

Biogenic emissions and gaseous precursors to forest aerosols

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(Manuscript received 5 May 2000; in final form 9 March 2001)

ABSTRACT

Measurements of ambient monoterpenes, sulphur dioxide, nitric acid, ammonia and particulate organic carbon were made in a Scots pine forest in southern Finland as part of the BIOFOR (Biogenic aerosol formation in the boreal forest) project in the summer of 1998 and spring of 1999. Scots pine branch emission measurements were made with the chamber technique for selected days. Steady state $\cdot\text{OH}$ and NO_3 concentrations were calculated and source terms for the production of secondary and condensable gases from the oxidation of terpenes and of SO_2 were determined. The purpose of the project was to investigate the source of new particles (nucleation events) observed at the site. Forest emission rates of monoterpenes were not found to be exceptionally high prior to or during the occurrence of events. Neither the relative composition of the monoterpene emission nor that of the forest concentrations showed significant deviations prior to or during event periods. Source terms for secondary organic compounds were only slightly higher (weakly significant) on event days as compared to non-event days and did not correlate to maxima in ultra-fine particle concentrations on event days. Nucleation events were not observed during nighttime when the production of secondary organic compounds, and probably of secondary organic aerosol was greatest. Thus, we conclude that the oxidation products of the terpenes were not the nucleating species observed at Hyytiälä. Correlations between nocturnal increases in particulate organic carbon and the source term for secondary organic compounds indicate that the increase could have been due to condensation processes if the aerosol yield was at least 10–15%. Sulphur dioxide and NH_3 concentrations, as well as the H_2SO_4 source term were significantly higher during event periods, and the H_2SO_4 source term together with the NH_3 concentration correlated well with the daily maxima in ultra-fine particle number concentrations. The results indicate that SO_2 and NH_3 were involved in the mechanism for nucleation events at Hyytiälä. The H_2SO_4 source term was not high enough to account for the entirety of the observed growth rate of the new particles. A substantial part of the growth ought to have been due to condensation of secondary organic material from the oxidation of terpenes. The data indicate that a secondary organic aerosol yield on the order of 10% would suffice.

1. Introduction

It has for many years been the generally accepted viewpoint that the oxidation of atmospheric monoterpenes leads in part to condensable products which by gas-to-particle conversion con-

tribute to the atmospheric aerosol. The first suggestion was made by Went (1960), and since then numerous laboratory studies have demonstrated aerosol formation from the oxidation of terpenes (Hooker et al., 1985; Hatakeyama et al., 1989, 1991; Pandis, et al., 1991; Grosjean et al., 1992; Odum et al., 1996; Hoffmann et al., 1997; Hoffmann et al., 1998; Christoffersen et al., 1998; Jang and Kamens, 1999; Nozière et al., 1999). A

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few studies have successfully identified terpene oxidation products in ambient air and/or aerosol samples (Cronn et al., 1977; Yokouchi and Ambe, 1985; Kavouras et al., 1998; Kavouras et al., 1999; Spanke et al., 2001).

The gas-to-particle conversion of condensable gases may occur in two ways: (1) by nucleation and creation of new particles or (2) by condensation onto existing particles. The nucleating potential is a function of the saturation vapor pressure of the products, their actual concentrations, temperature, and the surface area of the ambient aerosol. At "high" surface areas, condensation is expected to remove condensable gases faster than they can nucleate and in all cases, surface area competes with nucleation for the condensable gases (Clarke et al., 1999; Covert et al., 1996). Pankow (1994a) and Pankow (1994b) have suggested that condensation of organic material can occur even at concentrations below saturation concentrations, by absorption into existing aerosolic organic material. Odum et al., 1996 and Hoffmann et al. (1997) have subsequently demonstrated in laboratory studies, that yields of secondary organic aerosol (SOA) from the oxidation of organics are dependent on the organic mass concentration. Thus, the SOA yield from a given reaction does not have a unique value but is a function of temperature, the vapor pressure expressions for the individual products, and the pre-existing organic aerosol mass.

While many of the rate constants for the reaction of the terpenes with atmospheric oxidants are known, there still exist contradictory and incomplete knowledge of the yields of individual products and their vapor pressures. To date, it would seem that monoterpene reactions with O_3 and the NO_3 radical, leading to mono- and dicarboxylic acids and organic nitrates, respectively, are the most likely source of nucleating species (Christoffersen et al., 1998; Hoffmann et al., 1998; Jang and Kamens, 1999). Reactions with the $\cdot OH$ radical produce primarily keto-aldehydes (for example pinonaldehyde from α -pinene) and ketones (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Hoffmann et al., 1997; Calogirou et al., 1999) which may be absorbed by existing organic matter, but should not be important in nucleation processes (Nozière et al., 1999). Hoffmann et al. (1997) and Griffin et al. (1999) report strong SOA yields from the NO_3 reactions

with β -pinene and Δ^3 -carene in their smog chamber experiments. However, as the SOA is tentatively attributed to nitrated products, the yield may depend on NO_x levels. Wängberg et al. (1997) and Hallquist et al. (1999) found the NO_3 radical reactions with α -pinene and Δ^3 -carene to be quite different. While the molar yield of pinonaldehyde was greater than 60% for the α -pinene reaction, the yield of caronaldehyde from the Δ^3 -carene reaction was only a few percent. Neither of these carbonyls are expected to have large aerosol fractions. Hallquist et al. (1997) report a relatively large SOA mass yield for the Δ^3 -carene reaction (15%), which is in agreement with the results of Hoffmann et al. and Griffin et al., while the yield from the α -pinene reaction was found to be less than 1%.

In an experiment at a forest site in Idaho Hill, Colorado, Marti et al. (1997) concluded that SO_2 was the most probable source of nucleating species while terpene oxidation products probably condensed onto existing particles. They report only one event for which the data indicate a possible contribution to nucleation from organic species. Leitch et al. (1999), presenting data from a forest site in Nova Scotia, argue that the gas-to-particle conversion of terpene oxidation products was the probable cause of the observed increase in aerosol volume, while Kavouras et al. (1998) claim that they were the source of new particle formation in a Eucalyptus forest in Portugal.

Although it is known that the atmospheric oxidation of SO_2 is an important source of atmospheric particles, the mechanism and concentrations necessary for that formation is still a matter of research and discussion (Kulmala et al., 1998; Pirjola et al., 1998). For example, it has been shown that ternary nucleation, involving H_2SO_4 , H_2O , and NH_3 , can occur at lower H_2SO_4 levels than what is needed for binary nucleation (Marti et al., 1997; McMurry et al., 1995; Kulmala et al., 2000).

New particle formation, called nucleation events, has been observed at a coniferous forest site in Southern Finland (Mäkelä et al., 1997; Kulmala et al., 1998). Events were observed as early in the year as February-March, at which time ambient temperatures are low, which would seem to preclude the involvement of biogenics. However, neither emission nor concentration measurements have previously been made at these

latitudes at such an early time of year. A set of three campaigns were organized within the BIOFOR project (Kulmala et al., 2001a) to investigate the source of these forest aerosols. Here, we report the results of emission and concentration measurements of the biogenic monoterpenes as well as the concentration measurements of SO₂, NH₃, and HNO₃ and investigate their connections to the nucleation events.

2. Experimental

2.1. Field site

Measurements were made at the SMEAR II forest research station at Hyytiälä in southern Finland (61°51'N, 24°17'E) as part of the BIOFOR project (BIOgenic aerosol formation in the boreal FORest). The site is a coniferous forest dominated by Scots pine (*Pinus sylvestris*), with less than 5% coverage by other species, notably Norway spruce (*Picea abies*) and Downy birch (*Betula pubescens*). The leaf area index is 9 and the forest is homogeneous for 200 m in all directions. The ground vegetation is dominated by heather (*Calluna vulgaris*), lingonberry (*Vaccinium vitis-idaea*), and blueberry (*Vaccinium myrtillus*), and the dominant moss species is *Dicranum undulatum*. Measurements were made in two springtime and one summertime campaign: 14 April–22 May 1998; 27 July–21 August 1998; and 25 March–26 April 1999. For more detailed information about the site and a complete list of measurements, see Kulmala et al. (2001a). All times are given as local time (=Finnish winter time).

2.2. Aerosol measurements

Particulate carbon was measured with the ambient carbon particulate monitor (ACPM) (R&P, Series 5400). Ambient particles are collected on impactors with a D50 collection efficiency at 140 nm diameter. Two impactors were used alternately with a collection period of two hours each. After sampling, the impactor is heated to 340°C for 780 s, during which time organic carbon (OC) is oxidized, and then to 750°C for 480 s, which oxidizes the remaining elementary carbon (EC). The CO₂ emitted is measured with a non-disperse infrared (NDIR) spectrophotometer. Results are given in µgC m⁻³. Near real-time (10 min) aerosol

mass concentrations were recorded by the tapered element oscillating microbalance (TEOM), a gravimetric instrument that draws ambient air at a constant flow rate through a filter made of Teflon[®]-coated borosilicate glass. Sampling is done at above ambient temperature (50°C) to avoid humidity effects. The filter is "weighed" (frequency of vibration is recorded) every 2 s.

2.3. VOC measurements

Emission and concentration measurements of the monoterpenes, light carbonyls, and light hydrocarbons were made. Results of the concentration measurements for ethene and formaldehyde are used in the steady state [•]OH calculations, but as the light carbonyls and hydrocarbons are not potential precursors to particles, the measurements will not be included here.

2.3.1. Sampling and analysis. The monoterpenes were sampled on Tenax TA (200 mg in 1/4" stainless steel tubes) at 80 NmL min⁻¹ for 40 min. All sampling was steered by a system of timers and solenoid valves, and the mass flows monitored with Honeywell microbridge mass airflow sensors via ADAM[®] data acquisition modules (ADAM 4017 and 4520, Advantech Co., Ltd.). The samples were stored in a dry environment at room temperature, and analysed at the ITM laboratory in Stockholm by ATD-GC-MS.

Continuous measurement of the VOC was not possible, because of the limitations set by the number of tubes available and the time needed for transport, analysis and reconditioning. A sampling strategy had to be adopted. For the monoterpenes, the goal was to capture at least 2 representative nucleation events and 2 non-event days in each campaign. During the spring-99 campaign, we were able to make terpene concentration measurements essentially around the clock (every 2 h) throughout the campaign.

2.3.2. Branch emissions. Branch emission measurements were made with a 25 cm diameter, 17 liter all-Teflon chamber from Scots pine (*Pinus sylvestris*), the dominant tree species at the site, at a height of 12 m. The chamber was made of 0.05 mm transparent FEP-Teflon film which is tied around a 20–30 cm branch segment. Care was taken to avoid contact between the branch and

the walls of the chamber in order to avoid mechanical abrasion which is known to affect emission rates (Juuti et al., 1990). A fan ensured mixing but not excessive wind over the branch. The chamber was continuously flushed with 9 NL min^{-1} ambient air (Bronkhorst HI-TEC massflow controller), purified of ozone with a KI scrubber, and of particles with a $2 \mu\text{m}$ Teflon filter. The water content of the input air was reduced with a Peltier cooling element such that the relative humidity in the chamber was maintained at approximately the same level as ambient relative humidity. Temperature and relative humidity were continuously recorded from the inlet and chamber air with Rotronic MP-100 sensors, and photosynthetic active radiation (PAR) at the top of the chamber with a LiCOR LI-190SA quantum sensor. Uptake and release of carbon dioxide were also recorded during the spring-99 campaign with a Modell 41H ambient gasfilter correlation CO_2 instrument (Thermal Environmental Instrument Inc.). Samples were taken simultaneously at the inlet and outlet of the chamber. They were connected to the chamber via 8-way Teflon ports and 20 cm $0.03''$ ID teflon tubing. The meteorological and CO_2 data were continuously collected on a computer via ADAM[®] data acquisition modules (ADAM 4017 and 4520, Advantech Co., Ltd.).

Emission rates are determined from the difference in the BVOC mass flow at the inlet and outlet of the chamber, normalized to the branch needle dry weight (gdw):

$$E = (c_{\text{out}} - c_{\text{in}}) \cdot F_{\text{ch}} / g \text{ dw},$$

where c_{out} , c_{in} are the concentrations at the inlet and outlet and F_{ch} is the air flow through the chamber. Experiments with the empty all-Teflon chamber have shown that the system is free of artifacts for monoterpenes. Emission rate detection limits were less than $3 \text{ ng gdw}^{-1} \text{ h}^{-1}$ for all the terpenes.

2.3.3. Ambient concentrations. Monoterpene concentration samples were collected at the 2-m level with a semi-automatic system of timers and solenoid valves (max. 4 consecutive samples). All sampling was done through an ozone scrubber (MnO_2 coated copper screen) to avoid sampling artifacts. Breakthrough experiments (two tubes in series) have shown that the sampling efficiency was better than 95%. The detection limits for

concentrations of individual terpenes was less than 10 pptv.

2.4. Inorganic gas concentrations

Nitric acid and sulphur dioxide were measured with a parallel plate denuder-ion chromatograph (PPD-IC) and ammonia with a diffusion scrubber and flow injection analyzer (A-FIA). Briefly, the PPD is a continuously wetted wall denuder consisting of two parallel glass plates mounted 3mm apart and with a hydrophilic fabric of polyester glued to the inside walls. Hydrogen peroxide is added to the absorption liquid to capture SO_2 . Sampling time was 20 min and the detection limit was about 5 pptv (Rosman et al., submitted to *Atmospheric Environment*). The A-FIA samples ammonia from the ambient air stream with a diffusion scrubber and water as the absorbent. After sampling, ortho-phthalaldehyde (OPA) and sulfite are added to the sample solution which form a fluorescent product with the ammonia in solution. The product is detected by a fluorescence detector (Karlsson, 1997). The time resolution was 10 minutes and the detection limit 4 pptv. Sampling was done at the 2 meter level.

2.5. Data evaluation

Steady state $\cdot\text{OH}$ and NO_3 concentrations were calculated for the summer-98 and spring-99 campaigns. The generation of HO_x molecules occurs through the photolysis of O_3 and HCHO as well as the reaction between terpenes and O_3 . The major sink term is the reaction of $\cdot\text{OH}$ with NO_2 . The distribution between $\cdot\text{OH}$ and HO_2 was determined by the reaction of CO, CH_4 , terpenes, ethene, and HCHO with $\cdot\text{OH}$ and the reactions of NO and O_3 with HO_2 . The steady state NO_3 concentration was calculated by its source through the reaction of NO_2 and O_3 , its equilibrium with N_2O_5 , and its loss through reactions with NO and terpenes as well as its photolysis and the photolysis of N_2O_5 . Photolysis constants were calculated from solar zenith angles for clear sky conditions in accordance with Derwent and Jenkins (1990) and Demerjian et al. (1980), and adjusted to actual conditions of cloudiness with on-site UV-B (280–320 nm) measurements. The calculations do not take into account seasonal or day to day variations in the ozone column or

surface albedo. Springtime ozone is generally higher than what it is during the summertime which means that the springtime solar UV flux and therefore OH concentrations may be overestimated. On the other hand, springtime albedo is also higher due to ice and snow coverage, and this would mean that the springtime OH might be underestimated. Ozone and NO₂ concentrations were obtained from measurements at the station (Kulmala et al., 2001a), HCHO, ethene, and monoterpene concentrations from our measurements, while CO and CH₄ were set at 150 and 1700 ppbv, respectively. Because of the often low ambient concentrations and thereof high uncertainty, NO was calculated by the photostationary state approximation for O₃, NO₂, and NO.

Source terms for the production of secondary organic compounds (SOC) are defined by the reactions of the precursor gases with atmospheric oxidants:

$$Q_{\text{SOC}} = \sum k_i \cdot \text{OH} \cdot \text{terp}_i + \sum k_i \cdot \text{O}_3 \cdot \text{terp}_i \\ + \sum k_i \cdot \text{NO}_3 \cdot \text{terp}_i,$$

$$Q_{\text{H}_2\text{SO}_4} = k_i \cdot \text{OH} \cdot \text{SO}_2,$$

$$Q^* = Q_{\text{H}_2\text{SO}_4} \times [\text{NH}_3],$$

where Q_{SOC} and $Q_{\text{H}_2\text{SO}_4}$ are the source terms for SOC from the oxidation of monoterpenes and H₂SO₄ from the oxidation of SO₂, respectively, k_i is the relevant temperature dependent reaction rate constant, and terp_i includes α -pinene, β -pinene, Δ^3 -carene, and limonene. The unit is molecules cm⁻³ s⁻¹. The source term Q^* (pptv molecules cm⁻³ s⁻¹) is a working definition used here to investigate the role of ternary nucleation.

Not all of the products of monoterpene oxidation are condensable gases and not all of the condensable gases have a nucleating potential, as discussed above. However, as information on particulate phase product or even total SOA yields is incomplete, the application of yield factors in the above equation involves a good deal of uncertainty. Therefore, we will use the total and individual source terms Q_{SOC} , and Q_{SOC} (OH, O₃, or NO₃) in the following analysis.

The ultrafine particle number concentrations ($D_p < 10$ nm) and their peak values (N_{max}), have been taken from the DMPS data (differential mobility particle sizer) collected in the forest at 4 m above ground (Aalto et al., 2001). Surface

area has been approximated from the size distribution for the purpose of sorting the data.

3. Results and discussion

3.1. Classification of data

We concentrate our analysis on the summer-98 and spring-99 periods. The classification of nucleation events follows that of Mäkelä et al. (2000). Nilsson et al. (2001) have shown that all the observed nucleation events have occurred in arctic and polar air masses, usually during cold air advection. We therefore group the spring-99 data into three groups: group 1: days with well-defined nucleation events during cold air outbreaks, group 2: days with cold air outbreaks but without nucleation events, and group 3: All other non-event days. Days during which poorly defined event-like phenomena were observed are omitted. Aalto et al. (2001) report that no events were observed during periods when the pre-existing aerosol surface area was greater than 100 cm² cm⁻³. Thus, we want to limit our analysis to those days with smaller surface area concentrations. This leaves us with 10 days in group 1: (30 March, 2, 4, 5, 6, 8, 12, 13, 14, 19 April) and 3 in group 2: (25 March, 1, 16 April). All the remaining days of groups 2 and 3 had high pre-existing aerosol surface areas and are therefore omitted. 1 April of group 2 is actually a borderline case with surface areas just above 100 cm² cm⁻³, except during the morning period between 10:30 and 12:30. By the same criteria, 8 days of the summer-98 period were omitted and of the remaining days for which there is sufficient data, 6 were non-event days and 4 were "event" days. We use ' ' for the summertime "events" as a reminder that they were all class 3 or 0 events (Mäkelä et al., 2000), lasting only a short time and involving only hundreds of ultra-fine particles per cm⁻³, as compared to the 1999 events which were well defined, could last for several hours, and involved thousands of particles.

3.2. Branch emissions

The flux of monoterpenes from branches of Scots pine at Hyytiälä was dominated by α -pinene and Δ^3 -carene (Table 1).

The lack of Δ^3 -carene in the 1999 emission profile is an interesting but bothersome result. The

Table 1. Relative composition (%) of the monoterpene^a emissions from Scots pine. Number of samples in parentheses, first column

	tri.	α -p.	cam.	β -p.	myr.	Δ^3 -c.	lim.	β -ph.
April–May 1998: (44)	1 \pm 0.5	23 \pm 9	3 \pm 2	7 \pm 3	2 \pm 1	60 \pm 12	3 \pm 5	1 \pm 0.5
August 1998: (36)	1 \pm 0.5	33 \pm 6	6 \pm 2	5 \pm 2	5 \pm 1	44 \pm 7	0	3 \pm 2
March–April 1999: (77)	2 \pm 1	64 \pm 11	10 \pm 4	7 \pm 5	4 \pm 4	1 \pm 3	12 \pm 13	0

^atri. = tricyclene, α -p. = α -pinene, cam. = camphene, β -p. = β -pinene, myr. = myrcene, Δ^3 -c. = Δ^3 -carene, lim. = limonene, β -ph. = β -phellandrene.

spring and summer measurements were made on different branches of the same tree, while the 1999 measurements were made on an adjacent tree. Generally, trees of the same population are expected to emit the same relative composition of monoterpenes and Scots pine is expected to emit Δ^3 -carene (Janson, 1993; Juvonen, 1966; Hiltunen et al., 1975). Obviously, the particular tree chosen for the 1999 experiment was not representative for the Scots pine population at Hyytiälä since Δ^3 -carene was found to be one of the most abundant monoterpenes in the forest air, see below. These results demonstrate a major drawback with the chamber method when used to determine a forest flux, i.e., the problem of representativity.

No significant difference in the relative composition of the branch emission was observed for event days or the 24-h period prior to an event, as compared to non-event days, during any of the campaigns.

Emission rates varied from 10^1 to 10^2 ngC gdw⁻¹h⁻¹ and showed large variation, as is to be expected under varying conditions of temperature. Generally, monoterpene emissions are expected to adhere to a temperature dependence according to:

$$E = E_s \exp[\beta(T - T_s)], \quad (1)$$

where E is the emission ($\mu\text{gC gdw}^{-1} \text{h}^{-1}$) at temperature T , E_s is the standard emission at a reference temperature T_s , and β is an empirical constant. An overview of the data from the three campaigns, including the temperature correlations, is given in Table 2. The temperature correlation was poor in April 1998, as it was for the spring nighttime emissions in 1999, when temperatures ranged from -3 to 10°C . We find no correlation between the branch emission data and nucleation events, the latter occurring when emission rates were as low as $50 \text{ ng gdw}^{-1} \text{h}^{-1}$ and less, while there were examples of emission rates as high as

1000 or more which were not followed or accompanied by nucleation events.

3.3. Concentration of organic gases

Just a few days into the first BIOFOR campaign (25 April 1998), a very high concentration of monoterpenes, almost 14 ppbv and lasting just a few hours, was observed by three independent measurements about 6 h prior to the observance of an event beginning at 12 noon (see also Spanke et al. (2001)). The relative composition of the terpenes during the concentration episode was the same as that observed both before and after, suggesting that the source of the terpenes was the same. The episode occurred after sunrise and after the nocturnal boundary layer began to break up. Ambient temperatures during the 6-h period leading to the concentration episode were a few degrees above zero and very similar to the previous day, during which early morning terpene concentrations were a normal 400 pptv. Neither our branch chamber nor the SMEAR station cuvette measurements showed any abnormal behavior in terms of leaf monoterpene emissions, CO_2 exchange, water exchange, or stomata conductance between the 24th and 25th. Thus, the reason(s) for the high monoterpene concentration episode are unknown, and such high concentrations were not seen again, not even during the summer period. It can be noted that it was accompanied by an equally short period of high total aerosol number concentration and surface area, and that it was followed by a 7–8% increase in the organic fraction of the aerosol ($D_p > 140 \text{ nm}$). However, the nucleation event which followed was a class 3 (= poor) event.

Table 3 lists the average day and nighttime concentrations for the three campaigns. All data during periods with winds from the SW sector have been removed from the summer data due to

Table 2. Ranges of temperature and monoterpene emission rates ($\text{ngC gdw}^{-1} \text{h}^{-1}$) observed in the branch emission measurements made on Scots pine at Hyytiälä in 1998 and 1999

Period	Temp. ($^{\circ}\text{C}$)	MT emission	β	R^2	E (20°C)
April 1998: (12)	2–19	10–240	0.0527	0.0967	120
May 1998: (28)	2–25	10–1050	0.1365	0.7933	380
August 1998: (36)	5–25	60–450	0.0676	0.5458	200
March–April 1999	–3–25	<2–1600	0.1448	0.6723	390
daytime (08–17:30): (47)	0–25	5–1600	0.1663	0.7774	440
nighttime (23–05:30): (28)	–3–10	<2–110	0.1114	0.3176	280

In columns 4 to 6 are given the β coefficient (eq. (1)) and the correlation coefficient for the temperature dependences, as well as standard 20°C emission rates for each period ($\text{ngC gdw}^{-1} \text{h}^{-1}$). Number of samples in parentheses, first column.

Table 3. Average day and nighttime monoterpene concentrations (pptv) and their standard deviations measured in the Hyytiälä forest at 2 m height; number of samples in parentheses (night, day), first column

Period	night	day
April–May 1998: (17, 10)	700 ± 500	280 ± 90
August 1998: (17, 22)	1600 ± 2200	450 ± 160
March–April, 1999: (78, 112)	600 ± 1200	200 ± 180

possible contamination of samples from a saw mill in that sector which, whether in operation or not, emitted terpenes. As is usually the case, nighttime concentrations are higher than daytime. In spite of lower nighttime emissions caused by lower temperatures, concentrations in and at the top of the forest are often higher at night because of a shallower boundary layer and restricted vertical mixing. In the same manner, low daytime concentrations should not be interpreted as being primarily due to oxidation reactions, but rather vertical mixing through a deeper boundary layer (Johansson and Janson, 1993).

It can also be seen that both day and nighttime concentrations were generally higher during the summer period, a period which lacked well defined nucleation events. However, comparing concentrations on event days with those of non-event days of the spring-99 period, we find that average concentrations were in fact higher on event days, Fig. 1, although not with any high degree of confidence.

The relative composition of the ambient monoterpenes was very similar during all three campaigns, with α -pinene and Δ^3 -carene account-

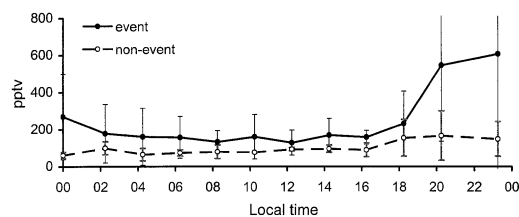


Fig. 1. Average diurnal variation (± 1 sd) of ambient monoterpene concentrations (pptv) during 10 event and 3 non-event days in the spring of 1999. Hyytiälä.

ing for $48 \pm 11\%$ and $23 \pm 5\%$, respectively (March–April 1999). Other terpenes identified were β -pinene (10%), limonene (10%), camphene (6%), myrcene (2%), tricyclene (2%), and occasional traces of sabinene. The proportion of α -pinene was slightly lower when winds were from the southern sector, 43% as compared to about 50% in the northern sector, reflecting differences in vegetation in the different sectors.

No difference in the relative composition of the terpenes in the forest air could be found for event as compared to non-event days.

3.4. Concentrations of inorganic gases

Sulphur dioxide concentrations ranged from below the detection limit (5 pptv) to 1600 pptv with an average of 310 ± 310 pptv during the spring-99 campaign, and from below 5 pptv to 3200 pptv, with an average of 90 ± 200 pptv, during the summer-98 campaign. Average concentrations during the ten spring-99 event days lay between 250 and 350 pptv, showed no significant diurnal variation, and were consistently higher than those of the three reference non-event days,

particularly during the morning hours, Fig. 2a. Relative standard deviations for the daytime averages (09:00–15:00 h) lay between 60% and 90%. The 7 to 9 o'clock excursion in the non-event-99 average is due to a short episode with up to 1 ppbv SO_2 at 8 a.m. on 1 April. The daytime summer-98 data did not differ significantly between four "event" and six non-event days, both sets of data averaging 40 pptv with relative standard deviations between 30% and 70%. August 6, also a class 0 day, is not included in the event-98

average. On that day, both the aerosol surface area and SO_2 concentrations were high (SO_2 up to 2 ppbv) during the morning. Both dropped at about noontime, SO_2 to 60–70 pptv, at which time a small particle burst was seen.

Nitric acid varied from 10 to 300 pptv with an average of 77 ± 54 pptv during the summer period and from 10 to 1000 pptv with an average of 130 ± 125 pptv during the spring-99 campaign. The lowest concentrations are generally observed in the early morning because of the combination

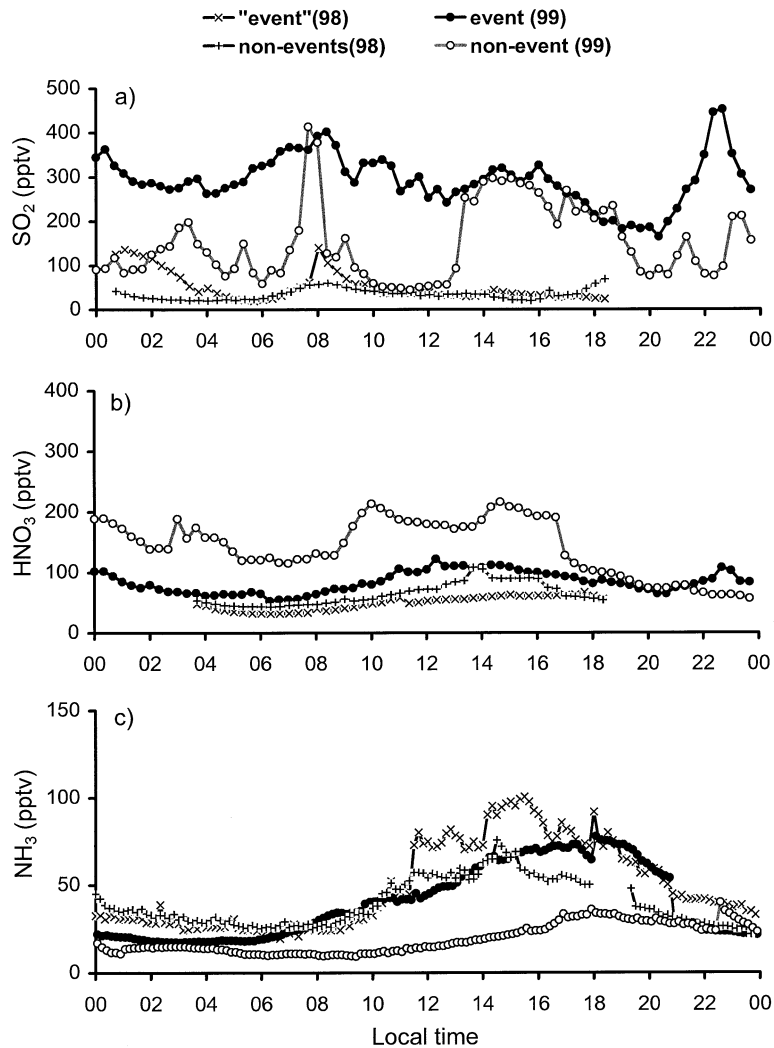


Fig. 2. Average diurnal variations of ambient (a) SO_2 , (b) HNO_3 , and (c) NH_3 concentrations (pptv) for 4 "event" and 6 non-event days between 30 July and 19 August 1999 and for 10 event and 3 non-event days between 25 March and 19 April 1999. Hyttiälä.

of dry deposition and nocturnal atmospheric stability. Average concentrations during the "event" and non-event days of the summer period, as well as for the event days of the spring period, show no significant differences (Fig. 2b). Generally higher concentrations were observed during the springtime non-event periods. The maximum concentration, 1000 pptv, was observed on a non-event day.

Generally, ammonia showed a strong diurnal variation with a concentration minimum in the early morning and maximum in late afternoon (Fig 2c). During the summer-98 period, concentrations ranged from 10 to 430 pptv, averaged 52 ± 43 pptv, and did not show significant differences between daytime "event" and non-event periods. Springtime concentrations ranged from 5 to 400 pptv, averaged 49 ± 58 pptv, and were significantly higher during event days. The noontime average for the 10 event days was 45 ± 36 pptv, while that for the 3 non-event days was 15 ± 9 pptv.

At the low values for HNO_3 and NH_3 observed here, the gas-particle partitioning equilibrium between $\text{HNO}_{3(\text{g})}$, $\text{NH}_{3(\text{g})}$ and $\text{NH}_3\text{NO}_{3(\text{p})}$ is of little interest.

3.5. Source terms for condensable gases

3.5.1. Oxidant concentrations. Steady state $\cdot\text{OH}$ and NO_3 concentrations were calculated for the summer-98 and spring-99 periods. Summertime $\cdot\text{OH}$ concentrations were on the order of 1×10^7 molecules cm^{-3} on sunny days and about 3×10^4 molecules cm^{-3} in the night (from the terpene + O_3 reaction). Concentrations were generally lower during the spring-99 campaign due to the lower zenith angle of the sun, with maximum values on the order of 6×10^6 molecules cm^{-3} . Average midday values were $3 \pm 1 \times 10^6$ molecules cm^{-3} on event days, while on the non-event days the values were lower, $1 \pm 0.8 \times 10^6$ molecules cm^{-3} . Nighttime NO_3 radical concentrations did not differ significantly between the summer and spring periods, or between the event and non-event days of the spring-99 period. Nighttime concentrations reached 1–2 pptv, which is quite low and depends on the the low NO_x concentrations. Ozone concentrations were generally higher in the spring, with values reaching 60 ppbv, while daytime concentrations during the summer period

were about 30 ppbv. Concentrations during the spring-99 event days averaged 50 ± 5 ppbv while concentrations on the three non-event days averaged 36 ± 4 ppbv.

3.5.2. Source term of secondary organic gases.

The average diurnal variation in the source term for secondary organic gases from the oxidation of monoterpenes Q_{SOC} , as well as the Q values for each oxidant, are shown in Fig. 3. Days with high aerosol surface area are not included. It can be seen that the average midday Q values on spring-99 event days are higher than those of reference non-event days, although the difference in the means is significant only at the 20% level. Daytime Q_{SOC} values were generally higher, $0.5\text{--}1 \times 10^7$ molecules $\text{cm}^{-3} \text{s}^{-1}$, during the summer-98 period, a result of the higher monoterpene and $\cdot\text{OH}$ concentrations. On the other hand, SOA yields can be expected to be lower because of the higher temperatures, $16 \pm 2^\circ\text{C}$ as compared to the $5 \pm 3^\circ\text{C}$ during springtime event days. No significant nucleation events were observed during the summer campaign. Looking at the spring-99 data, no correlations could be found between occurrence/non-occurrence of events, the ultra-fine particle number concentrations, or the daily maxima in ultra-fine particle number concentrations on the one hand and the Q_{SOC} values collectively or individually, average Q_{SOC} values for the periods 00–06 am, 06–12 am, or the 4 and 8 h periods prior to the observation of an event on the other. Neither did the relative contribution of the individual oxidants to terpene oxidation appear to be of any significance for nucleation events. Fig. 4 shows the $Q_{\text{SOC}}(\cdot\text{OH})$ and $Q_{\text{SOC}}(\text{O}_3)$ values (the two main oxidation pathways during daylight hours) plotted against the ultra-fine particle number concentration. In summary, we find little support in this data set for the hypothesis that terpene oxidation products are the precursors to the observed new particle formation. We can observe, however, that the values at the time of the observation of an event (ranging from 3×10^5 and 4×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ over 9 event days) are sufficiently high to maintain the observed condensational growth of new particles according to the calculations of Kulmala et al. (2001b), if the aerosol yield is on the order of 10%, 25% on event days with low Q values.

It can also be seen in Fig. 3 that the production

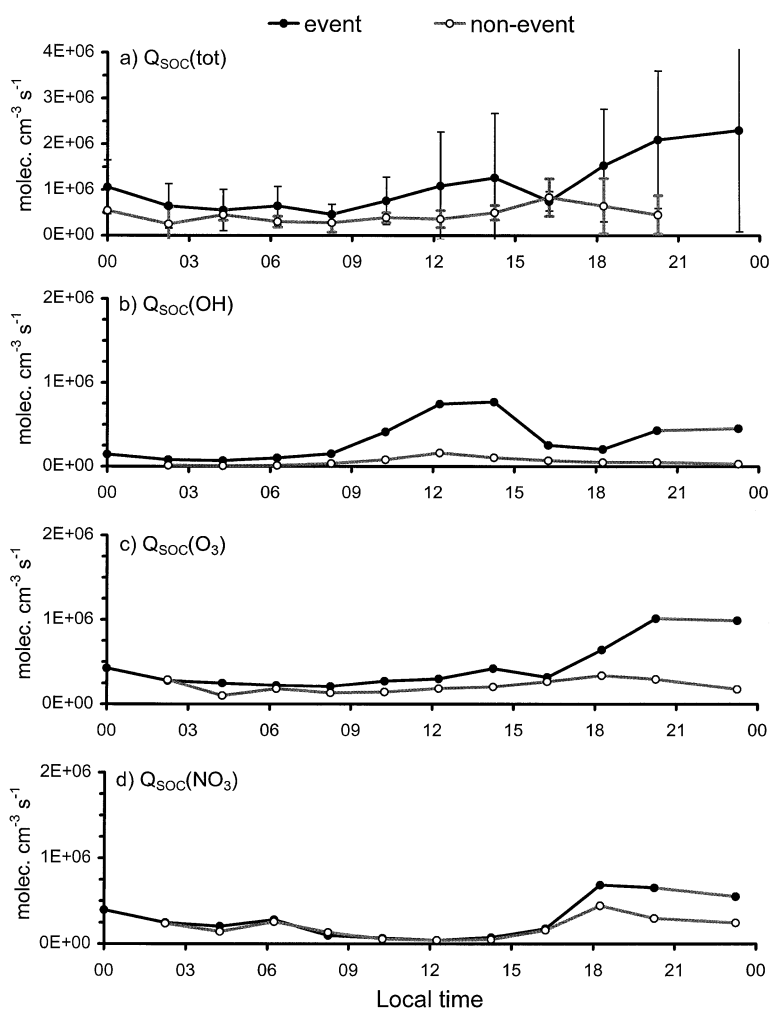


Fig. 3. Average diurnal variations for the source terms for monoterpene oxidation products (a) $Q_{\text{SOC}}(\text{tot})$, (b) $Q_{\text{SOC}}(\text{OH})$, (c) $Q_{\text{SOC}}(\text{O}_3)$, and (d) $Q_{\text{SOC}}(\text{NO}_3)$, (molecules $\text{cm}^{-3} \text{s}^{-1}$) for 9 event and 3 non-event days in the spring-99 campaign. Hyytiälä. Error bars are ± 1 sd.

of oxidation products increases in the late afternoon and evening, primarily a result of the increasing concentrations of terpenes. Generally, the OH radical accounted for 50 to 60% of the oxidation during the mid-day hours, O₃ for 30–40% around the clock, and the NO₃ radical only a few percent during the day, but 50 to 60% during nighttime. This means that not only is the production of secondary gases greatest at night, but also that the nighttime products may also be more condensable (i.e., have lower vapor pressures) than the daytime products (Hoffmann et al., 1997;

Wängberg et al., 1997; Hallquist et al., 1999; Griffin et al., 1999). At Hyytiälä, α -pinene and Δ^3 -carene accounted for about 50% and 25%, respectively, of the ambient monoterpenes. In light of the above mentioned laboratory studies, it is of interest to note that the aerosolic organic mass concentration (OC), as well as the organic mass fraction of the aerosol (%OC), both have maxima during the night, for both event and non-event periods (Fig. 5). In fact, we find a weak correlation ($R^2 = 0.4875$) between OC and the Q_{SOC} values during nighttime, but not during the day. The strongest

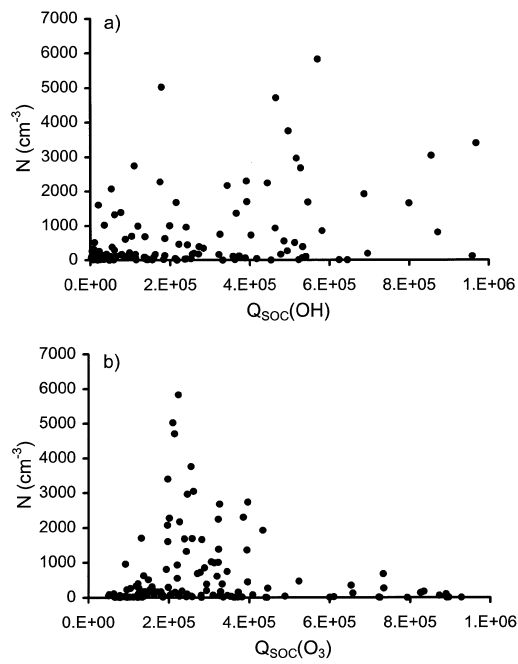


Fig. 4. The number concentration of ultrafine particles ($D_p < 10$ nm) plotted against the source term Q for products from the oxidation of terpenes by (a) $\cdot\text{OH}$ and (b) O_3 (see text). Data from periods with high aerosol surface area ($S > 100 \mu\text{m}^2 \text{cm}^{-3}$) are not included.

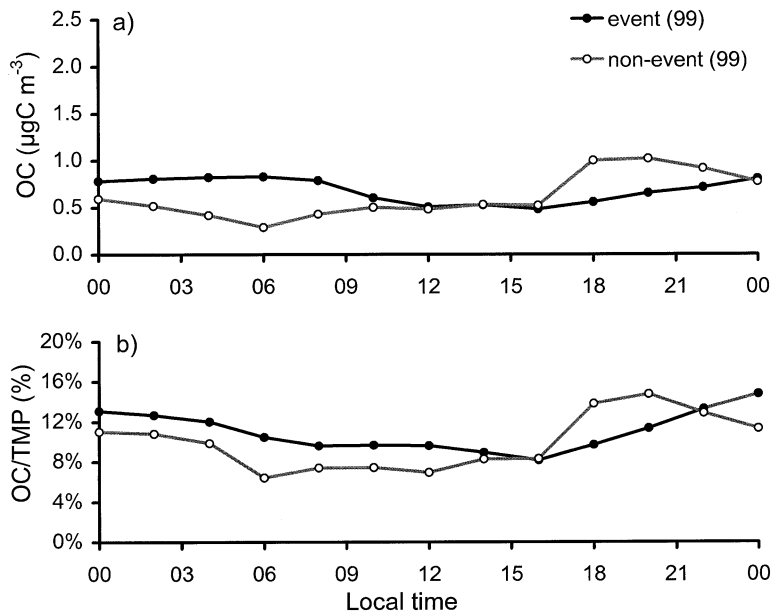


Fig. 5. Average diurnal variations of the (a) particulate organic carbon mass concentration ($\mu\text{gC m}^{-3}$) and (b) organic mass fraction of the aerosol mass (%) during 10 event and 2 non-event days in the spring of 1999. Hyytiälä.

correlation is seen for $Q_{\text{SOC}}(\text{NO}_3)$ (Fig. 6). We have investigated further the nocturnal increase in the OC mass concentration following 13 days during which the continuity of air mass identity could be assumed. We found that the increment in OC correlated with $Q_{\text{SOC}}(\text{O}_3)$, $Q_{\text{SOC}}(\text{NO}_3)$, and the sum of the two with $R^2 = 0.456$, 0.4275 , and 0.4827 , respectively. Since the OC data applies only to accumulation mode particles (instrument cutoff at $D_p = 140$ nm) and whereas condensation occurs to all sizes, it is of interest to consider the influence of the aerosol size distribution. The nighttime ratio between the surface area of the Aitken mode and that of the size bin $140 < D_p < 500$ nm ($S' = S_{\text{ait}}/S_{\text{acc}}$) was found to vary from 0.3 to 1.7 for the 13 periods studied here. The correlation between observed OC and the Q term can be expected to be poorer during periods of high aitken mode particle number, i.e., high S' . We therefore normalize the Q values with the ratio and find that the correlation between OC and the sum of the average normalized source terms $Q_{\text{SOC}}(\text{O}_3)$ and $Q_{\text{SOC}}(\text{NO}_3)$ is $R^2 = 0.7668$ ($n = 13$) (Fig 7). We can also observe that while the 6-h increase in organic aerosol mass concentration (OC) lay between 0.1 and $1 \mu\text{gC m}^{-3}$, the corresponding integrated production of secondary organic carbon from the O_3 and NO_3 reactions ($Q_{\text{SOC}}(\text{O}_3) + Q_{\text{SOC}}(\text{NO}_3)$) varied between 1.2 and $7.2 \mu\text{gC m}^{-3}$. For the increase in OC to be explained by condensation of monoterpene oxidation products, a SOA yield of at least 10 to 15% is needed.

Hämeri et al. (2001) report a decrease in the aerosol growth factor (a function of aerosol hygro-

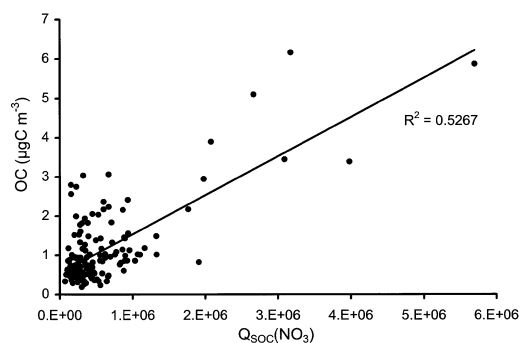


Fig. 6. Nighttime (20:00–06:00 h, local time) particulate organic carbon mass concentrations ($\mu\text{gC m}^{-3}$) plotted against $Q_{\text{SOC}}(\text{NO}_3)$ ($\text{molecules cm}^{-3} \text{s}^{-1}$).

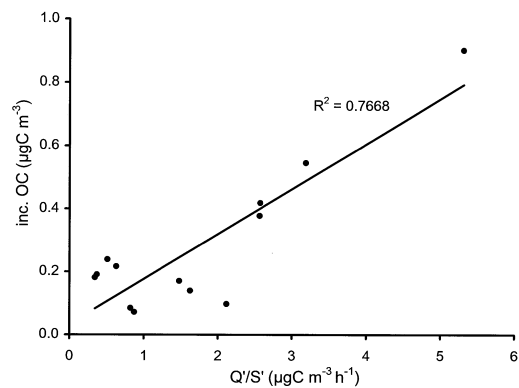


Fig. 7. Increase in the organic carbon mass concentration ($D_p > 140$ nm) plotted against the sum of the average source terms for the same period Q' ($=Q_{\text{SOC}}(\text{O}_3) + Q_{\text{SOC}}(\text{NO}_3)$), normalized to the ratio of the aitken to accumulation mode surface areas, S' .

scopicity) beginning in the late afternoon and continuing through the night to reach a minimum just prior to sunrise. Secondary organic aerosols from the oxidation of several monoterpenes have been reported to have low growth factors (Virkkula et al., 1999). Thus, our findings, that the production and condensation of secondary organic gases is greatest during the night, are consistent with the results reported by Hämeri et al. (2001).

The above results are consistent with the hypothesis that products of the atmospheric oxidation of monoterpenes contribute to the organic aerosol by means of condensation, but we find no evidence for their contribution to new particle formation. Indeed, if there existed species capable of nucleation among the oxidation products, then we should be seeing new particle formation during the nighttime when the production of SOA is highest and temperatures are lowest. We have not observed new particle events during the night at Hyytiälä. These results are in agreement with the findings of Marti et al. (1997) and Leaitch et al. (1999) but in contrast to those of Kavouras et al. (1998). However, the conclusions of Kavouras et al. rely heavily on chemical interpretations of co-varying diurnal variations where a meteorological interpretation might have been more appropriate.

3.5.2. SO_2 and NH_3 . As can be seen in Fig. 8, the daytime source term for H_2SO_4 , $Q_{\text{H}_2\text{SO}_4}$, and

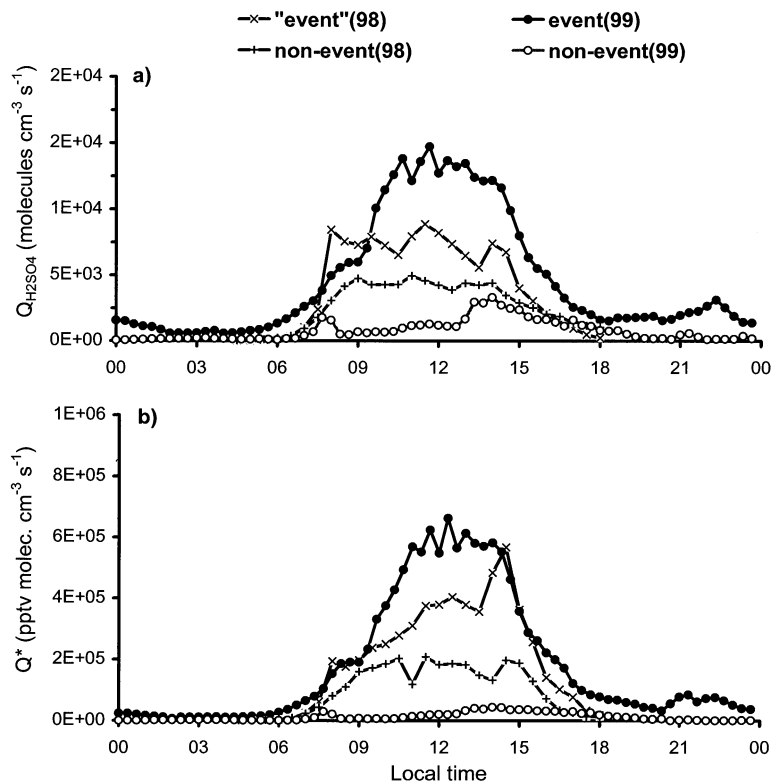


Fig. 8. Average diurnal variation of (a) H_2SO_4 source term ($\text{molecules cm}^{-3} \text{s}^{-1}$) and (b) Q^* ($=Q_{\text{H}_2\text{SO}_4}$ multiplied by the NH_3 concentration) for event and non-event days during the summer-98 and spring-99 campaigns. Hyttiälä.

even more so the term Q^* ($=Q_{\text{H}_2\text{SO}_4} \times [\text{NH}_3]$) was significantly higher on the event days of the spring(99) campaign. However, the correlation between $Q_{\text{H}_2\text{SO}_4}$ or Q^* and the ultrafine particle number concentration was poor, $R^2 = 0.2042$ and 0.3564 , respectively. If we look instead at the daily maxima in ultra-fine particle concentrations, N_{max} , and the average Q values for the morning hours 08 to 10 a.m. of the 10 event and 3 non-event days, then the correlation to Q^* , but not to Q , becomes stronger, $R^2 = 0.4686$, Fig 9a, but still somewhat dubious. Since there always exists a competition between nucleation and condensation, we might expect the pre-existing particle surface area to affect the correlation between the term Q^* and N_{max} . Normalizing Q^* to the surface area S ($3 < d_p < 500 \text{ nm}$) gives us a significant correlation with $R^2 = 0.7355$, if we omit one outlier, Fig. 9b. We cannot explain the outlier, 10 April, but only notice that the surface area was

exceptionally low on that day, the lowest observed. The correlation supports, but does not prov, the hypothesis that there is a connection between SO_2 and NH_3 on the one hand and nucleation events on the other, for example through ternary nucleation. However, the H_2SO_4 source terms, $Q_{\text{H}_2\text{SO}_4}$, averaged $8 \pm 5 \times 10^3 \text{ molecules cm}^{-3} \text{s}^{-1}$ at the start of event observations, which is lower than the concentration needed to account for the observed condensational growth, $1 \times 10^5 \text{ molecules cm}^{-3} \text{s}^{-1}$ (Kulmala et al., 2001b).

As mentioned earlier, the “events” of the summer period were brief observations of only hundreds of particles as compared to the thousands of particles observed during the springtime events. The source terms $Q_{\text{H}_2\text{SO}_4}$ and Q^* , as well as the terms normalized to the ambient aerosol surface area Q/S and Q^*/S , for both “event” and non-event days, were generally as high as the respective terms observed during the early morn-

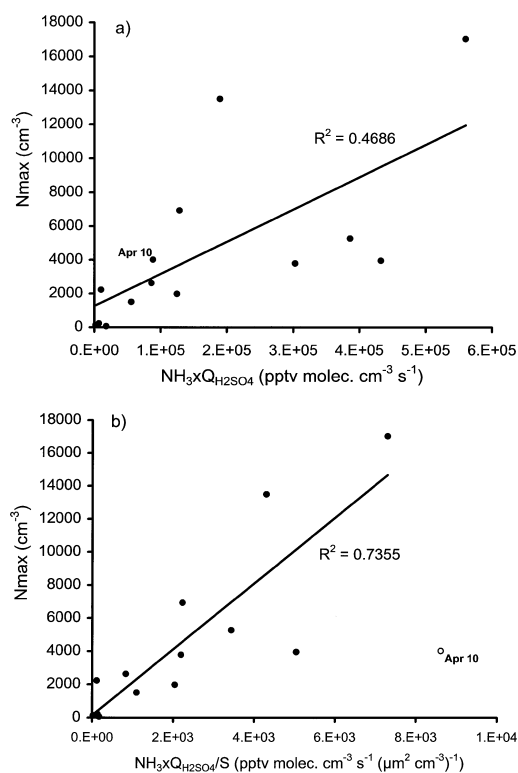


Fig. 9. Maxima in ultra-fine particle number concentrations plotted against averages in (a) Q^* ($Q_{\text{H}_2\text{SO}_4} \times \text{NH}_3$) and (b) Q^*/S (see text). The value for 10 April is not included in the trend line in 10b.

ing hours of the springtime event days, but lower during late morning and midday hours, Fig. 8. Still, the summer data can be sorted by the term Q/S . Non-event days had morning Q/S terms lower than $115 \text{ molecules cm}^{-3} \text{ s}^{-1} (\mu\text{m}^2 \text{ cm}^{-3})^{-1}$, while “event” days had values greater than $185 \text{ molecules cm}^{-3} \text{ s}^{-1} (\mu\text{m}^2 \text{ cm}^{-3})^{-1}$. The corresponding numbers for the spring99 campaign were 20 and $46 \text{ molecules cm}^{-3} \text{ s}^{-1} (\mu\text{m}^2 \text{ cm}^{-3})^{-1}$, respectively. Important to the comparison of spring and summer data are the results reported by Mäkelä et al. (2000), that the particle growth rates during the summer campaign were higher than those during the spring and that 10 times higher condensable vapor concentrations were needed to sustain those rates.

3.5.3. 5 April. On 5 April 1999, between 9 and 10 a.m., a nucleation event was observed with

about $15,000 \text{ new particles cm}^{-3}$ in the range $3 < D_p < 20 \text{ nm}$ and about $10,000$ of these below 10 nm . A distinct “cloud”, or maximum in number concentration could be seen in the DMPS data as the particles grew, and at 16:00 h there were $10,000 \text{ cm}^{-3}$ in the size range $8\text{--}30 \text{ nm}$. The average growth rate was $2\text{--}3 \text{ nm h}^{-1}$, and the increase in mass concentration for the size bin 3 to 30 nm associated with the growth, assuming a density of 1.5 g cm^{-3} , was 0.093 pg cm^{-3} , or $0.016 \text{ pg cm}^{-3} \text{ h}^{-1}$. Coagulation will shift the size distribution within the group, but not increase the mass. Thus, the mass accumulation represents condensational growth, assuming continuity of air mass identity. The number does not account for mass which was lost from the group during the 6 hour period by coagulation onto larger particles. From the SO_2 data and $\cdot\text{OH}$ approximation, we find that the oxidation of SO_2 and production of H_2SO_4 was on the order of $0.01 \text{ pg H}_2\text{SO}_4 \text{ cm}^{-3} \text{ h}^{-1}$ ($2 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$) during this period (Fig. 10). Condensation will not occur exclusively to this size bin and it is therefore doubtful that the oxidation of SO_2 could account for the observed particle growth, even if we include ammonia. Indeed, Kulmala et al. (2001b) have estimated a vapour source rate of about $1 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$ for the maintenance of the observed growth rate, which is an order of magnitude higher than the observed source term.

The daytime oxidation of monoterpenes by $\cdot\text{OH}$ and O_3 produced secondary organic material (assuming $M = 184 \text{ g mol}^{-1}$) at approximate rates of 0.4 and $0.2 \text{ pg cm}^{-3} \text{ h}^{-1}$, respectively. If we assume a daytime SOA yield of about 10%, then production of condensable material occurs at a rate of about $0.06 \text{ pg cm}^{-3} \text{ h}^{-1}$, or $5.5 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ (Fig. 10). From the ACPM data, we see that the mass concentration of organic carbon in the accumulation mode ($D_p > 140 \text{ nm}$) increases by 0.3 pgC cm^{-3} , or $0.02 \text{ pgC cm}^{-3} \text{ h}^{-1}$ between 10 a.m. and 4 p.m. This leaves about $0.04 \text{ pg cm}^{-3} \text{ h}^{-1}$ (still assuming a 10% yield) of condensable organic material for particles less than 140 nm during the midday hours. Thus it would seem that the oxidation products of the monoterpenes are the most likely (of the known) candidates to account for the growth of new particles. This conclusion is however, difficult to reconcile with the morning and daytime develop-

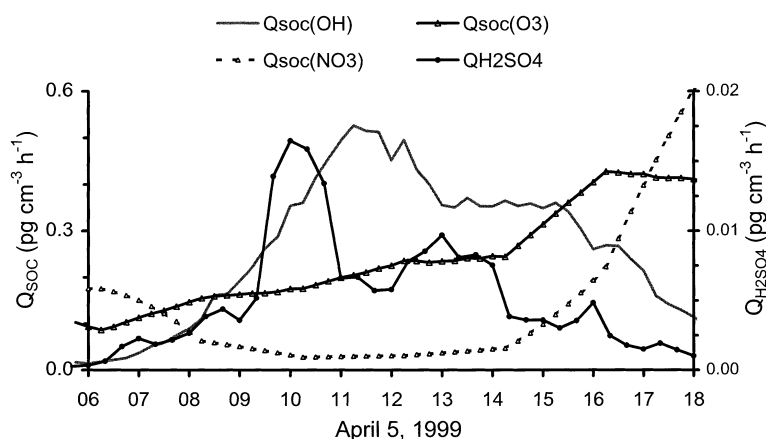


Fig. 10. Source terms ($\text{pg cm}^{-3} \text{h}^{-1}$) for the production of H_2SO_4 ($Q_{\text{H}_2\text{SO}_4}$), scale to the right, and secondary organic compounds ($Q_{\text{SOC}}(\text{OH})$, $Q_{\text{SOC}}(\text{O}_3)$, $Q_{\text{SOC}}(\text{NO}_3)$), scale to the left, during the nucleation event on 5 April 1999. Hyytiälä.

ment of the growth factor as reported by Hämeri et al. (this issue).

4. Summary and conclusions

Field data have been analyzed to investigate the possible links between organic and inorganic gases (monoterpenes, SO_2 , NH_3 , HNO_3) and new particle production, called nucleation events, observed at a forest site in Finland.

Forest emission rates of monoterpenes were found not to be exceptionally high prior to or during the occurrence of events.

Neither the relative composition of the monoterpene emission nor that of the forest concentrations showed significant deviations prior to or during event periods.

Both the concentrations of monoterpenes and the calculated source terms for secondary organic compounds produced from the oxidation of monoterpenes in the forest were slightly higher during event days, although the difference was not strongly significant.

No correlations could be found between the source term (Q_{SOC}) values, average values, or averages of values normalised to aerosol surface area on the one side and ultra-fine particle number concentrations or maxima in ultra-fine particle number concentrations on the other.

The nighttime production of secondary organic

compounds, and thereof probably the production of secondary organic aerosol, was found to be higher than daytime production. This observation, together with the fact that nighttime nucleation events were not observed, as well as the observation that daytime source terms did not correlate to ultra-fine particle concentrations during events, leads us to conclude that the oxidation products of the terpenes were not the nucleating species observed at Hyytiälä.

A correlation between the nocturnal increase in particulate organic carbon mass concentration and the nocturnal Q_{SOC} indicates that monoterpene oxidation products contribute to the secondary organic aerosol by way of condensation. A nocturnal SOA yield of at least 15% is needed to explain the observed increase in particulate organic carbon.

Both the concentrations of SO_2 and the corresponding source term for H_2SO_4 were significantly higher during event periods as compared to non-event periods. The product of the source term and the ammonia concentration was found to correlate to the maxima in ultra-fine number concentrations, implicating SO_2 and NH_3 in the mechanism for nucleation events. The H_2SO_4 source terms were, however, not high enough to account for the entirety of the observed particle growth during events. A substantial part of the growth ought to have occurred through the condensation of secondary organic material from the oxidation of

monoterpenes. A SOA yield of at least 10% would be needed, which is not unreasonable.

In conclusion, we find no evidence in this data set to support the hypothesis that the products from the atmospheric reaction of monoterpenes with $\cdot\text{OH}$, O_3 , and NO_3 , create new particles by gas-to-particle conversion. However, the data do indicate that they contribute significantly to the organic aerosol by way of condensation, and that they are important for the growth of new particles during nucleation events. The strongest argument can be made for SO_2 with the help of NH_3 , as the source of the new particles, but their concentrations are not high enough to account for the observed growth in its entirety.

5. Acknowledgements

We thank the personnel at the SMEAR II station and Hyytiälä Forestry Field Station, and in particular Toivo Pohja, for all their willingful

help. GC-FID and GC-MS analysis of the hydrocarbons was done by Katri Puhto and Ulla Wideqvist of this institute and HPLC analysis of the carbonyl compounds by Vaclav Vesely, also of this institute. Masahiko Shimmo from the University of Helsinki and Peter Tunved of Stockholm University made significant contributions during their stay at our institute, M. Shimmo in the field with the PPD-IC and A-FIA measurements, and P. Tunved in the field and with the evaluation of the BVOC measurements. Nuria Altimir from Helsinki University has supplied us with the SMEAR station cuvette measurements (CO_2 and H_2O exchange) and Petri Keronen, also of Helsinki University with the chemical and meteorological measurements from the mast (O_3 , NO_2 , wind, temperature, radiation). We thank the Stockholm Environmental Agency for lending us the CO_2 instrument. The project was financed by the R&D Programme Environment and Climate, project nr. ENV4-CT97-0405.

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