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Seasonal variations of trace gases, meteorological parameters, and formation of aerosols in boreal forests

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The data from observations made in the Hyytiälä background station over the period 1997–2003 were analyzed in order to investigate the possible links between physical, chemical and meteorological parameters for event and nonevent days during different seasons. The seasonal patterns of average trace gas (O_3, H_2O, $NO_x = NO + NO_2$, SO_2) concentrations, UV-A irradiation intensity, temperature, relative humidity and condensation sink were established and used for evaluating their influence on the seasonal dependence of the formation and growth rates of particles in the nucleation mode. For the forest region at Hyytiälä, an estimate was made on the contribution of the oxidation products of SO_2 and volatile organic compounds (VOCs) by O_3 and OH to the formation and growth of the nucleation mode particles. The condensation sink was shown to play a crucial role in the chemical dynamics of gaseous precursors and aerosol particles. The variability of the sink was attributed mainly to the humidification of the pre-existing aerosol particle population, depending thus strongly on the relative humidity. Our results indicate that the observed growth rate of new particles is connected with condensation of secondary organic compounds originating from the oxidation of terpenes.

Introduction

It has become more and more evident that the nucleation bursts contribute substantially to the production of CCN in the atmosphere and can thus affect the Earth's climate and weather conditions on our planet (Charlson and Heitzenberg 1995). The commonly accepted opinion is that nucleation bursts are connected with an additional production of nonvolatile substances that can then nucleate or condense on foreign nuclei or ions (Weber *et al.* 1997, Kulmala *et al.* 2001a, 2001b, 2004a, Nilsson *et al.* 2001b, Birmili *et al.* 2003). The production of nonvolatile substances, in turn, demands some special conditions concerning the emission rates of volatile organic compounds from plants, chemical composition of the atmosphere, rates of mixing and exchange processes between the lower and upper atmospheric layers, presence of foreign aerosol particles (submicron fraction, first of all) serving as condensation sink, and various interactions taking place in air masses from polluted or clean regions. Such a multitude of very diverse factors, most of which have a stochastic nature, prevents a direct attack on this effect. Phenomenological studies on correlations between various factors affecting the particle formation process and attempts of their systematization are thus of primary importance.

Recent observations provided impressive evidence that the particle formation and growth can be detected in different geographic locations and under quite diverse conditions (Kulmala *et al.* 2004a). A review of observations of ultrafine particles given in Kulmala *et al.* (2004a) showed that the formation rates of 3 nm particles in the boundary layer during regional nucleation events were 0.01–10 cm^{-3} s^{-1}. Typical particle growth rates were between 1 and 20 nm h^{-1}. The smallest reported growth rates, observed in clean polar areas, were around 0.1 nm h^{-1}.

A long-term data set concerning the particle formation events at a continental forest site (Hyytiälä, southern Finland) displays a strong seasonal variation in the number of occurrences of these events, with a maximum during springtime and a minimum in midsummer (Mäkelä *et al.* 2000, Aalto *et al.* 2001, Kulmala *et al.* 2004b). Particle growth rates (GR) during nucleation events in the Hyytiälä forest (Mäkelä *et al.* 2000, Dal Maso *et al.* 2005) as well as in rural (e.g. in Hohenpeisenberg; Birmili *et al.* 2003) and urban (e.g. in St. Louis; Qian 2003) locations have shown a strong seasonal variation with a maximum (GR = 4–17 nm h^{-1}) in summertime and minimum (0.5–2 nm h^{-1}) in winter. The reasons for the seasonal variability of GR are not yet fully understood. This is in particular related to our poor knowledge of the chemical composition of newlyborn particles within the size range 3–10 nm.

Independent of latitude, altitude and degree of pollution, a nucleation burst is a co-operative action of sources and sinks that produces a steady-state aerosol particle population not always visible by the existing instruments (a minimum detectable particle size is > 3 nm, Kulmala *et al.* 2000; on recent development *see* Kulmala *et al.* 2005). Particles with sizes distinguishable by the instruments can appear once a disbalance between the sources and sinks occurs in the atmosphere. The disbalance may have different reasons, including changes in the emission rates of precursor compounds, changes in the concentration of oxidants responsible for the production of nonvolatile compounds, or changes in external parameters (temperature, relative humidity, radiation, convection and advection transfer). For example, regular changes in sinks during the spring–summer period are related to daily variations in the relative humidity (RH), which in turn gives rise to the change in the total surface area of pre-existing aerosol particles and thereby in the condensation sink. Additionally, daily variations in the RH and temperature also change the absolute humidity, which affects the rates of chemical reactions forming the nucleating precursors and low-volatile compounds that are partitioning between the gas and aerosol phase.

Considerable variations in the balance of the source-to-sink ratio can be related to changes in the height of the boundary layer, convective and advective transfer, and changes in the concentration of all gaseous reactants. Air masses transported over polluted areas may contain very reactive pollutants like anthropogenic organic compounds or sulfur oxide. These pollutants can also break the steady-state picture.

Practically all sources and sinks have a seasonal pattern. Seasonal variations in concentrations of volatile organic compounds (VOC) are strongly connected with the biological activity of trees (Suni *et al.* 2003). Concentrations of VOC reach their maximum during the summertime (Hakola *et al.* 1994, 2003), since emissions of the most important biogenic VOCs depend on temperature (isoprene, monoterpenes, sesquiterpenes) and solar radiation intensity (isoprene). Seasonal variations in the wind direction, causing changes in the composition of air masses, are responsible for the opposite seasonal variability between the levels of SO_2 and VOCs.

The sinks of trace gases depend on meteorological conditions: the height of the mixing layer (maximum in summer), losses on surfaces (minimum in winter because of the snow cover) and losses in canopies (maximum in summer). As a result, seasonal variations in the particle formation process can be understood only on the ground of analysis of long-term, complex and simultaneous measurements of physical, chemical and meteorological parameters.

The major goals of this paper are to analyze the influence of trace gas concentrations and meteorological parameters on the seasonal dependencies of the formation and growth rates of particles in the nucleation mode, and to estimate the contribution of the oxidation products of SO_2 and volatile organic compounds to the formation of the nucleation mode in the forest region at Hyytiälä.

The paper is organized as follows. The first part considers the seasonal dependencies of basic physical and meteorological parameters obtained from measurements made at the Hyytiälä station in 2001 separately for event and nonevent days. In the second part the mean diurnal patterns of these parameters are investigated for different seasons of the whole measurement period (1997–2003). In order to be able to investigate the annual variation of formation and growth rates of atmospheric aerosol particles observed in 2001, the concentrations of oxidation products of SO_2 and VOC (monoterpenes) are calculated for this year. The results presented here are based on simultaneous, long-term measurements of different parameters conducted in the same location.

Measurements

Our analysis was based on the measurement data set obtained at the Hyytiälä station (southern Finland) in 1997–2003. The station is located in the extended area of Scots pines dominant forests with the conditions typical for a background location. The boreal forest, in which formation and growth of the smallest aerosol particles occur over large spatial scales, is one of the most important natural sources of biogenic boundary-layer aerosol particles.

Western winds dominated during all the seasons at the Hyytiälä station. More than 25% of the air masses arriving at Hyytiälä originated or passed over the Atlantic and Great Britain (Sogacheva *et al.* 2005). The fraction of air masses coming from the North Atlantic or Arctic was also substantial (20%–25% of air masses annually).

In the frame of this study, we analyzed the data from continuous measurements concerning the spectrum of solar radiation (280–580 nm), different gas (ozone, H_2O, $NO_x = NO + NO_2$, SO_2) concentrations, temperature, relative humidity (RH), wind direction, horizontal and vertical wind velocities and particle number concentration and size distribution. A detailed description of the SMEAR II station and complex instrumentation therein is given in Kulmala *et al.* (2001a).

Because our analyses focused on comparing the variations in physical and meteorological parameters for event and nonevent days, and on understanding their connections, we enumerate the criteria for the classification of the formation events. Particle formation events were classified according to the particle number concentration and the particle formation and growth rate (Mäkelä *et al.* 2000, Dal Maso *et al.* 2005). The nucleation event was considered to belong to the first class if an intense production of particles within the size interval 3–10 nm was observed. The particle growth rate for the events in this class reached 17 nm h^{-1} and the particle number concentration was sometimes over 10^5 cm^{-3}. Events with much less intense particle growth rate (5–7 nm h^{-1}) and ten times lower maximum particle number concentrations were attributed to the second class. Still the measurement of the kinetic characteristics was possible for the events of this type. Weaker events, for which the formation and growth rates could not be determined, were classified to the third class. Finally, there were so-called nonevent days, during which no clear evidence was obtained on newly-born aerosol particles.

Seasonal patterns

Below we consider the seasonal trends of monthly-mean values of meteorological parameters and concentrations of SO_2, NO_x, ozone and H_2O, and compare their variations for both event and nonevent days (Fig. 1).

Ozone, OH, UV-A irradiation and NO_x

Tropospheric ozone plays an important role in particle formation. First of all, ozone is a major source of hydroxyl radical (OH), the primary

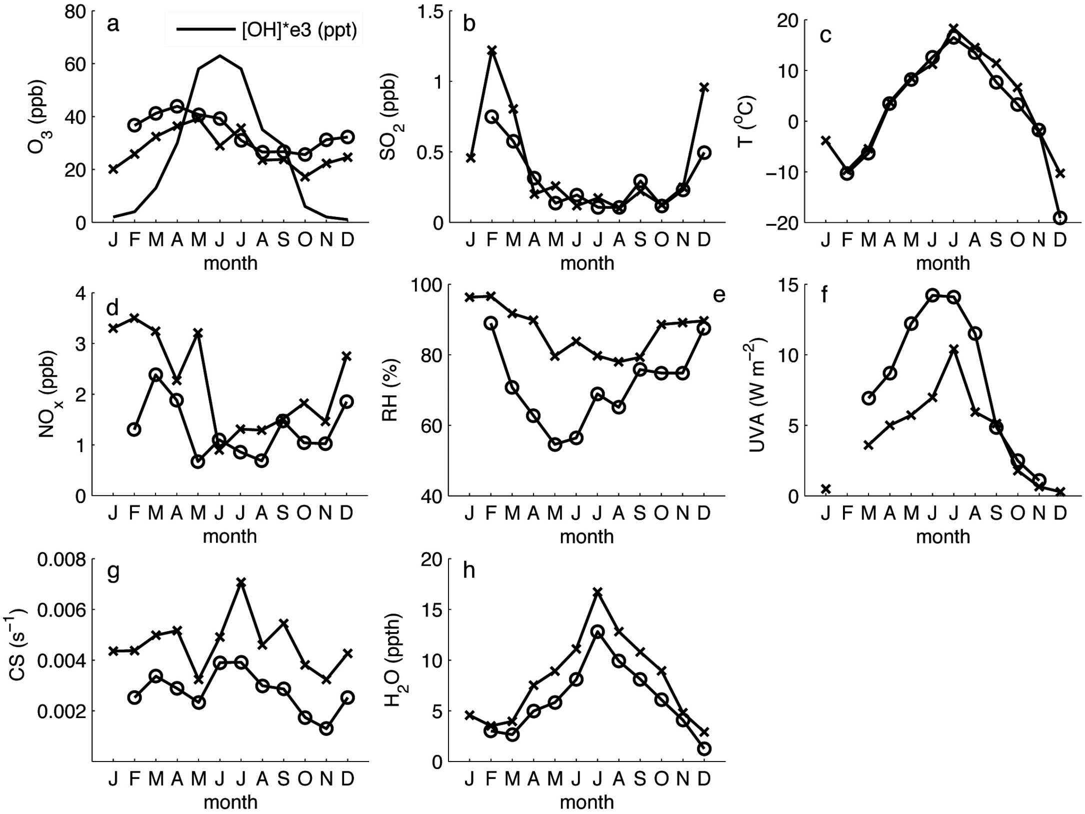

Fig. 1. Seasonal behavior of monthly-mean values of atmospheric parameters for event (empty circles) and non-event days (crosses) in 2001: (**a**) concentrations of O_3 and OH (solid line), (**b**) concentration of SO_2, (**c**) temperature, (**d**) concentration of $NO_x = NO + NO_2$, (**e**) relative humidity (RH), (**f**) short-wave UV-A (320–400 nm) irradiation, (**g**) condensational sink (CS), and (**h**) concentration of water vapor (H_2O). The monthly-mean concentrations of OH were calculated according to Hakola *et al.* (2003).

oxidant of trace gases in the troposphere. Next, ozone actively reacts with many atmospheric trace gases. Since oxidation is the main formation pathway for nucleating vapors and initiates the chemical sinks of atmospheric trace gases, ozone plays an indirect but crucial role in determining the oxidation potential of the atmosphere and the lifetime of many trace gases. The formation of OH is related to ozone photolysis via the following chain of reactions:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (1)$$

$$O(^1D) + H_2O \rightarrow OH. \quad (2)$$

The hydroxyl radical then interacts with SO_2 and VOC to produce low- or semi-volatile compounds. The oxidation of reactive VOCs by ozone is generally assumed to lead to the formation of low-volatile compounds (LVOC-O_3) such as dicarboxylic acids.

The typical concentration of OH radicals is low (10^6–10^7 cm^{-3}) and the rate of its production depends essentially on the rate of ozone photolysis and is therefore determined by the concentration of ozone. Equations 1 and 2 give the production rate of O(^{1}D), I[O(^{1}D)]:

$$I[O(^1D)] = \alpha I_{UV-A}[O_3]. \quad (3)$$

Here α is the reaction rate constant in Eq. 1 and I_{UV-A} is the short wave solar irradiation intensity (300–340 nm). Then, to the first approximation, the production rate of OH and thus the production rate of low-volatile vapors are related to the UV-A irradiation, total water vapor concentration and ozone concentration. During winter when $I_{\text{UV-A}}$ is extremely low, hydrogen radicals can be produced from the reaction of biogenic VOC with ozone (Paulson *et al.* 1998).

In the lower layer of the atmosphere two sources of ozone exist: the transport of ozone from upper layers and ozone production in intra-atmospheric chemical cycles. Ozone production depends on the concentrations of biogenic VOCs emitted by vegetation (Fuentes *et al.* 2000), anthropogenic VOCs and NO_x, as well as on the ratio between NO_x and VOC concentrations. Ozone sinks in forest regions are mainly determined by the stomatal uptake, deposition onto non-stomatal surfaces and ozone destruction in gas-phase chemical reactions.

The maximum monthly-mean ozone concentration at Hyytiälä was observed in April–May (spring), while minimum concentrations were seen in January and October (Fig. 1a). The observed springtime maximum of the ozone concentration is a typical feature for high latitudes, being linked to the substantial intrusion of O_3 by ozone enriched air from the upper layers of the troposphere peaking in early spring and photochemical production of ozone peaking in late spring and summer (Jenkin and Clemitshaw 2000). In summer the photochemical production of ozone in forest regions is related closely to high VOC emission. However, ozone losses in summer are increased considerably by the larger height of boundary layer, enhancement of mixing and increased ozone deposition due to the stomatal activity and dry deposition onto the canopy. The overall ozone concentration was lower in summer than in spring. As a rule, the concentration of ozone in the event days was higher than in nonevent days throughout the year.

The seasonal pattern of OH concentration is related closely to the variations in UV-A irradiation and ozone concentration. The monthly-mean maximum OH concentrations were observed in May–July, while the respective minimum concentrations were observed in November–January (Fig. 1a). This explains why the average OH concentration changed by a factor of 60 from 0.001–0.002 ppt in winter to 0.068 ppt in summer (Hakola *et al.* 2003).

The UV-A irradiation was higher during the event days for all seasons except for autumn when very little difference between the event and nonevent days was observed (Fig. 1f). The seasonal pattern of nitrogen oxide concentration was closely linked to that of OH (Fig. 1d). Increased concentrations of NO_x during the winter reflect the slower rates of photochemical oxidation reactions connected with the decreased OH concentrations of about an order of magnitude (Spivakovsky *et al.* 1990, Goldstein *et al.* 1995).

The concentration of NO_x was lower on event days compared with that on nonevent days throughout the year, being indicative of an enhanced photochemistry and intensified oxidation reactions during the event days. These reactions form compounds other than NO and NO_2, especially in winter and in May when the NO_x concentrations on event days were lower by a factor of 2–4 as compared with those on nonevent days.

SO_2 concentration

The highest monthly-mean sulfur dioxide concentrations were observed in winter, usually in February and December, whereas the lowest concentrations were observed in summer (Fig. 1b). This behavior is most likely related to wind directions, air masses and height of the mixing layer. In winter the boundary layer is shallow and convective mixing is weak. The shallow boundary layer in winter has a depth of about a half of that in summer (Holzworth 1967). In addition, the snow and ice cover may slow down the dry deposition of gases, leading to higher measured concentrations of SO_2 (Barrie *et al.* 1986, Barrie and Platt 1997, Ruuskanen *et al.* 2003). In summer the low concentrations of SO_2 can be explained by cleaner air masses from less polluted regions, by large losses of this gas due to its deposition onto the surface, by the increase in the height of mixing layer, by smaller emissions and by the consumption of SO_2 in chemical cycles.

In winter the concentration of SO_2 was lower on event days, being a result of either its reduced source rate or its intense loss by oxidation in atmospheric chemical cycles. During other seasons no significant differences in SO_2 concentrations between the event and nonevent days were observed.

Relative humidity and temperature

According to Weber *et al*. (1997), the ultrafine particle concentration and RH are negatively correlated (the correlation coefficient $r = -0.42$) at clean continental sites. At both Idaho Hill and Mauna Loa, aerosol formation was observed to take place at relative humidities as low as 30%. Similar results were obtained from Värriö (Vehkamäki *et al*. 2004), in which the RH was lower during event days than during nonevent days, except for the winter months when no clear difference in the RH between the event and nonevent days was observed.

Throughout the year, the RH was lower during the event days compared with that during nonevent days (Fig. 1e). The lowest nonevent-day values of RH were observed in April, May and June when the RH did not exceed 60%. In winter, particle formation events took place at the highest values of RH (~90%), but only a slight difference in the RH between event and nonevent days was observed. The influence of RH on the processes of particle formation can be connected via the positive correlation between the total particle surface area and relative humidity. This could result from an increase in particle hydration with increasing RH, which leads to larger particle surface areas and thereby larger condensation sinks.

In winter, the temperature was usually much lower on event days compared with that on nonevent days (Fig. 1c). In January–February the nucleation events occurred at temperatures < 20 °C, which is much below the mean temperature for these months. This fact is not so surprising, since the saturation vapor pressure of condensing vapors decrease exponentially with decreasing temperature. In spring and autumn temperature differences between event and nonevent days were small.

Condensational sink

The condensational sink (CS) determines the rate at which gaseous molecules are lost by condensation onto the surfaces of pre-existing aerosol particles. It can be calculated from

$$\mathrm{CS} = 4\pi D \int_0^\infty r\beta(r)n(r)dr, \qquad (4)$$

where r is the particle radius, $n(r)$ is the particle size distribution, D is the diffusion coefficient of the condensing species, and $\beta(r)$ is the Fuchs-Sutugin transition correction (Kulmala *et al.* 2001b, Dal Maso *et al*. 2005).

The condensation sink was calculated from measured aerosol size distributions for the year 2001. The value of CS (Fig. 1g) was lower in event days than in nonevent days throughout the year (Fig. 1g). The largest CS's were observed in June and July (CS = 7×10^{-3} s^{-1}) and the smallest ones in February, May and November (CS = 2×10^{-3} s^{-1}). The CS in the event days was approximately half of that in nonevent days.

Monthly-mean H_2O concentration

Throughout the year, the concentration of water molecules was lower on days with new particle formation as compared with that on nonevent days (Fig. 1h; *see* also Boy and Kulmala 2002, Boy *et al*. 2003). The smallest monthly-mean water vapor concentrations were observed in December, February and March. In summer (June–July) the concentration of water vapor reached the highest values when the particle formation rate was at its minimum. This fact agrees well with the data of Buzorious *et al*. (2003) who showed that nucleation rates increased with decreasing ambient water vapor concentration. At Hyytiälä a negative correlation ($r = -0.9$) between the absolute water content and particle formation probability in spring time was found (Buzorius *et al*. 2003). The laboratory experiments of Bonn *et al*. (2002) showed that the particle number concentration decreased with increasing water vapor concentration during the ozonolysis of both exocyclic (e.g. β-pinene, sabinene) and endocyclic (e.g. α-pinene, Δ^3-carene) monoterpenes. The authors observed a strong impact of water vapor content on exocyclic reactions even at very high monoterpene concentrations far above ambient conditions. The presence of water vapor led to suppression of nucleation in the laboratory. A similar but weaker influence of water was observed for endocyclic reactions.

This effect was not found for other oxidation reactions of monoterpenes with OH and NO_3 (Bonn and Moortgat 2002). However, according to the data of Spanke *et al*. (2001) and Hakola *et al*. (2003), the production of exocyclic terpenes was less than 25% of that of all terpenes over the Hyytiälä forest. The remaining 75% were endocyclic monoterpenes (α-pinene and Δ^3-carene).

Diurnal patterns

Here we consider the diurnal, hourly-average concentrations of trace gases for event and nonevent days. Similar dependencies of the meteorological parameters are also presented. Averaging was done over the whole measurement period at Hyytiälä station from 1997 to 2003.

Winter

The specific feature of the winter season was the small number of events. The average particle production rates for the events were equal to 0.21–0.45 cm^{-3} s^{-1}, the average growth rate being 2.21–2.68 nm h^{-1} (Mäkelä *et al*. 2000, Kulmala *et al*. 2004c). The nucleation mode in boreal forests at Hyytiälä was investigated by Kulmala *et al*. (2004b) whose analyses used the data set for five winters (1996–2001). No aerosol formation events were observed in December due to a lack of solar radiation and therefore lack of OH. A remarkable feature of events in January and February was the high relative humidity (RH = 77%–97%), low temperature (from –24 °C to –8 °C) and low condensation sink (CS = 2×10^{-4}–2×10^{-3} s^{-1}). However, from the daily patterns it can be seen that in winter period trace gas concentrations and relative humidity were high and temperature and radiation were low in all days (Fig. 2).

The average monoterpene concentration reached 97 ppt in winter, the main components of the monoterpenes being α- and β-pinene and Δ^3-carene (Hakola *et al*. 2003). The high monoterpene concentrations in winter can be explained by small but existing emissions and long atmospheric lifetimes. According to model estimates, the lifetime of α-pinene due to its reaction with the hydroxyl radical is 50 times longer in winter than in summer (Hakola *et al*. 2003).

The small number of nucleation events in winter was probably related to the deficiency of UV-A irradiation and ozone necessary for the formation of hydroxyl radicals, especially since the concentration of SO_2 was usually high. Low ozone concentrations and the absence of diurnal dynamics in winter can be explained by the stable inversion situation that suppresses the vertical mixing at this time of year, as well as by the decreased intrusion of ozone into boundary layer. In contrast, SO_2 concentrations increase in the boundary layer during the winter in the absence of strong mixing.

Ozone concentrations in winter were much higher (by 30%) during the event days as compared with those during nonevent days. The observed low temperatures and water contents indicate that the air masses arriving at our measurement site during the event days could have originated from or passed over high latitudes. Nilsson *et al*. (2001a) and later Sogacheva *et al*. (2004) found out that the new-particle formation events occurred predominantly in arctic and polar air masses that are typically colder, cleaner and drier than continental air masses. A diurnal pattern in the SO_2 concentration appeared regularly during the event days, showing a minimum at 12:00–18:00. This minimum was well-correlated with the maximums in PAR, UV-A irradiation and temperature as well as with the minimum in the relative humidity.

The factors that limited the formation of the nucleation mode in winter were the small amount of UV-A irradiation and low concentrations of O_3 and OH. On the other hand, high values of RH and concentration of SO_2 together with very low temperatures and CS provided favorable conditions for the particle formation.

Spring

The maximum frequency of event days was observed in spring when the particle growth rate was 2–5 nm h^{-1} and average particle formation rate was 6.5×10^{-1} cm^{-3} s^{-1} (Kulmala *et al*. 2004a, 2004b, Dal Maso *et al*. 2005).

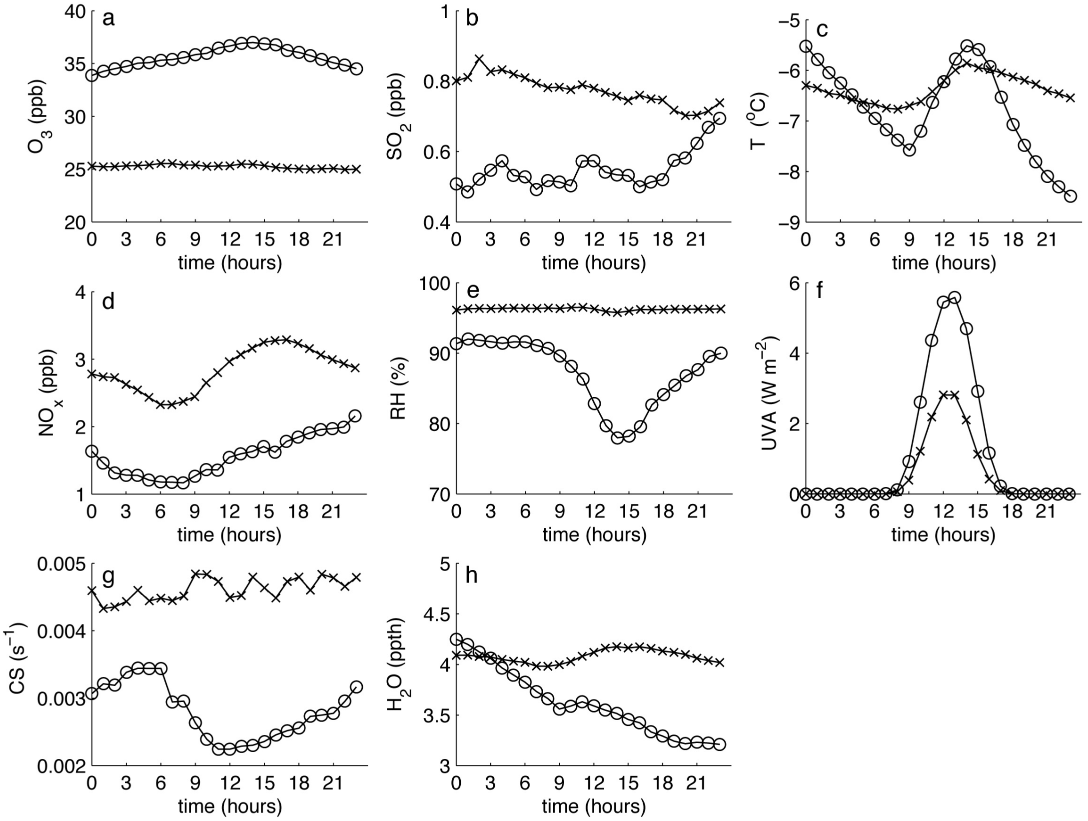

Fig. 2. Mean winter diurnal profiles of atmospheric parameters for event (empty circles) and nonevent days (crosses) in 1997–2003: (**a**) concentration of O_3, (**b**) concentration of SO_2, (**c**) temperature, (**d**) concentration of $NO_x = NO + NO_2$, (**e**) relative humidity (RH), (**f**) short-wave UV-A (320–400 nm) irradiation, (**g**) condensational sink (CS), and (**h**) concentration of water vapor (H_2O).

The beginning of the spring is accompanied by an increase in the UV-A irradiation, temperature and ozone concentration (Fig. 1). In contrast to winter months when no diurnal variations in *T*, RH and concentrations of H_2O and ozone were observed, clear diurnal patterns in these quantities were observed in spring (Fig. 3). Emissions of volatile organic carbon compounds increase due to the spring plant recovery and beginning of the photosynthetic process (Suni *et al.* 2003). At increasing temperatures, the emission potential of the monoterpenes grows in spring by a factor of 5–8 as compared with that in winter (Hakola *et al.* 2003). In spring the dominating monoterpene is Δ^3-carene (50%–80% of emissions) and the rest of monoterpene emissions is composed of α-pinene, β-pinene, terpinolene and β-phellandrene. The potential appearance of sesquiterpenes is important, since their oxidation products have a high potential to form secondary organic aerosol (Hoffman e*t al.* 1997, Bonn and Moortgat 2003). The lifetime of sesquiterpenes is generally shorter than two minutes during nucleation events with a minimum during spring and maximum during summer (Fig. 4).

The formation of the nucleation mode was accompanied by a decrease in SO_2 and NO_x concentrations. The maximum consumption of these gases was observed at 14:00–16:00 when a minimum in RH (43%) and maximum in O_3 concentration (47 ppb) were observed.

The average concentration levels of trace gases were much lower during the event days as compared with those during the nonevent days, whereas temperature, O_3 concentration and UV-A irradiation were considerably higher during the

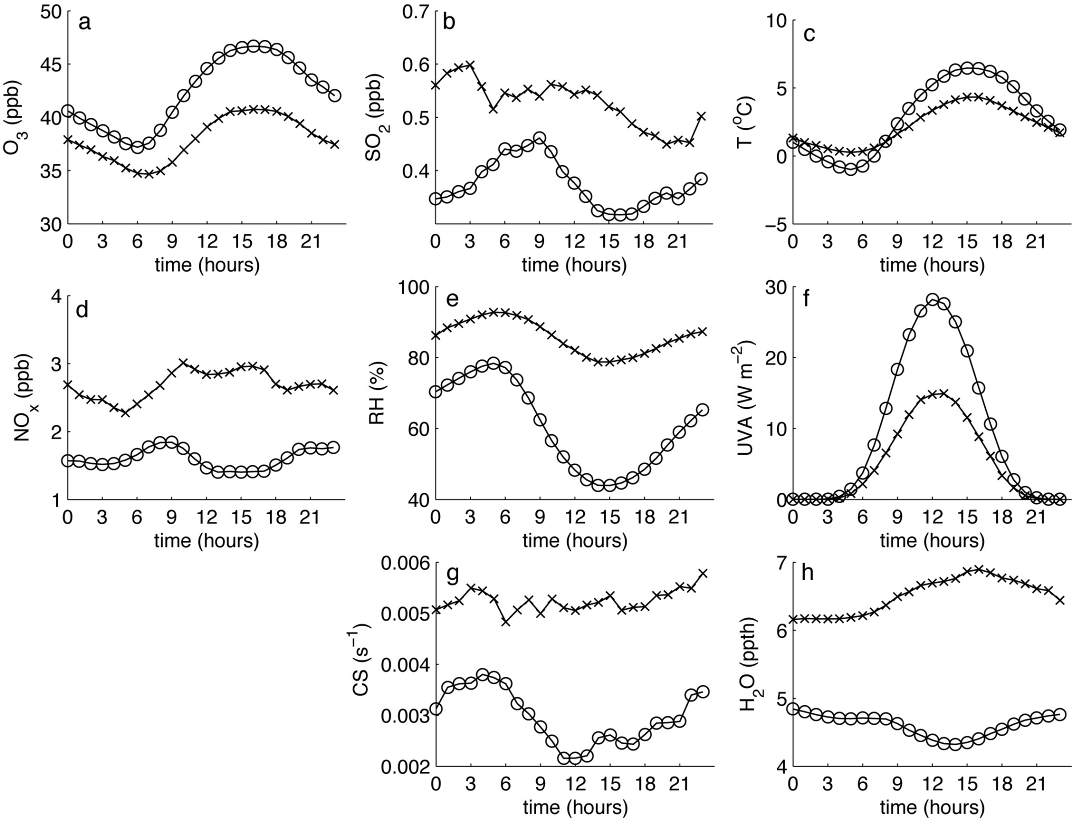

Fig. 3. Mean spring diurnal profiles of atmospheric parameters for event (empty circles) and nonevent days (crosses) in 1997–2003: (**a**) concentration of O_3, (**b**) concentration of SO_2, (**c**) temperature, (**d**) concentration of NO_x = NO + NO_2, (**e**) relative humidity (RH), (**f**) short-wave UV-A (320–400 nm) irradiation, (**g**) condensational sink (CS), and (**h**) concentration of water vapor (H_2O).

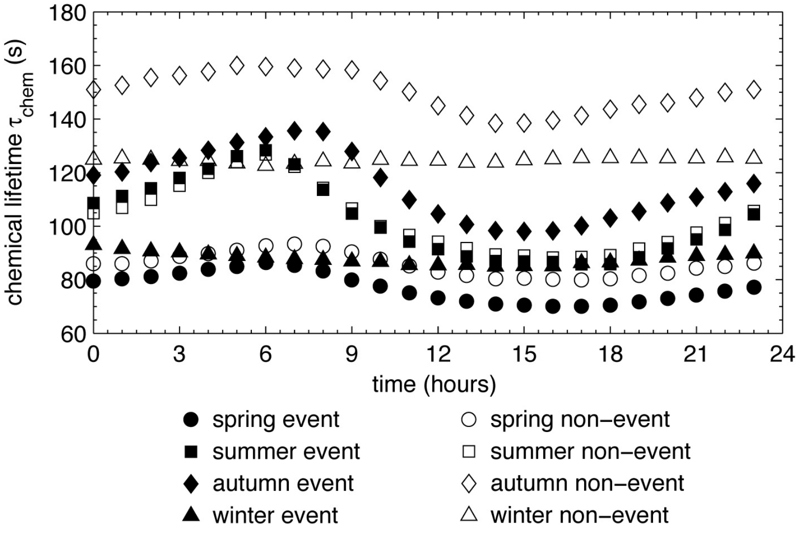

Fig. 4. Effect of ozone on the chemical lifetime of *β*-caryophyllene (sesquiterpene) for event and non-event days.

nonevent days. The ozone concentration showed a midday maximum, reflecting the entrainment of elevated ozone concentrations from aloft and influence of photochemical ozone production.

A sharp difference in the daily variability of RH between the event and nonevent days with respective minimum RH of 40% and 80%–90% was observed. On the nonevent days the high relative humidity stimulated the hygroscopic growth of pre-existing aerosol particles, which led to large values of the condensation sink ($CS = 5 \times 10^{-3}$ s^{-1}) preventing the formation of the nucleation mode. On the event days RH decreased during the daytime from 75% to 40%, such that the condensational sink decreased from 4×10^{-3} s^{-1} to 2×10^{-3} s^{-1}. In spring, therefore, new-particle formation was observed under the conditions of a maximum daytime temperature, high ozone concentration, high UV-A irradiation and very low relative humidity (40%). The diurnal behavior of CS was well-correlated with that of RH, which suggests that the value of CS was determined partly by the influence of RH on the pre-existing particle surface area.

Summer

During summer the frequency of nucleation events was low but the particle growth rate reached its maximum value of 5–17 nm h^{-1} (Kulmala *et al*. 2004b, 2004c, Dal Maso *et al*. 2005). Similar findings have been reported for other locations. In many cases nucleation and subsequent particle growth have been considered to be uncoupled under atmospheric conditions (Weber *et al*. 1997, Kulmala *et al*. 2000, 2004a, Janson *et al*. 2001, Birmili *et al*. 2003). The observed growth rates of nucleated particles cannot be usually explained by the condensation of sulfuric acid and associated inorganic compounds (H_2O and NH_3). Organic compounds having a very low saturation pressure are the most likely candidates for the growth of these particles.

Let us consider the links between the measured parameters from this point of view. Very low concentrations of SO_2 (0.2–0.1 ppb) and NO_x (0.7–0.3 ppb) were encountered in summer, whereas the values of UV-A irradiation, T and RH reached their maxima (Fig. 5). A high temperature and irradiation enhances substantially VOC emissions. The monthly-mean monoterpene concentration reached its maximum (0.25 ppb) in July and August. The main constituents of the monoterpenes in summer were α-pinene (0.1 ppb) and Δ^3-carene (0.06 ppb). In addition, the isoprene concentration began to grow in the beginning of June, whereas the maximum monthly-mean concentration of isoprene (0.1 ppb) was observed in July (Hakola *et al*. 2003). The maximum VOC emissions coincided with minimum SO_2 concentration levels.

The very high particle growth rates during the summer can probably be explained by the high VOC concentrations, effective conversion VOCs to non-volatile oxidized organic precursor and by the high values of T, UV-A irradiation and PAR. Nucleated particles were able to reach the Aitken or even accumulation size range in summer, but the concentration of nucleation mode particles was very large due to high VOC emissions, as has been suggested by model simulations (Pirjola 1999).

High observed water vapor concentrations can suppress the nucleation activity of VOCs. In summer, nucleation events occurred on days when the water vapor concentration was lower by 30%–40% compared with that on nonevent days. Similarly, the value of CS in event days was only half of that in nonevent days. A sharp decrease in the particle formation rate and increase in the product volatility due to the ozonolysis of monoterpenes with the increasing of the absolute water content has been demonstrated by Bonn *et al*. (2002). If compounds affecting new particle formation and growth originate significantly from sesquiterpenes, the oxidation of which is caused almost exclusively by ozone (Bonn and Moortgat 2003), the effect of water vapor is also involved in chemical reaction pathways.

Autumn

In autumn a second maximum in the frequency of formation events was often observed (Kulmala *et al*. 2004a, 2004b, Dal Maso *et al*. 2005). The observed particle growth rates of 3–5 nm h^{-1} can be attributed to the high concentrations of monoterpenes measured during this period. The

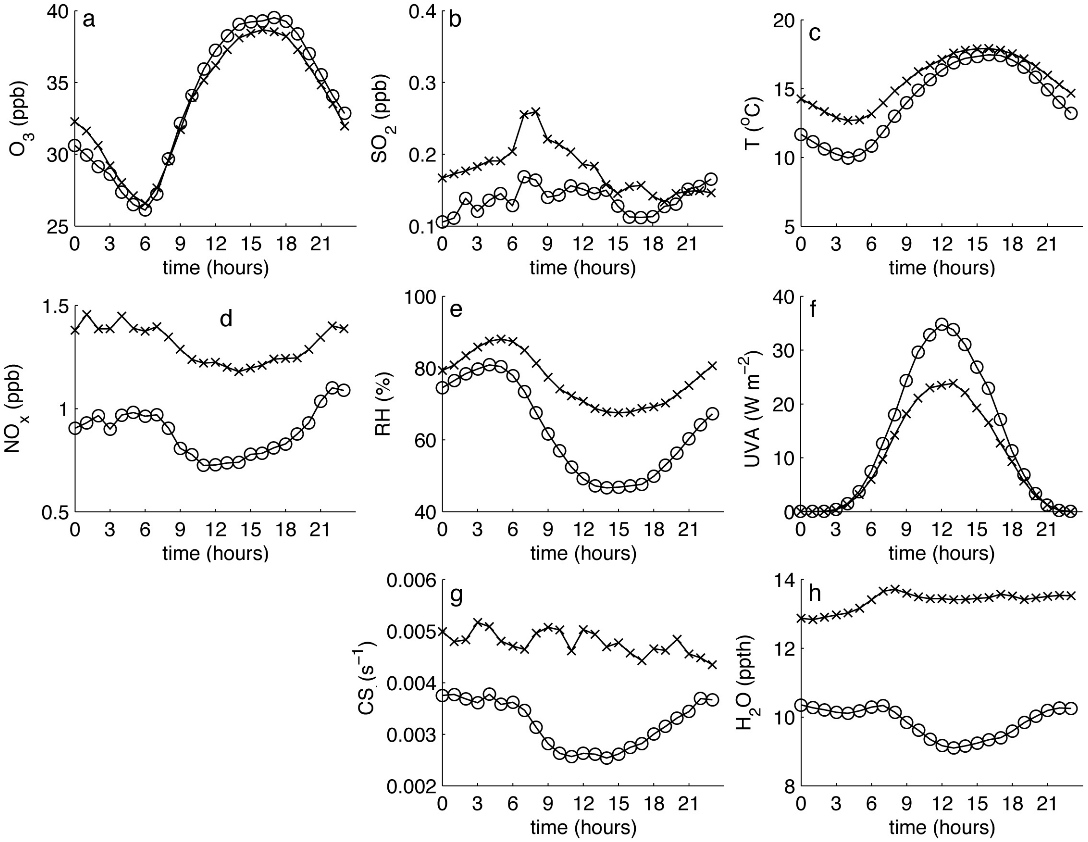

Fig. 5. Mean summer diurnal profiles of atmospheric parameters for event (empty circles) and nonevent days (crosses) in 1997–2003: (**a**) concentration of O_3, (**b**) concentration of SO_2, (**c**) temperature, (**d**) concentration of $NO_x = NO + NO_2$, (**e**) relative humidity (RH), (**f**) short-wave UV-A (320–400 nm) irradiation, (**g**) condensational sink (CS), and (**h**) concentration of water vapor (H_2O).

monthly-mean concentrations of monoterpenes in autumn were similar to those in summer (0.25 ppb, Hakola *et al.* 2003). The monoterpene composition did not differ strongly from that detected in summer.

The UV-A irradiation and temperature were higher on event days than on nonevent days (Fig. 6). The ozone concentration increased by 40% and CS decreased by 50% on event days. It is important that the diurnal pattern of CS did not coincide with that of RH. A maximum decrease in the value of CS was observed at 05:00–09:00 when RH remained approximately constant. It is worth to note that during autumn SO_2 concentrations reached their maximum during the morning hours indicating a downward transport from the free troposphere, followed by a decrease during the day.

Low-volatile vapors

Although considerable efforts have been undertaken in order to understand secondary aerosol formation, there is still no model that would correctly describe the particle formation and growth processes in a variety of the atmospheric conditions. The existing model calculations have related the formation of new particles to sulfuric acid originating from SO_2 oxidation, whereas the growth of these particles has been explained partly by sulphuric acid condensation and partly by the condensation of nonvolatile organic vapors (Kulmala *et al.* 2000a, 2004a, Korhonen *et al.* 2004).

The primary factor defining the particle formation and growth rate is the total concentration of nonvolatile vapors. Potential candidates for

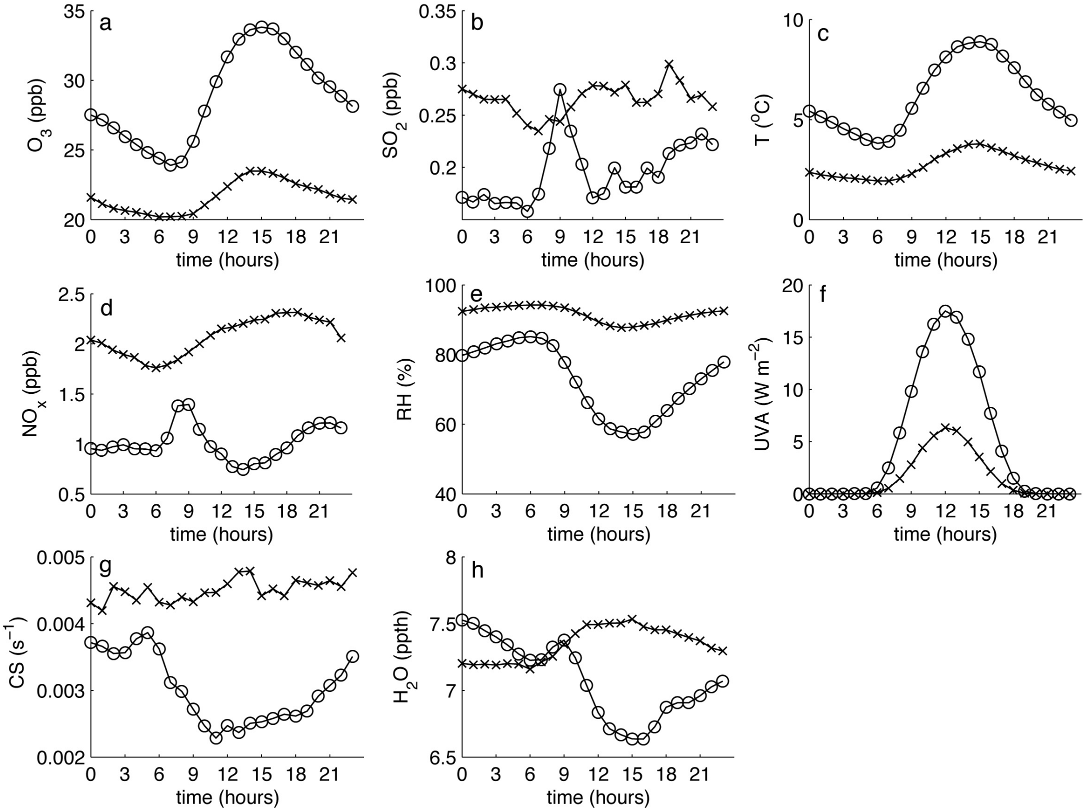

Fig. 6. Mean autumn diurnal profiles of atmospheric parameters for event (empty circles) and nonevent days (crosses) in 1997–2003: (**a**) concentration of O_3, (**b**) concentration of SO_2, (**c**) temperature, (**d**) concentration of NO_x = NO + NO_2, (**e**) relative humidity (RH), (**f**) short-wave UV-A (320-400 nm) irradiation, (**g**) condensational sink (CS), and (**h**) concentration of water vapor (H_2O).

such vapors are sulfuric acid and some as yet unidentified organic compounds formed by various oxidation reactions involving either SO_2 or VOCs (Kerminen *et al.* 2000). Nonvolatile vapor concentrations are expected to be positively correlated with the precursor gases and oxidants (hydroxyl radicals, ozone, nitrate radicals) and negatively correlated with the pre-existing aerosol particle concentration. The nucleation rate and particle growth rate are both expected to be positively correlated with the nonvolatile vapor concentration.

As for the gaseous precursors, the main yet unresolved question is the relative roles of SO_2 and VOCs (terpenes) in the gas-to-particle conversion process.

Sources producing secondary organic compounds (SOC) and H_2SO_4 are defined by the reactions of the precursor gases with the atmospheric oxidants (Atkinson 1997, Weber *et al.* 1997, Janson *et al.* 2001):

$$\begin{aligned} Q_{\mathrm{SOC}} &= \sum k_i[\mathrm{OH}]_3 \times [\mathrm{terp}]_i \\ &+ \sum k_i[\mathrm{O}\ \,] \times [\mathrm{terp}]_i \qquad (5) \\ &+ \sum k_i[\mathrm{NO}_3] \times [\mathrm{terp}]_i \end{aligned}$$

$$Q_{\mathrm{H2SO4}} = k_i[\mathrm{OH}] \times [\mathrm{SO}_2]. \qquad (6)$$

Here Q_{SOC} is the source term for SOC from the oxidation of monoterpenes, Q_{H2SO4} is the source term for H_2SO_4 from the oxidation of SO_2, k_i's are respective temperature dependent reaction rate constants, and $[\mathrm{terp}]_i$ includes the concentrations of α-pinene, β-pinene, Δ^3-carene and so on.

Monoterpene reactions with O_3 produce compounds with the lowest volatility among the three possible oxidation reactions. Reactions with the OH-radical produce primary carbonyl compounds, such as pinonaldehyde in the case of α-pinene (Hatakeyama *et al.* 1989, Arey *et al.* 1990, Hakola *et al.* 1994, Hofmann *et al.* 1997). The carbonyl compounds are not important in nucleation process directly because of their high saturation vapor pressures (Atkinson *et al.* 1997, Griffn *et al.* 1999, Noziere *et al.* 1999).

In order to estimate the possible contribution of different compounds to the formation and growth rate of nucleation mode particles during different seasons, we calculated the source rates and concentrations of gaseous H_2SO_4 and oxidation products of monoterpenes by O_3 (LVOC-O_3) and OH (LVOC-OH). The obtained source rates and concentrations were then compared with the monthly-mean formation and growth rates of nucleation mode particles. This was done for the year 2001, for which the seasonal VOC concentration measurements are available. In the calculations we used the monthly-mean concentration of O_3, OH and SO_2 (Fig. 1). The seasonal variation in the concentrations of monoterpenes, including α-pinene, β-pinene and Δ^3-carene, were taken from Hakola *et al.* (2003). The concentration of sulfuric acid was calculated using a steady-state approximation, i.e., we assumed that the primary removal mechanism for sulfuric acid is condensation onto pre-existing aerosol particles. In this case the concentration of sulfuric acid is

$$[\mathrm{H_2SO_4}] = \frac{k_i[\mathrm{OH}]\times[\mathrm{SO_2}]}{\mathrm{CS}}. \tag{7}$$

The values of CS were taken from measurements (Fig. 1) and $k_i = 8.5 \times 10^{-13}$ cm^3 s^{-1}. The concentrations LVOC-O_3's were calculated with a similar procedure by assuming the rate constants (k_i) of 86.6×10^{-18} cm^3 s^{-1}, 15×10^{-18} cm^3 s^{-1} and 37×10^{-18} cm^3 s^{-1} for the reaction of ozone with α-pinene, β-pinene and Δ^3-carene, respectively (Atkinson *et al.* 1997). The oxidation product yield of the ozonolysis of monoterpenes was taken to be 10%. The seasonal behavior of monthly-mean temperature, defining the temperature dependence of all reaction rates, was taken from measurements (Fig. 1c).

In calculating the source rate and the concentrations of LVOC-OH, we used the rate constants (k_i) of 53.7×10^{-12} cm^3 s^{-1}, 78.9×10^{-12} cm^3 s^{-1} and 88×10^{-12} cm^3 s^{-1} for the reaction of OH with α-pinene, β-pinene and Δ^3-carene, respectively (Atkinson *et al.* 1997). The oxidation product yield was taken to be 100%. Analogous products were calculated for isoprene in summer when the isoprene concentration was at its maximum (96 ppb) (Hakola *et al.* 2003). The rate constant of the isoprene-OH reaction is 1.0×10^{-10} cm^3 s^{-1} (Atkinson *et al.* 1997). The temperature dependencies of all the above reactions (the Arrhenius parameters) were taken from Atkinson (1994).

No clear difference in the seasonal behavior of the source rates of H_2SO_4 and LVOC-O_3 between the event and nonevent days were observed (Fig. 7). The concentration of nucleation-mode particles had two maxima, one in spring and the other in late summer coincident with the maximum in the sulfuric acid source. During midsummer the concentration of nucleation mode particles was very low.

The consideration of CS needed to determine the concentrations of condensable products changed the seasonal patterns essentially (Fig. 8). The concentrations of sulfuric acid and LVOC-O_3 were considerably higher for the event days as compared with those for nonevent days. The concentration of LVOC-O_3 exceeded the concentration of sulfuric acid by a factor of 3–5. The sharp difference in LVOC-O_3 concentrations between the event and nonevent days in autumn can also be explained by the variations in the magnitude of CS (Fig. 1g).

The annual patterns of the LVOC-O_3 concentration and nucleation mode particle concentration differed sharply from each other. The maximum LVOC-O_3 concentrations were observed in autumn when the particle formation rates were very low. The absence of a correlation between the LVOC-O_3 and nucleation mode particle concentrations at Hyytiälä confirms the results of Bonn and Moortgat (2003). They showed, using the laboratory data of Koch *et al.* (2000), that the individual monoterpenes have a high nucleation threshold (above 2 ppb). Since the total monoterpene concentration was always below that threshold, we conclude that monoterpenes are not able to produce new atmospheric particles at Hyytiälä. However, the recent measurements of the endocyclic sesquiterpene β-caryophyllene at Hyytiälä (Hakola *et al.* 2003) indicates that its concentration is high enough to make it a potential nucleation precursor due to its relative low nucleation

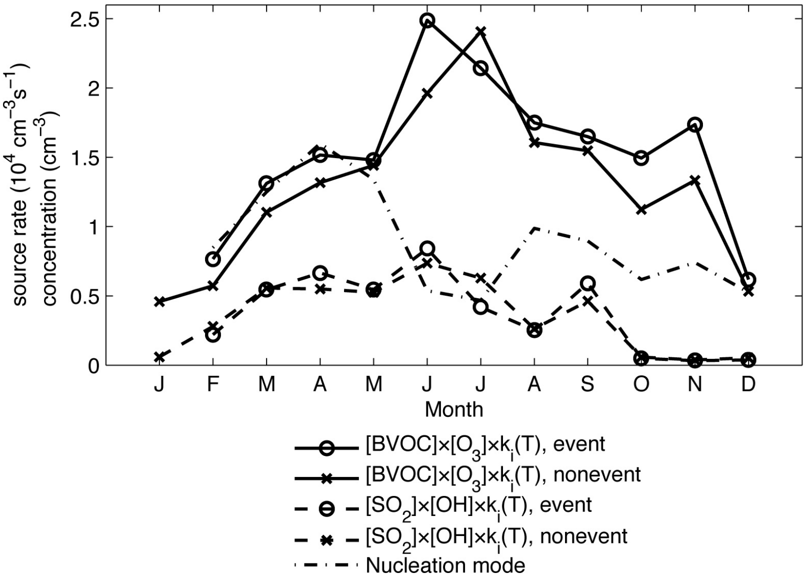

Fig. 7. Seasonal behavior of the nucleation mode (3–25 nm) particle concentration and the source rates of H_2SO_4 and LVOC-O_3 for event and nonevent days in 2001. The concentration of nucleation mode particles (cm^{-3}) is the monthly-mean value for event days in 2001. [BVOC], [O_3], [SO_2] and [OH] are the monthly-mean concentrations of monoterpenes (α- and β-pinene, Δ^3-carene), O_3, SO_2 and OH, respectively, and $k_i(T)$'s are the temperature-dependent rate constants. The oxidation product yield of the ozonolysis of monoterpenes was taken to be 10%.

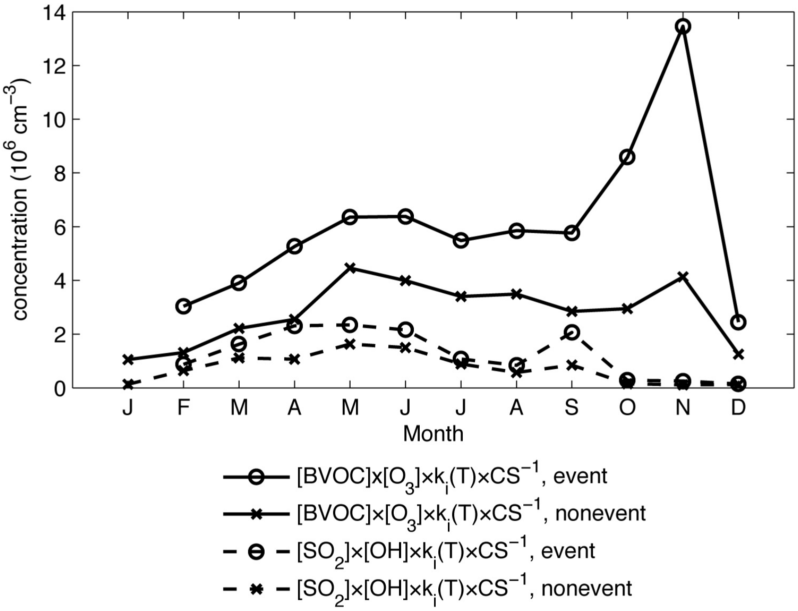

Fig. 8. Seasonal behavior of H_2SO_4 and LVOC-O_3 concentrations for event and nonevent days in 2001. [BVOC], [O_3], [SO_2] and [OH] are the monthly-mean concentrations of monoterpenes (α- and β-pinene, Δ^3-carene), O_3, SO_2 and OH, respectively, $k_i(T)$'s are the temperature-dependent rate constants and CS is the condensation sink. The oxidation product yield of the ozonolysis of monoterpenes was taken to be 10%. The monthly-mean concentrations of OH were calculated according to Hakola *et al.* (2003).

threshold (Bonn and Moortgat, 2003).

The seasonal pattern of the source rate (Fig. 9) and the concentration of monoterpenes oxidation products by OH (LVOC-OH) (Fig. 10), the main presumed participants in the particle growth, displayed sharp maxima in summer. For the event days the concentration of LVOC-OH was higher, which is especially well manifested in summer. This can be compared with the recent growth rate data by Dal Maso *et al.* (2005). Both data sets showed a similar annual behavior.

By using the monthly-mean concentration of oxidized monoterpenes (Fig. 10), we can estimate the growth rate of newly-born particles due to the condensation of the oxidation products onto the particle surface. Indeed, in the free-molecule regime

$$\mathrm{GR} = \frac{\pi v_{\mathrm{T}} \rho}{4\rho_{\mathrm{l}}}, \qquad (8)$$

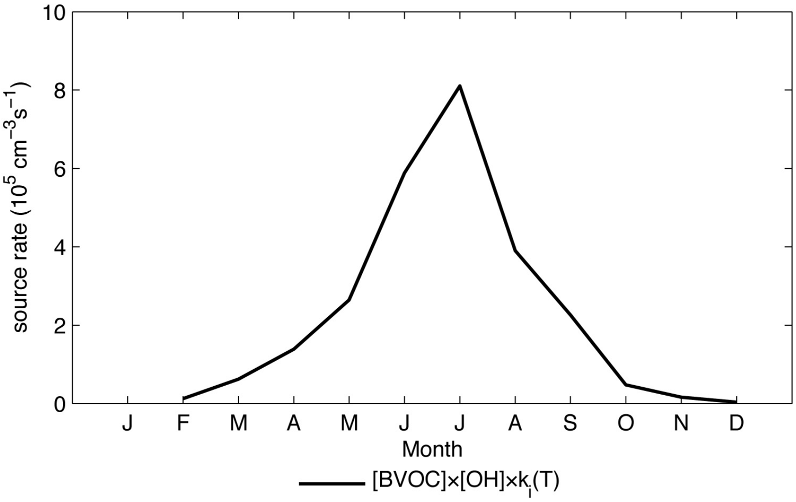

Fig. 9. Seasonal behavior of the source rate of the monoterpene (α- and β- pinene, Δ^3-carene) and isoprene oxidation products from their reaction with OH in 2001. [BVOC] represents the monthly-mean concentration of monoterpenes (α- and β-pinene, Δ^3-carene) and isoprene, [OH] is the monthly-mean OH concentration and $k_i(T)$'s are the temperature-dependent rate constants. The monthly-mean concentrations of OH were calculated according to Hakola *et al.* (2003).

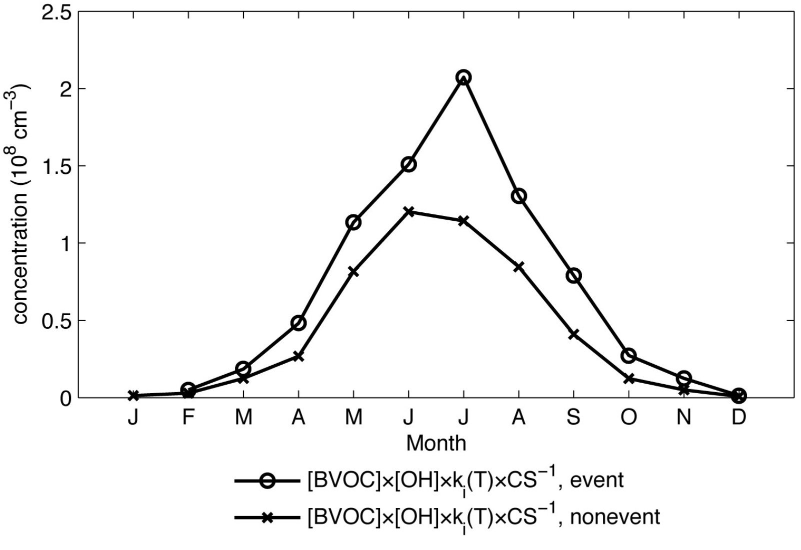

Fig. 10. Seasonal behavior of the concentration of the monoterpene (α- and β-pinene, Δ^3-carene) and isoprene oxidation products from their reaction with OH for event and nonevent days in 2001. [BVOC] is the monthly-mean concentration of monoterpenes (α- and β-pinene, Δ^3-carene) and isoprene, [OH] is the monthly-mean OH concentration, $k_i(T)$'s are the temperature-dependent rate constants and CS is the condensation sink. The monthly-mean concentrations of OH were calculated according to Hakola *et al.* (2003).

where v_T is the thermal velocity of condensing molecules, ρ is their atmospheric mass concentration and ρ_1 is the density of the condensate. Equation 8 gives GR = 10 nm h^{-1} for summer and GR = 1 nm h^{-1} for winter; measured values were 4.5 nm h^{-1} and 1.5 nm h^{-1}, respectively.

Conclusions

The data of observations at Hyytiälä in 1997–2003 were analyzed to investigate the possible links between different physical, chemical and meteorological parameters for event and nonevent days during different seasons.

In spring, new-particle formation was observed under the conditions of maximum daytime temperature, high ozone concentration and UV-A irradiation intensity, very low relative humidity (40%) and low values of condensation sink. The diurnal behavior of CS was shown to be well-correlated with that of RH, which suggests that changes in the surface area of pre-existing aerosol particles (CS) were connected mainly with changes in the relative humidity.

In winter, all events were observed at low temperatures (–5 °C > T > 20 °C), high RH (RH > 80%) and maximum observed monthly-mean concentrations of SO_2 and NO_x. The possibility for the nucleation mode in winter to appear was closely related to a substantial increase in the O_3 concentration (up to 30%) and UV-A irradiation, providing enhanced OH production necessary for the formation of nonvolatile vapors. The CS in winter was at minimum and the values of RH and CS were not correlated with each other.

The growth rate of nucleation mode particles was at its maximum in summer when the temperature and UV-A irradiation intensity were high, the concentrations of monoterpenes, hydroxyl radicals and water vapor were at their maximum, and concentrations of NO_x and SO_2 were at their minimum. The CS was at its maximum in summer. The daily patterns of CS and RH were well correlated with each other, and the daily dynamics of O_3 was determined by its production in the boundary layer. In the conditions of deficit of SO_2, a key parameter for suppressing nucleation in summer can be the high concentration of water vapor which prevents the formation of nucleating products from VOC. The calculated annual dependencies between LVOC-OH and LVOC-O_3 showed that the summer concentration of LVOC-OH exceeded that of LVOC-O_3 by a factor of 30–50. Therefore, the particle growth was mainly related to the oxidation products formed in the reaction cycles of VOC with OH in summer. In winter when the concentration of OH was at its minimum and thus the concentration of LVOC-OH was also at the minimum, the observed low particle growth rates are expected. In winter and autumn the concentrations of LVOC-OH and LVOC-O_3 were comparable in magnitude and in autumn the concentration of LVOC-O_3 could even exceed that of LVOC-OH. During these seasons both OH and O_3 reactions should be taken into account in calculating the particle growth rate.

The comparison of the seasonal behavior of the particle growth rate in the nucleation mode and oxidation products of monoterpenes in OH reactions clearly demonstrates their similarity, which means that the particle growth rate is linked to LVOC-OH. Equation 8 gives GR of 10 nm h^{-1} for summer and of 1 nm h^{-1} for winter; measured values were 4.5 nm h^{-1} and 1.5 nm h^{-1}, respectively.

The annual variation in the value of condensation sink showed that the limiting value of CS for a nucleation event to take place was about 5 × 10^{-3} s^{-1}. This practically coincides with the data obtained from Mauna Loa (Weber *et al.* 1997). There the largest surface area of pre-existing aerosol particles during nucleation events was 30 μm^2 cm^{-2} corresponding to condensation sink of 6 × 10^{-3} s^{-1}.

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