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Characteristics of the atmospheric particle formation events observed at a borel forest site in southern Finland

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We analysed 184 formation events of new atmospheric aerosol particles, observed at a boreal forest site in Hyytiälä, southern Finland. Recognition, selection and classification of the formation events was based on continuous experimental size distribution data for submicron particles from a period 31 January 1996–18 September 1999 (1327 days). The formation events were classified, and their characteristic features such as the starting time and duration of the particle formation, the number of new particles produced, the particle growth rate at the beginning of the formation burst, and the final particle size after the observed 8-hour growth subsequent to formation, were quantified. The formation rate of 3 nm particles, J_3, varied in the range 0.001–1 particles cm^{-3} s^{-1}. The ultrafine particle growth rates varied in the range 1–17 nm h^{-1}. The possible coupling between the apparent formation rate of new particles and their growth rate subsequent to formation was discussed.

Introduction

Formation of new ambient aerosol particles and, more generally, the processes affecting the total number concentration of ambient submicron particles, are current issues in atmospheric science (e.g. Seinfeld and Pandis 1998). Atmospheric aerosol have a significant influence on the global cloud albedo, radiative forcing of the atmosphere, ozone layer, acid rain, visibility (ICCP 1996), and the inhalation dose of particulate matter (Pope *et al.* 1995).

Ultrafine particle formation processes have been observed in the atmosphere for already a few decades. The appearance of ultrafine particles and their subsequent growth was originally

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observed in the ambient air ion spectra (Misaki 1964, Dhanorkar *et al.* 1991). From thereon, observations of the particle formation processes have been made based on measured rapid increase of the concentration of nucleation mode particles for example in Grawford Hill, NY (Hogan 1968), over the Arctic Ocean (Covert *et al*. 1992, 1996), in Mace Head, west coast of Ireland (O'Dowd *et al.* 1999), and in Jungfraujoch, a free-tropospheric mountain site in Switzerland (Weingartner *et al.* 2000). Nucleation events have recently been monitored also on the basis of ultrafine particle size distribution data at a forest-site in Hyytiälä, southern Finland (Mäkelä *et al.* 1997), in Izana, a free-tropospheric station in the isle of Tenerife (Raes *et al*. 1997), in Melpitz, a field station near Leipzig in Germany (Birmili and Wiedensohler 1997), in Munich, Germany (Brunnemann and Dlugi 1997), in Tähkuse, a coastal site in Estonia (Hõrrak *et al.* 1998), and over the Pacific Ocean in a plume downwind of Macquarie Island (Weber *et al*. 1998).

Based on the experimental data, quantitative estimates have been given in some of these studies for both the formation and growth rate of new particles. At the coastal site in Mace Head, the formation rate of the new particles (O'Dowd *et al.* 1999) was estimated to be on the order of 1000–10 000 particles $cm^{-3}\,s^{-1}$. The estimate was based on a short-time-scale variation of the ultrafine particle concentration. Weber *et al.* (1999) performed a comparison of data from various sites, and obtained nucleation rates on the order of 1–10 particles $cm^{-3}\,s^{-1}$ based on concentration changes and estimated time intervals over which the nucleation occurred. Ultrafine particle growth rates were estimated by Weber *et al.* (1997) at a clean continental site. Values of 1–2 nm h^{-1} were obtained from the subsequently measured size spectra. Similarly, over the South Pacific downwind from a penguin populated island (Weber *et al*. 1998), growth rates of 3–4 nm h^{-1} were obtained from the spatial evolution of the particle size distribution along the plume.

Continuous aerosol size distribution measurements with a twin-DMPS instrument (**D**ifferential **M**obility **P**article **S**izer) were started at the Hyytiälä measurement site (61°51´N, 24°17´E, 170 m a.s.l.) (Vesala *et al*. 1998) in January 1996. Since then, about 50–60 particle formation events have been observed annually. The continuous dataset spanning almost four years of ambient submicron number size distributions gives a good database for characterising the particle formation events for continental background aerosols in a boreal forest air.

Even though the particle formation events have been observed to occur quite frequently, the fundamental micro-physical nucleation process occurring in these events has remained unknown. Furthermore, the identities of the chemical species involved are not known. In our recent papers, it has been suggested that the formation events are connected with strong visible and UV radiation, vertical mixing of boundary layer air induced by sunlight (Mäkelä *et al.* 1997), and a flip-over of the vertical temperature profile (Kulmala *et al.* 1998a). The explanations of the ambient particle formation phenomenon usually include photo-chemical production of an unknown condensable vapour. Furthermore, the vertical mixing of the air parcels is assumed either to help the thermodynamics of the nucleation processes as well as the subsequent condensation (Nilsson and Kulmala 1998), or to introduce active precursor gases from the layers of air at different heights of the boundary layer. It may be that only one of these factors is important, or that both of them are required for the formation process to start. It is also possible that the particles are formed aloft during the morning hours, and then transported to ground level due to vertical mixing. The formation process may also occur due to several processes acting simultaneously, such as vertical mixing accompanied by favourable thermodynamics, emissions of distinct gaseous species, and photochemical formation of low-vapour-pressure species combined possibly with high humidity. Note that sunlight affects both the photochemical processes and the vertical mixing of the air, as well as possible emissions from the soil and trees. Therefore, it is very difficult to distinguish which of the observed phenomena connected to the particle formation events are prerequisite for particle formation to take place, and which (if any) are only secondary consequences of sunlight or related phenomena

and have actually nothing to do with the nucleation itself.

A full interpretation of the data is difficult, since the compounds involved have not yet been experimentally identified, the quantities of matter being vanishingly small. The compounds (a) initiating the nucleation and (b) providing the condensational growth may be different, and their chemical identity may vary (horizontally and vertically) between different locations in the troposphere.

There has also been some discussion on the microphysics of new particle formation and, furthermore, on the initial embryos of the nucleation. The nucleation could, in fact, be homogeneous, ion-induced (Hõrrak *et al.* 1998), or heterogeneous onto small (< 2 nm) thermodynamically stable clusters (TSCs; Kulmala *et al.* 2000). According to the recent discussion by Kulmala *et al.* (2000), the formation process of the TSCs could be a slow continuous ternary nucleation between water, ammonia and sulphuric acid vapours, taking place very frequently in the atmosphere. The observed particle formation could then be explained as a secondary heterogeneous nucleation process on previously-formed TSCs (which, because of their small size, are not directly detectable with the current instrumentation). The subsequent particle growth could be explained by condensation of local condensable species, which may vary from place to place. We have some evidence that some compounds involved in the growth of the ultrafine aerosol in forest air are non-hygroscopic and therefore possibly organic (Väkevä *et al.* 1998). This, however, does not relate (at least directly) to the nucleation of the ultrafine particles, but rather to their condensational growth subsequent to formation. Moreover, it should be noted that Misaki (1964) observed the formation process in the middle of the Arizona semidesert where organic sources are not necessarily present at very high concentrations.

In this paper, we outline the characteristics of the continental particle formation events based on our database. We will also keep in mind the possible hypotheses which match with the properties of the events and which, for the time being, cannot still be excluded.

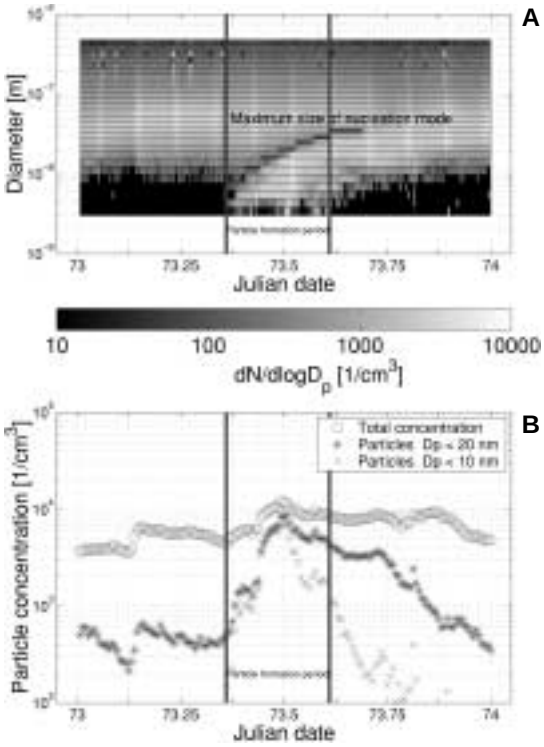

Fig. 1. — A: A typical particle formation event as a surface plot. Particle number size distribution in a boreal forest site in Hyytiälä on 13 March 1996. — B: Particle number concentration vs. time during the same day.

Methods

Definition of an event

The appearance of a typical particle formation event recorded by a DMPS-measurement can be seen in a surface plot (Fig. 1A), in which the submicron particle size distribution is presented as a function of time (Mäkelä *et al.* 1997, Kulmala *et al.* 1998a). At around midday, the newly formed particles enter the measurement range with initial sizes of 4–10 nm, and grow larger with a growth rate of few nanometers per hour, reaching 20–50 nm by the evening. This pattern is very distinctive and can be seen almost throughout the year, most often on sunny days (Mäkelä *et al.* 1997). The number concentration during our example day is shown in Fig. 1B.

The distinction between a particle formation

event and a non-event is sometimes difficult to make and is always somewhat subjective. The number of the nucleated particles may be small, or there can be a lot of background particles. In this work an event is assumed to have taken place if there is a clear increase of small (3–10 nm) particles and these particles grow during several hours.

Due to instrumental limitations we could not detect the very smallest ultrafine particles (less than 3 nm in diameter) connected with these bursts. Therefore, we assume that we are not discussing the nucleation directly. Most often the particles start to be observed at around 3–5 nm, which means that they have already grown for some time from their initial size, which is around one nanometer (a typical diameter for a nucleated molecular cluster). Because of the small size of the observed particles, it is, however, apparent that we are dealing with fairly new particles formed in a close vicinity to the measurement site. After their formation the particles grow to a detection limit and beyond. Alternatively, if the TSC-hypothesis is correct, we might be dealing with somewhat older clusters which only activate and grow in the vicinity of the site due to the condensable species. But, since growth rates of the order of several nanometers per hour are usually observed, we are still discussing relatively fresh particles.

One has to note that the evolution towards higher particle sizes seen in the particle size spectra during the particle formation process is always interpreted as a particle growth process. Since our fixed measurement spot actually records the data in an "Eulerian system", this interpretation of growth already includes the assumption that the aerosol must be quite homogeneous in a larger-scale air mass.

Selection

Utilizing the particle size distribution data, we can categorise the measurement period into different types of days, including the days during which some detectable new particle formation have occurred and the days with no significant particle formation (non-event days). From the particle formation days we can further select the ones on which the duration of particle growth was sufficiently long to permit the calculation of certain growth-related quantities. These days are termed event days. The events were divided into three separate classes with a quality number ranging from 1 to 3. The best ones, which showed a clear nucleation mode that was easily distinguishable until it had grown to the Aitken mode size, were classified as class 1. If there were only few nucleated particles, if there was some background, or if the growth was less distinct, the class was 2. In class 3 events, these factors were usually much worse, and it was difficult to see the nucleation mode at times. This classification is very subjective, especially for the classes 2 and 3 which may overlap somewhat.

Also a class 0 was introduced, as it became necessary to make a distinction between events and non-events. On these days, the criteria for an event were not met, but some particle formation was observed such that we wanted to rule these days out of the non-event group. This classification is even more subjective than the other ones. The days belonging to class 0 were not analysed any further.

Analysis

From the sets of DMPS-distributions we have estimated several features associated with the events, such as the particle formation rate (particles cm^{-3} s^{-1}) and particle growth rate (nm h^{-1}). Experimental detection of the actual nucleation rate, i.e. the formation rate of critical nuclei is beyond the present instrumentation. What we actually may obtain from the DMPS spectra is the rate of appearance of the particles into the measurement range. This may be best determined from the increasing rate of the particle number concentration in the nucleation mode. The growth rate of the nucleation mode may, on the other hand, be estimated either from the mean diameter of the nucleation mode as done by Kulmala *et al.* (1998a), or from the largest particles in the nucleation mode. The latter method actually would be a measure of the upper limit of the

particle growth rate.

Thus, the estimates for both particle formation and growth can be determined from the features of the nucleation mode. The main problem is to distinguish between the new and the pre-existing particles. If there is a lot of background aerosol prior to the particle formation, or if the size distribution fluctuates much, it is rather difficult to pinpoint which size classes belong to the event mode (nucleation mode). Therefore, one rather has to make an educated guess. Also the start and the end of an event are often difficult to determine because of fluctuations in the number concentrations in the smallest DMPS-channels. These difficulties could result in rather large uncertainties in the calculated values.

A program was written to calculate the apparent particle formation rate and growth rate from the DMPS data when given the starting and ending times of the event, together with the maximum size of the newly-formed particles. The input for the program was determined manually from the particle spectrum of an event day, displayed by the program. The upper size limit of the event mode was determined as a function of time at every hour (1, 2,..., 8 hours) from the start of the event and also at the end of the nucleation, as shown in Fig. 1A.

Given the input, the program calculated the apparent formation rate of 3-nm particles, J_3, with the equation:

$$J_3 = \frac{N_{\mathrm{nucl}}^{\mathrm{end}} - N_{\mathrm{nucl}}^{\mathrm{start}}}{t_{\mathrm{end}} - t_{\mathrm{start}}}. \qquad (1)$$

Here $N_{\mathrm{nucl}}^{\mathrm{end}}$ is the number concentration of particles smaller than the maximum event particle diameter at the end of the nucleation, $N_{\mathrm{nucl}}^{\mathrm{start}}$ is the respective concentration at the start of the nucleation, and t_{end} and t_{start} the ending and starting times of the event, respectively. It should be emphasized that J_3 is not the actual nucleation rate, nor even an average value for the nucleation rate over a period of time, but rather the appearance rate of particles larger than some distinct detectable size. Since the detected particles were usually in the size range 3–6 nm, and since we were dealing with particles mostly < 10 nm in size, we will call J_3 as the formation rate of 3-nm particles. This convention is assumed to be the most appropriate and relevant for the parallel and future modelling studies on atmospheric particle formation (e.g. Clement *et al.* 2000), and for making the best use of our results.

The maximum diameter, the apparent particle formation rate, the event starting and ending times, and the event classification were finally saved in a file, along with some other data such as the aerosol surface area at the beginning of the event, to be used later.

The results were compared with other data, namely gas, meteorology and radiation data measured in Hyytiälä, to find possible correlations. These data were obtained with a SMEAR II database program (Keronen and Laakso 1998). The program filters the data and uses the appropriate updated calibration coefficients to give 15-minute averages for radiation and 30-minute averages for other data. From these data, mean values for the time before nucleation (midnight-event start), nucleation time (event start–event end) and growth time (nucleation start–8 hours) were calculated.

Condensational sink and vapour removal rate

To describe the effective ability of the pre-existing aerosol particles to reduce the gas phase concentration of condensable species, we calculated the condensational sink, CS, which is related to the molecular number concentration of the condensable species, N_{a}, via the equation (Pirjola *et al.* 1999):

$$\frac{dN_{\mathrm{a}}}{dt} = -4\pi \times (\mathrm{CS}) \times D \times (N_{\mathrm{a}} - N_{\mathrm{a,a}}). \qquad (2)$$

Here D is the diffusion coefficient of the condensable species in the gas phase, and $N_{\mathrm{a,a}}$ is the the molecular number concentration of this species at the particle surface. The condensational sink is calculated by:

$$\mathrm{CS} = \int_0^\infty r\beta_i n(r)dr = \sum_i \beta_i r_i N_i, \qquad (3)$$

where r_i is the particle radius in the i:th size

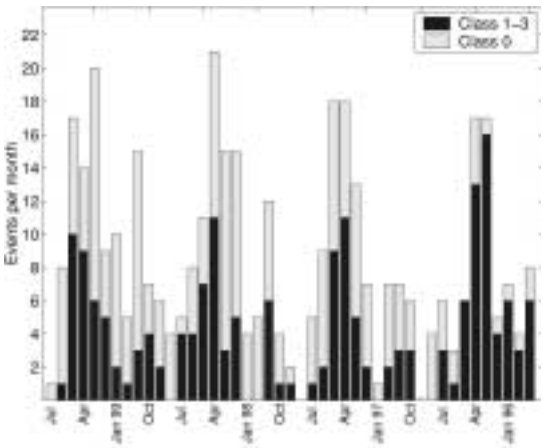

Fig. 2. Histograms of monthly occurrence of particle formation events in Hyytiälä during the 3.5-year period under investigation (January 1996–September 1999).

class, N_i is the respective number concentration and β_i is given by (Fuchs and Sutugin 1970):

$$\beta_i = \frac{(\mathrm{Kn})+1}{0.377(\mathrm{Kn})+1+\frac{4}{3}\alpha^{-1}(\mathrm{Kn})^2+\frac{4}{3}\alpha^{-1}(\mathrm{Kn})} . \quad (4)$$

Here the sticking coefficient α is assumed equal to unity, and Kn denotes the Knudsen number given by Kn = λ_v/r, where λ_v is the mean free path of the condensing vapour molecule. λ_v can be estimated using the diffusion coefficient of sulphuric acid in the air, calculated according to a binary formula given by Reid *et al.* (1987). The molecular masses and diffusion coefficients were chosen to be the same as in our recent paper (Kulmala *et al.* 1998a), where it was shown that their values have only little effect for the results of growth calculations.

Finally, the vapour removal rate R_A is calculated as

$$R_A = 4\pi \times (\mathrm{CS}) \times D . \quad (5)$$

The connection between R_A and the condensational sink CS is very simple, since the value of $4\pi D$ in Eq. 5 is approximately 1.3×10^{-4} m^2 s^{-1}. The calculation was performed with 30-minute temperature averages from the height of 16.8 meters. The program calculated the CS for both the pre-existing and the nucleated aerosol.

Table 1. Number of observed nucleation events in Hyytiälä 1996–1999. Different event classes refer to the clarity of appearance of the particle formation and subsequent growth (*see* text), Class 1 having the most recognisable pattern.

Year	Class 1	Class 2	Class 3	Total
1996	14	18	11	43
1997	12	17	14	43
1998	13	11	14	38
1999	18	19	23	60
Total	57	65	62	184

General results

Annual variation of occurrence of the events

We analysed submicron particle data from Hyytiälä for the period 31 January 1996 to 18 September 1999 (1327 days). On the average, 40–60 formation events are observed annually in Hyytiälä (Table 1). The overall coverage of the DMPS-data was about 97%–98%. However, the data for some days in 1998 was inadequate for determining the occurrence of the formation events, and thus the daily-based coverage for an event classification was only 93%. Therefore, the numbers may underestimate the occurrence, especially in 1998, by a few percent.

The analysed 1999 dataset ended in September, but a very frequent occurrence of class 1–3 events was seen throughout the year. When looking at the monthly number of observed events during the 3.5-year period (Fig. 2), a clear annual bimodal pattern was observed for the whole period, showing a larger peak in event number frequency in the spring (March–April–May) and a smaller one in the autumn (September–October). This also holds if the class 0 events were included. In mid-summer and mid-winter, frequency minima were observed. In December no events were observed to have taken place. This annual pattern has been discussed by Mäkelä *et al.* (2000).

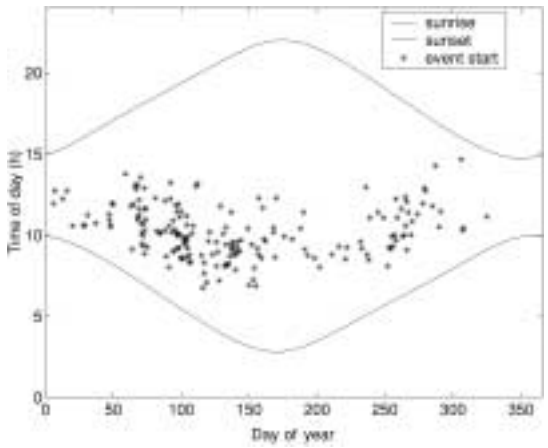

Fig. 3. Starting times of particle formation events vs. the day of year. The time of sunrise and sunset are shown as lines.

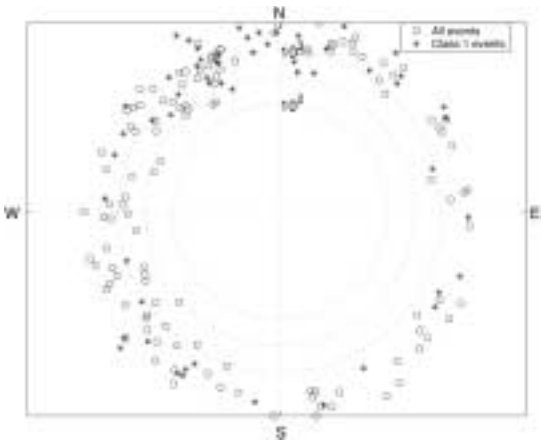

Fig. 4. Vapour removal rate R_A as a wind direction plot. The wind direction has been determined as a 30-min average value before the start of particle formation.

Time of day

The particle formation bursts always took place during daytime. No more than a single event was observed to occur per day. The events always started at least 2 hours after sunrise, and on the average 3–4 hours from sunrise (Fig. 3). It is also evident that the majority of the events started before noon.

Local wind direction

The uniformity of the particle growth such as that seen in Fig. 1 indicates that the appearance and growth of particles is a large scale phenomenon (*see also* Kulmala *et al.* 1988a). The time period of 8 hours corresponds to a horizontal scale of 100–300 km. This is also supported by the fact that there was no clear dependence of the event occurrence on the local wind direction. The calculated vapour removal rate R_A in the beginning of particle formation event showed an even distribution as a function of local wind direction prior to event (Fig. 4). The actual value of the vapour removal rate varied in the range of 0.00015–0.01 s^{-1} (corresponding to CS in the range 2–130 m^{-2}), which in practice means that without a continuous source, the vapour was removed from the gas phase within one or two hours.

The circle of data points in Fig. 4 is clearly tilted towards the lower right corner of the plot. Thus, the lowest values of R_A were found in the wind direction N–NW. This is understandable, since the northern air masses contained less pre-existing particles than the air masses arriving from central Europe, Belarus, southern Russia, or from the Baltic countries. Generally, the particle formation was seen to occur on all local wind directions.

4. Particle formation rate

The particle formation period lasted usually for several hours, the mean value calculated from the dataset being 4.8 hours. The duration of a nucleation event had two annual peaks coinciding with the spring and autumn frequency maxima of the events (Fig. 5).

The average yield of new particles within a one-day formation event also showed two annual maxima (Fig. 5B). On the average, events with duration of 2.5 hours and with a starting time of roughly 5 hours after the sunrise seemed to produce the highest concentrations of new particles. If the formation event started very late (with respect to the sunrise), the amount of new

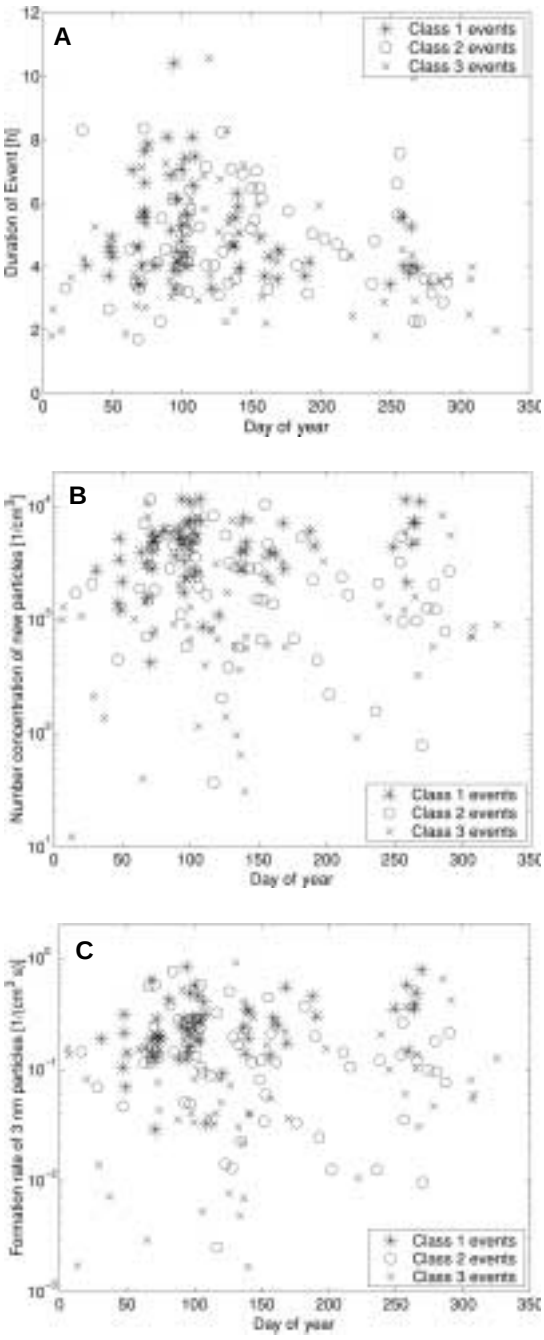

Fig. 5. — A: Duration of particle formation vs. the day of year. — B: New particle yield, i.e. the change in the number concentration of nucleation mode particle during the formation period. — C: Formation rate of 3-nm particles, i.e. the ratio between the new particle yield and the duration of particle formation.

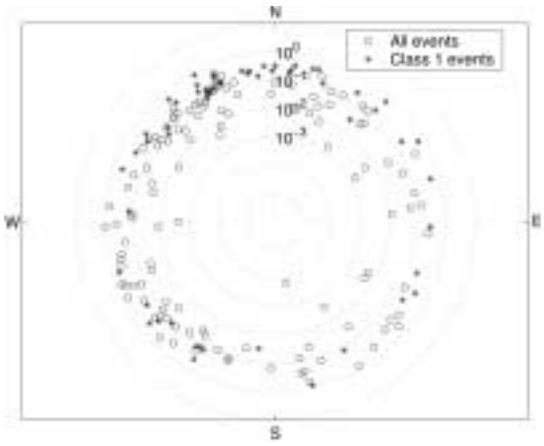

Fig. 6. Formation rate of 3-nm particles, J_3, as a wind direction plot.

particles remained usually relatively low. The duration of a nucleation event did not correlate directly with the final size of the particles.

From the two quantities, the yield of new particles and the duration of a particle formation period, one can derive the apparent new particle formation rate vs. the day of the year, as shown in Fig. 5C. Also the apparent formation rate was seen to have two annual maxima. The values obtained for the apparent formation rate of new particles ranged from 0.001 to 1 cm^{-3} s^{-1}. These values were very sensitive to the determination of the duration of an event. Significant fluctuations in the concentration of the smallest measured particles made the accurate determination of the duration difficult, so errors of even a few hours were possible.

The value of the formation rate of 3 nm particles was not very dependent on the wind direction (Fig. 6). The average formation rate may have been slightly lower for northerly winds than for other directions, and slightly higher for winds from SW. Furthermore, it can be seen that winds from N and NW favoured the occurrence of class one events. This preference may be connected with the low value of the condensational sink for those wind directions (Fig. 4).

In the previous figures, the apparent particle formation rate was derived as an average value for the whole formation period. For a "tempo-

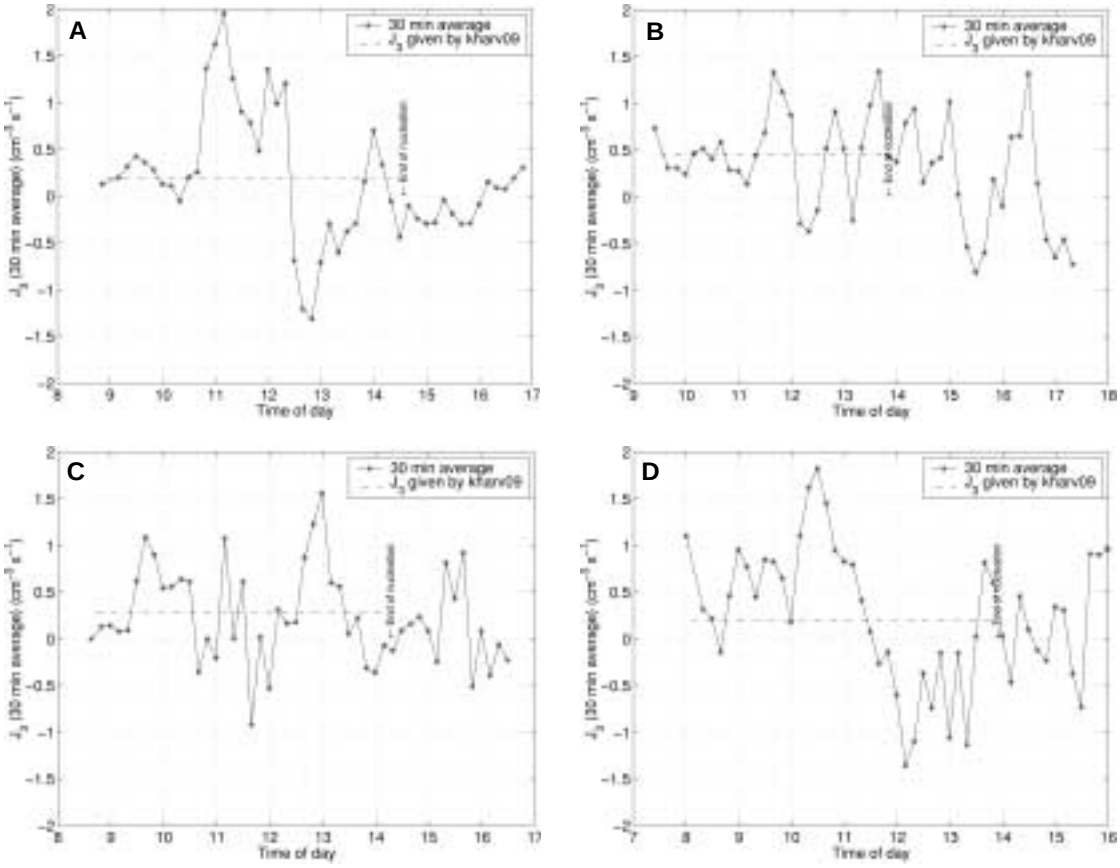

Fig. 7. Temporary particle formation rates (derived with a 30-min time window) for four cases of Class 1 events. — A: 13 March 1996, — B: 12 April 1996, — C: 13 April 1996, — D: 20 May 1998.

rary" formation rate with a time resolution finer than the actual duration, the experimental data produced sets of fluctuating values. As an example, the temporary formation rates, calculated as 30-minute moving averages, are shown for four cases of class one events in Fig. 7. Maximum values of 1.5–2.1 cm^{-3} s^{-1} were obtained (Fig. 7A and D), but also negative values were obtained already before the actual end of the formation period. In the two other example cases (Fig. 7B and C), the temporary particle formation rate practically fluctuated around a constant value throughout the whole formation period. The average values for the apparent particle formation rate, as calculated over the formation period, were non-negative in all of these four cases (0.25–0.45 cm^{-3} s^{-1}). The negative values of the temporary formation rate (Fig. 7A and D) are not anomalous, since in a large fraction of the events the temporary (30-min) particle formation rate clearly decreased to negative values before the end of the actual formation period. Two possible explanations are dilution due to growth of mixed layer height and the removal of particles by coagulation. In a more detailed process model, these effects will have to be accounted for to quantify the mechanisms.

Particle growth

Particle growth during the formation period and subsequent to it was estimated in several ways. The particle diameter growth was estimated (a)

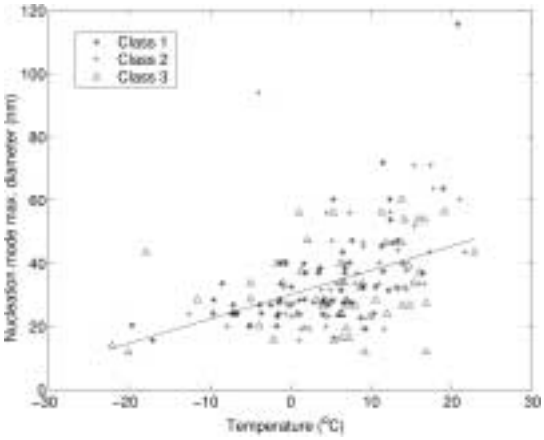

Fig. 8. Maximum diameter of event particles (8 hours after the start of an event) vs. the average temperature during formation. A correlation of $R^2 = 0.483$ was obtained.

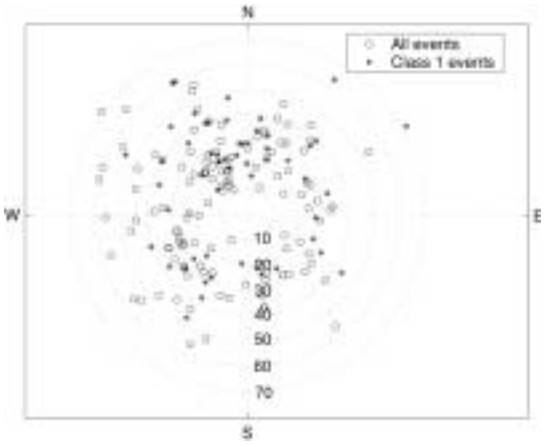

Fig. 9. Maximum diameter of event particles (8 hours after the start of an event) as a wind direction plot.

by determining the maximum size of the event mode (*see* Fig. 1) at eight hours from the start of event, and (b) by calculating the growth rate (dDp/dt in nm h^{-1}) from the evolution of maximum size of the event mode at 2 hours after the start of event. Secondly, the particle volume growth was studied (a) by calculating the increase of the total volume concentration of the event mode particles in $m^3\ m^{-3}$ (all particles smaller than the maximum size) at a given time after the start of event, and (b) by dividing the total volume increase by the particle number concentration in the nucleation mode, in order to obtain information on the volume change of a single particle.

Diameter growth of the particles

The maximum size of event particles at eight hours after the start of event showed a clear dependence on the temperature (Fig. 8), the correlation coefficient being $R^2 = 0.483$. The temperature has been determined as an average value over the particle formation period. One possible explanation for the correlation is the strong temperature dependence of biogenic vapour emissions (Jansson 1993). However, it is not known with certainty that the precursors of condensing species originate from vegetation, and the correlation seen here could as well be due to the temperature and light intensity depenences of photochemical reactions producing the condensable molecules, whatever the origin of the precursors.

The wind direction plot of the maximum size of the event particles at eight hours (Fig. 9) reveals that the wind directions 200–40 seemed to enable larger particle growth than the other directions. This may, again, be explained by the low values of condensational sinks in air masses arriving from these directions. Presumedly, when the condensational sink is low, the buildup of higher vapour concentrations becomes possible, enabling stronger particle growth.

The maximum size of event particles at eight hours after event start plotted vs. the day of year (Fig. 10A) reveals that the particles tended to grow larger during the summer. This is in fair agreement with the temperature correlation (Fig. 8); however it remains unclear why particle formation was not observed to take place in the mid-summer, when one would expect e.g. the highest monoterpene concentrations. The particle growth rate, derived from the maximum size of event particles (Fig. 10B), was seen to have an annual pattern with clearly higher growth rates towards summer. Note that growth rates as high as 8–17 nm h^{-1} were obtained for the summer period (day of year between 150 and 240).

It is somewhat surprising that a maximum in the particle growth rate was seen in the summertime, indicative of high condensable vapour

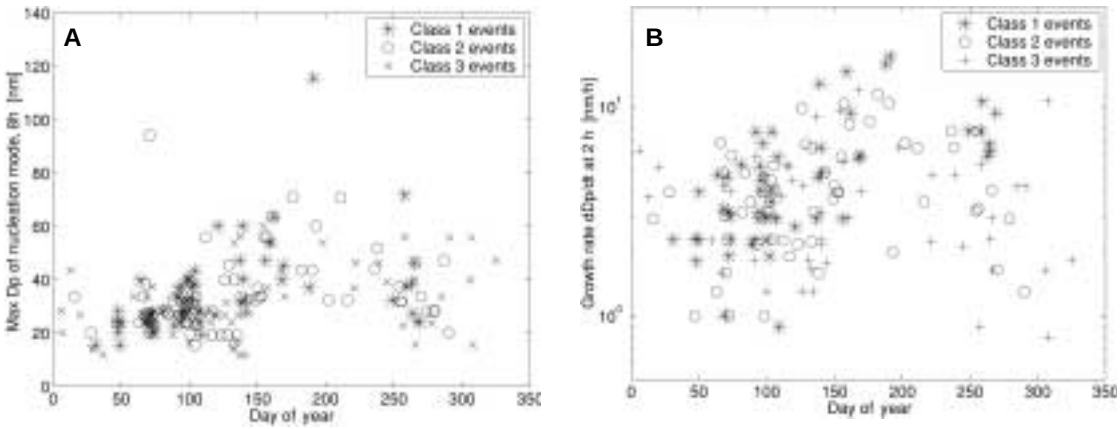

Fig. 10. — A: Maximum diameter of event particles (8 hours after the start of and event) vs. the day of year. — B: Particle growth rate vs. the day of year.

concentrations, but that particle formation events were rarely seen during that time. Mäkelä *et al.* (2000) observed an "event-like" growth pattern of Aitken mode particles in Hyytiälä in July 1996, just around the time when the particle growth rate reaches its annual maximum. It should be noted that the events were usually connected with a vertical mixing of air parcels in the lower troposphere. If the particle growth was very fast in the summertime and, moreover, if the particles were presumedly formed slightly higher up in the summertime, then, it is possible that all the particles grew in few minutes close to Aitken size already before getting to the ground level. In this case we actually would not observe the particle formation event in its conventional form anymore in the nucleation mode, but rather at higher sizes. If we e.g. consider the observed growth rate of 17 nm h^{-1}, it is clear that the particles will stay in the nucleation mode size range for less than one hour. Therefore, when measuring down at the ground level, it is possible that we actually miss a fraction of particle formation events with our present method of classifying them based on the ground level data only.

The volume growth of particles

The total increase in the ultrafine particle volume concentration, shown in Fig. 11A, may be interpreted as a measure of condensation. When the particle formation rate is higher, there is more condensation in a given time, i.e. the amount of condensed material is larger.

To show that the increased volume concentration was not only due to a higher number concentration of particles formed, we need to normalise the volume growth by the number of new particles. When plotting the ratio V/N as a function of the apparent particle formation rate, one should actually see whether the particle formation rate and single particle growth were linked to each other. Having done this (Fig. 11B), a slight upward trend was seen, but the dependence seemed very ambiguous. If the particle formation and growth were caused by the same vapour, we would expect a clear correlation between formation rate and V/N. On the other hand, if the condensation and nucleation were caused by two completely separate vapours, no correlation would be expected. However, if the phenomena were caused by two different vapours, both of which formed due to sunlight, a correlation of some degree would be expected. On the basis of the result (Fig. 11B) it is very difficult to exclude any of these cases.

The growth rate of maximum particle size in nucleation mode in the beginning of the event, derived from the maximum size of the event particles, is shown in Fig. 11C. The value of the estimated particle growth rate ($d\mathrm{Dp}/dt$) was on the average 6–8 nm h^{-1}. But, as shown in Fig. 10B, growth rates during the summer could be as high as 14–17 nm h^{-1}. The growth rate and the

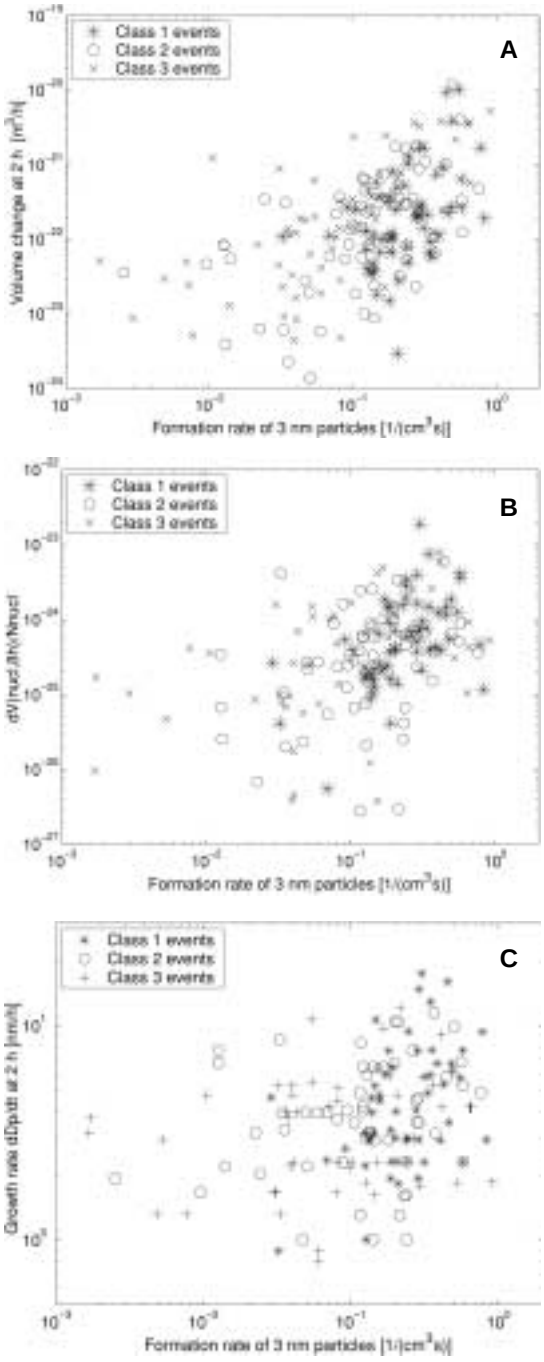

Fig. 11. — A: The change in total ultrafine particle volume concentration dV, 2 hours from the start of nucleation, as a function of J_3, the formation rate of 3-nm particles. — B: The 8-hour single-particle volume growth rate dV/dN vs. the formation rate of 3-nm particles. — C: The particle growth rate $d\mathrm{D}p/dt$ at 2 hours from the event start vs. the formation rate of 3-nm particles J_3.

apparent particle formation rate did correlate, but the large variability in the data points is suggestive of a very weak connection between the growth and formation. The slight de-coupling between the apparent formation rate and the growth is also seen from the combination of Figs. 6 and 9. While the formation rate was higher for wind directions SE and SW, the growth rates were highest for the sector SW–W–N–NE. Thus, there was a group of events from the wind direction SE having both high particle formation rates and not-so high growth rates.

The data in Fig. 11 include cases with a wide range of temperatures. Since we are aware that both condensation and nucleation phenomena are dependent on the prevailing temperature, we tested the data in Fig. 11C for narrower temperature ranges. It turned out that there is a better correlation for the data in the range +5 °C– +10 °C but the rest of the data do not verify the assumption. Therefore, at this point we conclude that the correlation presented in Fig. 11C is fairly weak.

Connection of particle formation events with other quantities

The amount of visible light as well as UV-radiation has been seen to correlate with the growth of the particles. In our data set, there was an increasing trend of final particle size with increasing amount of radiation, the correlation coefficient being $R^2 = 0.391$ (Fig. 12). It could be speculated that an increasing amount of UV-radiation increases the photochemical production of condensable species and, thereby, increases the particle growth. However, all types of radiation are directly linked with the total amount of sunlight, and therefore the extent of vertical mixing also correlates with both UVA and UVB.

To investigate the connection between the particle formation events and micrometeorology, we calculated the vertical gradient of the potential temperature $\Delta\theta/\Delta z$ derived from the temperature and pressure data from the measurement site. In Fig. 13, the histograms of two groups of the potential temperature gradient data are compared. The event day gradients were

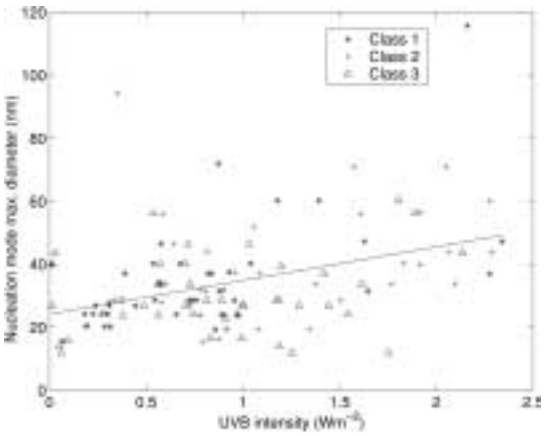

Fig. 12. The maximum size of event particles plotted versus average value of UVB-radiation intensity at 2 hours from the event start. A correlation of $R^2 = 0.391$ was obtained.

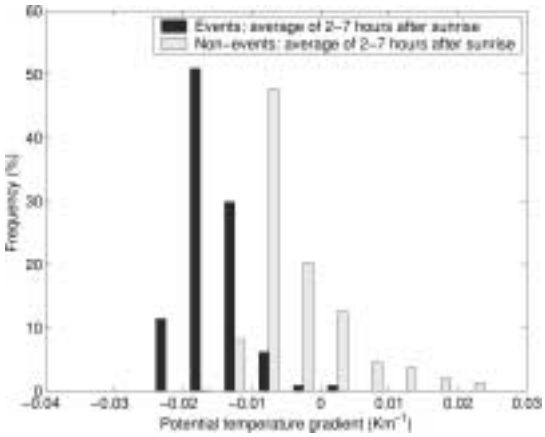

Fig. 13. Histograms of vertical potential temperature gradients on event days and non-event days.

calculated as one hour averages around the start of the particle formation, and for the non-event days the value was calculated as an hourly average around the daily minimum of $\Delta\theta/\Delta z$, which usually occurred around noontime. The set of event data suggests a mean value of –0.015 K m^{-1} for the typical vertical potential temperature gradient $\Delta\theta/\Delta z$ during the particle formation event. The reference data from non event days gave a mean value of –0.005 K m^{-1} for the gradient. From the $\Delta\theta/\Delta z$-distribution (Fig. 13), we conclude that the particle formation events are connected with vertical mixing and, furthermore, that the particle formation process is very likely to occur when the potential temperature gradient $\Delta\theta/\Delta z$ decreases below a value –0.015 K m^{-1}.

In addition to the data presented, we also searched whether the nucleation rate and the particle growth had any correlation with other quantities such as the relative humidity and the concentrations of NO_x, SO_2 and O_3. No clear correlation was found.

Conclusions

During the four years of continuous measurements of submicron aerosol size distributions at a boreal forest site, we have observed approximately 40–60 well-distinguishable particle formation events per year. The events took place at all local wind directions, even though the N–NW direction and the low values of the condensational sink seemed to favour the class one events, i.e. the events with the most recognisable pattern. A large amount of pre-existing particles was not seen to prohibit the particle formation significantly. The connection between the vapour removal rate R_A and a quantity defined as a ratio of global radiation to R_A has been discussed by Clement *et al.* (2000). Finding a lower threshold value for the fraction, below which particle formation is not observed to occur, indicates that low values of R_A indirectly allow an elevated concentration of the assumed condensable species, and therefore it may be assumed that the bursts should be more intensive when R_A is lower. In our data this appeared only as a weak preference of the most recognisable events towards N–NW wind directions which, on average, were seen to consist of lower condensational sinks.

The apparent particle formation rate, defined as an average rate over the burst, was observed to vary within the range 0.001–1 particles cm^{-3} s^{-1}. It may be noted that the observed particle formation rate never exceeded the value of the ion-pair formation rate, which in continental air is known to be on the order of 2–2.5 ion pairs cm^{-3} s^{-1} or more (Hensen and van der Hage 1994). Moreover, the calculated 30-min averages for the apparent particle formation rate stayed in the range < 3 particles cm^{-3} s^{-1}. Therefore,

based purely on this result, we cannot exclude the possibility of an ion-induced nucleation being responsible for the particle formation, although other studies (Kulmala *et al.* 2000) have found indirect indications that the ion-induced nucleation cannot be the only mechanism to generate new particles.

The apparent particle formation rate was found to have two clear annual maxima, one in spring and another in autumn. Also the duration of the formation period was found to exhibit maxima in these two seasons. An explanation for the apparent absence of the "typical" formation events in summertime can be given. The apparent absence was found to be connected with a high particle growth rate. In summertime the particles grew fast and were therefore not necessarily observed at nucleation mode size, providing that the actual nucleation occurred aloft and that it took some time for the particles to be transported to the measurement site. It should be noted that the final particle sizes after 8 hours of growth were on the order of 60–70 nm. A growth rate of 10 nm h^{-1} was frequently exceeded in June–August. In several cases, the growth was observed to continue to sizes as big as 100 nm and above (Kulmala *et al.* 1998b). The size of 60–70 nm is known to be sufficient for the particles to act as a cloud condensation nuclei in the atmosphere (Kulmala *et al.* 1998b).

The particle formation and growth rates were seen to correlate weakly with each other. This correlation does not necessarily mean that the vapours causing the formation and growth are the same, but rather that they may have a similar origin connected possibly with the sunlight. However, on the basis of the data no firm conclusions can be made, and it is quite possible that at least one of the compounds involved is not at all of photochemical origin. It should be remembered that the vapours participating the process and the actual composition of the new ultrafine particles have not yet been identified.

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References

Birmili W. & Wiedensohler A. 1997. New particle formation in the plume of a city. *J. Aerosol Sci.* 28: S717–718.

Brunnemann G. & Dlugi R. 1997. Dependence of the aerosol number size distribution on ambient air. *J. Aerosol Sci.* 28: S217–218.

Clement C.F., Pirjola L., Dal Maso M., Mäkelä J.M. & Kulmala M. 2000. Analysis of particle formation bursts observed in Finland. *J. Aerosol Sci.* 31. [In press].

Covert D.S., Kapustin V.N., Quinn P.K. & Bates T.S. 1992. New particle formation in the marine boundary layer. *J. Geophys. Res.* 97: 20581–20587.

Covert D.S., Wiedensohler A., Aalto P., Heinzenberg J., McMurry P.H. & Leck C. 1996. Aerosol number size distributions from 3 to 500 nm diameter in the Arctic marine boundary layer during summer and autumn. *Tellus* 48B: 197–212.

Dhanorkar S. & Kamra A.K. 1991. Measurement of mobility spectrum and concentration of all atmospheric ions with a single apparatus. *J. Geophys. Res.* 96: 18671–18678.

Fuchs N.A. & Sutugin A.G. 1970. *Highly dispersed aerosols.* Ann Arbour Science Publishers, Ann Arbour, London.

Hensen A. & van der Hage J.C.H. 1994. Parametrization of cosmic radiation at sea level. *J. Geophys. Res.* 99: 10693–10695.

Hogan A. 1968. An experiment illustrating that gas conversion by solar radiation is a majorinfluence in the diurnal variation of Aitken nucleus concentrations. *Atmos. Environ.* 2: 599–601.

Hõrrak U., Salm J. & Tammet H. 1998. Bursts of intermediate ions in atmosphere. *J. Geophys. Res.* 103: 13909–13915.

Jansson R.W. 1993. Monoterpene emissions from Scots pine and Norwegian spruce. *J. Geophys. Res.* 98: 2839–2850.

IPCC, Intergovernmental Panel on Climate Change. 1996. Cambridge Univ. Press, Cambridge.

Keronen P. & Laakso L. 1998. *Atmosphere-data*. Database program for SMEAR II station. University of Helsinki. Department of physics.

Kulmala M. Toivonen A. Mäkelä J.M. & Laaksonen A. 1998a. Analysis of the growth of nucleation mode particles observed in boreal forest, *Tellus* 50B: 449–462.

Kulmala M., Mäkelä J.M. Koponen I.K. & Pirjola L. 1998b. Formation of cloud condensation nuclei in boreal forest area. *J. Aerosol Sci.* 29: S567–S568.

Kulmala M., Pirjola L. & Mäkelä J.M. 2000. Stable Sulphate Clusters as a source of new atmospheric particles. *Nature* 404: 66–69.

Misaki M. 1964. Mobility spectrum of large ions in the New Mexico semidesert. *J. Geophys. Res.* 69: 3309–3318.

Mäkelä J.M., Aalto P., Jokinen V., Pohja T., Nissinen A., Palmroth S., Markkanen T., Seitsonen K., Lihavainen H. & Kulmala M. 1997. Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys. Res. Lett.* 24: 1219–1222.

Mäkelä J.M., Koponen I.K., Aalto P. & Kulmala M. 2000. One year data of submicron size modes of tropospheric background aerosol in Southern Finland. *J. Aerosol Sci.* 31: 595–611.

Nilsson E.D. & Kulmala M. 1998. The potential for atmospheric mixing processes to enhance the binary nucleation rate. *J. Geophys. Res.* 103: 1381–1389.

O'Dowd C., McFiggans G., Creasey D.J., Pirjola L., Hoell C., Smith M.H., Allan B.J., Plane J.M.C., Heard D.E., Lee J.D., Pilling M.J. & Kulmala M. 1999. On the photochemical production of new particles in the coastal boundary layer. *Geophys. Res. Lett.* 26: 1707–1710.

Pirjola L., Kulmala M., Wilck M., Bischoff A., Stratmann F. & Otto E. 1999. Formation of sulphuric acid aerosol and cloud condensation nuclei: An expression for significant nucleation and model comparison. *J. Aerosol Sci.* 30: 1079–1094.

Pope C.A.III, Dockery D.W. & Schwartz J. 1995. Review of epidemiogical evidence of health effects of particulate air pollution. *Inhalation Toxicology* 7:1–18.

Raes F., Van Dingenen R., Cuevas E. Van Velthoven, P.F.J. & Prospero J.M. 1997. Observations of aerosols in the free troposphere and marine boundary layer of the subtropical Northeast Atlantic: Discussion of processes determining their size distribution. *J. Geophys. Res.* 102: 21315–21328.

Reid R.C., Prausnitz J.M. & Poling B.E. 1987. *The properties of gases and liquids*, 4th edition, McGraw-Hill, New York, 441 pp.

Seinfeld J.H. & Pandis S.N. 1998. *Atmospheric chemistry and physics. From air pollution to climate change*, John Wiley & Sons, Inc., New York, 1326 pp.

Vesala T., Haataja J., Aalto P., Altimir N., Buzorius G., Garam E., Hämeri K., Ilvesniemi H., Jokinen V., Keronen P., Lahti T., Markkanen T., Mäkelä J.M., Nikinmaa E., Palmroth S., Palva L., Pohja T., Pumpanen J., Rannik Ü., Siivola E., Ylitalo H., Hari P. & Kulmala. M. 1998. Long-term field measurements of atmosphere-surface interactions in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry. *Trends in Heat, Mass & Momentum Transfer* 4: 17–35.

Weber R.J., Marti J.J., McMurry P.H., Eisele F.L., Tanner D.J. & Jefferson A. 1997. Measurements of new particle formation and ultrafine particle growth rates at a clean continental site. *J. Geophys. Res.* 102: 4375–4385.

Weber R.J., McMurry P.H., Mauldlin R.L., Tanner D.J., Eisele F.L., Brechtel F.J., Kreidenweis S.M., Kok G.L., Schillawski R.D. & Baumgardner D. 1998. A study of new particle formation and growth involving biogenic and trace gas species measured during ACE-1. *J. Geophys. Res.* 103: 16385–16396.

Weber R.J., McMurry P.H., Mauldlin R.L., Tanner D.J., Eisele F.L., Clarke A.D. & Kapustin V.N. 1999. New particle formation in the remote troposphere: A comparison of observations at various sites. *Geophys. Res. Lett.* 26: 307–310.

Weingartner E., Nyeki S. & Baltensperger U. 2000. Seasonal and diurnal variation of aerosol size distributions ($10 < D < 750$ nm) at high-alpine site. *J. Geophys. Res*. 104: 26809–26820.

Väkevä M., Hämeri K. & Mäkelä J.M. 1998. Hygroscopic properties of ultrafine aerosol particles measured at three sites in Finland. *J. Aerosol. Sci.* 29: S7–S8.

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