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OBSERVATIONS ON THE FIRST STEPS OF  
ATMOSPHERIC PARTICLE FORMATION AND GROWTH

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Academic dissertation

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Ilona Anniina Riipinen  
University of Helsinki, 2008

## **Abstract**

Atmospheric aerosol particles have a significant impact on air quality, human health and global climate. The climatic effects of secondary aerosol are currently among the largest uncertainties limiting the scientific understanding of future and past climate changes. To better estimate the climatic importance of secondary aerosol particles, detailed information on atmospheric particle formation mechanisms and the vapours forming the aerosol is required. In this thesis we studied these issues by applying novel instrumentation in a boreal forest to obtain direct information on the very first steps of atmospheric nucleation and particle growth. Additionally, we used detailed laboratory experiments and process modelling to determine condensational growth properties, such as saturation vapour pressures, of dicarboxylic acids, which are organic acids often found in atmospheric samples.

Based on our studies, we came to four main conclusions: **1)** In the boreal forest region, both sulphurous compounds and organics are needed for secondary particle formation, the previous contributing mainly to particle formation and latter to growth; **2)** A persistent pool of molecular clusters, both neutral and charged, is present and participates in atmospheric nucleation processes in boreal forests; **3)** Neutral particle formation seems to dominate over ion-mediated mechanisms, at least in the boreal forest boundary layer; **4)** The subcooled liquid phase saturation vapour pressures of C3–C9 dicarboxylic acids are of the order of  $10^{-5}$ – $10^{-3}$  Pa at atmospheric temperatures, indicating that a mixed pre-existing particulate phase is required for their condensation in atmospheric conditions.

The work presented in this thesis gives tools to better quantify the aerosol source provided by secondary aerosol formation. The results are particularly useful when estimating, for instance, anthropogenic versus biogenic influences and the fractions of secondary aerosol formation explained by neutral or ion-mediated nucleation mechanisms, at least in environments where the average particle formation rates are of the order of some tens of particles per cubic centimeter or lower. However, as the factors driving secondary particle formation are likely to vary depending on the environment, measurements on atmospheric nucleation and particle growth are needed from around the world to be able to better describe the secondary particle formation, and assess its climatic effects on a global scale.

Keywords: Atmospheric aerosols, particle formation and growth, vapour pressures, organic acids

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## List of publications

This thesis consists of an introductory review, followed by seven research articles. In the introductory part, these papers are cited according to their roman numerals.

- I** Kulmala, M., Laakso, L., Lehtinen, K.E.J., Riipinen, I., Dal Maso, M., Anttila, T., Hörrak, U., Vana, M., and Tammet, H. (2004). Initial steps of aerosol growth, *Atmos. Chem. Phys.*, 4:2553–2560.
- II** Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K.E.J. (2007). Connections between atmospheric sulphuric acid and new particle formation during QUEST III - IV campaigns in Hyytiälä and Heidelberg. *Atmos. Chem. Phys.*, 7:1899–1914.
- III** Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H.E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R.M., Hanson, I., Leung, C., Lehtinen, K.E.J., and Kerminen, V.-M. (2007). Toward direct measurement of atmospheric nucleation. *Science*, 318:89–92.
- IV** Riipinen, I., Kulmala, M., Manninen, H.E., Yli-Juuti, T., Boy, M., Sipilä, M., Ehn, M., Junninen, H., and Petäjä, T. (2008). Atmospheric nucleation: On the water solubility and composition of 2–10 nm particles in boreal forest. *Proc. Nat. Acad. Sci.*, submitted.
- V** Riipinen, I., Svenningsson, B., Bilde, M., Lehtinen, K.E.J., Gaman, A., and Kulmala, M. (2006). A method for determining thermophysical properties of organic material in aqueous solutions: succinic acid. *Atmos. Res.*, 82:579–590.
- VI** Koponen, I.K., Riipinen, I., Gaman, A., Kulmala, M., and Bilde, M. (2007). Thermodynamic properties of succinic, glutaric and malonic acids: evaporation rates and vapor pressures. *Environ. Sci. Technol.*, 41:3926–3933.
- VII** Riipinen, I., Koponen, I.K., Frank, G.P., Hyvärinen, A.-P., Vanhanen, J., Lihavainen, H., Lehtinen, K.E.J., Bilde, M., and Kulmala, M. (2007). Adipic and malonic acid aqueous solutions: surface tensions and saturation vapor pressures. *J. Phys. Chem. A*, 111:12995–13002.

# 1 Introduction

The air we breath does not consist of gas molecules only: each cubic centimeter of air typically carries several thousands of small aerosol particles. The term aerosol, by definition, stands for the combination of these liquid or solid particles and the carrier gas they are floating in. Examples of common atmospheric aerosol particles are cloud and fog droplets, dust, smoke and soot particles, airborne pollen and bacteria, as well as freshly nucleated molecular clusters formed from atmospheric vapours. The sizes of atmospheric aerosol particles range from nanometers up to hundreds of micrometers. Particles formed by the condensation of atmospheric vapours are referred to as secondary, whereas primary particles, for instance dust and sea salt, have entered the atmosphere in the condensed phase (see e.g. Seinfeld and Pandis, 2006). Aerosol particles are present practically everywhere in the Earth's atmosphere, and their concentrations vary over several orders of magnitude depending on the site. In very remote areas, such as Antarctica or the polar regions, concentrations as low as some tens of particles per cubic centimeter can be observed (see e.g. Koponen et al., 2003; Vehkamäki et al., 2004a). In polluted megacities, on the other hand, particle concentrations can reach several hundreds of thousands per cubic centimeter (e.g. Mönkkönen et al., 2005).

Atmospheric aerosol particles impact the Earth's radiation budget and therefore the climate in essentially a two-fold way. First, they directly scatter and absorb solar radiation, which can also be easily seen as a reduction of visibility in heavily polluted environments (e.g. Cabada et al., 2004). Second, aerosol particles act as condensation nuclei for cloud droplets – without such condensation nuclei, no clouds could be formed in atmospheric conditions. Atmospheric aerosols therefore influence the albedo and lifetime of clouds (Rosenfeld et al., 2000; Ramanathan et al., 2001; Lohmann and Feichter, 2005). Besides their impact on climate and visibility, aerosol particles cause adverse health effects when deposited in the human respiratory system (Stieb et al., 2002; Brunekreef and Holgate, 2002; Nel, 2005).

The Intergovernmental Panel on Climate Change (IPCC) has recognised the uncertainty in the radiative forcing caused by aerosols as the main single factor limiting the scientific understanding of future and past climate changes (IPCC, 2007). These uncertainties are related mostly to the aerosol-cloud interactions and the overall magnitude of aerosol concentrations in the past and future. It is still largely unclear how human activities affect the regional and global aerosol concentrations, and how the ratio of

anthropogenic to biogenic aerosols has and will evolve in time, particularly in the case of secondary aerosol. The aforementioned information is anyhow crucial in assessing the total climatic effects of human activities. Also the contribution of cosmic radiation to aerosol formation remains to be quantified.

Secondary aerosol formation via nucleation of atmospheric vapours accompanied with subsequent condensational growth of the particles is a global phenomenon proven to take place in a wide variety of high and low altitude environments (Kulmala et al., 2004a and references therein). After reaching large enough sizes, these particles are likely to have significant impact on the climate and air quality (Spracklen et al., 2006): according to a recent estimate by Spracklen et al. (2007), secondary aerosol formation increases regional cloud condensation nuclei concentrations with approximately 30 %. However, the exact particle formation mechanisms and the identities of the participating vapours in different environments are still unclear in many respects, mainly due to difficulties in direct atmospheric observations of nucleation and particle composition. This naturally has made estimations on the particle source caused by secondary aerosol formation challenging, as information on atmospheric nucleation mechanisms and the vapours participating in the particle formation and growth would be needed for accurate predictions.

In the past years, the commonly proposed candidates for the atmospheric nucleation mechanism have included kinetic (McMurry and Friedlander, 1979), binary (Doyle, 1961; Mirabel and Katz, 1974), ternary (Korhonen et al., 1999; Merikanto et al., 2007, ion-induced or ion-mediated nucleation (Yue and Hamill, 1979; Yu and Turco, 2000; Lee et al., 2003; Yu et al., 2007), and the activation and growth of persistent neutral or charged molecular clusters (Hoppel et al., 1994; Kulmala et al., 2000; Kulmala, 2003; Kulmala et al., 2006). These proposed particle formation schemes usually include water, sulphuric acid and sometimes ammonia or organic vapours participating in the nucleation and growth processes. Ion-induced nucleation is proportional to the intensity of cosmic rays arriving in the atmosphere, and is therefore closely related to solar activity.

The magnitude of the aerosol source provided by secondary particle formation has been demonstrated to be very sensitive to the processes taking place during the very first steps of particle formation and growth (McMurry and Friedlander, 1979; Weber et al., 1997; Kerminen and Kulmala, 2002). Direct observations on these processes are thus required to pin down the dominating particle formation mechanisms and



condensing vapours in different environments. In the case of charged particles, size distribution measurements reaching particle sizes of even 1 nm and below have been conducted during recent years in various environments (Hörrak, 2001; Laakso et al., 2004a; Kulmala and Tammet, 2007). These measurements have revealed that the typical concentrations of atmospheric ions are not enough to explain the observed total particle formation rates (e.g. Laakso et al., 2004a, Iida et al., 2006), giving first indications on the dominance of neutral over ion-induced nucleation. These data have also proven useful in determining the growth rates of the smallest particles (**Paper I**). However, a major limitation in understanding the first steps of atmospheric particle formation has been the lack of atmospheric observations on electrically neutral aerosol particles with sizes close to 1–2 nm, the size range at which nucleation and the initial steps of particle growth occur. Thus, recently a significant effort has been put into developing instruments that measure also neutral atmospheric particles of 1–3 nm in diameter (Kulmala et al., 2005; Mordas et al., 2005; **Paper III**; Sipilä et al., 2008). Measurements on the neutral fraction of the smallest particles complete the picture of atmospheric nucleation and initial particle growth, shedding light on the contribution of ions in particle formation. As noted above, the fraction of ion-induced nucleation, on the other hand, is directly connected to the relative importance of cosmic radiation compared to anthropogenic or biogenic activity in regulating the concentrations of atmospheric aerosols.

The composition of atmospheric particles is a major factor determining their effects on the climate (see e.g. Seinfeld and Pandis, 2006), visibility and human health. In the case of the smallest nanoparticles, their composition naturally reflects the mixture of vapours participating in secondary aerosol formation and growth. Several laboratory and field studies suggest that sulphuric acid and sulphate clusters are likely participants in atmospheric nucleation and growth (Weber et al., 1996; Hanson and Eisele, 2002; Berndt et al., 2005; Sihto et al., 2006; **Paper II**). However, there are also observations that imply that the ambient sulfuric acid concentrations cannot explain the observed nucleation and growth completely (Fiedler et al., 2005; Boy et al., 2005), particularly in rural environments. On the other hand, a clear link between atmospheric aerosol formation and the emissions of biogenic organics has been reported in several studies (O’Dowd et al., 2002; **Paper I** ; Kulmala et al., 2004b; Tunved et al., 2006). The relative roles of sulphurous and organic compounds in particle formation and growth can, among other things, be treated as a measure of the relative magnitudes of anthropogenic and biogenic effects on the secondary aerosol source. This is particularly true

in continental regions, where most of the gaseous sulphur is of anthropogenic origin.

Direct analytical composition measurements of atmospheric nanoparticles are difficult because of the minuscule mass of the particles. Therefore indirect methods, such as measuring the volatility or hygroscopicity (water-solubility) of the particles, need to be used (see e.g. Hämeri et al., 2000; Varutbangul et al., 2006). The water-solubility of the particles is also related to their ability to act as cloud condensation nuclei (CCN): the more water-soluble the particles, the more likely they are to serve as CCN. However, most of the current measurements give no information on the composition of particles smaller than 10 nm. In the work presented in this thesis we present data measured with a novel instrumental setup, which is capable of detecting the hygroscopic behaviour of 2–9 nm particles (Kulmala et al., 2007; **Paper IV**). The water-solubility of the smallest particles is directly related to the relative role of sulphurous compounds in comparison with biogenic organics, as the previous are expected to be more water-soluble than the latter.

Atmospheric sulphuric acid is theoretically expected to participate particle formation and growth and increase the CCN-activity of the particles, as its saturation vapour pressure is known to be very low (Kulmala and Laaksonen, 1990) and its affinity to water very high (see e.g. Seinfeld and Pandis, 2006). In the case of atmospheric organic compounds, the basic properties defining their partitioning between gaseous and particulate phase, such as saturation vapour pressures and surface tensions, are still largely missing. The scarcity of proper thermodynamics is one of the main limiting factors in identifying the compounds that are likely to form and grow particles (Kanakidou et al., 2005; Seinfeld and Pankow, 2003) from the vast variety of atmospheric organics. The current lack of information on the potential condensing organic compounds and their thermophysical properties, along with the aging processes of secondary organics aerosol (e.g. Barsanti and Pankow, 2004), result in large uncertainties in models aiming to predict the total production of secondary organic aerosol (Volkamer et al., 2006).

In the work presented in this thesis we have studied the atmospheric nucleation mechanisms and the vapours potentially participating in the formation and growth of atmospheric aerosols. We have applied novel instrumentation in the field to obtain direct information on the first steps of atmospheric particle formation and the composition of the freshly formed nanoparticles. Besides these field data, we have utilised laboratory measurements on the evaporation rates of droplets containing aqueous solutions of common organic acids to obtain information on the properties of atmospheric organics.

The main objectives of the work presented in this thesis thus include

- 1) investigating the relative contribution of sulphurous and organic compounds to particle formation and growth (**Papers I, II, IV**)
- 2) studying the role of persistent molecular clusters in atmospheric particle formation (**Papers II, III**)
- 3) estimating the ratio of ion-induced to neutral nucleation and growth (**Papers I, III**)
- 4) determining thermophysical properties of atmospheric organic acids (**Papers V–VII**).

## 2 Atmospheric particle formation events

Secondary particle formation and growth has been observed almost all over the world in varying environments and altitudes (see Kulmala et al., 2004a and references therein), including, for instance, remote continental (Weber et al., 1997; Mäkelä et al., 1997), urban (Stanier et al., 2004; Mönkkönen et al., 2005), alpine (Weingartner et al., 1999), savannah (Laakso et al., 2008), antarctic (Koponen et al., 2003) and coastal (O’Dowd et al., 2005) boundary layers.

Figure 1 illustrates a typical secondary aerosol formation and growth event as observed from 3–1000 nm particle size distributions. The event has been recorded on 24.4.2006 at the SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005), which is a remote boreal forest site with Scots pine (*Pinus Sylvestris L.*) as the dominating species. Most of the field data presented in this work (**Papers I–IV**) are based on measurements at the SMEAR II station.

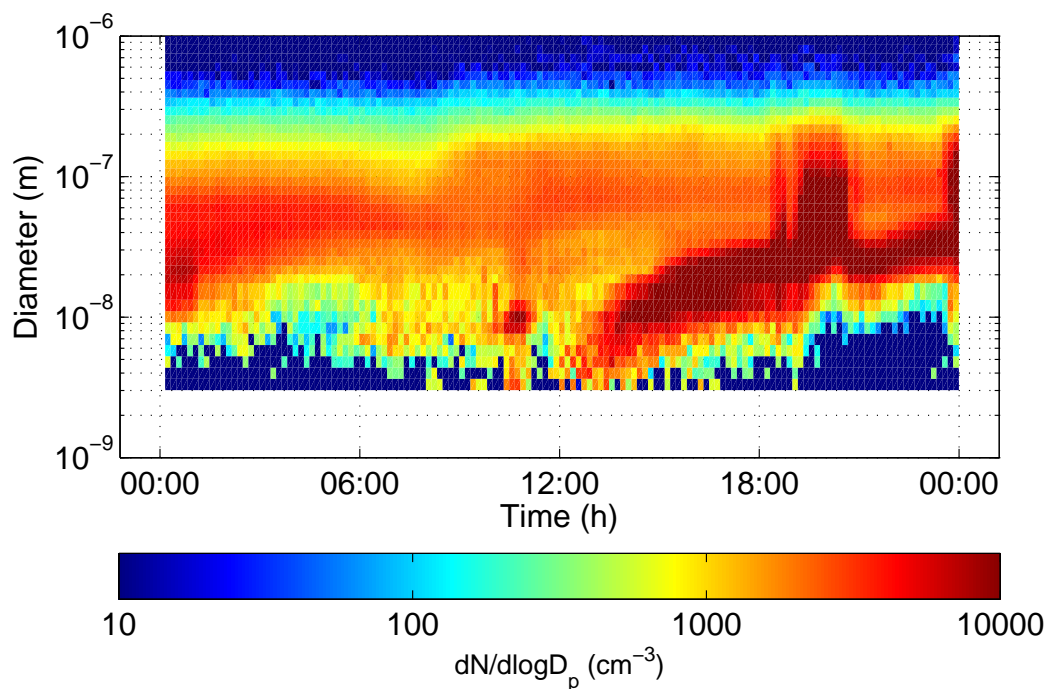


Figure 1: New particle formation event as measured with the DMPS system on 24.4.2006 at the SMEAR II station, Hyytiälä, Finland.

The size distributions have been measured with the Differential Mobility Particle Sizer (DMPS, Aalto et al., 2001) system. The DMPS consists essentially of a Differential Mobility Analyser (DMA) and a Condensation Particle Counter (CPC, see Stolzenburg and McMurry, 1991; McMurry, 2000). When the aerosol sample enters the device, it is charged with a bipolar charger to a known charge distribution. The particles are then classified according to their electrical mobility in the DMA. The mobilities can be converted to particle sizes (all particle sizes in this thesis are expressed in mobility equivalent diameters, see e.g. Mäkelä et al., 1996), and the concentrations in each size class are counted optically with a CPC after growing the particles to detectable sizes by condensing butanol vapour onto them. Data collected with the DMPS system are used in the analyses presented in **Papers I–IV**.

The features characterising atmospheric particle formation episodes are **1)** the appearance of new particle mode to the smallest observable size classes (at 3–25 nm in the DMPS measurement, see Fig. 1); **2)** the growth of the new mode, sometimes to sizes where the formed particles can directly act as cloud condensation nuclei (CCN). In Hyytiälä, the particle formation events typically start near midday, the growth continuing often for several hours (Dal Maso et al., 2005). This points to the connection of particle formation events and radiation (see e.g. Mäkelä et al., 1997): sunlight induces photochemical production of condensable vapours as well as the development of the atmospheric boundary layer, both of which have been observed to have a connection with NPF (Nilsson et al., 2001; Weber et al., 1997).

The DMPS data set on atmospheric particle formation events from Hyytiälä is by far the longest of its kind, with 12 years of continuous size distribution data. The yearly numbers of particle formation and growth events along with their monthly distribution are presented in Fig. 2 (see also Dal Maso et al., 2005; 2007). The numbers of days with particle formation vary between 60 and 120 per year, and their frequency shows a clear maximum in the spring time. The spring maximum is probably related to the increase in solar radiation and onset of biogenic activity in the forests.

The lower detection limit of the DMPS system is set to 3 nm by the detection efficiency of the CPC. The atmospheric particle formation and the initial growth processes, however, take place below 3 nm. Atmospheric nucleation cannot thus be directly reached with the DMPS system, and to estimate, for instance, the actual atmospheric nucleation rates the particle formation rates at 3 nm need to be scaled downwards (Weber et al., 1997; Kerminen and Kulmala, 2002; Lehtinen et al., 2007). This scaling, on the

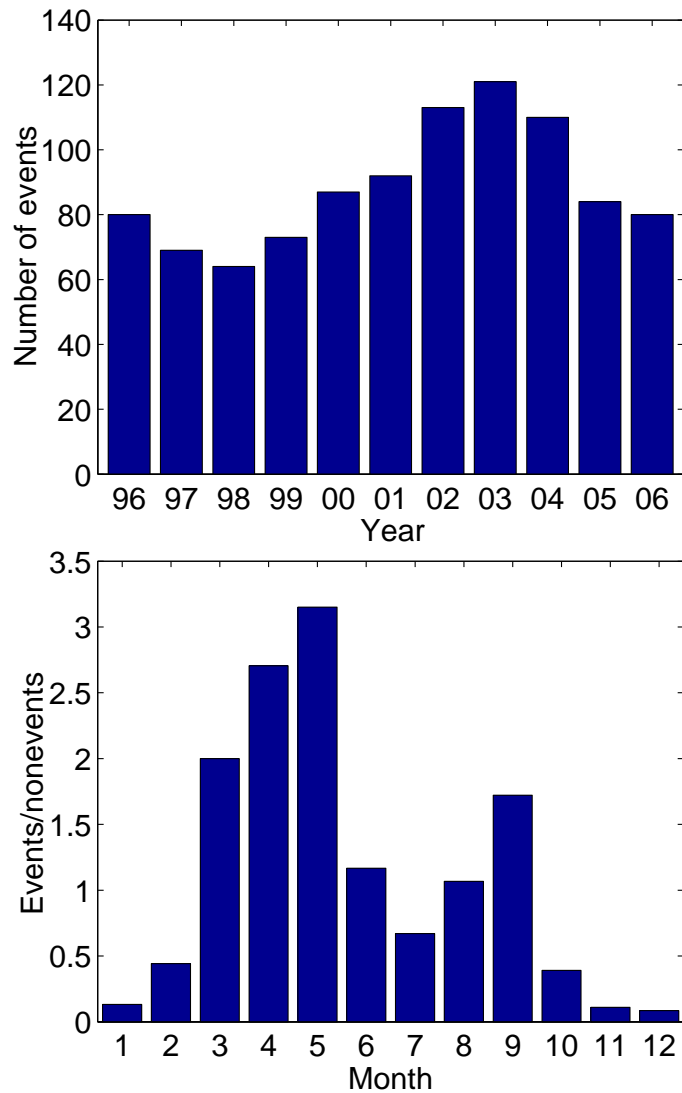


Figure 2: The yearly numbers of particle formation events observed in Hyytiälä (top) and the monthly event days divided by the number of days with no clear indications of particle formation and growth (bottom).

other hand, requires knowledge on the growth rates of particles below 3 nm as well as the actual size of the nucleating particles. If no measurements below 3 nm are available, these quantities need to be estimated, which results in considerable uncertainties in the predicted nucleation rates.

### 3 Measurements on the first steps of atmospheric nucleation and particle growth

To be able observe atmospheric nucleation and growth processes as directly as possible, measurements on the particle concentrations and size distributions at sizes close to 1–2 nm are needed. These measurements, however, are challenging, essentially because the smallest particles are easily lost by diffusion in tubings (see e.g. Hinds, 1999), difficult to charge and require very high supersaturations to grow inside the CPCs. Measurements on the composition of the freshly formed particles, on the other hand, would be required to obtain information on the vapours participating in the formation and growth processes. The main difficulty limiting atmospheric composition measurements of the freshly formed nanoparticles is the very small total mass carried by these particles. Therefore direct measurements on the particle composition, e.g. filter sampling and mass spectrometric studies, are typically limited to size ranges above 10–40 nm (see e.g. Mäkelä et al., 2001; Zhang et al., 2004a; Smith et al. 2005; Allan et al., 2006).

#### 3.1 Concentrations and size distributions of charged and neutral particles below 3 nm

The naturally charged fraction of atmospheric nanoparticles can be measured with ion spectrometers such as the Balanced Scanning Mobility Analyser (BSMA, Tammet, 2006) and the Air Ion Spectrometer (AIS, Mirme et al., 2007). When measuring only the charged fraction of the particles, no additional charging is required and the particle counting can be done by measuring the current carried by the particles. This allows the use of higher flow rates in comparison with instruments using CPCs, and therefore smaller losses inside the instrument. Therefore the BSMA and AIS can measure particle size distributions even down to 1 nm and below, the measured size range for both positive and negative polarity being 0.8–7.6 nm for the BSMA, and 0.8–40 nm for the AIS. The size classification is done in both instruments based on the electrical mobility of the particles. Data collected with these ion spectrometers were utilised in **Papers I, III and IV**. The positive and negative air ion size distributions measured by the AIS on the particle formation event day 24.4.2006 in Hyytiälä (see Fig. 1 for the DMPS data) are presented in Fig. 3. A particle formation and growth event similar to that measured with the DMPS is observed in the AIS data. However, the concentrations

are lower, as only the charged fraction of particles is measured, and a continuous pool of small cluster ions is observed in sizes smaller than 2 nm.

Because of their small lower detection limits, the ion spectrometers are useful tools in observing the first steps of aerosol formation and growth. However, the charged fraction of atmospheric nanoparticles is usually only of the order of 1 to 10 %, depending on the particle size (Hõrrak et al., 2001; Iida et al., 2006; Laakso et al., 2007). Thus, to detect the majority of the freshly nucleated particles, measurements of neutral particles below 3 nm are needed.

Recently, a lot of work has been put into developing instruments that can measure also neutral particles down to 1–2 nm and even below. Mordas et al. (2005) developed a prototype of a butanol-based CPC (UF-02proto), that could measure insoluble particles

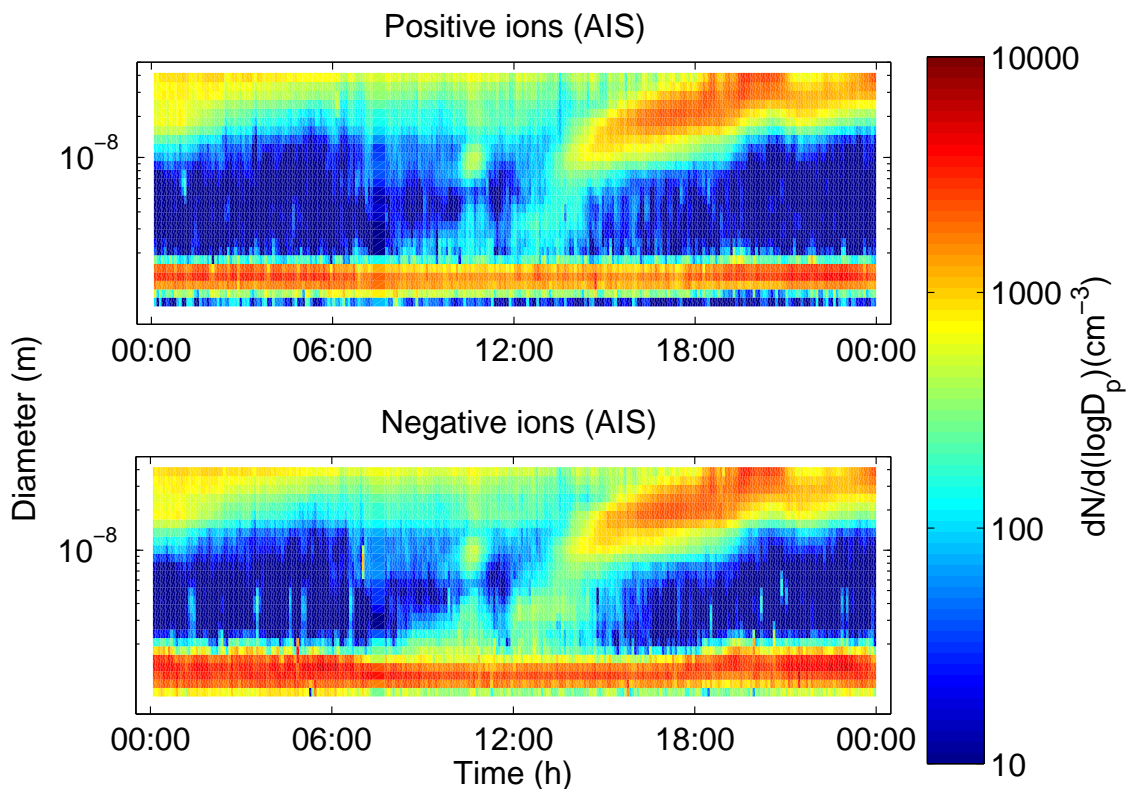


Figure 3: The particle formation event on 24.4.2006 as recorded with the AIS.



as small as 1.8 nm in diameter. Using a pair of UF-02proto CPCs in the field (one calibrated to 1.8 nm and another to 3 nm), preliminary data on two days with particle formation events were collected during spring 2006. This data is presented in **Paper III**. The Neutral cluster and Air Ion Spectrometer (NAIS) is a mobility spectrometer based on the AIS, but designed to measure also neutral particles in the same size range. This is achieved by equipping the instrument with a unipolar charger and an ion trap to remove the ions generated by the charger (see the Supporting Information of **Paper III**). A schematic figure of the setup of NAIS is presented in Fig. 4.

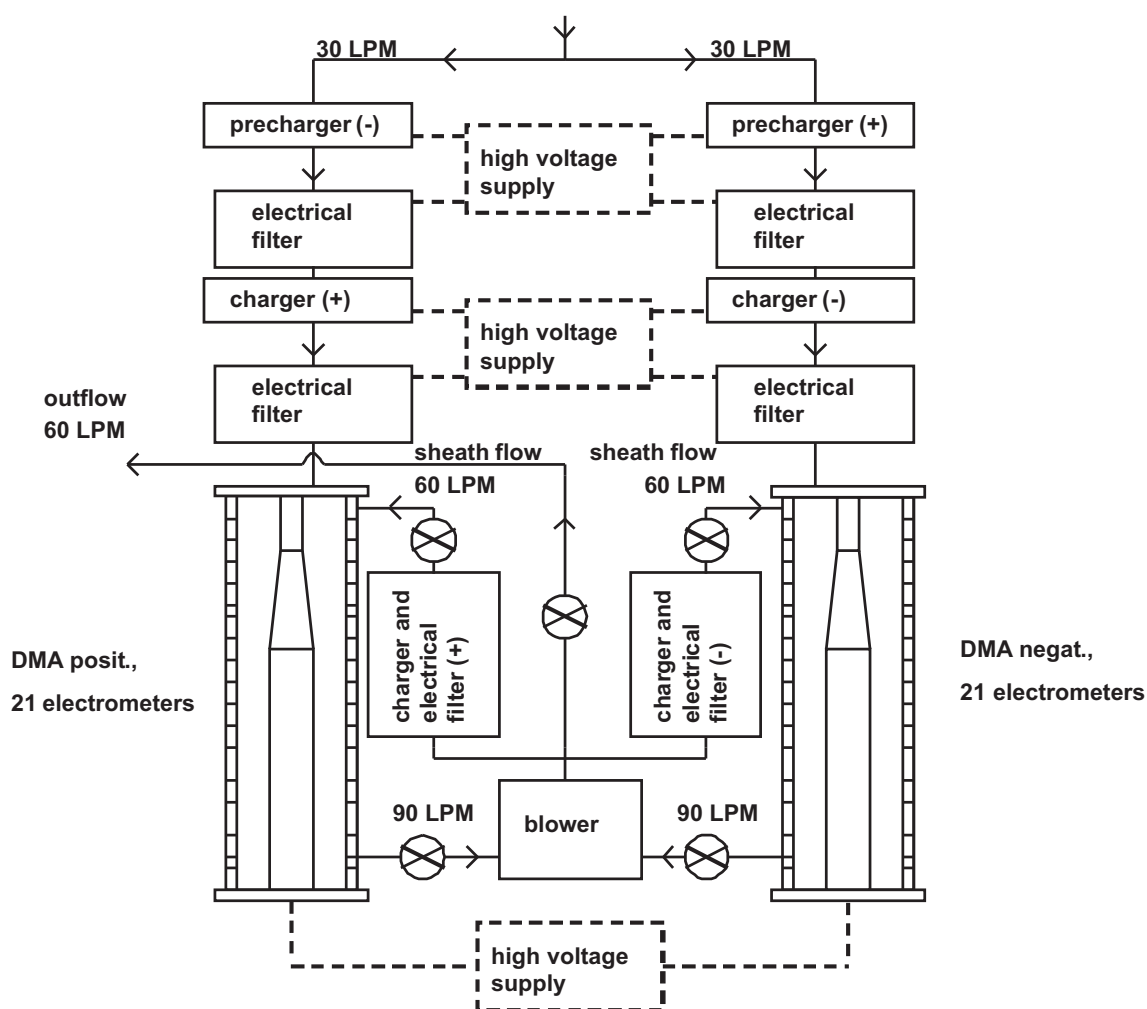


Figure 4: A schematic figure of the Neutral Cluster and Air Ion Spectrometer (NAIS, courtesy of Ms. Hanna Manninen and Dr. Aadu Mirme).

The total (neutral + charged particles) particle size distributions measured by the NAIS

on the example particle formation event day of 24.4.2006 in Hyytiälä are presented in Fig. 5. Again, the appearance of a new growing mode is seen, and similarly to the ion data, a continuous, yet more numerous, pool of clusters is present in sizes below 2 nm. The 2–3 nm particle concentrations measured by the NAIS at the SMEAR II station agree with those detected with the UF-02proto CPC pair, giving confidence in the results. Below this limit, however, the size distributions measured by the NAIS should be treated as qualitative rather than quantitative as no quantitative reference for these sizes exists yet. However, the work is ongoing and the results obtained with the NAIS for sub-2 nm particles are supported by the recent measurements reported by Sipilä et al. (2008), who used the Pulse Height -CPC (PH-CPC, see Marti et al., 1996; Dick et al., 2000) and Expansion-CPC (E-CPC, Kürten et al., 2005) techniques to detect atmospheric clusters even down to approximately 1 nm.

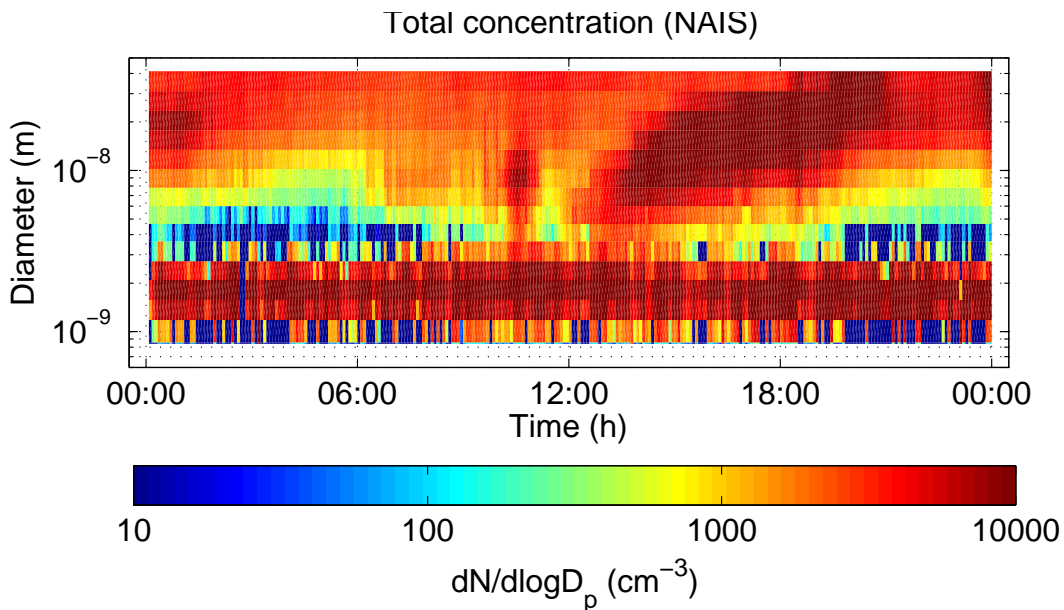


Figure 5: The particle formation event on 24.4.2006 as recorded with the NAIS.

### 3.2 Composition of the freshly nucleated particles

Because of the difficulties in direct particle composition measurements below 10 nm, indirect methods such as measurements of particle volatility or hygroscopicity (water solubility) are often used. However, also the conventional hygroscopicity and volatility

measurement setups (e.g. Hygroscopicity Tandem Differential Mobility Analyzer, HTDMA, see e.g. Hämeri et al., 2000; Volatility Tandem Differential Mobility Analyzer, VTDMA, e.g. Ehn et al., 2007a) are limited to larger than approximately 10 nm particles in atmospheric conditions, due to the relatively low concentrations of the small particles, particularly in remote environments (Ehn et al., 2007b). In a more polluted urban environment, on the other hand, Sakurai et al. (2005) measured the hygroscopicity of particles even as small as 4 nm.

One means of measuring the concentration and hygroscopicity of atmospheric particles even below 3 nm is to use the fact that the lower detection limit of a CPC depends on the composition of the detected aerosols. Recently Kulmala et al. (2007) presented a novel instrumental setup, the Condensation Particle Counter Battery (CPCB), which can be used to study the concentrations and constituents of particles even smaller than 3 nm. The CPCB consists of four CPCs, two working with butanol (TSI-3010 and TSI-3025, also referred to as CPC and UCPC, with 50% cut-off size calibrated to approximately 10 and 3 nm for silver particles) and two with water (TSI-3875 and TSI-3786, also referred to as WCPC and UWPCPC, with 50% cut-off size calibrated to approximately 10 and 3 nm for silver particles) as the condensing vapor. A schematic figure of the CPCB, as it was set up in the study reported in **Paper IV** is presented in Fig. 6.

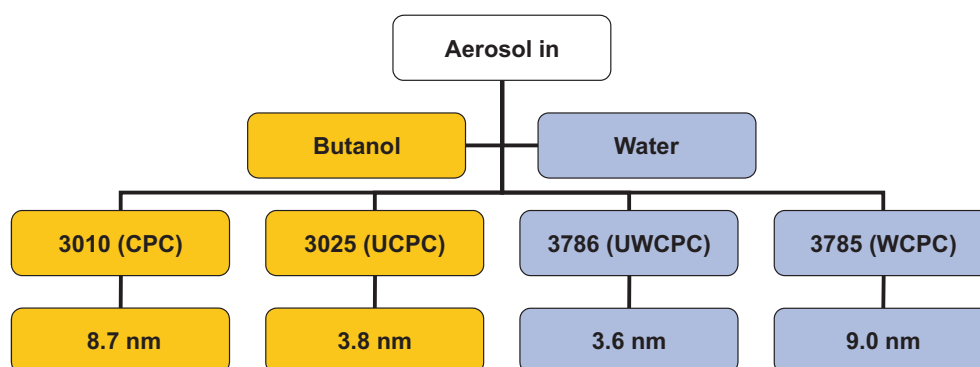


Figure 6: A schematic figure of the CPCB setup used in the field measurements presented in **Paper IV**.

The different condensing vapors lead to differences in the cut-off sizes of the CPCs depending on the composition of the sampled aerosol. If the smallest particles are clearly more soluble in water than in butanol, the detection limits of the water-CPCs are lowered compared to the butanol-CPCs. This is observed as increased particle concentrations detected by the water-CPC in comparison with the butanol-CPC having the same detection limit for insoluble particles. Highly water soluble particles (sodium chloride, ammonium sulphate) have been observed to decrease the detection limits of the water-CPCs significantly (Kulmala et al., 2007; Hering et al., 2005; Petäjä et al., 2006).

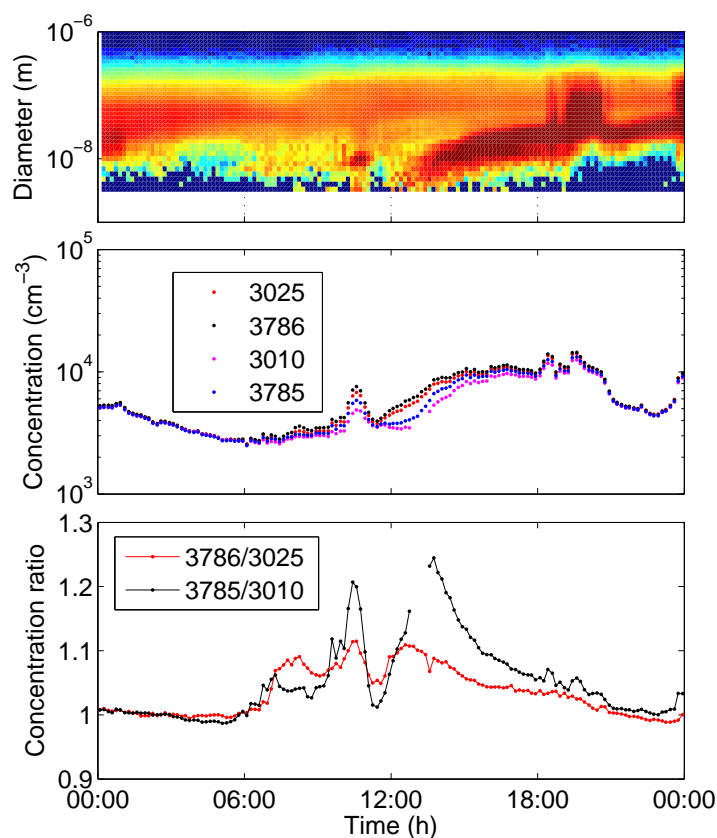


Figure 7: The concentrations (middle) and concentration ratios (bottom) measured by the water- and butanol-based CPCs during new particle formation on 24.4.2006. The corresponding DMPS spectra is given in the top panel.

Figure 7 illustrates the particle concentrations measured by the CPCB (middle) and the

corresponding concentration ratios of water to butanol CPCs (bottom) on 24.4.2006, along with the corresponding DMPS spectra (top, see also Figs. 1, 3 and 5). A clear increase in the concentration readings of the water-CPCs in comparison with the butanol-based instruments is observed during the particle formation and growth episode. This indicates that the detection limit of the water-CPCs is lowered, and thus the freshly-formed particles are more soluble in water than in butanol. In atmospheric conditions the TSI-3876 water-CPC has been shown to measure even down to 2 nm (Kulmala et al., 2007; **Paper IV**).

## 4 The vapours contributing to atmospheric particle formation and growth

As illustrated by Figs. 1 and 2, the beginning of new particle formation is correlated with the increase in solar radiation, on both annual and diurnal scales (see e.g. Dal Maso et al., 2005). It is therefore likely that the photochemistry induced by sunlight plays a major role in the production of atmospheric condensable vapours and thus aerosol particles. Hydroxyl radicals and ozone are common atmospheric oxidants which are formed via photochemical reactions. As these oxidants interact with atmospheric vapours such as SO<sub>2</sub>, NO<sub>2</sub> and volatile organic compounds (VOCs), new compounds are formed in the gas phase. These oxidation products typically have significantly lower saturation vapour pressures than their precursors (e.g. Asher and Pankow, 2002), and are potentially capable of nucleating and forming new particles or growing the pre-existing particles to larger sizes.

### 4.1 The connection between sulphuric acid and particle formation

Sulphuric acid is formed in the atmosphere via the oxidation of SO<sub>2</sub> by OH, and has been identified as a potentially important component in aerosol formation and growth, both experimentally and theoretically (Korhonen et al., 1999; Kulmala, 2003; Laakso et al., 2004a; Berndt et al., 2005). Several field studies such as Weber et al. (1997), Fiedler et al. (2005), Sihto et al. (2006), Kuang et al., (2007) and **Paper II** report a close connection between measured atmospheric sulphuric acid concentrations and new particle formation at different locations. However, the exact role of sulphuric acid in particle formation, as well as the processes limiting it are still under discussion.

Weber et al. (1996), Sihto et al. (2006), Fiedler et al. (2006), and **Paper II** reported that the freshly nucleated particle concentration and formation rate usually seem to follow the measured sulphuric acid concentration raised to the power of 1–2 (see Fig. 8 for an example from Hyytiälä during a particle formation event on 25.3.2003). Kulmala et al. (2006) proposed that atmospheric nucleation rates could thus be approximated with the simple semi-empirical formulas

$$J_{nucl} = A[\text{H}_2\text{SO}_4] \quad (1)$$

or

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

where  $J_{nucl}$  is the atmospheric nucleation rate,  $A$  and  $K$  are empirical nucleation coefficients, and  $[\text{H}_2\text{SO}_4]$  is the sulphuric acid concentration. The magnitudes of the nucleation coefficients  $A$  and  $K$  seem to vary depending on the site, being generally of the order of  $10^{-8}$ – $10^{-5}$   $\text{s}^{-1}$  for  $A$  and  $10^{-14}$ – $10^{-10}$   $\text{s}^{-1} \text{ cm}^3$  for  $K$  (Sihto et al., 2006; **Paper II**). The results imply that **1**) the diurnal behaviour of sulphuric acid (or something else with the same diurnal pattern) does seem to control the aerosol formation; **2**) homogeneous nucleation of sulphuric acid cannot explain the observed phenomena – as the binary and ternary nucleation theories involving sulphuric acid, water and ammonia would predict exponents clearly larger than 3 (Kulmala et al., 2006; Merikanto et al., 2007). Spracklen et al. (2006) implemented Eqs. 1 and 2 as the particle formation mechanisms in a global aerosol microphysics model. The model reproduced the observed secondary aerosol concentrations and the occurrence of new particle formation with good accuracy, proving that this kind of a simple parameterization has the potential to predict the occurrence of particle formation, at least in the boreal forest boundary layer.

Although a clear correlation between the atmospheric sulphuric acid concentrations and particle formation rates are observed, this cannot be directly interpreted as a sign of the dominance of sulphuric acid condensation in particle formation and growth. First, the diurnal profile of gaseous sulphuric acid is strongly correlated with the ambient OH concentration and further the UV radiation (Rohrer and Berresheim, 2006). This points to the possibility that besides sulphuric acid, some other compounds, also correlated with OH, might be participating or even dominating the particle formation. Second, as interestingly pointed out by Laaksonen et al. (2008), several laboratory studies report remarkably smaller sulphuric acid concentrations needed for the same particle formation rates if the sulphuric acid is produced via the photo-oxidation of  $\text{SO}_2$  (Friend et al., 1980; Berndt et al., 2005; 2006) compared with studies using sulphuric acid directly vaporized from a liquid sample (Viisanen et al., 1997; Ball et al., 1999;

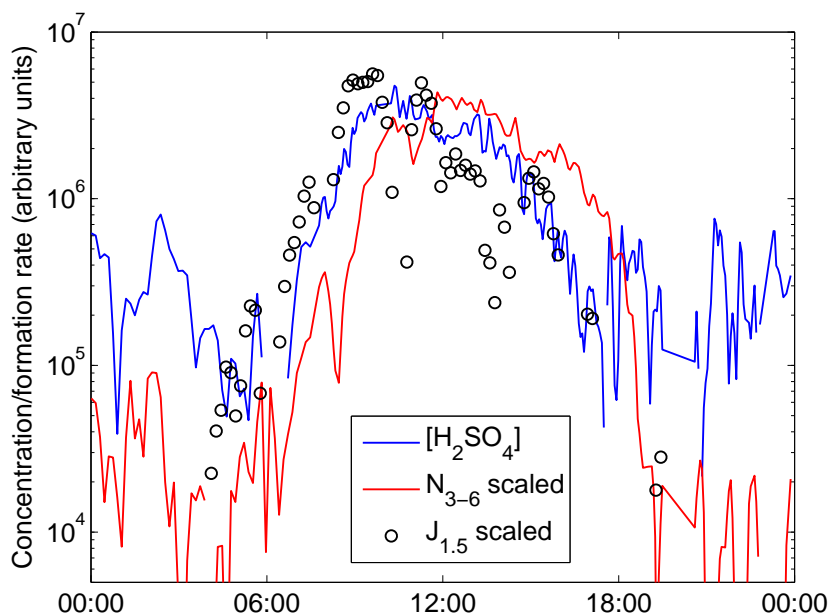


Figure 8: Measured sulphuric acid concentration, scaled 3–6 nm particle concentration, and scaled ( $A = 2.5 \cdot 10^{-7} \text{ s}^{-1}$ ) particle formation rate at 1.5 nm on 25.3.2003 in Hyttiälä.

Zhang et al., 2004b). The previous conditions naturally resemble those of the real atmosphere. These differences are illustrated in Fig. 9 (see also Laaksonen et al., 2008), which presents a summary of the particle formation rates as a function of sulphuric acid concentrations, as derived from atmospheric data and different laboratory studies: approximately three orders of magnitude lower sulphuric acid concentrations are required for the same nucleation rate if the acid produced in situ rather than taken from a liquid sample. It is also notable that the experiments using sulphuric acid produced in situ are roughly in accordance with the atmospheric data. This might indicate that the connection between particle formation and sulphuric acid does not actually point to direct involvement of sulphuric acid molecules in nucleation, but rather some other sulphur-containing molecules which correlate with sulphuric acid and are formed in the similar reactions.

The CPCB data presented in **Paper IV** revealed that the freshly formed aerosol particles are clearly more soluble in water than in butanol, close to both 2–3 and 8–9 nm. This observation supports the idea that sulphurous constituents do contribute



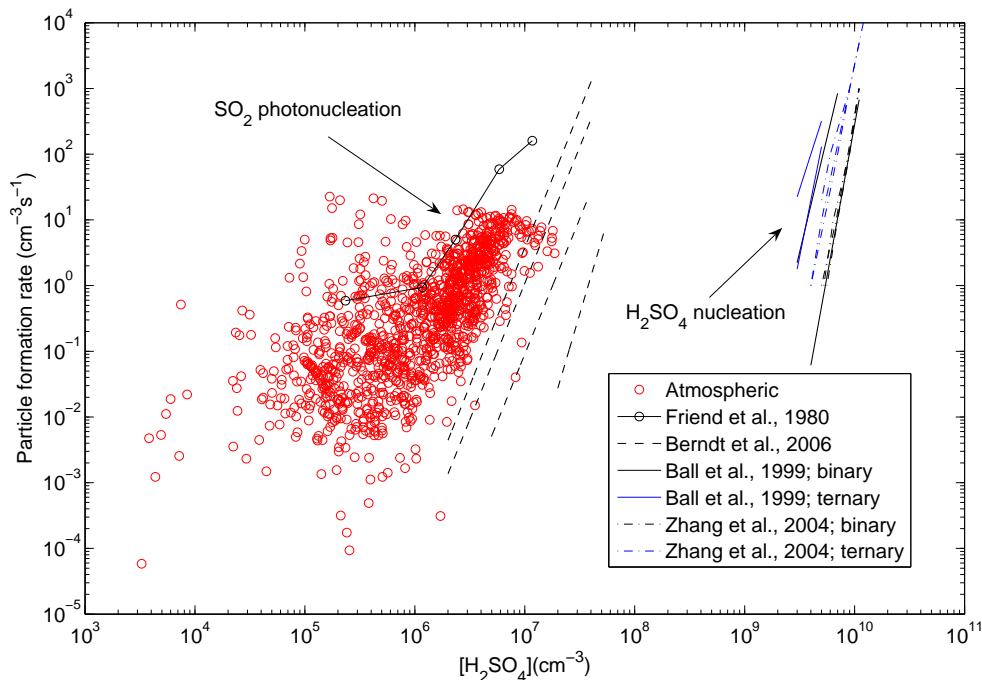


Figure 9: Nucleation rates from atmospheric observations and the binary water-sulphuric acid nucleation experiments of Friend et al. (1980) and Berndt et al. (2005; 2006) along with the binary and ternary experiments of Ball et al. (1999, water, sulphuric acid and ammonia) and Zhang et al. (2004b, water, sulphuric acid and organic acids) as a function of the sulphuric acid gas concentration. The different lines in the same experimental data sets correspond to different relative humidities.

significantly to the formation and growth of secondary particles, as sulphuric acid and related compounds such as ammonium sulphates are highly water-soluble. It was also noted that close to 8–9 nm the hygroscopicity seemed to increase with increasing sulphuric acid concentrations, indicating that increase in the gaseous phase sulphuric acid promotes its contribution to the growth from 2 to 9 nm. Interestingly this was not the case for the 2–3 nm particles, in other words the hygroscopicity of the very smallest particles did not seem to be controlled by the sulphuric acid concentrations.

The results on the water-solubility of 2–9 nm particles reported in **Paper IV** suggest, however, that although clearly hygroscopic, the freshly formed aerosol is generally less water-soluble than pure sulphate particles would be. This observation is in line with the particle growth rate analysis of Boy et al. (2005), Hirsikko et al. (2005) and Fiedler

et al., (2005), which report that even at the smallest sizes the observed particle growth rates cannot be explained by the condensational growth due to sulphuric acid alone. Both of these observations point to the role of atmospheric organic vapours in particle formation and growth.

## 4.2 Indications on the role of organic vapours

A clear link between atmospheric aerosol formation and the emissions of biogenic organics has been reported, particularly at continental sites (e.g. Kavouras et al., 1999; Kulmala et al., 2004b; Tunved et al., 2006). There are also significant amounts of laboratory data showing that the VOCs typically emitted by vegetation, for instance isoprene (Claeys et al., 2004a; 2004b), mono- (Pandis et al. 1991; Hoffmann et al., 1997) and sesquiterpenes (Bonn and Moortgaat, 2003), can act as precursors for condensable vapours forming and growing secondary aerosol particles.

In **Paper I** we reported, based on the AIS, BSMA, and DMPS data, that the particle diameter growth rates during particle formation events in Hyytiälä seemed to be clearly size-dependent. The growth rates consistently increase with particle size, suggesting that more material condenses on the particles as they grow. In **Paper I** this was seen as evidence of atmospheric particle formation being a two-step process, i.e. that the vapour nucleating and contributing to the initial steps of the growth are different from those growing the particles to CCN sizes. In the light of the observed close connection between atmospheric nucleation rates and sulphuric acid, it is likely that sulphurous compounds are present at the early stages of particle formation and growth. On the other hand, as mentioned also earlier, sulphuric acid condensation is not enough to explain the observed particle growth rates, pointing to the increasing role of organics in the later stages of the condensational growth processes.

Kulmala et al. (2004c) formulated the contribution of condensable organics in particle growth with the "nano-Köhler theory" (see also Anttila et al., 2004): the particles need to grow past a certain critical size to be able to grow further by the condensation of organics, similarly with the traditional Köhler theory of cloud droplet activation with water vapour (see e.g. Pruppacher and Klett, 1997). However, the observed increase in the growth rates with particle size could also be interpreted as an increase with time, as the photochemical production of condensable vapours increases with increasing sunlight. This would mean that the particle growth rates are limited by

the condensable vapour production, rather than the particle size. However, both ways of interpreting the data are consistent with the increasing role of organics, or at least the increasing variety of condensing vapours, as the particles pass the initial stages of growth.

The seasonal variation of growth rates as a function of size also supports the idea that the major condensation of organics starts after the particles have reached a certain size (for monthly median values of 1.5–3, 3–7 and 7–20 nm growth rates see Fig. 10 and Hirsikko et al., 2005). The growth rates of the 7–20 nm particles show a clear seasonal variation peaking in the summertime, whereas the 1.5–3 nm particles seem to grow with a similar rate throughout the year. The summer maximum coincides with the maximum in the emissions of biogenic organic vapours in Hyytiälä (Hakola et al., 2003; Tarvainen et al., 2007), showing correlation between atmospheric organics and the growth rates of the larger particles. Using eight years of DMPS data from Hyytiälä, Dal Maso et al. (2005) also reported a clear increase during summer in the 3–25 nm growth rates, whereas the particle formation rates were reported to peak in spring and autumn, similarly with the particle formation event frequencies (Fig. 2). This observation also supports the idea of atmospheric particle formation as a two-step process: the particle formation and further growth seem to be uncoupled (see also Kulmala et al., 2000).

The results on the water-solubility of the 2–9 nm particles, reported in **Paper IV**, also show indications on the role of organics in particle formation and growth. It was observed that the particles seem to become less hygroscopic as they grow in size. This is in line with the speculation on the increasing role of organic condensation as the particles grow in the atmosphere. It is also possible that the condensing organics oligomerize (Kalberer et al., 2004), catalysed by particulate phase sulfuric acid (Jang et al., 2002; Limbeck et al., 2003), and form a non-volatile - and probably also less hygroscopic - growing core to the particle, as has been observed also in previous studies (Wehner et al., 2005; Ehn et al., 2007a). On the other hand, as stated earlier, even the smallest 2–3 nm particles seem to be less hygroscopic than pure sulphuric acid or ammonium sulphate. This might mean that organics are present, although to a smaller extent, even at the very first steps of particle formation and growth. The size-dependent growth rates presented in Fig. 10 also indicate that sulphuric acid does not seem to be solely responsible for growth even in the smallest sizes: the typical 1.5–3 nm growth rates are approximately 1.5–2 nm/h, when the ambient sulphuric acid concentrations

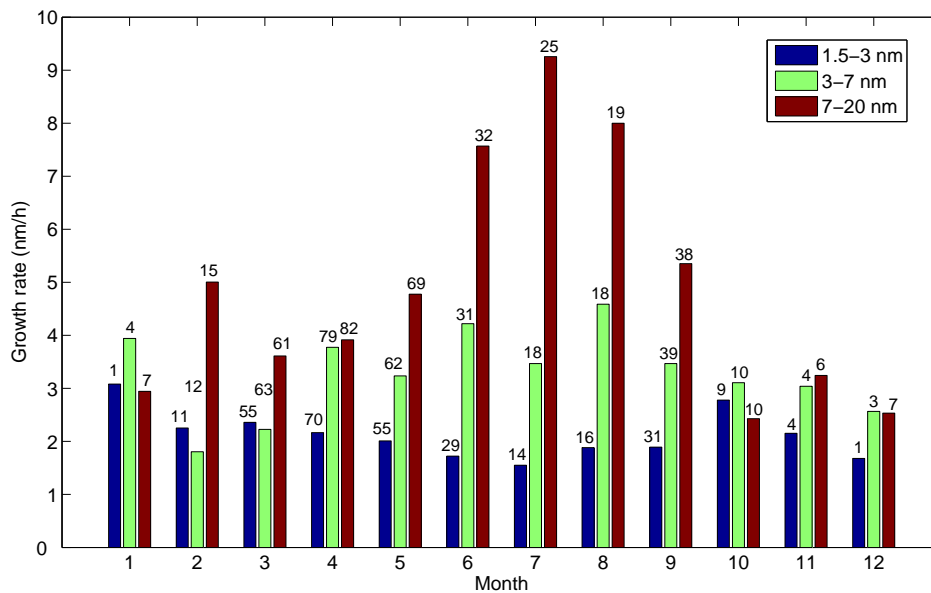


Figure 10: The median monthly growth rates of 1.5–3, 3–7 and 7–20 nm particles, as determined from the DMPS, AIS and BSMA data for years 2003–2007. The numbers refer to analysed particle formation events (courtesy of Ms. Taina Yli-Juuti, see also Hirsikko et al., 2005).

in Hyytiälä would explain particle growth rates of the order of 0.1–1 nm/h (e.g. Boy et al., 2005).

## 5 On the role of molecular clusters in atmospheric nucleation

It has been observed in several studies that homogeneous nucleation (i.e. the formation of particles from vapours without the presence of existing seed nuclei) is typically unable to produce atmospheric nucleation rates with atmospheric concentrations of the nucleating vapours (e.g. Spracklen et al., 2005a; 2005b), at least in the boundary layer. This is the case for binary water-sulphuric acid nucleation (Ball et al., 1999; Kulmala et al., 2006) as well as for ternary nucleation involving water, sulphuric acid and ammonia (Merikanto et al., 2007) or organics (Zhang et al., 2004b), which are thought to be the atmospheric vapours most likely to nucleate. Also, the observed linear or square relationship between atmospheric sulphuric acid and particle formation rates speaks against homogeneous nucleation of sulphuric acid as the main boundary layer nucleation mechanism, since in the case of homogeneous nucleation a significantly higher proportionality would be expected (Kulmala et al., 2006).

It has been suggested that the formation of new atmospheric aerosol particles is connected with the existence of small 1–2 nm clusters (Hoppel et al., 1994; Kulmala et al., 2000) that can act as seed particles for the nucleating vapours. Theoretical arguments predict the existence of such clusters (Kulmala et al., 2005; Kulmala et al., 2000), and suggest that they should play an important role in aerosol formation processes via their activation and growth by some condensable vapours (Kulmala et al., 2006). These clusters have been proposed to consist of sulphurous compounds (Kulmala et al., 2000; Hanson and Eisele, 2002; Vehkamäki et al., 2004b) or organics (Bonn et al., 2008). Cluster activation is closely related to heterogeneous nucleation: it has been known for decades that if seed particles are added to the vapour mixture, nucleation becomes energetically much more favourable, and smaller vapour concentrations are needed for particle formation (Fletcher, 1958).

Winkler et al. (2008) showed experimentally that the presence of nanometer-sized charged and neutral particles enhances nucleation significantly compared to the homogeneous case in the case of propanol vapour. Their results also indicate that the negatively charged clusters seem to activate with the lowest vapour concentrations, followed by the positively charged and neutral clusters. Finally, if the vapour concentration or saturation ratio increases further, homogeneous nucleation starts, resulting also in a higher proportionality between the nucleation rate and the vapour concentration as

compared with cluster activation. Atmospheric indications of the enhanced activation probability of negative air ions have been presented by Nieminen et al. (2007). A simplified scheme of the atmospheric particle formation processes outlined above and by e.g. Kulmala et al. (2007) is presented in Fig. 11.

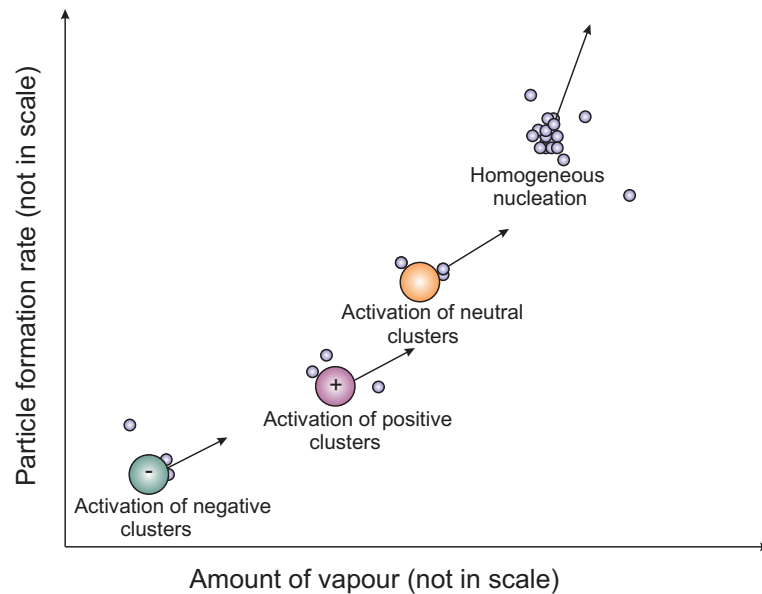


Figure 11: A schematic of atmospheric nucleation processes as a function of the amount of condensing vapour.

The hypothesis of cluster activation as the dominating particle formation mechanism results in a nucleation rate which is dependent on at least **1)** the concentration/saturation ratio of the condensing vapour; **2)** the concentration of the activated clusters; **3)** the activation probability of the clusters, which in turn depends on their charge and composition. According to calculations by Kulmala et al. (2006) the observed linear or square relationship between particle formation and sulphuric acid concentrations can be explained with cluster activation as the dominating atmospheric particle formation mechanism, depending on the composition of the clusters.

The existence of atmospheric ion clusters as small as 0.5–2 nm in diameter has been known for decades, and measurements with ion spectrometers, such as the AIS and BSMA, have demonstrated that such clusters are present practically all the time (Hörrak et al., 1998; Kulmala and Tammet, 2007). The production rates of ion clusters are, however, generally too low to explain the observed aerosol formation rates (Laakso et al., 2002; Eisele et al., 2006; Iida et al., 2006; Hirsikko et al., 2007). In

view of the insufficient numbers of ion clusters, the key to understanding atmospheric aerosol formation is clearly the presence of neutral clusters. However, until very recently (**Paper III**, Sipilä et al., 2008), no direct atmospheric evidence of the existence of neutral molecular clusters has been reported.

It is probable that no one or two compounds dominate the atmospheric cluster mode but that it is rather a mixture of clusters and molecules of various sizes and composition, depending on the ambient conditions. The results by Winkler et al. (2008) suggest that even the presence of some ionized pre-existing molecules might be enough to lower the nucleation barrier. The mixture of vapours capable of growing the clusters to larger sizes, that is, atmospheric vapours that have low enough saturation vapour pressures, might be much more specific. Fig. 12 shows the median diurnal behaviours of concentrations of negatively charged clusters in the BSMA channels corresponding to the size range 0.8–3.0 nm between April 2003 and March 2005, along with the median sulphuric acid (black line) on particle formation event (top) and non-event days (bottom). On the particle formation event days, concentrations in some of the larger channels (1.7–3.0 nm) seem to correlate with sulphuric acid, whereas a slight anticorrelation can be seen in the case of the smaller channels (1.1–1.4 nm). This behaviour can be interpreted as an indication of sulphuric acid activating the clusters/molecules in the smaller channels and growing them to larger sizes. Again, when discussing the composition of clusters to be activated, the role of organics comes into question. It is likely that part of the largest clusters/molecules observed in the atmospheric cluster modes consist of organics or organosulphates, as there are organic molecules present in the atmosphere that are considerably larger than, for instance, ammonium sulphates (e.g. Bonn et al., 2008).

## 5.1 On the concentrations of atmospheric neutral particles below 3 nm

In Figs. 3 and 5 we showed the size distributions measured by the AIS (positive and negative ions) and the NAIS (ions and neutral particles) on 24.4.2006 (see also **Paper III**). In both spectra, a clear particle formation and growth event can be seen. Both instruments also show a persistent pool of clusters below 2 nm. Similar pool of neutral clusters have also been observed by Sipilä et al. (2008), who use the PH-CPC and E-CPC techniques to observe particles below the detection limits of commercial

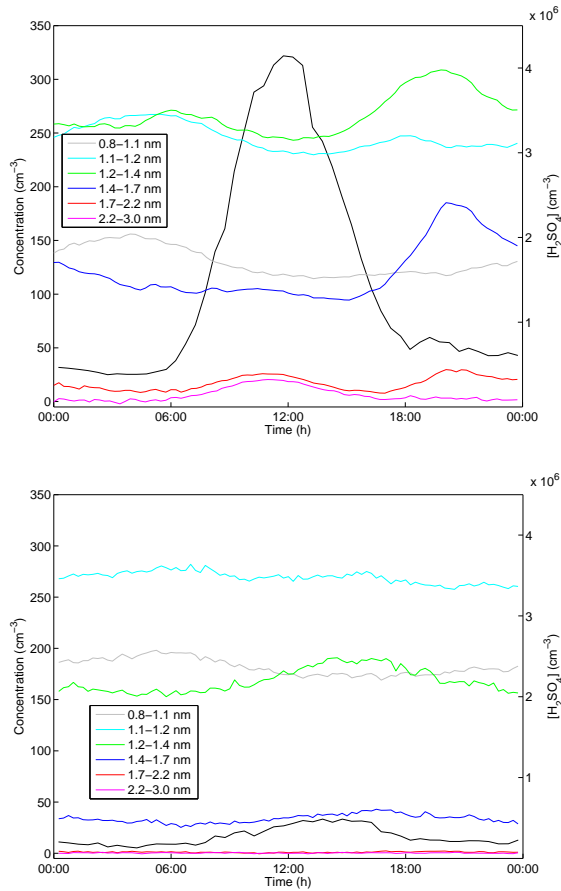


Figure 12: The median concentrations in the BSMA negative cluster channels, corresponding to the size range 0.8–3.0 nm (coloured lines), and ambient sulphuric acid (black line, calculated as described by Boy et al., 2005) on particle formation event (top) and nonevent (bottom) days between April 2003 and March 2005 (see Nieminen, 2008).

instruments. According to these pioneering studies, there does seem to be a persistent mode of atmospheric electrically neutral clusters, the concentration of which ranges from several thousands up to approximately  $100000 \text{ cm}^{-3}$ .

In **Paper III**, we also compared the 2–3 nm particle concentrations to those measured by the UF-02proto CPC pair, and a reasonable agreement was seen. These two independent measurements allow for particle measurements down to 2 nm, and, in the case of the NAIS, maybe even lower. This brings us closer to the direct detection of the atmospheric nucleation or cluster activation process, as it seems to happen close to 1.5–2



nm. These observations allow us, for instance, to calculate more reliable estimates for the atmospheric nucleation rates and the contribution of ions to particle formation, as well as estimate the cluster concentrations needed to explain the observed atmospheric nucleation rates.

The formation rates at 2 nm ( $J_2$ , including both charged and neutral particles) can be calculated from the 2–3 nm concentration data as

$$J_2 = \frac{dN_{2-3}}{dt} + CoagS_{2-3} \cdot N_{2-3} + \frac{GR_{2-3}}{1\text{nm}} N_{2-3}, \quad (3)$$

where  $t$  is the time,  $N_{2-3}$  is the 2–3 nm particle concentration,  $GR_{2-3}$  is the 2–3 nm growth particle rate, which can be estimated from the ion spectrometer data as described in **Paper I**, and  $CoagS_{2-3}$  is the coagulation sink for the 2–3 nm particles, expressed as (see Kulmala et al., citeyearkulmala2001)

$$CoagS(D_p, t) = \int_{D_{p0}}^{\infty} \beta(D_p, D'_p) n(D'_p, t) dD'_p, \quad (4)$$

where  $\beta$  is the collision frequency function for particles with sizes  $D_p$  and  $D'_p$  (see e.g. Seinfeld and Pandis, 2006). Then, assuming that **1**)  $J_2$  can be written as the sum of ion and neutral formation rates, i.e.

$$J_2 = J_2^+ + J_2^- + J_2^n, \quad (5)$$

where  $+$  and  $-$  refer to the polarities of the air ions and  $n$  to neutral particles; **2**) cluster activation and growth is the dominating nucleation mechanism; and **3**) that the activation probability of the ion clusters is always equal or larger than for neutral clusters (as was observed by Winkler et al., 2008), a minimum estimate for the neutral cluster concentrations can be calculated. For the details of the calculations see the Supporting Information of **Paper III**. In **Paper III**, these calculations were done for four example days, and neutral cluster concentrations of at least 7000–50000  $\text{cm}^{-3}$  were predicted for Hyytiälä conditions.

## 6 The contribution of ions to nucleation and particle growth

As discussed in the previous section, it has been shown both theoretically (e.g. Thomson, 1906; Kusaka et al., 1995) and experimentally (e.g. Katz et al., 1994; Winkler et al., 2008) that electrical charge enhances nucleation in both homogeneous and heterogeneous case by lowering the size of the critical cluster. Nadykto and Yu (2003) also argued, based on their model calculations, that the condensational growth of aerosol particles might as well be enhanced by electrical charging. In the atmosphere, on the other hand, molecules and clusters are known to be constantly ionized by the cosmic radiation, gamma radiation from the ground and airborne radionuclides (see e.g. Laakso et al., 2004b; Hirsikko et al., 2007). It has therefore been proposed that ions play a significant role in regulating atmospheric nucleation processes (Yu and Turco, 2000). Svensmark and Friis-Christensen (1997) even speculated the atmospheric ionization rates to be a major driving factor for global temperature changes through their interactions with clouds. However, depending on the study and the site, the estimates for the contribution of ion-induced nucleation seem to vary from negligible to 100 % of the total particle formation rates (Lee et al., 2003; Lovejoy et al., 2004; Iida et al., 2006; Eisele et al., 2006; **Paper III**; Yu et al., 2007; Laakso et al., 2007). To solve these discrepancies between different approaches, more laboratory and field data are crucially needed.

Atmospheric ions may affect the observed particle formation by **1)** enhancing homogeneous nucleation; **2)** enhancing the activation and growth of charged clusters; **3)** enhancing the growth rates of small charged particles; **4)** forming neutral atmospheric clusters (that can be activated and grown by vapours) by ion-ion recombination. In **Paper III** we estimated the contribution of ions to particle formation by calculating ion formation rates (i.e. the rates at which cluster ions are activated at 2 nm) according to

$$J_2^\pm = \frac{dN_{2-3}^\pm}{dt} + CoagS_{2-3} \cdot N_{2-3}^\pm + \frac{GR_{2-3}}{1nm} N_{2-3}^\pm + \alpha N_{2-3}^\pm N_{<3}^\mp - \beta N_{2-3}^\pm N_{<3}^\pm, \quad (6)$$

where + and - refer to the sign of the charge. The rates were then compared to the corresponding total rates calculated according to Eq. 3 from the NAIS and UF-02proto data, and used to estimate the neutral cluster concentrations as described

in the previous section. In the four example particle formation event days shown in **Paper III**, the ion formation rates contribute approximately 2–20 % to the total rates, depending on the day.

Medians of the 2 nm charged and neutral formation rates for both polarities and all the used instruments for spring 2006 (6.3.-31.5.2006) are presented in Fig. 13 (see also Riipinen et al., 2007). The days with clear positive or negative overcharging at 3 nm as observed with the ion-DMPS system have been separated from undercharged or neutral days (for details see Laakso et al., 2007; Kerminen et al., 2007). First, it can be seen that the magnitudes of the formation rates are consistent using different instruments. Second, the ion formation rates are clearly lower than the total formation rates. Third, it seems that the formation rates are highest on the days with undercharging detected with the Ion-DMPS. This supports the idea that also in the atmosphere the ions require less vapour to activate for growth than the neutral particles. As we know that there are always ion clusters present in Hyytiälä, this means that some fraction of atmospheric nucleation is always explained by the activation of ion clusters. However, we also know that the number of the activated ions is usually too small to account for the total rates. So, as depicted in Fig. 11, with increasing vapour concentration more and more neutral clusters start to activate and contribute to particle formation. If the vapour concentration increases further, it is possible that homogeneous nucleation starts to dominate. According to our observations, in particular in view of the linear or square relationship between particle formation and sulphuric acid, this is not likely to be the case in Hyytiälä. However, at locations with higher vapour production rates or lower sinks, for instance in the middle or upper troposphere (Lovejoy et al., 2004; Spracklen et al., 2005a; 2005b) or at urban sites with high sulphuric acid concentrations, homogenous nucleation might dominate.

Besides directly enhancing the nucleation of vapours, atmospheric ions may promote particle formation by colliding with each other and thus forming stable neutral clusters that can later be activated for growth. To assess this ion-mediated fraction of the neutral clusters, we estimated the maximum cluster concentrations produced by ion-ion recombination in **Paper III**. Steady state estimates for these cluster concentrations were obtained using the ion cluster measurements from the BSMA, and setting the balance equation

$$\frac{dN_{n,rec}}{dt} = a\alpha N_i^+ N_i^- - \beta N_{n,rec}(N_i^+ + N_i^-) - CoagS(N_{n,rec}N_{n,rec}) \quad (7)$$

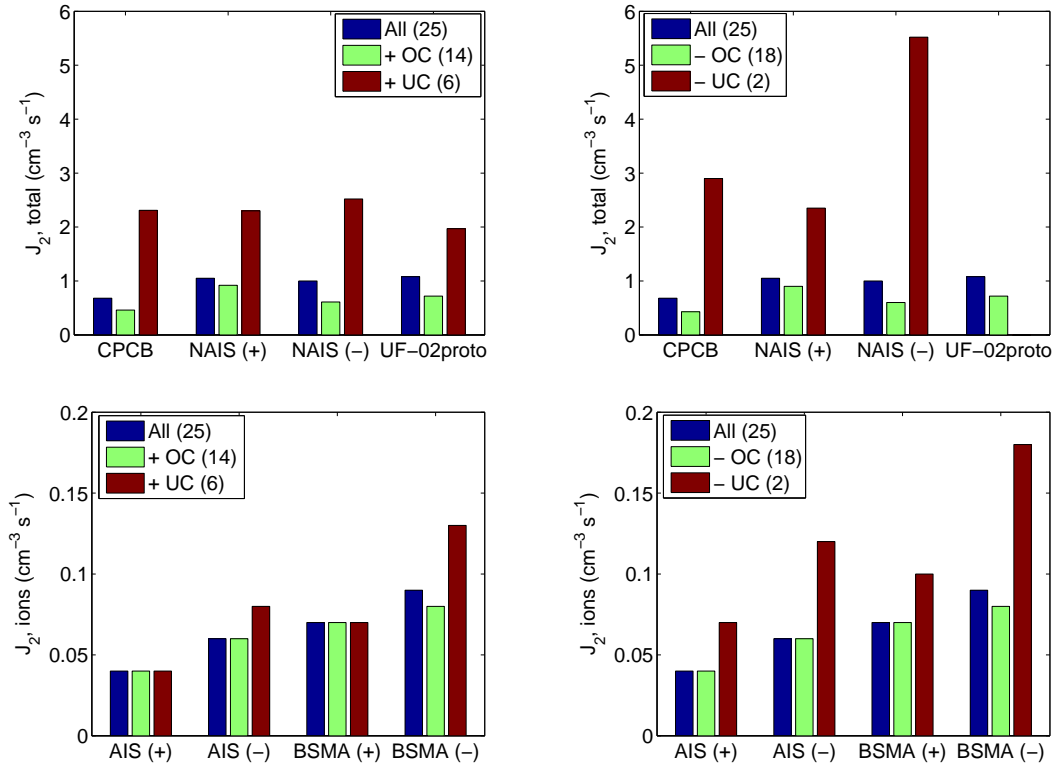


Figure 13: The medians of total (top) and charged (bottom) particle formation rates at 2 nm during spring 2006. The ion formation rates have been calculated from the BSMA and AIS data, and the total rates from the NAIS, UF-02proto CPC pair and CPCB data. The data have been grouped according to positive over- or undercharging (marked in the legend as +OC or +UC) on the left, and according to negative over- or undercharging (marked as -OC and -UC) on the right. The numbers in the legends refer to analysed cases during the measurement period.

to zero. In Eq. 7 the subscript  $n, rec$  refers to neutral clusters produced by ion-ion recombination,  $i$  to ion clusters and +/- to their polarity.  $a$  is the fraction of stable recombination products,  $\alpha$  the ion-ion recombination coefficient, and  $\beta$  the aerosol-ion attachment coefficient. Values of  $1.6 \cdot 10^{-6} \text{ cm}^3\text{s}^{-1}$  and  $0.01 \cdot 10^{-6} \text{ cm}^3\text{s}^{-1}$  were used for  $\alpha$  and  $\beta$ , respectively (Tammet and Kulmala, 2005). The maximum estimates were obtained by setting  $a$  to unity. On the four days presented in **Paper III**, the maximum neutral cluster concentrations resulting from recombination ranged from 115 to  $833 \text{ cm}^{-3}$ . These numbers correspond to at most 0.2–10 % of the minimum estimates of the neutral cluster concentrations, calculated as described in the previous section.

The charge-enhancement of particle growth rates (Nadykto and Yu, 2003) is another open question related to atmospheric aerosol formation and growth. The size dependent growth rates determined in **Paper I** give one point of view to this discussion. It was concluded that the atmospheric particle growth rates increase with size, whereas with solely ion-enhanced particle growth, a clear decrease with particle size would be seen (Lushnikov and Kulmala, 2004). This observation naturally does not rule out the case that ion-enhanced particle growth could play some role in the atmosphere, but clearly it is not the dominating effect determining the growth dynamics of atmospheric particles. It is even likely, according to detailed model simulations with the ion-UHMA model (Korhonen et al., 2004; Leppä, 2007), that the growth of the ion population observed with the AIS and BSMA actually follows that of the total (charged + neutral) aerosol. This results from the fact that the timescale of the atmospheric particle growth is typically much longer than the timescales related of the charging and neutralization of the particles.

## 7 Condensational growth properties of atmospheric organic vapours

Due to the wide variety of atmospherically relevant organic compounds, specific information on their ability to form particles and CCN is lacking for a large part. This results in large uncertainties in the secondary organic aerosol production predicted by current models (Volkamer et al., 2006). Recent papers by Kanakidou et al. (2005) and Seinfeld and Pankow (2003) stress the need of laboratory and modelling studies of the particle formation and growth potential of different organic species to be able to more accurately predict their partitioning between gas and condensed phase. Instead of treating each compound individually, methods based on, for instance, functional groups can be used (Asher et al., 2002 and references therein). Donahue et al. (2006), on the other hand, recently presented a framework where semivolatile organics are divided into bins according to their volatility. The framework can be used to model e.g. the partitioning, dilution and aging of atmospheric organics. However, even basic laboratory data against which these models could be tested are scarce, when it comes to compounds with potential relevance in particle formation and growth.

The partitioning of a compound between gas and condensed phases is mainly governed by its saturation vapour pressure and activity in the particulate phase (see e.g. Pankow, 1994). Therefore information on these properties, along with the liquid phase surface tensions, are needed in both nucleation and condensation studies on atmospheric organics. Direct measurements on saturation vapour pressures of compounds with low volatility are, however, challenging, as the very low saturation vapour concentrations are extremely difficult to detect. The low volatility compounds, on the other hand, are the ones most likely to partition in the particulate phase. Instead of detecting the saturation vapour pressure directly, one can infer it by detecting the condensation or evaporation rates of the studied compounds, and modelling them with a condensation/evaporation model. This is convenient and accurate, as the condensational growth and evaporation of liquid droplets is theoretically one of the most well-understood aerosol dynamic processes (e.g. Vesala et al., 1997). Accurate condensational growth modelling is thus mostly a question of accurate thermodynamics.

Aliphatic straight-chain dicarboxylic acids such as malonic, succinic, glutaric and adipic acids are water-soluble organic acids that are commonly found in atmospheric aerosol samples (Grosjean et al., 1978; Kawamura et al., 1996; Röhr and Lammel, 2002; Yu

et al., 2006). This implies that they partition to the condensed phase and therefore affect the formation and growth as well as the cloud droplet activation properties of aerosol. To understand these effects, information on the thermophysical properties of these acids is required. Malonic, succinic, glutaric and adipic acids have a general formula of  $\text{HOOC}(\text{CH})_n\text{COOH}$ , and are often referred to according to their carbon number (C3, C4, C5, C6 respectively). All the pure acids are solid under atmospheric conditions, but as theoretically shown by Marcolli et al. (2004), as the molecules are mixed in the particle phase, the liquid state could be the thermodynamically stable phase in atmospheric conditions. Solid state vapor pressures of these acids have been derived by Tao and McMurry (1989), Bilde and Pandis (2001), Bilde et al. (2003) using a TDMA system, by Ribeiro da Silva et al. (1999) with effusion methods, and most recently by Chattopadhyay and Ziemann (2005) and Cappa et al. (2007) with temperature programmed thermal desorption methods. The magnitudes of the reported vapor pressures are relatively low ( $10^{-6}$ – $10^{-3}$  Pa, varying significantly between different studies), suggesting that the acids may contribute to secondary aerosol formation. Apart from a study by Zardini et al. (2006) for malonic acid, measurements on the liquid phase vapour pressures of these acids were, however, missing.

In **Paper V** we present a method to determine the liquid phase vapor pressures of the dicarboxylic acids. The method is based on measuring the evaporation rates of aqueous acid solution droplets and modelling the evaporation with an accurate binary condensation model (see e.g. Vesala et al., 1997). In **Papers VI–VII** we applied the method to determine the subcooled liquid vapor pressures of the C3–C6 dicarboxylic acids. In **Paper VII** we also presented measurements and a parameterization for the surface tension of adipic acid aqueous solution.

## 7.1 Evaporation rate measurements

The evaporation rate measurement technique used in **Papers V–VII** is based on a Tandem-DMA system (Rader and McMurry, 1986), which has been modified to study aqueous liquid droplets (see Bilde et al., 2003). A schematic of the system is presented in Fig. 14 (see also **Paper VI**). Aqueous solution droplets were first generated by atomizing aqueous solutions of the studied species, after which an almost monodisperse fraction of the droplet population was selected with a DMA. The selected droplets were allowed to evaporate in a laminar flow reactor with a known flow rate and length.

During the evaporation, the droplet size was measured from four sampling ports along the length of the flow tube, yielding the droplet size as a function of time. Relative humidity and temperature were controlled throughout the system.

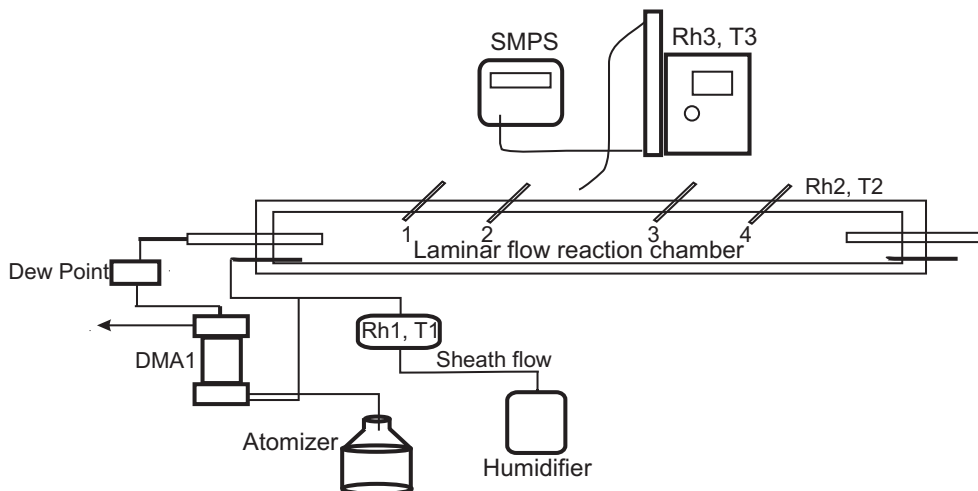


Figure 14: Schematic figure of the TDMA system used to study the evaporation rates of aqueous solution droplets of dicarboxylic acids. T and Rh refer to temperature and relative humidity measurements, respectively.

## 7.2 Evaporation modelling

The evaporation rates of the aqueous solution droplets of dicarboxylic acids were modelled with a binary condensation model BCOND (Vesala et al., 1997), to infer the saturation vapour pressures for the liquid phase acids. The model essentially solves the mass and heat transfer to/from a population of droplets in a gas mixture where no nucleation or coagulation takes place (see Kulmala and Vesala, 1991). This is done in practice by solving coupled differential equations for the droplet mass and composition, temperatures and partial vapour pressures of condensing/evaporating vapours far away from the droplet and at the droplet surface assuming a quasi-steady state. A schematic figure of the modelled system is presented in Fig. 15.

The mass flux of compound  $j$  to the droplet is calculated according to Kulmala and Vesala (1991):



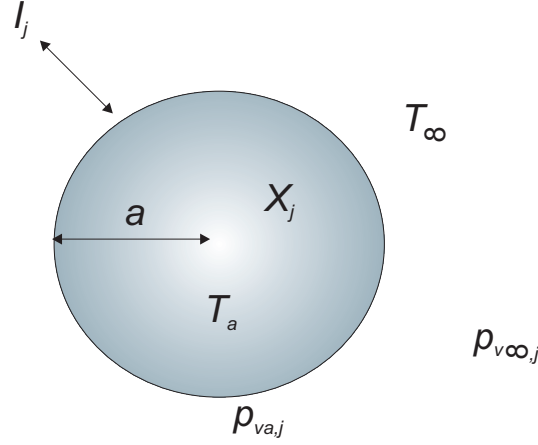


Figure 15: Schematic figure of the system modelled in the condensation/evaporation models.  $I_j$  refers to the mass flux of compound  $j$ ,  $a$  to the droplet radius,  $X_j$  to the mole fraction of  $j$  in the droplet, and  $T_a$ ,  $p_{va,j}$ ,  $T_\infty$  and  $p_{v\infty,j}$  to the temperatures and partial vapour pressures of  $j$  at the droplet surface and far away from the droplet.

$$I_j = \frac{4\pi a p M_j \beta_{m,j} D_j}{RT_\infty} \left[ C_j \ln \left( \frac{1 - \frac{p_{va,j}}{p}}{1 - \frac{p_{v\infty,j}}{p}} \right) \right], \quad (8)$$

where  $a$  is the droplet radius,  $p$  is the total pressure,  $M_j$  is the molar mass of the condensing species and  $D_j$  its diffusivity with respect to the gas mixture and  $T_\infty$  the temperature far away from the droplet.  $C_j$  is a temperature-dependent function taking into account the temperature dependence of the diffusion coefficient.  $\beta_{m,j}$  is the transitional correction factor for mass transfer (Fuchs and Sutugin, 1970)

$$\beta_{m,j} = \frac{1 + Kn_j}{1 + \left( \frac{4}{3\alpha_{m,j}} + 0.377 \right) Kn_j + \frac{4}{3\alpha_{m,j}} Kn_j^2}, \quad (9)$$

where  $Kn_j$  is the Knudsen number for the vapour  $j$  with respect to the studied particle, and  $\alpha_{m,j}$  the mass accommodation coefficient of vapour  $j$ . In the quasi-steady state, the vapour pressure of at the droplet surface during each time step corresponds to the equilibrium vapour pressure

$$p_{va,j} = p_{j,eq} = \Gamma_j X_j p_{j,sat} \exp \left( \frac{2\sigma v_{j,l}}{k_B T_a a} \right), \quad (10)$$

where  $\Gamma_j$  is the liquid phase activity coefficient of  $j$  the studied mixture,  $X_j$  the mole fraction of  $j$  in the droplet,  $p_{sat,j}$  represents the saturation vapour pressure of pure  $j$  over a flat surface,  $\sigma$  is the surface tension of the droplet,  $v_{j,l}$  the partial molecular volume of  $j$  in the droplet, and  $T_a$  the droplet temperature.

The heat transfer rate  $Q$  from the droplet is calculated according to Wagner (1982):

$$Q = 2\pi\beta_T a(k_a + k_\infty)(T_a - T_\infty) - \sum_{j=1}^n H_{jv} I_j, \quad (11)$$

where  $k_a$  and  $k_\infty$  are the thermal conductivities of the gas mixture at the droplet surface and far away from the droplet, and  $H_{jv}$  is the latent heat of evaporation of compound  $j$ .  $\beta_T$  is the transitional correction factor for heat transfer

$$\beta_T = \frac{1 + Kn_T}{1 + \left(\frac{4}{3\alpha_T} + 0.377\right)Kn_T + \frac{4}{3\alpha_T}Kn_T^2}, \quad (12)$$

where the Knudsen number has now been defined with the mean free path of the inert gas (in our case air).  $\alpha_T$  is the thermal accommodation coefficient.

The saturation vapour pressure values corresponding to the subcooled liquid phase acids were inferred from each data set (with different temperatures and relative humidities for different acids) by matching the modelled evaporation with the experimentally observed reduction in the particle diameter. As all the other relevant thermophysical properties could be found from the literature, this was done by varying the saturation vapour pressures of the acids.

### 7.3 Saturation vapour pressures of C3–C6 dicarboxylic acids

In **Papers V–VII** we presented evaporation rate measurements and the corresponding subcooled liquid phase saturation vapour pressures of the C3–C6 dicarboxylic (malonic, succinic, glutaric and adipic) acids at temperatures close to room temperature. We also presented temperature-dependent parameterisations of these vapour pressures, including the vapour pressures measured in our study and the boiling points of the acids. The obtained subcooled liquid vapour pressure values are presented at 298 K as a

function of the carbon number of the acids in Fig. 16, and compared to a representative selection of literature values (Bilde et al., 2003; Zardini et al., 2006; Cappa et al., 2007). The vapour pressures of the pure liquid phase acids are of the order of  $10^{-4}$ – $10^{-3}$  Pa ( $10^1$   $\mu\text{g m}^{-3}$ ). This is at the higher end of the volatility range still able to partition into the particulate phase, according to the "educated guess" by Donahue et al. (2006), suggesting that, in atmospheric conditions, these acids are unlikely to nucleate or condense in large amounts as such or as binary aqueous solutions. However, they can partition in the mixed particulate phase, as their equilibrium vapour pressures over real atmospheric particles might be significantly affected by the presence of some other compounds (see Eq. 10).

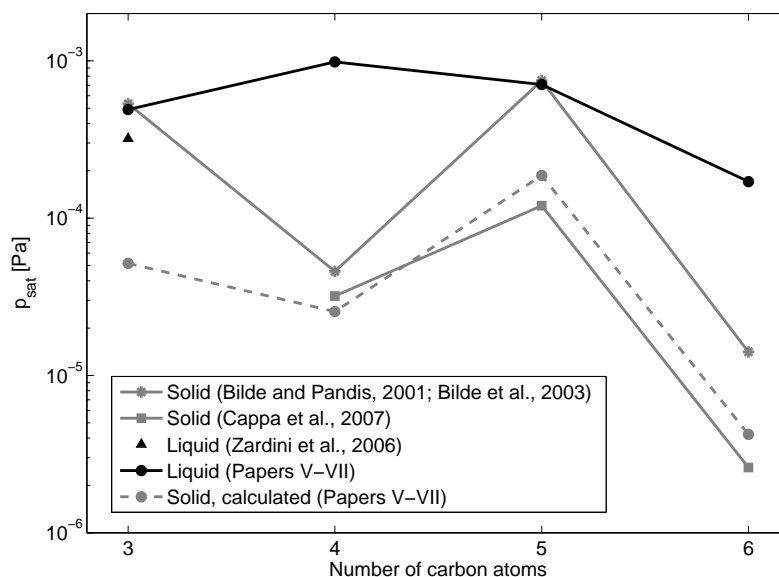


Figure 16: The saturation vapour pressures of malonic (C3), succinic (C4), glutaric (C5) and adipic (C6) acids at 298 K as a function of the carbon number.

The liquid phase saturation vapour pressure data determined in the work described in this thesis also contributes to the discussion about the solid state saturation vapour pressures of the acids. Depending on the study, the solid state vapour pressures of the dicarboxylic acids, particularly the odd acids, differ significantly. The solid state vapour pressures reported by Bilde and Pandis (2001), Bilde et al., (2003) and Cappa et al. (2007) are presented in Fig. 16 to represent the range of solid state values reported in the literature. The solid state values predicted from the liquid state values

determined in **Papers V-VII** are also presented (grey dashed line, see e.g. Prausnitz et al., 1986 for the prediction method). It can be seen that the liquid phase values presented in this work seem to be consistent with those presented by Cappa et al. (2007), although the methods used in the studies are quite different. In comparison with the work of Bilde and Pandis (2001) and Bilde et al. (2003), on the other hand, the liquid phase data for the odd acids reported in **Papers V-VI** seem to coincide with the solid state data. Assuming that the results presented in **Papers V-VII** are correct, one explanation for these results is that the presumably dry droplets studied by Bilde and Pandis (2001) and Bilde et al. (2003) might have contained some water, as speculated by Zardini et al. (2006) and Cappa et al. (2007).

## 8 Review of papers and the author's contribution

**Paper I** investigates the size-dependence of the particle growth rates in Hyytiälä (Finland), and compares the observations to the predictions of different hypotheses on the particle growth mechanisms. It is concluded that the particle growth rates seem to increase with size, indicating e.g. that **1)** the growth rate enhancement due to the charging of the particles seems not to play a role; **2)** the role of organic condensation increases with increasing particle size. It is suggested that the condensation of organics might display "nano-Köhler" -type behaviour, where the freshly formed particles are activated for growth by some condensing vapours, similarly as cloud droplets are activated for growth with water vapour (in traditional Köhler theory). In this work I contributed to the growth rate analysis and to a minor part of the writing.

**Paper II** reports a clear correlation between ambient sulphuric acid and 3–6 nm particle concentrations and formation rates, measured in Heidelberg (Germany) and Hyytiälä (Finland). It is concluded that sulphuric acid is likely to play a major role in the atmospheric new particle formation and growth episodes. The particle formation rates are reported to be proportional to sulphuric acid concentrations with either linear or square relationship. Cluster activation and kinetic nucleation are cited to explain these observations. I contributed in improving the data analysis methods used in the study, and did a major part of the data analysis and writing of the paper.

**Paper III** presents the first steps towards the direct detection of atmospheric nucleation. The results obtained with several individual measurements on neutral and charged atmospheric particles suggest that **1)** there is a continuous pool of numerous neutral clusters in the sub- 3 nm size range, **2)** the processes initiating atmospheric aerosol formation start from sizes around 1.5–2 nm, and **3)** neutral nucleation dominates over the ion-induced mechanism at least in boreal forest conditions. The first conclusion is in line with the observation on the linear (or square) relationships between sulphuric acid and new particle formation rates, as reported in **Paper II**. I contributed in designing the data analysis, did a major part it, and wrote a substantial part of the paper.

**Paper IV** contains the analysis of field data measured with the CPCB in Hyytiälä during spring 2006. The water-solubility and the composition of 2–9 nm particles, in particular the relative role of sulphuric acid and organics, is discussed. It is observed that the freshly-formed aerosol are more hygroscopic at sizes close to 3 nm than at 9 nm,

suggesting that the role of organics in the condensational growth of particles increases with the particle size, consistently with **Paper I**. However, it is also noted that the contribution of organics is needed to explain the results also near 3 nm: the ambient aerosol seems to be less hygroscopic than pure ammonium sulphate or sulphuric acid would be. In this paper I participated in designing the study, did a major part of the data analysis, and wrote most of the paper.

**Paper V** introduces a method for determining thermophysical properties, in particular saturation vapour pressures and vaporization enthalpies, of atmospheric organics with low volatility. The method combines the use of evaporation rate measurements with a laminar flow reactor to corresponding model calculations with a detailed evaporation/condensation model. As a first result, the saturation vapour pressure of succinic acid in subcooled liquid phase is reported. I contributed in designing the approach, did all the model calculations and the related data analysis presented in the paper, and wrote most of the paper.

**Paper VI** reports the subcooled liquid saturation vapour pressures for malonic, succinic and glutaric acids (C3-C5 dicarboxylic acids), as determined with the method presented in **Paper V**. The results are compared with the available literature data. I did all the model calculations and the related data analysis, and contributed to a major part of writing.

**Paper VII** presents results on the surface tension and subcooled liquid vapour pressures of adipic acid (C6 dicarboxylic acid), using the methodology of **Paper V**. Also a more complete set of data on the saturation vapour pressure of malonic acid is presented as a continuation for **Paper VI**. The results are compared to available literature data. Also, previous, partly contradictory, results on the solid state vapour pressures of C3-C6 dicarboxylic acids are discussed in the light of the subcooled liquid phase results. In this paper, I did all the calculations related to the saturation vapour pressure results. I also wrote most of the paper.

## 9 Conclusions and discussion

In the work presented in this thesis we studied atmospheric particle formation and growth in a two-fold way. On one hand, we analysed field measurements on the first steps of atmospheric particle formation and growth. On the other hand, we used detailed laboratory experiments and process modelling to determine condensational growth properties, such as saturation vapour pressures, enthalpies of vaporisation and surface tensions of dicarboxylic acids, which are organic acids often found in atmospheric samples. Our main conclusions are as follows:

1) At least in the boreal forest region, both sulphurous compounds and organics are needed for secondary particle formation and growth.

Ambient sulphuric acid concentrations showed a strong correlation with the observed particle formation rates, whereas the particle growth rates, particularly those of over 7 nm particles, seem to be correlated with the emissions of biogenic organics. It became clear that sulphuric acid alone is not likely to be the only component of the freshly formed particles. First, the ambient sulphuric acid concentrations were not enough to explain the observed particle growth rates. Second, we observed that even close to 2 nm, the atmospheric particles are usually less hygroscopic than pure ammonium sulphate of sulphuric acid would be. This suggests that the atmospheric organics participated even in the very first steps of particle formation and growth, although their importance significantly increased with particle size. Broadly speaking, however, our results indicate that the occurrence of particle formation episodes can be predicted with a reasonable accuracy based on ambient sulphuric concentrations, and the subsequent growth of the particles can be estimated with the help of organic emissions. As most of the atmospheric sulphur at the studied boreal forest site is of anthropogenic and the organics of biogenic origin, our results provide tools to, for instance, estimate the anthropogenic and biogenic fractions of secondary aerosol formation in boreal forests in past, present and future with regional and global models.

2) A persistent pool of molecular clusters, both neutral and charged, is present and participates in the atmospheric nucleation process at the boreal forest site in Hyytiälä, Finland.

To our knowledge for the first time, we found indications of a neutral cluster mode at sizes below 2 nm, with estimated concentrations ranging from some thousands to hun-

dreds of thousands per cubic centimeter. Our observations indicate that atmospheric nucleation takes place via interactions between condensing vapours and these clusters, as is it energetically more favourable than homogeneous nucleation of the vapours. According to our observations, these clusters are activated for growth at sizes close to 1.5–2 nm, which is later observed as particle formation in larger sizes as the particles grow further. The hypothesis of cluster activation and growth as the dominant particle formation mechanism is also in line with the linear or square relationship we observed between particle formation rates and sulphuric acid concentrations: in the case of homogeneous nucleation involving sulphuric acid, this dependence should be to much higher powers of the sulphuric acid concentration. The composition of these clusters and which are the vapours activating them for growth still remain somewhat an open question. For instance, it is not clear whether sulphurous compounds or organics are major constituents of the clusters or rather mainly the vapours growing them further. As our observations are restricted to a boreal forest site, more measurements in varying environments are needed to answer these questions, to add to our observations, and to give indications on the spatial and temporal variation of these clusters and their role in secondary particle formation.

**3)** Neutral particle formation seems to dominate over the ion-induced and -mediated mechanisms, at least in the boreal forest boundary layer.

This is indicated by the excessive total cluster concentrations and particle formation rates compared to those of charged clusters and nanoparticles we observed at Hyytiälä, Finland. The charged particle formation rates were typically 1–20 % of the total formation rates. Also, according to our calculations, ion-ion recombination as the sole source of the neutral cluster fraction was not capable of producing the numbers of clusters we observed. The estimated maximum fraction of neutral clusters produced by recombination was of the order of 0.1–20 %. The clear positive size-dependence of the growth rates indicates that the charge-enhancement of the growth rates does not seem to play a significant role in the atmosphere. These results suggest that cosmic rays seem not to be the key factor regulating secondary particle formation, at least not through their impact on ion-induced nucleation and growth. Again, more measurements in different locations and altitudes would shed light onto this subject in a more global scale.

**4)** The subcooled liquid phase saturation vapour pressures of C3–C9 dicarboxylic acids are of the order of  $10^{-5}$ – $10^{-3}$  Pa at atmospheric temperatures.



The values indicate that these acids are unlikely to condense as pure compounds or binary aqueous solutions in the atmosphere, and therefore also unlikely to be present in the very first steps of particle formation. They are, however, often found in atmospheric particulate matter. The presence of other substances in the particulate phase or, for instance, the aging of the aerosol are thus likely to strongly increase their partitioning into the condensed phase. More laboratory data are needed to pin down these processes. Anyhow, the vapour pressures determined in this work are readily usable to more accurately describe the partitioning of C3–C6 dicarboxylic acids in models predicting secondary organic aerosol formation.

The scientific work presented in this thesis gives tools to quantify the secondary aerosol source provided by the boreal forests, how it has changed due to human activity and how it will evolve in the future. These questions are unavoidable in investigating the interactions between the boreal forests, atmosphere and global climate. The idea of forests interacting with the atmosphere and even participating in the creation of their own microclimate is fascinating. However, to be able to describe the secondary particle formation and assess its climatic effects on a more global scale, more measurements on atmospheric nucleation and particle growth are needed from around the world, as the particle formation processes are likely to vary notably depending on the environment.

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