

# Is nucleation capable of explaining observed aerosol integral number increase during southerly transport over Scandinavia?

By P. TUNVED<sup>1\*</sup>, H. KORHONEN<sup>2</sup>, J. STRÖM<sup>1</sup>, H.-C. HANSSON<sup>1</sup>, K. E. J. LEHTINEN<sup>3</sup> and M. KULMALA<sup>4</sup>, <sup>1</sup>Department of Applied Environmental Science, Stockholm University, SE-106 91, Stockholm, Sweden; <sup>2</sup>Finnish Meteorological Institute, POB 503, FIN-00101 Helsinki, Finland; <sup>3</sup>Department of Applied Physics, POB 1627, FIN-70211, University of Kuopio, Kuopio, Finland; <sup>4</sup>Department of Physical Sciences, POB 64, FIN-00014 University of Helsinki, Finland

(Manuscript received 15 March 2005; in final form 3 November 2005)

## ABSTRACT

Using a pseudo-Lagrangian approach, changes in aerosol size distribution was investigated during southerly transport under clear sky conditions from Finnish Lapland to Hyytiälä. Seventy-nine individual transport cases were considered. The mean transport distance was 700 km and mean transport time 66 h. On average, a sevenfold increase in Aitken mode number concentration could be observed. An increase in number concentration was observed in virtually all the cases. Several of the studied cases were associated with indications of nucleation at the receptor site. Six of the cases were simulated in detail utilizing a box-model approach. Aerosol dynamics was evaluated using the University of Helsinki Multi-component Aerosol model. Particle formation was assumed to be controlled by a kinetic nucleation mechanism. Growth of particles was suggested to be controlled by, except water and ammonia, sulphuric acid, and some unknown species with saturation vapour pressure of  $3 \times 10^6 \text{ cm}^{-3}$ . This product was supposed to derive from terpene oxidation by hydroxyl radical, ozone, and nitrate radical.

The investigation strongly suggests nucleation events occurring over large scales to be responsible for the observed number increase during transport under modelled conditions.

Using a simplified two layer structure of the lowermost troposphere, we highlight the role of vertical exchange. Modelled growth rates were found to be in agreement with observational data, in the order of  $1\text{--}2 \text{ nm h}^{-1}$ . In order to reproduce the observed growth rates, a molar yield of condensable products from terpene oxidation of 10% was required. Concentration of sulphuric acid and condensable organic vapours were on average  $3 \times 10^6$  and  $1.5 \times 10^7 \text{ cm}^{-3}$ , respectively.

## 1. Introduction

Aerosols are likely to play a central role for the fate of climate in our changing atmosphere. In contrary to greenhouse gases warming the atmosphere, aerosols are capable of contributing with a negative forcing, cooling the climate accordingly. This forcing is caused by two different mechanisms. The first effect is often referred to as the direct effect (Charlson et al., 1991), including direct scattering of incoming solar radiation. The second mechanism is the indirect effect (Twomey, 1974), which is a result of the interplay between aerosols and water vapour. Increasing amounts of aerosols will probably lead to more, but smaller, cloud droplets. This will produce brighter clouds.

Nucleation events have been reported from variety of locations including free troposphere, marine boundary layer, and continental boundary layer. Nucleation is observed in urban, rural, remote rural, and coastal regions (Kulmala et al., 2004a and references therein). Nucleation is possibly a key process in producing high aerosol number concentration over large scales in remote areas as represented by the Nordic boreal background environment in this study. During recent years, nucleation has been frequently observed at a variety of locations in the Nordic region. Nucleation events are especially well studied at the Finnish background station Hyytiälä (e.g. Mäkelä et al., 1997; Kulmala et al., 1998, 2001; Mäkelä et al., 2000) Nucleation is further reported from Pallas and Värriö in Finnish Lapland (Komppula et al., 2003; Laakso et al., 2003, Tunved et al., 2003). Although not scantily examined, the qualitative and quantitative nature of nucleation is so far poorly understood.

---

\*Corresponding author.  
e-mail: peter.tunved@itm.su.se

Nucleation, as observed at background sites such as Hyytiälä, exclusively occurs during daytime, implying the importance of photochemistry. The number concentration of particles recently formed (3–6 nm) correlates with short-wave solar radiation and estimated OH (Boy et al., 2003), further indicating the role of photochemistry. Nilsson et al. (2001a) report nucleation to preferentially occur in arctic and polar air-masses during cold air outbreaks. Nilsson et al. (2001b) additionally conclude that new particle formation events are mostly associated with the onset of strong vertical mixing. This mixing often results in significant decrease in integral aerosol number prior detection of recently formed particles.

The most plausible mechanism for nucleation is ternary nucleation including  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  (Kulmala et al., 2000a). There is, however, some concern how the recently formed clusters have grown into stable particles. Also, no species capable of explaining subsequent growth of freshly formed aerosol has been found yet. The ambient concentration of sulphuric acid is only rarely present in high enough concentration to support observed growth rates. Oxidation products from terpene degradation are promising candidates contributing to the observed growth rate of nuclei mode particles up to sizes of cloud condensation nuclei (Janson et al., 2001; Kulmala et al., 2001; Boy et al., 2004). Terpenes are emitted from vegetation and abundant at concentrations ranging from some tens of ppt's up to several hundred ppt's depending on season, boundary layer conditions, and temperature (Janson et al., 2001; Spanke et al., 2001; Hakola et al., 2003).

In Scandinavia, a network of stations simultaneously observing aerosol size distributions has evolved during recent years. The network so far contributes with simultaneous size distribution observations back to the autumn of 1999 (Tunved et al., 2003). The stations Pallas (68°N) and Värriö (67.46°N) represent the northern rim of the network and are located some 200 km south of the coast of the Arctic Ocean. Assuming an average wind speed of  $5 \text{ m s}^{-1}$ , air arriving to the stations will spend a maximum of 10–20 h over land before reaching the stations. Except for industries located at the Kola Peninsula (e.g. Nikel and Monchegorsk, located east of Pallas and Värriö), there are no local sources of particulates or gases affecting the air as it is transported from the Arctic Ocean down to the two stations.

Hyytiälä is located some 700 km further south. Tunved et al. (2003) utilized a cluster analysis technique in order to investigate the difference in aerosol properties as air sharing a similar meteorological as well as source history arrived to different stations. It was clearly shown that a substantial increase in especially aerosol number was to be observed when comparing the southerly located stations (e.g. Hyytiälä) to the northerly located stations (e.g. Värriö). The nature of this increase did, however, remain unresolved. It is nevertheless clear that the time-scales associated with new particle formation and subsequent growth by condensation of these particles constitute a reasonable ex-

planation for the observed number increase as air is transported southwards.

In the present study, we explore the transformation of the aerosol size distribution as maritime air is transported southwards over the Finland countries. We perform qualitative and quantitative comparisons of the size distributions observed at the northerly and southerly located stations. One of the main questions posed in this study is whether nucleation is capable of explaining the observed changes of aerosol size distribution properties associated with southerly transport. For this purpose we adopt a pseudo-Lagrangian box-model approach in order to pinpoint the importance of both nucleation and dynamical aspects of the aerosol transformation as comparably clean marine air is transported from the north across Finland. The approach is not true lagrangian in that sense that we approximate flow conditions with single trajectories, and hence the term pseudo-lagrangian is used to highlight these conditions.

## 2. Methods

### 2.1. Size distribution observations

One year of size distribution observations is used in this study (June 1, 2000 to May 31, 2001). Data from three stations have been utilized (Värriö, (67.46°N, 29.35°E); The Matorova station in Pallas, (68.0°N, 24.14°E); and Hyytiälä, (61.51°N, 24.17°E)). All stations use similar instrumental setups for observations of aerosol size distribution (differential mobility particle sizer) and cover approximately the same size range. A more detailed description of the stations and instrumentation may be found in Tunved et al. (2003), Laakso et al. (2003), and Komppula et al. (2003). All instruments are built and calibrated using the same methods.

### 2.2. Trajectory analysis

Backward trajectories (120 h) with a resolution of 1 h have been calculated with the HYSPLIT4 model (Draxler and Hess, 1997; Draxler and Rolph, 2003). Four trajectories were calculated each day. Trajectories are calculated to arrive to the receptor 10 m a.g.l. These trajectories are used to represent the flow in the mixing layer. Based on NCEP/GDAS FNL reanalysis data, upon which the trajectory calculation relies, time-dependent meteorological output (RH, precipitation rate, temperature, pressure) is also supplied to each one of the trajectories.

The use of 10 m a.g.l. was motivated by the fact that measurements were performed at this typical height. However, due to vertical wind shear it is not guaranteed that the flow conditions described by these trajectories completely resembles average conditions in the mixing layer. This fact highlights the problems associated with the use of single trajectories to describe the origin of finite volumes of air.

### 2.3. Aerosol dynamic model

The aerosol particle dynamics was investigated using the University of Helsinki Multicomponent Aerosol model (UHMA) described in detail by Korhonen et al. (2004). The model incorporates the major microphysical processes that affect the aerosol under clear sky conditions, namely nucleation, coagulation, multicomponent condensation, and dry deposition.

In this study, the vapours condensing onto aerosol particles were sulphuric acid, ammonia, water, and a low-volatile organic compound following the nano-Köhler mechanism, suggested by Kulmala et al. (2004b), and were thus capable of contributing to the growth of newly formed particles after a threshold size of a few nanometres was reached. Although such low-volatile organic compounds have not been identified in the atmosphere, analysis of new particle formation events in boreal forest have shown that sulphuric acid can explain only a small fraction of the observed growth of nucleation mode particles (Boy et al., 2003). Furthermore, indirect experimental evidence indicates that the dominant compounds contributing to the growth of newly formed particles in forested areas are organic (O'Dowd et al., 2002).

The dry deposition rate of particles was calculated according to Rannik et al. (2003) over land and according to Slinn (1978) over sea. Nucleation was simulated according to the kinetically limited nucleation mechanism, which essentially gives the maximum nucleation rate under prevailing conditions. While the details of the atmospheric nucleation mechanism in the boundary layer are not known, Laakso et al. (2004) have shown that the observed particle formation events in Hyytiälä are more likely limited by gas-phase kinetics than by thermodynamics.

The particle size distribution was approximated with 55 size sections in the size range of 0.7 nm–2  $\mu$ m. Of the three size distribution descriptions available in UHMA, this study utilized the hybrid structure. In this structure, the particles are split into fixed size sections based on their core volume of sulphuric acid and condensable organic matter. The advantage of the approach is that it eliminates the numerical diffusion associated with the condensation of ammonia and water.

### 2.4. Treatment of chemistry

In the model, we assume two species, other than water vapour and ammonia, to control the growth and formation of particles: sulphuric acid, which is formed by oxidation of SO<sub>2</sub> by hydroxyl radical (OH) and some unidentified product from the degradation of terpenes formed by a reaction between terpenes and OH, ozone and nitrate radical (NO<sub>3</sub>). The concentration of OH is determined by steady-state calculations assuming balance between formation and degradation of HO<sub>x</sub> (OH, HO<sub>2</sub>). Sources of HO<sub>x</sub> are reactions of singlet oxygen (O<sup>1</sup>D), produced from photolysis of O<sub>3</sub>, and water vapour. Photolysis of HCHO and oxidation of terpenes also contributes to OH production. Relevant photolysis

constants are taken from Derwent and Jenkin (1990). Clear sky conditions are assumed. The sinks of odd oxygen are HO<sub>2</sub>–HO<sub>2</sub> self-reaction, OH–HO<sub>2</sub> reaction, and formation of nitric acid from a combination of OH and NO<sub>2</sub>.

The OH concentration calculated in this way is highly uncertain, mostly due to errors in the calculated photolysis constant. By using an observationally constrained chemistry model, Hakola et al. (2003) report average daytime OH concentration in the order of 0.03 ppt during late April/May 2000–2002. Our estimated OH concentration was scaled to approximately agree with these average daytime concentrations.

Nitrate radical is formed by reaction of NO<sub>2</sub> and O<sub>3</sub>. NO<sub>x</sub> and O<sub>3</sub> are taken from measurements at Hyytiälä. Bulk NO<sub>x</sub> is kept constant during transport but is partitioned in NO<sub>2</sub> and NO following typical observed diurnal variation. NO<sub>3</sub> is highly sensitive to photolytic degradation and reaches concentration close to zero during daytime. Temperature dependent dissociation and photolysis of N<sub>2</sub>O<sub>5</sub> also serves as a source of nitrate radical. NO<sub>3</sub> is consumed due to photolysis, NO<sub>3</sub>–NO reaction, NO<sub>3</sub>–NO<sub>2</sub> reaction, and reaction of NO<sub>3</sub> with terpenes.

Temperature dependent emissions of terpenes according to Lindfors et al. (2000) were implemented. This approach only considers bulk emissions of terpenes. Latitude dependent biomass density of spruce and pine was taken from Laurila and Lindfors (1999). Rate constants for primary oxidation steps were averaged for the most commonly encountered terpenes as reported by Janson et al. (2001). Oxidation of terpenes by NO<sub>3</sub>, OH, and O<sub>3</sub> is assumed to produce condensable products participating in aerosol growth with a molar yield of 10%. The saturation vapour pressure over flat surface for the condensable species is assumed to be 3  $\times$  10<sup>6</sup> molecule cm<sup>-3</sup>. According to Kulmala et al. (1998), an equally low vapour pressure is required to explain the observed growth of freshly formed nano-particles.

In the model runs, observational data of SO<sub>2</sub> from Värriö initialize the sulphur chemistry. During transport, SO<sub>2</sub> is linearly interpolated in space and time to the observed concentration at Hyytiälä. This allows some variation of the SO<sub>2</sub> during transport and implicitly accounts for possible sources and sinks during transport. Table 1 summarizes the model input of chemical species.

### 2.5. Treatment of boundary layer

In the box-model approach, we utilize a highly simplified approach to describe growth of the mixing layer and the resulting intrusion of air from aloft. In the base case, a two-layer structure of the lowermost troposphere is assumed. The lower layer is defined by the boundary layer height as given by the trajectory model. Above this layer a residual layer is assumed to exist. For simplicity, this residual layer height is constant at 2000 m. This height represents the approximate upper limit of the mixing layer during modelled cases. The residual layer defines a volume given by the difference in mixing layer height and the upper limit of

Table 1. Base case conditions

O <sub>3</sub>	NO <sub>2</sub>	NO	HCHO	CH <sub>4</sub>	CO	SO <sub>2</sub>	NH <sub>3</sub>	Terpenes	Meteoro-logical parameters
Mesure-ments <sup>a</sup>	From measured NO <sub>x</sub> <sup>a</sup>	From measured NO <sub>x</sub> <sup>a</sup>	0.4 <sup>b</sup>	1.700 <sup>b</sup>	0.150 <sup>b</sup>	(see text)	0.025	Temperature dependent <sup>c</sup> emissions <sup>c</sup>	From trajectory model

<sup>a</sup>Data from observations at Hyytiälä and Värriö (see text for details).

<sup>b</sup>Values taken from Janson et al. (2001).

<sup>c</sup>Terpene emissions according to Lindfors et al., 1999.

the residual layer. Diurnal variability in the mixing layer height governs the exchange of aerosols and gases between the two layers. This residual layer serves as a second reservoir of aerosol. Decreasing mixing layer height leave some of the components confined in the mixing layer to the residual layer. These components will partly be fumigated back into the mixing layer when the mixing layer height increases. Within the residual layer, the aerosol is only affected by coagulation, condensation, and nucleation. In the mixing layer, all processes including deposition will be active. Both layers are assumed to be internally well mixed.

### 3. Results

#### 3.1. General observations

Transport from 67.46°N 21°–29.5°E down to Hyytiälä (61.51°N, 24.17°E) was studied. The distance traversed by trajectories is roughly 700 km. Aerosol size distribution properties at the northerly source region were defined by size distribution observations at Pallas (68°N, 24.13°E) and Värriö (67.36°N, 29.35°E). The source aerosol size distribution used were approved for further studies only if the number size distribution observed at Värriö and Pallas deviated at a minimum over a 6-h period. This assures that the horizontal gradient of the aerosol is small. Further, only cases where the observed aerosol properties at Pallas and Värriö remained constant in the Aitken-accumulation mode size ranges of not less than 6 h were used. In total, 79 trajectories fulfilling the criteria above were found to describe transport from Värriö/Pallas to Hyytiälä during the year of study. The majority of cases were found during spring (mostly March and May) and autumn (September–October). In selecting the cases, trajectories crossing the area around Nikel and Monchegorsk (located at Kola Peninsula) were filtered out to reduce bias from the well-known heavy emitters of both particulates and SO<sub>2</sub> (e.g. Kulmala et al., 2000b; Komppula et al., 2003). The average transport time was 66 h.

The area in-between the stations are sparsely populated. A similar study but with reversed transport direction (Tunved et al., 2004) indicate that contributions from primary anthropogenic

emissions during transport over Scandinavia are small. The influence from anthropogenic activities is therefore assumed to be negligible in this study.

The median aerosol size distribution observations at Värriö and Hyytiälä are shown in Fig. 1. The modal parameters from fitted aerosol size distributions at source and receptor location are summarized in Table 2.

The observed number increase during southerly transport is typically confined to Aitken size range. We observe an almost sevenfold increase in number concentration in the Aitken mode. Modal diameters agree fairly well comparing Värriö and Hyytiälä. On average, accumulation mode number concentration increases by 50 cm<sup>-3</sup>. The integral number observed at Hyytiälä contains on average 1200 more particles cm<sup>-3</sup>. The observed mass increase is on average 0.80 μg m<sup>-3</sup>, assuming a density of 1.5 g cm<sup>-3</sup>. Only in one case do we actually observe a decrease in number concentration during transport. Mass decrease is observed in 17 cases. Median mass observed at Värriö is 1.2 and 2.0 μg m<sup>-3</sup> at Hyytiälä. The corresponding integral number concentration is 250 and 1800 cm<sup>-3</sup> at Värriö and Hyytiälä, respectively.

In total, the 79 trajectories describe transport between the source stations and the receptor station Hyytiälä during a period of 41 d (recall 4 trajectories were calculated each day). Of these 41 d included in the study, 25 d are associated with indications of nucleation at Hyytiälä according to the definition by Mäkelä et al. (2000).

In summary, observations indicate that both the number and mass increase during southerly transport as exemplified in the pseudo-Lagrangian approach described above. In the following, we perform a detailed investigation on how the aerosol size distribution may change during southerly transport under clear sky conditions.

#### 3.2. Model evaluation

**3.2.1. Model results.** Since we are lacking the means to specifically account for cloudiness during transport, we are forced to assume clear sky conditions in the base case. Several of the occasions where transport conditions were favourable

Fig. 1. Pseudo-Lagrangian evaluation of size distribution properties observed in the source region exemplified by observations at Pallas and Värriö, and size distribution properties observed at Hyttiälä, on average 66 h later. Data comprise size distributions from 79 individual transport cases. Units in  $dN/d\log D_p$ ,  $\text{cm}^{-3}$ .

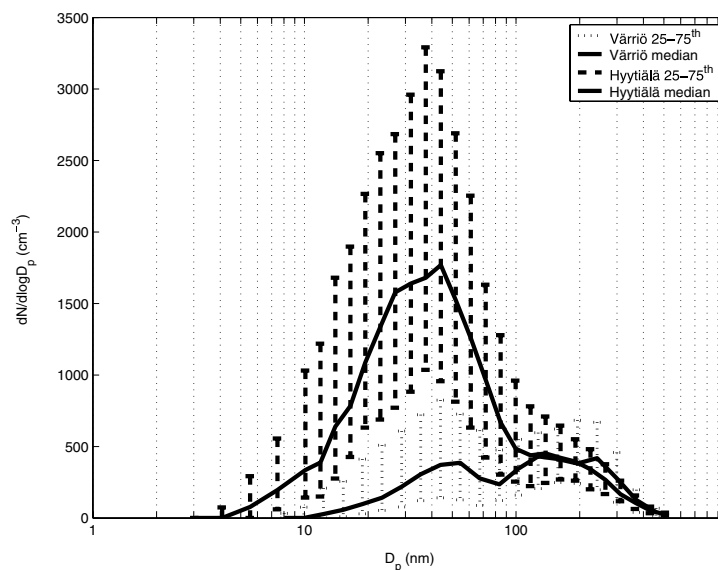


Table 2. Average model parameters for Värriö size distribution data preceding observations at Hyttiälä, on average 66 h later. The analysis comprises 79 observations. Percentile ranges of 25–75 are indicated within brackets

Värriö	D <sub>g</sub> (nm)	GSD	N (cm <sup>-3</sup> )
Nuclei	13.8 (12.6–15.1)	1.69 (1.38–1.88)	7 (2–54)
Aitken	39.0 (30–47.6)	1.48 (1.42–1.65)	162 (45–361)
Accumulation	179.7 (156–203)	1.56 (1.41–1.63)	118 (64–252)
Hyttiälä			
Nuclei	11.5 (9.4–13.3)	1.55 (1.37–1.79)	65 (20–320)
Aitken	39.2 (33.3–46.7)	1.60 (1.47–1.70)	1065 (435–1858)
Accumulation	184.5 (156.3–215.9)	1.51 (1.36–1.68)	176 (121–243)

for the purpose of this investigation, satellite images (NERC Satellite Receiving Station, Dundee University, Scotland, <http://www.sat.dundee.ac.uk/>) indicated cloudiness during some parts of transport. However, during the 11–15th of April we isolated a number of transport occasions where air arrived from our predefined source area and was advected under what we assume to be clear sky conditions during virtually the entire transport. This gave us six cases to model.

In Fig. 2, we exemplify the transport associated with the selected cases in mid April. Two branches of transport are detected: one going across Finland and Russia before arriving at Hyttiälä and the other crossing over Sweden and the Baltic Sea before arriving at Hyttiälä. The path of air going across Finland and Russia passes south of Monchegorsk, and we assume influence from anthropogenic sources to be negligible.

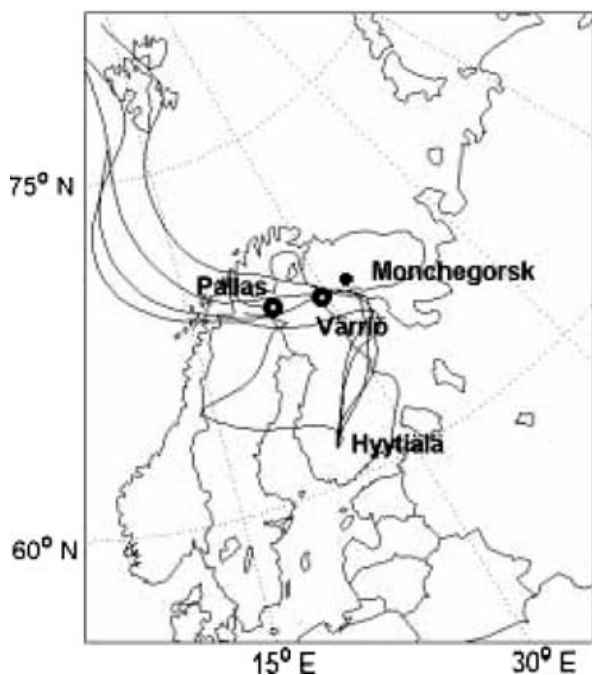
The time-dependent size distribution observed at Hyttiälä during the modelled period (April 11, 2001 to April 15, 2001) is shown in Fig. 3. During this period, all days indicate more or

less nucleation taking place at the station. During the first 4 d the weather situation is dominated by a very low degree of cloudiness over the area surrounding the station. However on the 15th of April a low pressure system arrives over Finland from the south-east and no more nucleation is observed. The modelled cases are indicated by arrows in Fig. 3. Transport time and arrival date and time (UTC) is given in Table 3.

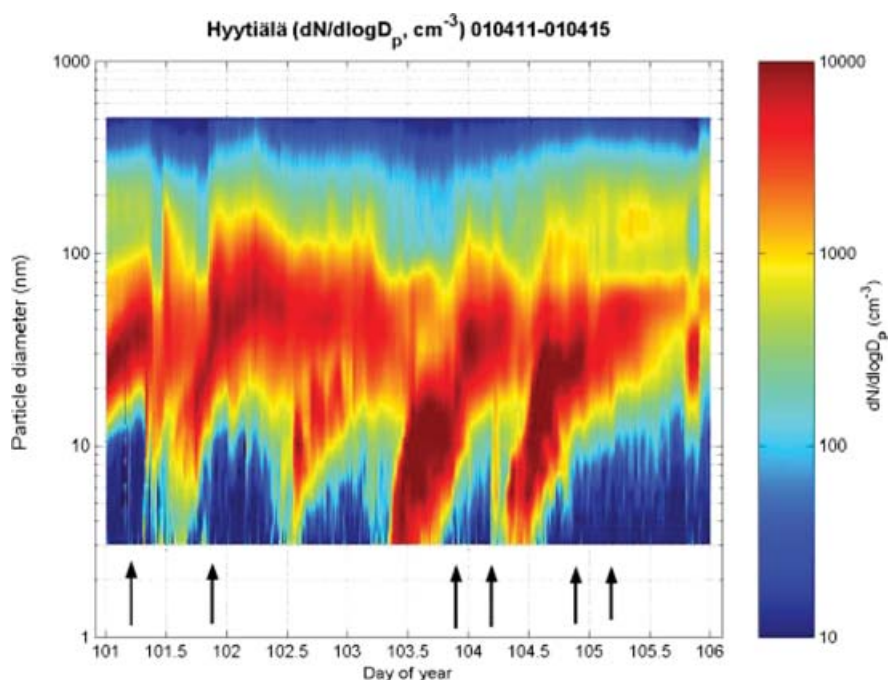
The box model was run along the trajectories in all six selected cases. Modelled daily average concentration of sulphuric acid was in the order of  $10^6$  molecules  $\text{cm}^{-3}$  with a daily maximum typically ranging from  $1.5 \times 10^6$ – $3.5 \times 10^6$  molecules  $\text{cm}^{-3}$ . Modelled terpene concentration was on average 80 ppt. Occasionally, during events with shallow boundary layer in conjunction with high temperatures, terpene concentration reached several hundred ppt. The amount of condensable species from terpene oxidation was on average  $1.5 \times 10^7$   $\text{cm}^{-3}$ , typically varying between  $0.5$  and  $3 \times 10^7$   $\text{cm}^{-3}$ . The concentrations of terpenes are in reasonable agreement with observations made at Hyttiälä (e.g. Janson et al., 2001).

The modelled growth rates are generally found to be in the order of 1–2 nm h. The modelled growth rates are in agreement with calculations performed by Tunved et al. (2003) during the same year as this study.

Figure 4 displays the modelled size distribution as the air arrives at Hyttiälä in four selected cases. Also shown in the figure are the 5–95th percentiles of observational data, giving a maximum and minimum observed aerosol concentration during a 6-h period. These selected cases, A–D, correspond to trajectories arriving at Hyttiälä during 04/13 at 23:00 UTC, 04/14 at 05:00 UTC, 04/11 at 05:00 UTC, and 04/14 at 23:00 UTC. Overall, the location of the dominating Aitken mode is rather well represented by the model as shown by the comparison in Fig. 4. Although the location of the mode agrees well with



*Fig. 2.* Trajectory orientation associated with five of the modelled cases. The source area is characterised by observations performed at Pallas and Värriö and changes of the aerosol size distribution is evaluated as transport from this source region down to Hyttiälä takes place. The trajectory model supplies relative humidity, temperature, pressure, and mixing layer height through transport.



*Fig. 3.* Observed aerosol size distribution properties at Hyttiälä during the studied period. Black arrows indicate the approximate arrival time (UTC) of trajectories associated with modelled cases.

observations, the number concentration is overestimated by the model in all cases but one (case F, not shown)

Cases A and B exemplify the cases where the model best captures the features of the observed size distribution. In case

A, there is almost a perfect match between modelled and observed data, although the location of the modelled Aitken mode is some 10 nm larger than observations. However, considering time-scales for growth, deviations of this magnitude are

Table 3. Observed 6 h median and modelled number ( $\text{cm}^{-3}$ ) and mass concentration ( $\mu\text{g m}^{-3}$ ) associated with each of the modelled cases A–F. A density of  $1.5 \text{ g cm}^{-3}$  is assumed

Case	Trp time (h)	N model ( $\text{cm}^{-3}$ )	N obs ( $\text{cm}^{-3}$ )	M model ( $\mu\text{g m}^{-3}$ )	M obs ( $\mu\text{g m}^{-3}$ )
A 20010411 05:00	105	6000	3200	2.3	1.1
B 20010411 23:00	117	8500	3500	0.6	0.7
C 20010413 23:00	72	10 500	4200	1.0	0.5
D 20010414 05:00	60	10 800	4200	1.7	1.2
E 20010414 23:00	69	9700	4300	0.8	1.3
F 20010415 05:00	99	2200	3700	1.2	1.1

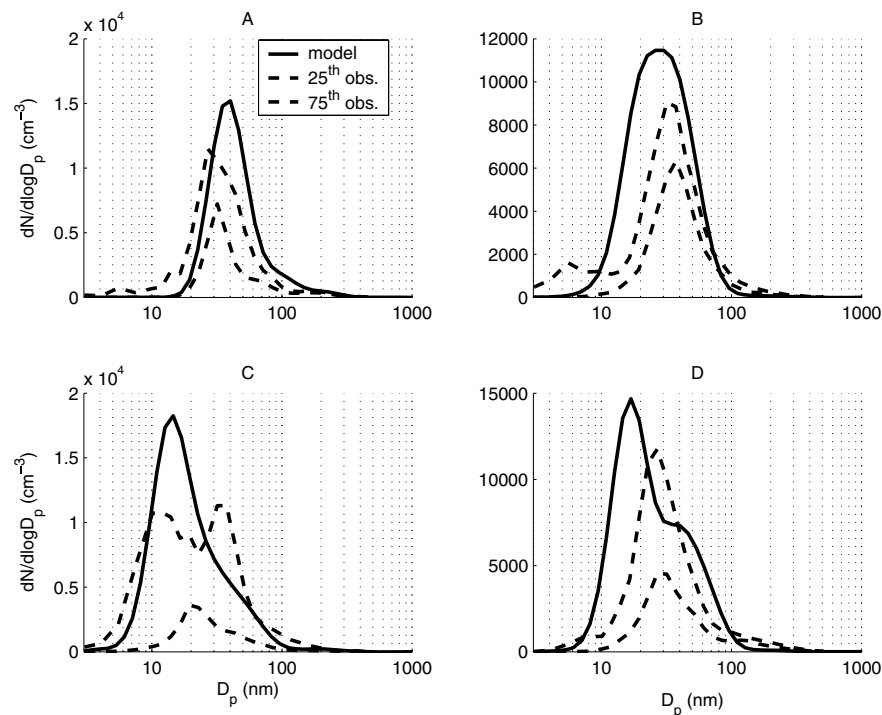


Fig. 4. Model and observation comparison of size distribution ( $dN/d\log D_p$ ,  $\text{cm}^{-3}$ ) at Hyttiälä. Dashed lines indicate 5th–95th percentiles of observed data and circles correspond to modelled size distribution. (A: 13 April at 23:00 UTC, B: 14 April at 05:00 UTC, C: 11 April at 05:00 UTC, and D: 14 April at 23:00 UTC).

considered to be of no importance (with a growth rate of 2 nm h according to both model and observations, there is only a 5 h difference between model and observations). In case B, the modelled size distribution is almost superimposed on observational data. The modelled size distribution, however, indicates a broader Aitken mode, and also a larger number concentration as compared with observations. In case C, the modelled data is within the ranges given by observations everywhere except in the 10–20 nm size range. In case D, the model indicates a bimodal structure of the Aitken mode. This does not agree with observations.

It should be highlighted that the simplified model gives a size distribution resulting from highly idealized conditions during transport. Naturally, the model does not include

small scale variations in nucleation rate, mixing properties in larger volumes of air, and other micro-scale features of the air-mass. In practice, these natural properties of the air-mass will invoke irregularities in observational data not possible to capture with this approach. These irregular variations of the size distribution data are clearly displayed in Fig. 3.

The average size distributions of all modelled cases are compared with 75th and 25th percentiles given by observational data at Hyttiälä in Fig. 5. On average, the model calculations result in slightly more particles than given by observations. This is especially observed in sub 50 nm size ranges. The larger particles of the aerosol size distribution are, however, fairly well represented by the model.

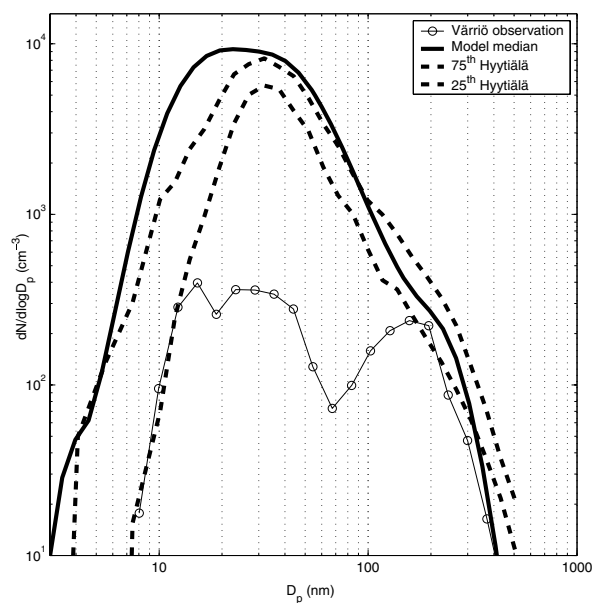


Fig. 5. Percentile ranges of 25–75 for observed size distribution ( $dN/d\log D_p$ ,  $\text{cm}^{-3}$ ) data associated with cases A–F compared with average model result. Average observed size distribution at the source region (Värriö, circles) is added for comparison.

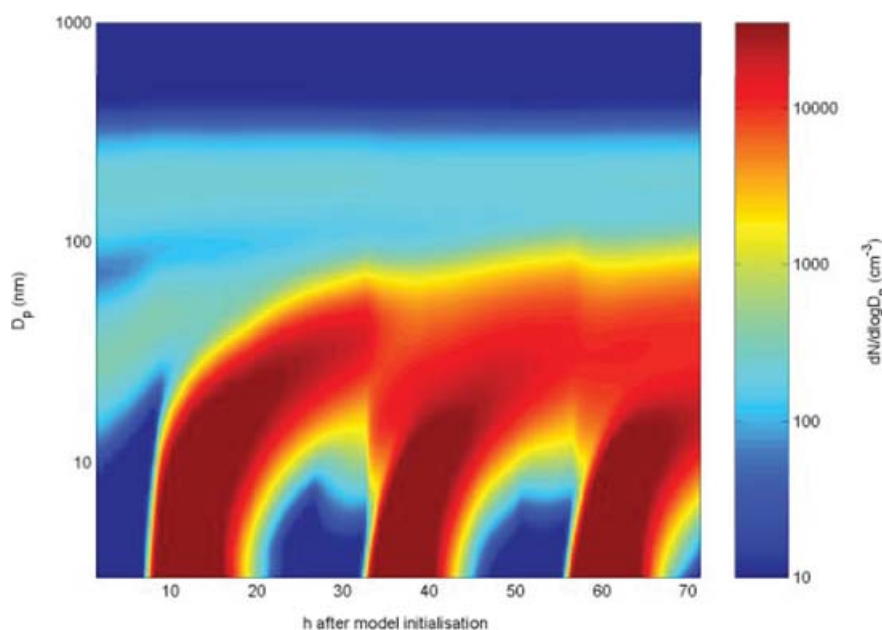


Fig. 6. Modelled size distribution evolution during 72 h of transport from the northerly source region to Hyytiälä, Case C, 13 April 2001,  $dN/d\log D_p$ ,  $\text{cm}^{-3}$ .

Mass and number concentrations of modelled cases were compared with observations (Table 3). Only particles of 10–450 nm were considered for consistency with observations. The modelled mass is on average overestimated by a factor of 1.3. Aerosol number is generally overestimated by a factor of two. Only in one case (case F) the model underestimates the number concentration.

In general, the time evolution of the aerosol size distributions shares some common properties in all modelled cases. These features are linked to diurnal variation of model input data such as boundary layer height and solar zenith angle. The time evolution of the aerosol size distribution during transport is exemplified by the model run in case C, Fig. 6. This case concerns air arriving at Hyytiälä on the 13th of April after crossing the vicinity of Värriö



and Pallas 72 h earlier. There are several interesting features associated with this case. The modelled case starts close to Värriö during night time. During the following day, a nucleation event is suggested by the model. The particles formed in this first nucleation grow undisturbed for a little more than 12 h. During the morning hours of the second day, there is an abrupt decrease in particle number and the number concentration associated with the growing Aitken mode observed previously is significantly reduced. At the same time smaller particles are introduced prior to the second nucleation event. These particles are not instantly produced, but represent remnants of the new particle production in the residual layer from the previous day. Some hours after the breakdown of the nocturnal boundary layer a new nucleation is initialized. During the following day the same pattern is repeated. This is the third and last nucleation event in the air parcel prior to the arrival to Hyttiälä. The timing of this nucleation event resembles the one observed at Hyttiälä during the day of the arrival of the trajectory (Fig. 3).

The sudden decrease in aerosol number concentration is typical for all modelled cases, and is linked to a large diurnal variability of the boundary layer height. This large variability in mixing layer height is characteristic for transport under clear sky conditions. The phenomenological boundary layer dynamics described in Section 2.5 obviously have large impact on the modelled properties of the aerosol size distribution within the boundary layer.

In the base case, the model is run to allow for nucleation both in the mixing layer and in the residual layer. The air in the mixing layer is in direct connection with sources of organic compounds. The air in the residual layer is only supplied with condensable organic vapours and precursors thereof via vertical pumping associated with the diurnal variation in mixing height. This means that the growth of the nucleated particles in the residual layer will be slow and further remnants of small particles will subsequently be mixed down during the morning hours of the following day. Well in contact with emission of organic compounds from vegetation they will either continue to grow or quickly be scavenged away depending on the aerosol concentration within the mixing layer. This behaviour is frequently observed in modelled cases, especially when a large diurnal variability of the mixing layer height is indicated. The sudden decrease in aerosol number concentration prior to nucleation is noticed rather often in observational data (e.g. Mäkelä et al., 1997, 2000). Also, the nucleation events associated with this study exhibit this typical feature. Recalling Fig. 3, it is clearly shown that a significant reduction in aerosol number occurs before the onset of nucleation observed during the 11th and the 13–14th of April. This behaviour is likely to be associated with the onset of vertical mixing as suggested by our simplified boundary layer dynamics.

### 3.3. Sensitivity to single parameters

In the present study, we use a highly simplified treatment of chemistry and boundary layer dynamics. It is therefore necessary

to test the sensitivity of the model to some of the most critical simplifications utilized in the study.

#### 3.3.1. Alternative treatment of the boundary layer dynamics.

In the base case, the phenomenological treatment of the boundary layer is implemented in the model. The simplifications are intuitively reasonable and the treatment allows us to reproduce some of the typical features associated with observed nucleation events from especially Hyttiälä. It is clear from previous investigations that condensation and coagulation sink associated with high loadings of preexisting aerosol likely quench the nucleation rate and particle growth under ambient conditions. As noticed in observational data and as a result of vertical mixing in the modelled cases, nucleation is often preceded by a reduction in aerosol number concentration. By excluding the two layer structure in the model, thereby neglecting any dilution effects, we test the response of the model.

In Fig. 7, case C represents the features of the aerosol size distribution evolution if no vertical mixing takes place. It is clear that the particles formed during the initial nucleation event are allowed to grow undisturbed throughout the entire model run. Under selected conditions, the subsequent nucleation events are significantly quenched by the preexisting aerosols and only minor fractions of small particles are added to the integral number of particles  $>10$  nm (compare with Fig. 6). This means that the effect of mixing is that the apparent nucleation rate is significantly increased compared with the cases where no mixing takes place. Running the model without mixing also indicates that the resulting Aitken mode modelled upon arrival at Hyttiälä is completely displaced compared with both the observation and base case model runs. We therefore confirm the necessity of mixing in the modelled case in order to dilute the aerosol concentration remaining from the previous nucleation events during transport to reproduce the observed aerosol features at Hyttiälä. This indicates the importance of vertical mixing in generating conditions where nucleation may occur to an extent agreeing with observations. The resulting size distribution with and without mixing is compared with observations in Fig. 8, top panel.

3.3.2. Sensitivity to OH concentration. The estimated OH concentration is associated with a high degree of uncertainty. In order to estimate the effect of changes in OH concentration two runs were performed, one where OH concentration was reduced by 50% and one case where the OH concentration was increased by a factor of four. The results are displayed in middle panel Fig. 8.

The daily maximum OH concentrations in the case where the reduction of OH was tested were in the order of  $6 \times 10^5$  cm<sup>-3</sup> and in the cases where OH was increased by a factor of four the daily maximum reached some  $6 \times 10^6$  cm<sup>-3</sup>. Increasing or decreasing the OH concentration affected sulphuric acid production as well as the generation of condensable vapours from terpene oxidation.

By decreasing the OH, we slightly improved the average result of the model compared with the base case conditions. It is,

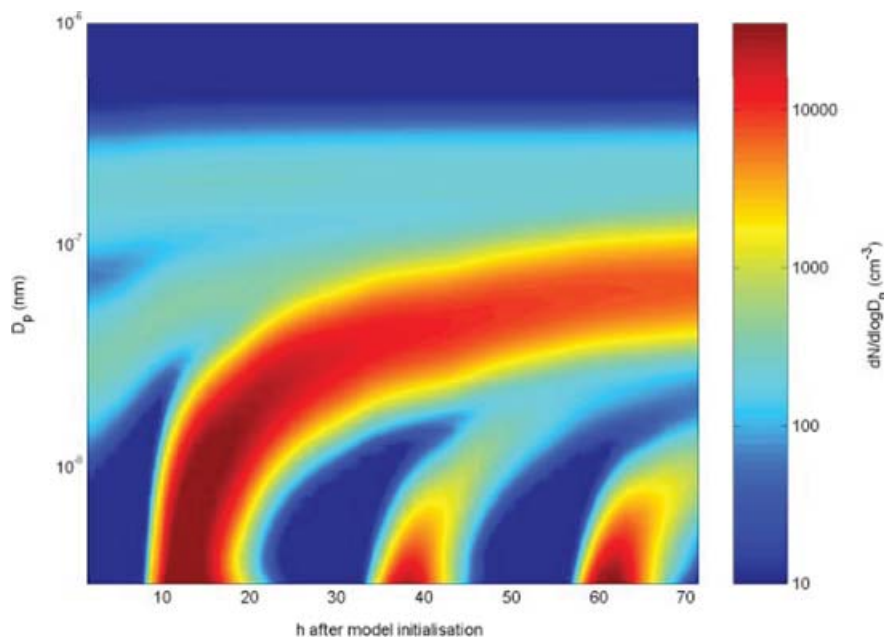


Fig. 7. Size distribution evolution during 72 h of transport associated with case C in absence of vertical mixing,  $dN/d\log D_p$ ,  $\text{cm}^{-3}$ .

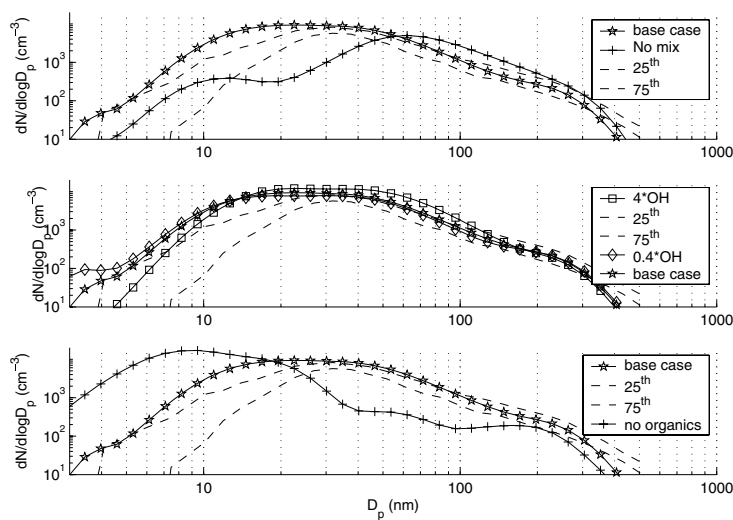


Fig. 8. Sensitivity to selected parameters, all cases. For comparison, aerosol size distribution resulting from base case conditions is shown in each frame. Top panel: comparison between cases with and without vertical mixing; middle panel: dependence on OH concentration; bottom Panel: role of condensable organic vapours. Dashed lines indicate observed size distribution properties at Hyytiälä. Units in  $dN/d\log D_p$ ,  $\text{cm}^{-3}$ .

however, clear that the implemented changes do not drastically alter the picture compared with the base case conditions. With a fourfold increase of the OH we worsen the modelled results, but still, by doing so we do retain the most prominent features of the modelled aerosol size distribution. It is clear, that over an order of magnitude of OH concentrations, with terpene emissions and concentration of other gases remaining unchanged, the basic features of the modelled size distribution remain the same, although the number concentrations differ between the cases. In these modelled cases, it is therefore concluded that sensitivity to the availability of oxidants is present, although the

system responds quite modestly even to large changes in oxidant concentrations.

**3.3.3. Organic vapours.** In the base case, we assume some unidentified product from terpene oxidation to participate in the growth of aerosol particles. The assumption is associated with a high degree of uncertainty since we do not know the yield of the products from oxidation; neither do we have data to support our estimated saturation vapour pressure of this conceptual oxidation product. However, as can be seen in the bottom panel of Fig. 8, by completely removing sources of condensable organic vapours, we clearly alter the structure of the modelled size distribution.

The resulting aerosol size distribution at Hyytiälä completely lacks resemblance with observations and base case conditions. The growth is significantly underestimated, supporting previous conclusions where some additional compound is argued necessary to support observed growth rates in boreal background locations such as Hyytiälä (e.g. Kulmala et al., 2001, 2004a; Boy et al., 2004). In the modelled cases, the aerosols typically grow up to 10–20 nm before the freshly formed particles are scavenged away. It is clear that sulphuric acid alone cannot be responsible for the growth rates commonly observed, at least not under modelled conditions. It is however noticed, that concentration of SO<sub>2</sub> in the order of ppb's may be sufficient to support growth rates as observed during nucleation events. However, such high concentration only rarely coincides with observed nucleation events and therefore it is argued that some additional species, most likely organic, are necessary to support the observed growth rates.

#### 4. Conclusions

In this study we have utilized a state-of-the-art aerosol dynamic model coupled to a Lagrangian model in order to investigate the importance of nucleation and other dynamical processes acting on the aerosol during southerly transport over Finland. Observations of aerosol number size distributions change associated with transport indicate a sevenfold increase of Aitken mode number concentration during advection from 68°N to Hyytiälä. The distance travelled by the trajectories was approximately 700 km and transport time was on average 66 h. Nucleation was often observed at the receptor station Hyytiälä. However, a single nucleation event prior to the arrival of the air to Hyytiälä is not sufficient to account for the observed aerosol properties. It is likely that a series of nucleation events are taking place during southerly transport. In this context, mixing plays a crucial role. In the absence of mixing, the model in many cases suggests that the first nucleation is sufficient to considerably quench subsequent nucleation events.

Modelled growth rates were found to be in the order of 1–2 nm h<sup>-1</sup>. This is in agreement with observations. Growth is largely assumed to be controlled by low-volatile products from terpene oxidation with an average vapour pressure of  $3 \times 10^6$  molecules cm<sup>-3</sup>. The average concentration of these compounds was modelled to be  $1.5 \times 10^7$  molecules cm<sup>-3</sup>.

On average the number was overestimated by a factor of 2.7 and the mass was overestimated by a factor of 1.3. The flow conditions in the mixing layer are represented by trajectories arriving at 10 m a.g.l. Due to the friction of underlying land, the average wind speed related to these trajectories is shorter compared to situations where the air would arrive at higher altitudes. It is clear that the calculated transport time (on average 66 h) represent an upper limit of the transport time in the mixing layer. A decrease in the transport time would result in smaller amount of emitted gases and consequently lower accumulated mass and likely also lower number concentration. This would then improve the agree-

ment between modelled and observed changes in particle mass and number concentrations. This clearly indicates that timing and extent of nucleation is crucial for an accurate description of the evolution of the size distributions during southerly transport over Finland.

Both model and observations indicate nucleation to largely control the sub 100 nm aerosol number evolution during southerly transport. This is indicated by a high frequency of observed nucleation events during the described transport situations. Further, modelled growth and number of nucleated particles are found sufficient to support nucleation as being the main cause of the observed number increase during southerly transport under clear sky conditions.

This means that nucleation and subsequent growth is sufficient to produce a large number of aerosols of CCN size over large areas on time-scales of a couple of days. Some species other than sulphuric acid is necessary to explain the observed growth. Based on the assumption that emissions and following oxidation of terpenes provide the low-volatile species necessary to support observed growth rates, the natural production of aerosols over the forest is central to the provision of accurate estimates of regional forcing caused by aerosols in the boreal region.

The present investigation provides a reasonable relationship between the nucleation and the observed number increase during southerly transport under almost completely clear sky conditions. It should however be pointed out that although a majority of the cases studied, but not modelled, are associated with a significant increase of number concentration although transport occurs under partially cloudy conditions. This might indicate the importance of nucleation also under partially cloudy conditions.

#### 5. Acknowledgments

This work was funded by the ASTA programme (International and National Abatement Strategies for Transboundary Air Pollution) of the MISTRA research foundation (Swedish Foundation for Strategic Environmental Research), Nordic Council of Ministers (NMR), and the Swedish Environmental Protection Agency, Environmental Monitoring Programme. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model used in this publication.

#### References

- Boy, M., Petaja, T., Dal Maso, M., Rannik, U., Rinne, J. and co-authors. 2004. Overview of the field measurement campaign in Hyytiälä, August 2001 in the framework of the EU project OSOA. *Atmos. Chem. Phys.* **4**, 657–678.
- Boy, M., Rannik, U., Lehtinen, K. E. J., Tarvainen, V. and co-authors. 2003. Nucleation events in the continental boundary layer: long-term statistical analyses of aerosol relevant characteristics. *J. Geophys. Res.* **108**, 4667, doi:10.1029/2003JD003838.

- Charlson, R. J., Langner, J., Rodhe, H., Leovy, C. B. and Warren, S. G. 1991. Perturbation of the northern hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols. *Tellus* **43B**, 152–163.
- Derwent, R. G. and Jenkin, M. E. 1990. Hydrocarbon involvement in photochemical ozone formation in Europe. AERE Report R13736 (HMSO), London.
- Draxler, R. R. and Hess, G. D. 1997. Description of the Hysplit.4 modelling system., NOAA Tech Memo, ERL, ARL-224.
- Draxler, R. R. and Rolph, G. D. 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory, Silver Spring, MD.
- Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellen, H. and co-authors. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* **37**, 1623–1634.
- Janson, R., Rosman, K., Karlsson, A. and Hansson, H. C. 2001. Biogenic emissions and gaseous precursors to forest aerosols. *Tellus* **53B**, 423–440.
- Komppula, M., Dal Maso, M., Lihavainen, H., Aalto, P. P., Kulmala, M. and co-authors. 2003. Comparison of new particle formation events at two locations in northern Finland. *Bor. Environ. Res.* **8**, 395–404.
- Korhonen, H., Lehtinen, K. E. J. and Kulmala, M. 2004. Multicomponent aerosol dynamics model UHMA: model development and validation. *Atmos. Chem. Phys.* **4**, 757–771.
- Kulmala, M., Hämeri, K., Aalto, P. P., Mäkelä, J. M., Pirjola, L., and co-authors 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* **53B**, 324–343.
- Kulmala, M., Kerminen, V. M., Anttila, T., Laaksonen, A. and O'Dowd, C. D. 2004b. Organic aerosol formation via sulphate cluster activation. *J. Geophys. Res.* **109**, Art. No. D04205.
- Kulmala, M., Pirjola, U. and Mäkelä, J. M. 2000a. Stable sulphate clusters as a source of new atmospheric particles. *Nature* **404**, 66–69.
- Kulmala, M., Rannik, Ü., Pirjola, L., Dal Maso, M., Karimäki, J. and co-authors 2000b. Characterization of atmospheric trace gases and aerosol composition at forest sites in southern and northern Finland using back trajectories. *Bor. Environ. Res.* **5**, 315–336.
- Kulmala, M., Toivonen, A., Mäkelä, J. M. and Laaksonen, A. 1998. Analysis of the growth of nucleation mode particles observed in Boreal forest. *Tellus* **50B**, 449–462.
- Kulmala, M., Vehkamäki, H., Petaja, T., Dal Maso, M., Lauri, A. and co-authors 2004a. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol. Sci.* **35**, 143–176.
- Laakso, L., Hussein, T., Aarnio, P., Komppula, M., Hiltunen, V. and Kulmala, M. 2003. Diurnal and annual characteristics of particle mass and number concentrations in urban, rural and Arctic environments in Finland. *Atmos. Environ.* **37**, 2629–2641.
- Laakso, L., Petäjä, T., Lehtinen, K. E. J., Kulmala, M., Paatero, J. and 2004. Ion production rate in a boreal forest based on ion, particle and radiation measurements. *Atmos. Chem. Phys. Discuss.* **4**, 3947–3973.
- Laurila, T. and Lindfors, V. (eds.), 1999. Brogenic VOC emissions and photochemistry in the boreal regions of Europe. Air Pollution Research Report No. 70, Commission of the European Communities, Luxembourg, 158 pp. ISBN 92-828-6990-3.
- Lindfors, V., Laurila, T., Harola, H., Steinbrecher, R. and Rinne, J. 2000. Modelling speciated terpenoid emissions from the European Boreal forest. *Atmos. Environ.* **34**, 4983–4996.
- Mäkelä, J. M., Aalto, P., Jokinen, V., Pohja, T., Nissinen, A. and co-authors 1997. Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys. Res. Lett.* **24**, 1219–1222.
- Mäkelä, J. M., Dal Maso, M., Pirjola, L., Keronen, P., Laakso, L. and co-authors 2000. Characteristics of the aerosol particle formation events observed at a boreal forest site in southern Finland. *Boreal Environ. Res.* **4**, 299–313.
- Nilsson, E. D., Paatero, J. and Boy, M. 2001b. Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer. *Tellus* **53B**, 462–478.
- Nilsson, E. D., Rannik, U., Kulmala, M., Buzorius, G. and O'Dowd, C. D. 2001a. Effects of continental boundary layer evolution, convection, turbulence and entrainment, on aerosol formation. *Tellus* **53B**, 441–461.
- O'Dowd, C. D., Aalto, P., Hämeri, K., Kulmala, M. and Hoffmann, T. 2002. Aerosol formation – atmospheric particles from organic vapours. *Nature* **416**, 497–498.
- Rannik, U., Aalto, P., Keronen, P., Vesala, T. and Kulmala, M. 2003. Interpretation of aerosol particle fluxes over a pine forest: dry deposition and random errors. *J. Geophys. Res.* **108**, 4544, doi: 10.1029/2003JD003542.
- Slinn, W. G. N. 1978. Parameterizations for resuspension and for wet and dry deposition of particles and gases for use in radiation dose calculations. *Nucl. Saf.* **19**, 205–219.
- Spanke, J., Rannik, U., Forkel, R., Nigge, W. and Hoffmann, T. 2001. Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modelling. *Tellus* **53B**, 406–422.
- Tunved, P., Hansson, H. C., Kulmala, M., Aalto, P., Viisanen, Y. and co-authors 2003. One year boundary layer aerosol size distribution data from five Nordic background stations. *Atmos. Chem. Phys.* **3**, 2183–2205.
- Tunved, P., Korhonen, H., Ström, J., Hansson, H.-C., Lehtinen, K. E. J. and co-authors 2004. A pseudo-Lagrangian model study of the size distribution properties over Scandinavia: transport from Aspöretten to Värriö. *Atm. Chem. Phys. Discuss.* **4**, 7757–7794.
- Twomey, S. A. 1974. Pollution and the planetary albedo. *Atmos. Environ.* **8**, 1251–1256.