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TELLUS

Characterization of new particle formation events at a background site in Southern Sweden: relation to air mass history

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ABSTRACT

Particle formation events were analysed from aerosol number size distribution data collected at a background station in southern Sweden between February 2001 and May 2004. Events occurred on about 36% of all days and were favoured by high global radiation values. The clearest events (class I, 20% of all days) were observed when the formation rate of activated hypothetical clusters around 1 nm diameter, J_1 was higher than $10^{(180*\mathrm{CondS}-0.60)}$, where CondS is the condensation sink (in s^{-1}). The median condensable vapour concentration, observed formation rate at 3 nm, and growth rate during class I events were 3.0×10^7 cm^{-3}, 1.1 cm^{-3} s^{-1} and 2.1 nm h^{-1}, respectively. On 7% of all days, it was possible to observe growth of the newly formed particles exceeding 30 nm geometric mean diameter during event days in the evening, which is important for the regional particle population, and thereby the climate. A trajectory analysis revealed that cleaner air masses were relatively more important for the contribution of Aitken mode particles than polluted ones. Class I events were registered on 36% of all days when trajectories had passed over the open sea, indicating that ship traffic can contribute to particle formation and growth.

1. Introduction

Numerous observations in different ambient environments worldwide show that natural sources can contribute significantly to the production of aerosol particles in the nanometre size range (see, e.g. Kulmala et al., 2004a). These particles nucleate from gaseous precursors and appear usually during the daytime, being indicative of the important role of photochemistry in atmospheric new-particle formation. Notable exceptions for this are the Amazon rain forest (Rissler et al., 2004) and the summertime Arctic Ocean pack ice region (Wiedensohler et al., 1996), where other mechanisms seem to be responsible for the formation of nucleation mode particles. The newly formed particles frequently grow into the Aitken mode size range (>30 nm in diameter) and are in many cases important for the production of cloud condensation nuclei (CCN) (Kerminen et al., 2005). However, the physical and chemical processes leading to their formation have not yet been clearly identified, partly due to difficulties in detecting and characterizing these nanometre-sized particles.

One of the theories behind particle formation assumes that there are numerous, stable clusters around 0.5–1.5 nm in diameter that are predicted to be nearly ubiquitous in the continental boundary layer (Kulmala et al., 2000). The activation of these clusters at around 1–2 nm in diameter and further growth in boreal forest environments via condensation of biogenic volatile organic vapour to detectable sizes above 3 nm diameter is proposed as the probable pathway for the initial formation (Kulmala et al., 2006). Recently, Kulmala et al. (2007) observed the presence of neutral sub-3 nm atmospheric particles, supporting the circumstantial evidence of their existence (Kulmala et al., 2005).

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However, the formation mechanism of these neutral clusters has not yet been elucidated (Kulmala et al., 2007). The atmospheric nucleation, and growth pathways, may differ, especially in polluted boundary layers, where the air contains other and more abundant precursor gases than those observed in the boreal forest environment (see, e.g. Zhang et al., 2004; Gaydos et al., 2005; Smith et al., 2005).

In this study, parameters that describe the dynamics and evolution of formation events in southern Sweden are calculated at the rural continental site Vavihill using almost 2 yr of aerosol particle number size distribution data (3–900 nm diameter). The calculations include the formation rate of 3 nm diameter particles, the growth rate of the nucleation mode, the resulting geometric mean diameter, the concentration of nucleation mode aerosol particles, global radiation, SO_2 in the gas phase, and the concentration and production rate of vapour responsible for the condensation growth of formation particles. The parameters are important for future studies identifying conditions leading to formation events in northern Europe. Moreover, a classification and an estimation of the frequency of events have been made to estimate how important these events are for the aerosol population and to assist the validation of models of the regional or global aerosol. The methodology of event classification and parameter estimation developed by Dal Maso et al. (2005) is novel and is intended to work for many sites worldwide. This comprehensive methodology is used for southern Scandinavian conditions to examine its applicability to environments other than the high latitude Nordic boreal forest, the only location where it has been tested so far (Dal Maso et al., 2007). Also, a hypothetical formation rate of 1 nm activated cluster particles based on the measured size distribution is also estimated using the methodology of Kerminen and Kulmala (2002). This rate corresponds better to those employed in models which simulate the global aerosol burden and use vapour concentration data as input (Spracklen et al., 2006).

Secondly, an investigation of the way in which the events at Vavihill may affect climate has been performed by analysing occasions when the geometric mean diameter of the nucleation mode increased to sizes larger than 30 nm. The measurements and the position of Vavihill between continental Europe and high latitude Nordic areas also provide an opportunity to investigate and compare the properties and frequency of formation events taking place at Vavihill when the air masses are both polluted and relatively clean.

2. Methods

2.1. Measurements

The measurements were performed at the EMEP background station Vavihill in Southern Sweden (56° 01′ N, 13° 09′ E, 172 m a.s.l., Fig. 1). There are no local pollution sources in the immediate vicinity of the site. However, the distances to the densely populated areas of Malmö, Copenhagen and Helsingborg southwest to west of the station are only 45, 40 and 25 km, respectively,

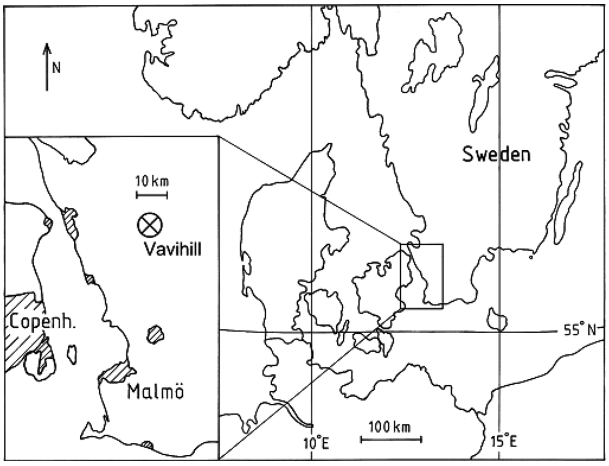

Fig. 1. Map showing the location of the Vavihill background monitoring station (⊗ in the enlarged insert).

and Vavihill is also close to the European continent in the south. When winds are coming from northwest to northeast, the air masses are often very clean.

Aerosol particle number size distributions have been measured continuously at the station since February 2001, using two similar differential mobility particle sizer (DMPS) systems. These were designed, constructed and calibrated at Lund University. The data used in this study were collected during the period February 2001–May 2004. There are only measurements available from 681 d during this time period and the longest time gaps are due to the fact that the DMPS was used in other campaigns. The DMPS, which is connected to a PM10 inlet (USEPA, 1991) is similar to the one described in more detail by Zhou (2001). The aerosol particles are first directed to a bipolar charger, which charges the particles according to a well-defined charge distribution. Then the flow is split into two parts; through two different Vienna-type differential mobility analysers (DMAs) (Winklmayer et al., 1991), where they are selected according to their size (electric mobility) by an electric field. The first flow goes through a nano-DMA that is used to scan from 21.5 down to 3.4 nm diameter, and the second through another DMA which simultaneously scans from 21.5 up to 857 nm diameter. The average ratio of particle counts between the DMA and the nano-DMA equalled 0.80 at 21.5 nm diameter during the measurement period. However, an analysis of data did not reveal whether nano-DMA concentrations were systematically overestimated or if DMA concentrations were underestimated, why data was left unaltered. The two DMAs are stepping in equal logarithmic diameter intervals, giving a total of 37 mobility channels, and the time required to measure one full number size distribution is 10 min. The condensation particle counters (models CPC 3025 and CPC 7610) (TSI Inc., Shoreview, MN, USA) are used to detect and count the mobility-classified particles exiting the nano-DMA and DMA, respectively. The algorithm for inversion of the DMPS data calculates the DMPS kernel matrix and uses the inverse of this to convert the measured mobility

distributions into particle number size distributions. Factors taken into account when calculating the matrix are: sampling line losses, bipolar charging probability, DMA transfer functions and CPC counting efficiency as a function of size (Zhou, 2001). Data is always presented as local wintertime (UTC + 1 h).

Two similar DMPS systems have been used in Vavihill. The first DMPS system measured the number size distribution until May 2002, and was run with dry (relative humidity, RH < 10%) external compressed air to maintain the laminar DMA sheath flows. The second DMPS, which has been in use since June 2002, has a closed loop sheath flow arrangement (Jokinen and Mäkelä, 1997). Depending on the status of the material drying the sheath air, the DMA RH for the second DMPS system varied between 1 and 45%.

Atmospheric temperature and RH were obtained from the weather station in Hörby, about 40 km east of Vavihill. Hourly averages of global radiation (W m^{-2}) were taken from Lund, about 30 km south of Vavihill, and finally SO_2 gas concentrations (μg m^{-3}) were determined with a filter pack method at Vavihill with a 24 h resolution (0–24 local wintertime, EMEP 2002).

2.2. *Classification of formation events*

The classification of formation events follows the method recently described by Dal Maso et al. (2005), and the reader is referred to that paper for more detailed information. The classification scheme classifies each day into one of five classes: class Ia and Ib and class II events, non-events, or un-defined events.

The aim of the classification is to separate the days with a regional-scale particle formation event from days with no formation events occurring. In principle, the particle formation takes place during the daytime followed by an almost linear particle diameter growth during the afternoon/evening (see e.g. Mäkelä et al., 2000). When particle formation is taking place over a larger area, this growth can be followed for a long time at a given site assuming horizontal advection. Unfortunately, other particle sources (such as local pollution or pre-existing particles) or arrival of an air mass with different properties can disturb or obscure this pattern. At the time of the present analysis, no computational algorithm existed to determine the occurrence of an event, and the classification was done manually. To reduce the subjective element, the event classes are determined by a group of three or more people, each making an independent classification of the size distribution data to reduce subjective bias.

The classification was based on the flowchart published in Dal Maso et al. (2005). Summarizing it, to classify as an event, a day had to fulfil the following criteria: (a) particles smaller than 25 nm had to be present; (b) these particles had to form a mode that had not existed before; (c) this mode had to persist over 1 h and (d) the particles in the new mode had to grow larger with time. Failure to fulfil the criteria (a), (b) and (c) resulted in a classification to the non-event class, and a failure to fulfil criterion (d) resulted in a classification to the undefined class.

In addition to these criteria, the classification into the event or non-event classes required agreement between all the participating scientists. If this was not the case, for example due to disagreement in interpreting whether an observed small mode was a new one or just a pre-existing mode that decreased in size, the day was classified as undefined. This criterion was used because it was deemed more important to eliminate possible false positives in these classes than to avoid false negatives. The purpose of the undefined class was to achieve a clear separation between the event and non-event days. It is likely that a fraction of undefined days are particle formation event days; however, it is highly unlikely that a non-event day is classified as an event or vice versa.

When a day was classified as an event day, it was further classified according to the possibility of further analysis. If it was possible to obtain the formation and growth rate of new particles, the day was classified as a class I event. For some days, while it was clear that the day was an event day, it was not possible to obtain these characteristics, due to for example strong fluctuations in the particle concentration. Such days were classified as class II events. Class Ia events are event days during which the new mode is clearly distinguishable from the pre-existing particle population for the whole duration of the event, making these days good candidates for modelling case studies.

A particle formation event search algorithm has recently been developed by Heintzenberg et al. (2007). It uses a pre-defined set of numerical criteria to select particle formation events, and has to be trained for each data set and event type separately. The classification obtained here will serve as a good basis for this training and as a reference for comparing the algorithm performance.

2.3. *Calculation of parameters describing the formation events*

The parameters relevant for formation events of class I calculated in this study include the 'apparent' and 'real' formation rate of 3 nm diameter particles determined from the DMPS (dN_3/dt, and J_3, respectively), the growth rate (GR) of the nucleation mode, the condensation sink (CondS) for condensing vapour, the condensable vapour concentration (C_{vapour}), the condensable vapour production rate (Q), the geometric mean diameter (GMD) and the number concentration (N_{nucl}) of the nucleation mode. Details on how these parameters are calculated can be found in Dal Maso et al. (2005), but are nevertheless briefly described and discussed below.

The three parameters characterizing each particle mode, GMD (nm), N_{nucl} (cm^{-3}) and the geometric standard deviation σ_g, are calculated based on a log-normal fitting routine developed by Hussein et al. (2005). GR (nm h^{-1}) is calculated by following the growth of the GMD of the nucleation mode. dN_3/dt (cm^{-3} s^{-1}) is calculated during formation events, starting from the time at which nucleation begins and continuing until the maximum number concentration is reached in the nucleation mode. J_3 (cm^{-3} s^{-1}) is the sum of dN_3/dt and the coagulation sink of the

nucleation mode particles, that is, J_3 is corrected for polydisperse intermodal coagulation losses with particles of larger sizes. Note that the nomenclature can be misleading in the literature, where J_x is sometimes used in place of dN_x/dt, where x denotes an arbitrary size (compare e.g. Mäkelä et al., 2000 with Dal Maso et al., 2005). The condensation sink (s^{-1}) is integrated over the entire humidified aerosol particle size distribution. The conversion from a dry to a humidified size distribution is based on the parametrization of Laakso et al. (2004) using the observed ambient RH. Although this parametrization is based on Finnish conditions, the situation at Vavihill should not be very different, and it is better to make this approximate correction for ambient RH than to make no correction at all (see, e.g. Dal Maso et al., 2002). The coagulation sink (cm^{-3} s^{-1}) used in the J_3-calculations is also based on the humidified distribution, and calculated as an average of the product between the coagulation sink in s^{-1} and N_{nucl} (cm^{-3}). The vapour concentration (cm^{-3}) and vapour production rate (cm^{-3} s^{-1}) are calculated indirectly via the GR. The exact compounds responsible for the condensational growth of the nucleation mode particles during formation events are still a matter of discussion. However, it is known that at least sulphuric acid takes part in this growth (Boy et al., 2005), so C_{vapour}, Q and CondS have been calculated assuming that the condensing vapours had the same properties as sulphuric acid. In reality the values of GR, C_{vapour}, Q and CondS are dependent on various vapour properties, including the molecular mass, saturation vapour pressure and mass accommodation coefficient of the condensing vapour, as demonstrated by Kulmala et al. (2001a).

The parametrization of Kerminen and Kulmala (2002) allows the calculation of the formation rate of the freshly activated particles (denoted J_1) assuming that they are around 1 nm in diameter. 1 nm was chosen here, since it is one of the most commonly used sizes in the literature. The parametrization can be calculated for any arbitrary size and it takes into consideration the calculated GR, the condensation sink of vapour and the polydisperse coagulation of nucleation mode particles with the pre-existing size distribution. The coagulation scavenging is taken into account by using a term $CondS^{|}$ (unit: m^{-2}) that is proportional to the condensation sink of vapours CondS (unit: s^{-1}). Physically, $CondS^{|}$ is a measure of the rate at which nanometre-size clusters coagulate with large pre-existing particles, so it does not require any prior knowledge of the condensing vapours, as opposed to CondS (s^{-1}). Three assumptions are made in the calculation of J_1:

1. Monodisperse coagulation (with particles in the same size mode, i.e. intramodal) can be neglected.
2. The population of the pre-existing aerosol particles remains unchanged during the event.
3. The nuclei grow by condensation at a constant diameter growth rate, GR.

$$J_1 = J_3 e^{\frac{\eta}{1}-\frac{\eta}{3}} \ (cm^{-3}\,s^{-1}), \tag{1}$$

where

$$\eta = \gamma \mathrm{CondS}^{|}/\mathrm{GR}\ (\mathrm{nm}) \tag{2}$$

and

$$\gamma = \gamma_0 (d_{mean}/150\ \mathrm{nm})^{0.048} (T/293\mathrm{K})^{-0.75}. \tag{3}$$

Since γ varies relatively weakly with different ambient parameters (Kerminen and Kulmala, 2002), it was approximated by a constant value of $\gamma_0 = 0.23\ nm^2\ m^2\ h^{-1}$. Recent ion and aerosol spectrometer data from Finland indicate that the GR could be lower for particles around 2 nm in diameter than for particles around 13 nm diameter (Kulmala et al., 2004b). Examination of 30 DMPS spectra from Vavihill gave no indication that the growth rate of smaller particles was generally lower than that of larger particles in this case, although it should be mentioned that no ion mobility data were available to confirm the growth rate of particles below 3 nm in diameter. In any case, the third assumption of constant GR probably leads to the greatest uncertainty in the J_1 calculations. However, as will be seen later, J_1 changes by several orders of magnitude between polluted and cleaner environments, and there is thus no reason to believe that this difference is not real.

2.4. Source region classification

An air mass classification was performed in order to examine how varying concentrations of precursor gases and overall pollution level influenced the Vavihill formation events. Back-trajectories were used to trace the air mass back to different source regions. The definitions of the various regions are shown in Fig. 2, and are similar to those used by Swietlicki (1989), displaying clear differences in pollution levels.

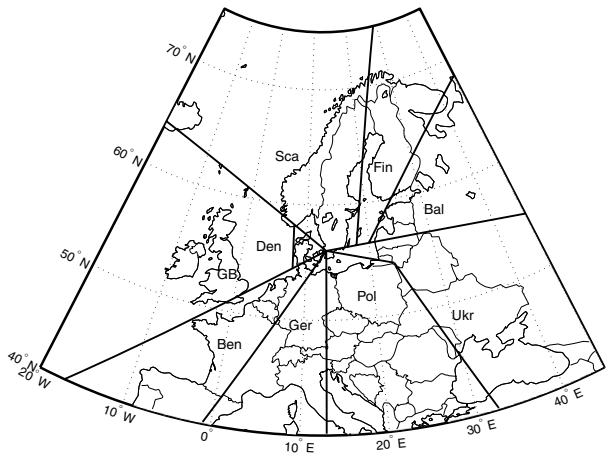

Fig. 2. Map showing region definitions with abbreviations. 'Den' = Danish air masses, 'GB' = British, 'Sca' = Scandinavian, 'Fin' = Finnish, 'Bal' = Baltic, 'Ukr' = Ukrainian, 'Pol' = Polish, 'Ger' = German and 'Ben' = Benelux countries.

The trajectories were calculated with the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory's HYSPLIT model using meteorological data from the FNL database (Draxler and Hess, 1997). The trajectories at 150 and 500 m a.s.l., which arrived at the Vavihill site at noon and 18:00 h every day, were used for the analysis. The higher altitude trajectory was used to establish whether there were different source regions for the aerosol in the residual layer overlaying the well-mixed boundary layer, and to check that the trajectories were consistent. When the 150 m trajectory passes a specific source area for a few hours within two days of arriving at Vavihill, it is labelled with the appropriate source region, which means that each event day may have one or more source regions associated with it. However, the third and fourth consecutive source regions are not considered in the analysis. 'Ben' (the Benelux countries = Belgium, the Netherlands, and Luxembourg) and 'Ger' (German) trajectories are not labelled as 'Den' (Denmark) even if they have passed over Denmark, since from data it does not seem to be important in terms of formation events whether 'Ben' or 'Ger' trajectories have passed Denmark or not on their way to Vavihill.

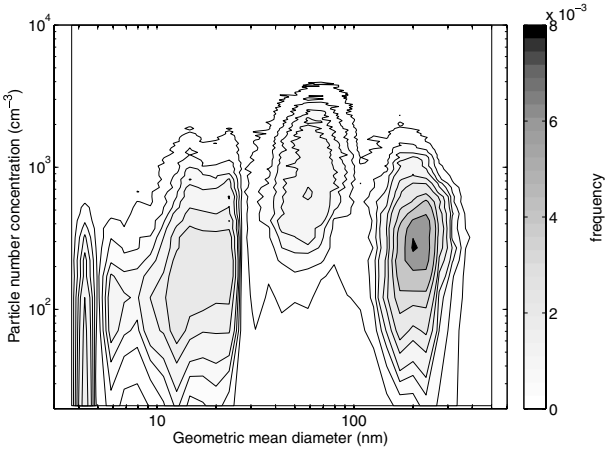

Fig. 3. Modal structure of the particle number size distribution measured at Vavihill summarized from the frequency of occurrence of individual modes within a certain interval of mode number concentration and geometric mean diameter (GMD). This figure consists of all the valid measured size distributions with 10-min resolution.

3. Results and discussion

3.1. Aerosol phenomenology

Following the methodology of modal fitting of the size distribution according to Hussein et al. (2005), three modes were used to fit the measured particle number size distributions at Vavihill. These were the nucleation, Aitken, and accumulation modes, respectively. The modal structure revealed that the accumulation mode usually had geometric mean diameters (GMD) between 100 and 300 nm with a number concentration of about 300 cm^{-3} (Fig. 3). The mode was observed in the entire data set indicating that these aerosol particles hold regional characteristics. The GMD of the Aitken mode ranged between 30 and 90 nm with a number concentration of around 800 cm^{-3}. Sources that are likely to sustain the Aitken mode population are either aged particles due to particle formation events or the production of primary particles such as those emitted from traffic. When produced 10–1000 km upwind from Vavihill, these particles have had time to grow to Aitken mode sizes before reaching the site. Contrary to the Aitken and accumulation modes, the nucleation mode was highly variable regarding both the GMD and number concentration; the GMD of the nucleation mode was mainly below 25 nm and rarely below 6 nm. The high variability in the nucleation mode parameters are mainly related to new particle formation events occurring around or upwind of the Vavihill site and scavenging of the newly formed particles by coagulation and deposition.

When separating the median size distribution into the four different seasons (Fig. 4 and Table 1), it is clear that the Aitken and accumulation mode particle number concentrations are highest during the summer months (about 30% higher than during winter). The median number concentration of the nucleation mode varies at most by about 15% between spring and winter implying that there is a frequent source of 10–25 nm particles during the entire year upwind of the Vavihill station as discussed above. Please note from Fig. 4 that the 75 percentile values of the nucleation mode throughout the year do not reveal the fact that particle formation events are actually more common during spring than during other seasons. However, 90 percentile values are clearly higher during spring (not shown here). Finally, the median sizes and widths of the modes remain nearly invariant as function of season, which is similar to the observations at another rural site in Sweden, at about 59°N (Aspvreten) (Tunved et al., 2003).

The Tunved et al. (2003) study also shows that there is a rather weak diurnal variation of the median size distribution at the Nordic stations when formation events are removed from the data set. The largest variation is found for the Aitken mode at Vavihill (about 30% relative variability in number concentration), see Fig. 5. The diurnal pattern follows that of the boundary layer evolution. In the evening, aerosol particles from formation events that have taken place further away from Vavihill and possibly also primary anthropogenic aerosol particles increase the Aitken concentration. During nighttime, the shallow and relatively stable nocturnal boundary layer prevents vertical mixing with air from aloft. Between sunrise and noon the following day, the break-up of the nocturnal boundary layer and mixing with relatively cleaner air from aloft slightly reduces the Aitken concentration. When formation events are considered, on the other hand, a much stronger diurnal pattern emerges for the nucleation and Aitken mode as has previously been demonstrated in the literature (e.g. Tunved et al., 2003). This implies that the aerosol

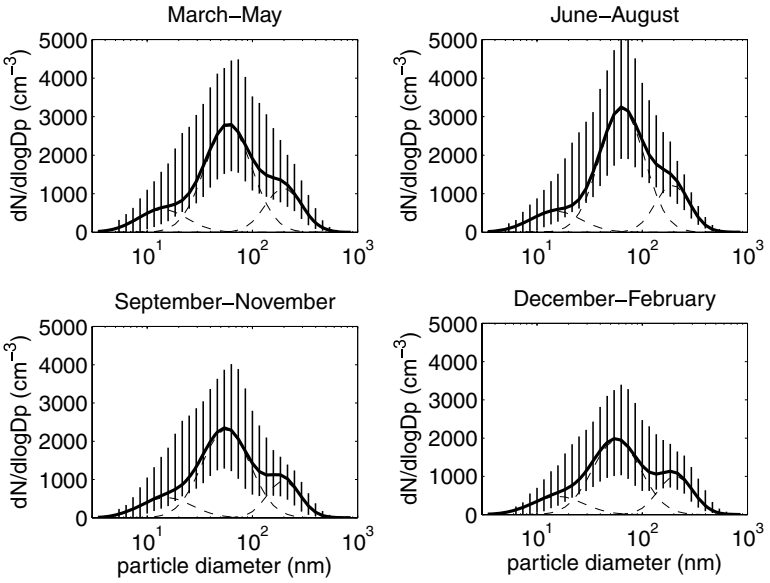

Fig. 4. Median number size distribution shown with a heavy line for the four different seasons based on the log-normal fitting method. Bars show the 25 and 75 percentile of number concentrations from raw data (not modal data). Please note that the median GMD and σ_g are constant for each season in this specific presentation (i.e. no percentile range is given for these values). The three modes which make up the size distribution are depicted with dashed lines.

Table 1. Median values of modal parameters using the fitting algorithm of Hussein et al. (2005), RH, temperature, sulphur dioxide (g) and global radiation as function of season at Vavihill

Modes	Median of modal parameters	Spring	Summer	Autumn	Winter
Nucleation mode	GMD (nm)	14.0	15.1	15.3	15.8
	σ_g	1.71	1.74	1.75	1.75
	N (cm^{-3})	350	330	320	290
Aitken mode	GMD (nm)	59	64	56	57
	σ_g	1.67	1.63	1.69	1.69
	N (cm^{-3})	1550	1700	1320	1120
Accumulation mode	GMD (nm)	197	193	197	206
	σ_g	1.49	1.45	1.43	1.47
	N (cm^{-3})	500	500	380	420
Total N (cm^{-3})		2400	2520	2020	1830
Total volume (μm^3 cm^{-3})		4.6	4.2	3.2	4.1
Frequency of events (%)	Class I + II	57	54	33	12
SO_2 (g) (μg m^{-3})	Diurnal average	0.60	0.38	0.36	0.68
RH (%)	1-h average	80	81	90	91
Temperature (°C)	1-h average	6.5	16.5	7.7	0.0
Global radiation (kW m^{-2})	3-h average (10:00–13:00)	0.44	0.57	0.20	0.062

population is influenced to a greater extent by photochemical activity and boundary layer evolution when local formation events occur.

The size distribution of southerly air masses arriving at Vavihill (trajectories from the Benelux countries, Germany, Poland and Ukraine) is shifted towards higher mass concentrations compared to relatively cleaner air masses from the Nordic countries. Northerly and southerly air masses contain on median 1410 and 2430 particles cm^{-3} larger than 25 nm diameter, whereas northerly air masses contain on median 570 cm^{-3} nucleation mode aerosols particles compared to 370 cm^{-3} in the polluted, southerly air masses. The lower mass concentration in the relatively cleaner, Nordic air masses allows for more formation events and a higher number concentration in the nucleation mode.

3.2. *Classification and characterization of formation events*

The results of the classification of the formation events are presented in Fig. 6, which shows that there were, on average, 36% event days in the 681 d classified (including days with events, non-events and undefined events, and days with missing or bad data were not classified). The events were of class Ia, Ib and II on about 5, 16 and 16% of the occasions, respectively. The rest were classified as undefined and non-events on 29 and 35% of the

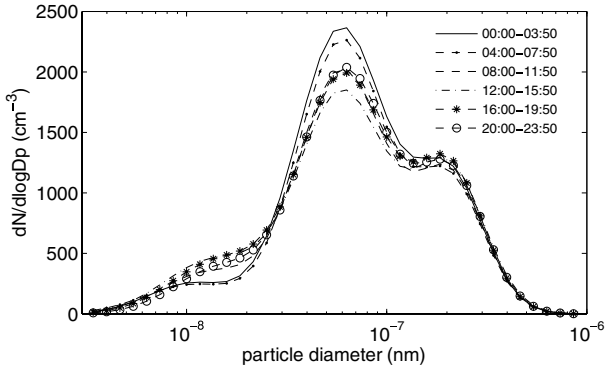

Fig. 5. The median size distribution of all Vavihill data excluding formation event days based on the log-normal fitting method by Hussein et al. (2005) as function of six different time intervals (UTC + 1 h) given in the figure legend.

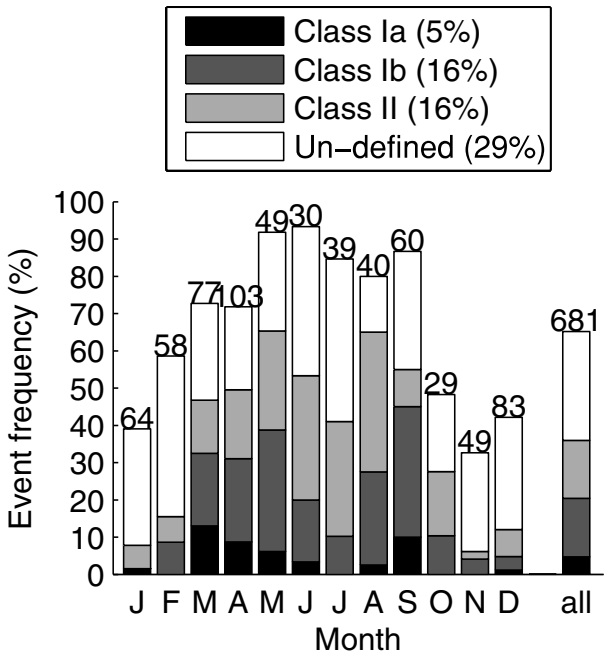

Fig. 6. The frequency of new particle formation events as a function of month. The first letter of the month is given below the bars. The last bar shows the average for all data. The average event frequency in percent is given in brackets next to the legend. The numbers on top of each bar give the number of data used in the calculations.

days, respectively. The fraction of events is higher in Vavihill than at the other Nordic stations Hyytiälä (61° 51′ N, southern Finland), Aspvreten (58° 46′ N, Sweden), Värriö (67° 46′ N, Finnish Lapland), and Pallas (67° 58′ N, Finnish Lapland) (Dal Maso et al., 2007), Abisko (68° 21′ N) (Svenningsson et al., 2008) and Utö (59° 47′ N, Baltic Sea) (Hyvärinen et al., 2008) where the fraction varied between 15 and 27%.

If only events and non-event days are considered as classified days, (i.e. undefined days are rejected), the event frequency

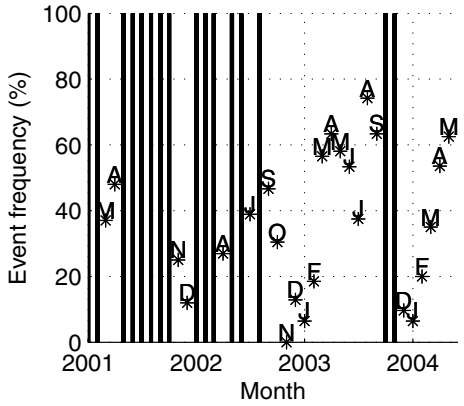

Fig. 7. The frequency of new particle formation events as function of time. Data are only shown for months in which at least 15 d were analysed. The first letter of the month is given above the data points. Grey bars indicate missing months. During May–October 2001, and January–March 2002, the DMPS was being deployed elsewhere.

increases to 51%, which is similar to the frequency found for Aspvreten and Hyytiälä, close to 50%. In Värriö and Pallas this frequency is about 27%, and at Abisko 26%. Considering the southern location of the Vavihill station, our findings here are in line with the north-south difference in event frequency reported by Dal Maso et al. (2007), where Lapland stations showed clearly lower particle formation frequencies than the more southerly stations.

The events are most frequent during spring and early autumn, and are slightly less common in June and July than in May and August. The average seasonal variation is similar to that observed at the other Nordic stations mentioned above residing inside or close to the boreal forest zone (Dal Maso et al., 2007; Hyvärinen et al., 2008). The greatest difference is that more events occur in June to August in southern Sweden than at the other sites. It should be remembered that most of the data for Vavihill are from the year 2003, when the frequency of formation events seemed to be higher than usual (Fig. 7). 2003 is also the year when the record amount of events were observed at the Hyytiälä station, as well as the year with the highest event/non-event ratio yet observed at the Aspvreten station. The seasonal frequency of events is different at rural continental sites in Germany and Italy, where other atmospheric circulation patterns might alter the seasonal conditions favourable for formation (Birmili and Wiedensohler, 2000; Birmili et al., 2003; Laaksonen et al., 2005; Rodriguez et al., 2005).

All the class I days in Vavihill were characterized with respect to the different parameters, and the results are presented in Table 2. The range of values of the different parameters is given as 10th and 90th percentiles.

The median GR is 2.1 nm h^{-1}, not very different from the other Nordic observations, which range from 2.0 nm h^{-1}, (Pallas) to 3.4 (Aspvreten). The median apparent formation rate,

Table 2. Statistics for the nucleation events for all class I days (139 of the 681 analysed days). See Dal Maso et al. (2005) for details on calculations

Parameter	Average	10th percentile	Median	90th percentile
J_1 (cm^{-3} s^{-1})[a]	620×10^3	3.3	59	72×10^3
J_3 (cm^{-3} s^{-1})[a]	4.3	0.41	1.89	8.3
dN_3/dt (cm^{-3} s^{-1})[a]	1.54	0.23	1.05	3.8
GR (nm h^{-1})[b]	2.5	1.12	2.1	4.2
N_{nucl} ($\times 10^3$ cm^{-3})[c]	3.8	0.43	2.8	8.3
GMD (nm)[c]	28	14.5	26	41
C_{vapour} ($\times 10^7$ molecules cm^{-3})[b]	3.5	1.56	3.0	6.0
Q ($\times 10^5$ molecules cm^{-3} s^{-1})[b]	2.5	0.41	1.39	6.2
CondS ($\times 10^{-3}$ s^{-1})[d]	5.4	1.23	3.5	10.8
SO_2 (g) (μg m^{-3})[e]	1.1	0.15	0.54	3.4
RH (%)[d,f]	59	37	59	77
Temperature (°C)[d,f]	11.4	1.85	12.4	19.2
Global radiation[g] (kW m^{-2})	0.51	0.23	0.54	0.72

[a]Calculated from the time at which nucleation began until the maximum number concentration had been reached in the nucleation mode.
[b]From the beginning of the formation event until growth became unstable or until the end of the day (anywhere between 14:00 and 24:00 UTC+1 h).
[c]At the end of GR calculation (see [2]).
[d]At the onset of formation.
[e]Diurnal average.
[f]1-h average.
[g]3-h average between 10:00 and 13:00 h local winter time.

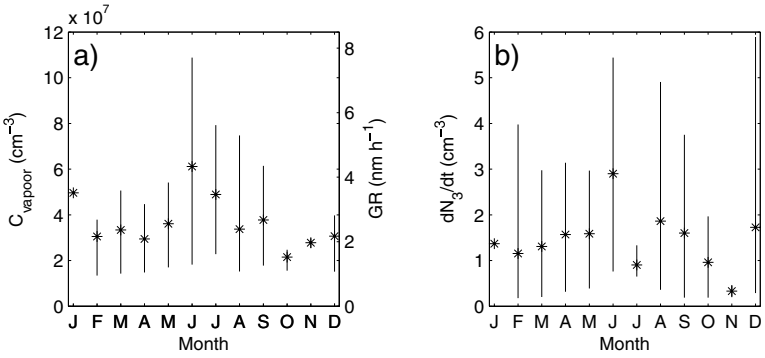

Fig. 8. C_{vapour} and GR (a), and dN_3/dt (b) for class I events as a function of month. Stars denote the average value, and the bars represent values between the 25 and 75 percentiles.

dN_3/dt is 1.05 cm^{-3} s^{-1}, about a factor 2 higher than in Hyytiälä, Finland. It is 5–10 times higher than at Aspvreten, Värriö or Pallas, which is however mainly caused by differing cut-off diameters of the instrumentation (Dal Maso et al., 2007). In general, the GR does not differ very much between different locations in Europe (Kulmala et al., 2004a), while the formation rate seems to become higher with increasing level of pollution (Kulmala et al., 2004a). One notable exception is the formation in clean coastal areas of Ireland, where both GR and dN_3/dt can be orders of magnitude higher than in all other environments (Dal Maso et al., 2002). The median source rate, Q of condensing vapours was 1.4×10^5 cm^{-3} s^{-1}, which is higher than observed in Finland (0.2–0.7 $\times$ 10^5 cm^{-3} s^{-1}), but similar to Aspvreten (1.3×10^5 cm^{-3} s^{-1}) (Dal Maso et al., 2007) and Utö (1.8×10^5 cm^{-3} s^{-1}) (Hyvärinen et al., 2008). Note that the value for Utö is an average, not a median.

The values of GR and C_{vapour} show a clear seasonal dependence with a maximum in the summer months (Fig. 8a). The seasonal variation of GR is similar to the other Nordic stations referenced above, and with the concentration of biogenic volatile organic oxidation products (Kulmala et al., 2004c), suggesting that biogenic volatile organic compounds may play a role in the growth process also at Vavihill. The seasonal pattern of dN_3/dt is furthermore similar to that at Hyytiälä and Aspvreten, with a clear minimum in July (cf. Fig. 8b and Kulmala et al., 2004c or Dal Maso et al., 2007), and the frequency of particle formation events is also lower in July. Kulmala et al. (2004b) suggested that one reason for the appearance of these minima in Finland may be that the average condensation sink in July is higher than in neighbouring months (Dal Maso et al., 2005) due to the higher frequency of subtropical air masses during this month. If the condensation sink is high prior to particle formation events, there is

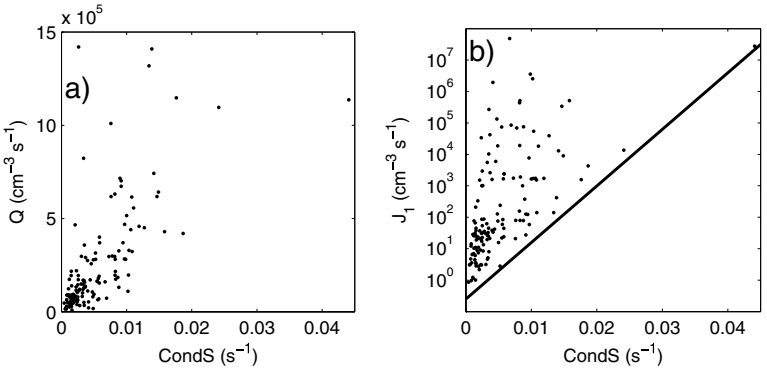

Fig. 9. Q (a) and J_1 (b) as function of the condensation sink just before the onset of nucleation for class I events. The heavy line in (b) separates the areas in the J_1-CondS-space where class I formations are observed and where they are not observed (equation: $J_1 = 10^{(180*\text{CondS}-0.60)}$).

a smaller chance of these events being detected, as is discussed below. At Vavihill, the median condensation sink collected from all available data is about 0.0085 s^{-1} during the adjacent months of May–June and August–September compared to 0.0093 s^{-1} during July. Such a small difference in the sink, however, does not necessarily explain the reduction in observed event frequency by about 40% in July compared to adjacent months (Fig. 6).

The formation rate of hypothetical clusters, J_1, the vapour source rate (Q), and the condensation sink (CondS) do not show such a strong seasonal dependence as GR, C_{vapour}, and dN_3/dt. Instead, they depend strongly on air mass history.

Polluted air masses often contain a relatively high number of aged accumulation or Aitken mode particles. This produces a large particle surface area or, in other words, a large condensation sink for low volatile vapours. Therefore, a high vapour production rate (Q) is required in polluted air for the growth of the newly formed particles to occur. In a corresponding way, the production rate of freshly activated particles (J_1) needs to be higher. Otherwise, the particles are readily scavenged by polydisperse coagulation before they reach detectable sizes (Kerminen et al., 2001). Since polluted air masses generally contain a higher concentration of condensable gases, naturally Q and J_1 are higher. Figs. 9a and b indeed shows that Q and J_1, respectively increase with the size of the condensation sink during formation events.

Figure 9b further shows that there is a minimum particle formation rate as function of CondS, below which class I events are not observed for the Vavihill data (heavy line in the figure given by $J_1 = 10^{(180*\text{CondS}-0.60)}$, where J_1 and CondS are in units of cm^{-3} s^{-1} and s^{-1}, respectively). Therefore, this seems to represent a threshold for southern Scandinavia, where regional events cannot be observed due to coagulation scavenging as J_1 values are below the line.

3.3. Comparison between polluted and clean air masses

It has been assumed that southerly air masses arriving in Vavihill will have a higher condensation sink of particles prior to formation events. Fig. 10a shows all the data and the median of the condensation sink during class I events for the different air masses defined above. Clearly, the air arriving from the regions 'Ben', 'Ger', 'Pol' and 'Ukr' have a higher median condensation sink ($\sim$0.01 s^{-1}) and are therefore referred to as polluted air masses. The three source regions from the Nordic countries ('Den', 'Fin' and 'Sca') have a lower condensation sink ($\sim$0.0025 s^{-1}), and are hereafter referred to as clean air masses. Two moderately polluted air masses are also evident, the 'GB', and the 'Bal' air masses (condensation sink $\sim$0.005 s^{-1}). It can be seen in Fig. 10b and c that J_1 and Q are about 100 and 5 times higher, respectively, in the polluted air masses than in the cleaner ones. Nevertheless, the formation rates given by the DMPS (dN_3/dt) in both types of air masses are comparable (Fig. 10d), that is, on the order of 1 cm^{-3} s^{-1} due to the higher polydisperse coagulation and condensation sinks in polluted air.

A question that naturally arises is: how does the degree of pollution affect the frequency of formation events? To answer this question, Fig. 11 is presented, where it can be seen that clean air masses, on average, have a high probability of leading to class I formation events in Vavihill (around 20%). Note that each event class may be associated with two source regions. However, no general conclusion can be drawn from a cursory inspection of Fig. 11 regarding the event frequency at Vavihill in polluted air masses. In fact, it appears that polluted air masses can produce both rather high and low numbers of class I events. The frequency of class I events in Polish air masses is 20%, while it is only between 5 and 10% in air from the Ukrainian and Baltic regions.

The high frequency of events in air from the clean northerly and northwesterly air masses is not surprising, since this has previously been reported in Hyytiälä, Finland (Kulmala et al., 2001b). The vapour production rate Q is highest in the Polish air masses, at least during the particle formation events when DMPS data can be used to estimate Q (Fig. 10c). If the same holds also for the other days, it might explain the higher frequency of events in the Polish air masses compared to the other polluted sectors.

Another question that arises is whether a certain pattern can be discerned within similarly polluted air masses when events are observed compared with occasions when they are not observed. The trajectories reveal that in 22 of 39 Benelux, German and Polish class I cases, the air has spent less than 2 d over the polluted areas before reaching Vavihill. Conversely, there are 79

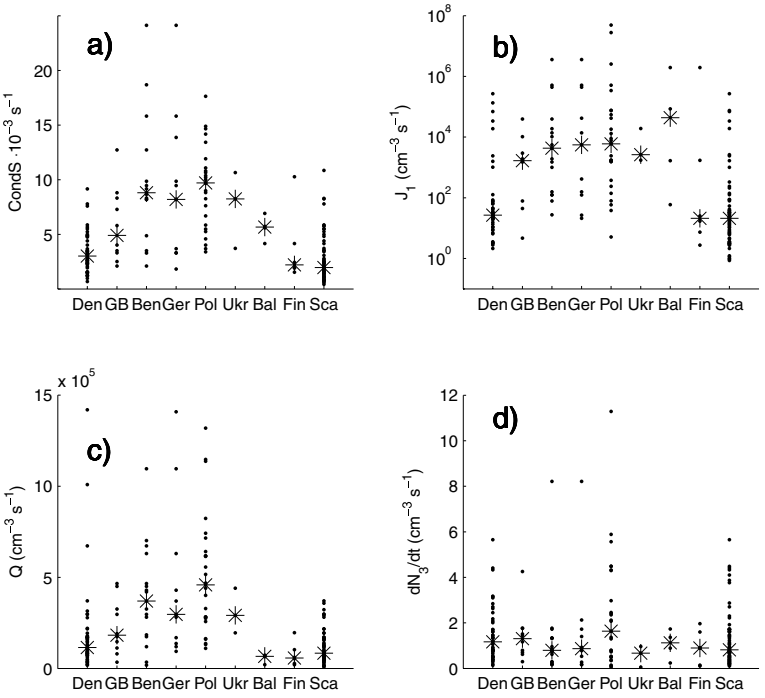

Fig. 10. (a) Condensation sink just before the onset of nucleation; (b) J_1; (c) Q; and (d) dN_3/dt, as a function of air mass source region for class I events. Stars denote median values, and each dot represents one measurement.

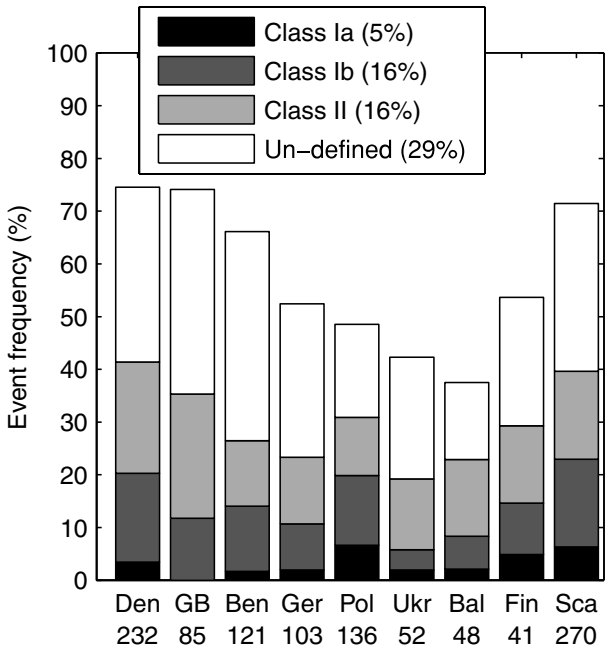

Fig. 11. The frequency of nucleation events at Vavihill (in %) as a function of air mass source region. The numbers on the bottom of the histogram give the number of times the trajectories have passed over the source region.

non-events associated with air residing more than 2 d over polluted areas, and only 27 occasions of non-events when the air has resided less than 2 d over polluted areas. Hence, it is more probable that nucleation events will occur in southerly air masses if the air has not persisted over polluted areas. A possible explanation of why events should occur in these cases is that the air was very clean to start with, and then passed over polluted areas for 1 or 2 d. This may not have been a sufficiently long time for particles to form and grow into large accumulation mode sizes, at the same time as the accumulation of a high concentration of vapour, needed for the formation events, took place. Hence, the air movement may have resulted in high concentrations of condensable vapours, while the condensation sink was kept on a level low enough to observe formation events. This explanation is partly supported by the fact that the condensation sink is much greater on several non-event occasions when air has persisted for longer times over the polluted areas.

Not surprisingly, the median duration of an event (duration of elevated levels of particles appearing in the lowest size channel of the DMPS instrument) in polluted air masses is shorter, about 3.5 h compared to about 5.5 h in cleaner air. This again should be a result of the higher polydisperse coagulation and condensation loss in polluted air. There is no significant difference between the start of the formation event between polluted and clean air, and the start of an event usually follows an annual pattern with a time lag of a few hours after the sunrise. The duration of an event is highest in spring, about 5.5 h, and only about 4 and 3.5 h in summer and autumn/winter, respectively. Note that the similarity between these numbers and the median duration of the events in polluted and clean air masses is circumstantial, and does not mean that events in clean air masses are only observed during spring, and the rest of the year for the polluted cases. Rather, the events are evenly distributed between polluted and clean cases during the year. The annual pattern of the start and duration

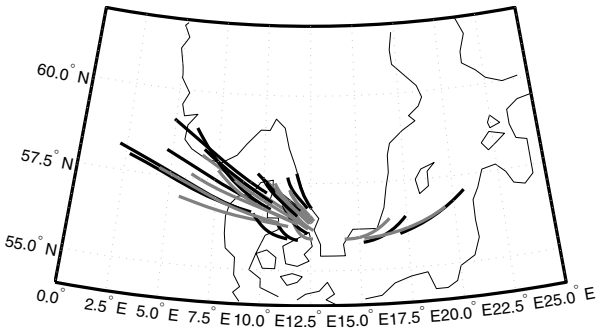

Fig. 12. Map showing the trajectories crossing over the open sea and reaching Vavihill at 20:00 and 23:00 (grey and black, respectively, 150 m arrival height) during 15 class I event days. Only the section when the UTC + 1 h time is between 9:00 and 17:00 h along the trajectory is shown, since the formation events are initiated during this time.

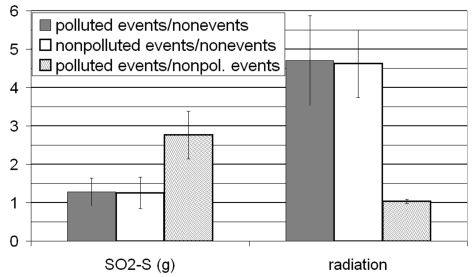

Fig. 13. The ratio of median SO_2 in the gas phase and median radiation between different air masses or event and non-event occasions. Polluted air masses are Polish, Benelux, German, and Ukrainian, and clean air masses are Danish, Scandinavian, and Finnish. Error bars show the variability of the ratios using the error of propagation formula and standard deviations of the median values. SO_2 values are diurnal averages (μg m^{-3}) and global radiation values are 3-h averages between 10:00 and 13:00 h local winter time (W m^{-2}).

of an event is similar to the boreal Finnish forest, except that the duration shows another peak during autumn for the Finnish forests (Mäkelä et al., 2000).

Another interesting feature discovered when studying the trajectories in detail is that formation events with clear growth are also observed when the trajectories only pass over the Danish mainland (Jutland) and islands without passing over any other continental area. The particle growth can be followed for at least 10 h in Vavihill. This means that formation probably takes place all over Denmark, since it takes about 10–12 h to traverse Denmark before reaching Vavihill.

The trajectories were also used to separate air masses that had passed over as little land as possible before reaching Vavihill. This was done in order to test whether formation events with continuous subsequent growth (class I events) can take place over the open sea surrounding Vavihill, mainly the straits of Skagerak separating Jutland-Norway and Kattegatt (Jutland-Sweden) and parts of the Baltic Sea east of Vavihill. Also 3000 m trajectories (free troposphere) were investigated to further ensure consistency in air mass origin between different altitudes. Two trajectory arrival times (20:00 and 23:00) were selected for each day, Altogether 42 occasions could be identified with trajectories that had previously passed over the open sea between 9:00 and 17:00 h, the time when particle formation is normally occurring. Out of these, 15 occasions contained class I events, corresponding to a formation event frequency of 36%, higher than for any other air mass. Fig. 12 shows that the trajectories of 13 of these 15 class I events cross the main Kattegatt ship lanes that run between the northern tip of Jutland (Skagen) and through the straits of either Öresund, the Great Belt or the Little Belt.

Since the growth of the nucleation mode particles from formation events is still observed at evening time for class I events, it appears that a significant fraction of the actual particle conception and subsequent continuous condensational growth took place over the open sea, and not over land. Note that this was concluded from observations at Vavihill only, since no size distribution data along the trajectory was available.

This finding is somewhat surprising, since earlier studies at Finnish stations did not observe any clear or strong formation events with continuous growth in air masses passing over the Norwegian Sea (Tunved et al., 2006). That study concluded that the nucleation mode particles from formation events could only accumulate a significant mass concentration if the air masses had been transported over the Nordic land areas. However, the Kattegatt ship lanes are among the most heavily trafficked in Europe with ~200 ships passing each day (Gustafsson, 2007), emitting large quantities of SO_2, NO_x and VOC (Vestreng, 2003). The SO_X (SO_2 and SO_3) emissions per unit area are actually higher for Kattegatt and Skagerak with a reported range from about 1 to 4 Mg km^{-2} than for the surrounding land in Denmark (ranging from about 0.1 to 2 Mg km^{-2}, average about 0.5 Mg km^{-2}) and Sweden (ranging from about 0.01 to 2 Mg km^{-2} for southern Sweden) (EMEP 2007). On the other hand, the non methane volatile organic carbon compounds (NMVOC) emissions from these sea areas are reported to be 1–2 orders of magnitude smaller than for the Danish mainland (EMEP 2007), while NO_X emissions are on the same order of magnitude, that is, ~5 Mg km^{-2} (EMEP 2007). The findings from this study however, need to be confirmed by measurements conducted over the open sea to be able to make any conclusive statement of the ability of ship traffic to account for new particle formation events.

Although SO_2 is required as a precursor for sulphuric acid which takes part in both particle formation and growth (Boy et al., 2005), the available SO_2 data at Vavihill (daily averages) can not be used to predict the occurrence of formation events. The median ratio of Vavihill SO_2 concentrations between events and non-events is slightly higher than unity in both polluted and cleaner air masses (Fig. 13). In contrast, global radiation is 4.5 times higher on median between events and non-events, showing that meteorology is more important for the onset of nucleation

than the availability of SO_2. Birmili and Wiedensohler (2000) have shown similar results for a German continental site. The seasonal event frequency at Vavihill in polluted air is similar to that in cleaner air, despite that polluted air contains ∼2.5 times higher concentrations of SO_2 (Fig. 13), again supporting atmospheric conditions as the more important trigger mechanism of formation events. The condensation sink at Vavihill in polluted air is only about a factor 4 lower than in Pittsburgh (Stanier et al., 2004), whereas the availability of SO_2 is about 30 times higher in Pittsburgh (Vavihill average ∼0.90 μg m^{-3}, Pittsburgh average ∼30 μg m^{-3}, Wittig et al., 2004). Despite the much higher levels of SO_2, the frequency of formation events in Pittsburgh is comparable to polluted air masses in Vavihill, that is, about 30%. This again implies that an input of excess SO_2 does not necessarily increase the frequency of formation events.

3.4. Implications for climate

Events with a growing GMD of the nucleation mode to sizes above 30 nm diameter or larger in the evening of the same day were considered to likely affect aerosol climate forcing. This 30 nm criterion was used as a compromise, since it is often not possible to follow the air parcel over several days to observe the full growth of the Aitken mode particles to sizes where they are likely to act as CCN and thereby contribute to the indirect aerosol effect on climate (Pirjola et al., 2004). In northern Finland, aerosol particles activate to form cloud droplets between 50 and 128 nm diameter, with an average activation size of 80 nm diameter (Komppula et al., 2005). Since growth is often observed during the subsequent day at Vavihill, these Aitken particles can also be regarded as indication of regional formation and growth events, having a fingerprint of around 300–600 km.

The characteristic time scale (the time required to reduce the population by 63%) of 30 nm diameter particles subject to coagulation losses as they grow to cloud activation sizes is roughly 2 d, when calculated as the inverse of the coagulation sink in s^{-1}. The 30 nm diameter Aitken mode aerosol is assumed to be lost by coagulation with an accumulation mode aerosol typical for spring conditions at Vavihill using values in Table 1. In a corresponding fashion, the dry deposition characteristic time scale of the 30 nm particle is calculated by dividing a typical boundary layer height of 500 m with a typical dry deposition velocity of about 0.01 m s^{-1} for a boreal forest (Grönholm et al., 2007). The resulting time scale of about 14 h should be regarded as a lower limit, since Vavihill is also surrounded by agricultural and sea areas, where the dry deposition velocities are much smaller. As the particles grow beyond 30 nm, their characteristic lifetimes also become higher. In other words, the time scale should be on the order of at least 1 day.

For the few class I events when growth could be observed from the onset of particle formation all the way up to 80 nm or slightly smaller, the time required for growth from 30 to 80 nm was on the order of ∼1 d. Hence, the estimated particle loss time scales are comparable to the time it takes for a 30 nm particle to grow to 80 nm, meaning that the 30 nm diameter particles have a realistic chance to survive losses and take part in climate effects.

During 34% of the class I events (7% of all days), the GMD becomes larger than 30 nm by the end of the event day. Polluted air masses ('Ben', 'Ger' & 'Pol') contribute about 40% to these cases (see Fig. 14a). Ukrainian and Baltic air masses were previously regarded as being less important for the frequency of class I events appearing at Vavihill, and in Fig. 14a they are not even represented when GMD > 30 nm. This confirms that Vavihill formation events in these air masses have less impact on climate. Formation events in the Finnish air masses are only observed to give GMD > 30 nm on one occasion during a 2-yr period, and could probably also be disregarded in the discussion about potential climate effects.

What is triggering the growth of aerosols above 30 nm? One of the factors for a high growth rate is probably the vapour production rate. Calculations show that the median value of Q is about a factor 2 higher when GMD is higher than 30 nm than when it is lower than 30 nm.

Cleaner air masses are able to produce a slightly higher number concentration (median) of particles from formation events at the end of the day (∼3·10^3 cm^{-3}) than more polluted air masses (1.5–3 × 10^3 cm^{-3}) (Fig. 14a). The fraction of nucleation mode particles compared to the total concentration measured by the DMPS is also higher in the cleaner air masses (around 70%)

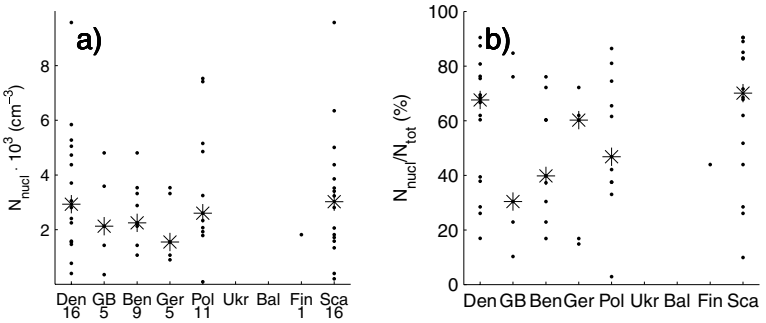

Fig. 14. (a) N_{nucl}, and (b) N_{nucl}/N_{tot} when GMD > 30 nm at the end of the class I event day (end of GR calculation) as a function of source region. Stars denote median values. The numbers of observed events in each of the source regions are given at the bottom of panel (a).

compared to polluted air (30–60%, see Fig. 14b). This indicates that each formation event in cleaner air has a relatively higher impact on climate compared to an event in polluted air. The fact that aerosol particles in cleaner air masses typically activate to form cloud droplets at lower sizes (50–100 nm diameter) than in polluted air (higher than 100 nm diameter) further strengthens this conclusion (Komppula et al., 2005).

Regardless of the relative importance of CCN production in polluted and non-polluted formation events, it is still difficult to say how much of the CCN produced arise from formation events compared with other sources. The Scandinavian stations are densely spaced, which offers a unique opportunity to model the CCN contribution from aerosol formation over the boreal forests of Scandinavia using a common database. Work has been initiated to model the aerosol and CCN concentrations globally including formation events through the binary water–sulphate homogeneous nucleation (Spracklen et al., 2005). More recently Spracklen et al. (2006) have used recent theory of activation of clusters including growth by organics (see Kulmala et al., 2006), and they were able to reproduce observed atmospheric nucleation in the Hyytiälä case. Quantitative efforts already exist to estimate the 'first indirect' radiative forcing due to CCN production from nucleation bursts in the boreal forest worldwide, where figures between –0.03 and –1.1 W m^{-2} are put forward (Kurten et al., 2003). Here, the Finnish trees around Hyytiälä are used as proxy for boreal forests.

4. Conclusions

Almost 2 yr of DMPS data from the background station Vavihill in southernmost Sweden show that there are 36% event days of classes I and II. The mean frequency and seasonal pattern are comparable to those in southern Finland (Hyytiälä). GR, dN_3/dt, C_{vapour} and Q were calculated during the formation of class I events. Furthermore, N_{nucl} and CMD were calculated for the formation of class I events at the end of the day, and the condensation sink prior to formation. The seasonal pattern of GR, C_{vapour} and dN_3/dt are similar in Vavihill and Finland, suggesting that similar compounds take part in particle formation and growth on many occasions, although other mixtures of compounds might influence the nucleation in Vavihill when the air is more polluted.

Vavihill is a suitable place to study the influence of polluted versus less polluted air masses on class I events. The main conclusions drawn from this comparison are as follows.

The production rate of condensing vapours and of freshly activated nano-particles (~1 nm diameter) are much higher in polluted than in cleaner air masses. Therefore, events with clear growth are still frequently observed at Vavihill in polluted air despite the higher rate of coagulation scavenging and loss of condensable vapours to the pre-existing particle population. The frequency of events is higher if the air has not resided over the polluted area for more than 2 d. Polluted air masses can moreover lead to the growth of the nucleation mode to a GMD higher than 30 nm that should be relevant for climate effects with comparable frequency to cleaner air masses, which happens during 7% of all analysed days. Generally however, the frequency of all events and the relative number concentration of newly formed nucleation mode particles are higher in cleaner air masses.

The analysis of individual source regions reveal that the impact of formation events observed at Vavihill in air masses from the source areas, 'Ukr', 'Bal' and 'Fin' is probably rather small. Furthermore, trajectories show that events take place over the entire area of Denmark. The highest frequency of events with a clear growth seems to take place over the open sea surrounding Vavihill, where ship emissions might be the most important source.

Finally, the analysis of which conditions should lead to formation events shows that global radiation is more important for the probability of events than gaseous SO_2, and that regional events are observed when $J_1 > 10^{(180^* \mathrm{CondS} - 0.60)}$.

It must be remembered, though, that even if some air masses were not able to produce particle formation events at Vavihill, nothing here is concluded about the origin of the 'pre-existing' aerosol particle load arriving at Vavihill during both events and non-events. Many of these aged particles might as well have been formed during earlier formation events.

5. Acknowledgments

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