DIRECT DETECTION OF ATMOSPHERIC PARTICLE FORMATION USING THE NEUTRAL CLUSTER AND AIR ION SPECTROMETER

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Academic dissertation

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Direct detection of atmospheric particle formation using the Neutral cluster and Air Ion Spectrometer

Hanna Elina Manninen
University of Helsinki, 2011

Abstract

Aerosol particles play an important role in the Earth’s atmosphere and in the climate system: they scatter and absorb solar radiation, facilitate chemical processes, and serve as seeds for cloud formation. Secondary new particle formation (NPF) is a globally important source of these particles. Currently, the mechanisms of particle formation and the vapors participating in this process are, however, not truly understood. In order to fully explain atmospheric NPF and subsequent growth, we need to measure directly the very initial steps of the formation processes.

This thesis investigates the possibility to study atmospheric particle formation using a recently developed Neutral cluster and Air Ion Spectrometer (NAIS). First, the NAIS was calibrated and intercompared, and found to be in good agreement with the reference instruments both in the laboratory and in the field. It was concluded that NAIS can be reliably used to measure small atmospheric ions and particles directly at the sizes where NPF begins. Second, several NAIS systems were deployed simultaneously at 12 European measurement sites to quantify the spatial and temporal distribution of particle formation events. The sites represented a variety of geographical and atmospheric conditions.

The NPF events were detected using NAIS systems at all of the sites during the year-long measurement period. Various particle formation characteristics, such as formation and growth rates, were used as indicators of the relevant processes and participating compounds in the initial formation. In a case of parallel ion and neutral cluster measurements, we also estimated the relative contribution of ion-induced and neutral nucleation to the total particle formation.

At most sites, the particle growth rate increased with the increasing particle size indicating that different condensing vapors are participating in the growth of different-sized particles. The results suggest that, in addition to sulfuric acid, organic vapors contribute to the initial steps of NPF and to the subsequent growth, not just later steps of the particle growth. As a significant new result, we found out that the total particle formation rate varied much more between the different sites than the formation rate of charged particles. The results infer that the ion-induced nucleation has a minor contribution to particle formation in the boundary layer in most of the environments. These results give tools to better quantify the aerosol source provided by secondary NPF in various environments. The particle formation characteristics determined in this thesis can be used in global models to assess NPF’s climatic effects.

Keywords: atmospheric aerosols, aerosol measurements, air ion spectrometers, mobility diameter, new particle formation and growth, corona discharge
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This thesis consists of an introductory review, followed by six research articles. In the introductory part of this thesis, these papers are cited according to following roman numerals.


1 Introduction

Aerosol particles exist everywhere in the atmosphere, they are diverse and complex, and they are in a constant movement and interaction with their surroundings. Aerosol particle sizes range from nanometer sized molecular clusters up to approximately 100 μm cloud droplets. The particle number size distribution changes constantly as particles are formed by nucleation, grown by condensation, become smaller by evaporation, and are lost by deposition. The lifetime of the particles is roughly from hours to a few weeks depending on natural removal processes (Sienfeld and Pandis, 2006). Particles are transported in the atmosphere anywhere from a few hundred meters to several thousands of kilometers. All this makes aerosol particles extremely difficult to measure. The very small size of these particles causes several difficulties in sampling and analysis.

Aerosol particles have global effects on Earth’s climate and regional effects on air quality. In its 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 affect Earth's radiation budget and climate in several ways. For example, they can scatter sunlight back to space, thereby cooling Earth’s surface. Even more importantly, however, they play a crucial role in cloud formation (Ramanathan et al., 2001; Rosenfeld et al., 2008). Clouds both reflect sunlight, which cools the Earth, and trap heat in the same way as greenhouse gases, thus warming the Earth. On a regional scale, other aerosol effects also become important, mainly the degradation of visibility due to absorption and scattering of light (Bohren and Huffman, 1983), and the adverse health effects (Brunekreef and Holgate, 2002) caused by the inhalation of aerosol particles.

The main characterizing parameters of atmospheric particles are their size, concentration, and composition. Primary particles are directly released into the atmosphere by wind, combustion processes, or anthropogenic sources. Secondary particles are those that form in the atmosphere via phase transition of atmospheric vapors. Secondary new particle formation (NPF) increases the total particle concentration and decreases the median particle size. Under favorable conditions, nucleated particles grow into sizes in which they are able to act as cloud condensation nuclei (Kerminen et al., 2005; Laaksonen et al., 2005; Whitehead et al., 2009; Wiedensohler et al., 2009; Kuang et al., 2009). Sulphuric acid is considered to be one
of the key components in these particle formation events (Weber et al., 1997; Petäjä et al., 2009). The growth of freshly-nucleated atmospheric aerosol particles cannot usually be explained without a significant contribution by vapors other than sulphuric acid (Birmili et al., 2003; Smith et al., 2008), and both indirect and direct chemical measurements indicate that organics are present in nm-sized and larger particles during atmospheric NPF events (O'Dowd et al., 2002; Smith et al., 2006, 2008; Riipinen et al., 2009).

Atmospheric NPF by nucleation takes place frequently in the continental boundary layer (BL), as well as in the free troposphere (e.g. Mäkelä et al., 1997; Kulmala et al., 2004a; Kulmala and Kerminen, 2008; Venzac et al., 2008; Mirme et al., 2010; Hirsikko et al., 2011), the overall magnitude of this source is still extremely poorly understood compared to any other major sources. At least two reasons for this exist. Firstly, atmospheric aerosol formation is driven by processes involving particles below 3 nm in diameter, which is a size range below the detection limit of most of the current instruments. Secondly, the nucleation mechanism initiating aerosol formation is likely to vary with location and atmospheric conditions. The detailed formation and growth mechanisms of these freshly formed particles are still unclear in many respects. Where, when and why are the particles formed? What is the contribution of ions to particle formation?

Several formation mechanisms for atmospheric aerosol particles have been suggested. These include activation of stable neutral clusters (Kulmala et al., 2005, 2006; Sihto et al., 2006), kinetic nucleation (Weber et al., 1996), ion-induced (Laakso et al., 2002, Lovejoy et al., 2004) and ion-mediated nucleation (Yu et al., 2008), as well as binary and ternary homogeneous nucleation (Kulmala et al., 1998; Korhonen et al., 1999; Vehkamäki et al., 2002), some of which might further be affected by meteorological processes such as turbulent fluctuations, atmospheric waves and mixing (Wehner et al., 2010; Nilsson and Kulmala, 1998). The existence of neutral clusters has been suggested by theoretical arguments (Kulmala et al., 2005), laboratory (Hanson and Eisele, 2002) and field experiments (Paper I; Lehtipalo et al., 2009; 2010; Sipilä et al., 2008). The relevance of ion-induced nucleation in NPF is still under discussion (Iida et al., 2006, Laakso et al., 2007, Kazil et al., 2008; Yu et al., 2008, Hirsikko et al., 2011, Papers V-VI).

From a physical point of view, two very different cluster types in the sub-3 nm size range can be distinguished: charged (air ions or ion clusters) and neutral species. The
existence of atmospheric ion clusters as small as 0.5-1 nm in diameter has been known for decades (Israël, 1970; Tammet, 1970; Tammet et al., 1995; Flagan et al., 1998; Hörrak et al., 1998a), and measurements with ion spectrometers, such as the Air Ion Spectrometer (AIS, Mirme et al., 2007) and Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006), have demonstrated that such clusters are present practically all the time (Hirsikko et al., 2011). The production rates of ion clusters are, however, generally too low to explain the observed aerosol formation rates (Laakso et al., 2004).

In view of the insufficient numbers of ion clusters, the key to understanding the atmospheric aerosol formation is clearly the presence of neutral clusters. Theoretical arguments predict the existence of such clusters (Kulmala et al., 2005) and suggest that they should play an important role in aerosol formation processes via their activation (Kulmala et al., 2006). The presence of the neutral atmospheric clusters has not been experimentally verified until recently (Paper I; Sipilä et al., 2008; Lehtipalo et al., 2009, 2011), since commercially available instruments cannot reliably detect neutral aerosol particles smaller than about 3 nm in diameter. One of the key problems in elucidating the atmospheric nucleation is the importance of ion-induced nucleation. As a solution, simultaneous measurement of the concentrations of charged and neutral nanoparticles is a viable method to detect it (Iida et al., 2006; Lehtipalo et al., 2009; Gagné et al., 2010; Hirsikko et al., 2011; Papers I, V-VI).

The recently developed Neutral cluster and Air Ion Spectrometer (NAIS, Mirme et al., 2010, Papers I-VI) can be reliably used to measure ions and neutral species near the sizes where atmospheric particle formation begins. The main purposes of the NAIS are to: 1) charge particles efficiently in sub-3 nm size range, 2) detect the fraction concentration of charged particles down to 10 cm$^{-3}$ in air, 3) measure with a high enough time resolution that enables the detection of rapid changes in size spectra during particle formation bursts, and 4) cover the whole size range from cluster molecules up to 42 nm, which approaches the climatically relevant sizes where the particles act as cloud condensation nuclei.

In this thesis, ion spectrometers were used to measure the mobility distributions of charged aerosol particles and clusters down to molecular sizes (Tammet, 2006; Mirme et al., 2007) in various locations across Europe (Paper V-VI). In addition, several NAIS systems measured the mobility distribution of neutral particles larger than 2 nm in diameter by charging the aerosol sample with unipolar corona chargers. In general, ions were measured in the mobility diameter range of 0.8–42 nm, whereas neutral
particles were detected in the range of ~2–42 nm. Atmospheric nucleation and cluster activation takes place in the mobility diameter range of 1.5–2 nm (Nieminen et al., 2009) or even somewhat smaller (1.2–1.5 nm) (Sipilä et al., 2010). Therefore, ion spectrometers allow direct measurements exactly at the size where atmospheric nucleation occurs. In addition to characterizing the spatial and temporal variability of the nucleation events, this enables the investigation of several parameters relevant to nucleation events, including the particle formation and growth rates and, in the case of parallel ion and neutral cluster measurements, also the contribution of ions to the NPF.

Several large-scale modeling studies have demonstrated that more reliable nucleation parameterizations than currently available are urgently needed to evaluate the importance of nucleation in climate (Spracklen et al., 2006; Makkonen et al., 2009; Merikanto et al., 2009; Pierce and Adams, 2009; Yu, 2010). The instrumental developments described here, observing neutral clusters about a nanometer smaller than any earlier measurement technique, offer a chance to test the existing nucleation theories against real atmospheric data. By conducting measurements similar to those reported here in a few carefully-selected locations, it should be possible to develop simple yet sufficiently accurate nucleation parameterizations for large-scale modeling.

This thesis aims to increase the understanding of secondary particle formation and the importance of ions in this process, in order to address the question of how particles are formed in the atmosphere. The main objectives of the work presented in this thesis are:

1) to introduce the Neutral cluster and Air Ion Spectrometer as a reliable tool to directly observe atmospheric particle formation (Paper I-VI),
2) to calibrate and intercompare multiple NAIS instruments (Papers II-III),
3) to verify the performance of the corona-needle charger used in the NAIS (Paper III),
4) to establish continuous field measurements of ions and particles using the multiple (N)AIS systems (Papers IV-VI),
5) and to investigate the relative contribution of atmospheric ions to observed atmospheric particle formation using NAIS (Papers I, V-VI).
2 Atmospheric nucleation

The occurrence of atmospheric NPF events is controlled by a number of factors including the origin of air masses, production of low-volatility vapors, concentrations of aerosol precursor vapors, pre-existing aerosol population, meteorological parameters and radiation (e.g. Nilsson et al., 2001; Boy and Kulmala, 2002; Kulmala et al., 2005; Sogacheva et al., 2005, 2008). Understanding the temporal variation of the NPF phenomenon and quantifying its effect on the climate and air quality requires both intensive field campaigns and long-term, continuous field measurements.

Throughout this thesis, all sub-3 nm particles are referred as clusters and all diameters are reported as Millikan-Fuchs equivalent mobility diameters (Mäkelä et al., 1996; Ku and Fernandez de la Mora, 2009; Ehn et al., 2011). A cluster, by definition, consists of two or more molecules which may – or may not – be weakly bound and may – or may not – be made up from same or similar charged or uncharged units.

2.1 Identifying particle formation events in the sub-3 nm size range

Formation of atmospheric particles by nucleation of vapors and subsequent growth of the particles by condensation are observed world-wide in various environments (Kulmala et al., 2004a, Kulmala and Kerminen, 2008, Hirsikko et al., 2011). Several studies have reported NPF observations in remote continental (Weber et al., 1997; Mäkelä et al., 1997; Birmili et al., 2003; Yli-Juuti et al., 2009), polluted urban (Mönkkönen et al., 2005; Iida et al., 2008; Wu et al., 2007), alpine (Weingartner et al., 1999), savannah (Laakso et al., 2008), Antarctic (Siingh et al., 2007; Asmi et al., 2010) and coastal (Vana et al., 2008; Whitehead et al., 2009) boundary layers as well as in high altitude sites (Venzac et al., 2007; 2008).

Prior to the Neutral cluster and Air Ion Spectrometer (NAIS) measurements, the particle size distribution was typically measured with a Differential Mobility Particle Sizer (DMPS, Hoppel et al., 1978). The longest time series of atmospheric NPF studies ever performed using a DMPS system were performed in a boreal forest site called SMEAR II in Hyytiälä, Finland (Hari and Kulmala, 2005). In Hyytiälä, Mäkelä et al. (1997) observed NPF events on sunny days when the pre-existing particle background concentrations were low, in agreement with Birmili and Wiedensohler (2000). This indicates that direct solar radiation enhances the photochemistry needed
to form both nucleating and condensing vapors. Particle formation (30% of all days) usually takes place during daytime as the NPF starts before noon and the growth of the particles continues all afternoon to CCN sizes (Mäkelä et al., 2000; Aalto et al., 2001). On an annual scale, particle formation is most frequent in the springtime (March-May) and during the autumn (September) (Dal Maso et al., 2005).

NPF occurs when nucleated particles grow to a size that can be detected with instruments lower detection limit. Typical particle size distributions together with NAIS derived ion distributions from Hyytiälä during NPF events are presented in Fig. 1. The figure shows particle and ion size distributions in the size ranges of 2-1000 nm and 0.8-40 nm, respectively, during 12 consecutive days. On all the days the distinct shape of the formation and growth (Dal Maso et al., 2005), called a ‘banana’ event, were observed. In Fig. 1, the formation of sub-3 nm particles began before noon and the growth of the particles continued for several hours; in other words, clusters activated in the morning and started growing by condensation.

Figure 1. Particle size distribution measured with the NAIS in the size range 0.8–20 nm and with the DMPS in the size range 20–1000 nm (top). Negative (middle) and positive (bottom) ion distributions were also measured with the NAIS (0.8–42 nm) on 12 consecutive particle formation event days 8–19 April 2007 in Hyytiälä, Finland (adapted from Paper IV).
Because growth of the secondary particles is seen to continue for hours as measured at a fixed measurement site (Mäkelä et al., 2000), particle formation and growth must occur over a large area. Crumeyrolle et al. (2010) investigated the spatial extent of NPF phenomenon using instrumented aircraft. The overall horizontal extent of NPF bursts seem to be between 100 and 1000 km (Vana et al., 2004; Hussein et al., 2009; Crumeyrolle et al., 2010). The air mass back-trajectory analyses suggest that the origin of the air mass is relevant for occurrence of the NPF (Mäkelä et al., 2000; Tunved et al., 2006; Hussein et al., 2009). Particle formation is also connected to the mixing state of the BL (Nilsson et al., 2001). The elevation of the BL can lead to dilution, which reduces condensable surface area for non-volatile vapors and encourages nucleation.

The ion spectrometers are widely used in atmospheric nucleation studies in sub-3 nm size ranges due to their ability to measure down to molecular sizes. In Fig. 1, the time series of negative and positive ion size distributions were similar to that of the neutral cluster size distribution. Typically, the observed formation and growth of the particles and ions seemed to be almost simultaneous. Nevertheless, on some days that have been classified as NPF event days, the charged cluster concentrations increased somewhat before a corresponding increase in total cluster concentrations (Paper IV-V). The term “total cluster” refers to the sum of charged and neutral clusters.

A significant effort has recently been put into developing instruments that measure neutral atmospheric particles of 1–3 nm, which is close to size range at which nucleation and the initial steps of the particle growth occurs. Very recently, the Airmodus A09 particle size magnifier (Vanhanen et al., 2011) has been able to extend the detection range of Condensation Particle Counters (CPC, McMurry, 2000) down to approximately 1 nm. Jiang et al. (2011) reported on measurements of the 1-2 nm nano condensation nuclei with the Diethylene Glycol Scanning Mobility Particle Sizer (DEG SMPS). Until then, the most compelling evidence of the existence of neutral clusters (at least during NPF) was given by the NAIS measurements.

2.2 Parameters characterizing formation and growth

In particle formation event analysis based on measured number size distributions, the first step is to classify all available days into event, non-event, and undefined days, according to methods introduced by Dal Maso et al. (2005) and Hirsikko et al. (2007). The days which do not fulfill the criteria of event or non-event days are categorized as
undefined. The classification is done visually using daily contour plots of size distributions such as those shown in Fig. 1. The second step in the analysis is to calculate NPF parameters, such as the particle growth and formation rates, in order to characterize the processes leading to nucleation. McMurry et al. (2005) and Kuang et al. (2010) introduced a parameter $L$, the ratio of the particle scavenging loss rate to the particle growth rate, as a means of predicting whether or not NPF would occur on a particular day.

Typically condensation of vapor molecules to the particle surfaces is the most important process behind the observed growth of aerosol particles in the atmosphere (Stolzenburg et al., 2005). The rate (in nm h$^{-1}$) at which the newly formed aerosol population grows can be determined from the measured number size distributions (Fig. 1). A normal distribution function was fit to the time series of the particle concentrations in a certain size bin. After determining the moment corresponding to the maximum concentration in each of the size bins, the growth rate was obtained by a linear least square fit through the data points in the selected size classes. These calculated growth rates can deviate from the real atmospheric growth rates by up to a factor of two because of the observational uncertainties (Kulmala et al., 2004b; Hirsikko et al., 2005).

The total particle formation rate at 2 nm ($J_{2}^{\text{total}}$, in cm$^{-3}$ s$^{-1}$), i.e. the flux of particles into the 2–3 nm size range, can be calculated from the total particle concentrations by taking into account the losses due to coagulation scavenging to the larger pre-existing particles, as well as the growth out of the 2–3 nm size range as (Paper I)

$$J_{2}^{\text{total}} = \frac{dN_{2-3}}{dt} + \text{CoagS}_{2-3} \cdot N_{2-3} + \text{GR}_{3} \cdot N_{2-3}, \quad (1)$$

where $t$ is time, $N_{2-3}$ is the measured 2–3 nm particle concentrations, $\text{CoagS}_{2}$, is the coagulation sink (Kulmala et al., 2001), and $\text{GR}_{3}$ is the particle growth in the size range 2–3 nm (Paper I, see supporting online material).

In the case of charged particles, the losses due to ion-ion recombination and sources due to charging of 2–3 nm neutral particles need to be taken into account. The ion formation rate of 2–3 nm size range is estimated by

$$J_{2}^{\pm} = \frac{dN_{2-3}^{\pm}}{dt} + \text{CoagS}_{2-3} \cdot N_{2-3}^{\pm} + \text{GR}_{3} \cdot N_{2-3}^{\pm} + \alpha \cdot N_{2-3}^{\pm} \cdot N_{<3}^{\mp} - \beta \cdot N_{2-3} \cdot N_{<2}^{\pm}, \quad (2)$$
where the superscript ± refers to the polarity. The ion-ion recombination coefficient, $\alpha$, and ion-neutral attachment coefficient, $\beta$, were assumed to be equal to $1.6 \times 10^{-6}$ cm$^3$ s$^{-1}$ and $0.01 \times 10^{-6}$ cm$^3$ s$^{-1}$, respectively (e.g. Israël, 1970). Suggestive uncertainty estimations for the formation and growth rate calculations are presented in Paper V. The values for the real $J_2$ appear to be approximately a factor of 2 lower or higher than the calculated total formation rates. A closer analysis revealed that the growth out of the size range dominates the $J_2$ calculations.

According to the method described in Paper I, the total nucleation rate can be expressed as a sum of neutral and ion-induced nucleation rates as

$$J_{2 \text{total}} = J_{2 \text{neutral}} + J_{2}^{+} + J_{2}^{-}. \quad (3)$$

In case of parallel ion and total cluster measurements, we can estimate the contribution of ions to particle formation (i.e. the ion-induced fraction) using the calculated ion and total formation rates. Paper VI contains only the ion-induced fraction in different environments. The fraction of ion-induced nucleation (IIN) can be written as

$$\text{IIN} = \frac{J_{2}^{+} + J_{2}^{-}}{J_{2 \text{total}}}. \quad (4)$$

As ions may contribute to neutral nucleation by producing neutral clusters via ion-ion recombination (Arnold, 1980; Yu and Turco, 2008), in Paper V the ion-ion recombination rate $J_{2 \text{rec}}$ was also included into the total particle formation:

$$J_{2 \text{rec}} = a\alpha N_{i}^{+} N_{i}^{-}, \quad (5)$$

where $a$ is the probability that a collision between two ions of opposite polarity leads to a formation of a stable cluster (when the electrical forces holding each of the charged particles together vanish). The size bins for the ion concentrations $N_{i}^{+}$ and $N_{i}^{-}$ were selected in such a way that the diameter of the resulting cluster (i.e. the ion-ion recombination product) was in the size range of 2-3 nm. The recombination coefficient $\alpha$ describes the collision rate of opposite polarity ions and is, therefore, the maximum rate coefficient for the production of the stable neutral particles via recombination.

In terminology, IIN means nucleation in the presence of electric charges (a special case of heterogeneous nucleation), while ion-mediated (IMN) particle formation also takes into account the ion-ion recombination in the small ion size range (Yu and
The fraction of IMN is obtained when the ion-ion recombination products as described in Paper I (supporting online material), are involved in IIN, and it may be expressed as

$$IMN = \frac{J_2^+ + J_2^- + J_{rec}^2}{J_{total}^2}. \quad (6)$$

An example of utilizing calculated nucleation parameters in atmospheric NPF studies is presented in Paasonen et al. (2010). They investigated the relative contribution and spatial variability of sulphuric acid and organic vapors in atmospheric NPF. Figure 2 illustrates the correlation between the neutral particle formation rate calculated from NAIS data (Eq. 3) and sulphuric acid concentration measured with chemical ionization mass spectrometer in Hyytiälä (Finland), Hohenpeissenberg and Melpitz (Germany), and San Pietro Capofiume (Italy). At three out of four measurement sites the nucleation rate was closely connected to sulphuric acid concentration, whereas in Hohenpeissenberg low-volatility organic vapors were observed to be dominant. Under atmospheric conditions, both sulphuric acid and low-volatility organic vapours, in addition to ammonia and possibly amines, are likely participants in nucleation.

Figure 2. Neutral particle formation rate $J_2$ as a function of sulphuric acid concentration. The lines present the 90th and 10th percentile values of the ratio between the observed $J_2$ and the modelled rate (courtesy of Pauli Paasonen, see also Paasonen et al., 2010).
3 Experimental methods and laboratory experiments

The measurement of sub-3 nm aerosol particles is challenging. The smallest particles are easily lost by diffusion during transport, difficult to charge for electrical classification, problematic for collecting representative samples for electrical detection, present in insufficient amounts for chemical analysis, and require a very high super saturation to grow large enough for optical detection. Typically, the measurement set-ups for atmospheric nucleation studies include complementary instruments for detecting both negative and positive ions as well as neutral aerosol particles. In addition to NAIS measurements, different methods have been used in this thesis to determine their concentration and evolution in order to avoid artifacts (Papers I, IV-VI). The calibration of the instruments under laboratory conditions is essential to confirm that the results are comparable (Papers II-III).

3.1 Aerosol size distribution measurements

Size is probably the most fundamental parameter describing aerosol particles. Particle size is determined by the formation processes and subsequent physical and chemical processes in the atmosphere. The appropriate particle size definition depends primarily on the type of measurement made. In this thesis, we focus on electrical mobility analysis. The motion (or terminal velocity, to be exact) of charged particles in an electric field determines their mobility equivalent size, the so-called mobility diameter. The instruments, which measure mobility, do not yield all the information whether the detected nano-particle is a particle, cluster, or a large molecule.

The differential Mobility Analyzer (DMA) was introduced by Hewitt (1957) and later Knutson and Whitby (1975) for particle size selection. Typically, DMAs operate with a constant voltage with each measurement channel corresponding to a fixed mobility (Flagan, 1998). The size-selected particles are transported in an electric field through a particle-free sheath flow and extracted to sample flow. A typical sample-to-sheath flow ratio is 1:5-1:20, depending on the design of the DMA. All DMAs are designed to operate under laminar flow conditions so that, ideally, no mixing occurs between these two streams. Particles with higher mobilities (smaller particles) deposit on the collecting electrode upstream of the sample extraction port. Particles with low mobilities (larger particles) deposit further downstream or are discharged with the excess sheath flow. To determine the size of particles transmitted through the DMA,
transfer functions, i.e. the transmission efficiency of particles as a function of their mobility, need to be known (Stolzenburg, 1988).

For example, simplified cross sections of two cylindrical DMAs are presented in Figure 3. Only particles with a specific electrical mobility will enter into the slit in the central electrode of Vienna-type DMA (University of Vienna DMA commercialized by Hauke, Winklmayr et al., 1991). In the case of the Vienna-type DMA, the classification is literally differential since only a small mobility fraction is classified at a time, whereas in a Mirme-type DMA (Mirme et al., 2007, 2010) the entire size distribution is measured continuously. In the Mirme DMA, the size distribution is acquired by coating the outer cylinder walls with 21 electrometers, and the sample is introduced to the inner cylinder, i.e. the reserve of the Vienna-type DMA. The radial electrical field is generated by connecting a potential to different sections of the inner cylinder.

Figure 3. Schematic cross sections of different types of cylindrical Differential Mobility Analyzers (DMAs): Vienna-type DMA (left panel) is used in the Differential Mobility Particle Sizer (DMPS) and Mirme-type DMA (right panel) in the ion spectrometers.

A limitation of the DMA is that it can only size-select charged particles. Therefore, it is necessary to bring the sample to an equilibrium charge distribution using forced charging. In many applications this is achieved with artificial unipolar or bipolar charging (Flagan, 1998). The advantage of the unipolar, over bipolar, diffusion charging is the higher charging efficiency, which can be a critical factor at the smaller, 1–10 nm, particle sizes where the charged fraction remains small (only around 0.5–
However, the resulting aerosol charge distribution depends strongly on the charging conditions, on the flow rate, and also, in the case of highly pre-charged particles, on the initial charge distribution (Biskos et al., 2005).

The concentration of ultrafine particles can be determined by measuring a current delivered by a flow of charged particles to an electrometer or by condensing vapor on them and growing them to larger sizes where they can be detected with optical methods. The limitation of electrometers is their sensitivity, whereas the condensational techniques are sensitive to the chemical composition of the particles. The most common method to measure ultrafine particle number size distribution is Differential Mobility particle Sizer (DMPS). In the DMPS system a charger is placed in front of a DMA, and the voltage is scanned (continuously or) step-wise while the concentration is recorded. To obtain the particle size distribution, \( \frac{dN}{d(\log D_p)} \), from the raw data (which is particle concentration, or current signal induced by charged particles) vs. DMA voltage, one has to know the charge distribution of the aerosol particles, analyzer flows rates, the DMA transfer function, the detection efficiency of the detector and losses in the sampling lines. Transformation from voltage-concentration (or voltage-current) space to diameter-concentration space is called inversion.

Electrical mobility spectrometers can detect atmospheric charged clusters even smaller than 1 nm (Iida et al., 2006; Tammet et al., 2006; Mirme et al., 2007). The natural charge of the ions enables electrical detection (Flagan 1998) if concentrations are large enough. Neutral clusters in sub-3 nm size range are challenging to classify and detect with mobility spectrometers, in many respects. Recent instrumental development has pushed the neutral particle detection limit below 2 nm in size (e.g. Sipilä et al., 2008; Iida et al., 2009; Jiang et al., 2011; Vanhanen et al., 2011) also with various condensation/activation techniques. In the case of condensation techniques the activation efficiency determines the smallest detectable particle size (McMurry, 2000; Kulmala et al., 2007; Winkler et al., 2008; Iida et al., 2009).

The electrical detection of clusters is a challenging task due to small concentrations, transport losses, and insufficient charging efficiency of small neutral particles. Thus, electrical instruments need to be sensitive enough to distinguish the minuscule signal brought in by the clusters from the instrument background. To tackle the difficulties in the electrical techniques, high flow rates are used to minimize the ion diffusion losses.
and also increase the sensitivity to the ion concentrations. By utilizing a unipolar charger, the charging efficiency can be improved by employing high ion concentrations. However, high particle loss within the charger, resulting in a small percentage of charged particles exiting the chargers, is typically the case for unipolar chargers.

3.2 Ion spectrometers

The Air Ion Spectrometer (AIS, Mirme et al., 2007) measures the mobility distributions of both negative and positive air ions simultaneously in the range between 3.2 and 0.0013 cm$^2$ V$^{-1}$ s$^{-1}$, which corresponds to a mobility diameter range of 0.8–42 nm. Hereafter the mobility diameter, i.e. the Millikan diameter, is applied when converting the measured mobility to particle diameter (Mäkelä et al., 1996). The AIS consists of two parallel cylindrical DMAs, one for classifying negative ions and the other for positive ions. The ions are simultaneously classified according to their electrical mobility with differential radial electric field and collected to 21 electrically isolated sections (Fig. 3). Each section has its own electrometer to measure the currents carried by the ions. The total flow into the AIS is 60 L min$^{-1}$, whereas the sample and the sheath flows of the DMAs are 30 and 60 L min$^{-1}$, respectively.

The Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006) measures the mobility distributions of small air ions and naturally charged aerosol particles of both negative and positive polarity. The mobility range of the BSMA is 3.2–0.032 cm$^2$ V$^{-1}$ s$^{-1}$, corresponding to the diameter range of 0.8–8.0 nm. The BSMA consists of two plate capacitors (DMAs), one for each polarity, and a common electrical amplifier (electrometer) connected to a balanced bridge circuit. Thus, as both DMAs use the same electrometer, only one polarity is measured at a time while on the other polarity all ions are removed from sampled air with an electrostatic filter (±250 V). The electrostatic pre-filters (±500 V) are used also to clean the sheath flow. The total flow into the BSMA is 2400 L min$^{-1}$.

The advantage of the AIS is a high time resolution (minimum 60 s) since both polarities are measured in parallel, whereas the disadvantages include possible turbulence in the analyzer and under-estimation of multiply charged particles. The drawbacks of the BSMA compared to the AIS are the narrower measurement range, decreased time resolution (minimum 10 min), and practical sampling difficulties due
to high inlet flow rate. However, the high flow rate minimizes the ion losses efficiently. Ehn et al. (2011) reported a good agreement between the ion mobility spectrometers and atmospheric pressure interface time-of-flight mass spectrometer (API-TOF; Junninen et al., 2010) at small ion sizes. Together with previous validation of the instruments at sizes above 5 nm (e.g. Vana et al., 2006; Paper II), it can be stated that the ion spectrometers can measure the whole size range that is important for NPF.

![Figure 4](image_url)

Figure 4. A channel-by-channel comparison of the AIS and the API-TOF during 5 days in Hyytiälä. The background of each subplot is colored according to the amount of sulfate, nitrate, and other (mainly organic) compounds in each bin as measured by the API-TOF (courtesy of Mikael Ehn).

Figure 4 illustrates a channel-by-channel comparison of the time series of the AIS and the API-TOF negative ion signals (Ehn et al., 2011). A similar comparison was performed for the BSMA data. To get good agreement some corrections had to be made for the ion spectrometer transfer functions and mobility channels. Nevertheless, the mass and mobility spectra complement each other, with the API-TOF giving superior chemical information on the small ions, whereas the mobility spectrometers are better suited for quantitative concentration measurements.
3.3 Neutral cluster and Air Ion Spectrometer (NAIS)

Although the ion spectrometers detect freshly formed charged particles in the size range well below 1.5–2 nm, the majority of these freshly formed particles are uncharged (Wiedensohler 1988; Lehtipalo et al., 2009, 2010; Paper I). Therefore, measurements of neutral particles below 3 nm are necessary. The Neutral cluster and Air Ion Spectrometer (NAIS) is a modified version of the AIS instrument and includes several improvements. A controlled charging of the aerosol sample with a needle-corona charger, together with electrical filtering of the corona charger ions, enables one to measure neutral aerosol particles as well. The mobility range of the NAIS is 3.2–0.0013 cm² V⁻¹ s⁻¹, which corresponds to a diameter range of 0.8–42 nm.

![Diagram of the NAIS](image)

Figure 5. A schematic figure of the NAIS (a more detailed figure is presented in Paper IV).

The NAIS consists of two independent spectrometer columns, one of each polarity, where the ions are classified by a cylindrical DMA (Fig. 3, right panel). The NAIS may be divided into two units: aerosol processing and aerosol detection unit (Fig. 5). The processing unit consists of two corona charger and electrostatic filter pairs, where
the aerosol sample is treated according to the operation mode prior to the mobility analyzers. In the detection unit the charged sample is classified and collected in the 21 electrometer rings in the outer cylinder according to their electrical mobility, and the ion currents are measured with the electrometers. The channels up to 12 are located quite densely on the mobility scale to provide higher mobility resolution at the cluster ion range (negative cluster ions >1.7 cm$^2$ V$^{-1}$ s$^{-1}$, positive >1.3 cm$^2$ V$^{-1}$ s$^{-1}$). The sample and sheath flows of the analyzers are 30 and 60 L min$^{-1}$. The main working principle of the NAIS is described in more detail in Paper IV. The main parts of the NAIS are presented in Fig. 6.

![Figure 6. The Neutral cluster and Air Ion Spectrometer.](image)

The ion and the particle spectra are measured with the NAIS using three operational modes: ion, particle, and offset (Table 1). In the ion mode both pairs of corona chargers and electrostatic filters are switched off. Therefore, the instrument classifies and detects ions according to their ambient charge. In the particle mode only the main corona charger and the main filter is switched on. The charger polarity is equal to the analyzer polarity. Therefore, all the particles carried to the DMA are either uncharged
or charged with the same polarity as the analyzer. In addition to particle mode, the
NAIS has a mode called alternate charging, where the sampled particles are exposed
to the corona ions of an opposite sign before the main charging section. The purpose is
to bring particles closer to an equilibrium charge distribution. In addition to the
operation modes presented in Table 1, the NAIS has an additional mode to measure
only neutral particles with an ion trap in front of the inlet, and an ion background
mode to detect ion production inside the instrument.

<table>
<thead>
<tr>
<th>Ion mode</th>
<th>Particle mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pos. ions</td>
<td>Neg. Ions</td>
</tr>
<tr>
<td>Discharger</td>
<td>off</td>
</tr>
<tr>
<td>Pre-filter</td>
<td>off</td>
</tr>
<tr>
<td>Main Charger</td>
<td>off</td>
</tr>
<tr>
<td>Main filter</td>
<td>off</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pos. charging</th>
<th>Neg. charging</th>
</tr>
</thead>
<tbody>
<tr>
<td>on, pos. HV</td>
<td>on, neg. HV</td>
</tr>
<tr>
<td>on, pos. HV</td>
<td>on, neg. HV</td>
</tr>
<tr>
<td>on, pos. HV</td>
<td>on, neg. HV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Offset mode</th>
<th>Alternate charging mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pos. polarity</td>
<td>Neg. polarity</td>
</tr>
<tr>
<td>Discharger</td>
<td>on, neg. HV</td>
</tr>
<tr>
<td>Pre-filter</td>
<td>on, pos. HV</td>
</tr>
<tr>
<td>Main Charger</td>
<td>off</td>
</tr>
<tr>
<td>Main filter</td>
<td>off</td>
</tr>
</tbody>
</table>

Table 1. The functioning of the aerosol processing unit during different operation modes: ion measurements (ion mode), particle measurements (particle mode), and background measurements (offset mode). The high voltage (HV) feeds the electric filters and corona charger needle.

The reliability of the offset measurements very much defines the accuracy of the
instrument itself and, clearly, the final spectra. The measurement errors and noise are
electrometer specific while the mobility spectrum is measured with 21 individual
electrometer rings. In the offset mode the first pair of the unipolar corona discharger,
which has the opposite polarity to the analyzers, and the electrostatic pre-filters are
switched on (Fig. 7). The opposite charging together with the filtration enables us to
measure the noise and the offset of the electrometers, when no particles or ions are
carried to the DMA. Similar electrical filtration is used also for cleaning the re-
circulated sheath air.

The high voltage (HV) supplies feed the electric filters (50-150 V) and corona charger
needles (2-3 kV). The main charger current is set to 25 nA for the positive charger and
to –22 nA for the negative one. The difference in charging currents compensates for
the difference in the charging efficiency of the chargers (due to the different mean
mobility of positive and negative ions). A schematic cross section of the NAIS aerosol
processing unit is shown in Fig. 7.

Figure 7. A cross section of the NAIS aerosol processing unit and upper part of the mobility
analyzer (courtesy of Aadu Mirme, Airel Ltd and University of Tartu).

The corona currents and filter voltages are adjusted by varying the HV supply feed
voltage according to an active feedback loop. The corona charger’s efficiency is
directly determined by the charging current. The charger ion concentration is
maintained at a constant level. Thus, the pre-charger and the main charger are
controlled with a feedback loop driven by the current measured from the surrounding
electrode. The post-filter is controlled according to the current measured on the first
channels in particle mode. In the NAIS the blowers are also actively controlled
according the measured aerosol flow signals.
Although bipolar radioactive chargers are the most widely used chargers due to their well defined charge distribution (Reischl et al., 1997; Wiedensohler et al., 1988), unipolar diffusion chargers can attain much higher charging levels. Therefore, the NAIS uses unipolar corona discharge ionization. Chen and Pui (1999) reported that their corona charger achieves 90% and 95% charged particle penetration efficiency with 22% and 48% extrinsic charging efficiency at 3 and 5 nm particle sizes, respectively. But these levels differ greatly between different charger designs and usage time (Intra and Tippayawong, 2009). The charging efficiency of the corona charger can change over time, since the electrode (i.e. corona needle/wire) gets worn out. For this reason the NAIS corona needles need to be cleaned regularly.

The sampled particles are assumed to be in charge equilibrium. The particle charging probability is predicted by Fuchs’ diffusion charging theory (Fuchs and Sutugin, 1971). At a constant corona-wire current the aerosol charging depends mainly on the particle size, charger ion concentration and the residence time of the aerosol in the charging region. The product of the latter two is called nt-product. The model that calculates the NAIS inversion takes into account aerosol volume flows, particle charging probabilities, the loss factor, and the charging parameter (i.e. nt-product). The charging probabilities use a calibrated charging parameter $\alpha = 6$, which translates to $nt = 2.22 \times 10^6$ for a mobility of $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Paper I, supporting online material). According to these numbers, 1% of 1 nm particles and 5% of 5 nm particles are singly charged. Alguacil and Alonso (2006) reported that substantial fractions of doubly charged particles occur for particle diameters above 15 nm. The use of the corona charger for accurate aerosol sizing should therefore be limited to the particle size range below 15 nm. For larger particles, multiple charging is not negligible and data inversion becomes complicated, though not impossible.

Although the data inversion assumes that the sampled particles are in charge equilibrium, the unipolar charger does not neutralize the aerosol sample entering the NAIS (McMurry et al., 2009). If the sample is highly overcharged, this can lead to overestimation of the particle concentrations. On the other hand, the electrostatic losses inside the corona charger during charging process lead to underestimation of the particle concentration (Alonso et al., 2006; Huang and Alonso, 2011). The diffusion losses decreases and electrostatic loss increases as the charger voltage is increased, whereas charging efficiency increases with particle size and charger voltage. Electrostatic loss of small particles increases with decreasing particle diameter.
<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of an extra charger and filter pair to aerosol conditioning unit</td>
<td>To measure both charged and neutral particles in particle mode (AIS → NAIS)</td>
</tr>
<tr>
<td>Ion trap to the aerosol inlet (ion background and filter ion measurement modes)</td>
<td>To measure ion background caused by radon decay in the inlet tubing, or get an ion-free sample</td>
</tr>
<tr>
<td>Decrease of inlet sample flow</td>
<td>To decrease turbulence in the aerosol processing unit, and improve size resolution</td>
</tr>
<tr>
<td>Additional current feedback</td>
<td>Faster response to changes in environmental conditions (charging, filtering, flow rates)</td>
</tr>
<tr>
<td>New data acquisition software</td>
<td>Extended charger control range and automatic control improves stability and usability</td>
</tr>
<tr>
<td>Constant monitoring of all flows</td>
<td>To provide more information used later in inversion algorithm and data analysis</td>
</tr>
<tr>
<td>Constant volume sample flow regardless of air pressure</td>
<td>To keep the analyzer particle sizing constant (airborne measurements; Mirme et al., 2010)</td>
</tr>
<tr>
<td>Nets removed from venturi tubes</td>
<td>To increase the inter-cleaning time (dirty nets increase flow resistance)</td>
</tr>
<tr>
<td>Improved mechanical construction</td>
<td>To improve air tightness, and minimize leaks/losses</td>
</tr>
<tr>
<td>Single blower flow system was changed to a three blower system</td>
<td>To enable better adjustment and stability of the air flows</td>
</tr>
<tr>
<td>Two blowers in series for air sampling</td>
<td>Efficient sampling, wider adjustment range</td>
</tr>
<tr>
<td>Improved inversion algorithm</td>
<td>Enhanced final mobility spectra</td>
</tr>
<tr>
<td>Internet site Wiki for ion spectrometer users</td>
<td>To exchange the latest information</td>
</tr>
<tr>
<td>Organization of regular air ion and aerosol workshops</td>
<td>To improve information exchange with user meetings (Kulmala and Tammet, 2007)</td>
</tr>
<tr>
<td>Organization of regular calibration workshops</td>
<td>Improved maintenance and stability of the instruments</td>
</tr>
</tbody>
</table>

Table 2. Modifications made to the ion spectrometers during the last few years.

The NAIS has undergone several improvements since the prototype was introduced in the spring of 2006 in order to increase its sensitivity (e.g. in clean air chamber studies (Duplissy et al., 2010)), reliability (e.g. in continuous field measurements (Venzac et al., 2008; Boulon et al., 2010; Paper V-VI)), and to extend its operation to variable altitudes (e.g. airborne measurements (Laakso et al, 2007; Mirme et al., 2010)). The development of the NAIS is an outcome of an open co-operation between the manufacturer Airel Ltd. (University of Tartu, Estonia) and the (N)AIS users (e.g.
Kulmala and Tammet, 2007; Mirme et al., 2007, 2010; **Paper I-IV,VI**. Some of the more recent (N)AIS modifications and improvements are listed in Table 2.

Currently, the total number of the (N)AIS instruments in the world is 18, which includes 6 AISs, 5 NAISs and 7 ‘new generation’ NAISs. The new generations of instruments contain all of the modifications listed in Table 2. Figure 6 shows a photo of a new generation NAIS built in 2009. The most visible difference between this NAIS and the one presented schematically in Fig. 5 is the replacement of single blower system with a three blower construction.

### 3.4 Calibration of ion spectrometers

The laboratory verification and calibration of the ion spectrometers were performed during the ion spectrometer calibration and intercomparison workshops, held in February 2008 and June 2009 in Helsinki, Finland (**Paper II** and Gagné et al., 2011). Several methods were used to cover the whole size range of the instruments. In the size range of the smallest cluster ions and neutral particles the calibration is a challenging task due to capability of reference instruments, proper calibration aerosols, and instrumentation for the size-separation. All of the ion spectrometers were calibrated using state-of-art instrumentation: 1) in the sub-3 nm size range the high resolution H-DMA (Herrmann-DMA; Herrmann et al., 2000) was used for size-separation to determine the transfer function at 1-10 nm, 2) monomobile standards (Ude and De la Mora, 2005) were used for a mobility calibration, 3) a Hauke DMA (Winklmayr et al., 1991) was used for mobility and concentration calibration in the size range of 4-40 nm, and 4) the flows of the ion spectrometer were determined using a special pressure difference sensor apparatus.

The first calibration workshop aimed to verify the (N)AIS instruments so that they could be reliably used for long-term studies. Considering the short time period of development and the fact that the instruments are also used to detect nanometer-sized ions and particles in the size range below 3 nm, their performance for both mobility and concentration measurements was discovered to be good (**Paper II**). The mobilities seemed to be slightly overestimated in both polarities. The (N)AIS systems detected similar concentrations as the reference instruments at the concentrations corresponding to those observed during particle formation events, but as the calibration aerosol concentration decreased significantly, the (N)AISs detected elevated concentrations.
In the ion concentrations, a small background caused by the noise of the electrometers was always present. In the particle measurements this background became more significant. The ion concentrations measured with the AIS were higher compared to the ones measured with the NAIS (Paper IV; Gagné et al., 2011).

One of the most important conclusions of the first workshop was that, according to the size distribution of corona charger ions, it is possible to measure neutral particles down to 2 nm using the NAIS (Paper II). The positive and negative corona ions measured with the high resolution DMA were clearly below 1.8 and 1.5 nm in diameter, respectively. However, the mobility standard calibrations showed that the monomobile ion peaks extended to approximately 3 to 5 channels in both polarities of the (N)AIS. The transfer function broadening is due to diffusion losses of ions and the ratio between aerosol and sheath flow used in the (N)AIS.

The second calibration workshop focused on ensuring that the instruments had sustained their performance during the EUCAARI field measurements (Paper VI) and to experimentally determine the (N)AIS transfer functions for all the ion spectrometers. Gagné et al. (2011) aimed to compare the instruments in field-like conditions to offer guidance for data analysis. They performed a mobility and concentration comparison to reference instruments and also compared the ion spectrometers to each other. Again, all the instruments showed sufficient agreement in terms of particle number concentration and size. A repetition of the inter-comparison also suggested that the ion spectrometers sustain their measurement stability after operating continuously in a variety of different conditions given that the instruments are properly maintained.

### 3.5 Characterization of the NAIS corona charger

The corona charger ions complicate NAIS particle detection in the measurement range that overlaps the size range of these charger ions. According to Papers II and III, the positive and negative charger ions were smaller than 1.8 and 1.6 nm, respectively, which results in the lower detection limit of approximately 2 nm for the NAIS particle measurements. Therefore, particles below a diameter of ~2 nm cannot be reliably distinguished from the corona charger ions. An efficient filtering of the charger ions, but not the charged particles, at different operating conditions is essential for achieving the lowest possible size limit for the electrical detection of charged particles.
Challenges in adjusting the main filter, the so-called post-filter, are discussed in detail in Paper IV. The lower detection limit of the NAIS is determined by the charging probability, ion concentration and the charger ion masses and mobilities. Corona chargers have been studied widely (reviewed by Intra and Tippayawong, 2009; 2011).

The size distribution of the positive and negative corona charger ions, shown in Fig. 8, illustrates the effects of carrier gas and impurities in the sample lines on the size distribution observed during laboratory experiments. Paper II and Paper III both used the main charger of the NAIS to generate these charger ions. Basically, the only difference between the experiments is the design of the sample lines and the exact composition of the carrier gas, as the charger current stayed constant in both experiments. In Fig. 8, the black dots represent corona-generated ions carried by filtered compressed air and the gray stars represent charger ions carried by room air. The room air contains e.g. more water vapour compared to the compressed air.

![Figure 8. The size distribution of positive and negative corona charger ions measured with a high resolution H-DMA by Paper II and III.](image)

This surprising result found an agreement with earlier publications and indicated that the size and concentration of charger ions generated in the corona charging process depend both on corona voltage and on the properties and composition of the carrier gas. Therefore, in field conditions the corona charger ion size and composition changes with time. Again, this observation brings additional challenges to post-filtering of the corona-generated ions in the field.
The corona charger ions were characterized with a high resolution H-DMA in Papers II and III (Fig. 8), which has nearly monomobile transfer functions (sample to sheath flow ratio ~1:100). This has to be considered when determining the lower detection limit of the NAIS. The ratio of sample and sheath flows of the NAIS-DMA is 1:2, widening the measurement channel transfer functions (Knutson and Whitby, 1975) and spreading the detection of corona ions to several channels (Fig. 9), as discussed earlier. Therefore, a part of these ions is detected also at larger sizes by the NAIS.

The size distribution also depends on where in the size spectrum the peak is located; if the size happens to be between fraction bins the distribution is broad. According to our results, the lowest detection limit can be set to between 2-3 nm. Particles below this limit cannot be distinguished from the charger ions. However, the limit can be further decreased if the measured small particle concentration is high (when an even larger fraction of the charger ions is used to charge the sample particles).

![Figure 9. The size distributions of four different sizes of neutral silver particles measured with the NAIS-DMA. The shaded area represents the size range of corona charger ions.](image)

The performance of the electrical mobility spectrometer depends on the quality of aerosol charging. Here, the neutralized silver particles in the size range 2.4-4.5 nm were used to verify the aerosol charging inside the NAIS charger. Figure 9 shows the size distribution of different sized neutral particles measured with the NAIS-DMA using positive corona charging. The silver particles were size selected using a high resolution H-DMA. Prior to the NAIS inlet the sample was neutralized using an $^{421}$Am source and all ions were removed using an ion trap (70 V). As can be seen from Fig. 9, the charger ions were smaller than 2 nm and the particle sizes were well resolved. The corona-generated ions are slightly smaller when negative charging is used (Fig. 10a,b).
Clearly, the post-filtering had an effect on both the charger ion and the charged particle concentrations with increasing filtration efficiency as the particle size decreases. The result is in agreement with the experiments presented in Paper III. The results presented in Fig. 9 and 10 were measured in particle mode (neutralized aerosol sample). In sub-5 nm range almost all of the generated silver ions were neutralized. The same aerosol sample (without neutralization) was measured also with the NAIS ion mode. An empty neutralizer and ion trap (0 V) was placed before the NAIS inlet to ensure the same diffusion losses. Interestingly, the concentrations were much higher in ion mode than in particle mode, even if the charger ions were excluded, indicating high electrostatic losses for small ions even when the sample was 100% overcharged.
4 Field observations of atmospheric particle formation and growth

Measuring the ion concentration and charge distribution of aerosol particles offers an effective method to study particle formation mechanisms. Few years ago, the lowest measurement limit of neutral particles was approximately 3 nm, whereas the small air ions could be measured down to molecular sizes. At that time, the ion spectrometers were the only instruments able to measure directly the early stages of atmospheric nucleation and subsequent growth. In this thesis, the ion number size distribution was measured with following ion spectrometers: the Balanced Scanning Mobility Analyzer (BSMA, Tammet 2006) and the Air Ion Spectrometer (AIS, Mirme et al 2007). NPF event analysis – event classification, particle formation, and growth rate calculations – for ion spectrometer data already has well-defined guidelines (Hirsikko et al., 2005, 2007; Vana et al., 2006; Paper I, V).

Based on the calibration and good agreement with the reference instruments (Sections 3.4-3.5), the Neutral cluster and Air Ion Spectrometer (NAIS) can be reliably used as the first instrument to measure in addition to ions also neutral particles near the sizes where atmospheric particle formation takes place. In this section, NAIS observations of atmospheric particle formation are reported from a variety of settings. The field measurements reported here were carried out in Hyytiälä, Finland, (Papers I, IV-V) and at 11 other field sites across Europe: Pallas (Finland), Vavilhill (Sweden), Mace Head (Ireland), Cabauw (The Netherlands), Melpitz and Hohenpeissenberg (Germany), K-Puszta (Hungary), Jungfraujoch (Switzerland), Puy de Dôme (France), San Pietro Capofiume (Italy) and Finokalia (Greece) (Paper VI).

4.1 Direct observation of atmospheric nucleation using NAIS ion measurements

Over the last 30 years, ion spectrometers have been utilized in continuous field measurements and intensive campaigns in various environments (Hirsikko et al., 2011, and references therein). Although a large number of observations have shown that atmospheric particle formation takes place frequently in the continental BL (Kulmala et al., 2004a; Kulmala and Kerminen, 2008), the role of ions in this process is not well quantified (e.g. Kulmala and Tammet, 2007; Enghoff and Svensmark, 2008b; Arnold, 2008; Gagné et al., 2008; Yu and Turco, 2008; Kulmala et al., 2010; Paper VI). Ion
losses occur due to recombination with oppositely charged ions and through attachment to larger aerosol particles or surfaces. The loss rate varies mainly according to the amount of aerosol particles and the production according to the amount of radon in the air (Laakso et al., 2004; Hörrak et al., 2008). A typical ion-production rate in continental areas is considered to be 10 pairs cm$^{-3}$ s$^{-1}$ (Chalmers, 1967; Israël, 1970). Small ions exist all the time in the atmosphere outside of clouds (Lihavainen et al., 2007; Hirsikko et al., 2011, and reference therein), and the average concentrations of positive and negative small ions are typically 200–2500 cm$^{-3}$.

For instance in Hyytiälä on the NPF event days, an increase in the median concentration of 1.8–3.0 nm ion clusters is typically detected around noon, reaching a maximum at midday. On average, these small air ions reach the maximum concentration approximately ~1 hour earlier than total particles in the corresponding size range (Paper IV, Fig. 5). During the events, the ratio of total to charged cluster decreases. This observation suggests that the relative fraction of neutral clusters changed during the event. The decrease in neutral cluster fraction is connected to overcharging of the atmospheric ions (Laakso et al., 2007; Gagné et al., 2008). During the overcharging of particles, higher atmospheric ion concentrations are detected than in charge-equilibrated air.

Figure 11 shows the ion number size distribution and concentration time series on a selected NPF event day in Hyytiälä. During the NPF event, the concentrations of the cluster ions smaller than 1.7 nm decreased, whereas the amount of the 1.7-6.5 nm intermediate ions started to increase almost simultaneously with the increase in the gas phase sulfuric acid concentration (supporting observations by Nieminen et al., 2009; Gagné et al., 2010). As sulfuric acid is one of the key components taking part in the initial steps, we can conclude that the ion measurements directly detect NPF occurrence. The decrease of cluster ion concentration can be due to ion-induced nucleation or an increased sink after the NPF burst.

Based on the spring-time data (Paper V), the median growth rate of 1.3–3 nm charged particles in Hyytiälä was 2.3 nm h$^{-1}$, varying from 0.6 nm h$^{-1}$ to 7.7 nm h$^{-1}$. The median growth rate showed an increase with an increasing particle size. The median observed formation rate of 2 nm charged particles was 0.03 cm$^{-3}$ s$^{-1}$ varying from 0.01 to 0.09 cm$^{-3}$ s$^{-1}$. The size-dependent growth rates obtained from the different ion spectrometers gave consistent results with each other (Papers V-VI).
Figure 11. Upper panel: Negative ion number size distribution during a selected particle formation day measured with the NAIS. Lower panel: Concentration of negative cluster ions (<1.7 nm), intermediate ions (1.7-6.5 nm), large ions (5.6-42 nm) and gas phase sulphuric acid (gray solid line) on 5 May 2007 in Hyytiälä.

4.2 Added value from the NAIS particle measurements

The lowest detection limit of the NAIS is set to approximately 2 nm, depending on the mobility of the charger ions and efficiency with which these ions are separated from the charged particles (Paper II). The added value of the NAIS particle measurements relies especially on the 2-3 nm size range. Figure 12 presents the particle size distribution measured on the same day as shown in Fig. 11. Clearly, the NPF has started already at smaller sizes than what is detected with the NAIS particle measurements. The particle size distribution measured with the NAIS compliments well the one measured with the DMPS system. The DMPS system below 6 nm has also some uncertainties due to low charging of aerosol sample, diffusion losses, and the particle detection efficiency.
Figure 12. Particle size distribution measured with the NAIS in the size range 2.5–20 nm and with the DMPS in the size range 20–1000 nm on 5 May 2007 in Hyytiälä.

Figure 13. Upper panel: Concentrations of 2-3 nm particles measured with the NAIS, 3-6 nm particles with the DMPS, and sulphuric acid. Lower panel: Ion and particle formation rates during the NPF event on 5 May 2007 (see also Paper V, Fig. 7).
On this day the concentration of 2-3 nm particles measured with the NAIS started increasing at almost the same time as the 3-6 nm particle concentration measured with the DMPS (Fig. 13, upper panel). The growth rates were 1.7 and 4.5 nm h⁻¹, respectively, for 1.3–3 and 3–7 nm charged particles and 5.2 nm h⁻¹ for total particles in 3-7 nm size range. The ion concentration in the 1.7-6.5 nm size range started to increase already around 9 a.m., whereas the total concentration of 2-6 nm particles started to increase at 11 a.m. The upper panel in Fig. 13 also shows the gas phase sulfuric acid concentrations during the event. The initial increase in sulfuric acid begins at 6 a.m, whereas small particles did not begin to increase until 11 a.m.

Nieminen et al. (2009) studied the connection between sulfuric acid concentration and 2-3 nm particle concentration measured with NAIS more closely, and they concluded, in line with Paper I, that atmospheric nucleation seems to start from sizes very close to 2 nm as they observed simultaneous increase in sulfuric acid and small particle concentrations.

Generally speaking, in Hyytiälä the time series of negative and positive ion size distribution are similar to that of the total particle size distribution, even though the ion concentrations are about two orders of magnitude smaller (e.g. Fig. 1). This result suggests that the intermediate ions typically detected during NPF events are the naturally charged fraction of the total particles. However, further studies are needed. For instance, the concentration of sub-3 nm neutral clusters was much higher than the concentration of sub-3 nm ion clusters due to the low charging probability of the particles at these sizes (e.g. Paper I and IV). In charge equilibrium, 1% of all 3 nm particles will be charged, and 99% will be neutral. For 10 nm particles, 5% will be charged and 95% neutral. Lehtipalo et al. (2009, 2010) measured that in Hyytiälä on average ~1% of 1.5-3 nm nano-CN (i.e. clusters; Zhao et al., 2010) are charged.

As already mentioned, increased ion concentrations are observed during overcharging of atmospheric particles compared to charge equilibrium, whereas in undercharged situation reduced concentrations are detected (Laakso et al., 2007; Kerminen et al., 2007; Gagné et al., 2008). The different activation properties of charged and neutral particle are visible in Fig. 13 (lower panel): the ion-induced formation rates increased somewhat before a corresponding increase in the total J₂ is seen. The fraction of ion-induced nucleation becomes less important in the middle of the event (Gagné et al., 2010). Ion-induced nucleation is more important at the beginning of the event, which agrees with the thermodynamic principle described in Kulmala et al. (2007) and
observed by Winkler et al. (2008), according to which charged particles activate with a smaller supersaturation ratio than the neutral particles.

One of the most essential uses of the ion and particle size distributions measured by the NAIS is the estimation of the contribution of ions to total particle formation (using Eqs. 1-6). During the spring-time, the median formation rates of 2 nm total and charged particles were 0.65 cm$^{-3}$ s$^{-1}$ and 0.03 cm$^{-3}$ s$^{-1}$, respectively (Paper V). The estimated ion-ion recombination rates were about the same order of magnitude as the ion-induced formation rates. According to Eq. 6, these results imply that the ion-mediated nucleation contributes approximately 10% to the boreal forest NPF events. The importance of ion-induced nucleation is discussed in detail later. Papers V-VI conclude that in most continental environments total and charged particle formation rates differed from each other by approximately an order of magnitude.

Figure 14. The ion-induced fraction calculated from the NAIS measurements and the Ion-DMPS measurements for NPF events in Hyytiälä 2006-2007 (Gagné et al., 2010).

Figure 14 presents a reasonable agreement between the ion-induced fractions at 2 nm derived from the NAIS measurements and those calculated based on the number size distributions measured by the ion-DMPS (Gagné et al., 2010). One should note that these two methods are completely independent from each other. The Ion-DMPS (Mäkelä et al., 2003; Kerminen et al., 2007; Laakso et al., 2007) measures directly the charging state of particles larger than 3 nm, from which the relative role of the neutral and ion-induced particle formation can be estimated. The charging state describes
whether the particles are in a charge equilibrium or if they are over- or undercharged. It still remains unclear how reliable indicator the NAIS would be for the charging state or charged fraction due to the difference between unipolar corona charger used in the NAIS and bipolar charger used in the ion-DMPS (Kerminen et al., 2010; Gagné et al., 2011).

As mentioned in Section 3.4, when the NAIS was used to measure ion concentrations (in ion mode), a small background, caused by the noise of the electrometers, was always present (Paper II). When in particle mode, the detected charged particle concentrations are multiplied with charging probabilities, and the background becomes more significant. The background complicates reliable measurements of very low concentrations with the NAIS. Therefore, the agreement between NAIS and other instruments improves significantly when the number concentrations increase. In the size range of small particles, the adjustment of the post-filter and the broad transfer functions can also cause background noise in size bins (Papers II-IV). In the larger particle sizes (>15 nm, Alguacil and Alonso, 2006), the concentrations are overestimated due to multiply charging of the particles, which NAIS inversion is not able to take into account (Paper IV) due to the lack of a pre-impactor.

Figure 14 presents a time series of total particle concentrations between 1.5–3 nm and 3–5 nm in a coastal environment (Mace Head, Ireland). The concentrations measured with the pulse height CPC (Sipilä et al., 2008; Lehtipalo et al., 2009, 2010) and the NAIS agree very well in both size classes, especially during particle formation bursts at daytime low tides (Vana et al., 2008). Lehtipalo et al. (2009) performed the same comparison in a boreal forest (Hyytiälä, Finland) where in the size range 3–5 nm the measurements agree remarkably well, but in the 1.5–3 nm range the concentrations are only of similar order. The problem was likely due to the corona charger ions, which extend well above 1.5 nm. The same problem occurs in Mace Head as well but it’s not as clearly visible due to much higher natural concentrations of 1.5–3 nm particles.

The particle size distributions measured by the NAIS can be used as supporting information for the interpretation of atmospheric aerosol data (Fig. 15). For instance, Riipinen et al. (2009) estimated the ambient cut-off sizes of the water-CPC in the CPC battery (CPCB, Kulmala et al, 2007) by comparing the water-CPC and butanol-CPC concentration ratios and the size distributions measured with the NAIS. The comparison was done by weighting the NAIS size distribution data with the detection efficiency curves of the CPCs. The analysis suggested that for ambient aerosol the cut-
off sizes for the water-based instruments were lowered with 0.8–0.9±0.3 nm as water-soluble compounds were present during the NPF events.

Figure 15. The total concentration of 1.5–3 nm and 3–5 nm particles in Mace Head 13–16 June 2008 measured with the NAIS (red and blue dots for positive and negative charging, respectively) and the pulse height CPC (PH-CPC) data (black dots). Vertical solid lines indicate the times of a low tide (courtesy of Katrianne Lehtipalo).

Figure 16. Estimation of the ambient cut-off size of the water-CPC (UWCPC) in Hyytiälä on April 23, 2006 (adapted from Manninen, 2007). The NAIS channels corresponding to diameters 1.8-4.1 nm detect the same particle concentration as the difference between ultrafine CPCs (the ultrafine butanol-CPC (UCPC) was calibrated to ~4 nm with insoluble particles).
4.3 Atmospheric particle formation in different environments

The data set presented in Paper VI is unique. To date, the EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality interactions; see e.g. Kulmala et al., 2009, and Kerminen et al., 2010) ion spectrometer measurements are the most comprehensive effort to experimentally characterize nucleation and growth of atmospheric clusters and particles at ground-based observation sites on a continental scale. The twelve field sites represent a wide variety of environments, such as marine, coastal, remote continental, suburban, rural and mountainous regions. The field sites are located at different altitudes ranging from sea level to several thousands of meters above sea level. NPF was observed to occur at all the sites and the observations were used as indicators of the particle formation mechanisms. Particle formation rates and size-dependent growth rates were examined to obtain information on NPF and subsequent growth.

Overall, the EUCAARI data revealed that the observed fraction of nucleation event days varied between 57% in Melpitz, Germany, and 21% in Pallas, Finland. As presented in Fig. 17, the median number of NPF event days had a maximum in May and the non-event days around December–January in most of the environments (Paper VI). A high event frequency in spring time is consistent with many earlier studies (e.g. Hõrrak et al., 1998b; Birmili and Wiedensohler, 2000; Birmili et al., 2003; Dal Maso et al., 2005; 2007; Vana et al., 2008), suggesting a clear connection of the NPF to the presence of solar radiation (i.e. enhanced photochemistry) and to the onset of biogenic activity (i.e. source of condensing vapors, Dal Maso et al., 2009). The monthly event distribution varied from site to site also due to local meteorological and geographical conditions, and regional air mass history and background aerosol concentration (Paper VI, see Appendix).

The nucleation bursts were almost exclusively observed during daytime, and mostly started before noon according to the time series of particle formation observed during EUCAARI field measurements (Paper VI). In addition to the prevailing result that the NPF takes place only during daytime and typically with the help of enhanced photochemistry, we observed occasional night-time particle formation on some sites, e.g. in Hyytiälä (Finland), Mace Head (Ireland), and Finokalia (Greece). Similar observations were reported by Junninen et al. (2008), Lee et al. (2008), Suni et al. (2008), Kalivitis et al. (2011), and Lehtipalo et al. (2011). Junninen et al. (2008)
suggested that NPF mechanisms or vapours participating in particle formation and growth are different during day- and night-time. Kalivitis et al. (2011) showed that the air mass origin was relevant also to the night-time nucleation.

Figure 17. The median monthly number of particle formation event, undefined and non-event days for all the twelve sites from April 2008 to April 2009 within the EUCAARI project (adapted from Paper VI). The numbers above the figure refer to the median number of days included in the analysis.

Typically, atmospheric particle growth rates vary in the range of 1–20 nm h\(^{-1}\) in different environments (Kulmala et al., 2004a; Hirsikko et al., 2011). In Paper VI, the growth rates of new particles were found to be of the order of a few nanometers per hour, varying within a factor of 3 between the different environments. The highest median (~5 nm h\(^{-1}\)) and momentary (~10-20 nm h\(^{-1}\)) growth rates are observed at the sites with the strongest and most frequent nucleation bursts (e.g. Cabauw, Hohenpeissenberg, and Mace Head). Median growth rates observed in polluted urban areas, such as Mexico City (15–40 nm h\(^{-1}\); Iida et al., 2008) or South Africa (3–21 nm h\(^{-1}\); Laakso et al., 2008), were significantly higher. At most of the 12 sites, the particle growth rate increased with increasing particle size. The size-dependence of the particle growth rates is consistent with earlier observations from Hyytiälä (Kulmala et al., 2004b; Hirsikko et al., 2005; Paper V), Tumbarumba in Australia (Suni et al., 2008) and K-Puszta (Yli-Juuti et al., 2009).

The increase of growth rate with particle size suggests that the condensing vapors that participate in the first steps of particle growth may be different than the vapors contributing to the later steps of the growth depending on their saturation vapor pressures (e.g. Kulmala et al., 2004b). This could also be related to differences in the production rates of condensable vapors as a function of time. The particles formed in a
given NPF event typically reach 20-nm size several hours after their initial formation. It is possible to assume that the concentration of condensable vapors and their relative ratios has changed from the initial conditions due to, e.g. differences in the oxidation pathways and photochemistry leading to the condensable products (e.g. Yli-Juuti et al., 2009).

The formation rates of 2 nm ions were in the range of 0–1.1 cm\(^{-3}\) s\(^{-1}\) according to earlier publications (reviewed by Hirskikko et al., 2011). On the other hand, the total particle formation rates at 2 nm varied between 0.001 and 60 cm\(^{-3}\) s\(^{-1}\). In agreement with these numbers, the median total formation rate at 2 nm varied by more than an order of magnitude between the EUCAARI sites ranging from 0.9 to 32 cm\(^{-3}\) s\(^{-1}\), whereas the formation rate of the charged particles showed much less variation (Paper VI). This indicates that the ion cluster concentration is much more stable regardless of the surroundings, whereas the neutral cluster concentration is dependent on the environment. Gagné et al. (2010) concluded that the larger concentrations of new particles were produced during the days with a smaller fraction of ion-induced nucleation.

### 4.4 The role of ions in particle formation

Gas phase ions can reduce the concentration of aerosol precursor molecules required for nucleation, as they greatly stabilize the molecular clusters with respect to evaporation (Kazil et al., 2008; Winkler et al., 2008). Therefore, the ions are a potential source for the aerosol particles. For instance, when the contribution of ion-induced nucleation (IIN) to particle formation is said to be 10 %, it means that 10% of all the particles are charged while ion activation is taking place. Ion-induced nucleation is always limited by the number of ions, so if the nucleation process consumes up all the ions, ion-induced nucleation can not occur anymore.

According to Laakso et al. (2004), the average ion-production rate in Hyytiälä calculated from aerosol particle size distribution and air ion mobility distribution measurements was 2.6 ion pairs cm\(^{-3}\) s\(^{-1}\), and based on external radiation and radon measurements, 4.5 ion pairs cm\(^{-3}\) s\(^{-1}\). As mentioned, the median formation rates of 2 nm total and charged particles were 0.65 cm\(^{-3}\) s\(^{-1}\) and 0.03 cm\(^{-3}\) s\(^{-1}\), respectively (Paper V). The lifetime of the ions is very short and only a small fraction of the molecular ion clusters will grow to 2 nm due to losses by ion-ion recombination and
by attachment to the larger particles. As ion-induced nucleation relies on the ion-production rate and the losses of the ions, the ions are not enough to explain the observed total particle formation.

Gagné et al. (2008) reported that, on average, the NPF events in Hyytiälä were clearly dominated by neutral particle nucleation and the pathway of IIN made only a minor contribution. They observed a median contribution of the ion-induced nucleation to be approximately 6.4%, ranging from 1.7 to 16.5%. Lehtipalo et al. (2010) concluded that recombination of ions can explain ~5% of nano-CN in Hyytiälä. In Boulder, Colorado, the average contribution of IIN was approximately 0.5% in both polarities (Iida et al., 2006). Therefore, both studies showed a minor contribution of IIN to the total particle formation.

Eisele et al. (2006) measured size and mobility distributions of charged molecular clusters and aerosol particles in Atlanta, Georgia, and found that while the ions contributed to the formation of the small charged sulfate clusters, charged nucleation did not play a significant role in aerosol production during these measurements. On the other hand, Yu and Turco (2008) reported that their model of IMN was able to explain all of particle formation observed during QUEST IV campaign in Hyytiälä during spring 2005.

In Mace Head and Melpitz, ion-induced nucleation started earlier than neutral nucleation, whereas the starting time between the nucleation of negative and positive ions did not differ from each other. In these places the contribution of ion-induced nucleation is most significant in the beginning of the event. The same observations have been made earlier in Hyytiälä (Paper V). On the other hand, at Cabauw, Hohenpeissenberg and Jungfraujoch, both the ion and the total nucleation start at about the same time. The different starting times of charged and neutral particle formation can be indicative of the dynamics and chemistry of the nucleation process. Heterogeneous nucleation experiments have shown that charged particles are activated before the neutrals (Winkler et al., 2008).

Gagné et al. (2010) concluded that the fraction of ion-induced nucleation is typically higher on warmer, drier and sunnier days. On the other hand, Curtius et al. (2006) and Yu (2010) suggested that ion-mediated particle formation mechanisms are important with low temperature and pre-existing aerosol surface area (i.e. particle sinks), together with high ion and sulphuric acid concentrations. Table 3 shows a summary of
the contribution of ion-induced nucleation to the total nucleation rate at different sites based on literature and studies from this thesis. The contribution of ion-induced nucleation to total particle formation at 2 nm was typically in the range of 1–30% (Paper VI).

<table>
<thead>
<tr>
<th>Measurement site</th>
<th>Instrument</th>
<th>IIN fraction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boulder</td>
<td>IGMA *)</td>
<td>0.5 %</td>
<td>Iida et al. 2006</td>
</tr>
<tr>
<td>Cabauw</td>
<td>NAIS</td>
<td>2 %</td>
<td>Paper VI</td>
</tr>
<tr>
<td>Hohenpeissenberg</td>
<td>NAIS</td>
<td>6 %</td>
<td>Paper VI</td>
</tr>
<tr>
<td>Hyytiälä</td>
<td>Ion-DMPS</td>
<td>6 %</td>
<td>Gagné et al. 2008,</td>
</tr>
<tr>
<td></td>
<td>PH-CPC</td>
<td>5 %</td>
<td>Lehtipalo et al., 2009</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>NAIS</td>
<td>27 %</td>
<td>Paper V</td>
</tr>
<tr>
<td></td>
<td>NAIS</td>
<td>22 %</td>
<td>Paper VI,</td>
</tr>
<tr>
<td>Mace Head **)</td>
<td>NAIS</td>
<td>2 %</td>
<td>Boulon et al. 2010</td>
</tr>
<tr>
<td>Melpitz</td>
<td>NAIS</td>
<td>1 %</td>
<td>Paper VI</td>
</tr>
<tr>
<td>Pallas</td>
<td>NAIS</td>
<td>18 %</td>
<td>Paper VI</td>
</tr>
</tbody>
</table>

*) Inclined Grid Mobility Analyzer (Iida et al. 2006)

**) Regional events only

Table 3. The median fraction of the observed ion-induced nucleation (IIN) from total particle formation in various environments.

The systematic measurements performed within this thesis support the earlier observations on the contribution of ions to total particle formation in the boreal forest (Laakso et al., 2007; Kulmala et al., 2007; Gagne et al., 2008; Lehtipalo et al, 2009) and in other environments (e.g. Iida et al., 2006; Eisele et al., 2006; Mirme et al., 2010; Boulon et al., 2010). The results infer that ion-induced nucleation has a minor contribution to particle formation in the boundary layer in most environments.
5 Review of papers and author’s contributions

Paper I introduces the first steps towards the direct measurements of atmospheric particle formation using NAIS. The measurements were performed mainly in spring 2006 in Hyytiälä, Finland. The NAIS was compared with several independent methods to measure atmospheric neutral and charged nano-sized clusters. The results suggest that the neutral clusters were detected consistently in the sub-3 nm size range and that neutral nucleation dominates over ion-induced nucleation, at least in boreal forest conditions. The processes initiating atmospheric particle formation seem to start from particle sizes of ~1.5-2 nm. In this work, I contributed to the measurements and to the data analysis, as well as to the writing.

Paper II reports the results from the first ion spectrometer calibration and intercomparison workshop, held in January-February 2008 in Helsinki, Finland. All the ion spectrometers which were used to perform measurements for this thesis were calibrated using state-of-art reference instruments. The results verified that the ion spectrometers were adequate for both size and concentration measurements, especially at high aerosol concentrations. The instruments were found to be accurate and reliable enough for field measurements. The lowest cut-off size of the NAIS in neutral particle measurements was determined to be in the size range ~1.5-3 nm, depending on the conditions and polarity. In this paper, I contributed to planning and performing the calibrations and to the data processing as well as to the writing.

Paper III presents a study of the properties of the corona charger ions used in the NAIS to charge aerosol particles, as a continuation to Paper II. The experiments were performed using a high resolution DMA. The corona ions were below 1.7 nm (positive) and 1.6 nm (negative) in diameter. The size and concentration of the charger ions generated in the corona charging process depended on both the corona voltage and on the physical and chemical properties of the carrier gas (such as chemical composition and relative humidity). The electrical filtering of the charger ions (but not the charged particles) plays an important role in determining the lowest detection limit of the NAIS. I took part in the planning and conducting the laboratory measurements, performed a large part of the data analysis, and wrote major part of the paper.

Paper IV contains the results from the first continuous field measurement using the NAIS in Hyytiälä, Finland, during 2006-2007. The total concentration of 1.8-3.0 nm particles were at least an order of magnitude larger than corresponding ion cluster
concentration, highlighting the importance of neutral nucleation. Also these concentrations had different diurnal cycles on particle formation event days compared to the ion clusters, suggesting a varying importance during NPF events. A comparison with the other aerosol and cluster instrumentation showed 1) a continuous background at low concentration in the NAIS signal, as reported already in Paper II, and 2) that especially during the NPF event, as the particle concentrations exceed these values the NAIS is a capable tool for quantitative measurements, consistent with Paper I and II. I contributed to the measurements, performed a major part of the data analysis, and wrote most of the paper.

Paper V demonstrates a methodology for experimentally determining the neutral particle formation rates, which we were able to estimate using the difference between the total and ion-induced formation rates, while also taking into account ion-ion recombination. The particle and ion number size distributions and total particle concentration measurements were done at a boreal forest site in Hyytiälä, Finland, during the spring 2007 EUCAARI field campaign. The total and charged particle formation rates differed from each other by approximately an order of magnitude. The ion-induced nucleation involving the ion-ion recombination products, (i.e. ion mediated nucleation), comprises approximately 10% of the boreal forest NPF events, as suggested in Paper I. I contributed to the measurements, performed a major part of the data analysis, and wrote most of the paper.

Paper VI reports the results from the EUCAARI ion spectrometer measurements at 12 European sites during March 2008 – May 2009. The measurements were conducted in a wide variety of environments, including coastal and continental locations as well as sites at different altitudes (both in the boundary layer and in the free troposphere). The NPF parameters were determined using the methods described in Paper V. The dominance of neutral over ion-induced nucleation is consistent with the findings presented in Papers I and IV-V. In this paper, I contributed to organizing and carrying out the field measurements, processing and analyzing the data, and wrote a major part of the paper.
6 Conclusions

In the work presented in this thesis, the recently developed Neutral cluster and Air Ion Spectrometer (NAIS, Airel Ltd.) was used in a wide variety of laboratory experiments to verify its performance, and in field studies to characterize atmospheric particle formation. In order to understand the particle formation and growth processes, we investigated the magnitudes of the particle formation and growth rates at the size where the atmospheric nucleation and activation occur. In the case of parallel ion and neutral cluster measurements, we could also estimate the relative contribution of ion-induced and neutral nucleation to the total particle formation. The main conclusions are the following:

1) The first field measurements proved that the NAIS is a reliable tool to measure atmospheric ions and neutral particles close to sizes where nucleation occurs (Paper I, IV).

The NAIS proved to be consistent and enduring instrument in comparison with other cluster instrumentation used in Hyytiälä. The atmospheric nucleation seems to start from sizes very close to ~1.5-2 nm. Size distribution measurements by the NAIS revealed that, similar to cluster ions, there appears to be a large pool of neutral clusters in the atmosphere all the time. The concentration of small ions is, however, typically not high enough to explain the observed atmospheric particle formation rates in the boundary layer. The charged fraction calculated from NAIS number size distributions give a good estimate of the charged fraction and its behavior in time, when the sample is not too overcharged (in agreement with later studies by Vana et al., 2006; Gagné et al. 2010, 2011).

2) Multiple (N)AIS systems measured concentrations that were consistent with those measured by reference instruments at conditions representing particle formation events, whereas mobilities were slightly overestimated (Paper II).

The NAIS was successfully verified and intercompared during the two calibration and intercomparison workshops organized by the University of Helsinki (Paper II, Gagné et al., 2011), though the results from latter workshop are not included in this thesis. The NAIS showed adequate agreement with the reference instruments and with respect to each other. The comparison to other instrumentation in field strongly
supports these laboratory observations (Paper I, IV; Sipilä et al., 2008; Lehtipalo et al., 2008, 2009; Riipinen et al., 2009; Ehn et al., 2011). The NAISs sustain their measurement stability after operating continuously in a variety of conditions given that the instruments are properly maintained Gagné et al. (2011).

3) Based on our laboratory experiments, the lowest detection limit for the NAIS in the particle mode is approximately 2 nm (Papers II-III).

The corona-needle charging process used in the NAIS was studied using a high resolution DMA and a time-of-flight mass spectrometer. The lower detection limit of the NAIS in particle mode is determined by the charging probability, cluster concentration, and the mass and mobility of the charger ions. The corona charger ions have a diameter range of 1.0-1.6 nm (1.3–0.8 cm² V⁻¹ s⁻¹). These sizes define the absolute lower detection limit of the NAIS. The electrical filtering of the charger ions and inability to remove all the charged particles plays an important role in determining the lowest detection limit. The main filter is used to cut-off the corona ions generated by the charger, and consequently the small charged particles are filtered out together with ions used for charging.

4) The ion spectrometer measurements performed within the EUCAARI project (Kulmala et al., 2009; Kerminen et al., 2010) present, so far, the most comprehensive effort to experimentally characterize nucleation and growth of atmospheric molecular clusters and nanoparticles at ground-based observation sites on a continental scale (Paper VI).

The particle formation events seem to take place on a regional scale. The list of locations and altitudes where frequent aerosol formation has been observed is still growing as new measurement campaigns are organized and field sites established. The phenomenon was observed to take place frequently in various environments in the boundary layer as well as in the free troposphere. The observed site-to-site variations are evidence of differences in the particle formation limiting factors, which include sources of nucleating and condensing vapors, scavenging by pre-existing particles and meteorological effects. Atmospheric ions participate in the initial steps of NPF, although their contribution was minor in the boundary layer (Papers I, V-VI). The highest atmospheric particle formation rates were observed at the most polluted sites where the role of ions was the least pronounced (Paper VI). Furthermore, the increase
of particle growth rate with size suggests that enhancement of the growth by ions was negligible.

5) **Neutral particle formation seems to dominate over ion-induced and ion-mediated nucleation, at least in the continental boundary layer (Papers I, V-VI).**

The results obtained from the NAIS particle and ion measurements agree well with separate independent measurements performed with other electrical mobility spectrometer (Ion-DMPS, Gagné et al, 2010) and condensation based (PH-CPC, Lehtipalo et al., 2009) techniques. The formation rates of charged particles at 2 nm accounted for 1-30 % of the respective total particle formation rates. As a significant new result, we found out that the total particle formation rate varied much more between the different sites than the formation rate of charged particles. Several nucleation mechanisms may be operating in parallel or over the course of the day. Nevertheless, the ion-induced nucleation may have more important role in the particle formation events under substantially different atmospheric conditions or in other locations or altitudes of the atmosphere.

The observed global occurrence of atmospheric aerosol formation provides a good reason to include this phenomenon in large-scale atmospheric models, such as regional air quality models and global climate models. The instrumental developments described in this thesis have made it possible to observe small neutral particles about a nanometer smaller than previously measured. This offers a possibility to test existing nucleation theories against real atmospheric data. By conducting continuous measurements in different environments and altitudes, it should be possible to develop simple yet sufficiently accurate nucleation parameterizations for large-scale modeling using the data presented in this thesis (e.g. Paasonen et al., 2010; Nieminen et al., 2011).

In order to understand the role of atmospheric aerosol particles in the climate change and radiative forcing and feedbacks related to it, long-term measurements are crucially needed. Continuous time series are essential to understanding difference between seasonal and long-term interannual variability (Thoring et al., 1989). As an example, continuous particle size distribution measurements at SMEAR II in Hyytiälä (Hari and Kulmala, 2005) since 1996 can be seen as a good starting point towards the right direction.
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