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ANALYSIS OF ATMOSPHERIC PARTICLE FORMATION
EVENTS

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Academic dissertation

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Analysis of atmospheric particle formation events

Miikka Ilmari Dal Maso
University of Helsinki, 2006

Abstract

Atmospheric aerosol particle formation events can be a significant source for tropospheric aerosols and thus influence the radiative properties and cloud cover of the atmosphere. This thesis investigates the analysis of aerosol size distribution data containing particle formation events, describes the methodology of the analysis and presents time series data measured inside the Boreal forest.

This thesis presents a methodology to identify regional-scale particle formation, and to derive the basic characteristics such as growth and formation rates. The methodology can also be used to estimate concentration and source rates of the vapor causing particle growth.

Particle formation was found to occur frequently in the boreal forest area over areas covering up to hundreds of kilometers. Particle formation rates of boreal events were found to be of the order of $0.01\text{--}5\text{ cm}^{-3}\text{s}^{-1}$, while the nucleation rates of 1 nm particles can be a few orders of magnitude higher. The growth rates of over 3 nm sized particles were of the order of a few nanometers per hour. The vapor concentration needed to sustain such growth is of the order of $10^7\text{--}10^8\text{ cm}^{-3}$, approximately one order of magnitude higher than sulfuric acid concentrations found in the atmosphere. Therefore, one has to assume that other vapors, such as organics, have a key role in growing newborn particles to sizes where they can become climatically active.

Formation event occurrence shows a clear annual variation with peaks in summer and autumns. This variation is similar to the variation exhibited the obtained formation rates of particles. The growth rate, on the other hand, reaches its highest values during summer. This difference in the annual behavior, and the fact that no coupling between the growth and formation process could be identified, suggest that these processes might be different ones, and that both are needed for a particle formation burst to be observed.

Keywords: Atmospheric aerosols, nucleation, particle formation and growth

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List of publications

This thesis consists of an introductory review, followed by five research articles. The papers are reproduced with the kind permission of the journals concerned.

- I Jyrki M. Mäkelä, Miikka Dal Maso, Liisa Pirjola, Petri Keronen, Lauri Laakso, and Markku Kulmala: "Characteristics of the atmospheric particle formation events observed at a boreal forest site in southern Finland", *Boreal Environment Research* 5 (4) : 299-313, (2000)
- II Markku Kulmala, Miikka Dal Maso, Jyrki M. Mäkelä, Liisa Pirjola, Minna Väkevä, Pasi P. Aalto, Pasi Miikkulainen, Kaarle Hämeri, and Colin D. O'Dowd: "On the formation, growth and composition of nucleation mode particles", *Tellus* B 53 (4): 479-490, (2001)
- III Miikka Dal Maso, Markku Kulmala, Kari E. J. Lehtinen, Jyrki M. Mäkelä, Pasi P. Aalto, and C. D. O Dowd: "Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers" *Journal of Geophysical Research*, 107 (19D), 8097, 10.1029/2001jd001053, (2002) *Reproduced by permission of American Geophysical Union.*
- IV Miikka Dal Maso, Markku Kulmala, Ilona Riipinen, Robert Wagner, Tareq Hussein, Pasi P. Aalto and Kari E. J. Lehtinen: "Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland", *Boreal Environment Research* 10 (5): 323-336, (2005)
- V Miikka Dal Maso, Larisa Sogacheva, Pasi P. Aalto, Ilona Riipinen, Mika Kompula, Peter Tunved, Laura Korhonen, Ville Suur-Uski, Anne Hirsikko, Theo Kurtén, Veli-Matti Kerminen, Heikki Lihavainen, Yrjö Viisanen, Hans-Christer Hansson, and Markku Kulmala: "Aerosol size distribution measurements at four Nordic field stations: identification, analysis and trajectory analysis of new particle formation bursts", submitted to *Tellus* (2006)

1 Introduction

The Earth’s atmosphere is one of the most important environmental factors influencing human activity and the biosphere in general. Its chemical and physical properties, such as temperature, composition and permeability to radiation, affect our life in countless different ways.

The atmosphere is a mixture of a number of gaseous species and small liquid- or solid-phase particles. Thus, it can be called an ‘aerosol’, defined as “*a suspension of fine solid or liquid particles in gas*” (Merriam-Webster Online Dictionary, 2006). These suspended particles, for example cloud droplets or road dust, can have a significant effect on the atmosphere’s physio-chemical properties.

Because of the climatic and health implications caused by atmospheric aerosol loading, the aerosol budget especially in the troposphere has been a target of growing scientific investigation. This can be seen in Figure 1, where the number of hits for some relevant search terms as a function of the article publication year are given.

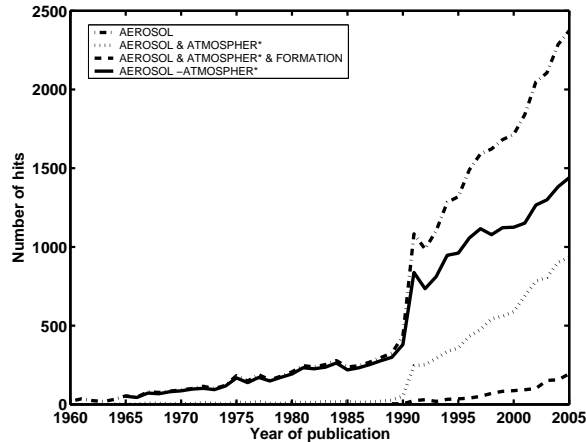


Figure 1: Number of references found with the search terms given in the legend when using the ISI Web of Science article search (ISI Web of Science, 2006).

The two main directions of atmospheric aerosol studies are the environmental effects of aerosols and the aerosol health effects. Particulate pollution causes visibility degradation as the suspended particles absorb and scatter solar radiation in the visible band (Chan et al., 1999). Aerosol particles can also provide surfaces for heterogeneous reactions and thus influence the concentrations of atmospheric pollutants (see e.g. Dentener and Crutzen, 1993; Tie et al., 2001). Probably the most important and much studied effect is the role of atmospheric particles on climate and the ongoing climate change (IPCC, 2001). In addition to the absorbing and scattering of incoming solar radiation, aerosols also affect outgoing thermal radiation, thus altering the Earth’s radiative balance. Additionally, aerosol particles play a critical role in cloud formation by acting as

cloud condensation nuclei (CCN) upon which water condenses to form cloud droplets (Pruppacher and Klett, 1997). Clouds in turn play a major part in regulating the radiative properties of the atmosphere, absorbing, emitting and reflecting solar and thermal radiation. These radiative properties are sensitive to changes in cloud droplet numbers and size (Albrecht, 1989; Twomey, 1991; Hu and Stannnes, 2000), which again are partly defined by the size and composition of the CCN. Climate effects of sulphate particles have been studied extensively (Haywood and Ramaswamy, 1998; Graf et al., 1997; Ghan et al., 2001), but also the effects of e.g. aerosols containing organic matter have been investigated (Cruz and Pandis, 1998, 1997; Hegg et al., 2001; Novakov et al., 1997). Regarding the health effects, urban particulate loading has been shown to link with increased risk of asthma attacks in children and increased mortality (Slaughter et al., 2003; Goldberg et al., 2001). Ultrafine particles can enter the bloodstream from the lungs (Nemmar et al., 2002) and may even be deposited in the brain (Oberdorster et al., 2004).

This thesis focuses on the formation of secondary aerosol in the lower troposphere. Already in the 19th century, when John Aitken was doing his pioneering work in aerosol measurements, he reported the following results from his measurements in Ireland: *“When the wind is from the N.W. the number of particles is always very low, [...] but [...] when the sun came out then numbers rapidly increased [...] to many thousands in the afternoon”* (Aitken, 1894). With advances in technology, similar observations have been made in various environments (see for example Kulmala et al. (2004c) for a review). These bursts of new aerosols could be a significant source of tropospheric aerosol number concentration and thus affect our environment in the ways described above. The University of Helsinki measurement station SMEAR II at Hyytiälä, Finland, (Hari and Kulmala, 2005) has measured the longest available time series of aerosol size distributions containing bursts of aerosol formation. The scientific knowledge gained by analyzing this set for data can lead to better understanding on how and why these particles are formed and what is their influence on the atmosphere and climate.

Before declaring the specific research aims of this thesis I shall say a few words on the ‘research chain’ ideology underlying this and other atmospheric research (Kulmala et al., 2005). The Earth’s atmosphere as a whole is a huge, complex and inherently chaotic system with a large number of processes that are currently less than well understood. Many of its processes interact in numerous ways, making studying them independently very challenging; to correctly describe larger-scale phenomena one needs to understand the different subprocesses and also vice versa. To tackle this problem the idea of a research chain comes in useful: research should be performed in a way that it interfaces with research done on both a smaller scale, as well as with the larger scale, acting as a link between the different scales. The research chain in the study of atmospheric aerosol formation could now be given as (A) Studies on molecular properties of atmospheric constituents – (B) Nucleation and cluster studies – (C) Aerosol dynamics, field experiments – (D) Box modeling – (E) Regional aerosol studies, 3D

models – (F) Global modeling. This thesis is at (C) in this chain, taking and giving information to theoretical work on understanding the processes leading to particle formation (B) and also providing analyzed field data to box model studies while using box model simulations (D) to refine analysis methods and interpret field measurement results. The results are then further propagated up and down the chain to increase the total understanding on all levels.

The aims of this study can be crystallized as

- to develop a method to identify and quantify particle formation events
- to develop and test methods to obtain characteristics of events from measured size distribution data
- to give a quantitative description of the extent of occurrence and characteristics of atmospheric particle formation in the boreal forest

In this introduction I will give a short description of general features of atmospheric aerosols and their size distributions and describe the most important aerosol dynamics relevant to particle formation events. After this, an overview of the methodology used in the event analysis will be given, after which follows a review of particle formation characteristics in the boreal forest boundary layer.

2 Atmospheric aerosols

The main characterising parameters of atmospheric particles are their size and composition. Both of these parameters can vary greatly in different environments and conditions, ranging from grains of Saharan dust of several hundred micrometers in size to just-formed nucleation clusters with a diameter of a nanometer or even less.

The atmospheric aerosol number size distribution usually comprises several modes. The largest particles belong to the *coarse mode*, usually considered to consist of particles larger than $1\ \mu\text{m}$. The main sources of these particles are wind blown mineral dust from deserts and salt particles born as a result of oceanic bubble bursting. These particles also dominate the mass spectrum of particles.

Particles smaller than $1\ \mu\text{m}$, called *fine particles*, are usually found in at most three modes. The *accumulation mode* (ca. $90\ \text{nm} - 1\ \mu\text{m}$ in diameter), is named so because particles in its size range have low deposition velocities and thus long lifetimes, causing particles to accumulate in this size range. *Aitken mode* particles, with a size range of $25-90\ \text{nm}$, are often particles which have grown from the *nucleation mode* ($3-25\ \text{nm}$, also called *ultrafine* particles) by condensation. Fine particles can be formed by various

mechanisms, for example anthropogenic burning processes. One important source of fine particulates is the formation of stable nanosized clusters or particles from gaseous matter. This particle formation mechanism, called nucleation, is the main object of study of this thesis. Such formation often occurs as bursts, called *nucleation events*, in which new nucleation mode particles appear in the ambient size distribution and grow to larger sizes.

2.1 Atmospheric particle formation events

A nice example of the size distribution evolution during a particle formation event can be seen in Figure 2. The basic feature of a particle formation event is an increase of particle number, especially in the nucleation mode (3-25 nm) (A). The formed particles then grow for several hours (B) until they have reached sizes of 50-100 nm, where they can activate as CCN. During the growth the particles coagulate with pre-existing particles, and their number is therefore reduced (red line). An often observed feature of formation events is the reduction of pre-existing particle number, characterized by the condensation sink *CS* (blue line). This may be the result of the growth of the planetary boundary layer (black line) after sunrise. If no combustion sources are nearby, the only possible source of such small particles is transformation of gas-phase matter to the particle phase either by homogeneous or heterogeneous nucleation (activation) or condensation onto some very small and thus undetectable clusters. The growth of the particles is caused by condensation of a vapor or vapors onto the surface of the particles, while the decline in fresh particle number concentration is mainly due to coagulation. These three processes will be covered in more detail in the following section.

2.2 Aerosol dynamical processes

The atmospheric aerosol size distribution is constantly undergoing changes that result from the particles' interaction with each other and the surrounding gas mixture. These interactions result in both increases and decreases in aerosol number and mass, and are often strongly dependent on the particle size. Especially at the start of their lifespan aerosol particles go through vigorous transformations. In the following I will describe the most important aerosol dynamical processes that are relevant when analyzing newborn secondary aerosol. In this treatment the aerosol is thought of in a very simplified way, as spherical droplets with no coulomb- or other interactions with each other except when colliding.

Nucleation Nucleation is the first and critical step of new aerosol particle formation from precursor vapors. The transformation of matter in the vapor phase to the liquid

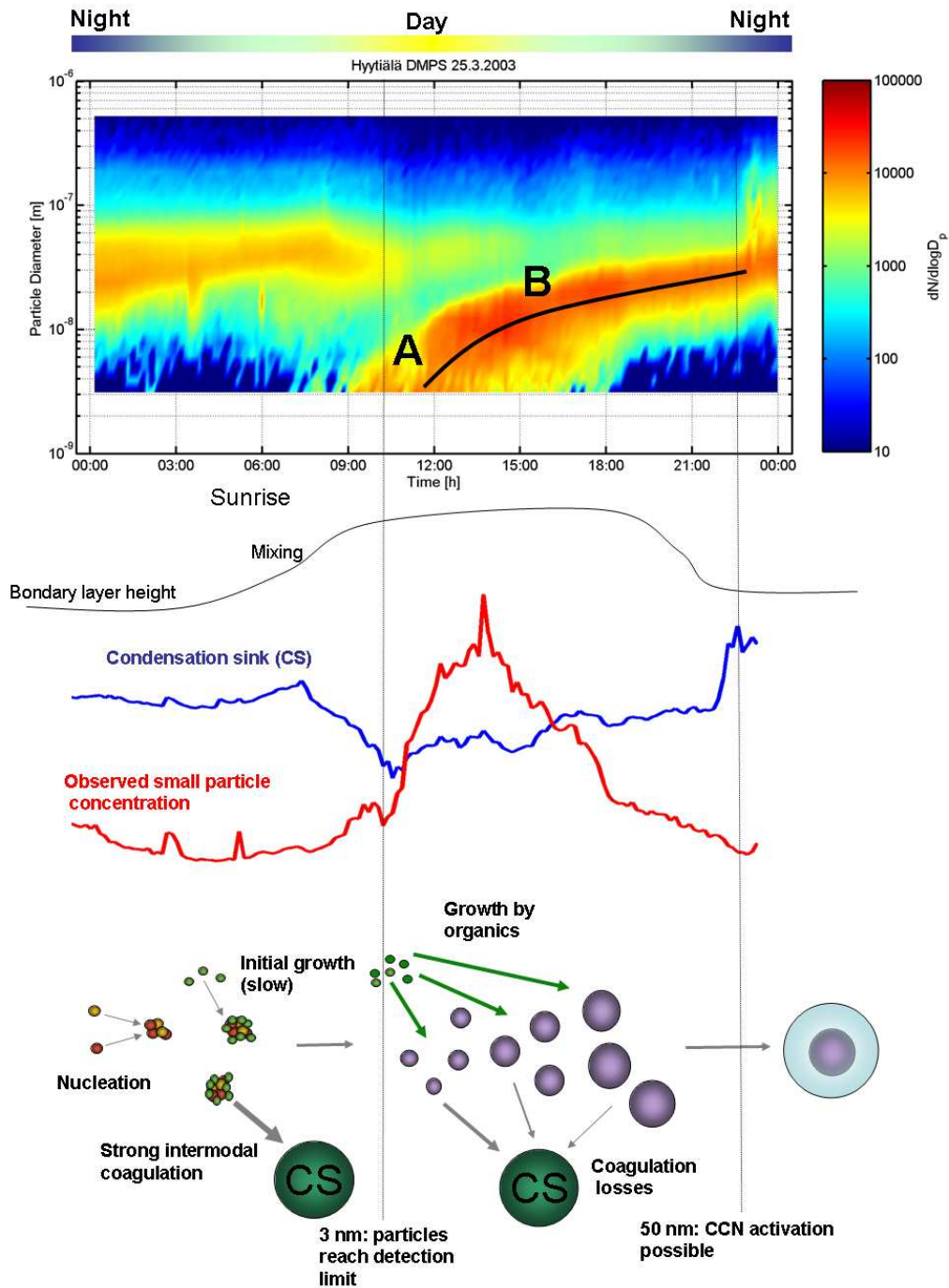


Figure 2: *Top:* A size distribution measured at Hyytiälä during a particle formation event. *Red line:* The number of particles with diameter < 25 nm *Blue line:* The condensation sink evolution *Black line:* Schematic of the evolution of the boundary layer height *Bottom:* Schematic of the processes going on during a particle formation event.

phase does not happen instantly when the vapor is saturated. First, small clusters of the new phase are formed in the supersaturated vapor. These clusters are considered to be ca. 1 nm in diameter (Kulmala et al., 2000a), too small to be detected by conventional aerosol instrumentation. The species participating in atmospheric nucleation are still to a large degree unknown, but sulfuric acid is thought to be a major candidate along with water vapor. This ‘binary homogeneous’ nucleation mechanism is one of the most studied ones in atmospheric nucleation studies (Jaeger-Voirol and Mirabel, 1987; Kulmala et al., 1998; Vehkamäki et al., 2002). The theoretical nucleation rates predicted for the binary sulfuric acid–water system in tropospheric conditions are too low to explain observed nucleation rates. Therefore, it is likely that some other species, for example ammonia or some organic acids, are also participating in atmospheric nucleation processes (see e.g. Ball et al., 1999; Napari et al., 2002; Bonn and Moortgat, 2003). Another factor that is studied is the influence of charges on the nucleation physics (ion-induced nucleation, see e.g. Lovejoy et al., 2004; Eisele et al., 2006; Laakso et al., 2002). Recently, studies on the formation rate dependence of sulfuric acid concentrations have shown support to activation theory, in which clusters containing one sulfuric acid are activated for further growth due to heterogeneous nucleation, heterogeneous chemical reactions or activation of soluble clusters (Kulmala et al., 2006; Sihto et al., 2006).

Nucleation as a process is still not very well understood. The molecular clusters in question are comprised of few molecules, and using thermodynamic properties of bulk matter to describe such clusters is not very well justified. It is, however, often the only way, because measuring the properties of these clusters is at present a challenge that has not been overcome. Nucleation studies are important, because nucleation is the sole source of secondary aerosol number in the atmosphere.

Condensation Once a new liquid phase particle has been formed, its surface is continuously bombarded by gas molecules. If the droplet is not in equilibrium with the surrounding vapor, there is a net flux of molecules either towards (condensation) or away from (evaporation) the droplet surface. Condensation is the main mechanism that grows atmospheric aerosol particles. It is driven by the difference of vapor pressures (or concentrations) at the droplet surface p_s, c_s and the vapor pressure far away from the droplet, p_∞, c_∞ . The relation between the rate of the diameter change and the concentration difference in the case of unary condensation of spherical particles can be given as (Seinfeld and Pandis, 1998)

$$\frac{dd_p}{dt} = \frac{4D_i M}{\rho d_p} \beta_M (c_\infty - c_d) \quad (1)$$

where d_p is the particle diameter, D_i is the binary diffusion coefficient in air for the condensing vapor (Poling et al., 2001) and M is the molecular mass of the condensing vapor. β_M is the transitional correction factor, introduced to account for the difference

in the condensation flux at small and large droplet sizes. At small sizes the particles see the vapor molecules as discrete entities (free molecular regime), while at large particle sizes the condensing vapor is seen as a continuous medium (continuum regime). The size scale is characterized by a dimensionless group, the Knudsen number

$$Kn = \frac{2\lambda}{d_p} \quad (2)$$

where λ is the effective mean free path of the condensing vapor in the gas (air). The form of the transitional correction factor β_M used throughout this thesis is the one proposed by Fuchs and Sutugin (1971), given by

$$\beta_M = \frac{1 + Kn}{1 + (\frac{4}{3\alpha} + 0.337)Kn + \frac{4}{3\alpha}Kn^2}. \quad (3)$$

α is the mass accommodation coefficient (also called the sticking coefficient) which describes the probability of an impinging molecule sticking to the surface. Unless otherwise stated, it is assumed to be unity, based on the results obtained by Winkler et al. (2004).

Condensation is generally very well understood, and in laboratory conditions, when the growth or evaporation rate of droplets of a known vapor can be determined accurately, condensation theory can be used to acquire knowledge of the participating vapor properties. In the atmosphere, however, the condensing vapor is often unknown and the determination of the growth rate can be problematic.

Coagulation When aerosol particles move in the carrier gas they occasionally collide and stick to each other, forming a single particle. This process is called coagulation. The coagulation rate of a particle population depends of the particle concentration and the coagulation efficiency of the particles. The coagulation efficiency in turn depends on the relative velocity of the colliding parties and their interception cross area. There are several ways that cause particles to move relative to each other, among others gravitational settling, turbulence and Brownian motion. Brownian coagulation is one of the main sinks of ultrafine aerosol particles. In this thesis, other coagulation mechanisms are omitted, and mentions of coagulation refer solely to Brownian coagulation.

The coagulation coefficient $K(u, v)$ (also called the coagulation kernel) describes the coagulation efficiency of two particles with volumes between $[u, u + du]$ and $[v, v + dv]$. Similar effects due to the free molecular and continuum regime that have to be considered for condensation also apply to coagulation. In this work, the calculation of the coagulation coefficient has been performed following the Fuchs (1964) treatment where the coagulation coefficient is given by

$$K(v, u) = \frac{K_C}{\frac{r_{uv}}{r_{uv} + \sigma_{uv}} + \frac{4D_{uv}}{c_{uv}r_{uv}}}. \quad (4)$$

Here

$$K_C = 4\pi r_{uv} D_{uv} \quad (5)$$

is the coagulation coefficient in the continuum regime, and $r_{uv} = \frac{1}{2}d_p(u) + d_p(v)$ is the interception distance of the particles. The binary particle diffusion coefficient D_{uv} can be given as $D_u + D_v$ if the particles are assumed to move independently. $\overline{c_{uv}} = \sqrt{\overline{c_u^2} + \overline{c_v^2}}$ is the relative thermal velocity of the particles and σ_{uv} is a distance parameter resulting from the flux matching approach. Coagulation is most efficient between particles with a large difference in size, when the big but slowly moving particle scavenges the small particle which moves with a large velocity. This means that just-formed, nanometer-sized particles are most susceptible to coagulation scavenging, and Brownian coagulation is one of the key processes determining whether particles produced by nucleation ever reach detectable sizes, let alone CCN sizes.

3 Measurement and data analysis

3.1 Aerosol size distribution measurements

The instrument John Aitken used for his pioneering work only counted the number of particles without giving any insight into the size distribution of particles. Additionally, the instrument used was only capable of detecting particles larger than ca. 20 nm, which ruled out the possibility to investigate the formed particles at the early states of development. The situation remained like this for almost a century, until the development of instrumentation to generate calibration aerosols caused measurements to “evolve from art to science” (McMurry, 2000) in the 1970’s. Later advances in technology, especially the advent of the Differential Mobility Particle Sizer (DMPS) in the early 90’s, have enabled routine and continuous measurements of particle size distributions from sizes down to 3 nm. The DMPS is currently the most widely used, and best (Wiedensohler et al., 1994) instrument for measuring ultrafine size distributions; it is also the instrument used to obtain the aerosol data analyzed in this work. In the following I shall give a short description of this instrument.

The DMPS consists of a differential mobility analyzer (DMA; see Liu and Pui, 1974; Knutson and Whitby, 1975) and a particle detector, usually a condensation particle counter (CPC). The aerosol is first brought to a Boltzmann charge equilibrium (Wiedensohler, 1988) and then it is taken to the DMA. In the DMA the particles are exposed to an electrical field which is used to select a fraction of the particles based on their electrical mobility. This fraction is then taken to the CPC where they are exposed to a supersaturated vapor which causes them to grow, enabling their optical detection. When the instrument air flows, the DMA voltage and the particle number counts are known, the DMPS transfer function can be calculated and the ambient size

distribution is obtained. The DMPS systems used in this study scan a size distribution between 3-500 nm in 10 minutes.

A large part of the data analyzed in this work is measured at the SMEAR II station in Hyytiälä, Central Finland. The DMPS system at this site is a 'twin-DMPS', which means that it consists of two DMAs and two CPCs, each subsystem measuring different size ranges and overlapping at some point. This increases the resolution in both time and particle diameter as less time is needed to cover the size range. A thorough description of the Hyytiälä DMPS system can be found in Aalto et al. (2001)

When the Hyytiälä size distribution measurements were started in January 1996, there was very little observational data of aerosol size distributions during particle formation events. Continuous measurements of ultrafine aerosol concentrations, let alone size distribution measurements, were very rare. Therefore, it was somewhat of a surprise that in a relatively short time, a number of particle formation events were observed (Mäkelä et al., 1997). Similar observations had been made by Birmili et al. in the plume of Leipzig in 1996-1997 (Birmili and Wiedensohler, 2000) and by Raes and coworkers already in 1994 (Raes et al., 1997) at Tenerife. These observations, however, were only short-term measurements, whereas the Hyytiälä measurements were kept running continuously, providing at present the longest submicron aerosol size distribution time series known to the author.

Because measured size distributions of particle formation bursts were so rare, there was also very little literature of a methodology to be used when identifying and characterizing particle formation bursts. These tasks are of prime importance in determining the extent and importance of particle formation in the atmosphere, as well as in investigating the processes leading to the formation itself. Developing this methodology is one of the focal points of this thesis and will be reviewed in the following sections.

3.2 Identifying particle formation events

The first step in the analysis of particle formation events is the identification and classification of the formation time periods from the data. To do this, one needs to keep in mind the process leading to the observable phenomenon, described in section 2.1. The formation process, regardless of the exact pathway, leads to a sharp increase in the number concentration of very small, nucleation mode particles. Subsequent condensation of low-volatile vapors causes the new particles to grow in diameter thus causing the mean size of the formed particles to shift towards larger sizes as time goes by.

The area where this process is taking place affects the shape and evolution of the measured size distributions. If the particle source is a point (or a relatively small area)

or a line close to the measurement site, then the shift towards larger sizes will not be observed if there is any horizontal advection (which is the case virtually always in the atmosphere). However, if formation is occurring over a larger area, the formation can be seen in a time series of size distributions as a distinct shape, as shown in Fig. 2. This shape is sometimes referred to as ‘the nucleation banana’ due to its tropical appearance when plotted as a colored surface plot. This thesis focuses mainly on the analysis of the regional kind of particle formation events, with the exception of **Paper III**, where some case studies of a line particle source are considered. The data features of such events are well visible in Fig. 2: The appearance of a new small particle mode (**A**), and the growth of this mode to larger sizes (**B**).

The identification and classification of particle formation was performed for a day at a time. This is justified by the observation that the formation bursts appear with great regularity during daytime, mostly in a time window centered at noon, while nighttime events are extremely rare. So instead of marking time periods as formation periods, this approach allowed the classification of days as either event days or non-event days.

The classification was performed visually, based on the color plots of the time series of the number size distributions. In **Paper I** the classification was done by a single person; the analyses in **Papers IV and V** were performed by groups of three or more persons to reduce the subjective aspect of the classification.

While identifying particle formation bursts is in principle simple, there are some complications that required refinements in the classification guidelines. One of the main assumptions in the analysis was that the measurement is made in a uniform air mass with the same properties for an extended period of time. Because of the inherently turbulent nature of the atmosphere, the validity of this assumption varies. This causes fluctuations in the observed size distributions which can make the analysis of the event properties more difficult, or even make the distinction between particle formation and transported aerosol difficult. Therefore it was early noted that a classification system was needed to somehow get a measure on the amount of trust that could be placed in the derived characteristics.

In **Paper I** the classification was a 3-class classification with class 1 being the most clear case with little or no fluctuations and the nucleation mode visibly separate from any pre-existing aerosol in the measured distributions. Classes 2 and 3 were then progressively lower in quality, with concentration of the nucleation mode, uniformity of the growth and interference with pre-existing aerosol being the main factors weighing in on the classification. A class 0 was also introduced, for days that could not be analyzed but might still be formation event days.

In later analysis of the Hyytiälä dataset it was found that the subjective grouping into three different classes was difficult to maintain, as there were no set criteria separating the classes. Therefore, a new classification system was introduced. In the new system

the main focus was on separating event and non-event days; this was done as group work and following some simple guidelines (**Paper IV**, Fig. 3). Any days where the event or non-event status was doubtful, was classified as ‘undefined’.

Now that the events were clearly separated from the other days, they were classified further into classes I and II, representing events that could be analyzed for event characteristics (I), and events that exhibited too much fluctuations or background aerosol interference to be analyzed (II). This classification system has the benefit that each class has a well-defined set of criteria according to which a day can be classified into it. The system was used for the classification of several aerosol time series in **Papers IV and V**.

3.3 Formation characteristics

The aerosol formation and growth process can be crudely termed as gas-to-particle transformation, but in reality there are complex subprocesses affecting the evolution of the aerosol. These subprocesses are grouped under the heading ‘Aerosol dynamics’ and cover among others condensation, coagulation and nucleation.

Theory The evolution of the aerosol population in time can be described by the general dynamic equation (GDE) (Seinfeld and Pandis, 1998)

$$\begin{aligned}
\frac{\partial n(d_p, t)}{\partial t} &= \frac{1}{2} \int_{d_{p0}}^{(d_p^3 - d_{p0}^3)^{1/3}} (K([d_p^3 - d_p'^3]^{1/3}, d_p') \\
&\times n([d_p^3 - d_p'^3]^{1/3}, t) n(d_p', t) dd_p') \\
&- n(d_p, t) \int_{d_{p0}}^{\infty} K([d_p, d_p'] n(d_p, t) n(d_p', t) dd_p' \\
&- \frac{\partial}{\partial d_p} \left[\frac{dd_p}{dt} n(d_p, t) \right] \\
&+ J(d_p) \delta(d_p - d_{p0})
\end{aligned} \tag{6}$$

in which the third and fourth terms on the right hand side describe condensation and nucleation, respectively. The first term on the right hand side is the coagulation production term, i.e. the formation rate of particles of radius d_p from smaller particles. The second term is the coagulation loss term, i.e. the removal rate of particles of radius d_p because of collisions with particles of any size. J is the nucleation rate and β the collision frequency function. As stated in equation (1), assuming a negligible vapor

pressure, the growth rate of the particle diameter in the condensation term depends on the condensing vapor concentration C_{vapor} in the following way:

$$\frac{dd_p}{dt} = \frac{4m_v\beta_m DC_{vapor}}{d_p\rho} \quad (7)$$

Here m_v is the molecular mass of the condensing vapor, β_m is the transitional correction factor for the mass flux (Fuchs and Sutugin, 1971), D is the vapor diffusion coefficient and ρ is the particle density.

Well established numerical methods to solve the GDE exist (e.g. Gelbard and Seinfeld (1980), Raes and Janssens (1986), Jokiniemi et al. (1994), Jacobson (1995)). However, in this case we are looking for simple, analytical order-of-magnitude estimates, which also provide insight into the relative importance of different aerosol dynamical mechanisms. Thus, we will first simplify the GDE by neglecting terms, based on a simple order of magnitude analysis.

The coagulation production term can be neglected for most particle formation events because the production rate is very low, causing negligible particle growth, as shown in **Paper III**.

Thus the coagulation term can be simplified to the product of $n(d_p)$ and a coagulation sink

$$CoagS(d_p, t) = \int_{d_{p0}}^{\infty} K([d_p, d'_p])n(d'_p, t)dd'_p \quad (8)$$

yielding for the GDE

$$\begin{aligned} \frac{\partial n(d_p, t)}{\partial t} &= -n(d_p, t)CoagS(d_p, t) \\ &- \frac{\partial}{\partial d_p} \left[\frac{dd_p}{dt} n(d_p, t) \right] \\ &+ J(d_p)\delta(d_p - d_{p0}) \end{aligned} \quad (9)$$

Coupled with the GDE, one has to solve a balance equation also for the condensing vapor:

$$\frac{dC_{vapor}}{dt} = Q - CS \cdot C_{vapor} \quad (10)$$

where Q is the source rate and CS is the condensation sink. The condensation sink is the value of how rapidly condensable vapor molecules will condense on the existing

aerosol (the whole particle size distribution). Its unit is 1/s. It is obtained from (see also Pirjola (1999))

$$CS = 2\pi D \int_0^\infty d_p \beta_m(d_p) n(d_p) dd_p = 2\pi D \sum_i \beta_i d_{pi} N_i \quad (11)$$

Here the second form of the CS definition is for a discrete size distribution, and d_{pi} is the diameter of a particle in size class i and N_i is the particle concentration in the respective size class.

[A NOTE TO THE READER: In **Paper I** the notation for the condensation sink differs from the one used in this thesis and the rest of the included papers. In the paper in question, CS refers to the integral part of the above expression, while R_A , the vapor removal rate, corresponds to the CS used elsewhere.]

In Equations (4) and (10) the observable quantities for particle formation bursts are the particle growth rate $GR = \frac{dd_p}{dt}$, the condensation and coagulation sinks CS and $CoagS(d_p)$ and the time change of the particle concentration in size range $[d_{p1}, d_{p2}]$, $dN_{d_{p1}-d_{p2}} = \frac{\partial}{\partial t} (\int_{d_{p1}}^{d_{p2}} n(d'_p, t) dd'_p)$. These quantities characterize the dynamics of the particle formation event and if they are known, we can gain estimates on more fundamental properties of the phenomenon, such as the concentration and source rate of the condensing vapor and the nucleation rate of clusters that are too small to be detected. In the following I will present the methods of extracting these quantities from the measured aerosol number size distributions.

The growth rate Our aim was to derive the rate at which the newly formed aerosol population grows, $\frac{dd_{p,nuc}}{dt}$. In the literature several detailed ways of deriving the growth and formation rates can be found (e.g. Weber et al. (1995)). For the data analysis performed in this work we needed a robust method, which copes well with fluctuating data and is straightforward to use.

The main question is defining the representative diameter, that is the diameter that is considered to represent the recently formed particle population, and extracting this diameter from the data. The first approach, applied in **Paper I**, used the maximum size that the nucleation mode particles reached after a given time from the first appearance of particles as the basis of the growth rate determination. Another method involved visual determination of the mode centerpoint and its change in time (**Paper II**). Both methods relied strongly on user input, and gave results with a large error range. Therefore, the development of more well-defined methods that would give reproducible results was deemed necessary.

A straightforward way to determine the growth rate would have been to follow the temporal change of the mean diameter or the geometric mean diameter. However, this

presented the problem of defining the size range over which to average. If the averaging is performed over a range containing large particles (>25 nm), the result is influenced by pre-existing particles that are not formed recently. On the other hand, if the range is limited only to small particles and the growth rate is large, it may happen that the particles grow quickly out of the averaging range and our parameter does not represent the new population in its entirety.

A method where the evolution of the new mode is determined by following the concentration of each channel (mobility size range) of the DMPS is another possibility. In this method, the peak in each channel caused by the mode passing its size range is identified, for example by fitting a normal distribution to the time series of the channel concentration (Lehtinen and Kulmala, 2003). By recording the instants when peaks occur in each channel, we could then derive the growth rate. This method, while being efficient for sub-10-nm particles (Hirsikko et al., 2005), proved ill suited for our analysis. The logarithmically spaced channels caused a broadening of the peaks, making it difficult to identify the exact time of peak passage at larger particle sizes. Additionally, the method is sensitive to fluctuations in the mode concentration, which is usual in our data, requiring careful user input to select the correct peak.

After long testing by trial and error, the best approach to derive the growth rate was to parametrize each size distribution expressing it as a sum of one or more lognormal distributions. The parameters of each distribution (or 'mode' as it is often called), namely the geometric mean diameter \bar{d}_{pg} , the geometric standard deviation σ_g and the modal concentration N , were obtained by a least-square fitting procedure. The reason this parametrization was not used prior to **Paper IV** is the time-consuming nature of the fitting procedure. Only after an automated procedure for performing the fitting became available (Hussein et al., 2005) this method could be used for larger datasets.

The modal geometric mean \bar{d}_{pg} , which is obtained as a result of the fitting procedure is a good choice for growth rate analysis. In a log-normally distributed population \bar{d}_{pg} is also the median diameter (Seinfeld and Pandis, 1998), meaning that the majority of the particles are of a size close to \bar{d}_{pg} .

To obtain the growth rate, a first order polynomial is fitted to the geometric mean diameters of the nucleation mode during the formation burst. If the new particle mode is not well-behaved over the whole time period that it is visible in the measured size distributions, a time period where the growth was close to constant is chosen, with a time period close to the beginning of the burst being preferred.

Vapor and particle sinks To quantify condensation and coagulation processes during new particle formation, it is of use to calculate the condensation sink and the coagulation sinks. CS describes the ability of the size distribution to remove condensable

vapors from the atmosphere. In practice, the vapor is assumed to have a very low vapor pressure at the surface of the particle, and molecular properties similar to sulfuric acid.

The coagulation sink in turn is a measure of the pre-existing aerosol’s ability to scavenge small recently-formed particles. It is a function of both the pre-existing size distribution and the diameter of the scavenged particle. Smaller particles are more easily lost to coagulation than larger particles.

Both sink parameters are strongly dependent on the shape of the number size distribution. The DMPS system at the SMEAR II station measures the size distributions in a dried sample flow; this causes a reduction in particle sizes depending on their hygroscopicity. To get the correct value for the sinks in ambient air, this hygroscopicity effect should be taken into account. In **Paper IV** a parametrized hygroscopic growth scheme was applied to calculate the growth factor of the measured particles, adopted from Laakso et al. (2004):

$$GF(d_p, RH) = \left(1 - \frac{RH}{100}\right)^\gamma \quad (12)$$

Here GF is the growth factor of a particle of size d_p in a relative humidity RH . γ is a parameter derived by a least-square fit to hygroscopicity data measured during the BIOFOR campaign in Hyytiälä in 1999 (Hämeri et al., 2001), given by

$$\gamma = 3.1116 \cdot 10^5 \cdot d_p - 0.0847. \quad (13)$$

The GF was restricted so that it could not exceed the GF of ammonium sulphate. Using this parameterization increased the CS value usually by a factor between 1.1 and 2.0, with a mean and median of 1.62 and 1.48, respectively.

Formation rate The particle formation rate refers to the flux of particles into the observable size range. Because no information is available of the temporal behavior of the real formation rate, a constant particle source that is active during a time period $[t_{1,start}, t_{1,end}]$ is assumed. The produced particles then appear in the observable size range between the times $[t_{2,start}, t_{2,end}]$, where the time difference $t_{2,start} - t_{1,start}$ depends on the growth rate of the freshly formed particles. During this time, a fraction of the particles is lost due to coagulation processes. The flux of particles into the observable size range, J_{obs} , can be calculated from the following equation (see for example Kulmala et al. 2004 and references therein):

$$J_{obs} = \frac{dN_{nuc}}{dt} + F_{coag} + F_{growth} \quad (14)$$

where N_{nuc} is the nucleated particle concentration, F_{coag} is the loss of particles due to coagulation and F_{growth} is the flux of particles out of the size range. The size range for

the nucleated particles (N_{nuc}) was chosen to be from 3 nm up to 25 nm, allowing one to neglect the growth term in equation 14, as particles rarely grew over this size before formation ended. Smaller ranges could be used to gain insight into the time dependence of the formation rate; however, the aim was to obtain a more general average formation rate, so a more stable size range was used. In some cases the particles grew out of the 3–25 nm range; to analyze these cases N_{nuc} was also calculated from the fitted modal concentration of the nucleation mode. This concentration was generally equal to the concentration in the 3–25 nm size range. To calculate $\frac{dN_{nuc}}{dt}$, $t_{2,start}$ and $t_{2,end}$ was determined by choosing the period when the particle number showed a linear increase. Then a first-order polynomial was fitted to the values of N_{nuc} . F_{coag} was calculated from

$$F_{coag} = CoagS_{nuc}N_{nuc} \quad (15)$$

where $CoagS_{nuc}$ is the coagulation sink of particles in the nucleation mode. The reference size for $CoagS_{nuc}$ was taken to be the GMD of the fitted nucleation mode.

Condensing vapor concentration and source rate We see from equation (7) that the particle growth rate depends on the concentration of the condensing vapor. Integrating this equation, one arrives at (Kulmala, 1988)

$$C_{vap} = \frac{\rho \left[\frac{d_p^2 - d_{p0}^2}{8} + \left(\frac{4}{3\alpha} - 0.623 \right) \frac{\lambda}{2} (d_p - d_{p0}) + 0.623 \lambda^2 \ln \frac{2\lambda + d_p}{2\lambda + d_{p0}} \right]}{\Delta t D m_v} \quad (16)$$

where α is the mass accommodation coefficient and λ is the vapor mean free path. Assuming a constant growth rate from d_{p0} to d_p and integrating from 3 to 20 nm this expression simplifies to

$$C_{vap} = A \cdot \frac{dd_p}{dt} \quad (17)$$

where the constant $A = 1.39 \cdot 10^7 \text{ nm}^{-1} \text{ cm}^{-3} \text{ h}$. This is because the size range is in the free molecular regime, and the growth rate is independent of the particle diameter.

If no sudden injections or depletions of vapor are taking place, we can assume a steady state situation and set $\frac{dC_{vap}}{dt} = 0$ in equation (10), which gives for the vapor source rate

$$Q = CS \cdot C_{vap}. \quad (18)$$

In all these calculations the saturation vapor pressure over surface of the particle is assumed to be negligibly small. This is the case for sulfuric acid; whether this assumption holds also for other condensing species, for example organic oxidation products, is still debatable.

Nucleation rate To link the observations of particle formation to theoretical work on the formation mechanism, one has to know the rate at which particles are formed. The problem here is, however, that present instrumentation can not detect particles smaller than ca. 3 nm in diameter, whereas the initial size of the nucleated particles is considered to be around 1 nm (see e.g. Kulmala et al., 2000a). Because coagulation is very efficient between particles with differing sizes, a significant part of the nucleated particles can be lost before they grow large enough to be detected by aerosol instruments. Therefore, one has to solve for the nucleation rate J in the GDE with knowledge of only particles larger than the instrument’s minimum detection size.

In the following I will give a short overview on how this was done in this thesis, specifically in **Papers II and III**. The approach is based on discretising the particle number density distribution $n(d_p, t)$, dividing it into size classes for which one can calculate the coagulation loss rate. The main assumptions made are

- a) the size distribution is in steady state. This means that the size distribution reacts quickly to changes in the coagulation and growth rates and settles then again in a new steady state, where the time change in each size class can set to zero, $\frac{dN_i}{dt} = 0$.
- b) the growth rate is constant during the formation burst period, with respect to both time and particle size. This means that we can use the growth rate obtained from the analysis of the observed particles and assume that it represents the growth of below-detection particles.
- c) Self-coagulation is negligible. This means that the growth caused by nucleated particles colliding with each other, as well as the number reduction of said particles, can be neglected.
- d) Condensation out of the largest size class is negligibly small. This can be achieved by choosing a suitable size range for determining $\frac{dN_{obs}}{dt}$.

Depending on the way of discretising the size distribution and how the coagulation losses are calculated, different forms of the equation for J can be derived. Their general form is

$$J = \frac{1}{P_{surv}} \left[\frac{dN_{obs}}{dt} + CoagS_{obs}N_{obs} \right] = \frac{1}{P_{surv}} J_{obs} \quad (19)$$

where P_{surv} is the probability of a formed cluster to survive to detectable size, related to the loss probability by $P_{loss} = 1 - P_{surv}$.

The formula proposed for P_{surv} in **Paper II** is

$$P_{surv} = e^{-Kt} = e^{-K \frac{2nm}{GR}} \quad (20)$$

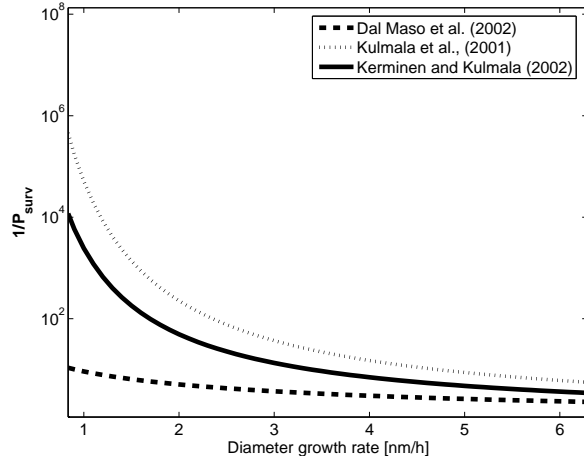


Figure 3: The dependence of the factor $\frac{1}{P_{surv}}$ on the growth rate for typical formation-time conditions in Hyytiälä. For comparison, the value of a widely-used formula by Kerminen and Kulmala (2002) is also given.

where $K = CoagS_{1-3}$ is the average coagulation sink during the growth of the particles from 1 to 3 nm in diameter and t is the growth time. This method is quite sensitive to errors in the growth rate and the calculation of the average sink, and therefore an improved method with additional discretization was introduced in **Paper III**, which gave

$$P_{surv} = \frac{C_1 C_2}{(CoagS_1 + C_1)(CoagS_2 + C_2)} \quad (21)$$

where C_i is the condensation growth flux out of size class i , given by $C_i = \frac{GR}{\Delta d_{p,i}}$, $\Delta d_{p,i}$ being the size class width.

In figure 3, one can see the dependence of the factor $\frac{1}{P_{surv}}$ on the growth rate for a typical event-time situation in Hyytiälä. The factor grows exponentially as the growth rate gets smaller, and the difference between the methods can be several orders of magnitude with small growth rates. From the figure one can also see that J is quite sensitive to errors in the GR determination. For comparison, the values obtained using the expression proposed by Kerminen and Kulmala (2002), published after the publication of **Papers II and III** and currently often used, is also given.

Recently Hirsikko et al. (2005) published results on an analysis of charged atmospheric particles with sizes below 3 nm during particle formation. Their analysis showed that assumption b), which is integral to the J estimation methods, is probably not justified because the particles grow slower during the initial stages of their existence. This, coupled with the large sensitivity of the J estimation at lower growth rates, is a major worry when considering the validity of the estimated J . There have been several studies on the subject (Kulmala et al., 2004b,a), but the exact growth behavior during the initial growth is still unclear. Therefore, in the longer time series analysis in **Papers**

IV and V estimation of the nucleation rate was excluded from the analysis, and only the observable formation rate was reported.

4 Characteristics of Boreal particle formation

The developed methodology was used for data analysis of observed particle formation bursts. The main body of the analyzed data was measured at the Hyytiälä station for measuring ecosystem-atmosphere relationships SMEAR II (**Papers I-V**). Data from other stations was also analyzed: data measured during the PARFORCE campaign in Mace Head, Ireland, (**Paper III**; O’Dowd et al. (1999); O’Dowd (2000)), and data from three other stations in the Nordic area, all inside the Boreal forest (**Paper V**; Tunved et al. (2003)). The focus in this thesis is on the boreal forest particle formation characteristics, which will be summarized in the following.

Event occurrence The classification and selection of event and non-event days revealed that tropospheric particle formation in the boreal forest is quite common, at least more common than previously assumed. At the Hyytiälä field station, roughly every fourth day was found to contain a particle formation burst when the long time series was analyzed (**Papers IV and V**).

Taking a look at the times of particle formation, some clear patterns could be found. The bursts are almost exclusively observed during daytime, at least 2 hours after sunrise and on average 3-4 hours after sunrise (**Paper I**) but mostly before noontime. The start time of the bursts followed the variation of the time of sunrise (**Paper I**, figure 3.) On the annual scale, two clear peaks in the formation frequency were found, one in springtime (March-May) and another centered around September (see e.g.. **Paper V**, figures 1-4). During these periods, the event fraction was over 50% of all days, and even higher than that if undefined days were removed from the statistics. In contrast, wintertime (November to mid-February) is a very inactive time for particle formation. In summer a dip in the frequency is observed.

The classification revealed that also some interannual variation was present in the Hyytiälä time series. From 1998 to 2003 a clear increasing trend could be observed, during which the number of classified event days increased from 63 to 120 *per annum*. The trend does not continue beyond 2003. A similar trend could be seen at the Aspöretten station in southern Sweden, but not at Lapland stations. The cause for the increase is yet unknown.

Conditions favoring particle formation As already mentioned, particle formation occurs during daytime, some time after sunrise. Sunlight is, a few exceptional days

during the polar night at Värriö excluded, a necessary prerequisite for particle formation (see also Mäkelä et al., 1997). Incoming radiation was found to correlate with the growth rate of the new particles (**Paper I**), which lead to speculation that increasing amounts of radiation increase the photochemical production rate of condensing vapor, which increases the growth rate of the particles. This in turn increases the probability of particles surviving the early stages of growth until they are detectable.

While investigation of the local wind direction did not lead to conclusive findings of a dominant direction from which air leading to particle formation could originate (**Paper I**), later investigations showed that the direction NW of Hyytiälä was the predominant source of such air. Trajectory studies by Nilsson et al. (2001), Kulmala et al. (2000b), and Sogacheva et al. (2005) showed that North Atlantic air and especially outbreaks of cold polar air are favorable to particle formation. Air arriving from the direction of the North Atlantic was also found in **Paper V** to promote particle formation at all the investigated boreal stations.

Particle formation is also connected to the mixing state of the planetary boundary layer. This was reported in connection with the Hyytiälä formation events by Nilsson and Kulmala (1998), and briefly touched upon in **Paper I**. There it was seen that a strong potential temperature gradient, indicative of vertical mixing, was favorable for particle formation.

The pre-existing aerosol, well characterized by the condensation sink CS , has a strong case of being the most important limiting factor of particle formation. This has been discussed extensively in the literature (e.g.. Weber et al., 1997; Clement et al., 2000)). A low condensation sink was also in this work found to be important, and event-time condensation sinks were clearly lower than the sink of non-event days (**Papers IV and V**). A study by Hyvönen et al. (2005) applied data mining techniques to the classification presented in **Paper IV** and other atmospheric data measured in Hyytiälä, and found that CS (or the logarithm of it) and relative humidity are the two parameters that most effectively separate event days from non-event days.

Other atmospheric parameters such as concentrations of the trace gases SO_2 , O_3 or NO_x did not significantly correlate with particle formation events.

Event characteristics The growth rates of new particles were found to be of the order of a few nanometers per hour. At Hyytiälä, the average growth rate in the 1996-2004 period was 3.0 nm/h (median 2.5 nm/h), but values in the range of 0.5 – 15 nm/h were found (**Papers I-V**). Similar values were also found for the other analyzed boreal stations (see **Paper V**). To sustain such growth rates, a condensing vapor concentration of $0.7 \cdot 10^7 - 2.0 \cdot 10^8 \text{ cm}^{-3}$ would be expected in the ambient air. Measurements of sulfuric acid concentrations, performed at the Hyytiälä station during the QUEST project, revealed that H_2SO_4 concentrations were considerably lower than this value

(Boy et al., 2005; Sihto et al., 2006). This means that the growth is mainly caused by some other vapor, and the best candidates are oxidation products of organic species, for example terpenes, that are emitted by the boreal trees. The estimated source rate of the condensing vapor varied between $5 \cdot 10^3$ and $6.4 \cdot 10^5 \text{cm}^{-3} \text{s}^{-1}$ in Hyytiälä, and between $6 \cdot 10^2$ and $2.4 \cdot 10^6 \text{cm}^{-3} \text{s}^{-1}$ in the data of the four boreal stations analyzed in **Paper V**.

The observed formation rates at the Hyytiälä station varied between 0.06 and $5.0 \text{cm}^{-3} \text{s}^{-1}$ with a mean of $0.8 \text{cm}^{-3} \text{s}^{-1}$. At the other stations the observed formation rates were somewhat lower; however, one has to take into account that the instrumentation was not identical between the stations, and this may affect the determination of the formation rate more than the growth rates. The estimated formation rates of particles were, depending on the analysis method, from 10-100 $\text{cm}^{-3} \text{s}^{-1}$ (**Paper II**) or 8-20 $\text{cm}^{-3} \text{s}^{-1}$ (**Paper III**). These values should, as mentioned in section 3.3, be approached with caution, as the real growth rate of below-detection nuclei most probably differs from the growth rate of larger particles. If the growth rate of 1-3 nm particles is lower, as reported by Hirsikko et al. (2005), then the formation rate of 1 nm nuclei will be significantly higher.

The formation event characteristics showed annual variation that could shed some light on the mechanism behind the formation. The growth rate is highest during summer, when the mean GR is around 5 nm/h and values of 10 nm/h are not uncommon. The formation rates, in turn, show two maxima in spring and autumn, around the same times than the formation event frequency peaks.

5 Review of the papers

The thesis consist of five articles published in peer-reviewed journals.

- **Paper I**

Paper I is the first longer time series analysis with focus on analyzing the growth and formation rates of the selected particle formation events. The connections between the growth and formation rates and a variety of environmental parameters were studied, and the possible coupling of the formation and growth processes are discussed. The author did the major part of the analysis in this paper and participated in the writing.

- **Paper II**

Paper II is a methodology paper that develops methods to derive formation and growth properties from size distribution data. Together with hygroscopicity data also basic composition properties could be estimated. The paper contains the

description of the methodology and some case studies from during the BIOFOR campaign at Hyytiälä, in which the developed methods are utilized. The author was responsible for most of the size distribution data analysis and a minor part of the writing.

- **Paper III**

Paper III is another methodology paper where another method for estimating the nucleation rate of 1 nm clusters is presented and condensing vapor concentrations and sinks are calculated for particle formation events observed at Mace Head, on the Irish west coast, and Hyytiälä, Finland. The results of the two sites are compared and the vapor and particle concentrations were found to be much higher during coastal events. The author was responsible for most of the analysis and a major part of the writing.

- **Paper IV**

In Paper IV the methods presented earlier are used for analysis of an eight-year time series of aerosol particle size distributions from the boreal forest, measured at Hyytiälä, Finland. The event selection and classification is redefined and methods of acquiring the growth and formation rates are improved from Paper I. Particle formation at Hyytiälä was confirmed to be frequent, with clear annual variation in event occurrence, growth and formation rates. The author was responsible for most of the analysis and the writing.

- **Paper V**

The same methodology was again utilized, this time for analysis of several time series measured inside the boreal forest, in Lapland at Värriö and Pallas, as well as in southern Sweden at Aspvreten. The results were then compared to results obtained from Hyytiälä, which were also updated by one more year of data. The formation occurrence was found to show a north-south dependence, with the southern stations exhibiting a greater event/non-event ratio than the Lapland stations. Growth rates were also higher at the southern stations. Particle formation was confirmed to be occurring on regional scale in the boreal forest. Trajectory analysis strengthened the assumption that air resulting in particle formation often originates from the North Atlantic. Events were also found to occur in air with lower condensation sinks; this effect was found to be stronger at the southern stations. The author was responsible for most of the analysis and the writing.

6 Conclusions

In the course of the work described in this thesis several long time series of aerosol size distributions have been analyzed with focus on particle formation events. A set

of guidelines have been established to identify regional-scale particle formation, and methods to derive the basic characteristics such as growth and formation rates have been developed. The methodology can also be used to estimate concentration and source rates of the vapor causing particle growth. The methodology used has proven to be useful in the analysis of long time series of particle number size distribution data.

The analysis shows without doubt that secondary particle formation from vapors is occurring frequently in the boreal forest area, and the frequency and spatial extent of the formation are such that they can be considered a significant source to the tropospheric aerosol load. Particle formation rates of boreal events were found to be of the order of $0.01\text{--}5\text{ cm}^{-3}\text{s}^{-1}$, while the nucleation rates of 1 nm particles can be a few orders of magnitude higher, depending on the growth rate of particles below the detection limit of the measuring instrument. These formation rates are higher than predicted by classical nucleation theory of a binary water-sulfuric acid system (Kulmala et al., 1998), so this mechanism can be ruled out as a cluster source. Cluster activation or possibly kinetic nucleation of sulfuric acid (Kulmala et al., 2006; Lushnikov and Kulmala, 1998), however, are possible candidates for the nucleation mechanism. The role of other mechanisms, such as ternary water-sulfuric acid-ammonia nucleation or ion-induced nucleation remains to be investigated.

The growth rates of over 3 nm sized particles were found to be of the order of a few nanometers per hour, which is a common value for particle formation in rural areas (Kulmala et al., 2004c). The vapor concentration needed to sustain such growth is of the order of $10^7\text{--}10^8\text{ cm}^{-3}$, approximately one order of magnitude higher than sulfuric acid concentrations found in the atmosphere. Therefore, one has to assume that other vapors, such as organics, have a key role in growing newborn particles to sizes where they can become climatically active.

Formation event occurrence shows a clear annual variation with peaks in summer and autumns. This variation is similar to the variation exhibited by the obtained formation rates of particles. The growth rate, on the other hand, reaches its highest values during summer. This difference in the annual behavior, and the fact that no coupling between the growth and formation process could be identified, suggest that these processes might be different ones, and that both are needed for a particle formation burst to be observed.

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