

REPORT SERIES IN AEROSOL SCIENCE
N:o 151 (2014)

**LONG-TERM TRENDS AND LARGE-SCALE SPATIAL VARIABILITY OF
NEW PARTICLE FORMATION IN CONTINENTAL BOUNDARY LAYER**

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Academic dissertation

*To be presented, with the permission of the Faculty of Science of
the University of Helsinki, for public criticism in Physicum auditorium E204,
Gustaf Hällströmin katu 2a, on May 27th, 2014, at 12 o'clock noon.*

Helsinki 2014

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ISBN 978-952-5822-94-6 (printed version)
ISSN 0784-3496
Helsinki 2014
Unigrafia Oy

ISBN 978-952-5822-95-3 (pdf version)
<http://ethesis.helsinki.fi/>
Helsinki 2014
Helsingin yliopiston verkkojulkaisut

Long-term trends and large-scale spatial variability of new particle formation in continental boundary layer

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University of Helsinki, 2014

Abstract

Atmospheric aerosol particles affect our lives in various ways. One of the largest sources of aerosols is their formation in the atmosphere via nucleation from precursor vapours. These new particle formation (NPF) events have been observed to occur globally. The climatic effects of secondary aerosol are among the largest uncertainties limiting our scientific understanding of future and past climate changes. Characterizing the processes controlling the formation and growth of aerosols is crucial in order to estimate their effects on air quality, human health, and eventually, global climate.

The work presented in this thesis is based on measurements of aerosol formation under various conditions at 12 field sites across Europe, as well as long-term, comprehensive observations of aerosol properties at a boreal forest site in Finland. The results show that new particle formation is a frequent phenomenon at both clean background and polluted Central European sites. On the sites where measurements of both charged and neutral particles were performed, the total particle formation rates at 2 nm size varied in the range $0.9\text{--}32\text{ cm}^{-3}\text{ s}^{-1}$, whereas the charged particle formation rates were on the order of $0.05\text{--}0.16\text{ cm}^{-3}\text{ s}^{-1}$. Further evidence of the minor role of ions in continental boundary layer particle formation was obtained from the long-term observations, which did not show any connection between variation in the galactic-cosmic-ray-induced ionization and new particle formation. In confirmation of earlier observations, sulphuric acid was found to be closely connected to particle formation rates, but to have only a minor role in their subsequent growth. At the boreal forest site, a long-term decreasing trend in the concentrations of sulphuric acid and aerosol particles was observed, whereas the particle formation and growth rates had a slight increasing trend. Finally, a proxy for the global distribution of nucleation-mode particle concentrations based on satellite data was developed.

The results of this thesis give tools to quantify the source rate of atmospheric aerosol from new particle formation in various environments. The characteristics of particle formation determined in this thesis can be used in global models to evaluate the climatic effects of NPF events. The results support previous observations of atmospheric NPF, and give significant new results in particular about the role of ions in NPF in various environments, and the long-term changes in NPF.

Keywords: atmospheric aerosols, particle formation, particle growth, ion-induced nucleation, sulphuric acid, long-term trends

Acknowledgements

The research presented in this thesis was carried out at the Department of Physics of the University of Helsinki. The head of the department until 2013, Prof. Juhani Keinonen is acknowledged for providing me with work facilities. I thank the head of the Division of Atmospheric Sciences and my supervisor Prof. Markku Kulmala for all the possibilities to participate in various interesting projects over the years. Working at the division and in your group has truly been a privilege and a front-row seat to top-level research on atmospheric aerosols. Prof. Veli-Matti Kerminen is acknowledged for always finding time for my questions and giving excellent comments, especially while I was finishing this thesis. I thank Docs. Miikka Dal Maso and Ilona Riipinen for their guidance and help during the first years of my research career. Professor Markus Olin and Doc. Harri Kokkola are acknowledged for reviewing this thesis, and Dr. Eimear Dunne for her prompt proof-reading of the final version of the text.

This thesis would not have been possible without the co-operation and help of all my co-authors. Particularly I would like to thank Dr. Hanna Manninen for the excellent scientific collaboration and all your support, Dr. Taina Yli-Juuti for being the best officemate ever and sharing your knowledge on theoretical aerosol questions, and Dr. Pauli Paasonen for many insightful discussions on aerosol phenomenology. The researchers and technicians who have been installing, maintaining and repairing the instruments at the SMEAR II station and in various field campaigns are gratefully acknowledged. I thank all my colleagues at the Division of Atmospheric Sciences for creating a welcoming and inspiring work environment. Especially I would like to thank Ale, Arnaud, Daniela, Hanna, Katrianne, Maija, Misha, Sigi, Simon, Stéphanie, and Taina for being my friends and sharing your time with me also outside the workplace.

Finally, I would like to thank my mum and dad for all your love, care, encouragement and support.

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List of publications

This thesis consists of an introductory review followed by 7 research publications. In the introduction these publications are referred to by the following numbers. Papers II and VII are reprinted with permission from the publisher, and all other papers under the Creative Commons Attribution License.

- I Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10 nm particle growth by vapor condensation - effects of vapor molecule size and particle thermal speed. *Atmos. Chem. Phys.* 10, 9773–9779, 2010.
- II Nieminen, T., Manninen, H. E., Sihto, S.-L., Yli-Juuti, T., Mauldin, R. L., Petäjä, T., Riipinen, I., Kerminen, V.-M., and Kulmala, M.: Connection of Sulfuric Acid to Atmospheric Nucleation in Boreal Forest. *Environ. Sci. Technol.* 43, 4715–4721, 2009.
- III Manninen, H. E., Nieminen, T., Asmi, E., Gagné, S., Häkkinen, S., Lehtipalo, K., Aalto, P., Vana, M., Mirme, A., Mirme, S., Hörrak, U., Plass-Dülmer, C., Stange, G., Kiss, G., Hoffer, A., Töro, N., Moerman, M., Henzing, B., de Leeuw, G., Brinkenberg, M., Kouvarakis, G. N., Bougiatioti, A., Mihalopoulos, N., O’Dowd, C., Ceburnis, D., Arneth, A., Svenningsson, B., Swietlicki, E., Tarozzi, L., Decesari, S., Facchini, M. C., Birmili, W., Sonntag, A., Wiedensohler, A., Boulon, J., Sellegri, K., Laj, P., Gysel, M., Bukowiecki, N., Weingartner, E., Wehrle, G., Laaksonen, A., Hamed, A., Joutsensaari, J., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: EUCAARI ion spectrometer measurements at 12 European sites - analysis of new particle formation events. *Atmos. Chem. Phys.* 10, 7907–7927, 2010.
- IV Nieminen, T., Paasonen, P., Manninen, H. E., Sellegri, K., Kerminen, V.-M., and Kulmala, M.: Parameterization of ion-induced nucleation rates based on ambient observations. *Atmos. Chem. Phys.* 11, 3393–3402, 2011.
- V Kulmala, M., Riipinen, I., Nieminen, T., Hulkkonen, M., Sogacheva, L., Manninen, H. E., Paasonen, P., Petäjä, T., Dal Maso, M., Aalto, P. P., Viljanen, A., Usoskin, I., Vainio, R., Mirme, S., Mirme, A., Minikin, A., Petzold, A., Hörrak, U., Plass-Dülmer, C., Birmili, W., and Kerminen, V.-M.: Atmospheric data over a solar cycle: no connection between galactic cosmic rays and new particle formation. *Atmos. Chem. Phys.* 10, 1885–1898, 2010.
- VI Kulmala, M., Arola, A., Nieminen, T., Riuttanen, L., Sogacheva, L., de Leeuw, G., Kerminen, V.-M., Lehtinen, K. E. J.: The first estimates of global nucleation mode aerosol concentrations based on satellite measurements. *Atmos. Chem. Phys.* 11, 10791–10801, 2011.
- VII Nieminen, T., Asmi, A., Dal Maso, M., Aalto, P. P., Keronen, P., Petäjä, T., Kulmala, M., and Kerminen, V.-M.: Trends in atmospheric new particle formation: 16 years of observations in boreal forest environment. *Boreal Env. Res.*, in press, 2014.

1 Introduction

The atmosphere of our planet is a complex mixture of several gases, together with liquid and solid particles suspended in the gas. This mixture is called an aerosol. Aerosol particles can be directly emitted into the atmosphere as primary particles (for example sea salt or dust), or they can be secondary particles formed in the atmosphere by gas-to-particle phase nucleation of vapours. Analysis of this secondary new particle formation (NPF) is the focus of the work presented in this thesis. Typical primary atmospheric aerosol particles include dust, soot and smoke particles, airborne pollen, fungi and bacteria, sea spray and cloud droplets. The size of aerosol particles in the atmosphere ranges from molecular clusters with one-nanometre diameters up to cloud droplets with diameters of some hundreds of micrometres. Particle concentrations vary from 10–100 cm⁻³ or even less in clean background environments up to more than 10⁵–10⁶ cm⁻³ in heavily polluted urban areas (e.g. Koponen et al., 2003; Mönkkönen et al., 2005). Several dynamical processes, including condensation and evaporation, coagulation and deposition, as well as cloud processing, affect particle concentrations and their composition, and as a consequence, the typical atmospheric aerosol lifetime in the troposphere (the lowest part of the atmosphere) ranges from hours to a couple of weeks (Seinfeld and Pandis, 2006).

Atmospheric aerosol particles have diverse effects on air quality, human health, and the global climate. The first two of these effects are very much connected to each other, because in densely populated urban areas, exposure to high particulate matter concentrations has been shown to cause health problems such as respiratory effects and cardiovascular diseases (Brunekreef and Holgate, 2002; Nel, 2005), and even to increase mortality rates (Samet et al., 2000). From a health perspective, the most harmful particles seem to be ultra-fine particles (smaller than 100 nm in diameter), as they can deposit in the human respiratory system or even enter into the circulatory system (Nel et al., 2005). On a regional scale, aerosol particles also affect visibility, with the most extreme case of this being smog episodes in large megacities in Asia (e.g. Wang et al., 2013).

From a global and regional perspective, aerosol particles influence the radiation balance of the Earth. Compared to greenhouse gases, aerosol particles are short-lived climate forcers, as they only stay in the atmosphere for periods of a few weeks, whereas the lifetime of (for example) carbon dioxide in the atmosphere is several decades (Seinfeld and Pandis, 2006). Aerosols directly affect the global climate in two ways: firstly, by scattering sunlight back to space and thereby cooling the climate; and secondly, by absorbing solar radiation and thus heating the atmosphere (especially soot particles; Skeie et al., 2011). Soot particles can also decrease the albedo of snow and ice by depositing on them (Hansen and Nazarenko, 2004). The

indirect effect of aerosol particles on climate occurs via their role in cloud formation as cloud condensation nuclei (CCN; Twomey, 1991). Without aerosol particles, no cloud droplets would form under atmospheric conditions. The number and properties of aerosol particles that are able to act as CCN affect both the albedo of the clouds (Twomey, 1974) and their lifetime (Albrecht, 1989). The more CCN there are, the smaller the cloud droplets will be, and as a result the clouds will be brighter and longer-lived (Andreae and Rosenfeld, 2008). This leads to a larger fraction of solar radiation being reflected back to space and has a net cooling effect on the climate. In the latest report from the Intergovernmental Panel on Climate Change (IPCC, 2013), it is estimated that these indirect aerosol effects cause a significant cooling effect on the global climate, and may therefore cancel out some of the global warming caused by the long-lived greenhouse gases. However, the uncertainty due to the effects of aerosol particles on global climate is estimated to be large, and the level of the scientific understanding currently still low (IPCC, 2013).

Atmospheric new particle formation – the formation and growth of secondary aerosol particles by nucleation from trace gases – has been observed around the world in various environments in both the planetary boundary layer and in the free troposphere (see Kulmala et al., 2004a and references therein). NPF has been shown to increase CCN concentrations regionally (Kerminen et al., 2012), and it is estimated that several tens of per cent of the global CCN concentrations could originate from atmospheric NPF (Spracklen et al., 2008; Merikanto et al., 2009; Yu and Luo, 2009). Despite extensive research during the past two decades or so, the exact mechanisms by which atmospheric NPF takes place in different environments in the continental boundary layer are still unclear in many respects. In particular, it is essential to understand the processes taking place during the initial steps of particle formation and growth in order to be able to include NPF accurately in regional and global climate models.

The research presented in this thesis aims to increase our understanding of atmospheric NPF, its variation between different environments, the role of ions in NPF, and the possible existence of long-term trends or changes. The work utilizes field observations of NPF on a continental scale, as well as a decade-long time series of aerosol and trace-gas concentrations measured in a boreal forest. Global estimates of the magnitude of NPF over continental areas are made utilizing satellite observations.

The main objectives of the work are

- 1) to quantify the connection between sulphuric acid and the formation and growth of nucleation-mode particles in a boreal forest environment;
- 2) to investigate and quantify possible long-term trends in several quantities related to atmospheric new particle formation, based on observations in a boreal forest

environment;

- 3) to characterize the spatial and temporal variation of new particle formation and the contribution of ion-induced nucleation on a continental scale based on field observations;
- 4) to find out whether there is any connection between changes in cosmic-ray-induced ionization and new particle formation in boreal forest environment;
- 5) to develop proxy variables for estimating the distribution of nucleation-mode particles on a global scale.

The following section describes the main dynamic processes affecting the atmospheric aerosol size distribution. Section 3 introduces the instrumentation and data-analysis methods that have been used in this thesis. Sections 4 and 5 give a review the papers and the main results, with references to relevant research that has been done after the publication of the original papers. Finally, Section 6 summarizes the main conclusions of this thesis research.

2 Dynamics of atmospheric aerosols

Under typical atmospheric conditions, the distribution of aerosol number concentration as a function of particle size can be represented as a sum of 2–4 log-normally distributed modes (Raes et al., 2000). One mode is formed by particles larger than 1 μm in diameter. These are called coarse-mode particles. Sources of coarse-mode particles include sea salt particles, wind-blown dust, and various biogenic particles such as pollen, fungi and bacteria. Although their number concentration is typically very small, the coarse-mode particles contribute most to the total aerosol mass concentration. The majority of aerosol particles by number consists of particles smaller than 1 μm in diameter. These fine particles are further divided into nucleation-, Aitken-, and accumulation-mode particles. Particles in the Aitken (25–100 nm) and accumulation modes (100 nm–1 μm) are always present in the atmosphere due to slow removal processes in these size ranges, especially for accumulation-mode particles. Nucleation-mode particles (smaller than 25 nm) are present during atmospheric new-particle-formation events or in the vicinity of other sources, such as various antropogenic combustion processes or traffic especially in urban areas. Aerosol particles in the atmosphere interact constantly with their environment and with other particles, and as a result their concentrations, size, and chemical composition are continuously changing.

Nucleation is, by definition, the first step in first-order phase transition phenomena. When the term new particle formation (NPF) is used in this thesis, it refers to a transition from the gas phase to either liquid or solid phase, i.e. nucleation of liquid or solid clusters and particles from gas-phase precursors. Nucleation can occur either homogeneously or heterogeneously. In homogeneous nucleation, one or more nucleating vapours form a critical cluster, the size of which depends on the prevailing conditions – the concentration of the vapours, ambient temperature and pressure – which determine the saturation ratio of the nucleating vapour (Seinfeld and Pandis, 2006). Clusters smaller than the critical size are not thermodynamically stable and will tend to evaporate, whereas larger clusters continue to grow. In the case of heterogeneous nucleation the critical cluster is formed around a pre-existing particle or on a surface, and thus heterogeneous nucleation does not increase the number concentration of particles. Heterogeneous nucleation is more energetically favourable compared to homogeneous nucleation and will therefore happen at lower vapour supersaturation. A special case of heterogeneous nucleation is ion-induced nucleation, where the critical cluster is formed around a charged seed particle. The electrostatic interaction between the vapour molecules and the charged cluster reduces the evaporation rate from the cluster. Therefore, if ions are present, ion-induced nucleation will occur first, followed by heterogeneous nucleation on neutral surfaces, and finally, when the vapour supersaturation is high enough, it will nucleate

homogeneously (Vehkamäki and Riipinen, 2012). In the atmosphere, ion-induced nucleation is limited by the ion-pair production rate, which in the boreal forest environment is not high enough to explain the observed particle formation rates (Laakso et al., 2004).

Based on numerous field observations it is very likely that sulphuric acid participates in the nucleation of atmospheric particles in most continental environments (e.g. Weber et al., 1995, Fiedler et al., 2005; Riipinen et al., 2007; Kuang et al., 2008; **Paper II**). However, at the typical sulphuric acid concentrations observed in the continental boundary layer (10^6 – 10^7 cm⁻³ daytime maxima in the rural boreal forest; Petäjä et al., 2009), binary nucleation of sulphuric acid and water is not able to explain the observed particle formation rates. In recent laboratory experiments, it has been shown that ammonia and particularly amines and oxidized organics can enhance the sulphuric acid–water nucleation rates to levels comparable to those observed in the atmosphere (Kirkby et al., 2011; Almeida et al., 2013; Ehn et al., 2014).

Condensation is the main process by which aerosol particles grow under most atmospheric conditions. It is driven by the difference of vapour concentration at the particle surface $c_{v,s}$ and far away from the particle c_v (Seinfeld and Pandis, 2006). The mass flux to the particle phase (increase rate of the particle mass m_p) is given by (**Paper I**)

$$\frac{dm_p}{dt} = 2\pi m_v (d_p + d_v) (D_p + D_v) \beta_m (c_v - c_{v,s}) \quad (1)$$

as a function of the vapour molecule mass m_v , diameters of the particle d_p and vapour molecule d_v , diffusivities of the particle D_p and vapour molecule D_v . The Fuchs-Sutugin transition-regime correction factor β_m accounts for the difference in the condensation flux at large and small particle sizes (Fuchs and Sutugin, 1970). If the ambient vapour concentration is lower than the concentration at the particle surface then *evaporation* from the particle phase into gas phase occurs. Above a curved surface the equilibrium vapour pressure is increased compared to a flat surface case, because of the reduced binding between surface molecules on the curved surface (Seinfeld and Pandis, 2006). This Kelvin effect limits the condensation of most atmospheric vapours onto the smallest particles, which have diameters of only a few nanometres. One notable exception in this regard is sulphuric acid, which has a very low saturation vapour pressure, often approximated to be zero (Marti et al., 1997).

Coagulation refers to a collision between two aerosol particles, resulting in their sticking together to form a larger particle or agglomerate, thus reducing the particle number concentration. Gravitational settling, turbulence and in particular their Brownian motion relative to each other cause atmospheric particles to come into contact with each other (Seinfeld and Pandis, 2006). Coagulation is most efficient between particles with a large difference in their sizes, because the larger particles

efficiently collect the faster-moving small particles. For nucleation-mode particles, coagulation is the main sink process.

Dry deposition removes particles from the atmosphere when they come into contact with and are attached to macroscopic surfaces such as walls, tree needles, and leaves. The efficiency of dry deposition depends on the strength of atmospheric turbulence, the size of the particle and the properties of the surface with which the particle comes into contact. For the largest aerosol particles, over 10 μm in diameter, gravitational settling onto surfaces becomes important. In *wet deposition* particles are scavenged from the air by falling rain droplets, snow flakes or ice crystals. Aerosol particles can also be removed from the air by being activated to cloud droplets and precipitating, or in clouds by colliding with cloud droplets. Based on observations at a boreal forest site, wet deposition is more efficient particle removal mechanism than dry deposition for all particle sizes, and for the smallest particles below 10 nm coagulation is the main removal mechanism (Laakso et al., 2003; Lyubovtseva et al., 2005; Kyrö et al., 2009). The ratio between the particles' condensational growth rate and the coagulation scavenging during their growth determines how large a fraction of nucleated particles will eventually reach sizes of climatic importance (around 50–100 nm diameter depending on the particle composition).

Aerosol measurements considered in this thesis have been performed mainly within the *atmospheric boundary layer*, which is the lowest part of the troposphere. Properties inside this layer are influenced by changes at the Earth's surface on time scales of a few hours or less. The height of the boundary layer varies from tens of meters to a few kilometres from the surface depending on atmospheric stability and properties of the surface. Wind shear and convection caused by solar heating of the surface during daytime produce turbulence in the air inside the boundary layer. This results in vertical mixing of aerosols and gases throughout the boundary layer (Stull, 1988).

3 Instrumentation and data-analysis methods

3.1 Measurements of charged and neutral particle size distributions

Studying the first steps of atmospheric new particle formation requires instruments which are able to detect particles of 1–2 nm in diameter. In this thesis, aerosol number concentration size distribution data is obtained using four different types of instruments: Differential Mobility Particle Sizer (DMPS; **Papers V, VI and VII**), Balanced Scanning Mobility Analyzer (BSMA; **Paper III**), Air Ion Spectrometer (AIS; **Papers III and IV**) and Neutral cluster and Air Ion Spectrometer (NAIS; **Papers II, III, IV and V**).

The DMPS measures the number-concentration size distribution of the total aerosol population, including both the charged and neutral particles. For a detailed description of a typical DMPS setup, see e.g. Aalto et al. (2001). In the DMPS, the sample air is first led through a dryer and then charged using a bipolar charger, which produces both negative and positive ions. Particles of a specific electrical mobility are selected using a Differential Mobility Analyzer (DMA). In a DMA, the particles move across an electric field which deflects their movement depending on their electrical mobility. Particles' charge and mass mobility determine their mobility, which can be converted to size. All particle sizes in this thesis are given as mobility equivalent diameters (Mäkelä et al., 1996). The number concentration of the size-selected particles is determined using a Condensation Particle Counter (CPC; the working principles of CPCs are described by e.g. McMurry, 2000). By varying the strength of the electric field in the DMA, particles of different mobilities can be selected making it possible to measure the full aerosol size distribution. The lower detection limit of DMPS systems is set by the detection efficiency of the CPC, which is typically 3 nm or larger. Therefore, they cannot be used to directly observe the initial steps of atmospheric particle formation.

The BSMA and AIS ion spectrometers are also based on DMAs used to classify particles according to their electrical mobility. The particle concentration is measured from the electric current carried by the particles to electrodes on the walls of the analyzers. The BSMA (Tammets, 2006) and AIS (Mirme et al., 2007) do not have chargers for the sample air and therefore measure only the naturally charged particles. The measurement size range of the BSMA is 0.8–7.5 nm, and that of the AIS is 0.8–42 nm. The NAIS, on the other hand, can also detect neutral particles, as the aerosol sample can be charged using a corona charger (Mirme and Mirme, 2013). The lowest detection limit of the NAIS for neutral particles is set by the requirement that it be possible to distinguish the charger ions produced by the corona charger from the charged particles in the sample air. Based on laboratory calibrations, the lower detection limit of NAIS is around 2 nm depending on the ambient conditions

(Manninen et al., 2011). Besides providing measurement data of particles smaller than the widely used DMPS setups, the NAIS is also useful in analyzing the ion-induced nucleation mechanism since it is able to measure both the charged and total particle number-concentration size distributions. This data was utilized in **Papers II, III, IV and V**.

During the last few years it has become possible to measure neutral particles in the sub-2 nm size range. CPCs using working fluids that have a low saturation vapour pressure and high surface tension can detect particles down to sizes around 1.5 nm (Iida et al., 2009). One of these instruments is the Particle Size Magnifier (PSM; Vanhanen et al., 2011) which uses diethylene glycol as the working fluid. PSM has already been utilized in several laboratory and field measurements, often together with the ion spectrometers (e.g. Lehtipalo et al., 2010; 2011; Almeida et al., 2013).

3.2 Analysis of atmospheric new particle formation

Analysing new particle formation events from atmospheric aerosol measurements typically involves several steps. First, the data is visualised by plotting the particle number size distributions as a function of time. From these plots, the NPF events are identified visually. The guidelines for the NPF event classification which were used in this thesis are presented by Dal Maso et al. (2005) and Yli-Juuti et al. (2011). The main focus of this work was to identify regional-scale NPF events. This means that formation of new particles and their subsequent growth can be followed from stationary measurements over a period of several hours. The decision-making portion of the NPF event identification is usually performed by a small group of researchers in order to reduce the subjectivity of the event classification process. Typically the classification of NPF occurrence is made on a daily basis because most NPF events occur at daytime in a time window of a few hours around noon. In this classification, days are divided into three categories: event (days with clear NPF), non-event (days without NPF) and undefined (days when NPF might have occurred).

An example of a typical NPF event is seen in Fig. 1. The event was observed at the University of Helsinki SMEAR II field station in Hyytiälä, Finland (Hari and Kulmala, 2005). In the morning hours, the pre-existing particle concentrations decrease due to efficient mixing into the growing boundary layer. This reduces the sink for smaller particles. During a few hours around noon, particles below 10 nm are detected by DMPS and NAIS, and the ion measurements by NAIS show the particle formation starting from the cluster ion pool below 2 nm. The total concentration of particles larger than 1.6 nm measured by PSM starts increasing about one hour before corresponding increase in the larger than 3-nm particle concentration detected by DMPS (Fig 1. bottom panel).

Calculating the rate at which particles are formed requires knowledge of the particle

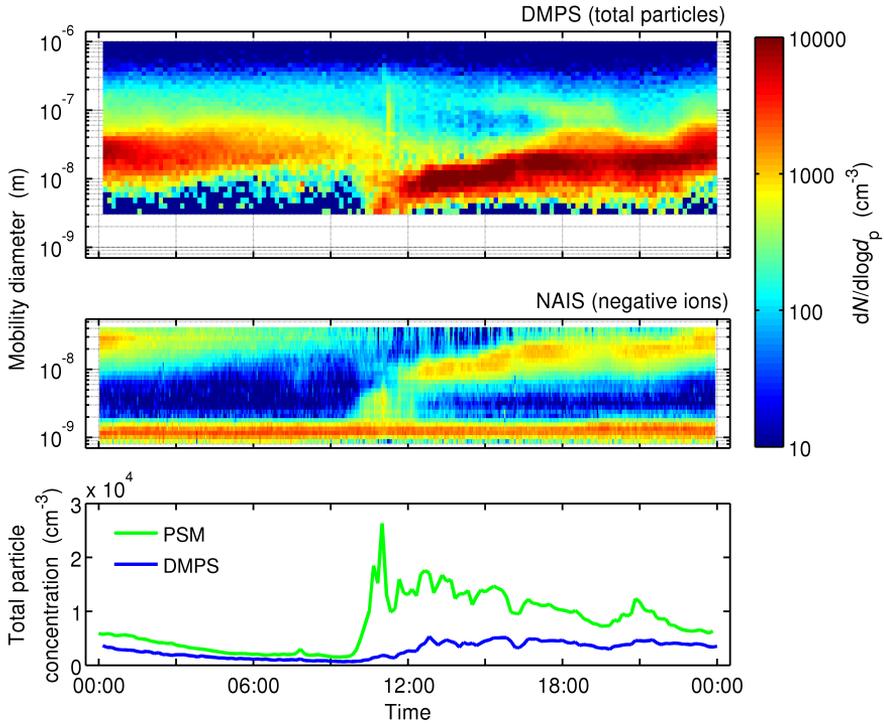


Figure 1. Example of a new particle formation event observed in Hyytiälä on March 26, 2011. The first and second panels from the top show the total particle size distributions measured by DMPS and the negative ion size distributions by NAIS, respectively. The total particle number concentration measured by PSM (particles larger than 1.6 nm) and DMPS (particles larger than 3 nm) is presented in the bottom panel.

concentration in a certain size range. Using the number concentration size distribution data measured with instruments described in Section 3.1, the concentration of particles with diameters between d_{p1} and d_{p2} can be calculated. The balance equation for the number concentration $N_{dp1-dp2}$ can be written as

$$\frac{d N_{dp1-dp2}}{dt} = J_{dp1} - F_{coag} - F_{growth}. \quad (2)$$

Here, J_{dp1} represents the formation rate of particles into the size range from d_{p1} to d_{p2} . The coagulation flux F_{coag} is a loss term representing the scavenging of the particles in the considered size range by collisions with all larger particles. It can be expressed using the coagulation sink $CoagS$ which is calculated from the measured aerosol number concentration size distributions (Kulmala et al., 2012). The condensational growth flux out of the size range $d_{p1}-d_{p2}$ is

$$F_{\text{growth}} = \frac{\text{GR}}{\Delta d_p} N_{\text{dp1-dp2}} \quad (3)$$

where Δd_p is the width of the size range and GR is the growth rate over the size range. By solving J_{dp1} from Eq. 2 we obtain

$$J_{\text{dp1}} = \frac{dN_{\text{dp1-dp2}}}{dt} + \text{CoagS}_{\text{dp1}} \cdot N_{\text{dp1-dp2}} + \frac{\text{GR}}{\Delta d_p} N_{\text{dp1-dp2}}. \quad (4)$$

When calculating the formation rate of charged particles only, the ion-ion recombination and diffusion charging of neutral particles need to be taken into account. In this case the formation rate can be written as

$$J_{\text{dp1}}^{\pm} = \frac{dN_{\text{dp1-dp2}}^{\pm}}{dt} + \text{CoagS}_{\text{dp1}} \cdot N_{\text{dp1-dp2}}^{\pm} + \frac{\text{GR}}{\Delta d_p} + \alpha \cdot N_{\text{dp1-dp2}}^{\pm} N_{<\text{dp2}}^{\mp} - \beta \cdot N_{\text{dp1-dp2}}^{\pm} N_{<\text{dp1}} \quad (5)$$

where the superscripts + and – refer to positively and negatively charged particles, respectively. A typical estimate for the ion-ion recombination coefficient α of 2–3 nm ions is $1.6 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$, and for the ion-neutral attachment coefficient β $10^{-8} \text{ cm}^3 \text{ s}^{-1}$ (Tammet and Kulmala, 2005).

The contribution of ions to the observed particle formation rates can be assessed by writing the total particle formation rate as a sum of the neutral and charged formation rates and recombination rate,

$$J_{\text{tot}} = J_{\text{neutr}} + J_{\text{ion}} + J_{\text{rec}} \quad (6)$$

where J_{rec} refers to the recombination rate of ions producing stable neutral clusters, and J_{neutr} and $J_{\text{ion}} = J^- + J^+$ are the neutral and ion formation rates, respectively. Equation 6 is typically referred to as ion-mediated nucleation (IMN; Yu, 2006). If the contribution of the recombination product formation is not included, then the corresponding particle formation rate is typically referred to as ion-induced nucleation (IIN). Ion-induced nucleation is a special case of heterogeneous nucleation, in which nucleation takes place around a charged particle. The fractions of ion-mediated nucleation and ion-induced nucleation from the total particle formation rate can be expressed as

$$f_{\text{IMN}} = \frac{J^- + J^+ + J_{\text{rec}}}{J_{\text{tot}}}, \quad f_{\text{IIN}} = \frac{J^- + J^+}{J_{\text{tot}}}. \quad (7a), (7b)$$

In this thesis, the growth rates GR of the particles were determined from particle size distribution data with two different methods. In the case of particle size distributions measured with the DMPS, log-normal modes were fitted to the size distributions using an automatic algorithm presented by Hussein et al. (2005). The growth of the nucleation mode is determined by following the time evolution of the geometric mean of the fitted nucleation mode. Atmospheric aerosol measurements are almost always

performed at a fixed measurement location, which means that the air masses that are sampled are continuously changing due to advection. This imposes some limitations on the conditions in which particle growth rates can be reliably determined from atmospheric measurements. Firstly, there can not be any sudden changes in the sampled air masses, because this is typically observed as a sharp change in the aerosol size distribution and complicates the interpretation of whether the observed changes in particle size are due to growth of the particles or the fact that particles of different origin are sampled at different times. The assumption in the case of regional-scale NPF events is that aerosol formation occurs rather homogeneously over a geographically large area. This assumption is supported by the fact that the growth of the newly formed particles can typically be followed for several hours in observations from stationary measurement sites.

The particle growth rates determined from size distributions can be linked to condensable vapour concentrations. In **Paper I** it was shown that when analyzing the condensation growth of sub-10 nm particles the size of the vapour molecules and the thermal speed of the particles need to be taken into account. The growth rate GR of the particle diameter caused by vapour concentration C_v can be expressed as

$$\text{GR} = \frac{\gamma}{2\rho_v} \left(1 + \frac{d_v}{d_p}\right)^2 \left(1 + \frac{m_v}{m_p}\right)^{1/2} \left(\frac{8kTm_v}{\pi}\right)^{1/2} C_v, \quad \gamma = \frac{4}{3} \text{Kn}\beta_m. \quad (8)$$

Here ρ_v is vapour density in the condensed phase, m_p and m_v are the masses of the particle and vapour molecules respectively. The parameter γ takes into account the differences in vapour condensation flux onto the particle in different size regimes, and it depends on the Knudsen number Kn and transition regime correction factor β_m (Seinfeld and Pandis, 2006; **Paper I**). The particle growth rate as function of particle size is shown in Fig. 2 for two different vapours. The enhanced growth of sub-10 nm particles is clearly visible. It should be noted that Eq. 8 assumes a negligible saturation vapour pressure for the condensing vapour. If this is not the case, GRs will decrease with particle size due to the Kelvin effect's increasing of the equilibrium vapour pressure over the particle surface (compare with Eq. 1). For particles smaller than 10 nm Eq. 8 can be simplified and integrated over the particle size range from d_{p0} to d_{p1} to obtain the vapour concentration required to grow the particles over this size range in the certain time Δt (**Paper I**):

$$C_v = \frac{2\rho_v d_v}{\alpha_m m_v \Delta t} \sqrt{\frac{\pi m_v}{8kT}} \left[\frac{2x_1+1}{x_1(x_1+1)} - \frac{2x_0+1}{x_0(x_0+1)} + 2 \ln \left(\frac{x_1(x_0+1)}{x_0(x_1+1)} \right) \right]. \quad (9)$$

Here $x_0=d_v/d_{p0}$ and $x_1=d_v/d_{p1}$ are the ratios of the sizes of the vapour molecule and the particle at the low and high ends of the size bin, and α_m is the mass accommodation coefficient (often assumed to be unity). Earlier, Kulmala (1988) derived an equation for the vapour concentration required for a certain particle growth rate. Compared to

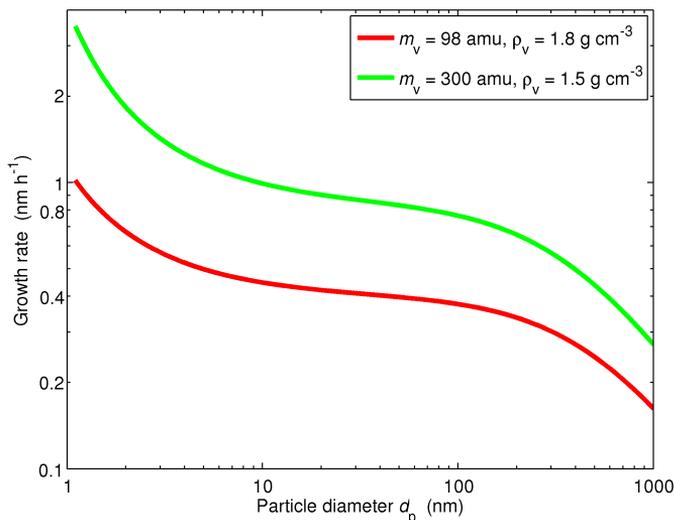


Figure 2. Growth rate as a function of particle diameter calculated according to Equation 8 from condensation of a vapour with gas-phase concentration of 10^7 cm⁻³. The red line shows the GR from condensation of pure sulphuric acid, and the green line from a vapour with molecular properties estimated to be typical for oxidized organic compounds in boreal forest environment (Ehn et al., 2014).

their approach, the result from Equation 8 shows that in the sub-10 nm size range, the necessary vapour concentration is about 1.5 times less than that calculated using the approach of Kulmala (1988). This method of calculating vapour concentrations was used in the study of Paasonen et al. (2010) to obtain the concentration of low-volatility oxidized organic compounds that is sufficient to explain observed particle growth rates when taken in combination with sulphuric acid vapour.

3.3 Proxy variables

A proxy variable (sometimes also called a proximity measure) is a variable that is used to predict the value of an unobservable quantity of interest. One typical example of a proxy is the estimated value of atmospheric sulphuric acid concentration via measurements of sulphur dioxide, UV-B radiation and condensation sink (Petäjä et al., 2009). In a steady state, the concentration is given by the ratio of the production and sink terms. In the atmosphere, sulphuric acid is mainly produced via oxidation of SO₂ by OH radicals, and the OH concentration can be approximated by the UV-B intensity (Rohrer and Berresheim, 2006; Petäjä et al., 2009). The sink term is due to condensation onto pre-existing particles as described by the condensation sink CS. Thus, the proxy concentration for H₂SO₄ is

$$[\text{H}_2\text{SO}_4]_{\text{proxy}} = k \frac{[\text{SO}_2] \cdot \text{UVB}}{\text{CS}} \quad (10)$$

where the scaling coefficient k needs to be evaluated from a comparison of the proxy to measured concentrations. In this thesis proxies were also used to estimate the concentrations of oxidation products of volatile organic compounds (**Paper VII**) as well as the global distribution of nucleation-mode particle concentrations (**Paper VI**).

3.4 Trend analysis

Several statistical methods have been developed for detecting and estimating trends in environmental data-series. In **Paper VII**, we calculated linear trends by fitting a linear model

$$\log_{10}(y) = A \cdot t + B \quad (11)$$

to the datapoints of variable y as a function of time t . Because the model of Eq. 11 uses logarithmic values of the datapoints, the slope A is the relative trend (in units of % per year) of the property in question. Relative trends enable direct comparison of the trends determined from different stations. The use of logarithmic values in Eq. 11 is reasonable for determining trends of aerosol and trace gas concentrations, since these are typically log-normally distributed.

The statistical significance of the calculated trends was estimated using a moving-block bootstrapping method (MBB; Mudelsee, 2010). In this method, blocks of residuals (differences of the datapoints from the fit) are randomly selected with replacement to construct a new data-series, which is then fitted again with Eq. 11 giving a new slope A' . This procedure is repeated a large number of times (1000 times using a block size of one year in the analyses of **Paper VII**) to obtain a distribution of fitted slope values A' . The confidence interval of the original fit was taken to be the 5th to 95th percentile range of this distribution. If the confidence interval does not contain zero (i.e. the 5th and 95th percentiles have the same sign), the sign of the actual trend A was regarded to be statistically significant.

4 Results

4.1 Connection between sulphuric acid and atmospheric particle formation

Sulphuric acid has been observed to be closely connected to atmospheric new particle formation already in studies from the 1990s (Weber et al., 1995), and later in many other investigations (e.g. Fiedler et al., 2005; Riipinen et al., 2007; Kuang et al., 2008; Paasonen et al., 2010; **Paper II**). In most atmospheric observations, the formation rate of particles correlates with sulphuric acid concentration with a power between 1 and 2. Theoretically, a direct dependence can be understood as an activation-type nucleation (Kulmala et al., 2006),

$$J_{\text{act}} = A[\text{H}_2\text{SO}_4]. \quad (12)$$

On the other hand, if the particle formation rate correlates with sulphuric acid to power of 2,

$$J_{\text{kin}} = K[\text{H}_2\text{SO}_4]^2, \quad (13)$$

the nucleation can be described as the kinetic nucleation of two sulphuric acid molecules or clusters containing sulphuric acid (McMurry and Friedlander, 1979). Larger exponent values of three or even higher have also been reported, especially from polluted environments where the coagulation scavenging of newly formed particles is efficient (Wang et al., 2011). It should be kept in mind, however, that in many atmospheric studies, particle formation has been observed at sizes larger than those where the actual nucleation occurs, and this has been shown to affect the observed correlations (Sipilä et al., 2010). Therefore, the comparisons of formation rates with sulphuric acid concentrations using Equations 12 and 13 do not necessarily imply that the actual nucleation mechanism could be deduced from these correlations (Vehkamäki et al., 2012). In order to reduce the uncertainties related to processes occurring between the nucleation of particles and their observation at some larger size, measurements of sub-3 nm particle size distributions are needed. **Paper II** was the first study to correlate 2-nm particle formation rates with measured sulphuric acid concentrations. The Neutral cluster and Air Ion Spectrometer NAIS was used to detect the total particle concentration in the 2–3 nm size range. According to the recent results by Kulmala et al. (2013), this size range is already very close to the expected atmospheric nucleating particle size of 1.5 ± 0.3 nm. In the dataset consisting of 30 NPF events analysed in **Paper II**, the exponent values with respect to sulphuric acid varied between 1 and 2, and the overall dependence of the particle formation rates on sulphuric acid seemed to suggest activation type nucleation to occur more favourably than kinetic nucleation. After the publication of **Paper II**, advances in

condensation particle counting techniques have enabled the detection of clusters and particles smaller than 2 nm in diameter. The Particle Size Magnifier (PSM; Vanhanen et al., 2011) was used by Kulmala et al. (2013) to obtain formation rates of 1.5 nm particles. According to their results, the correlation of these formation rates with sulphuric acid concentration has a power dependence close to one with the power increasing when examining formation rates at larger particle sizes.

Measurements of atmospheric sulphuric acid concentrations are typically performed during dedicated campaigns lasting from a few weeks to couple of months. To gain more insight on the connection between sulphuric acid and particle formation, in **Paper VII**, formation rates of 3 nm particles determined from DMPS data were correlated with a proxy for the concentration of sulphuric acid over 16 years. The exponent dependence of particle formation rates was observed to have a clear temperature dependence, being close to 2 at the coldest temperatures and decreasing to about 1.6 with increasing temperature. The smaller exponent values in higher temperatures can be interpreted as an indication of vapours other than sulphuric acid having a larger contribution to the formation and initial growth of the particles.

The prefactors A and K (“nucleation coefficients”) in Eqs. 12 and 13 contain all the physical and chemical details of the nucleation mechanism. In the campaign study of **Paper II**, the fitted nucleation coefficient values were observed to vary by more than an order of magnitude, between $4.6 \cdot 10^{-8}$ – $2.1 \cdot 10^{-6} \text{ s}^{-1}$ for A and $1.9 \cdot 10^{-14}$ – $2.2 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for K . This is in line with earlier studies at the same measurement site, as well as similar correlation studies from sites in Central Europe (Sihto et al., 2006; Riipinen et al., 2007; Paasonen et al., 2009; Paasonen et al., 2010). In Heidelberg in particular, a site influenced by anthropogenic pollution, the nucleation coefficients have been reported to be one order of magnitude higher than in Hyytiälä, which is a rural background site (Riipinen et al., 2007). Trace gases such as ammonia and amines emitted by anthropogenic activities have been shown in laboratory experiments to already enhance nucleation rates at very low concentrations (Kirkby et al., 2011; Almeida et al., 2013). In **Paper VII**, the formation rate of 3 nm particles was found to vary up to three orders of magnitude as a function of temperature at a certain constant sulphuric acid concentration. This is probably not due to the increased temperature itself enhancing atmospheric nucleation, but is rather related to changes in emissions of biogenic volatile organic compounds (BVOC) with temperature. The highest temperatures correspond to summer time, when the emissions and also concentrations of BVOCs, especially monoterpenes, are at their highest in Hyytiälä (Hakola et al., 2012). The oxidation products of BVOCs are low-volatility vapours which can participate in both nucleation and the initial growth of the nucleated particles (Kulmala et al., 2013; Ehn et al., 2014). One more argument supporting the importance of oxidized organics to NPF is the observation that sulphuric acid concentration alone does not separate NPF days from non-NPF days very effectively.

On the other hand, a much better association is observed between NPF probability and the formation rate of 2-nm particles, and the product of proxy concentrations of both sulphuric acid and low-volatility oxidized organic vapours (Paasonen et al., 2010; **Paper VII**).

Nucleation-mode particle growth rates were observed in **Paper VII** to be negatively correlated with sulphuric acid proxy concentrations at the Hyytiälä SMEAR II site. On the other hand, the fraction of the growth rates explained by sulphuric acid condensation was clearly positively correlated with sulphuric acid. The median fraction of the contribution of sulphuric acid condensation to nucleation mode particle growth varied from 15% in wintertime to 1–2% in summertime. As with particle formation rates, the nucleation-mode particle growth rates increased with increasing temperature, reaching their highest values during the summer months. Both these facts – the minor role of sulphuric acid in growing the particles and the growth rate correlation with temperature – support the importance of BVOC oxidation products in the NPF in the boreal forest environment.

4.2 Observations of atmospheric particle formation around Europe

During the EUCAARI (European Integrated Project on Aerosol Cloud Climate and Air Quality Interactions; Kulmala et al., 2009) project, measurements of aerosol number size distributions were performed from March 2008 to April 2009 at 12 field sites around Europe (Figure 3; **Paper III**). These sites were located in a range of

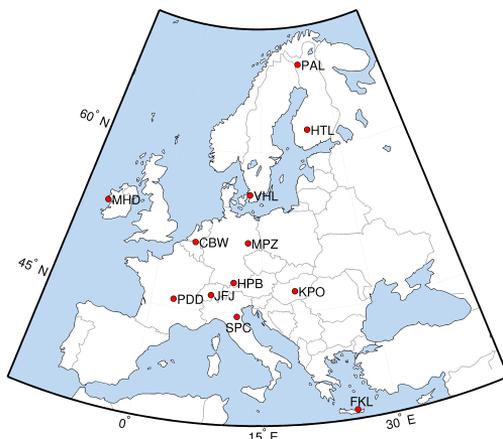


Figure 3. Measurement sites during the EUCAARI project (Paper III): Pallas (PAL; Finland), Hyytiälä (HTL; Finland), Vavihill (VHL; Sweden), Mace Head (MHD; Ireland), Cabauw (CBW; Netherlands), Melpitz (MPZ; Germany), Hohenpeissenberg (HPB; Germany), Puy de Dôme (PDD; France), Jungfrauoch (JFJ; Switzerland), K-Pusztá (KPO; Hungary), San Pietro Capofiume (SPC; Italy) and Finokalia (FKL; Greece).

different environments, from remote background to suburban and coastal locations. The altitude of the sites also varied from sea-level to mountain-top (partly in the free troposphere). In addition to a DMPS/SMPS instrument, an ion spectrometer (BSMA, AIS or NAIS) was installed at each site in order to observe also the contribution of charged particles to NPF.

The frequency of NPF occurrence varied quite markedly between the sites. At the Central-European, anthropogenically influenced sites, more than 50% of measurement days were NPF event days, whereas in Pallas in Northern Finland, NPF was observed on only 21% of the days. Overall, the most favourable time for NPF was late spring: the fraction of NPF days from all analysed days peaked in May and had a minimum in December-January (Fig. 4). The frequent NPF occurrence during spring-time at various continental sites has also been observed in many other studies (e.g. Birmili and Wiedensohler, 2000; Birmili et al., 2003; Dal Maso et al., 2007; Vana et al., 2008; Jaatinen et al., 2009; Yli-Juuti et al., 2009), supporting a general picture of the connection of atmospheric NPF to emissions of biogenic organic compounds and their photo-oxidation to low-volatility species in the presence of solar radiation. Only in Finokalia NPF was most frequent in wintertime. At Pallas, Hohenpeissenberg, Puy de Dôme and San Pietro Capofiume the seasonal distribution of NPF frequency was less clear than at the other sites. In a previous study, Paasonen et al. (2009) reported NPF days in Hohenpeissenberg to be most frequent in wintertime. This shows the importance of long-term measurements in order to observe year-to-year variations in NFP characteristics.

The regional-scale particle formation and growth events occurred almost entirely during the daytime with a typical starting time before noon. However, there was also evidence of night-time growth episodes of clusters. This was detected with the ion

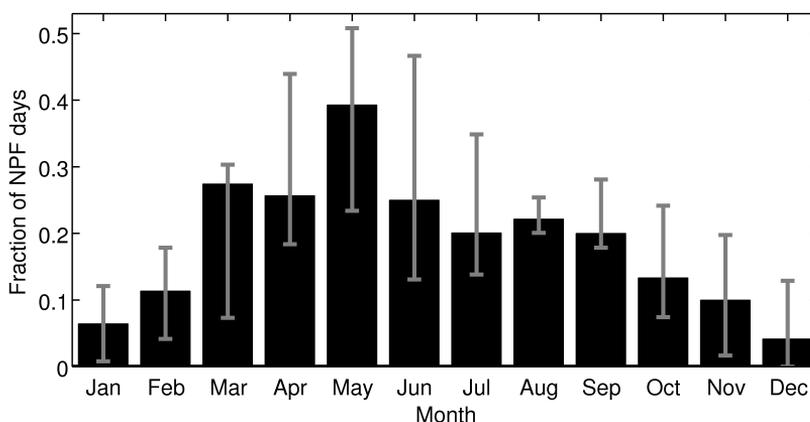


Figure 4. The median monthly fraction of NPF event days from all analysed days at the EUCAARI sites in 2008–2009 (adapted from **Paper III**). Errorbars show the 25th to 75th percentile range of the monthly NPF day fractions.

spectrometers (BSMA and NAIS) as growth of the cluster ions to sizes of 2–3 nm without further growth into larger sizes, and was therefore clearly different from the daytime NPF events where particle growth could be followed over several hours. Observations of similar night-time cluster ion growth events have been reported by Junninen et al. (2008), Suni et al. (2008) and Kalivitis et al. (2012).

In **Paper III** the formation rates of 2-nm ions were calculated at each of the 12 EUCAARI sites, and at 6 of the sites it was also possible to obtain the total formation rate (i.e. charged and neutral particle formation rate) from the NAIS data. The ion formation rates at 2 nm at all of the sites were very close to each other, with site-specific median ion formation rates varying in the range 0.05–0.16 cm⁻³ s⁻¹. This is similar to the ion formation rates observed at other locations, according to the review of atmospheric ion observations by Hirsikko et al. (2011). Total particle formation rates were markedly different from ion formation rates. Firstly, the total particle formation rates varied in much larger range between the sites than ion formation rates. Secondly, the total formation rates were on the order of 10–100 times higher than the corresponding ion formation rates at each of the sites where both ion and total particle measurements were available, meaning that the fraction of ion-induced nucleation at these sites was on average 1–10%. The site-specific median total formation rates were 0.9–32 cm⁻³ s⁻¹. More specifically, at the sites where the NPF events were most frequent and strongest (Melpitz, Mace Head and Cabauw), the ion-induced fraction from total formation rates was very low, on average a few per cent. A similar result has been obtained from the Hyytiälä site by Gagné et al. (2010) who reported based on ion-DMPS measurements that particle formation rates were higher in NPF events which had a smaller ion-induced nucleation fraction. Within the EUCAARI sites, the ion-induced nucleation had the largest significance (18–27% of the total formation rates) at the remote and mountainous sites of Pallas and Jungfraujoch where the lowest total formation rates were observed.

Growth rates of the newly formed particles were analyzed from the EUCAARI dataset in three size-ranges: 1.5–3 nm, 3–7 nm and 7–20 nm. The median particle growth rates calculated over all sites were 2.8 nm h⁻¹, 4.3 nm h⁻¹ and 5.4 nm h⁻¹, respectively (**Paper III**). These values are similar to the growth rates reported from many other locations as well (Kulmala et al., 2004a; Hirsikko et al., 2011), except for heavily polluted urban areas such as Mexico City where growth rates up to 15–40 nm h⁻¹ have been observed (Iida et al., 2008). The variation of growth rates between the sites was within a factor of 3, which is much smaller than the variation observed in total formation rates. In most of the sites, particle growth rates increased with increasing particle size, which is a common feature in studies from other locations as well (Suni et al., 2008; Manninen et al., 2009; Yli-Juuti et al., 2009, 2011). Exceptions to this trend were the Mace Head, Hohenpeissenberg and Pallas sites. At these sites, the initial growth rates of 1.5–3 nm particles were typically the highest. In

Mace Head, which is a coastal site, particle formation has been shown to be connected to the emissions of iodine vapours from “hot spots” of sea weed along the coast line (Mäkelä et al., 2002), creating NPF events which differ from typical regional-scale events (see Fig. 5 in **Paper III**). Hohenpeissenberg and Pallas, on the other hand, are situated on top of small mountains where the diurnal dynamics of the boundary layer might influence growth rate observations.

The observed size dependency of particle growth rates at the EUCAARI sites could be explained by different vapours contributing to the growth of different-sized particles. Since sulphuric acid is clearly connected to particle formation, its contribution to the initial growth is probably also significant. Later in the growth process, oxidized organic compounds with low enough saturation vapour pressures are also able to condense on the particles due to the decreasing Kelvin effect with increasing particle size or via the nano-Köhler mechanism if the condensing organic vapours are water soluble (Kulmala et al., 2004b; 2013). It should be kept in mind, however, that particles typically grow in the atmosphere over several hours, and therefore both the ambient conditions, and the chemical composition and concentrations of the condensable vapours might change during the growth.

The sink caused by pre-existing particles has been suggested as one factor which suppresses the occurrence of atmospheric NPF (Kerminen et al., 2004; Kuang et al., 2010). At the EUCAARI measurement sites analyzed in **Paper III**, the frequency or magnitude of NPF events did not correlate with the condensation sink. However, the condensation sink values were clearly lower during NPF days than on non-NPF days, except at Pallas and Jungfraujoch, where the overall level of the condensation sink was low (below 10^{-3} s^{-1}). Opposite to our findings, Jaatinen et al. (2009) observed slightly higher levels of condensation sink in Melpitz on NPF than on non-NPF days. This finding suggests that the NPF can be governed either by anthropogenic emissions of nucleating vapours (which is typically associated with higher levels of particulate matter), or by biogenic emissions in more remote areas, where the increased concentrations of pre-existing particles cause suppression of NPF. It should be kept in mind that the observation period covered in **Paper III** was one year, and there is probably year-to-year variation in the levels of particulate matter concentration due to e.g. the prevailing airmass transport patterns, which are influenced by large-scale meteorological conditions.

4.3 Contribution of ions to atmospheric particle formation

From an energetic point of view the presence of ions and charged clusters enhances nucleation and the initial growth of particles. In ion-induced nucleation, the new particle formation occurs around a charged particle, and the nucleation barrier is reduced compared to the corresponding case of nucleation onto a neutral particle or without a seed particle (e.g. Vehkamäki and Riipinen, 2012).

During the measurement campaign at Hyytiälä during spring 2007, a clear difference in the diurnal behaviour of the cluster ion concentrations was observed between NPF and non-NPF days (**Paper II**). Firstly, the average concentration of cluster ions with diameters smaller than 1.7 nm is higher on NPF days compared to non-NPF days. Secondly, during NPF days the concentrations of cluster ions have a minimum during daytime when NPF is typically observed, and at the same time the concentration of intermediate ions between 1.7–2.9 nm have a maximum in their concentrations. The increase of this intermediate ion concentration starts just after the increase in gas-phase sulphuric acid concentration, with a very short time delay (on average 10 minutes) (**Paper II**). Changes in the coagulation scavenging efficiency of cluster ions during the day do not explain the observed decrease in cluster ion concentrations on NPF days, since the coagulation sink typically has a minimum during active NPF periods (Kulmala et al., 2013). The NPF daytime cluster ion concentration decrease might be explained by more efficient mixing of the boundary layer, because NPF days are typically sunny, which causes turbulent convection (Lyubovtseva et al., 2005). After the publication of **Paper II**, developments in instrumentation have enabled the detection of neutral clusters in the sub-2 nm size range. The diurnal variation of the concentrations of neutral clusters smaller than 2 nm shows a clear daytime maximum on NPF days in all the size classes down to cluster sizes around 1.2 nm (Kulmala et al., 2013). This is a direct observation of the dominance of the neutral nucleation pathway compared to ion-induced or ion-mediated nucleation in the boreal forest boundary layer. The small fraction of ion-induced nucleation from the total nucleation rate may be sufficient to cause the decrease in cluster ion concentrations during NPF. Gagné et al. (2010) observed that in Hyytiälä the fraction of cluster ions removed during NPF days varies between 10–16%, which is comparable to the ion-induced nucleation fraction calculated from observed nucleation rates at the same site (**Paper III**). The fraction of activated cluster ions during NPF was higher in events with higher IIN fraction, and was larger for negatively than for positively charged ions (Gagné et al., 2010). The preference of negatively charged nucleation involving sulphuric acid has also been observed in laboratory experiments as well as in quantum chemical calculations (Winkler et al., 2008; Kurtén et al., 2009).

The fraction of 2-nm particle formation explained by ion-induced nucleation is shown in Fig. 5 at seven measurement sites. Ion-induced fractions of 50% and higher were only observed at two of the sites, Jungfraujoch and Pallas. However, these are also the sites where the total formation rates were lowest (medians 0.9 and $1.2 \text{ cm}^{-3} \text{ s}^{-1}$, respectively). As the total formation rate increases to $1\text{--}10 \text{ cm}^{-3} \text{ s}^{-1}$, the ion-induced fraction decreases to 1–10%. In Melpitz and Mace Head, where total formation rates above $10 \text{ cm}^{-3} \text{ s}^{-1}$ were observed, the ion-induced fractions were even lower than this. It should be noted that Fig. 5 shows only the fraction of ion-induced nucleation and does not include the contribution from ion-ion recombination. However,

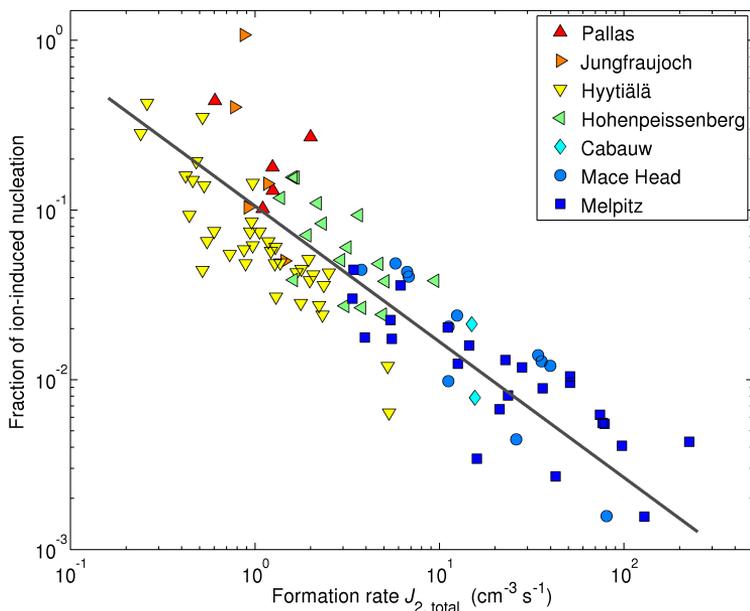


Figure 5. Ratio of ion-mediated nucleation rate to the total nucleation rate at 2 nm as a function of the total nucleation rate J_2 at seven measurement sites in Europe. Data adapted from Manninen et al. (2009) and **Paper III**. The line shows a linear fit through all the data points.

Manninen et al. (2009) showed that in Hyytiälä, the ion-mediated fractions of particle formation (including the ion-ion recombination products, Eq. 7a) does not increase the contribution of ions to total particle formation rates considerably. In their study, the median of ion-ion recombination rates in the 2–3 nm size range were between 0.03 and 0.1 $\text{cm}^{-3} \text{s}^{-1}$. In a later study from the same site, Kontkanen et al. (2013) concluded that in sub-2 nm size range the median fraction of ion-ion recombination products was only 1.5% of all neutral clusters.

The extensive ion size distribution measurements during the EUCAARI campaign 2008–2009 were used to develop parametrizations of ion-induced nucleation rates in **Paper IV**. The parametrizations are given in two forms. When data on the concentration of gas-phase sulphuric acid is available, the formation rate of 2-nm ions is obtained from

$$J_2^\pm = C^\pm N_{\text{clust}}^\pm \left([\text{H}_2\text{SO}_4] + [\text{Org}] \right)^2 \quad (14)$$

where the fitting coefficient C^\pm is $2.0 \cdot 10^{-19} \text{ cm}^6 \text{ s}^{-1}$ and $1.9 \cdot 10^{-19} \text{ cm}^6 \text{ s}^{-1}$ for negative and positive ion formation rates, respectively. Org is the concentration of oxidized organic vapours that, together with the measured sulphuric acid, explain the observed condensational growth of the particles after their formation. As sulphuric acid is not

routinely measured due to technical challenges, its concentration is often approximated using different proxies. The simplest proxy is based on scaling the solar radiation intensity, since the production rate of sulphuric acid depends on OH radical concentration, which follows the solar radiation (e.g. Petäjä et al., 2009). In this case, the parametrization for ion formation rate is

$$J_2^\pm = C_{\text{rad}}^\pm N_{\text{clust}}^\pm \text{GlobRad}^2. \quad (15)$$

Here GlobRad is the global radiation intensity, and the fitting coefficients C_{rad}^\pm are $7.86 \cdot 10^{-10}$ and $7.95 \cdot 10^{-10} \text{ W}^{-2} \text{ s}^{-1}$ for negative and positive ions, respectively. It should be noted that without including the cluster ion concentration N_{clust} , neither of the parametrizations (Eqs. 14 and 15) would work as well compared to the observed ion-induced nucleation rates. This suggests that cluster ions are involved in the ion-induced nucleation process, and also supports the interpretation that the observed minimum in cluster ion concentrations during active NPF (**Paper II**) is caused by the activation of the cluster ions during the nucleation process. In the case of Eq. 14, including the oxidized organics concentration was also essential in order to obtain good correlation with observed nucleation rates, indicating the involvement of the oxidized VOCs in the ion-induced nucleation process. The cluster ion concentrations can be estimated based on ion-pair production rate and background aerosol coagulation sink. Thus, especially Eq. 15 provides a computationally efficient parameterization for estimating the ion contribution to particle formation even in global scale models.

It has been suggested that variation in the intensity of galactic cosmic rays (GCR) and subsequently in the ion production rate in the atmosphere is linked to the observed variation in the global cloud cover (Svensmark and Friis-Christensen, 1997; Marsh and Svensmark, 2000; Svensmark et al., 2009), although this connection has been disputed in several later studies (e.g. Sloan and Wolfendale, 2008; Dunne et al., 2012; Krissansen-Totton and Davies, 2013). The suggested mechanism behind this connection is the ion-aerosol clear-sky hypothesis, which proposes that ions produced by GCR enhance atmospheric particle formation and subsequently cloud condensation nuclei concentrations via ion-induced nucleation (Carslaw et al., 2002). Based on the analysis of NPF event frequency and intensity observed in Hyytiälä during the years 1996–2008, atmospheric NPF in boreal forest boundary layer does not seem to be correlated with GCR on either a seasonal or an inter-annual basis (**Paper V**; updated figure of the yearly number of NPF events and CRII intensity shown in Fig. 6). None of the investigated NPF characteristics (the frequency of NPF events, particle formation and growth rates, and nucleation-mode particle concentrations) had statistically significant correlations with the cosmic-ray induced ionization (CRII) intensity. The concentrations of Aitken- and accumulation- mode particles (which can be used as proxies for actual CCN concentrations) also showed

no correlation with CRII. As was observed in **Paper III**, ion-induced nucleation typically contributes on the order of 10% or less to the total observed particle formation rates in Hyytiälä. The ion-pair production rate from GCR at ground level varied between 1.9–2.15 $\text{cm}^{-3} \text{s}^{-1}$ in Hyytiälä during the studied period, meaning that changes in the GCR flux could account for a maximum change of around 1% in total particle formation rates. Since not all nucleated particles end up growing to CCN particle sizes, the changes in the formation rate of CCN active particles would be even smaller than this. Pierce and Adams (2009) used a general circulation model with two different parametrizations of ion-induced nucleation to estimate the change in CCN concentrations over a solar cycle. They concluded that the change in CCN concentrations was far too small to account for any changes in cloud properties and thus to have a significant role in global climate change. In the upper troposphere, the ionization rate from GCRs is higher than at ground level, and therefore ion-induced nucleation at higher altitudes could be enhanced compared to ground-level observations. However, results from airborne measurements over Central Europe during the EUCAARI project in 2008 showed that the fraction of ions from total particle concentrations in the sub-3 nm size range was lower than 10% throughout the troposphere up to 12 km altitude (Mirme et al., 2010; **Paper V**). The small contribution of ion-induced nucleation to total nucleation therefore seems to be valid throughout the tropospheric column.

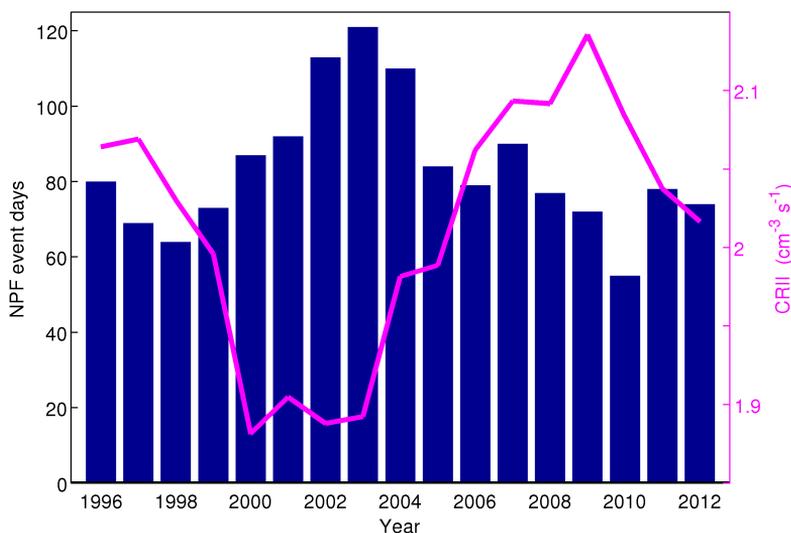


Figure 6. The yearly number of NPF event days (blue bars) and the annual median cosmic-ray-induced ionization rate (magenta line) in Hyytiälä during 1996–2012. Figure updated from **Paper V** using CRII data calculated from the World Neutron Monitor Network observations (<http://cosmicrays oulu.fi/phi/phi.html>).

4.4 Estimates of the global distribution of nucleation mode particle concentrations

Only a limited amount of information can be obtained on the large-scale variation of atmospheric new particle formation from point-wise measurements performed on the ground or from larger scale airborne observations. In **Paper VI** we developed proxies to estimate the distribution of concentrations of nucleation-mode (3–25 nm diameter) particles over continental regions. The proxies are based on the assumption that particle formation rates are proportional to sulphuric acid concentration to power 1 or 2, which is a relation that has been observed in many field studies, as was discussed in Section 4.1. In the case where the particle formation rate is directly proportional to sulphuric acid, the nucleation-mode proxy concentration is given by

$$N_{\text{nuc}} = \frac{[\text{SO}_2] \cdot \text{UVB}}{\text{CS}^2}. \quad (16)$$

The loss term, which is the coagulation sink of nucleation-mode particles, is proportional to condensation sink CS (Lehtinen et al., 2007). In order to obtain the global distribution of N_{nuc} , the CS in Eq. 16 is approximated by the aerosol optical depth (AOD), which can be obtained from remote sensing satellite data. Replacing the coagulation sink with AOD is a crude assumption for several reasons. Firstly, the coagulation sink is calculated from aerosol size distributions measured at ground level, whereas the AOD is a column-integrated quantity. Secondly, the dependence of the AOD and the coagulation sink on particle size is not exactly the same. As a result, the shape of the ambient aerosol size distribution will affect the correlation between AOD and coagulation sink. Thirdly, the chemical composition of aerosol particles also affects their light scattering and absorbing properties and thus their contribution to the AOD, whereas the coagulation sink is determined only by the particle size. In the literature, there are only a few comparisons between ground-based aerosol measurements and column-integrated aerosol properties. Sundström et al. (2013) compared the condensation sink calculated from aerosol size distributions measured on the ground at several sites in South Africa to the AOD derived from satellite observations. The correlation coefficient between these quantities was 0.2–0.3 depending on location. Boundary layer height was observed to affect the correlation somewhat, but other factors, such as the effect of dust on AOD, were likely to have a stronger impact (Sundström et al., 2013).

Paper VI presents the results of the global nucleation-mode particle proxy as seasonal averages (Fig. 7). The proxies show a spatial distribution that is roughly consistent with both the available ground-based measurement data on nucleation-mode particle concentrations and global model simulations. The very frequent and strong NPF events observed in South Africa in all seasons (Laakso et al., 2008; Vakkari et al., 2011), as well as the strong nucleation-mode particle source in

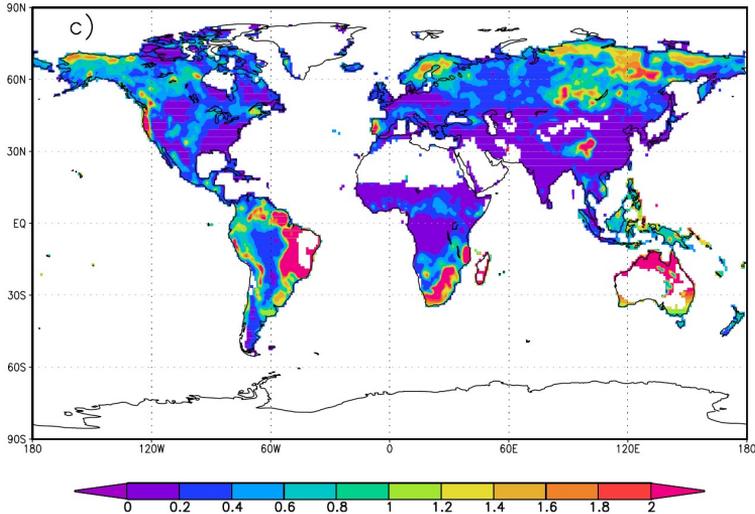


Figure 7. Distribution of the nucleation mode proxy concentration calculated from Equation 16 for June–August 2006 (adapted from **Paper VI**). The color scale shows the relative differences in nucleation mode particles concentrations, not the absolute concentration values.

Eastern Australian rainforest areas (Sun et al., 2008), are reproduced well by the proxy. The boreal forest areas in the Northern hemisphere also have high nucleation mode proxy concentrations during the spring and summer, consistent with observations (Tunved et al., 2006; Dal Maso et al., 2008). On the other hand, frequent nucleation events observed in Eastern China (Wang et al., 2011; Herrmann et al., 2014) are completely missing in the proxy concentrations. This is probably due to the fact that sulphur dioxide concentrations in these polluted areas are very high, leading to a dominance of sulphuric acid driven nucleation. Since the satellite-based detection of SO_2 is not sensitive enough to distinguish any differences in the column SO_2 concentration over polluted and clean areas, this nucleation mode particle production could not be reproduced by our proxy. Another area where the proxy concentrations seem to contradict ground-based observations is the Amazon rainforest. The proxy predicts high nucleation mode concentrations in this region, whereas the few available studies do not show evidence for regional-scale NPF occurring there (Ahlm et al., 2009).

Crippa et al. (2013) have developed the approach of **Paper VI** further and constructed a satellite-data-based proxy for the number concentration of 6–100 nm particles. In addition to SO_2 , UV radiation and AOD data, their approach also utilizes NH_3 concentration and the aerosol Ångström exponent. At selected ground-based measurement sites in eastern North America, the proxy developed by Crippa et al.

(2013) performs better than the proxy from **Paper VI** in predicting nucleation-mode concentrations, especially during autumn. The additional parameters utilized by Crippa et al. (2013) show the importance of other vapours besides sulphuric acid (such as ammonia) in atmospheric NPF, especially in areas of high anthropogenic influence. However, since no results of the proxy performance outside of the Eastern US were presented by Crippa et al. (2013), the performance of their proxy especially at remote areas with low pollution levels is not known.

4.5 Long-term trends in particles, trace gases, and NPF in the boreal forest

To be able to understand the role of atmospheric aerosol in the climate system and the feedbacks related to it, long-term measurements of aerosol properties are required. Compared to many meteorological datasets, continuous aerosol measurements have been started relatively recently. The longest continuous time series of aerosol size distribution measurements is available from the SMEAR II station in Hyytiälä, Finland. In **Paper VII**, we analyzed the interannual variability and trends of the sources and sinks of aerosol particles based on a 16-year data series from the Hyytiälä station. It was seen that the concentration of sulphur dioxide and the condensation sink have a decreasing trend in Hyytiälä. Similar decreasing trends have been observed throughout Europe as a result of efforts in controlling air pollution (e.g. EDGAR, 2011). Although the levels of air pollutants in Finland are lower than in Central Europe, similar decreasing trends of SO₂ and particulate matter as in Hyytiälä have been observed also in other areas of Finland (Anttila and Tuovinen, 2010). The particle number concentrations in nucleation, Aitken and accumulation mode size ranges also have a statistically significant decreasing trend in Hyytiälä. All of these decreasing trends were in the range of 1–2%/year.

The annual frequency of NPF in Hyytiälä was observed to be influenced by the air-mass origin, explaining a large part of the interannual variability in the number of NPF event days (**Paper VII**). NPF occurrence is most probable when airmasses arrive at Hyytiälä from the Northern Atlantic over Scandinavia, as has also been observed by Sogacheva et al., (2005). During 2002–2004 airmasses arrived to Hyytiälä from north-northwest on 24–28% days per year, and in these years the most NPF event days (over 100) were observed. Dal Maso et al. (2007) showed that north-western airmasses favoured NPF at all Scandinavian measurement sites. The seasonal variation of NPF probability in Hyytiälä has remained the same as reported in previous studies from the same site, with a clear maximum in spring-time (Dal Maso et al., 2005). The proxy concentration of sulphuric acid was found to have a decreasing trend, whereas the proxy concentration of oxidation products of organic vapours is increasing. In contrast, the trends in nucleation-mode particle formation and growth rates are smaller than the corresponding trends in the nucleation-mode

Table 1. Trends in new particle formation analysed at four European measurement sites. Trends that were reported to be statistically significant are shown in bold.

Measurement site (observation period)	Trend			Reference
	NPF event frequency	Formation rate	Growth rate	
Melpitz (1996–2006)	Decrease (–45% over the observation period)	Decrease (–68% over the observation period)	Increase (+22% over the observation period)	Hamed et al., 2010
Hyytiälä (1996–2012)	No clear trend	Increase (+0.4% per year)	Increase (+0.5% per year)	Paper VII
Värriö (1998–2011)	Decrease (–3.7% per year)	Increase (+9.6% per year)	No clear trend	Kyrö et al., 2013
Pallas (2000–2010)	No clear trend (decreasing 2000–2003, increasing 2003–2010)	No clear trend (minimum in 2003)	No clear trend	Asmi et al., 2011

particle concentration. There is also much more differences between seasons in the formation and growth rate trends compared to the trends of nucleation-mode concentrations. Because both sulphuric acid and low-volatility oxidized organics have an influence on atmospheric NPF, their opposite trends could partly explain the absence of any statistically significant trend in the observed particle formation and growth rates.

A similar study by Kyrö et al. (2014) of the trends in NPF characteristics in Värriö in Northern Finland showed much larger decreases in the SO₂ and sulphuric acid proxy concentrations and the condensation sink than those observed in Hyytiälä. These decreasing trends were linked to the decreasing sulphur emissions in Kola Peninsula. As a consequence, the NPF event frequency has decreased substantially in Värriö. On the other hand, the formation rate and concentrations of nucleation-mode particles had an increasing trend, which was attributed to the considerably decreased condensation sink. At Pallas, another Northern Finnish site, no clear trends were observed in NPF frequency or the magnitude of the formation and growth rates (Asmi et al., 2011). At Melpitz in Central Europe, the effect of decreasing SO₂ concentrations was seen to decrease both the yearly number of NPF event days and the particle formation rates, whereas the particles' growth rates had an increasing trend (Hamed et al., 2010). Of the four measurement sites where long-term changes in atmospheric NPF have been analyzed, the changes in NPF characteristics were clearly largest in Melpitz (Table 1), where the decrease in SO₂ concentration was also the

largest of the four sites. In Hyytiälä and especially in Pallas, the overall level of SO₂ concentrations is lower compared to Melpitz, and consequently the NPF event frequency was not observed to change as much at these two sites. Asmi et al. (2013) studied the aerosol the aerosol number concentration trends at several sites around the world and found clear decreasing trends at majority of the sites, and suggested the cause to be the decreased antropogenic emissions of primary particles and SO₂. Interestingly, at two sites studied also in this thesis, Melpitz and Pallas, Asmi et al. (2013) determined the aerosol concentrations to have either no trend (Melpitz) or an increasing trend (Pallas), although these might be affected by gaps in the data.

These differing trends in the NPF characteristics observed at the three Finnish and one Central European measurement sites show the importance of long-term and large-scale observations. Especially in the areas away from antropogenic influence, such as the boreal forest areas of the Northern hemisphere, observations of NPF would be crucial. These areas are probably strong sources of atmospheric nucleation as was shown in **Paper VI**.

5 Review of the publications and author's contribution

In **Paper I**, a revised form of the condensation growth equation was derived, taking into account the size of the vapour molecules and the thermal speed of the particles. Both these effects enhance the growth rates of sub-10 nm particles compared to the traditional kinetic-regime condensation calculations. A parametrization for calculating the growth caused by hydrated sulphuric acid molecules as a function of RH is presented. In this paper, I did the model calculations, and wrote most of the text.

Paper II presents observations of the connection between gas-phase sulphuric acid and formation of 2-nm charged and neutral clusters. Formation rates were correlated with sulphuric acid concentration to a power between one and two, with a very short time delay. Coefficients for the activation and kinetic type nucleation mechanisms were calculated. Typical diurnal cycles of the cluster ions on new particle formation (NPF) and non-NPF days were investigated, revealing information on the participation of the sub-2 nm clusters on particle formation. In this paper, I performed the data analysis and wrote the major part of the text.

Paper III presents the results of ion spectrometer measurements at 12 European field sites during the EUCAARI project 2008–2009. Particle formation and growth rates are derived for different types of environments and also different altitudes, including measurement sites partly in the free troposphere. A general seasonal cycle in NPF with a maximum in spring-time was observed in the majority of the measurement sites. Ion-induced nucleation was observed to make only a minor contribution to total particle formation rates. Growth rates of particles were typically observed to increase as function of size. I participated in the planning of the paper, and contributed to the data analysis and interpretation of the results. This paper was also included in the thesis of Dr. H. E. Manninen.

In **Paper IV**, parametrizations for ion-induced nucleation rates were developed. The data is taken from ion spectrometer measurements performed during the EUCAARI project 2008–2009. These parametrizations are simple enough to be included in all atmospheric models containing size-resolved aerosol dynamics, including global models. Because the parametrizations are based on direct field measurements of particle formation rates, they do not have the uncertainties of nucleation rate parametrizations traditionally derived from nucleation theories. I participated in derivation of the parametrizations, in the interpretation of the results, and wrote majority of the paper.

In **Paper V**, the connections between galactic-cosmic-ray-induced ionization (CRII) and NPF are analysed based on 12 years of observation at the SMEAR II station. It was found that neither the amount of NPF days nor the particle formation rates

correlate with CRII. The main reason behind this is the minor contribution of ion-induced nucleation to the total particle formation at the site. Campaign-wise measurements of vertical profiles of ion fraction also revealed that in the continental troposphere, ions contribute only a few per cent or less to the total concentrations of sub-10 nm particles. I participated in the planning of the paper, did all the data-analysis related to the long-term observations, and contributed to the writing of the paper.

In **Paper VI**, global distributions of ground-level nucleation-mode particle concentrations are presented based on proxies. Several proxies are developed based on different assumptions of the functional dependence of the formation rates on the nucleating vapour concentrations. The results of the proxy calculations are compared to measured nucleation-mode concentrations at the SMEAR II station in Hyytiälä, Finland, and predictions on the global distribution of nucleation mode particles are presented based on satellite data. In this paper, I participated in the planning of the paper and the data analysis.

Paper VII presents an analysis of the long-term trends in atmospheric particle formation in the boreal region. Connections between NPF occurrence and particle formation and growth rates are analysed based on proxy concentrations of sulphuric acid and oxidized organic compounds. In this paper, I did all the data analysis and wrote the majority of the paper.

The introduction part of this thesis is written entirely by the author.

6 Conclusions and outlook

The work presented in this thesis characterizes atmospheric new particle formation in different environments and its long-term changes. Several proxy variables have been developed and utilized in addition to measurement data. The main conclusions are as follows:

- 1) In the boreal forest environment, the formation rate of 2 nm particles correlates with sulphuric acid concentration to a power between one and two. From long-term observations, it was seen that the magnitude of particle formation rates varied by up to 3 orders of magnitude at a certain sulphuric acid concentration. The main factor explaining this variation seems to be temperature, pointing towards the participation of biogenic volatile organic compounds in atmospheric NPF. The fraction of observed particle growth explained by sulphuric acid condensation varied from around 15% in winter to a few per cent in summer.
- 2) A decreasing trend was observed in sulphur dioxide, particulate matter, sulphuric acid proxy and particle number concentrations during the years 1997–2012 whereas the particle formation and growth rates had a slightly increasing trend during the same period at the Hyytiälä boreal forest site. In contrast to sulphuric acid, the proxy concentration for oxidized organics had an increasing trend.
- 3) During a year-long measurement campaign at 12 European field sites, the frequency of NPF days varied between 21–57%. A larger site-to-site variation was observed in the total particle formation rate than in the ion-induced nucleation rates. Charged particle formation rates at 2 nm typically contributed 1–10% to the total particle formation rates at the same size range, with the largest fraction (up to 27% in median) occurring at the remote high-altitude sites where the total particle formation rates were smallest.
- 4) Neither new particle formation frequency nor the concentrations of nucleation-mode particles at the Hyytiälä measurement site shows a correlation with the changes in galactic cosmic ray intensity reaching the ground level. As ion-induced nucleation was observed to make a minor contribution to the total particle formation rates, any variation in particle formation characteristics at this site due to the changes in cosmic rays is too small to be detected in our data set.
- 5) Proxy variables to estimate the global distribution of nucleation-mode particle concentrations over continents based on satellite data were developed. Challenges in obtaining reliable input data from satellite data products were related to estimating the particle sink term from column-integrated aerosol optical depth, and omitting the influence of sulphur dioxide variability to particle production efficiency. Comparison to existing knowledge on nucleation-mode particle

concentrations in various environments shows that the proxy is qualitatively consistent with observations in the boreal forest zone as well as parts of Australia and southern Africa.

Atmospheric new particle formation is a globally occurring phenomenon that is important for total aerosol number concentrations. In its latest report the Intergovernmental Panel on Climate Change concluded that the largest source of uncertainty in estimating the radiative forcing is due to aerosols (IPCC, 2013). The results presented in this thesis provide tools to include the aerosol formation into regional and global scale models via parametrizations, as well as to estimate the future changes and feedbacks related to NPF based on long-term direct field observations. Further continuous long-term measurements of aerosol size distributions would be needed in order to observe the response of NPF to changes in anthropogenic emissions due to efforts of mitigating climate change, as well as changes in biogenic emissions due to changing climate.

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