measured over the rainforest (Zimmerman et al., 1988; Helmig et al., 1998).

Generally methane reached a daytime maximum sometime between 06:00 and 11:00, decreasing towards the onset of the nocturnal boundary layer. Daytime higher methane mixing ratios were generally observed when the wind blew from northwest to northeast.

Methane mixing ratios ranged between 1.79–1.88 ppmv during the campaign with clear trends in the diel profile. The daytime maximum occurred between 06:00 and 11:00 and higher methane mixing ratios were generally observed when the wind blew from northwest to northeast. There are no grounds to say that the forest soil was a source.

Shown in Fig. 3 is SO_2 whose predominant regional source is anthropogenic (e.g. fossil fuel burning). SO_2 mixing ratios were highly variable exhibiting both daytime and night-time maxima up to 2 ppbv or 4.2×10^{10} molec. SO_2/cm^3. This is in contrast to H_2SO_4 which showed a distinct diurnal cycle (see Fig. 4) with maxima up to 2×10^7 H_2SO_4 molec./cm^3 for the period between 17 April and 2 May.

From Fig. 2 we may compare the number of particles in the range of 3–850 nm detected by the DMPS at the site with the meteorological parameters. The aerosol concentrations decrease from circa 3000 cm^{-3} on 17 April to 350–500 cm^{-3} on 19 April. Low levels persist until the 23 April when concentrations rise and describe a broad peak lasting 5–6 days, centred on 27 April. Superimposed on these undulating background levels are several distinct events, defined as strong deviations from the underlying background (see also Fig. 6). In particular, there is a broad event on 30

April (hereafter termed Event 1) during which particle concentrations increased from circa 2000 to 6000 particles/cm^3 for approximately 6 h. Between the 25 and 28 April a series of short, intense particle bursts occurred. In such events (hereafter collectively termed Event 2), particle concentrations were observed to increase by an order of magnitude over the background (circa 30 000 cm^{-3} over 3000 cm^{-3}).

5.2 Vertical distribution of VOCs

Vertical profiles of the VOCs were obtained by sampling over the 4 sampling levels previously described, from the evening of 17 and before sunrise on 23 April. They are presented in Fig. 5 as 5–95% box and whisker plots for methanol, acetone, the sum of monoterpenes and acetonitrile with separate daytime (solid lines) and night-time (dashed lines) vertical profiles. The vertical gradients within the forest were not strong (<15%) for any of the VOCs although night-time gradients were usually slightly stronger than those seen by day. This is probably due to the stronger mixing occurring by day. Fallen needles may be the possible source of monoterpenes close to the ground. Nocturnal mixing ratios for methanol and monoterpenes were significantly higher than diurnal levels throughout the vertical profile. The vertical profiles for acetone, acetonitrile, benzene and toluene showed no significant difference between the diurnal and nocturnal mixing ratios.

5.3 Variation of VOCs and other trace gases in the particle events

Two distinct particle events were identified for examination in this study: Event 1 (daytime: 30 April) was a threefold increase in particles lasting several hours; Event 2 (night-time: 27–28 April) was a series of short duration, 10 fold increases in the monoterpene mixing ratios. In this section we examine the relationship between organic and inorganic compounds, and particles during these events.

Prior to the start of the VOC measurements, relatively strong nucleation events were observed almost every day in daylight between 28 March and 17 April, clearly discernible in DMPS spectra as the aerosol particle size distribution shifts from small (<3 nm) to larger aerosol particles (usually up to 100 nm). Some of these events have been discussed in detail by Riipinen et al. (2007). Occasionally, a nucleation event extended into the following day, resulting in a size distribution with two independent size modes. Between 19 and 25 April, there was a conspicuous absence of nucleation events and considerably fewer particles were counted over the measurement range of 3 nm to 850 nm. Back trajectories for this period indicate relative steady Artic winds crossing Finland.

In the upper panel of Fig. 6, the number of particles counted for a certain size interval is quantitatively colour marked for intensities between 1 and 10^5 particles per cm^3 for 1 week of measurements in which Event 1 and Event 2 took place. A clear increase in intensity ($dN/d\log D_p > 3000$ particles/cm^3) for particles between 20 nm and 300 nm is visible between 25 until noon of 29 April 2005. During this period acetonitrile mixing ratios were also observed to increase.

5.4 Event 1 (daytime)

The nucleation event “Event 1” took place on 30 April (between ~09:30 and ~18 h). Figure 6 shows the typical growth in the aerosol particle size following a nucleation event. The particle growth appears to stop abruptly after about 8 h coincident with the onset of the nocturnal boundary layer, shortly before sunset. The observed formation rate of 3 nm particles is 0.84 cm^{-1} s^{-1}, and growth rate 2.6 nm/h. These values are pretty typical in Hyytiälä (Kulmala et al., 2004; Dal Maso et al., 2005).

From Fig. 7a it can be seen that during Event 1 daytime temperatures were warmer at the surface than at the highest measurement level (74 m), and that the monoterpene mixing ratios were low (<0.2 ppbv). The mixing ratios of methanol, acetone and acetaldehyde were observed to increase only slightly (circa hundred pptv) and remained elevated until 17:00, whereupon the particle number concentration dropped sharply and a clear change in the ratio [methanol]/[acetone] was observed. The air monitored after 17:00 was richer in methanol. Likewise, the toluene to benzene ratio scattered between 0.1 and 0.8 as commonly observed during this day except between 12:00 and 13:00 when it exceeded 1 pointing at fresh anthropogenic pollution. Night-time air-masses are found to be richer in methanol compared to acetone and richer in toluene compared to benzene.

Methane mixing ratios decreased from 1.83 ppmv to 1.79 ppmv throughout Event 1 owing to the low chemical reactivity of methane, it is unlikely to have played a significant role in the nucleation process. However, for every peak in the particle concentration during Event 1, there is a peak in the methane mixing ratio as well.

At dawn on 30 April, there was a change in wind direction from NNE to NE and from around 09:35, the wind became easterly. The highest total particle concentrations were observed when the wind direction was approximately 75±17°, and the enhanced particle event was observed to end when the wind direction shifted slightly to circa 100±17° (taken from the 16.8 m level shown in Fig. 7b). The wind speed was variable by day (enhanced mixing) and more constant by night (suppressed mixing). At 74 m, wind speeds increased from 4–6 m/s around dawn to 10–11 m/s at half past ten in the morning. Nearer the ground the wind speed was lower consistent with a surface friction resistance. The wind speed decreased throughout Event 1. From noon, the wind speed decreased until at dusk the speed was similar to dawn.

Backward trajectories ending at Hyytiälä on 30 April indicate the airmass originated from the north, but turned northeasterly so that it crossed central Finland two days before arrival at the site. According to the NOAA Hysplit model, the airmass stayed close to the surface in the two days before arrival than on the days before.

Between dawn and 13:30, the relative humidity (RH) dropped from 84% down to 42% on all measurement levels of SMEARII with the strongest decline before 09:40. A strong correlation was noted between the observed humidity, the wind direction and the particle concentration during Event 1 (see Fig. 7b). The absolute humidity increased by 0.2 g/m^3 between 8 and 13 on all levels of SMEARII. After a short decline between 13:00 and 13:30, the absolute humidity was relatively constant until 15:00 whereafter it increased in parallel with the total particle concentration until ~17:00.

A study by Easter and Peters (1994) has shown that a high relative humidity favours homogenous binary nucleation of sulphuric acid and water (as in the beginning of Event 1 marked by the increase in smaller sized aerosol particles D_p<6 nm). In contrast, a study by Korhonen et al. (1999) found that ternary nucleation involving ammonia seemed to be independent of the relative humidity. Ammonia was not measured during Event 1. We note that its concentration was below 0.4 μg/m^3 between 17 and 25 April in absence of strong nucleation events and between 1 and 4 μg/m^3 during the week prior to VOC measurements during which several nucleation events occurred.

CO_2 is known to be removed from the atmosphere by vegetation during photosynthesis and a minimum in the daytime CO_2 mixing ratios was observed. CO_2 mixing ratios decreased from 404 ppmv at dawn to 394 ppmv at the end of Event 1, but was not considered to be related to its occurrence (Fig. 8a). Ozone mixing ratios (Fig. 8b) were similar to those observed on the previous day when no nucleation event occurred nevertheless suggested advection of polluted air. Carbon monoxide data did not show signs of diel variation on Friday 29 and Saturday 30 April but varied between 130 and 160 ppbv. CO mixing ratios were somewhat lower between 09:00 and 15:00. A typical commuter traffic related NO peak was observed between 04:30 and 09:30 with maximum mixing ratios of 0.15 ppbv between 07:00 and 08:00 (corresponding to slightly higher CO mixing ratios) and occurring under a declining total aerosol number concentration. No such clear peak in NO has been observed in the afternoon and evening suggesting a more temporally dispersed traffic.

Several peaks in NO_2 (up to 1.2 ppbv) have been observed during the night of 29 to 30 April, each lasting several hours and coinciding with increases in the particle concentration of 1200 cm^{-3}. The daytime NO_2 peak (up to 1 ppbv) was not as narrow as the night time peaks and closely resembled the aerosol particle concentration (Fig. 8c).

Radiative measurements (see Fig. 9a) indicated that Event 1 took place under mostly clear sky conditions until 11:10 with a few very brief disturbances reducing the direct sunlight around 09:40, the start of Event 1. Thereafter, the sky became overcast. Two compounds that can be connected with the occurrence of Event 1 are SO_2 and its photo-oxidation product H_2SO_4. The observed concentration of SO_2 (mixing ratios 0.2–0.4 ppbv) were 10 000–50 000 times higher than the concentration of H_2SO_4 during the night and 1000–10 000 times higher during daytime of 30 April. H_2SO_4 showed maximum concentrations of $\sim 4 \times 10^6$ molecules H_2SO_4/cm^3 before noon under clear sky conditions. For Event 1, the drop in the sulphuric acid concentration is synchronous with the cut off in the 3–6 nm aerosol particles. From all nucleation events arising during this campaign, we conclude that there is a certain condition upon which nucleation occurs and the strength of a nucleation event is not equivalent to the locally measured mixing ratio of H_2SO_4. This could possibly be explained by the competition between the growth of freshly formed particles and their loss by scavenging, rather than a limit in the initial particle production by nucleation of sulphuric acid (Riipinen et al., 2007).

As a first approximation and in absence of real-time wind fields, plain fetch calculations were done for Event 1 on the assumption that the monitored airmass had been transported towards the site from the measured wind direction and speed. Figure 9b shows that a tracer released three, six and nine hours back in time, could have had sources between, respectively 15 to 30 km, 30 to 90 km, and 60 to 130 km distant to the site. Airmasses coming from the East-North East were loaded with H_2SO_4 concentrations up to 4×10^6 molecules per cm^3. Possible sources of SO_2 and/or H_2SO_4 are indicated in Fig. 9c. These include a city of Jyväskylä at ca. 60° NE and approximately 88 km away from Hyytiälä.

In summary we note that Event 1 occurred by day in the absence of a temperature inversion. The event was strongly correlated to changes in wind direction and humidity and to a lesser extent on wind speed. Event 1 is characterised by a correlation with sulphuric acid, which in turn depends on the solar radiation and SO_2 levels. No correlation with monoterpenes or other VOCs was found. Event 1 took place under relatively elevated levels of ozone and slightly elevated NO_x, under slightly increased CO, and under naturally declining CO_2. The nucleation event is characterised by a shift in particle size distribution from smaller to larger-sized aerosol particles.

5.5 Event 2 (night-time)

Event 2 refers to the series of strong particle bursts which occurred during the night of 27 to 28 April 2005 under unusual meteorological conditions. Similar bursts to those observed in Event 2 occurred during the nights prior to Event 2 but could not be investigated in detail as the meteorological and trace gas dataset was incomplete.

The stratification of the nocturnal surface layer under investigation was apparent in the ambient temperature, humidity, wind speed and wind direction measured at SMEARII. Even though ambient temperatures remained positive, they dropped by 9°C at 4.2 m and by 5°C at 67.2 m (Fig. 10a) over the course of the night. The first particle peak of Event 2 occurred when the inversion was formed and strengthening. Before 00:45, there were short gusts of somewhat warmer air interrupting the cooling of the air within the canopy. These gusts occurred in between the particle bursts. Otherwise, the wind blew relatively steadily from the South-East at 16.8 m, which is above the tree tops. The angular deviation of the wind with height became more apparent after midnight with deviations of 15–30° between the different levels.

The RH generally increased from dusk (19:00) to dawn (04:30) on all levels with a stronger increase after midnight. The RH increased from 44 to 53% before midnight and increased further to 68% at 04:30 at 4.2 m above the forest floor, whereas at 67.2 m RH was around 39% before midnight and increased only to 50% just before sunrise.

The remarkably intense bursts of aerosol particles were strongly correlated with exceptionally high concentrations of monoterpenes (Fig. 10a). These peaks were observed only a few hours after the onset of the nocturnal boundary layer (~0.2 ppbv). Monoterpene mixing ratios increased to ~7.1 ppbv, ~10 ppbv and 15.9 ppbv and corresponded to 18 000, 32 000 and 25 000 particles/cm^3, respectively (see peaks labelled P, Q and R in Fig. 10).

In contrast to Event 1, during which the particles grew from small to big particles, both small and large particles were present right from the beginning of the first peak of

Event 2. As for the subsequent peaks, they transported mainly larger particles with a reduced number of smaller particles to the site.

Each peak was marked by exceptional increases in CO_2 and NO_x and drops in O_3 on all measurement levels (see below for further details). This was also observed for the subsequent peaks (collectively labelled by S) which were much lower in particle concentration (<10 000 particle/cm^3) and in monoterpenes (<1.5 ppbv) around 01:00, 03:00 and 04:00 o'clock. Striking are the occurrences of peaks (P, Q and R) under declining SO_2 mixing ratios before midnight. This is in contrast to substantial increases in in SO_2 mixing ratios on all measurement levels afterwards (from ~0.3 ppbv up to 1.8 ppbv at canopy level). The most substantial increase in SO_2 after midnight was observed above 30 m.

Strong increases in compounds like benzene, toluene, C_2- and C_3-benzenes during the first part of the night points to fossil fuel combustion processes. The ratio [toluene]/[benzene] went up to 5, but was on average 2 between 19:30 and 01:00. A maximum ratio of 1 but on average 0.5 was calculated for the rest of the night. Although toluene declined at daybreak, benzene increased until 09:00, similar to SO_2.

This data indicates that Event 2 can be related to a nearby source (or sources) which was a strong emitter of monoterpenes and several other organic compounds. Strong increases were observed in methanol, acetone and acetaldehyde which are known to be released during biomass burning, although this source type can be eliminated as there was no substantial increase in acetonitrile during Event 2.

The methane mixing ratios increased with the onset of the nocturnal boundary layer (18:00) from 1.78 ppmv to 1.81 ppmv. While this increase in methane matched Peak P (see Fig. 10a), there was no correlation with any of the subsequent peaks, the particle concentrations or any of the VOCs.

Interestingly, during Event 2 increased signals have also been observed on *m/z* 69 and *m/z* 71 which have previously been attributed to isoprene and its primary oxidation products MACR+MVK. In some previous studies, isoprene was shown to be correlated with benzene during winter indicating a traffic source (Reimann et al., 2000; Borbon et al., 2001). This was not observed in this data set. However, a strong correlation between toluene and *m/z* 69 was found during Event 2. As these peaks occurred during the night, they are very unlikely to be natural isoprene emission which is driven by light.

Event 2 was marked by peaks in the CO_2 mixing ratios extending beyond the natural fluctuation. Similar peaks have also been observed on several occasions during this campaign together with peaks in monoterpenes, particles and NO_2 and drops in O_3. Between dusk and dawn, there was a clear vertical gradient in ozone with mixing ratios within the forest consistent with a surface or chemical loss. The gradient in ozone during Event 2 was as strong as 5–12 ppbv, much stronger than the gradient of less than 2 ppbv seen on nights without particle concentration increases.

The highest peak in NO_2 was observed coincident with burst "S", with NO_2 mixing ratios up to 7.5 ppbv within the canopy and occasionally spiking up to 14 ppbv of NO_x at the 33.6 m (offscale in Fig. 11c). Remarkably, only the first peak around 20:00 was accompanied by a very strong increase in the CO mixing ratios from 140 to 200 ppbv on all measurement levels. Half an hour later, CO mixing ratios returned on all levels to values between 140 and 160 ppbv until 01:00. After that, CO mixing ratios increased only gradually to reach values between 160–180 ppbv along with SO_2.

4-Day backward trajectories indicate that for Event 2, the air came from Central and Southern Finland between 26 and 28 April and show that the airmass has remained close to the surface (>500 m) for several days. The lifetime of e.g. α-pinene with respect to ozone under the conditions of Event 2 was 16 to 22 min. A fetch plain has been calculated for Event 2 using a steady southeasterly wind to locate the source area. These empirical calculations, purely based on the measured wind speed and direction as measured at 16.8 m, suggest that air parcels released one, two and three hours back in time would have covered a distance of approximately 1 to 10 km, 6 to 16 km, and 10 to 25 km (see Fig. 12b). This footprint area is much smaller than prevalent for Event 1. At slightly more than 6 km distance and 131 degrees South-East of the SMEAR II station, the Korkeakoski sawmill is located in the town Juupajoki (the yellow square in Fig. 12b represents the location of the Korkeakoski sawmill relative to the SMEAR II observatory at the origin). This sawmill has an annual production capacity of 330 000 cubic metres of softwood products, notably for the joinery industry and in this respect a very plausible source of the massive monoterpene emissions plus other pollutants.

In summary, Event 2 is characterised by a very clear correlation with monoterpenes and no correlation with SO_2 or sulphuric acid. The aerosol bursts in Event 2 were observed at night under the influence of a temperature inversion, at low wind speeds and with clear wind direction dependence, the optimum being at ~130°. Particle bursts correlate with CO_2 emissions beyond those of the normal forest respiration. Intense peaks in NO_2 and a concomitant drop in the ozone mixing ratios were observed for all peaks, whereas strong emissions of CO were found only for the first burst. Event 2 correlates with many volatile organics, mostly unknown but predominantly monoterpenes. Event 2 exhibited a different aerosol size distribution compared to Event 1 with generally larger aerosol particles present.

6 Discussion and conclusions

Rural background mixing ratios for the boreal forest have been determined for several VOCs during the transitional period between winter and spring when airmasses come from the North crossing Finland. Most of the analysed non methane hydrocarbons in this generally clean air did not show distinct diel profiles. Of the VOCs measured methanol, acetone and acetaldehyde were the most abundant daytime organic species present. The biogenic VOCs observed during this study predominantly result from coniferous trees as the deciduous trees were still leafless at this time of the year.

Elevated levels of anthropogenic pollutants were observed typically in the morning and the evening, presumably by commuter traffic or on occasions when airmasses had passed over urbanized areas, marked by e.g. peaks in NO_2 and SO_2.

In this study, a daytime and a night-time aerosol event exhibiting high particle concentrations, were analysed using the available meteorological, organic and inorganic trace gases measurements. Figure 4 shows that Event 1 (daytime; 30 April) was characterised by a fivefold increase in the total aerosol number concentration ($dN/d\log D_p$) lasting several hours and Event 2 (night-time, 27–28 April) was of short duration with 11 fold increase in $dN/d\log D_p$.

Event 1 is characterised by a correlation with sulphuric acid. No evidence was found that monoterpenes or other volatile organic compounds measured during campaign were involved in the growth of particles during nucleation Event 1. Rough fetch calculations suggest that the SO_2 emissions from Jyväskylä and its surroundings were the likely source of this event. H_2SO_4 plays an important role in atmospheric new particle formation which is generally thought to occur due to homogeneous or ion-induced nucleation of sulphuric acid (Kulmala, 2003; Lovejoy et al., 2004). Recently, Laaksonen et al. (2008) and Berndt et al. (2008) suggested a new particle formation mechanism in which the free HSO_5 radicals are formed prior to the H_2SO_4 formation. They suggest that at temperatures above 250 K these radicals produce nuclei of new aerosols much more efficiently than H_2SO_4 as well as that the HSO_5 radicals will react with other trace species, and that the resulting molecules act as nuclei for heterogeneous nucleation of H_2SO_4 vapour which will initiate the growth of the new particles. Recently Kulmala et al. (2006) suggested that activation of existing clusters might be the actual atmospheric nucleation mechanism. The existence of those clusters have later been shown (Kulmala et al., 2007). On the other hand, a study by Väkeva et al. (2000) indicated that somewhat larger deviations in the wind direction may interrupt the conditions favourable for the growth of particles which might have been also the case for Event 1. However, the growth of the particles may have been interrupted, in following of the abovementioned new particle formation mechanism, by a reduced number of HSO_5 radicals formed after the sudden overcast, with a clear relapse in the concentration of H_2SO_4.

In contrast, particle Event 2 is characterised by a very clear correlation with monoterpenes and no correlation with SO_2 or sulphuric acid. During Event 2, sulphuric acid concentrations were found to be relatively low and SO_2 mixing ratios declined during the intensive night-time bursts in aerosol particles before midnight. The source was characterised as releasing more toluene relative to benzene; more methanol relative to acetone; and above all, releasing massive amounts of aerosol particles, monoterpenes and NO_2. Here we suggest the wood industry and more specifically the Korkeakoski sawmill as the likely source. Monoterpenes and possibly toluene may have come directly from the cut wood whereas the NO_x from the generators/cutting tools used.

Additional support for this source identification was obtained from the detailed analyses of the monoterpenes by TD-GC-MS which includes an enantiomeric separation. It was shown that (+)-α-pinene, (+)-δ-3-carene, (−)-α-pinene and (−)-β-pinene were the most abundant monoteprenes above the boreal forest. This monoterpene composition resembles to that found in the emission of *P. sylvestris* with low (+)-δ-3-carene chemotype in the branch enclosure cuvette study (Yassaa and Williams, 2007). Daytime enantiomeric ratios of [(+)-α-pinene]/[(−)-α-pinene] varied between 1.6 and 2 during this campaign, generally increasing from the break-up to the onset of the nocturnal boundary layer. This enantiomeric ratio was significantly higher than 2 during nocturnal monoterpene peaks. Such peaks on 26 and 27 April were believed to be of similar kind as monitored by the PTR-MS during Event 2, with much higher α-pinene enantiomeric ratios of 3–5. Subsequent study of the enantiomeric composition of monoterpenes from intact and damaged or wounded Scots pine has been conducted with solid-phase microextraction (SPME) combined with dynamic branch enclosure cuvettes and enantioselective GC-MS. The detached needles from *P. sylvestris*, the dominant forest species, exhibited different enantiomeric emission patterns for the most important chiral monoterpene α-pinene. Damaging the plants seems to induce modifications not only to the emission rate of monoterpenes but also on their enantiomeric compositions. In the wounded plant materials, while the emission rates of monoterpenes increase by several order of magnitude, the [(+)-α-pinene/(−)-α-pinene] enantiomeric ratios pass from ∼2 for intact plants to ∼6 for damaged trees, similarly to what was observed in the Event 2. Therefore, the substantial increase in the mixing ratios of monoterpenes together with the [(+)-α-pinene/(−)-α-pinene] enantiomeric ratios observed during the Event 2 strongly supports the hypothesis that the wood industry is the very likely source of monoterpenes during the Event 2.

A study by Schade and Goldstein (2003) has mentioned 10-fold increases of monoterpene emissions from a pine plantation as a result of mechanical disturbances. During the period of measurements we noted some deforestation activities nearby although we did not notice any burning during the campaign. Thinning is a routine forest management operation that changes tree spacing, number, and size distribution which can affect the emission of VOC from vegetation to the atmosphere. A study by Vesala et al. (2005) has shown some effects of thinning on physical processes like wind speed normalized by the friction velocity, light penetration, and particle deposition. Some of these forest management activities undoubtedly can have implications for regional air quality management, likely both in terms of ozone chemistry and secondary aerosol formation (Goldstein et al., 2004). However, in this case the strong dependence on the wind direction strongly suggests that the sawmill was the source of these bursts.

It is well established that secondary aerosol particles can be formed during monoterpenes oxidation, but is this process sufficient enough to deliver more than 20 000 particles/cm^3 in half an hour under atmospheric conditions? Event 2 bears some resemblance to laboratory studies (Bonn and Moortgat, 2002) focussing on the ozonolysis of monoterpenes and the resultant particle nucleation, coagulation and condensation processes. Bonn and Moortgat (2002) reported that due to the low rate constant of the reaction of α- and β-pinene with ozone (α: 8.66×10^{-17} and β: 1.5×10^{-17} cm^3 molecule^{-1} s^{-1}) the reaction proceeds relatively slowly. They performed ozonolysis experiments on α- and β-pinene under laboratory conditions, meaning 500 ppbv of pinene and 500 ppbv of ozone. As they followed the reaction, various products of different volatility non-, semi- and volatiles were observed. The non-volatile products reached their saturation vapour pressure and started to nucleate homogeneously. This was observed during the ozonolysis reaction in an intense nucleation during the first four minutes of the experiment. At this stage of the reaction, the more volatile products (semi-volatile) were able to condense on the surface of the pre-formed particles and cause an increase in particle size and aerosol volume. This behaviour was observed in a broadening and a shift of the particle size distribution to larger diameters (centred around 60 nm in diameter at 50 min reaction time) due to both the coagulation as well as the condensation. The authors measured a $dN/d\log D_p$ of 10^6 particles/cm^3 distributed around 20 nm after 4 min, and 7.10^5 particles/cm^3 distributed around 60 nm after 12 min. Interestingly, we have found aerosol particles of similar sizes during Event 2 as reported in this laboratory experiment. Even though the aerosol particle size distribution matched well with those obtained from the laboratory experiments under controlled conditions, Event 2 is characterised by interludes of airmasses which bear the characteristics of the undisturbed nocturnal situation.

Recently Junninen et al. (2008) investigated night-time particle production events. Typically strong night particle production in Aitken and accumulation modes was connected to local pollution.

More than 50 sawmills similar to the Korkeakoski sawmill are spread over entire Finland besides plywood, paper- and fibreboard mills (FFIF, 2006). Wood waste is a potential source of methane and non-methane hydrocarbon production due to its high degradable organic carbon content and an on-site storage that is conducive to development of anaerobic conditions.

We may conclude from this study that the Sawmill industry can substantially influence air chemistry and the formation of secondary aerosol particle over the boreal forest, especially under stable meteorologically conditions.

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Table 1. Summary of VOC mixing ratios for April 2005 compared to other spring time measurements of VOCs observed at Hyytiälä, Finland.

	(ppbv)	This study colder period	This study warmer period	Sellegri et al. (2005)	Hellén et al. (2004)	Ruuskanen et al. (2009)
m*/*z	**Compounds**	**25 p–75 p**	**25 p–75 p**	**25 p–75 p**	**mean**	**5 p–95 p**
33	Methanol	0.64–1.00	1.23–2.01	0.75–1.1		0.31–1.74
42	Acetonitrile	0.03–0.05	0.05–0.07	0.05–0.10		0.02–0.06
45	Acetaldehyde	0.14–0.21	0.21–0.32	0.09–0.04	0.18	0.21–0.39
59	Acetone	0.74–0.96	1.21–1.40	0.23–0.42	0.52	0.40–1.31
69	Isoprene	0.04–0.08	0.05–0.10			0.02–0.10
71	MACR+MVK	0.01–0.03	0.02–0.04			0.03–0.13
79	Benzene	0.08–0.12	0.08–0.13			0.06–0.11
93	Toluene	0.01–0.04	0.03–0.07			
137	Monoterpenes	0.06–0.18	0.17–0.64	0.32–0.84		0.03–0.20

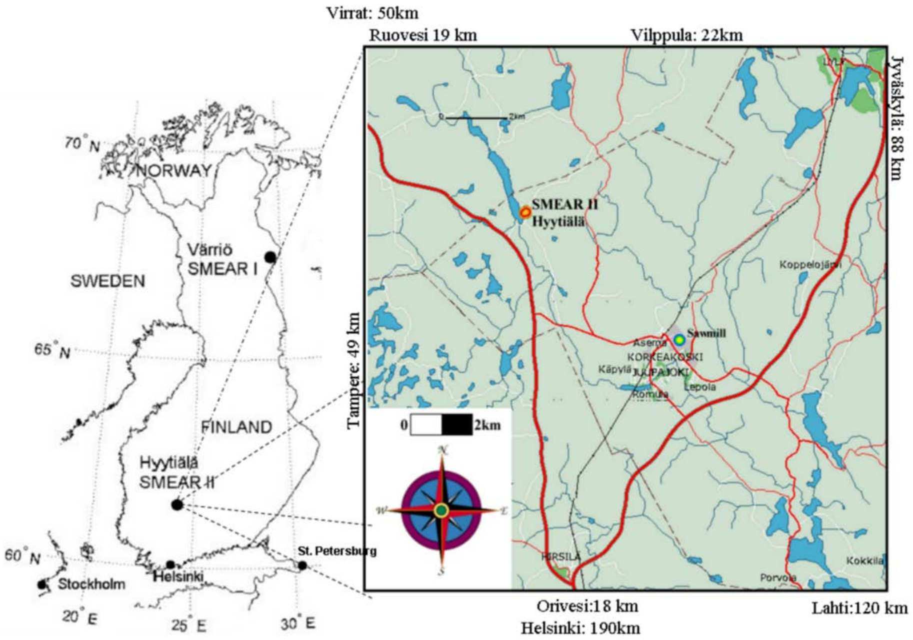

Fig. 1. Location of Hyytiälä on the map with its surrounding settlements and cities.

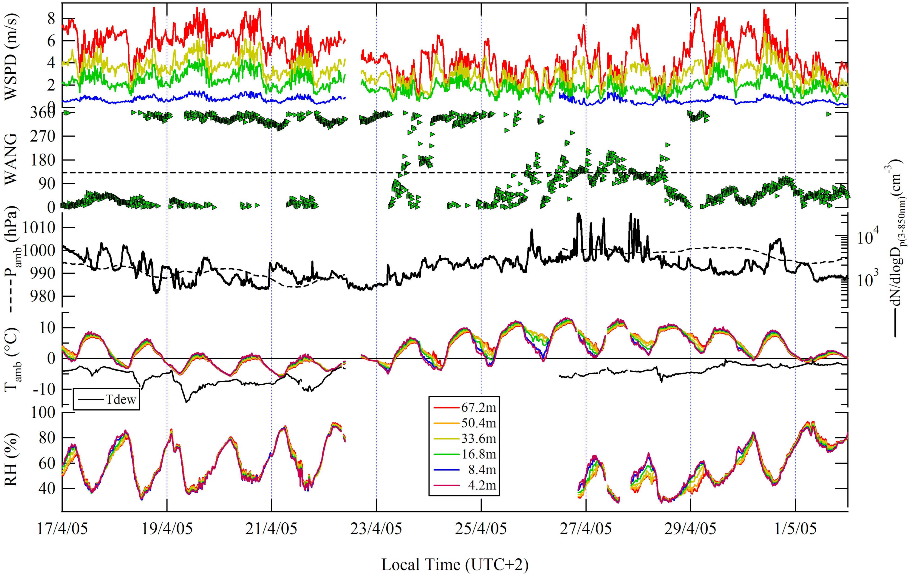

Fig. 2. Time series of basic meteorological parameters (left vertical axis) and aerosol total number concentration over the measurement range of the DMPS-analyser on the (right vertical axis) and aerosol total number concentration over the measurement range of the DMPS-analyser on the (right vertical axis) from the SMEAR II main mast (74 m).

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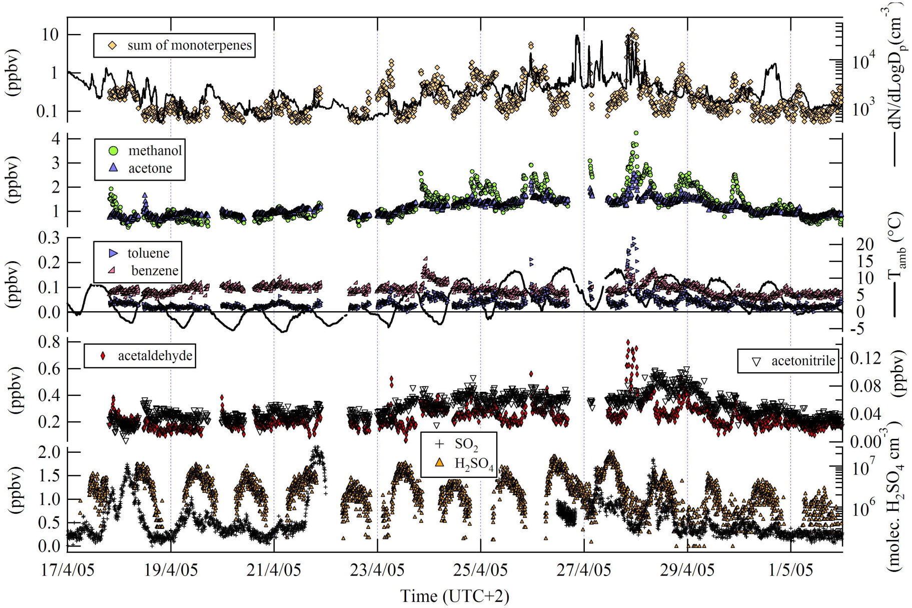

Fig. 3. 10 minutely averages of inorganic and organic trace gases, total aerosol particle concentration (3–850 nm) measured for the springtime BACCI/QUEST IV campaign at Hyytiälä.

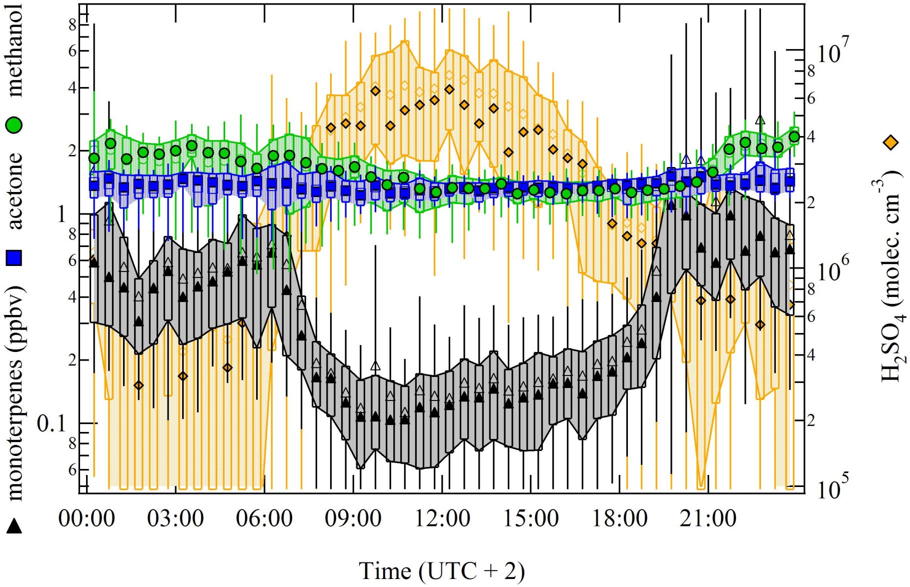

Fig. 4. Diurnal profiles of methanol, acetone, monoterpenes and sulphuric acid for the period between 23 and 30 April 2005.

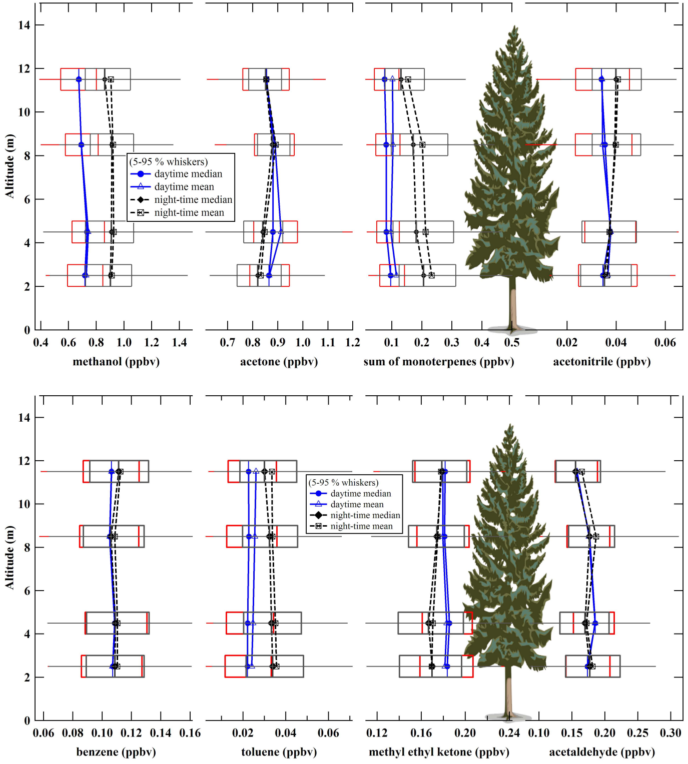

Fig. 5. Vertical profiles within the canopy for VOCs for the clean airmasses without elevated aerosol particle concentrations (17–23 April 2005).

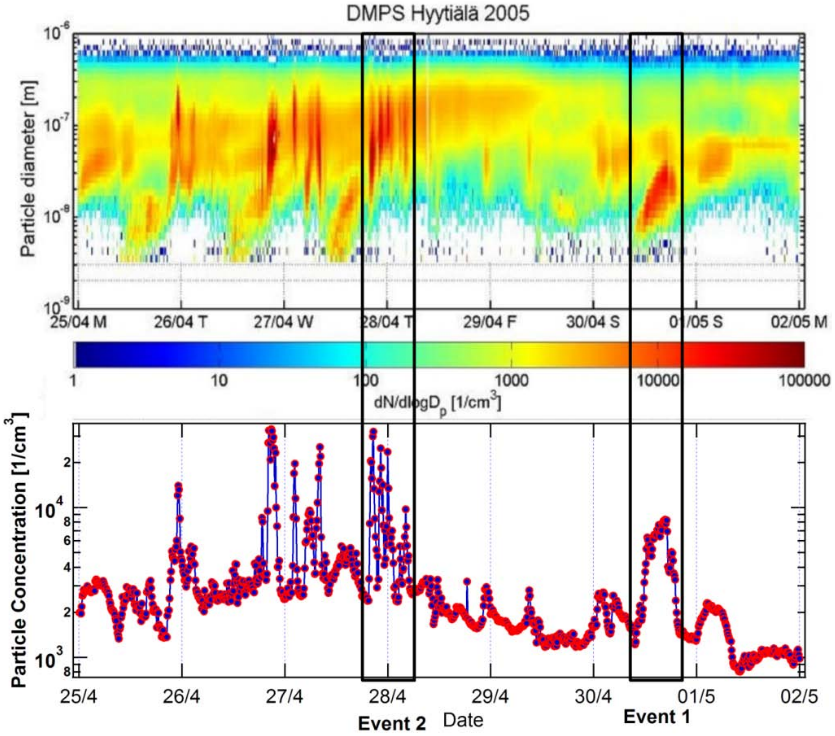

Fig. 6. Differential mobility size spectra between 3 nm and 850 nm for one week during which Event 1 and 2 occurred. Event 1 is a broad event on 30 April; Event 2 is a series of shorter, more intense particle bursts during the night of 27 to 28 April.

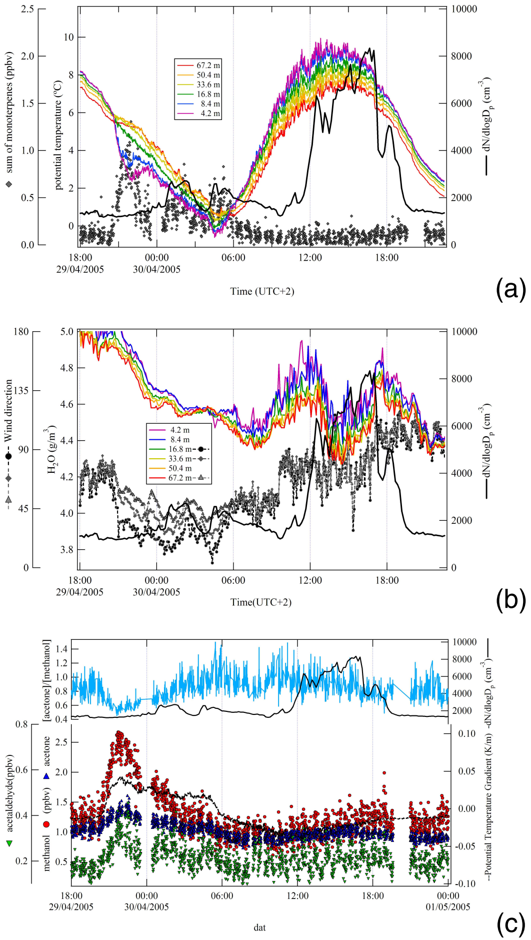

Fig. 7. Total aerosol number concentration (black solid lines) in relation to **(a)** the potential temperature **(b)** wind direction and humidity measured at SMEAR II and **(c)** OVOCs for Event 1.

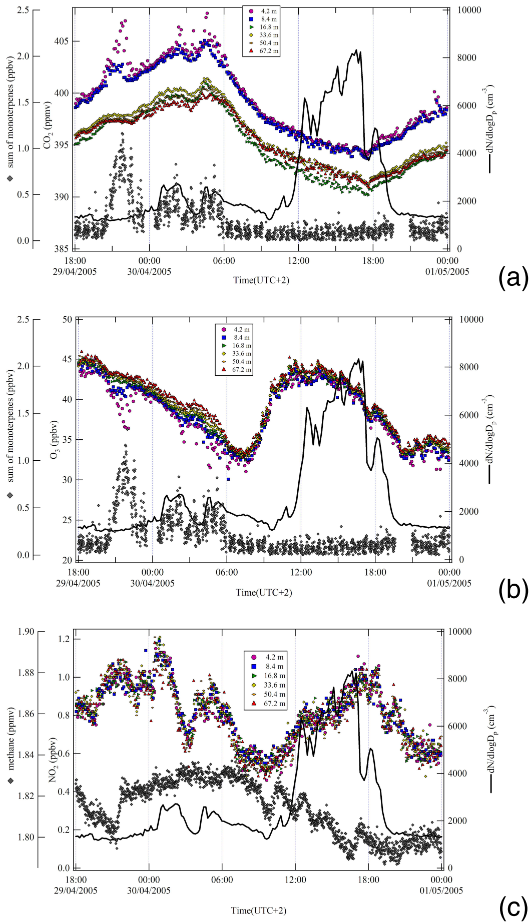

Fig. 8. (a) CO$_2$, **(b)** O$_3$ in relation to monoterpenes and aerosol particle concentration, **(c)** NO$_2$ and CH$_4$ mixing ratios for Event 1 and the foregoing night.

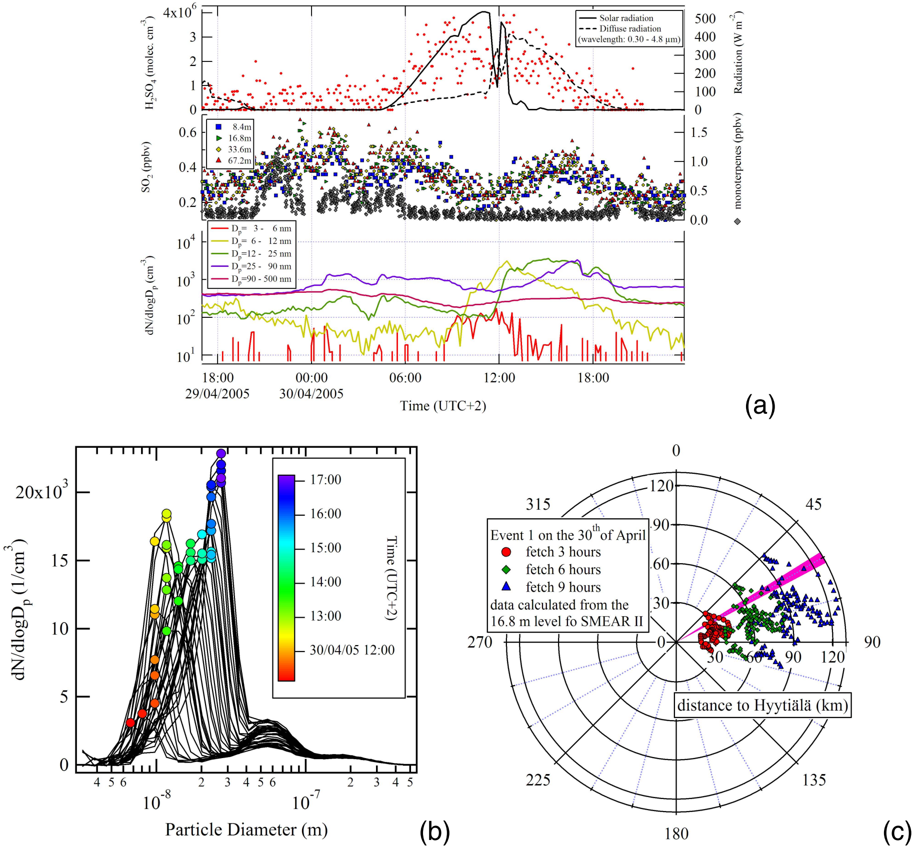

Fig. 9. **(a)** H_2SO_4, SO_2 and the sum of monoterpenes as function of time for Event 1. **(b)** shift in the particle size distribution **(c)** Three-, six- and nine-hour plain fetch calculated for 30 April in kilometres to the site. Highlighted wind direction corresponds to the relative position of the big city Jyyväskylä, approximately 88 km away from Hyytiälä.

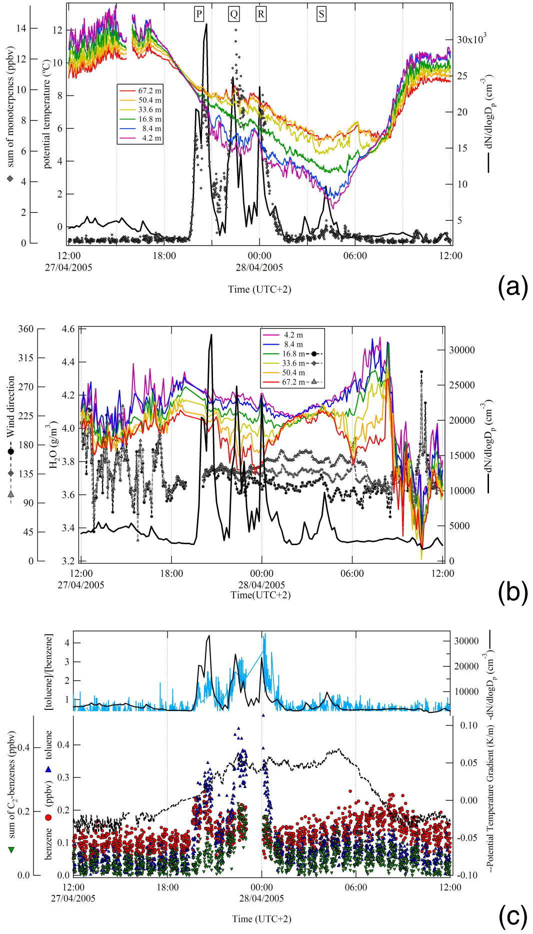

Fig. 10. Total aerosol number concentration (black solid lines) in relation to the potential temperature and monoterpenes **(a)** wind direction and humidity **(b)**, measured at SMEAR II and **(c)** the ratio of toluene to benzene for Event 2.

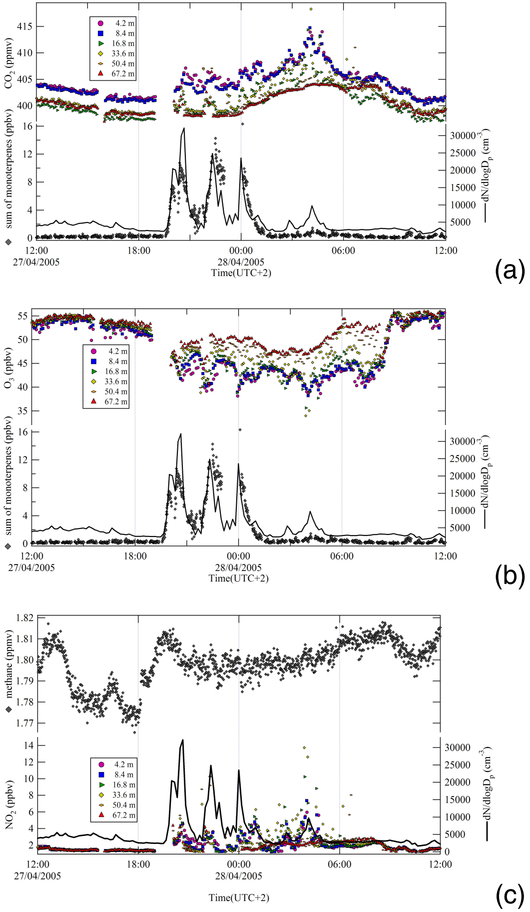

Fig. 11. **(a)** CO_2, **(b)** O_3 and **(c)** CH_4 and NO_2 mixing ratios for Event 2.

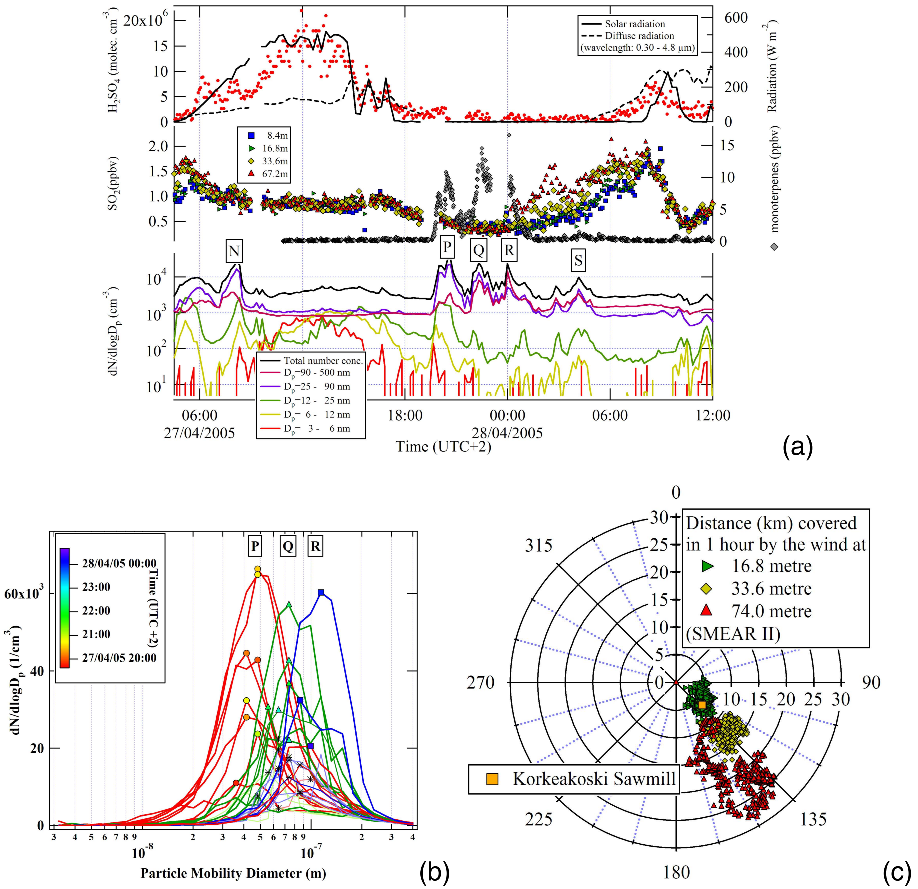

Fig. 12. **(a)** H_2SO_4, SO_2 and the sum of monoterpenes as function of time for Event 2. **(b)** shift in the particle size distribution for the different peaks P, Q and R. **(c)** Fetch calculated for a tracer with an atmospheric lifetime of 1 h arriving at the SMEAR II at different heights during Event 2.

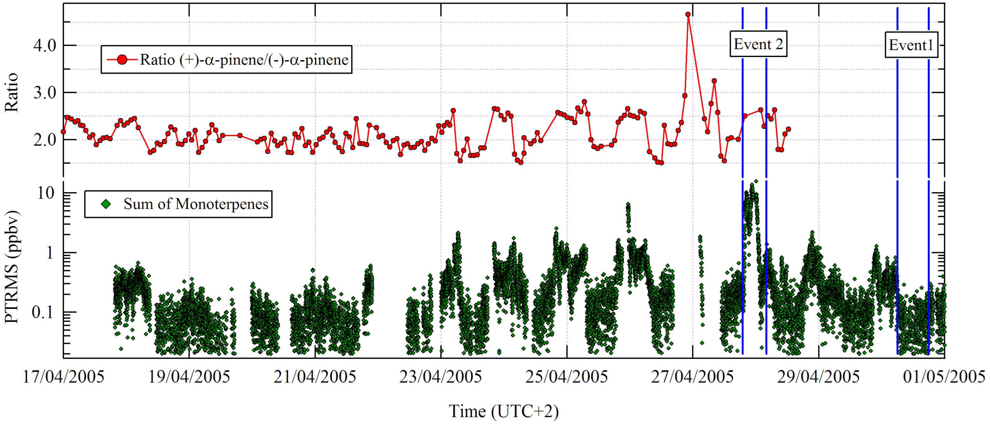

Fig. 13. Enantiomeric ratio of (+)-α-pinene to (−)-α-pinene as function of time in connection to the sum of all monoterpenes for the entire period of investigation.