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UNDERSTANDING THE CHEMISTRY OF ATMOSPHERIC AEROSOL  
PARTICLE FORMATION VIA OBSERVATIONS OF PHYSICAL  
PROPERTIES

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Academic dissertation

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# **Understanding the chemistry of atmospheric aerosol particle formation via observations of physical properties**

Mikael Kristian Ehn

University of Helsinki, 2010

## **Abstract**

It is widely accepted that the global climate is heating up due to human activities, such as burning of fossil fuels. Therefore we find ourselves forced to make decisions on what measures, if any, need to be taken to decrease our warming effect on the planet before any irrevocable damage occurs. Research is being conducted in a variety of fields to better understand all relevant processes governing Earth's climate, and to assess the relative roles of anthropogenic and biogenic emissions into the atmosphere. One of the least well quantified problems is the impact of small aerosol particles (both of anthropogenic and biogenic origin) on climate, through reflecting solar radiation and their ability to act as condensation nuclei for cloud droplets. In this thesis, the compounds driving the biogenic formation of new particles in the atmosphere have been examined through detailed measurements.

As directly measuring the composition of these newly formed particles is extremely difficult, the approach was to indirectly study their different characteristics by measuring the hygroscopicity (water uptake) and volatility (evaporation) of particles between 10 and 50 nm. To study the first steps of the formation process in the sub-3 nm range, the nucleation of gaseous precursors to small clusters, the chemical composition of ambient naturally charged ions were measured.

The ion measurements were performed with a newly developed mass spectrometer, which was first characterized in the laboratory before being deployed at a boreal forest measurement site. It was also successfully compared to similar, low-resolution instruments. The ambient measurements showed that sulfuric acid clusters dominate the negative ion spectrum during new particle formation events. Sulfuric acid/ammonia clusters were detected in ambient air for the first time in this work.

Even though sulfuric acid is believed to be the most important gas phase precursor driving the initial cluster formation, measurements of the hygroscopicity and volatility of growing 10-50 nm particles in Hyytiälä showed an increasing role of organic vapors of a variety of oxidation levels.

This work has provided additional insights into the compounds participating both in the initial formation and subsequent growth of atmospheric new aerosol particles. It will hopefully prove an important step in understanding atmospheric gas-to-particle conversion, which, by influencing cloud properties, can have important climate impacts. All available knowledge needs to be constantly updated, summarized, and brought to the attention of our decision-makers. Only by increasing our understanding of all the relevant processes can we build reliable models to predict the long-term effects of decisions made today.

Keywords: Atmospheric aerosols, aerosol measurement, air ions, particle formation and growth, hygroscopicity, volatility

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## List of publications

This thesis consists of an introductory review, followed by five research articles. In the introductory part, these papers are cited according to their roman numerals. Papers **I**, **II**, **IV**, and **V** are reprinted under the Creative Commons Attribution 3.0 License.

- I Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostianen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R. (2010). A high-resolution mass spectrometer to measure atmospheric ion composition. *Atmos. Meas. Tech.*, 3, 1039-1053.
- II Ehn, M., Junninen, H., Petäjä, T., Kurtén, T., Kerminen, V.-M., Schobesberger, S., Manninen, H. E., Ortega, I. K., Vehkamäki, H., Kulmala, M., and Worsnop, D. R. (2010). Composition and temporal behavior of ambient ions in the boreal forest. *Atmos. Chem. Phys.*, 10, 8513–8530.
- III Ehn, M., Junninen, H., Schobesberger, S., Manninen, H. E., Franchin, A., Sipilä, M., Petäjä, T., Kerminen, V.-M., Tammet, H., Mirme, A., Mirme, S., Hörrak, U., Kulmala, M., and Worsnop, D. R. (2010). An instrumental comparison of mobility and mass measurements of atmospheric small ions. *Aerosol Sci. Tech.*, accepted for publication.
- IV Ehn, M., Petäjä, T., Birmili, W., Junninen, H., Aalto, P., and Kulmala, M. (2007). Non-volatile residuals of newly formed atmospheric particles in the boreal forest. *Atmos. Chem. Phys.*, 7, 677-684.
- V Ehn, M., Petäjä, T., Aufmhoff, H., Aalto, P., Hämeri, K., Arnold, F., Laaksonen, A., and Kulmala, M. (2007). Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid. *Atmos. Chem. Phys.*, 7, 211-222.

# 1 Introduction

The atmosphere is a complex system. It governs Earth's climate through processes studied in a variety of scientific fields, including (but not limited to) physics, chemistry, meteorology, biology, geography, and hydrology. If also considering anthropogenic, i.e. human, influence, the list can be extended to include fields such as sociology and economy. With this in mind, it is not surprising that much controversy surrounds the on-going debate on climate change, and the role of anthropogenic influence. Although the major consensus is that the burning of fossil fuels has increased the level of carbon dioxide (CO<sub>2</sub>) in the atmosphere (IPCC, 2007; Hansen et al., 2008; Hofmann et al., 2009), enhancing the green house effect and heating Earth's surface, many open questions still remain, both related to CO<sub>2</sub> and other anthropogenic emissions. In a system as complex as the atmosphere, the only way to achieve a complete picture is to construct climate models incorporating all the available knowledge. Unfortunately, our knowledge is not complete, and small errors can accumulate to large discrepancies in the models as all the processes are intricately linked to each other. The reliability of climate models is, however, improved every time a gap in our knowledge is filled.

In their last report, the Intergovernmental panel on climate change (IPCC) listed atmospheric aerosol particles as the most poorly understood part of the climate system (IPCC, 2007). Aerosol particles are solid or liquid particles suspended in air (Hinds, 1999). For simplicity, they are assumed to be spherical, and their diameter is used as the measure of size. While typical gas molecules in the atmosphere have diameters below 1 nm ( $10^{-9}$  m), aerosol particle diameters range from 1 nm up to around 100  $\mu$ m ( $10^{-4}$  m). For larger particles, gravitation causes the particles to reach a surface fairly quickly, and therefore they are not considered aerosol particles. Aerosol particles affect Earth's climate in several ways, as they can scatter sunlight back to space, thereby cooling Earth's surface, but even more importantly, they play a crucial role in cloud formation. For cloud droplets to form, water has to condense onto pre-existing aerosol particles (termed cloud condensation nuclei, CCN). If the concentration of available CCN is low during cloud formation, the clouds will contain few, but large, cloud droplets. On the other hand, in the event of high CCN concentrations, a cloud with many, but small, droplets will form. The latter cloud will typically have a longer lifetime and be brighter than the former, reflecting more sunlight back into space. Thus, if human activity would increase the amount of aerosol particles in the atmosphere, the net result would be a cooler climate (Twomey, 1977). However, this might be an over-simplification, as aerosol-

cloud-climate interactions are extremely complex (Ramanathan et al., 2001; Rosenfeld et al., 2008).

In a global perspective, the most crucial aerosol effect stems from their impact on the climate. On a regional scale, other aerosol effects also become important, mainly the degradation of visibility due to absorption and scattering of light (Bohren & Huffman, 1983), and the adverse health effects (Brunekreef & Holgate, 2002) caused by the inhalation of aerosol particles.

Aerosol particles are produced in many different ways. Direct emissions (primary production) derive from e.g. sea spray from oceans, dust storms, volcanoes, traffic and different types of burning processes. In addition to these, gas-to-particle conversion is also occurring in the atmosphere (Kulmala et al., 2004), and is believed to be the dominant source of aerosol particles in the atmosphere (Merikanto et al., 2009). This gas-to-particle conversion (secondary production) produces new particles through a process beginning with a few gas molecules colliding to form a cluster of 1-2 nm in diameter (Kulmala, 2003). Subsequently more molecules attach to the cluster, and they can be considered aerosol particles, which starts to grow by condensation, typically at a rate of 1-10 nm h<sup>-1</sup> (Kulmala et al., 2004; Kulmala & Kerminen, 2008). Small clusters are easily lost by coagulation, i.e. collisions with larger particles, and deposition, i.e. collisions with surfaces such as the ground or leaves on a tree. If the particles grow above 50 nm, they can potentially start scattering light and act as CCN, which is when they become relevant from a climate point of view. Both primary and secondary aerosol production can be either biogenic, anthropogenic, or a combination of the two.

Although the process of gas-to-particle conversion and subsequent growth, simply termed new particle formation in this work, is qualitatively understood as outlined above, the exact compounds participating in each step are far from clear. The main reason is the difficulty of measuring the composition of particles smaller than 50 nm in diameter due to their minuscule mass. Below 3 nm, where the first steps of new particle formation take place (Kulmala et al., 2007b), measuring the number of particles/clusters is already a difficult task, let alone measuring their chemical composition. Above 3 nm, the number concentration of particles is routinely measured, but composition measurements below ~50 nm are still scarce. Above this limit, the mass of the particles is large enough to be measured with a number of different instruments, either online (real-time measurements) or offline (e.g. sample collection on filters for later analysis). To date, reliable composition measurements of sub-50 nm particles are extremely rare (Smith et al., 2004; Smith et al., 2008), and even these cannot unambiguously determine the complete composition of the particles, though they have given some indications down to around 10 nm. As the



mass of a spherical particle scales as the third power of the diameter and the initial steps of particle formation take place around 2 nm, the mass of the original 2 nm core will make up less than 1% of the mass once the particle has grown to 10 nm. Therefore, without reliable sub-10 nm composition measurements, we are still lacking information on a very crucial part of the formation process.

As direct measurements have not been successfully employed to measure the composition of the smallest particles, indirect methods have been developed to gain insight into this problem. Such measurements have been based on measuring some characteristic of the particles, such as their affinity (uptake ability) of different liquids, most commonly water (Sakurai et al., 2005), but also alcohols (Vaattovaara et al., 2005; Kulmala et al., 2007a). Another regularly measured characteristic is the response of the particles to elevated temperatures (Wehner et al., 2005). With knowledge of these physical properties, one can constrain the composition, even though a full picture will still be missing. Both the direct and indirect methods have been applied in various environments and the chemical composition is expected to differ a great deal between e.g. Mexico City, rural Germany, and the Finnish boreal forest, to list a few of the measurement sites of the above-referenced studies.

Another indirect approach is to measure a subset of the sub-3 nm clusters and molecules by only studying the naturally charged ions (Laakso et al., 2004; Eisele et al., 2006; Arnold, 2008). Constant ion production takes place in the atmosphere due to high energy particles, produced mainly from cosmic rays and the radio-active decay of radon, which causes a small fraction of the neutral clusters and molecules to acquire charge. This greatly facilitates their detection and characterization. However, the charging mechanism is highly selective and can thus not give a complete picture of all compounds in this size range. Nevertheless, the method has proven to be an efficient way to detect several critical species and their correlation with new particle formation (Eisele, 1989; Eisele et al., 2006).

To understand the processes and compounds participating in new particle formation and growth is, and has been for the past few decades, one of the major goals in the field of atmospheric aerosol research. Many advances have been made during this time, but more work is undoubtedly still needed. In this thesis, the focus was on experimentally identifying compounds, or groups of compounds, taking part in biogenic new particle formation in the lower troposphere, through indirect methods. More specifically, the detailed objectives were:

1. To develop, test and deploy instruments in the field to obtain information on the chemical compounds involved in new particle formation and growth up to 50 nm (**Papers I-V**).

2. To chemically characterize naturally charged ambient small ions, and to indirectly link their properties to the behavior and chemistry of neutral clusters and molecules during the first steps of new particle formation (**Papers I-III**).
3. To measure physical properties of the growing new particles to indirectly gain insight into the condensing vapors responsible for new particle growth (**Papers IV-V**).

## **2 Indirect methods to measure chemical composition**

When available, direct approaches provide conclusive information on the composition of the measured particles. The amount of inorganic compounds in particles larger than 50 nm in diameter has been quantitatively measured online with several instruments, such as particle-into-liquid samplers (PILS, Weber et al., 2001), using ion chromatography for the chemical analysis, and the Aerodyne aerosol mass spectrometer (AMS, Jayne et al., 2000; Canagaratna et al., 2007). The AMS is also able to quantitatively measure the total organic mass spectrum, though after considerable fragmentation of the original molecules. Nevertheless, several different organic compound types can be distinguished (Lanz et al., 2007; Jimenez et al., 2009). Direct measurements of sub-50 nm particles are not possible with the PILS or AMS, but the thermal desorption chemical ionization mass spectrometer (TDCIMS) developed by Smith et al. (2004) can measure particles down to around 10 nm. Due to the ionization technique, the results are only qualitative, but it still has provided evidence of several compounds in these small particles (Smith et al., 2008; Smith et al., 2010). Additionally, the nanoaerosol mass spectrometer (NAMS) allows direct and quantitative measurements of particles around 10-20 nm (Wang & Johnston, 2006; Wang et al., 2006). The drawback of the instrument is that it only provides elemental bulk composition of the particles due to the high-energy laser ionization. Nevertheless, this technique has shown itself capable of clearly separating between hydrocarbon-like traffic emission particles and sulfate driven new particle formation (Zordan et al., 2008). In summary, below 10 nm, there are no direct techniques available for composition measurements, and in the range of 10-50 nm, improvement is still needed.

While the direct techniques are further developed, additional insight can be acquired using different indirect techniques currently available. This has been the main focus of this work, and the utilized instruments will be described in section 3. This section describes the aims, theory and basic concepts of measuring some select indirect properties of molecules and particles.

## 2.1 Ions

Ions are constantly produced and lost in the atmosphere, but depending on the height, the ionization, ion concentration, and ion composition will be very different. For simplicity, in this work we will focus solely on the lower troposphere. Galactic cosmic rays and high-energy particles originating from the radio-active decay of radon can interact with gas molecules and produce a cascade of high-energy collisions. These collisions will have sufficient energy to ionize gas molecules by removing electrons from the molecules, resulting in primary ions such as  $\text{N}_2^+$  and  $\text{O}_2^+$  (e.g. Arnold, 2008). The free electrons rapidly attach to electronegative molecules, producing negative ions such as  $\text{O}_2^-$ . The reason for these ions being the typical primary ions is their great abundance: nitrogen (N) and oxygen (O) together make up roughly 98-99% of the atmosphere. Water, argon and  $\text{CO}_2$  together account for around 1-2%, and the most abundant gas after that is neon with a contribution of less than 0.002%. Even though the other trace gases make up only a marginal part of the atmosphere, there are constant collisions between gas molecules (every molecule collides around  $10^{10}$  times every second) and once an ion collides with a molecule, the charge may be transferred if it is energetically favorable. In practice, this means that the molecules with the highest electron affinity will end up with the extra electron. Later on in the reaction chain, not only electron transfer will take place, but reactions including bond breaking may also occur. Less energy is typically required to add/remove a proton than an electron from a molecule, and in the later steps of the ion-neutral collisions, proton transfer will therefore dominate. The negative charge will end up on the ion with the lowest proton affinity. A low proton affinity is equivalent with high acidity and it has been found that the negative ion spectrum consists mainly of strong acids, both inorganic (e. g. sulfuric and nitric acid) and organic (e. g. malonic acid) (Eisele, 1989; **Paper II**). Similarly, molecules with the highest proton affinities (bases, such as ammonia, amines, pyridines) will collect the positive charges (Eisele & Tanner, 1990; **Paper II**).

Losses of ions occur due to recombination of positive and negative ions and through collisions with aerosol particles or surfaces (Hörrak et al., 2008). The loss rate mainly varies according to the amount of aerosol particles, and the production according to the amount of radon in the air. At the earth's surface, this competition results in ion concentrations in the order of  $1000 \text{ ions cm}^{-3}$  for each polarity. This can be compared to the total amount of molecules available, which is around  $2 \cdot 10^{19} \text{ cm}^{-3}$ . In other words, only a fraction of the gas phase molecules are charged, but still the ion composition reflects the composition of trace gases in the atmosphere. The most obvious example is sulfuric acid ( $\text{H}_2\text{SO}_4$ ) which is formed in the atmosphere

through oxidation of sulfur dioxide ( $\text{SO}_2$ ), causing a strong diurnal behavior (i.e. variation between day and night) of the acid, as oxidation is strongly photochemically driven. Typical  $\text{H}_2\text{SO}_4$  concentrations night-time are around  $10^5 \text{ cm}^{-3}$  or below, and day-time around  $10^6$ - $10^7 \text{ cm}^{-3}$  (Eisele & Tanner, 1993; Petäjä et al., 2009).  $\text{H}_2\text{SO}_4$  is one of the strongest acids in the atmosphere and will thus become charged in a collision with any negative ion, and thus the amount of  $\text{HSO}_4^-$  ions is closely linked to the concentration of neutral  $\text{H}_2\text{SO}_4$ , denoted  $[\text{H}_2\text{SO}_4]$ . During a day with  $[\text{H}_2\text{SO}_4] > 5 \cdot 10^7 \text{ cm}^{-3}$ , the negative ion spectrum can be completely dominated by  $\text{HSO}_4^-$  and its clusters with  $(\text{H}_2\text{SO}_4)_n$ ,  $n = 1$ -3, as reported in **Paper II**. Interestingly, during the same day a strong new particle formation event also took place. Although far from conclusive, this measurement of ions and ion clusters indirectly implies that  $\text{H}_2\text{SO}_4$  can play a key part in new particle formation. Unfortunately, the dominating feature of  $\text{HSO}_4^-$  in the negative ion spectrum can also have a drawback, since if there exists more important participating compounds, they will not be detected with this method as their proton affinities are lower than that of sulfuric acid.

## 2.2 Hygroscopicity

The hygroscopicity of a particle is a measure of how readily it absorbs water at subsaturation, i.e. at relative humidities (RH) below 100%. It is often measured in terms of a diameter growth factor (GF) at a certain RH, typically around 90% (Swietlicki et al., 2008; Paper V). If a 100 nm particle is taken from completely dry conditions ( $\text{RH} \approx 0\%$ ) and exposed to high RH, causing it to grow to a 150 nm particle through water uptake, the GF would be reported as 1.5. This gives an indirect measure of the chemical composition of the particle. Obviously, as the particles can contain thousands of different molecules, a single number is not enough for a full understanding of the particle composition. Nevertheless, there is a large variation in GF for different compounds, with organic compounds typically having  $\text{GF} < 1.3$  and inorganic salts typically having  $\text{GF} > 1.5$  (Hämeri et al., 2000; Hämeri et al., 2001; Peng et al., 2001; McFiggans et al., 2006). Simplified illustrations are given in Figure 1, where the growth from 0% to 90% is depicted for a non-hygroscopic organic particle (A) and a hygroscopic inorganic particle (B). In the atmosphere, particles usually contain a mixture of inorganic and organic compounds (C0 in Figure 1), and the compounds in the particles are often assumed to absorb water independently of each other (Stokes & Robinson, 1966). Thus, we can again apply some constraints on the composition based on measured GF. For instance, if a particle has a  $\text{GF} = 1.0$ , it has not absorbed any water, and can therefore not contain any inorganic species such as ammonia, nitrate or sulfate, which are typically abundant in atmospheric aerosols. On the other hand, if the GF of a

particle is 1.6, the particle can be mostly pure ammonium sulfate ( $GF=1.65$ ), or a mix of sodium chloride (typical in marine environments,  $GF=2.3$ ) and some organics with low hygroscopicities. In reality, excluding marine environments, the  $GF$  typically falls somewhere in between these two example values, as most particles contain mixtures of many different molecules.

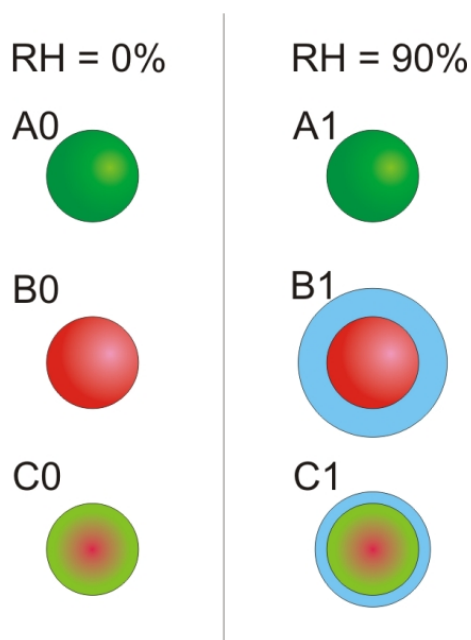


Figure 1: Hygroscopic growth of different particle types. A0 represents an organic, non-hygroscopic particle, which does not take up water when humidified to 90% RH (A1). B0 represents a particle containing ammonium sulfate, which is very hygroscopic and takes up much water when humidified (B1). If a particle is a mix of A and B, the latter will absorb water independently of the organics, and only grow slightly. The water-absorbing molecules in B and C will dissolve upon humidification.

In addition to giving hints on the chemical composition, measuring the hygroscopicity is also important for other reasons. Firstly, the impact of aerosols on light scattering is partly determined by their actual size in the atmosphere, but particle size distributions are typically measured after drying as conducting measurements at ambient RH is often difficult due to the high sensitivity to temperature (Nessler et al., 2003; Wang et al., 2003; Birmili et al., 2009). With a measured hygroscopicity and ambient RH, the dry size distribution can, at least to some extent, be used to recalculate the true ambient distribution. Secondly, many composition measurements are based on measuring the total aerosol mass, such as

filter collection and many aerosol mass spectrometers. These may not give an accurate picture of the aerosol as one has to assume that all particles have the same composition. As a clarifying example, if a filter measurement shows that 50% of the particle mass consisted of hydrocarbons and 50% was ammonium sulfate (AS), it can still not be determined if every single particle was composed of a 50-50 distribution of organics and AS (termed an internal mixture), or if half the particles were purely organic, and half were pure AS. With a measurement of the hygroscopicity, this problem is solved as the data will either show that the particles had two completely different growth factors (A1 and B1 in Figure 1) in the latter case, or a single GF in the 50-50 mixture case (C1 in Figure 1).

## 2.3 Volatility

The volatility of a compound can be defined by how easily it will evaporate from a condensed phase. Compounds that are mostly found in the gas phase at ambient conditions are considered volatile, those that stay in solid or liquid form are considered non-volatile, and finally, if some fraction of a compound is found in both gas and condensed phase, it can be considered semi-volatile (Robinson et al., 2007). The volatility of a particle is measured by heating the air in which the particle is suspended to a certain temperature, and later measuring how much of the mass evaporated (Huffman et al., 2009; Cappa & Jimenez, 2010). To achieve the maximum information from the measurement, a thermogram can be measured. A thermogram depicts evaporation as a function of temperature, which in practice means that the temperature is ramped from room temperature up to several hundred degrees Celsius, while the evaporation is monitored. Each compound will come off at a certain temperature range, and again an indirect measure of the composition is acquired.

Figure 2 illustrates the evaporation of three different particles types, the same as in Figure 1, after heating to 100 C and 200 C, respectively. As the decrease in diameter after heating to these two temperatures is clearly different for each particle type, this measurement enables us to constrain the particle composition.

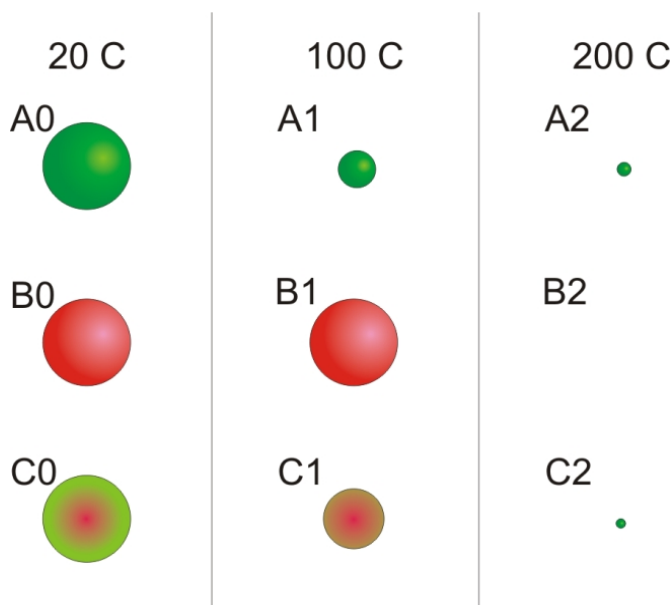


Figure 2: Volatility of different particle types. When heated to 100 C, the organic particle (A0) will shrink (A1) due to evaporation. However, if the organic particle is a mix of numerous different organic molecules, some may stay in the particle even after heating up 200 C (A2). Ammonium sulfate particles (B0) evaporate at around 150 C, which means that heating to 100 C (B1) will hardly affect the particles, but at 200 C the entire particle has evaporated (B2). For the mixed particles (C0), heating to 100 C will cause evaporation of most of the organics (C1), but at 200 C all the ammonium sulfate has evaporated and only a small organic fraction remains.

When measuring the volatility, it is important to keep in mind that the aerosol particles are hardly ever in equilibrium, but rather in some pseudo steady-state, meaning that evaporation and condensation take place continuously. Additionally, the evaporation is not instantaneous, and thus the residence time in the heated section of the instrument will influence the result (Cappa, 2010; Riipinen et al., 2010).

## 2.4 Additional indirect methods

Some less commonly used indirect methods to probe sub-50 nm particle composition are listed in the following. Hygroscopicity is a measure of the water affinity of the particles, and similarly the affinity to other liquids can also be studied. Growth factors have been measured by introducing particles to high sub-

saturation ratios of ethanol (Joutsensaari et al., 2001; Vaattovaara et al., 2005). A drawback of this approach compared to growth in water, is that the ethanol can react chemically with some of the organics in the particles, changing the composition of the particles. Another method involves comparing the condensation of water and butanol onto particles at super-saturations. If either vapor condenses more readily than the other, the particles are thought to be more soluble in the corresponding liquid. This method has been used in the condensation particle counter battery presented by Kulmala et al. (2007a). High solubility in water typically means high inorganic content, while solubility in alcohols suggests high organic content. However, the difficulties with generating similar saturation profiles in different instruments makes the interpretation challenging. Finally, indirect methods can also be combined for additional information, the most common being the measurement of hygroscopicity after some part of the particle has been evaporated (Johnson et al., 2004; Ristovski et al., 2010). This method can be very powerful, but requires careful measurements to be certain which part of the resulting size change is due to evaporation and which to water uptake.

### **3 Experimental methods**

In this section, the most important instruments utilized in this study are presented, together with a description of the site where the majority of the measurements were conducted (**Papers II-V**). **Paper I** presents mainly laboratory data, together with brief results from Helsinki, Finland.

#### **3.1 Basic instrument building blocks in aerosol science**

There are two instrument building blocks, the condensation particle counter (CPC) and the differential mobility analyzer (DMA), that have played a central role both in the field of aerosol science as a whole, and in this thesis. Therefore, these will be described first, facilitating the following introduction to the instruments themselves.

##### **3.1.1 The condensation particle counters (CPC)**

Particles larger than a few hundred nm scatter light, and can thus be detected optically using lasers. Smaller particles, including the range where all the work presented in this thesis were performed, are too small to efficiently scatter incident light, and can therefore not be directly detected optically. The principal idea behind a CPC is to grow all particles large enough to be detected (McMurry, 2000). This is accomplished by introducing all particles into a flow containing an extremely high saturation ratio of typically butanol or water. Under these supersaturated conditions,



the butanol/water molecules will condense onto the particles, growing them enough to easily be detected by an optical particle counter.

When the particle diameter decreases below 10 nm, the curvature of the particles start playing a more important role. This is called the Kelvin effect, which in practice means that increasing curvature decreases the amount of neighboring molecules at the surface, and they will evaporate more easily. The Kelvin effect increases exponentially when further decreasing the particle diameter. Traditionally, no commercial CPCs could grow particles smaller than 2.5-3 nm, and only a few research groups had managed to optimize customized CPCs that extended below this limit (Saros et al., 1996; Gamero-Castano & de la Mora, 2000; Mordas et al., 2008; Sipilä et al., 2008). Very recently, the Airmodus A09 particle size magnifier has been able to extend also the detection range of commercial CPCs down to around 1 nm (Vanhanen et al., 2010).

### 3.1.2 The differential mobility analyzer (DMA)

A DMA (Knutson & Whitby, 1975; Winklmayr et al., 1991) allows us to select a monodisperse particle sample (i.e. particles of only one size) from a polydisperse distribution (different sizes). The selected particles can then continue to another device for processing, conditioning, sizing, counting, or any other of a multitude of different applications incorporating DMAs. A limitation of the DMA is that it can only size-select charged particles, since it relies on the particles moving in an electric field. A simplified schematic cross-section of a cylindrical DMA is shown in Figure 3. A sheath flow of particle-free gas (typically air) enters at the top of the DMA. The flow inside the DMA is kept laminar, and the sample flow containing the polydisperse aerosol is introduced at the outer edge of the sheath flow. A typical sample-to-sheath flow ratio is 1:10. A voltage of up to several kV can be applied to the central rod (marked with "V" in Figure 3) while the rest of the DMA is grounded, producing an electric field between the rod and the outer cylinder. The neutral particles will continue with the sample flow on the outer edge, but the electric field will exert a force on the charged particles, either towards or away from the central rod depending on the polarity. The particles with opposite sign to the central rod will move towards it at a speed corresponding to their size (or electrical mobility, to be exact). In Figure 3 this is depicted by three different particle sizes, of which all will travel at the same speed along the cylinder, but the smallest particles will impact on the central rod, while the largest will never reach it during the time spent inside the DMA. Only the particles with a specific size, in this case the intermediate sized particles, will come close to the slit in the central rod through which they will follow the outgoing sample flow.

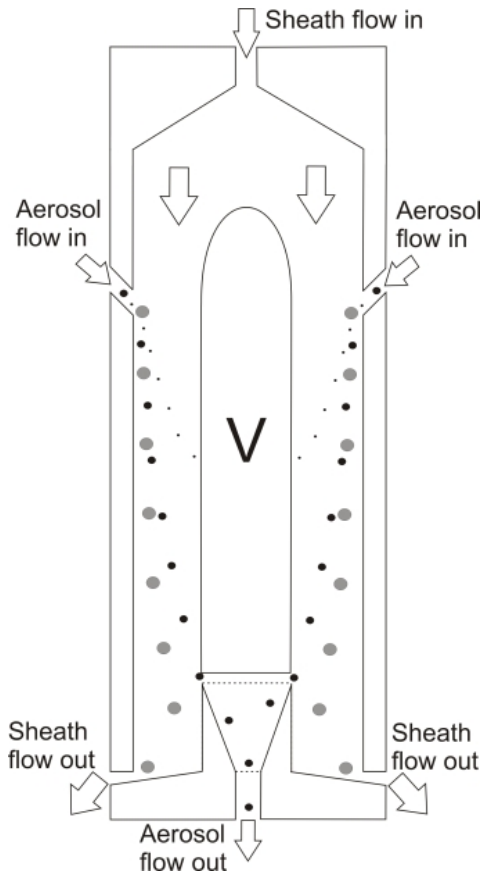


Figure 3: Schematic cross section of a differential mobility analyzer (DMA). Particles enter the laminar flow at the outer edge of the cylinder, and due to the electric field, only particles of a certain size are attenuated to find the narrow slit on the inner cylinder.

### 3.2 Differential mobility particle sizer (DMPS)

One of the simplest applications utilizing a DMA and a CPC is the DMPS (e.g. Aalto et al., 2001). The basic principle is that the sample is passed through the DMA, with a certain voltage applied to the central rod to select only a certain, chosen particle size which is subsequently passed to a CPC for counting. After a certain counting time (typically on the order of a few seconds), the voltage on the central rod is changed to pass through another particle size, and this process is repeated until the entire particle size range of interest has been scanned. The

concentration measured at each size is logged, and a particle number size distribution is obtained.

As a DMA only measures charged particles, a charger is typically used in front of the DMA to produce particles in charge equilibrium. It has been found that when there are enough charges available, particles of a certain size will always reach a certain charge distribution (Hoppel & Frick, 1986; Wiedensohler, 1988). For instance, in charge equilibrium, 95% of all 10 nm particles will be neutral, and 5% will be singly charged. For 100 nm particles, 66% will be neutral, 28% singly charged, and 6% doubly charged. A doubly charged 100 nm particle will have the same mobility as a singly charged 68 nm particle. Post-processing of the measured CPC concentrations will take into account the equilibrium charge distribution, accounting for multiply charged particles, diffusion inside the DMA, and imperfect sizing, to produce a best estimate for the complete size distribution of all particles in the sample.

### **3.3 Volatility scanning mobility particle sizer (VSMPS)**

A scanning mobility particle sizer (SMPS, Wang & Flagan, 1990) is similar to a DMPS, with the only exception being that the voltage over the DMA in the DMPS is stepped, while in the SMPS the voltage is scanned continuously over the size range. In practice, the instruments measure the same quantity, but scanning allows for faster measurements than stepping, while making the data analysis more complex. The VSMPS additionally contains an oven in front of the SMPS in order to evaporate some part of the aerosol particles (Wehner et al., 2005; **Paper IV**). The oven can either be set to a certain temperature, or be scanned or stepped to obtain a thermogram. The instrument also needs to incorporate a bypass for the oven, or have another SMPS/DMPS measuring concurrently, as the non-heated size distribution also needs to be measured to be able to calculate how much of the particles has evaporated. In this way, an indirect measure of the particle composition can be obtained.

### **3.4 Hygroscopicity tandem differential mobility analyzer (HTDMA)**

The working principle of a HTDMA is to measure the growth of aerosol particles upon humidification (Rader & McMurry, 1986; **Paper V**). This is realized by using two DMAs in series, followed by a CPC for particle counting (Figure 4). A humidification unit is placed between the DMAs. The polydisperse particle sample is first passed through a dryer which removes most of the water vapor before entering the first DMA (DMA1). In DMA1, a certain dry size is selected, and these

particles are subsequently humidified to a high relative humidity (RH), typically 90%. Depending on the composition, particles will grow by absorbing water. Inorganic species like ammonium sulfate or sodium chloride, both typical atmospheric aerosol constituents, will absorb large amounts of water, whereas hydrocarbons and soot particles will hardly absorb any water. After humidification and possible growth, the particles enter the second DMA (DMA2) which scans the particle size range while the concentration at each size is measured by the CPC. After this, the voltage on DMA1 is changed to pass through another dry size and DMA2 will scan the resulting humidified size distribution. The HTDMA thus produces hygroscopicity data for all selected dry sizes, and this data can be used to indirectly derive information on the particle composition, in a similar manner as with the VSMPS.

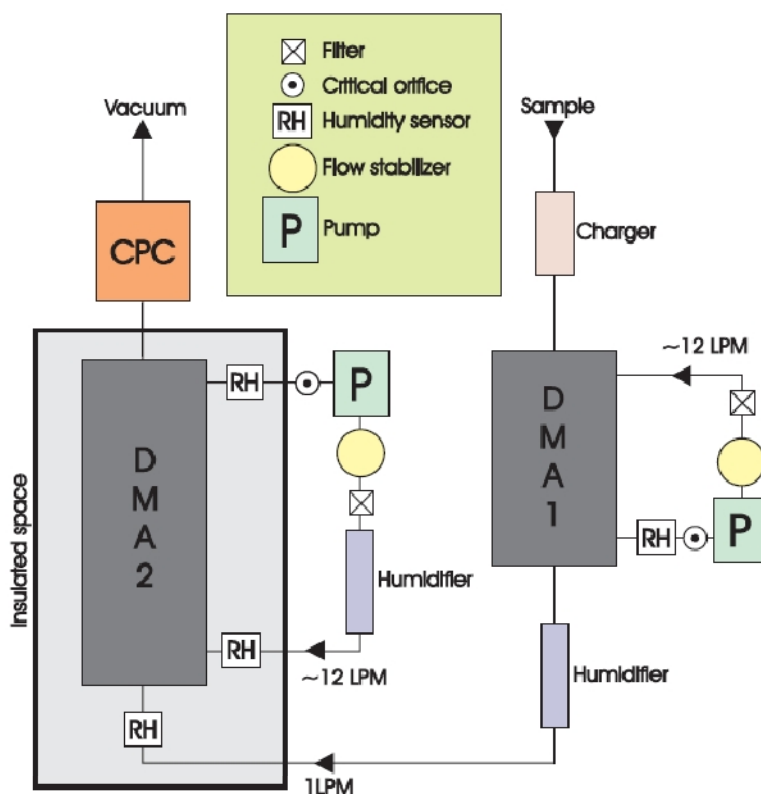


Figure 4: A schematic of the hygroscopicity tandem DMA (from Paper V). The sample travels from the top right to top left. First the sample is neutralized to charge equilibrium with a radio-active charger, then a monodisperse aerosol sample is selected in DMA1, after which the sample is humidified to a high RH and the resulting size distribution is scanned with DMA2 and a CPC.

### 3.5 Atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF)

The purpose of the APi-TOF is to measure the mass of small ions below a few nm with minimal perturbation of the sample (**Papers I-III**). Typically mass spectrometers always use an ionization mechanism, and to decrease the possible confusion with atmospheric pressure ionization, often abbreviated API, the “i” in APi-TOF is lowercase. The instrument consists of two parts: the atmospheric pressure interface (APi) and the time-of-flight mass spectrometer (TOF). The APi, in turn, consists of an inlet (a critical orifice) drawing a sample flow of about  $0.8 \text{ l min}^{-1}$ , two guiding quadrupoles and an ion lens assembly. The purpose of the quadrupoles and the lenses is to guide all the ions through the APi while gas is pumped away to achieve the vacuum needed for the TOF. Once the ions reach the TOF, the pressure is roughly  $10^{-6}$  mbar, i.e. 9 orders of magnitude lower than ambient pressure. There are also ion losses in the APi, and the typical transmission in the range 50-1500 Da is around 0.1-1%. The high resolution of the TOF allows accurate determination of the chemical composition, as will be shown in section 4.1. The dalton (Da) is used as the unit of mass, and is equal to the atomic mass unit, i.e. one twelfth of the mass of the carbon ( $^{12}\text{C}$ ) atom. To be exact, all mass spectrometers measure mass/charge, and not directly mass. In the TOF, the ions are accelerated in an electric field giving each ion the same kinetic energy  $E$ . The acquired velocity ( $v$ ) will depend on the mass ( $m$ ) of the ions according to  $E = \frac{1}{2}mv^2$ . The flight path of the ions leads to a detector, and their flight time ( $t$ ) is measured. As  $t$  is inversely proportional to  $v$ , the mass of each ion can be calculated purely based on the time-of-flight. The assumption in the previous calculation is that the ions are singly charged, which is typically the case for such small ions, especially in the absence of strong ionization processes. All APi-TOF results in this thesis will for simplicity be presented as a function of mass, assuming that all observed ions were singly charged.

As the ion mass is measured in vacuum, evaporation may take place inside the instrument before detection. Additionally, in the quadrupoles the pressure is still relatively high, which means that collisions between gas molecules and the ions occur. If these collisions are energetic enough, especially weakly bound clusters can fragment. This is not believed to be a large problem, as shown in **Paper III** when comparing the APi-TOF to ion mobility spectrometers, but needs to be kept in mind during analysis.

## 3.6 Ion mobility spectrometers

Ion mobility spectrometers come in a variety of different configurations (Flagan, 1998). The ones used in this work apply the same method of size separation as the DMA. In addition to this, they also incorporate detectors and can thus measure the ion size distribution as stand-alone instruments. The detection is not based on optical methods as in a CPC, since the ions are typically smaller than can be detected by CPCs. Instead, they use electrometers which measure the current produced by the ions impacting on the detector. The currents involved are extremely small (on the order of femtoamperes), and thus the instruments require large flows to obtain a decent signal-to-noise ratio. However, as the measured ions are very small, high flows are needed to keep the diffusional losses at a minimum. Below are short descriptions of the ion mobility instruments used in this thesis.

### 3.6.1 Balanced scanning mobility analyzer (BSMA)

The BSMA (Tammet, 2006) utilizes plane-type DMAs instead of cylindrical DMAs, but the working principle is the same. The instrument consists of two separate DMAs, one for each polarity. The voltages over the DMAs are scanned simultaneously, but as both DMAs use the same electrometer, only one polarity is measured at a time while ions of the other polarity are removed with a pre-filter. The total flow into the BSMA is  $2400 \text{ l min}^{-1}$ .

### 3.6.2 Air ion spectrometer (AIS)

The AIS (Mirme et al., 2007) consist of two completely separate cylindrical DMAs, one for each polarity, with fixed classifying voltages. The size distribution is acquired by lining the outer cylinder walls with 24 electrometers each, and the sample is introduced at the inner cylinder, i.e. inversely to the DMA presented in Figure 3. The smallest ions will impact on the first electrometers, while the larger ions with higher inertia will impact further down in the DMA. The entire size distribution for both polarities is measured continuously. The drawback of the AIS is the low achievable mobility resolution. The sample flow of the instrument is  $60 \text{ l min}^{-1}$ .

## 3.7 Station for measuring ecosystem-atmosphere relations (SMEAR)

The measurements in **Papers II-V** were all conducted at the SMEAR II station (Hari & Kulmala, 2005) in Hyytiälä, Finland. The station is located in a fairly homogenous Scots pine stand, and represents a boreal coniferous forest that covers

roughly 10% of the earth's surface (Bonan, 2008). The closest large city is Tampere, located 60 km southwest of the station. The anthropogenic influence at the site is believed to be low, and the new particle formation studies conducted there are indicative of pure biogenic particle production.

## **4 Chemistry and physics of atmospheric aerosol particle formation and growth: Review and thesis results**

In this section, the current knowledge concerning atmospheric new particle formation in the lower troposphere will be reviewed. The results obtained in this work can be distinguished by the citations to the five papers (**Papers I-V**) making up this thesis. As previously stated, different environments may have very different compounds participating in the particle formation, and thus the emphasis will be put on biogenic, mainly boreal forest, environments where most of the measurements in this thesis were performed. However, many aspects will be applicable also to other environments where new particle formation occurs (Kulmala et al., 2004). Much of the work performed in this work was funded by the EU project EUCAARI (Kulmala et al., 2009), and a review of the results on new particle formation in the project is presented by Kerminen et al. (2010).

As discussed in section 2.3 on volatility, some compounds prefer to remain in gas phase, while others prefer solid or liquid phase. This implies that for gas-to-particle conversion to occur, there must be low-volatility compounds in the gas phase that want to condense, i.e. have low volatility. These compounds may either condense onto pre-existing particles or nucleate to form new particles. The two most common mechanisms in the atmosphere that can produce such super-saturated conditions are:

- 1) Temperature changes. Evaporation is more efficient at high temperatures, which means that semi-volatile species will dominantly remain in the gas phase. However, if the temperature decreases, the preferred state of the compound can shift to the condensed phase, and a super saturation of the compound is produced. As an example, super saturation of water vapor means that the relative humidity (RH) surpasses 100%. Assuming a bath room where a hot shower is running, both the temperature and the RH will increase. If there is a colder window or mirror in the room, the air close to it will contain the same amount of water vapor, but at a lower temperature, causing condensation onto the window/mirror.
- 2) Oxidation. The atmosphere contains radicals such as OH, NO<sub>3</sub> and ozone (O<sub>3</sub>) which are highly reactive. When these react with another gas phase

molecule, the result is usually addition of oxygen to the molecule. Higher oxygen content, in turn, tends to decrease the volatility of the compounds, making them more likely to condense. For instance,  $\text{SO}_2$  is a gas typically present in the atmosphere at concentrations on the order of  $10^{10} \text{ cm}^{-3}$ , and can react with OH and water to form low-volatility  $\text{H}_2\text{SO}_4$ . Another purely biogenic example is the oxidation of volatile organic compounds (VOCs) such as monoterpenes ( $\text{C}_{10}\text{H}_{16}$ ) emitted by vegetation. As their name suggests, these compounds are volatile and will prefer to stay in the gas phase, but if oxidized, their volatility decreases, and after a certain amount of oxidation steps they will readily condense.

Temperature decrease usually happens in the evening and at night, whereas oxidation is stronger during daytime when solar radiation produces more oxidizing radicals. As the majority of reported new particle formation events occur during the day (Kulmala et al., 2004), oxidation is considered to be the more important of the two above-mentioned processes. Additionally, oxidation can be considered an irreversible process, whereas later increases in temperature can cause re-evaporation of compounds.

A typical particle formation event observed in Hyytiälä is plotted in Figure 5, with new particles appearing just before noon and growing throughout the day and night. On average, these events occur in Hyytiälä every fourth day, but they are not evenly spread out over the seasons (Dal Maso et al., 2005). During spring and autumn the frequency is the highest, and during winter the lowest, indicating that biological activity is important for the particle formation process in Hyytiälä (Dal Maso et al., 2009). It is worth keeping in mind that since the measurement is stationary and the air is always moving with the wind, the fact that both formation and growth are observed in Hyytiälä means that the site is surrounded by a large, roughly homogeneous area where particles are produced and grow.

The presence of low volatility compounds in the gas phase, i.e. super saturation, is not necessarily enough to produce new particles. As an extreme example, water will condense onto surfaces, as mentioned above, at super saturation ( $\text{RH} > 100\%$ ). Depending on the level of super saturation, water will also condense onto aerosol particles, in which case the aerosol particles function as cloud condensation nuclei. However, in the absence of surfaces and aerosol particles, the water will not homogeneously nucleate to form particles on its own before the RH reaches several hundred percent (Wölk et al., 2002). The reason is that the initial clusters formed purely by water molecules are not stable enough, and molecules will detach (i.e. evaporate) from the clusters faster than new ones attach. This same phenomenon is true for a variety of other compounds. However, aerosol particles are always present



in the atmosphere, which means that if low volatility compounds cannot form new particles, they will eventually condense onto pre-existing particles. This shows the need to divide the study of particle formation into a step of initial cluster formation, often termed nucleation, and subsequent growth through multi-component condensation.

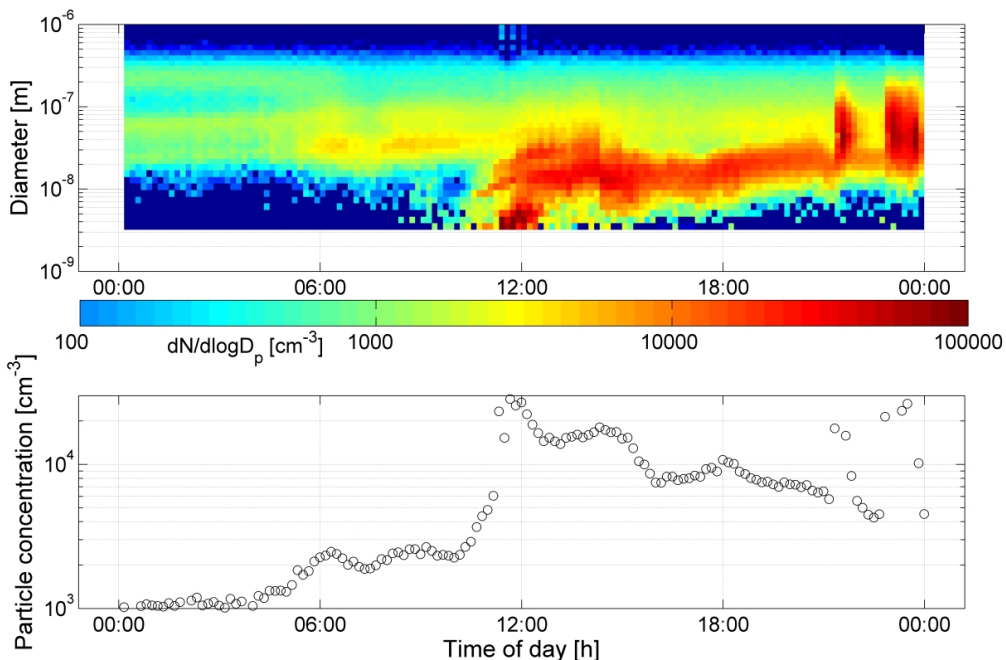


Figure 5: A new particle formation event observed in Hyytiälä, Finland, on 2 May, 2005. The top panel shows the size distribution of particles according to the color scale below. The x-axis goes from midnight to midnight, and the y-axis from 1 to 1000 nm. The bottom graph shows the total particle concentration for the same period. New particles appear around 3 nm just before noon, the concentration increasing ten-fold, and the particles grow during the evening up tens of nm.

## 4.1 Cluster formation

The compounds that can form at least somewhat stable clusters of only a few molecules are the best candidates for explaining the first step of new particle formation. Sulfuric acid has been identified as an important constituent in atmospheric new particle formation (Weber et al., 1996; Eisele & Hanson, 2000; Kulmala et al., 2004; Nieminen et al., 2009; Zhao et al., 2010; **Paper II**), both

through field and laboratory measurements. Sipilä et al. (2010) even speculate that  $\text{H}_2\text{SO}_4$  alone could explain the observed formation rates in most places where new particle formation has been observed. However, there is also a wide agreement that sulfuric acid can only explain a fraction of the later growth of the new particles. Additionally, typical atmospheric  $\text{H}_2\text{SO}_4$  concentrations are always well below saturation, which means that for  $\text{H}_2\text{SO}_4$  to remain in the particles, bond formation needs to occur in the cluster to bind it in the particle phase. As  $\text{H}_2\text{SO}_4$  is an acid, the addition of a base (like ammonia,  $\text{NH}_3$ ) will facilitate formation of a salt (like ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ ) which will have much lower volatility. Amines can also produce salts, as will be discussed later, and even water can act as a base, keeping sulfuric acid in the condensed phase. Water is typically present at a concentration of  $10^{16}$ - $10^{17}$   $\text{cm}^{-3}$ , and can thus be assumed to always reach steady state almost instantaneously (e.g. Kerminen, 1997). Concentrations of trace gases such as sulfuric acid and ammonia are typically  $10^5$ - $10^{10}$   $\text{cm}^{-3}$ , and it can thus take seconds, or even minutes, before a cluster collides with a specific molecule. Therefore, the initial clusters need to be stable enough to not evaporate faster than new molecules can be added.

For clusters containing two sulfuric acid molecules, quantum chemical calculations have shown that the addition of ammonia makes the clusters more stable than the addition of water (Kurten et al., 2007; Ortega et al., 2009) and the addition of an amine enhances the stability even more than ammonia (Kurten et al., 2008). However, it is still debated whether or not this is the case also for larger clusters. Clusters of 1-4 molecules will henceforth be referred to as monomer, dimer, trimer and tetramer, respectively. Recent laboratory measurements (**Paper I**) have shown that charged clusters with 4 or more sulfuric acid molecules will readily cluster with ammonia, whereas clusters smaller than the tetramer contain no ammonia (Figure 6). The same results also suggest that charged clusters containing only sulfuric acid and water will not grow above 4-5  $\text{H}_2\text{SO}_4$  molecules unless highly super-saturated, but with the addition of one ammonia, the cluster can grow by 4-5 additional  $\text{H}_2\text{SO}_4$  molecules. Adding a second ammonia may increase this size even further, as the clusters with two ammonia become more abundant than the ones with one ammonia at 9 sulfuric acid molecules (Figure 6). Also clusters with three ammonia become visible at larger cluster sizes. Similar measurements have not been available previously, and thus the role of ammonia may have gone unnoticed in earlier “pure” sulfuric acid nucleation studies, as even trace amounts of ammonia may be enough to stabilize the  $\text{H}_2\text{SO}_4$  clusters, which by themselves might not be able to form particles at ambient concentrations. As these types of measurements are now available, research on this topic is likely to move forward rapidly.

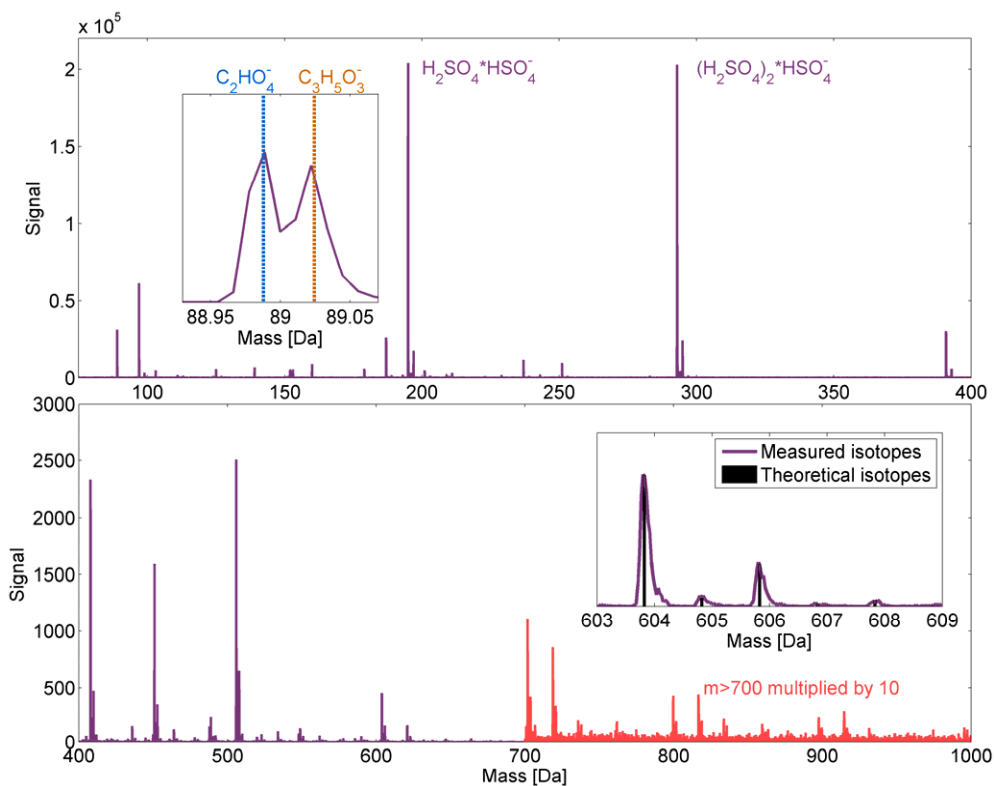


Figure 6: Cluster distribution measured by the APi-TOF of room air with added sulfuric acid from **Paper I**. In the top panel the mass spectrum between 80 and 400 Da is plotted, with the dominant peaks being the sulfuric acid monomer-tetramer. The high-resolution spectrum at integer mass 89 Da is plotted in the inset to show that the APi-TOF can distinguish between ions separated by only a few hundredths of Da for the smallest ions. In the bottom panel, the 400-1000 Da mass range is shown (note the different scale on the y-axis), and the signal above 700 Da has been multiplied by 10. The dominating peaks are no longer the pure sulfuric acid peaks, but instead the cluster with sulfuric acid and 1-2 ammonia. The inset figure shows the distribution around the cluster of six sulfuric acid and one ammonia. At that high mass, the resolution alone is not enough for identification, but the isotopic pattern clearly verifies the ion as the above-mentioned cluster.

Figure 6 also contains inserts to depict two methods used to identify the observed ions. In the top panel, the spectrum around unit mass 89 Da is shown, and two different peaks are observed: oxalic acid (88.988 Da) and lactic acid (89.024 Da). These two peaks are clearly distinguishable at this small mass. At larger ion sizes, the peaks become wider, and the possible combinations of elements making up the molecules/clusters increase exponentially. Thus another way to limit the amount of possibilities is to study the isotopic pattern. Roughly 95% of the sulfur on Earth is

$^{32}\text{S}$ , but ~4.5% is  $^{34}\text{S}$ , which causes molecules to spread out over several different integer masses. An example is shown in the bottom panel of Figure 6, where the measured distribution around the cluster of 6 sulfuric acid and one ammonia is plotted, together with the theoretically calculated isotopic distribution (black bars). The good agreement validates the identification.

Quantum chemical calculations predict that ammonia will attach to pure sulfuric acid charged trimers and larger clusters (Ortega et al., 2008). According to API-TOF measurements (**Paper I**), ammonia forms clusters with tetramers and larger clusters. Thus, experiments and models are still not in complete agreement concerning the charged clusters, but the trends are similar. This gives more confidence that the models can also be applied to molecules and neutral clusters, which currently cannot be measured, but where most of the atmospheric new particle formation takes place (Kulmala et al., 2010). According to Ortega et al. (2008), ammonia stabilizes even smaller neutral clusters, but these will not be able to grow as large as charged clusters with the same amount of ammonia. In **Paper II**, we detected pure sulfuric acid charged clusters up to the tetramer, and also the tetramer clustered with one ammonia, in ambient air in Hyytiälä (Figure 7). The top panel shows a 2 h average mass spectrum during a day with high  $\text{H}_2\text{SO}_4$  concentration, and the spectrum is completely dominated by sulfuric acid and its clusters. The tetramer and tetramer clustered with ammonia are small peaks, but still distinguishable as seen in the inset figure (top right). Even though the amount of different organic molecules at the site is likely huge, the main correlation with new particle formation was found with sulfuric acid. During the day with the highest  $\text{H}_2\text{SO}_4$  concentration, also the charged tetramer clustered with  $\text{NH}_3$  was observed. This indicates that the amount of ammonia in the neutral clusters is probably even larger, suggesting that ammonia, and possibly amines, are important in the first steps of particle formation due to their stabilizing effect on the  $\text{H}_2\text{SO}_4$  clusters.

To demonstrate the differences between day- and night-time ion spectra, the bottom panel in Figure 7 depicts a typical nocturnal ion distribution. The sulfuric acid peaks are reduced to a minor contribution, and nitrate and organic peaks have increased. The peaks around 300-400 Da have not yet been unambiguously identified, but they are believed to be highly oxidized organics containing one nitrogen atom. The sulfuric acid peaks are strongly dependent on the amount of sun light during the days, but the night-time organic peaks have appeared every night during the spring and summer measurements conducted at SMEAR II. No connection between the particle formation events and these organic ions has been found.

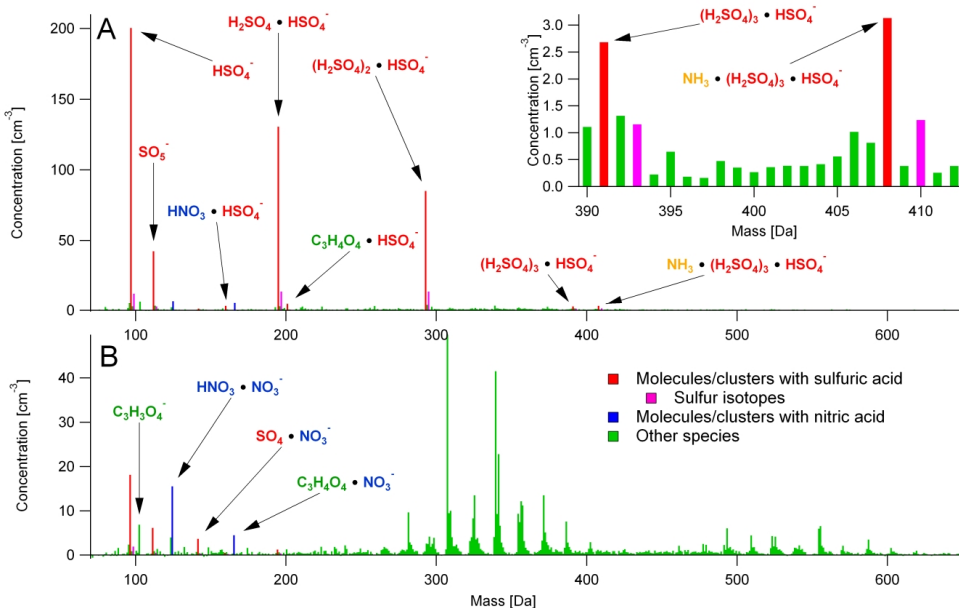


Figure 7: Ambient small ion distribution in Hyytiälä on 30 April, 2009 (from **Paper II**). The top panel corresponds to a 3 h average during the day (9:00-12:00), and the bottom panel to a 3 h night-time average (0:00-3:00) (figure modified from Paper II). The day-time spectrum was measured during a day with exceptionally high H<sub>2</sub>SO<sub>4</sub> concentrations and a strong nucleation event. The sulfuric acid peaks comprise the major part of the spectrum, and also the tetramer clustered with ammonia is visible at 408 Da, as seen in the inset figure. The nocturnal spectrum in the bottom panel strongly contrasts the top panel, with many more peaks visible, and only a minor contribution of sulfuric acid.

Whereas ambient ion measurements rely on natural sources of the charge, and ion reaction times on the order of minutes (Tanner & Eisele, 1991, **Papers I-III**) mass spectrometers using chemical ionization have also been employed to study neutral molecules and clusters, mainly of sulfuric acid. In this case, nitric acid ions are introduced into the sample flow, and as one of the few stronger acids available is sulfuric acid, this method can be used to quantitatively measure the gas phase sulfuric acid concentration (Eisele & Tanner, 1993). If the reaction time between sample and ions can be varied, good estimates can also be given for the smallest sulfuric acid clusters. Zhao et al. (2010) found elevated concentrations of neutral sulfuric acid clusters up to the tetramer during particle formation events in Colorado, USA. No ammonia containing clusters were reported in that study, but instrumental limitations would have made these clusters hard to distinguish for the tetramer and larger clusters. For smaller neutral clusters of H<sub>2</sub>SO<sub>4</sub> and NH<sub>3</sub>, the

charging may cause rapid evaporation of  $\text{NH}_3$ , in which case the detected ion will be a pure sulfuric acid cluster.

Equally interesting as the results on  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$ , is the lack of organic molecules detected in the smallest clusters during particle formation events, both in the laboratory (**Paper I**) and the field (Eisele et al., 2006; Zhao et al., 2010; **Paper II**). Paper II does report an organosulfate and its cluster with sulfuric acid, which track  $\text{H}_2\text{SO}_4$ , but no larger cluster were detected and their role in new particle formation could not be determined. Some studies (e.g. Metzger et al., 2010) claim to have shown the contribution of organics already in the cluster formation step in chamber studies under typical ambient conditions. However, these results are not based on measurements of the clusters directly, and require a fair amount of assumptions. It is ultimately very hard to decouple the cluster formation step from the initial condensational growth with the measurements conducted in studies like the one by Metzger et al. (2010). Sulfuric acid is the strongest acid available, and will take the charge from most molecules and clusters given the chance, but no hint of organic involvement was detected in the ambient ions, nor by Zhao et al. (2010) during on-going particle formation events. It is possible that these clusters are so weakly bound that they evaporate in the APi-TOF, but as shown in **Paper III**, when comparing to ion mobility spectrometers such as the AIS and BSMA no considerable fragmentation was found to occur in the instrument. This is all in accordance with many studies showing sulfuric acid to be the compound that best explains the formation rate of new particles (Sipilä et al., 2010). This, however, does not apply to the growth of these clusters after their initial formation.

## 4.2 Growth from clusters to particles

Compared to the cluster formation, the role of organics in the condensational growth step is much less controversial. The concentration of sulfuric acid has been found to be insufficient to alone explain the observed growth rates (eg. Kulmala et al., 2001), and both indirect (Kulmala et al., 2001; Wehner et al., 2005; Riipinen et al., 2009; **Papers IV-V**) and direct (Allan et al., 2006; Smith et al., 2010) measurements have indicated that organics play a large role in the growth from a few nanometers up to 50 nm and above. This is in accordance with total aerosol mass measurements which have shown a large organic fraction in the particles (Zhang et al., 2007; Jimenez et al., 2009). Combining both gas and particle measurements, it is estimated that  $10^4$ - $10^5$  different organic compounds have been measured in the atmosphere (Goldstein & Galbally, 2007; Hallquist et al., 2009). Whenever low-volatility vapors are condensing onto freshly nucleated particles, some part will also condense onto the larger pre-existing particles, and if no

nucleation has occurred, all the condensation will happen onto the large particles. This will not increase the total particle number, only the size and mass of the particles.

In a recent laboratory study, Wang et al. (2010) produced 2-20 nm particles through  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation and introduced three different organic compounds in a drift tube. All the compounds caused the particles to grow, but the processes were found to be different. The addition of trimethylamine caused growth through the formation of aminium salts in the particles. 2,4-hexadienal produced large low-volatility polymers through acid-catalyzed reaction in the particles. Finally, glyoxal also formed smaller polymers in the aqueous particles, but to a smaller extent as this reaction was not acid-catalyzed. This shows the inherent complexity of the new particle formation process, where a wide range of different compounds are involved, and both gas and particle phase reactions constantly alter the composition. The particle size is also important, as Wang et al. (2010) also found that 2,4-hexadienal only grew particles of 4 nm and larger, whereas 2-3 nm particles remained unaffected. Although only one molecule, this again is in line with the hypothesis that  $\text{H}_2\text{SO}_4$  is important in the smallest clusters, and organic molecules become involved in the growth from a few nm.

The direct ambient measurements of 10 nm particles in Hyytiälä performed by Smith et al. (2010) were based on chemical ionization, which means that there is some selectivity involved. Their results showed large concentrations of organic acids and amines in the particles, and it was speculated that the formation of organic aminium salts in the particles was one reason for the low volatility of the particles. In the afternoon, sulfate only made up a few percent of the observed signal. Allan et al. (2006) conducted quantitative measurements of the chemical composition of particles larger than 50 nm with an aerosol mass spectrometer (Canagaratna et al., 2007) in Hyytiälä, and found them to be completely dominated by organic compounds. This indicates that the importance of sulfuric acid decreases rapidly as particles grow larger. The question is, at what point does this happen? As a completely hypothetical example, if the growth to 10 nm was purely by sulfuric acid, and the growth from 10 to 50 nm was by organics, the 50 nm particles would contain only 0.8% sulfuric acid by mass. Obviously, there is no such sharp limit, but the example shows the need for knowledge of the composition throughout the growth process. Organics are likely to be important well below 10 nm, as the measurements by Riipinen et al. (2009) suggest, and sulfuric acid will likely condense to some extent throughout the growth.

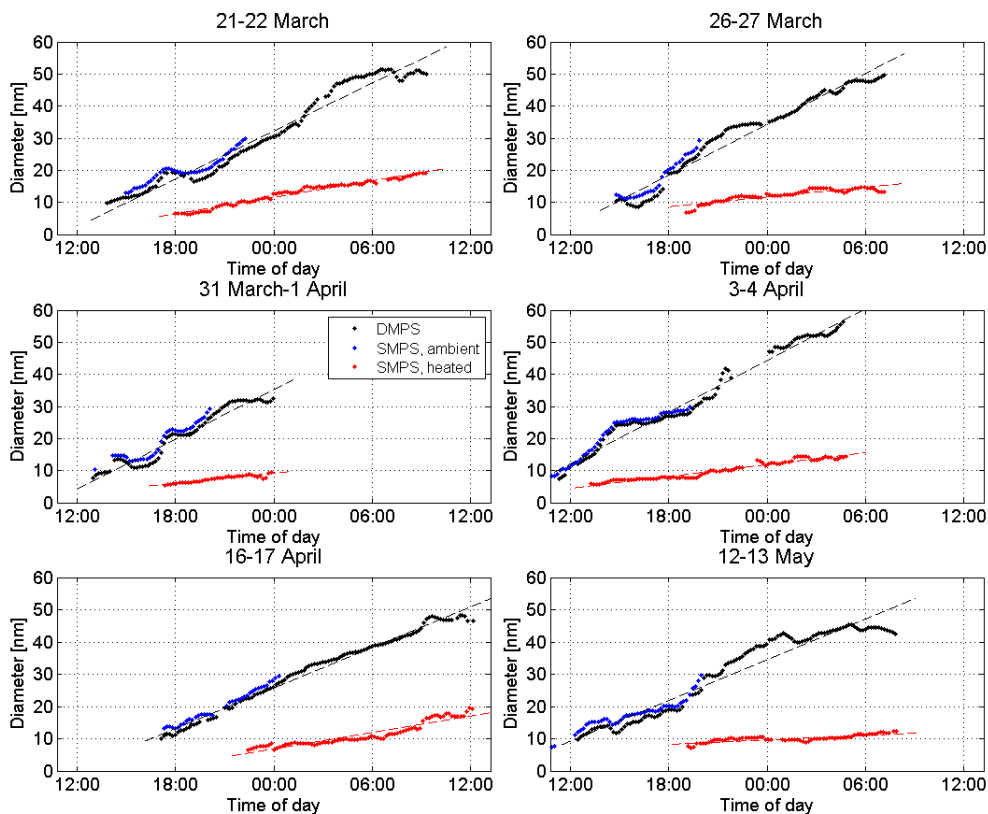


Figure 8: Mean size of the newly formed particles during 6 days in 2005, together with the size of the non-volatile core (from **Paper IV**). During the particle growth, also the non-volatile matter increases steadily during the event.

Volatility measurements conducted in Hyytiälä show that all new particles typically contain substances that do not vaporize at 280 C (**Paper IV**). In mass, the amount of non-volatile substances accounted for roughly 1-7% depending on the event, and this fraction stayed fairly constant (Figure 8), indicating that also the non-volatile material in the particles was increasing during the growth. The blue and black traces are two different measurements (DMPS and VSMPS, non-heated) of the mean size of the newly formed particles during six nucleation events in 2005. The red trace shows the mean size of those particles after heating to 280 C. The diameter ratio of the heated to non-heated is on average around 0.3. Sulfuric acid vaporizes at around 50 C, and ammonium sulfate at 150-200 C. In other words, this non-volatile material was likely of organic origin. The extremely low volatility can have a number of different explanations. It is possible that the condensed organics polymerize in the particle, thus making them less volatile, as found in laboratory



studies by Kalberer et al. (2004) and Wang et al. (2010). Alternatively, according to Huffman et al. (2009), when sufficiently oxidized, organic molecules can become sufficiently non-volatile as to not evaporate even at 300 C. The fact that the non-volatile fraction decreased at night when also the temperature decreased, points toward the latter alternative, since the polymerization process in the particles is not expected to decrease at night. On the other hand, as the temperature decreases during night, less oxidized and more volatile molecules can condense onto the particles causing the non-volatile fraction to decrease. Regardless of the exact reason, organic molecules need to be involved in the growth process to explain the observed volatility.

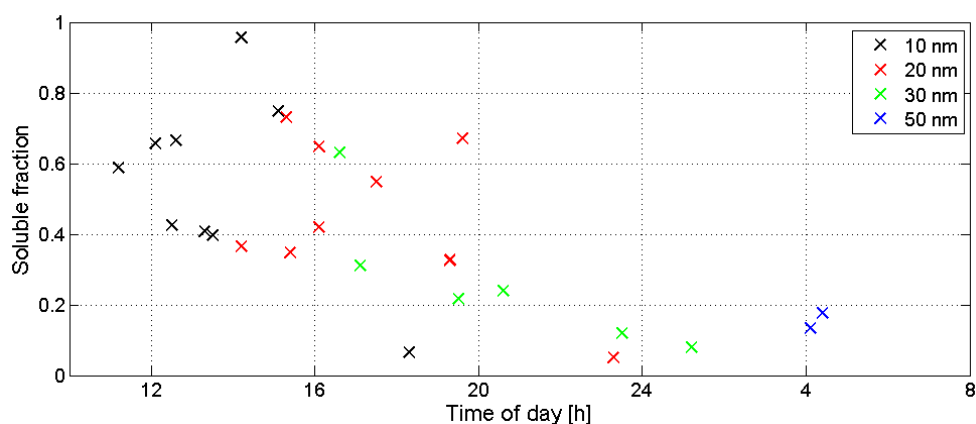


Figure 9: The soluble fraction, a size-independent surrogate for the hygroscopicity, of the newly formed particles during 9 different days (from **Paper V**). Each point signifies the time when the growing mode of new particles passes the selected sizes. Only during two days did the particles grow to 50 nm in such a well-defined way that the hygroscopicity could be measured. The hygroscopicity of the particles constantly decreases during the growth from 10 to 50 nm, implying a decrease in condensing compounds as the particles grow larger.

The hygroscopicity of 10, 20, 30 and 50 nm particles during new particle formation events in Hyttiälä were also measured (**Paper V**). During each of the 9 case studies analyzed, the 10 nm particles contained the most hygroscopic material, and during each event, the average hygroscopicity of the condensing vapors decreased during the growth (Figure 9). The markers indicate the time and hygroscopicity of the new particles when they grow past the measured dry sizes (10, 20, 30 and 50 nm). Due to the Kelvin effect, particles of 10 and 50 nm will not have the same growth factor even though they have the same composition. Therefore, a size-independent measure of the hygroscopicity, the soluble fraction, is used. In practice, this number

denotes the mass fraction of ammonium sulfate (AS) in the particle, if the particle only consisted of AS and a non-hygroscopic compound. Pure AS particles would thus have a soluble fraction of 1. For the growth from 20 to 50 nm, only a fraction of the growth could be due to sulfuric acid or other inorganic species since these have fairly high hygroscopicities. The low hygroscopicities also indicate that the organic vapors on average are not highly oxidized, as recent studies have shown that hygroscopicity is closely linked to the level of oxidation of the organic aerosol (Jimenez et al., 2009; Raatikainen et al., 2010). In other words, by simply measuring the hygroscopicity of the particles during the growth, we can deduce that the main vapors contributing to the growth with high certainty are moderately oxidized organic compounds.

## 5 Review of papers and author's contribution

**Paper I** describes a newly developed mass spectrometer, the APi-TOF, capable of measuring charged molecules and clusters. The instrument is characterized for sensitivity, measurement range, mass accuracy and resolution. The data analysis and peak identification procedures are presented, and applied to the first ambient measurements of naturally charged ions in Helsinki, Finland. I performed a large part of the laboratory and ambient measurements and the data interpretation. I wrote the majority of the instrumental description and the results sections.

**Paper II** presents the first results on ambient ion composition and temporal behavior at the boreal forest site in Hyytiälä, measured with the APi-TOF presented in **Paper I**. The negative ion spectrum was found to be dominated by strong inorganic and organic acids, whereas the positive ions consisted of strong bases, such as amines and pyridines. During new particle formation, the negative ions were dominated by sulfuric acid and its clusters, suggesting that  $\text{H}_2\text{SO}_4$  may play an important role in the first steps of new particle formation. I performed a large part of the APi-TOF measurements, and did most of the data analysis and writing, with the exception of the parts concerning the quantum chemical calculations.

**Paper III** compares ambient ion measurements in Hyytiälä performed with the APi-TOF and two different ion mobility spectrometers. The paper discusses the relationship between mobility, mass, and diameter for ions below a few nm, and the importance of knowing the transfer functions of each instrument. Several comparisons are presented where the instruments are found to agree well with each other, and the ranges where the disagreement is worse are discussed. The good overall agreement is taken as proof that the instruments work as expected, and they

are complementary in many aspects. I was responsible for planning and conducting a large part of the APi-TOF measurements, performed all the data analysis, and almost all the writing.

**Paper IV** investigates the volatility of newly formed particles in Hyytiälä during their growth from below 10 nm up to around 50 nm. The particles were heated to 280 C before the size distribution was measured and compared to the non-heated ambient size distribution. The difference is attributed to evaporated compounds, and only the non-volatile fraction of the particles remained. This fraction was found to stay fairly constant during the growth of the new particles, with only some slight variation which correlated with the ambient temperature. The conclusion was that either extremely low-volatility vapors are condensing onto the particles, or polymerization processes are taking place in the particles, making the compounds less volatile. In any case, this non-volatile core is likely of organic origin. I made the laboratory and comparison measurements, analyzed most of the data, and did most of the writing.

**Paper V** studies the hygroscopicity, of 10-50 nm particles in Hyytiälä. The focus was on the difference between days with and without new particle formation, and to understand the changes in hygroscopicity during the growth of the new particles. The diurnal behavior was more pronounced during days with new particle formation. During the growth from 10 to 50 nm, the hygroscopicity was seen to decrease rapidly, meaning that the growth of the particles was due to condensation of vapors with low hygroscopicities. This suggests that organic compounds dominate the growth of the particles. I built and deployed the instrument and performed the hygroscopicity measurements and the data analysis. The sulfuric acid data was supplied by MPI Heidelberg. I also did most of the writing.

## 6 Conclusions

The rapid development of new measurement techniques, especially mass spectrometric techniques, has greatly increased our understanding of aerosol chemistry and physics. Measurements of particles smaller than 50 nm in diameter still pose a challenge in many ways, and this is the size range where many important processes take place, mainly related to secondary aerosol formation. In this thesis, the chemistry of biogenic new particle formation was studied with different indirect physical approaches. A novel mass spectrometer, the APi-TOF, was characterized and used to measure ambient ions. It was also compared to existing low-resolution spectrometers for validation. Hygroscopicity and volatility measurements of 10-50 nm particles were carried out with two separate self-constructed instruments.

This APi-TOF was first characterized for sensitivity, resolution and accuracy in the laboratory, and deployed for ambient measurements in an urban environment. During the laboratory measurements, it proved its ability to measure cluster distributions of sulfuric acid-ammonia ion clusters up to 1000 Da. The distributions showed that ammonia was only present in larger clusters (tetramer and above), and no pure H<sub>2</sub>SO<sub>4</sub> clusters were found above the pentamer, which is in qualitative agreement with predictions from quantum chemistry. As no instruments can yet measure neutral clusters, this agreement is of great importance as it validates the model calculations, which can be extended also to neutral clusters.

The APi-TOF was subsequently deployed at the SMEAR II boreal forest station in Hyytiälä, and measurements during new particle formation events showed spectra dominated by sulfuric acid and its clusters, strengthening the idea that H<sub>2</sub>SO<sub>4</sub> is a key compound in the cluster formation process. Additionally, also clusters with ammonia were observed, which in conjunction with quantum chemical calculations indicates the presence of several more H<sub>2</sub>SO<sub>4</sub>/NH<sub>3</sub> clusters on the neutral side. Although the ion signal and sulfuric acid concentrations were clearly lower, the ambient cluster distribution looked similar to the one produced in the laboratory at high H<sub>2</sub>SO<sub>4</sub> concentrations. No large clusters containing organic molecules were detected to correlate with particle formation, neither in the laboratory or ambient measurements. During the measurements at the SMEAR II station, the APi-TOF was also compared to previously characterized low-resolution mobility spectrometers, and good agreement was found. This suggests that no considerable fragmentation occurs inside the instrument, although the low resolution of the mobility spectrometers limits the comparison.

In the 10-50 nm range, reported direct measurements of particle composition are extremely rare. We designed and deployed two instruments, a VSMPS and a HTDMA, to measure two physical properties of these particles: hygroscopicity and volatility. The results provided indirect information on the chemical composition of particles in this size range. Measurements during new particle formation events at the SMEAR II station showed that the hygroscopicity of the particles always decreased during the growth in the 10-50 nm range, indicating a dominant role of organics in the condensational growth. Increased oxygen content in the organic aerosol typically leads to increased hygroscopicity, which indicates that the condensing species were only moderately oxidized. However, extremely low-volatility compounds were also detected in the particles, and since volatility typically decreases with increased oxidation, it is also likely that some fraction of the organics was highly oxidized, or alternatively, polymerization occurred in the particles. This indicates a wide range of different organic compounds being

involved in the growth process, which is not unexpected in such a complex environment as the boreal forest.

Directly measuring the neutral cluster composition below 2-3 nm is still a major goal within this research field, and new techniques are being pursued. Meanwhile, mass spectrometric measurements of charged clusters, combined with quantum chemical and kinetic modeling is one of the strongest approaches to study sub-2 nm clusters. The 2-10 nm particles make up another important range to focus on, as no direct measurements in this range have yet been made, and even indirect methods are very limited. In the 10-50 nm range, direct methods, although available, are still in practice limited to one-two instruments, and therefore indirect methods such as those presented in this thesis are still extremely valuable.

This thesis presents measurements of cluster formation and condensational growth during atmospheric new aerosol particle formation in the lower troposphere. The results will hopefully find their way into models where they can fill gaps in the knowledge or improve parameterizations. The hygroscopicity and volatility measurements are not unique, but they are the first and most comprehensive measurements of their kind in the boreal forest, making the data applicable over a large area of Earth's surface. The high mass and time resolution cluster measurements, on the other hand, are completely novel, and should in the near future be expanded into many different environments, as well as to laboratory nucleation experiments. This study contains the first step towards mapping out ion cluster distributions during particle formation in different environments, and thereby indirectly helping us understand the mechanisms and compounds driving neutral particle formation in the atmosphere.

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