

REPORT SERIES IN AEROSOL SCIENCE  
N:o 124 (2011)

ON THE CHARGING STATE OF ATMOSPHERIC  
AEROSOLS AND ION-INDUCED NUCLEATION

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Academic dissertation

*To be presented, with the permission of the Faculty of Science  
of the University of Helsinki, for public criticism in auditorium E204,  
Gustaf Hällströmin katu 2, on June 1st, 2011, at 12 o'clock noon.*

**Helsinki 2011**

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ISBN 978-952-5822-45-8 (printed version)

ISSN 0784-3496

Helsinki 2011

Yliopistopaino

ISBN 978-952-5822-46-5 (pdf version)

<http://ethesis.helsinki.fi>

Helsinki 2011

Helsingin yliopiston verkkojulkaisut

## Acknowledgements

The research presented in this thesis was carried out at the Department of Physics of the University of Helsinki and the Helsinki Institute of Physics. I wish to thank Prof. Juhani Keinonen and Prof. Dan-Olof Riska for providing me with working facilities.

I would like to thank Markku Kulmala for giving me an opportunity to work in his division, and also for his supervision, guidance and understanding during my Ph.D. studies. I would like to thank Markku for taking me as a intern during my B.Sc. studies, only based on my CV and a few emails. It is the once in a lifetime chance that introduced me to the exciting world of aerosol research -and got me hooked.

I wish to thank Dr. Madis Noppel and Prof. Risto Hillamo for reviewing this thesis, and Dr. Erik van Dongen for proofreading it.

Many thanks to Drs Lauri Laakso and Tuukka Petäjä, for guiding and advising me through all my research projects. You both always had good ideas and good comments, and I would like to thank you both for all the careful reviewing of all my texts during the years. More precisely, I would like to thank Lauri for introducing me to ion-induced nucleation and providing me with the relevant literature, but also for his support; and Tuukka for teaching me all the lab tricks, for resolving many practical matters, and for his encouragement. I would like to thank Veli-Matti Kerminen who commented on many of my manuscripts, and answered to all my questions about the world of publications. I would also like to thank Miikka Dal Maso who was supervising my work as an intern in summer 2004 and taught me the basics of new particle formation event analysis and also for introducing me to the light side of Finland. I must also thank my supervisors in my first two B.Sc. internships, Prof. Patrick Fournier and Prof. Serge Jandl, at the Quantum Material Laboratory, Université de Sherbrooke, for teaching me how science is done “in real life” and also for believing in me and encouraging me.

I would like to thank Erkki Sivola and Pasi Aalto for building and characterizing the Ion-DMPS just a few months before I came to Finland, and passing it down to me. This instrument is the core of this thesis, and naturally, it couldn't have been done without your remarkable work.

Sciences, and physics in particular, is increasingly becoming a matter of (international)

cooperation. Hence I would like to thank all my co-authors whose names appear in the papers presented in this thesis. Without you all, this work wouldn't have been possible. Thank you for your invaluable help. I also wish to thank all those with whom I share other publications, and other projects: EUCAARI people, CLOUD people, and all others. Cooperation and scientific interactions are among the elements that make science exciting and enjoyable. It has been nice working with you all and I hope our cooperation will extend beyond this degree.

As a foreign student, I could not publish this thesis without thanking all those who became my friends and helped me get through the days, for the past six years. First, I would like to thank everybody at Tsemppi -an organization for international degree students at the University of Helsinki- for providing a nice social environment where I have met many of my good friends. I would also like to thank all the Finnish members of Tsemppi for making us feel so welcome. I could not name everyone with whom I befriended, but I would like to single out three: Yana Tzaneva, Dora Shivute and Erik van Dongen. Thanks for being there throughout the past six years, for all the good times, and for your support when the times were not so good.

Besides co-authorship, I have had the chance to work with formidable colleagues. It is great to wake up in the morning and know that a bunch of nice and enthusiastic people are going to be there when I get to work. Thanks also for listening to all my complaints. Again, there are too many names and I must highlight some and leave some in the shadow. But I do not forget you. Special thanks to Alessandro Franchin, Maija Kajos, Katrianne Lehtipalo, Risto Makkonen, Hanna Manninen, Stephany Mazon, Matt McGrath, Tuomo Nieminen, Mikhail Paramonov, Siegfried Schobesberger and Taina Yli-Juuti.

Finally, I would like to thank my parents, Rosella and Jacques Gagné who were always supportive and even encouraged me to move all the way to Finland for my studies. Thanks for your trust, support, and understanding. Many thanks also go to my friends and fellow physics students in Québec as well as my CEGEP friends for keeping in touch, for visiting me in Finland, or hosting me when I'm visiting. Your friendship is important to me.

In the end, I would like to thank my husband, Erik, for being there, always supporting me, sharing academic concerns, academic writing, many discussions, and making my life so much more interesting.

Stéphanie Gagné

University of Helsinki, 2011

## **Abstract**

Atmospheric aerosol particles (particles suspended in the air) have significant effects on the Earth's climate. They affect the Earth's radiation budget directly by scattering radiation, and indirectly by acting as cloud condensation nuclei, influencing the brightness and lifetime of clouds. Nucleation (new particle formation and growth) accounts for about half of the cloud condensation nuclei. Several nucleation mechanisms have been proposed. We can divide these mechanisms into two main groups: ion-induced and neutral mechanisms.

The charged fraction of an aerosol population is needed in order to determine the fraction of particles formed through ion-induced nucleation (IIN). The charging state is a quantity directly related to the charged fraction, but which conveys more physical meaning in a dynamical aerosol particle population. The charging state is defined as the ratio of the ambient charged fraction to the charged fraction of the same sample at bipolar equilibrium.

The Ion-DMPS is an instrument that was specifically designed to measure the charging state of aerosol populations as a function of size and time. Its switchable neutralizer and bi-polar DMA combination allows for the measurements of the aerosol size distribution in four modes with the very same inlet and losses. The ratio of the neutralized and ambient modes, for each polarity, gives us the charging state.

In this thesis, the behavior of the charging state as a function of particle diameter is theoretically described. The Ion-DMPS is presented and used to estimate the IIN fraction for the first time. Methods to analyze the charging state are developed, described and evaluated. The IIN fraction, derived from extrapolated charging states, was found to be around 6% in rural background Hyytiälä and around 1% in urban Helsinki, on average. IIN varies from a place to another and from one day to another. It is more important when the ion-pair production rate is high or when neutral nucleation is limited by too low vapor saturation ratios or too high temperatures. In Hyytiälä, where the IIN fraction varies from day to day, the IIN fraction was higher in summer and very small in winter, and negative IIN was more common than positive IIN. In Helsinki, no seasonal tendency appeared. Days with an important neutral contribution yielded higher nucleation mode particle concentrations. IIN seems to survive in conditions in which neutral nucleation takes place difficultly. However, in favorable conditions, neutral nucleation thrives.

Keywords: Atmospheric aerosols, Ion-induced nucleation, Charging state, Ion-DMPS, Particle formation and growth

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## List of publications

This thesis consists of an introductory review, followed by six research articles. In the introductory part, these papers are cited according to their roman numerals. **Paper I** is reproduced with the kind permission of John Wiley and Sons and **Paper IV** is reproduced by permission of American Geophysical Union. **Papers II, III, V** and **VI** are reproduced under the Creative Commons Attribution 3.0 License.

- I Kerminen, V.-M., Anttila, T., Petäjä, T., Laakso, L., **Gagné, S.**, Lehtinen, K.E.J., and Kulmala, M. (2007). Charging state of the atmospheric nucleation mode: implications for separating neutral and ion-induced nucleation. *J. Geophys. Res.*, 112, D21205, doi:10.1029/2007JD008649.
- II Laakso L., **Gagné, S.**, Petäjä, T. Hirsikko, A., Aalto, P.P., Kulmala, M. and Kerminen, V.-M. (2007). Detecting charging state of ultra-fine particles: instrumental development and ambient measurements. *Atmos. Chem. Phys.*, 7, 1333-1345.
- III **Gagné, S.**, Lehtipalo, K., Manninen, H. E., Nieminen, T., Schobesberger, S., Franchin, A., Yli-Juuti, T., Boulon, J., Sonntag, A., Mirme, A., Mirme, S., Hörrak, U., Petäjä, T., Asmi, E. and Kulmala, M. (2011). Intercomparison of air ion spectrometers: an evaluation of results in varying conditions. *Atmos. Meas. Tech.*, 4, 805-822.
- IV **Gagné, S.**, Laakso, L., Petäjä, T., Kerminen, V.-M. and Kulmala, M. (2008). Analysis of one year of Ion-DMPS data from the SMEAR II station, Finland. *Tellus*, 60B, 318-329.
- V **Gagné, S.**, Leppä, J., Petäjä, T., McGrath, M., Vana, M., Kerminen, V.-M., Laakso, L. and Kulmala, M. (2011). Measurements of charging states in Helsinki, Finland. *Atmos. Chem. Phys. Discuss.*, Accepted.
- VI **Gagné, S.**, Nieminen, T., Kurtén, T., Manninen, H.E., Petäjä, T., Laakso, L., Kerminen, V.-M., Boy, M. and Kulmala, M. (2010). Factors influencing the contribution of ion-induced nucleation in a boreal forest, Finland. *Atmos. Chem. Phys.*, 10, 3743-3757.

# 1 Introduction

As global warming threatens human populations, biodiversity and ecosystems, scientists strive to understand the causes, effects and feedback mechanisms, and to make predictions or propose means for mitigation. Externally imposed changes in the Earth's radiative budget, which influences the climate, are called radiative forcings. They are expressed in Watts per square meter. Anthropogenic radiative forcings include, for example, greenhouse gases, stratospheric and tropospheric ozone, surface albedo (land use and black carbon on snow) and, finally, the total aerosol effect.

The level of scientific understanding of aerosol effects is among the lowest of all radiative forcings (IPCC, the Intergovernmental Panel on Climate Change, 2007). Besides having an important effect on the climate, aerosols are also a potential geoengineering tool to mitigate the warming effect of greenhouse gases (e.g. Tuck et al., 2008; Mitchell and Finnegan, 2009; Rasch et al., 2009; Pierce et al., 2010 and Korhonen et al., 2010). Aerosols can affect the climate in two ways: directly and indirectly. The direct effect consists in scattering the incoming and outgoing radiation (e.g. Myhre et al., 2009). The indirect effect consists in changing the cloud albedo: aerosol particles larger than about 100 nm act as cloud seeds, or cloud condensation nuclei (CCN). The number of such CCNs influences the size of each cloud droplet (a lot of smaller droplets, or a smaller number of larger droplets), and thus changes the cloud's albedo, and possibly its lifetime (e.g. Twomey, 1991; Lohmann and Feichter, 2005; Andreae and Rosenfeld, 2008; Stevens and Feingold, 2009; Wang and Penner, 2009). The IPCC, the Intergovernmental Panel on Climate Change (2007) estimates that the total aerosol forcings have a cooling effect between  $-2.7 \text{ Wm}^{-2}$  and  $-0.4 \text{ Wm}^{-2}$  with a most probable value of  $-1.2 \text{ Wm}^{-2}$ . These values are comparable in magnitude to the warming due to the greenhouse gas  $\text{CO}_2$  ( $\sim 1.66 \text{ Wm}^{-1}$ ). Aerosols thus have a significant influence on the climate.

Aerosols consist of particles (solid or liquid) suspended in a gas. The air that surrounds us is an aerosol. In order to float in a gas, aerosol particles have to be very small, and cannot be seen with the naked eye: their size varies from  $\sim 1 \text{ nm}$  to  $100 \mu\text{m}$  ( $10^{-9} - 10^{-4} \text{ m}$ ). Due to their small size, they can lodge themselves efficiently in our lungs as we breath in and out, and they can affect our health (Brunekreef and Holgate, 2002). The health effect due to traffic-related air pollution is a good example of harmful ambient aerosols (Hoek et al., 2002). In this thesis, we concentrate on particles smaller than 42



nm in diameter, with a special attention to particles smaller than 15 nm.

Aerosol particles can be emitted directly (primary emissions), through human activity or naturally, or they can be formed in-situ in the atmosphere (secondary emissions). Different sources of primary particles may be, for example, industrial activities, road traffic, breaking sea waves, dust, pollens, bacteria; whereas secondary particles are formed in all kinds of environments where there exist enough vapors for particles to nucleate and grow (Kulmala et al., 2004). This conversion from gas phase (vapors) to liquid or solid phase (particles) is called nucleation. Once they are in the atmosphere, aerosol particles can stay suspended in the atmosphere and can travel around the world for anything between a few hours to a few weeks before they are removed through various scavenging processes, evaporation or deposition.

Secondary aerosol particles formed through nucleation is estimated to contribute to about half of the global CCN population at 0.2% supersaturation (Merikanto et al., 2009), and thus affect the Earth’s climate significantly (Lohmann et al., 2007). The growth of newly formed particles to CCN sizes has been observed in different environments (see e.g. O’Dowd, 2001; Lihavainen et al., 2003; Kuwata et al., 2008; Laaksonen et al., 2005; Whitehead et al., 2009; Wiedensohler et al., 2009 and Sihto et al., 2010). While primary emissions are fairly easy to quantify at their source, secondary emissions involve a few more formation steps that are still poorly understood. Hence, understanding these steps is of great importance. New particle formation (NPF) has been observed to take place frequently in several environments around the world (for reviews see Kulmala et al., 2004; Hirsikko et al., 2011): for example in the African Savannah (Laakso et al., 2008; Vakkari et al., 2011), in the marine coastal areas (Vana et al., 2008), in an eucalyptus forest (Suni et al., 2008), on mountain tops (Venzac et al., 2007, 2008) and in the boreal forest (e.g. Dal Maso et al., 2005). During an NPF event new particles emerge in the nucleation mode (particles of sizes ranging between 2 and 25 nm). This emergence, the entire new particle formation process and their further growth to larger sizes, or the so-called “banana-type” events, can be observed by measuring the size distribution of particles as a function of time. Observation of three such events is shown in Figure 1, measured with different instruments. In this synthesis, as well as in the papers, we will use “charged particles” to designate particulates bigger than 2 nm in diameter, and “small ions” or “cluster ions” for particulates smaller than 2 nm. We will designate the sum of neutral and charged particles as total particles.

The formation of new particles, or nucleation, and their growth to climatically relevant

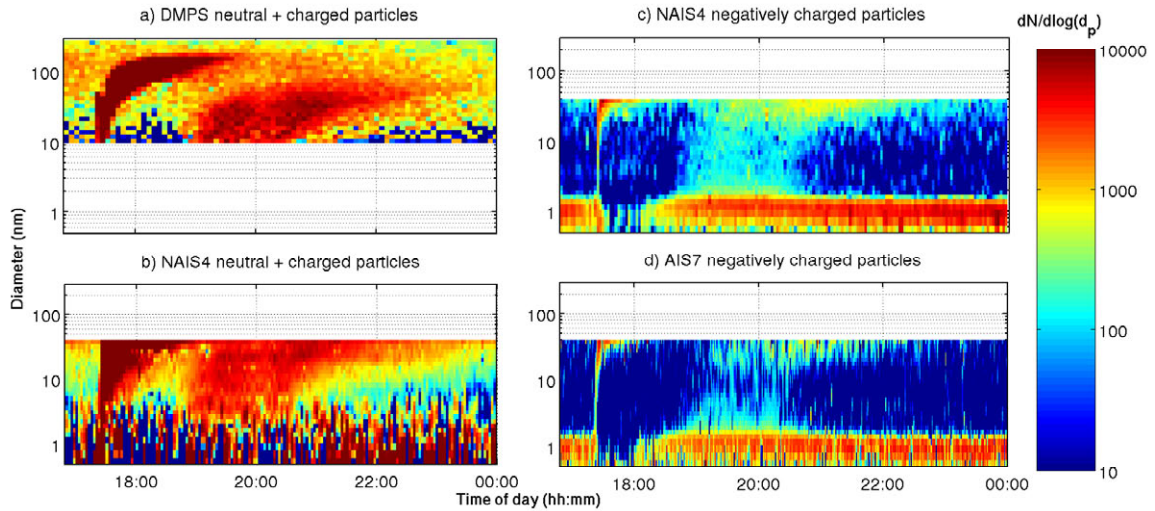


Figure 1: Three NPF events (at ca. 17:20, 18:50 and 20:00), provoked by peeling citrus fruits during the air ion spectrometer calibration and intercomparison workshop (**Paper III**): a) measured with a Differential Mobility Particle Size (DMPS), showing the concentration of total particles; b) measured with a Neutral cluster and Air Ion Spectrometer (NAIS), showing the concentration of total particles; c) measured with an NAIS, showing the concentration of negatively charged particles; and d) measured with an Air Ion Spectrometer (AIS), showing the concentration of negatively charged particles as a function of the particle diameter and time.

sizes could involve several possible nucleation mechanisms: classical binary homogeneous nucleation (Seinfeld and Pandis, 1998), ternary nucleation (Kulmala et al., 2000), ion-induced nucleation (Raes and Janssens, 1985, 1986), ion-mediated nucleation (Yu and Turco, 2000), kinetic nucleation (Laakso et al., 2004a) and nucleation through cluster activation (Kulmala et al., 2006). The contribution of each of these mechanisms to the formation of new particles is not well known. It even appears that more than one mechanism can be at work at the same time during new particle formation events (**Papers II, IV, VI** and e.g. Laakso et al., 2007 and Kazil et al., 2008). The particles can be formed by nucleation of vapors only, or by the condensation of vapors on a seed particle. We know that water and sulfuric acid vapors participate in nucleation (Weber et al., 1996; Sihto et al., 2006; Riipinen et al., 2007; Kuang et al., 2008; Sipilä et al., 2010), but so do ammonia, amines, and volatile organic compounds (Ehn et al., 2010; Kirkby and the CLOUD collaboration, 2011). In this thesis, we emphasize two classes of nucleation mechanisms independently of their internal chemistry: neutral nucleation

and ion-induced nucleation (IIN). Neutral nucleation includes all mechanisms that do not involve electric charges; ion-induced nucleation includes all mechanisms involving one or more electric charges. Ion-mediated nucleation (IMN) encompasses the product of the recombination of oppositely charged small ions in addition to ion-induced nucleation.

Diverse modeling studies propose that ion-induced nucleation may be an important, or even dominant nucleation mechanism, at least in certain conditions. According to Yu and Turco (2001), IMN can explain most part of a major NPF event observed in the marine boundary layer, and conclude that IMN works best at relatively low ionization rates, low condensation sink, high sulfuric acid concentration when nucleation is principally limited by the availability of ions. A model by Yu (2010) also suggests that ion-mediated newly formed particles are more abundant at lower temperature, and higher relative humidity in accordance with the model presented by Laakso et al. (2002). Moreover, a kinetic model by Lovejoy et al. (2004) “predicts that IIN of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  is an efficient source of new particles in the middle and upper troposphere”. However, Lovejoy et al. (2004) disagree with Yu and Turco (2001) and note that IIN is generally not important for NPF events in the boundary layer. Boy et al. (2008) modeled four NPF event days from Hyytiälä and found that IIN can explain up to 15% of the total amount of new particles formed in the 3-10 nm size range.

Ion-induced nucleation is all the more important because it is at the heart of the link between the solar cycle, galactic cosmic rays (GCR), the cloud cover, and finally, climate change (Svensmark and Friis Christensen, 1997). This observation led the public into questioning the role of humans in global warming. Since then, a lot of research, models and experiments have been published on this subject (e.g. Carslaw et al., 2002; Kazil et al., 2006; Sloan and Wolfendale, 2008; Kirkby, 2007; Kulmala et al., 2010 and Duplissy et al., 2010). The current scientific consensus is that the variability of GCRs, modulated by solar activity, may play a minor role in changing the cloud cover, but does not challenge the role of humans in global warming. In most places where the IIN has been estimated through measurements, the fraction of IIN was well below 30% on average (Iida et al., 2006, 2008; Manninen et al., 2009a, 2010 and **Papers II, IV and V**). Nevertheless, ion-induced nucleation may be important, or even dominant, in the upper troposphere (Curtius et al., 2006), and in elevated areas, such as mountain tops (Manninen et al., 2010).

The charging state, the ratio between the concentration of ions in an ambient sample

to the concentration of this sample at charge equilibrium, enables us to evaluate the fraction of ion-induced nucleation taking place in an NPF event. The principal objective of this thesis is to increase the knowledge and know-how on the charging state of aerosol populations, and its use to evaluate the importance of ion-induced nucleation as a nucleation mechanism. In order to attain the principal objective, the work was divided into smaller goals. These goals were:

- to develop and master instruments capable of measuring the charging state or the charged fraction as a function of time and particle size (**Papers II & III**), in order to understand the role of ions in aerosol dynamics,
- to develop and evaluate theoretical tools to understand the behavior of the charging state in order to obtain information about the fraction of ion-induced nucleation in a new particle formation event and its dynamical features (**Papers I & V**),
- to estimate the importance of ion-induced nucleation in different environments (**Papers IV & V**),
- to start understanding the factors influencing the participation of ion-induced nucleation to new particle formation (**Papers V & VI**), and
- to investigate the behavior of the charging state as a function of time during an NPF event (synthesis of the papers).

## 2 Theoretical background

In the atmosphere that surrounds us, electrically charged and neutral particles coexist and interact. We know that both positively and negatively charged particles are present, which makes the atmosphere a bipolar aerosol. If the air is given enough time to interact, the aerosol population in the air sample will reach the bipolar steady-state, or equilibrium (Wiedensohler, 1988). However, if the aerosol population is undergoing some dynamical process, the distribution of charged particles may be outside of the equilibrium. The different dynamical processes that affect ions are: ion-ion recombination, ion-neutral attachment, coagulation, ionization (production of ions) and condensation/evaporation. These processes are summarized in Figure 2.

Ion-ion recombination involves two small ions of opposite polarities combining to form a bigger, neutral particle. Ion-neutral attachment involves an ion (negatively or positively charged) combining with an electrically neutral particle to form a bigger charged particle. Coagulation is when a charged particle merges with a neutral particle. Ionization, which is the source of ions in the atmosphere, happens when a neutral molecule or particle is excited by a photon of sufficient energy to liberate an electron and produce two ions of opposite charges. Possible ionizing sources in the environment come from radon decay (Hatakka et al., 1998; Laakso et al., 2004b), galactic cosmic rays (Carslaw et al., 2002) or other ionizing sources such as power transmission systems (e.g. Ling et al., 2010). Finally, condensation (or evaporation) does not alter the number of charges of each polarity in the aerosol population, but it changes the size of the particles. Some vapors may have a chemical affinity for negatively charged particles (like in Figure 2) or for positively charged particles. This results in an advantage of charged particles over neutral or oppositely charged particles, and it may help them capture a larger quantity of vapor and enhance their growth (Nadykto and Yu, 2003; Lushnikov and Kulmala, 2004). However, the magnitude of this enhancement factor is not well known. All these processes may push the aerosol population outside of its charge equilibrium, and we use this behavior as a tool in this thesis.

## 2.1 Charged fraction and charging state

The charged fraction  $f$  is the fraction of particles that are electrically charged in a given aerosol population. The charged fraction can be calculated separately for negatively and positively charged particles, or for both together. Since the equilibrium charged fraction varies depending on the particle size, the charged fraction is usually defined for a given particle size range. In bipolar equilibrium situations, the charged fraction  $f_{eq}$  is given in Figure 3. When the charged fraction of the population is higher than the bipolar equilibrium value, the aerosol population is called overcharged; when it is lower, it is called undercharged.

The charging state, or charging ratio,  $S$ , is the ratio of the sample's charged fraction to the sample's bipolar equilibrium charged fraction, so that overcharged aerosol populations have a charging state above one, and undercharged below one. The charging ratio is usually calculated separately for each polarity as a function of the diameter  $d_p$  and is defined as:

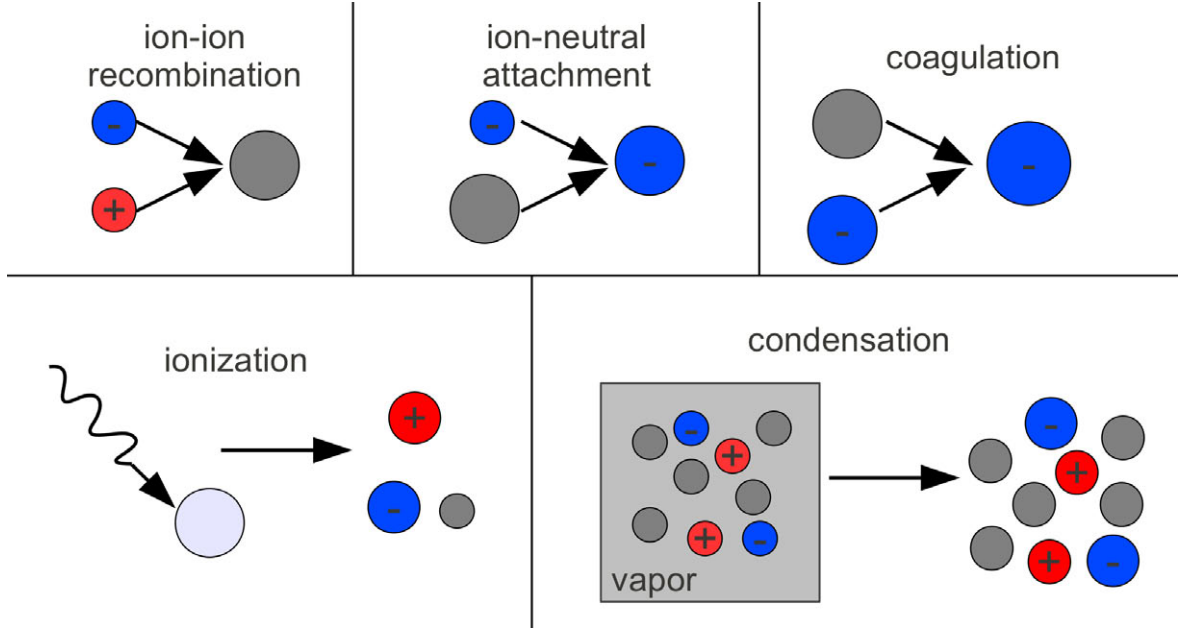


Figure 2: Five processes that affect the distribution of charged particles in the atmosphere: ion-ion recombination, ion-neutral attachment, coagulation, ionization and condensation.

$$S^\pm(d_p) = \frac{f^\pm(d_p)}{f_{eq}^\pm(d_p)} \quad (1)$$

where  $f^\pm$  is the charged fraction of the air sample for positive or negative particles (indicated by the superscript). Since the charged fraction of the sample and the equilibrium charged fraction are a function of particle size, and the dynamical processes differ at different particle sizes, the charging ratio as a function of particle size gives us hints about the nucleation mechanisms affecting the aerosol population. An equation describing the behavior of the charging ratio as a function of the diameter can be derived based on the balance equations, describing the dynamics of the charged particles, and using a number of simplifying assumptions (**Paper I**):

$$S^\pm(d_p) = 1 - \frac{1}{Kd_p} + \frac{(S_0 - 1)Kd_0 + 1}{Kd_p} e^{-K(d_p - d_0)} \quad (2)$$

where

$$K = \frac{\alpha N_c^\pm}{GR} \quad (3)$$

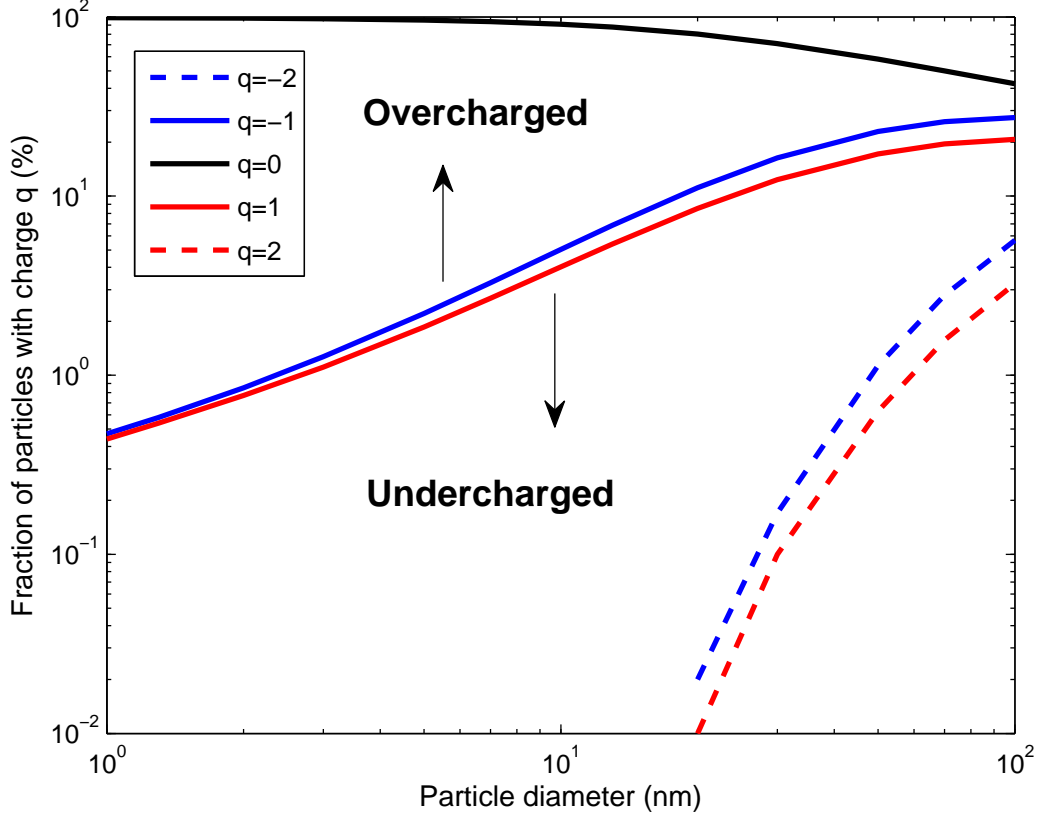


Figure 3: Fraction of particles with charge  $q$  (where  $q$  varies from -2 to +2 electronic charges) for different particle sizes, at bipolar equilibrium. The bipolar equilibrium is taken from Wiedensohler (1988).

and  $S_0$  and  $d_0$  are the charging state and diameter of newly formed particles, respectively,  $N_c^\pm$  is the number concentration of positive or negative small ions, GR is the particle growth rate and  $\alpha$  ( $\sim 1.6 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$ ) is the ion-ion recombination coefficient. The parameter  $K$  contains information about the charging state “memory” of the aerosol population: when  $K$  is large, the growth rate is small or  $N_c^\pm$  is large and the particles recombine and lose their charged fraction information before they become large enough to be measured: they have lost their memory of the charging state.

There exist some cases where the charge steady-state in a natural aerosol population is not the charged fraction of the bipolar equilibrium. This can happen when the concentration of positively charged small ions,  $N_c^+$ , is significantly different from the

concentration of negatively charged small ions,  $N_c^-$ . The theoretical framework that should be applied in such cases is presented in detail in Leppä et al. (2011). In this case, the steady-state charged fraction,  $f_{asym}^\pm$ , is the equivalent asymmetric equilibrium value and is equal to  $f_{eq}^\pm N_c^\pm / N_c^\mp$ . We can then define an asymmetric charging ratio,  $S_{asym}$ , which shows how far from the asymmetric equilibrium the charging ratio is.

$$S_{asym}^\pm(d_p) = \frac{f^\pm(d_p)}{f_{asym}^\pm(d_p)} \quad (4)$$

and the equation describing the behavior of the asymmetric charging state as a function of particle size becomes:

$$S_{asym}^\pm(d_p) = 1 - \frac{1}{K^\pm d_p} + \frac{(S_{asym,0}^\pm - 1)K^\pm d_0 + 1}{K^\pm d_p} e^{-K^\pm(d_p - d_0)} \quad (5)$$

and

$$K^\pm = \frac{\alpha N_c^\mp}{GR} \quad (6)$$

## 2.2 Ion-induced nucleation in NPF events

Observations of new particle formation events suggest that the contribution of ion-induced nucleation to newly formed particles can vary greatly, from nearly 0% to almost 100% in certain conditions (e.g. **Papers IV** and **V**; Yu and Turco, 2008). In order to understand the conditions that favor ion-induced nucleation over neutral nucleation, it is important to have tools to estimate the fraction of ion-induced nucleation. There are several ways to estimate the ion-induced nucleation fraction. In this thesis, we concentrate on the two ways that are most used in the literature.

The first such way is based on the charged fraction at the size where nucleation occurs,  $d_0$ . The sum of the negative and positive charged fractions at  $d_0$  is assumed to be representative of the fraction of ion-induced nucleation. The rationale behind this method is that the particles that are charged at the size where nucleation occurs are ion-induced particles, which tend to charge equilibrium as they grow. This method assumes that the particles are in a pseudo-steady-state and that the sink of those particles is equal to their source. Consequently, the fraction of ion-induced nucleation is  $f^+(d_0) + f^-(d_0)$ .



The second method is based on the formation rate of charged ( $J_{ion}$  or  $J^+ + J^-$ ) and total ( $J_{tot}$ , neutral + charged) particles at  $d_0$ . The ratio between the two formation rates is then a good estimate of the fraction of ion-induced nucleation. The rationale behind this method is straightforward: the concentration of charged particles formed per unit of time, divided by the same physical quantity for total particles ( $J_{ion}(d_0)/J_{tot}(d_0)$ ) represents the fraction of ion-induced nucleation.

The fraction of ion-induced nucleation gives us information about the share of particles that were formed through ion-induced nucleation in a given NPF event. However, it does not give any information about the absolute number of particles formed either through ion-induced nucleation or neutral mechanisms. In order to evaluate the contribution of each mechanism to the global climate forcing (through modeling), it is important to be able to estimate the number of particles that are formed through each pathway and in different conditions. The second method makes the retrieval of the number of particles easier, since we know  $J_{ion}$  and  $J_{tot}$ . With the first method, however, the total number of particles has to be calculated separately. Both methods are compared in Kerminen et al. (2010) and in **Paper VI**.

### 3 Instruments

The charging state of an aerosol population is a quantity that has been measured in a few places only. However, there exists a large number of ways to measure it. One way is to use a combination of instruments: one instrument that measures the size distribution of all particles regardless of their charge such as a Differential Mobility Particle Sizer (DMPS, Hoppel, 1978; Aalto et al., 2001) and an ion spectrometer, for example an Air Ion Spectrometer (AIS, Mirme et al., 2007). Iida et al. (2006) in Boulder, Colorado, and Vana et al. (2006) in Hyytiälä, Finland, also used a combination of instruments. In the first case, the combination consisted of a DMPS and an Inclined Grid Mobility Analyzer (IGMA, Tammet, 2002b and 2003). In the second case, the authors used a DMPS and an Electrical Aerosol Spectrometer (EAS, Tammet, 2002a) to measure the number size distribution, and an AIS and a Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006) as ion spectrometers. Another way to measure the charging state is to use a single instrument that measures in different operation modes. The Neutral cluster and Air Ion Spectrometer (NAIS, Asmi et al., 2009; Manninen et al., 2009b and **Paper III**) and the Ion-DMPS (**Paper II**) are the only two instruments

so far that can measure the charging state singlehandedly. They are described in more detail in the following sections.

### 3.1 Ion-DMPS

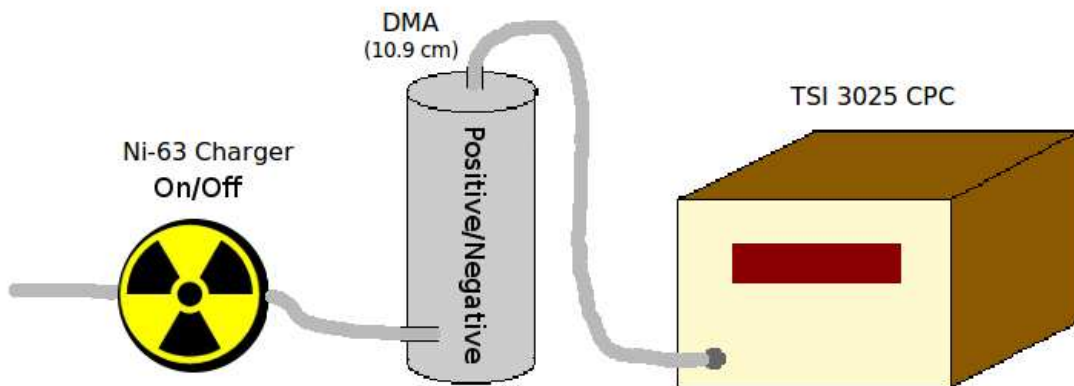


Figure 4: The Ion-DMPS consists of a neutralizer (bipolar charger, Ni-63) that can be switched on or off, a DMA that can be selecting positively or negatively charged particles and a CPC TSI 3025 to count the particles.

The Ion-DMPS measures the number size distribution of aerosol particles. It consists of three parts: a bipolar charger (also called a neutralizer,  $\beta$ -active Ni-63), a Hauke-type Differential Mobility Analyzer (DMA, Winklmayr et al., 1991) in a closed loop flow arrangement (Jokinen and Mäkelä, 1997) and a Condensation Particle Counter (CPC, TSI 3025, Stolzenburg and McMurry, 1991). The neutralizer induces the steady-state charged fraction in the sample by ionizing it. This neutralizer is also equipped with a special shield which blocks the ionizing radiation from reaching the air sample when it is in a certain operation mode. Consequently, the neutralizer can be either in the “on” or “off” position. When it is switched on, the aerosol population is neutralized, i.e. the charged fraction as a function of the particle size is known (Wiedensohler, 1988) and the Ion-DMPS acts as a DMPS. When the neutralizer is turned off, the sampled aerosol population conserves its original charged fraction, the Ion-DMPS then acts as an ion spectrometer. After the air sample has gone through the neutralizer, it is directed to the DMA, where the positively or negatively charged particles (alternatively) of specific sizes are selected. The DMA was scanning stepwise for equivalent electrical

mobility diameters usually between 3 and 15 nm. Finally, the CPC measures the charged particle concentration. By combining the operation modes of the neutralizer and those of the DMA, the Ion-DMPS can measure in four different modes:

- Neutralized negative: the neutralizer is switched on, so the charged fraction of the sample after passing through the neutralizer is known. The DMA selects negatively charged particles of given sizes. The CPC gives the number concentration of negatively charged particles when the charged fraction is at steady state.
- Ambient negative: the neutralizer is switched off, so the charged fraction of the sample after passing through the neutralizer is the ambient fraction. The DMA selects negatively charged particles of given sizes. The CPC gives the number concentration of negatively charged particles with the ambient charged fraction.
- Neutralized positive: the neutralizer is switched on, so the charged fraction of the sample after passing through the neutralizer is known. The DMA selects positively charged particles of given sizes. The CPC gives the number concentration of positively charged particles when the charged fraction is at steady state.
- Ambient positive: the neutralizer is switched off, so the charged fraction of the sample after passing through the neutralizer is the ambient fraction. The DMA selects positively charged particles of given sizes. The CPC gives the number concentration of positively charged particles with the ambient charged fraction.

The charging ratio for negative particles is obtained from the ratio of the ambient negative concentration to the neutralized negative concentration. Similarly, the charging ratio for positive particles is obtained from the ratio of the ambient positive concentration to the neutralized positive concentration. An example of a new particle formation event day, detected through the Ion-DMPS, is presented in Figure 5

The main strength of the Ion-DMPS is that the sampled air passes through the exact same inlet system in each operation mode, hence the diffusional losses are the same and no corrections need to be applied to get the charging state. However, the time resolution depends on the integration time and the number of size channels, and a complete cycle of four modes can vary between 10 and 30 minutes. The Ion-DMPS is used in all of the papers presented in this thesis.

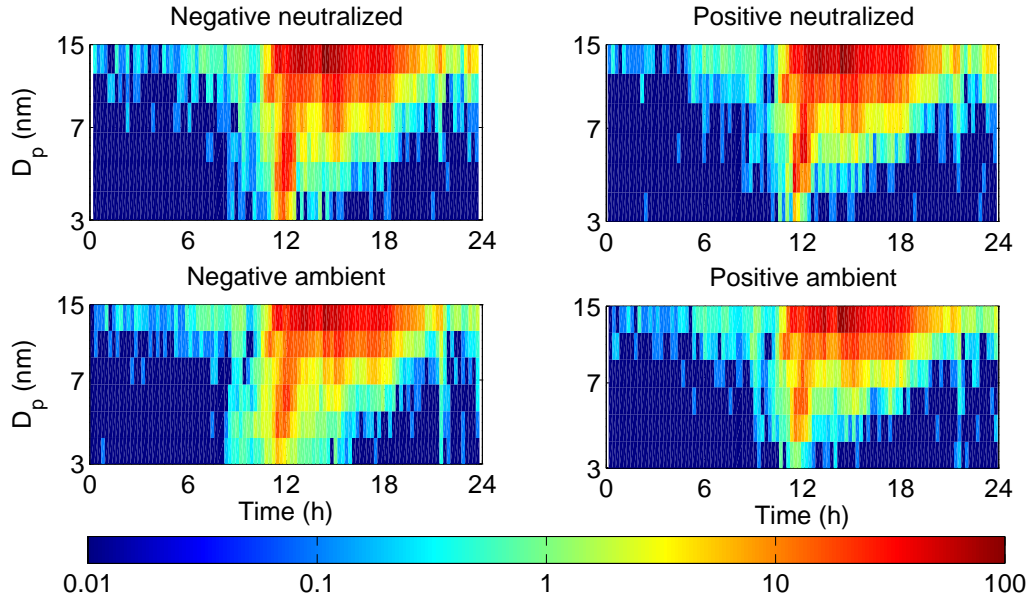


Figure 5: The size distribution of aerosol particles on 2 May 2005 as measured by the Ion-DMPS. The negative polarity is shown on the left side, with the neutralized sample on top and the ambient sample at the bottom. Similarly, the positive polarity is shown on the right, with the neutralized sample on top and the ambient sample at the bottom. The concentration, in particles  $\text{cm}^{-3}$ , is represented by the color bar.

### 3.2 NAIS and AIS

The NAIS was developed by Airel Ltd. based on their earlier AIS instrument. The NAIS consists of two concentric cylindrical DMAs operating in parallel (one for each polarity). The central cylindrical electrode provides an electrical field which projects the charged particles onto 21 vertically stacked electrometers such that the instrument measures between roughly 0.8 and 40 nm, on 21 size channels. While the AIS only measures the ion size distribution, the NAIS can measure in two modes: a mode measuring the naturally charged particle size distribution, and a mode measuring the total particle size distribution. The latter mode relies on unipolar corona chargers where the particles in the air sample acquire unipolar charges in predefined conditions. The current of these charges is then measured by the electrometers, and the total particle concentration is estimated based on calibrations made in similar charging conditions. The charged fraction is the ratio of the ion concentration to the total particle concen-

tration. The charging state can be estimated using the steady-state charged fraction. In **Paper III**, an NPF event was provoked and measured by the Ion-DMPS and the NAIS simultaneously. It was found that the charged fractions measured with both instruments agreed well with each other above 3 nm.

Since both polarities and all size bins are measured simultaneously, the strengths of the NAIS reside in its good size and time resolution. The integration time is user-defined but is usually set between 2 and 5 minutes. It is also capable of measuring below 3 nm because of the use of electrometers rather than a CPC with a minimum cut-off size. However, both the ion and particle mode of the NAIS have a background concentration at the smaller sizes. This is probably due to corona charger ions produced in the total particle mode or to traces of radon in the instrument (**Paper III**). This background makes measurements below 1.7 nm in particle mode unreliable (Manninen et al., 2011). Another possible problem with the NAIS is the effect of the initial charged fraction in the air sample. It is not clear whether the unipolar charger can produce a charged fraction in the aerosol population that corresponds to the calibrations values when the sampled air is overcharged. This means that the total particle concentration would be overestimated in overcharged cases, leading to underestimated charged fractions and ion-induced fractions. This phenomenon is currently under investigation.

### 3.3 BSMA

Although the work presented in this thesis focuses mostly on the Ion-DMPS, with a noticeable contribution from the NAIS, other ion spectrometers are also of interest. For example, the BSMA has been used as a supporting instrument in **Papers II, III, IV, V** and **VI**.

The BSMA is an ion spectrometer that consists of two parallel plane-type DMAs connected in a balance bridge circuit arrangement. The electrical current of the particles is measured while the electrical field in the DMA is scanned. The very high sampling flow of  $22 \text{ l s}^{-1}$  per polarity reduces the ion losses in the inlet of the instrument. The diameter measured with this instrument ranges from 0.4 to 7.5 nm. A complete ion size distribution is obtained in a cycle of ca. 3 minutes.

In the BSMA, no charging modules introduce any background concentrations. This instrument is thus very trustworthy to measure the size distribution of small ions and

charged particles of both polarities. Moreover, it compared well with an Atmospheric Pressure interface Mass Spectrometer (APi-TOF, Ehn et al., 2010)

## 4 Methods to analyze the charging state

### 4.1 Classification of NPF events based on their charging state

The first step to analyze measurement data is to divide the measured days into different categories: NPF event days, non-event days, and undefined days. The classification scheme was inspired by Dal Maso et al. (2005) and adapted to the size range of the Ion-DMPS. The method is described in detail in **Papers II, IV and VI** and summarized here:

- **NPF Event** days are days when formation of 3–5 nm particles and their subsequent growth was observed.
- **Non-event** days are days when no formation and growth of new particles was observed.
- **Undefined** days are days that did not belong to the event nor to the non-event class (e.g. either no growth, or no new 3-5 nm particle formation was observed, but some dynamical features were observed).
- Days on which the instrument was malfunctioning or classification was impossible are classified as **bad/no data** days.

Since our interest mostly lies in new particle formation, only NPF event days were kept for further analysis. Each NPF event day was classified further into 4 categories: overcharged, undercharged, steady-state (equilibrium) or bad. This classification was made for each polarity separately.

- **Overcharged** events are events for which the aerosol particle population had a higher charged fraction than the bipolar equilibrium.
- **Undercharged** events are events for which the aerosol particle population had a lower charged fraction than the bipolar equilibrium

- **Steady-state** or **equilibrium** events are events for which the aerosol particle population had a similar charged fraction than the bipolar equilibrium (within the uncertainty of the instrument).
- **Bad** events are events for which the general charging state could not be determined.

In terms of Ion-DMPS data, this means that the particle size distributions in neutralized and in ambient mode were compared visually, concentrating on the smallest sizes because the charging state usually reached the charge equilibrium before 5-7 nm. In Figure 5, the classification is difficult because the particle population is overcharged at the beginning and at the end of the event, but undercharged at its core. It was classified as undercharged in **Paper II** because it was undercharged on average.

## 4.2 Determination of the charging ratio from measurements

Since the behavior of the charging ratio is described as a function of diameter in Eqs. 2 and 5, we want to determine the charging ratio as a function of diameter. Despite knowing that the charging ratio can change during a new particle formation event (Laakso et al., 2007), it is most practical to give only one average charging ratio value for an event, independently of time. In the papers presented in this thesis, we present one average charging state value per new particle formation event per particle size and polarity.

In this thesis, two methods to retrieve the charging ratio are used. The first method, used in **Papers II, IV** and **V**, consists in finding the average charging ratio for each diameter during the period where the newly formed particles are present for a given size, as presented in Figure 6. The charging ratio is calculated by dividing the ambient concentration by the neutralized concentration at each point in time. The uncertainty on the diameter is calculated based on flow fluctuations in the DMA as well as the DMA's transfer function. The uncertainty on the charging ratio for this method depends on the integration time of the CPC (uncertainty of the concentration), and the concentrations in each measurement mode (uncertainty of the concentration ratio).

The second method, used in **Paper V**, also yields a single average value during the period of the event, but this time relies on a least-mean square fit (forced to pass

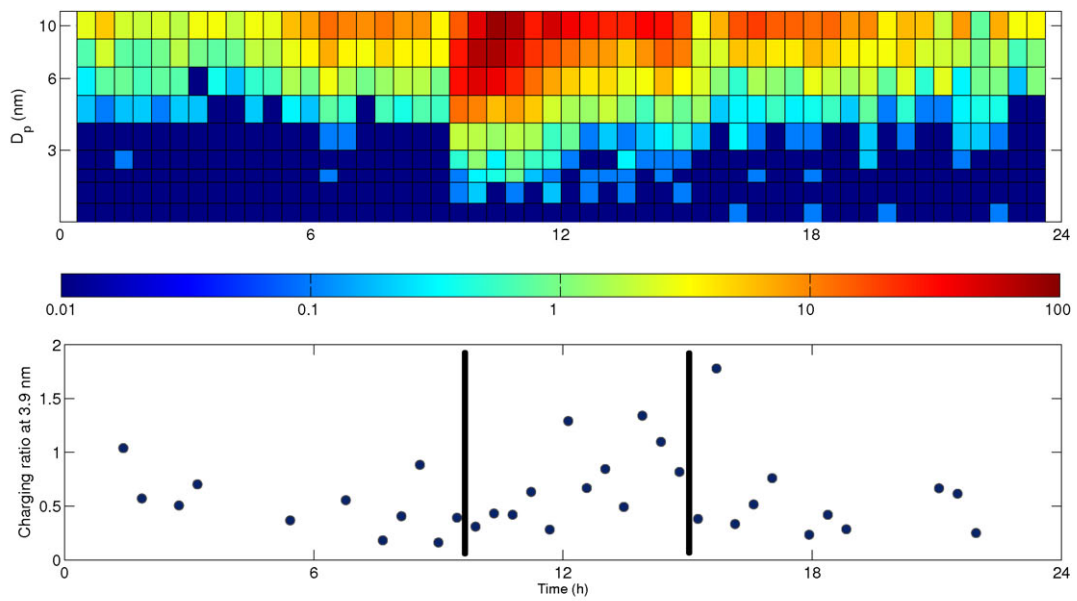


Figure 6: The time average method consists in selecting the timespan (indicated by black vertical bars) of new particle formation at a given size, here at 3.9 nm, and calculating the average of the ratio of the ambient concentration to the neutralized concentration during this period. The size distribution is shown in the upper panel to guide the eye, and the charging ratio for a given size is shown on the lower panel, as a function of time.



through the origin) of the concentration of particles in the ambient mode as a function of the concentration of particles in the neutralized mode. The slope of such a fit then becomes the average charging ratio (see Figure 7). The uncertainty on the diameter is the same as for the time averaging method. The uncertainty on the charging ratio is the sum of the uncertainty on each point (maximum estimate) and the uncertainty related to the scatter around the linear fit.

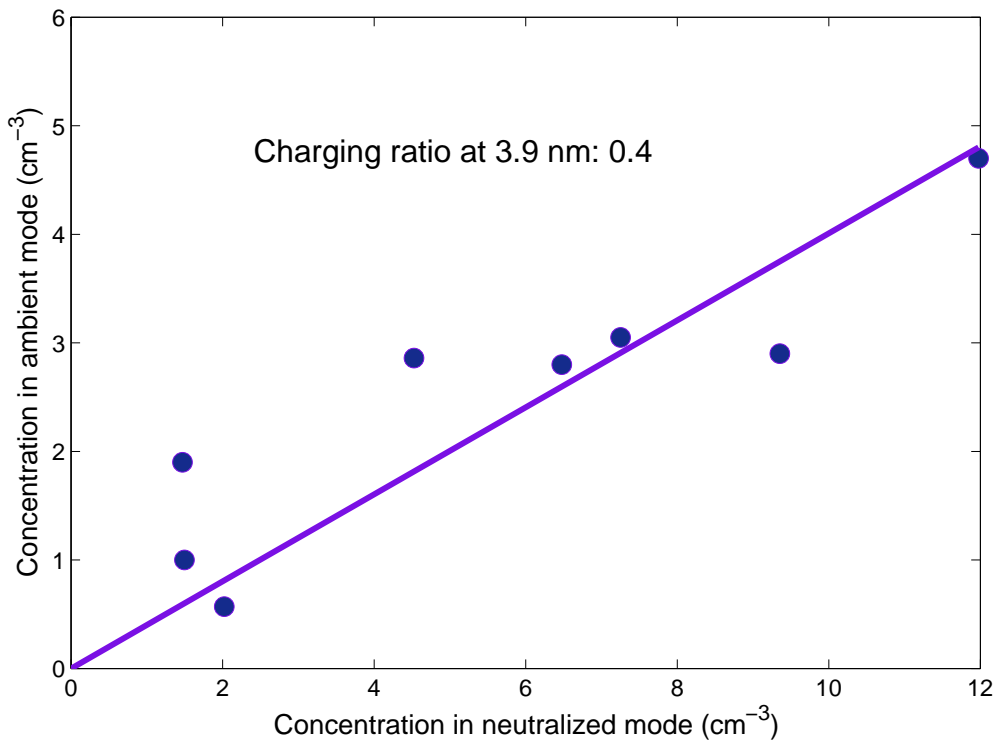


Figure 7: The slopes method consists in plotting the concentration of particles in the ambient sample as a function of the concentration of particles in the neutralized sample for a given size, here 3.9 nm. The selected concentrations were measured during the same timespan as indicated in Figure 6. The slope of the linear fit is the average charging ratio.

The superiority of the second method, the slopes method, over the time averaging method is demonstrated in **Paper V**. The two methods gave consistent results for the charging state. However, the median average deviations (MADs) using the slopes method were halved compared to MADs using the time averaging method. Using the second method reduces the uncertainty on the ion-induced fraction.

### 4.3 Estimation of the charging state for an event

The charging state can be estimated by fitting the curves described by Eqs. 2 and 5 to the measured charging ratios. In practice, however, the curve's shape can vary widely depending on the position of each charging ratio. For example, if the charging ratios are all oscillating around one, the optimal fit will follow the one-line and jump up or down at the smallest diameter. This behavior is not physically justified. To avoid such biases, the free parameters  $S_0$  and  $K$  are limited.  $S_0$  is allowed to vary between -10 and 100% ion-induced nucleation. Even though a negative charging state is physically impossible, the parameter is allowed to get this low to give more freedom to the fitting curve. The parameter  $K$  is allowed to vary between 0.1 and 5 or 10. When  $K$  is larger than two, it is unlikely that the aerosol population retained the charging state information. To account for these biases,  $S_0$  was replaced by zero for all fits for which  $S_0$  was smaller than zero, and fits for which  $K$  was bigger than 2 were discarded. Also, Eqs. 2 and 5 were fitted 2,000 times through randomly generated charging ratios normally distributed inside their uncertainty boxes. The median charging state,  $S_0$ , and the value of  $K$  of the same curve are kept as an average curve for one event. The uncertainty is estimated using the MAD of the 2,000 fits. An example of such a fit is shown in Figure 8. Each fit can be given a quality value, describing how well they fit the experimental data (see **Paper V**).

### 4.4 Growth rate estimations from the charged fraction

In **Paper V**, the growth rate of a new particle formation event is estimated based on behavior of the charged fraction as a function of the diameter (Eq. 7; Leppä et al., 2011).

$$GR_f^\pm = \frac{df^\pm}{dd_p}^{-1} (\beta_0 N_c^\pm - \alpha f^\pm N_c^\mp) \quad (7)$$

where  $GR_f$  is the growth rate derived from the charged fraction,  $f$  is the charged fraction,  $d_p$  is the diameter,  $N_c$  is the concentration of small ions,  $\beta_0$  is the attachment coefficient between a neutral particle and a charged small ion and  $\alpha$  is the attachment coefficient between a small ion and an oppositely charged particle. In this method,  $\frac{df^\pm}{dd_p}$  was determined from the measurements and the charged fractions were calculated

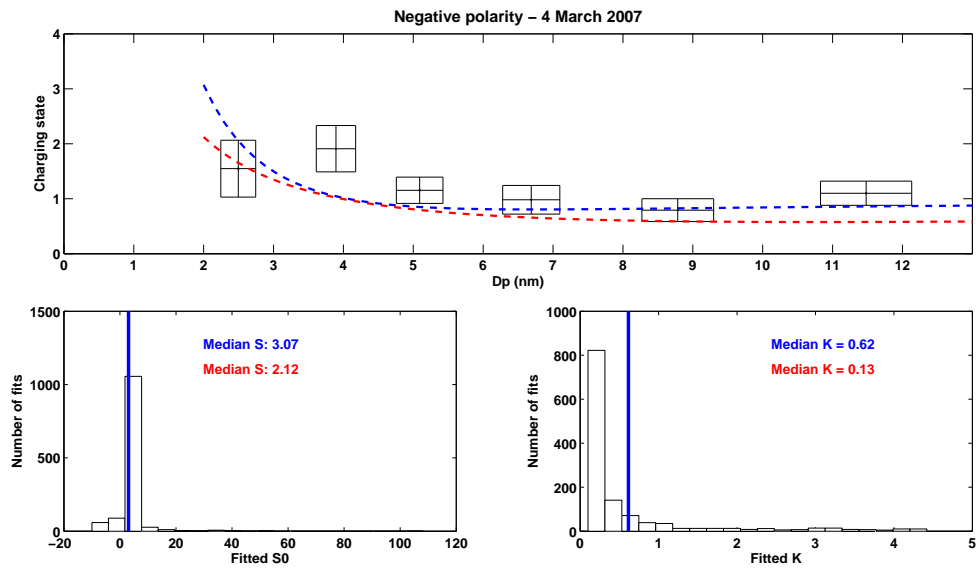


Figure 8: Example of a fit of Eq. 5 through measured charging ratios for 4 March 2007, Hyytiälä. The measured charging ratios with their uncertainties (boxes; the measured point is in the middle of the box) as a function of the diameter is shown in the upper panel. The curve is fitted to randomly generated points normally distributed within the boxes two thousand times. The distributions of fitted  $S_0$  and  $K$  values are shown in the lower left and right panels, respectively. The curve with the median  $S_0$  value and the corresponding  $S_0$  and  $K$  are shown in blue, whereas the curve with the median  $K$  value and the corresponding  $S_0$  and  $K$  are shown in red. The blue vertical bars show the values associated with the median  $S_0$  that is kept for analysis.

from Eq. 7. The growth rate was obtained by iteratively changing its value to match the calculated and measured charged fractions.

The method described by Eq. 7 was applied to undercharged events and compared to  $GR_{PSD}$  in **Paper V**. The growth rates to which this method was applied were small, and could be determined with the traditional methods, which makes comparisons possible.  $GR_f$  were overestimated compared to  $GR_{PSD}$ , but the growth rates corresponded within their uncertainty values.

A better method was developed in the meantime. In this method, the charged fractions were obtained by solving the differential equations 8 and 9. The growth rate and charged fractions at the lowest size boundary were changed iteratively until the calculated and measured charged fractions match. The new method optimizes the fitting with the same growth rate for both polarities but still allows for different charged fraction:

$$GR_f = \frac{df^{-1}}{dd_p} \left( (1 - f^- - f^+) \beta_0^- N_c^- - \alpha f^- N_c^+ \right) \quad (8)$$

$$GR_f = \frac{df^{+1}}{dd_p} \left( (1 - f^- - f^+) \beta_0^+ N_c^+ - \alpha f^+ N_c^- \right) \quad (9)$$

This method can be used in a wider range of cases and is being tested at the moment. The method is especially practical in situations where it is difficult to follow the peak of the size distribution as a function of time ( $GR_{PSD}$  see e.g. Dal Maso et al., 2005). A similar method was developed and applied by Iida et al. (2008) on NPF events in Mexico City where the observed growth rates were as fast as 40 nm/h, and the peak of the distribution could not be followed. The advantage of the method described here over the method of Iida et al. (2008) is that the concentration of small ions and the charged fraction of particles do not have to be the same for the negative and positive polarity.

## 5 Results

### 5.1 Comparison of the Ion-DMPS and the NAIS

The study of the charging state or the charged fraction has yielded valuable results. The charged fraction and the charging state can be measured using the Ion-DMPS, the NAIS or a combination of instruments measuring the charged and the total concentration for a given size range (for example, a combination of a particle sizer and an ion spectrometer, or a CPC battery with a switchable ion precipitator; Duplissy et al., 2010). Figure 9 shows the charged fraction measured with the Ion-DMPS and an NAIS during an NPF event taking place in Hyytiälä. At smaller diameters (2.8 and 3.9 nm), the Ion-DMPS measures higher charged fractions than the NAIS, but they agree remarkably well at larger diameters. Since corona ions do not affect the measurements above 1.7 nm, the most likely explanations are that a) the sample is too strongly overcharged for the unipolar chargers and the total concentration is overestimated, and/or b) the bipolar equilibrium charged fraction is underestimated at small sizes. Overall, however, the behavior of the charged fraction as a function of the size and as a function of time is similar for both instruments. The NAISs and the Ion-DMPS also compared well in **Paper III**.

In **Paper VI**, the ion-induced fraction determined using the Ion-DMPS and the NAIS are compared. The Ion-DMPS method uses charging ratios extrapolated using Eq. 2; the NAIS method uses the formation rates of ions ( $J_{ion}$ ) divided by the formation rate of total particles ( $J_{tot}$ ). The agreement is good for charged fractions below 20% (see Figure 2b of **Paper VI**). Points with a large Ion-DMPS but a small NAIS ion-induced fraction are due to event days where the charging ratio was not well-behaved and the fit to Eq. 2 went up at the smallest diameter to reduce its residual. However, points with a small Ion-DMPS but a large NAIS ion-induced fraction are due to days for which  $J_{ion}$  was almost as large as  $J_{tot}$  or when  $J_{tot}$  was small.

### 5.2 Analysis of the fraction of ion-induced nucleation

The ion-induced nucleation fraction was calculated based on the extrapolation of the charging state in **Papers II, IV and V**. These papers, as well as Manninen et al. (2010) and Kerminen et al. (2010), show that the ion-induced fraction varies from one place

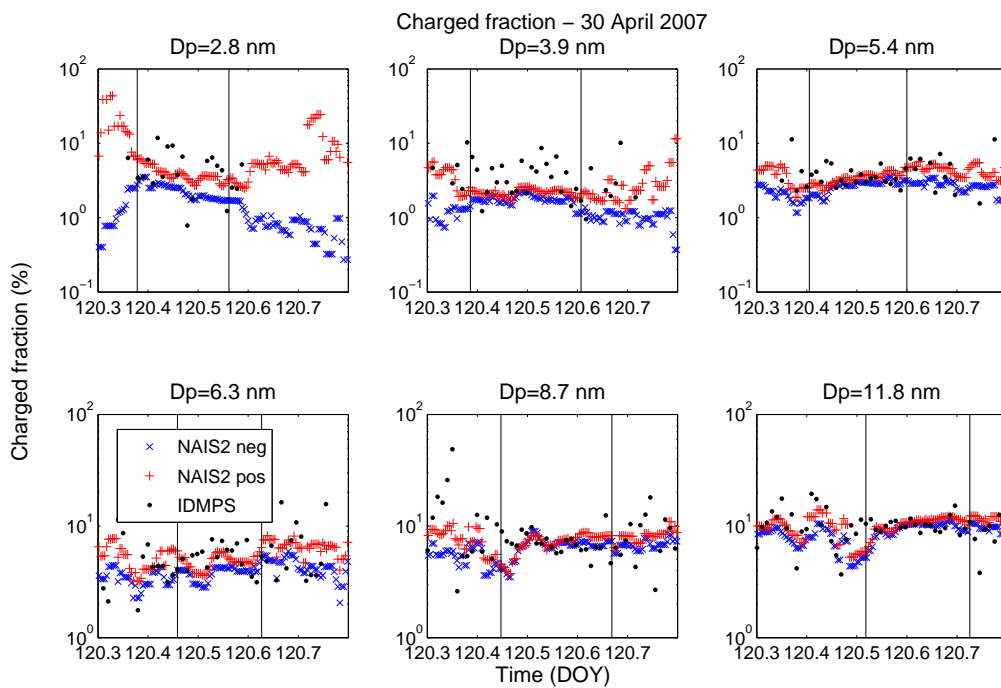


Figure 9: Charged fraction measured with an Ion-DMPS and an NAIS in Hyytiälä on 30 April 2007, an overcharged day, at different particle sizes. The Ion-DMPS measurements are represented by black dots, the NAIS charged fraction (negatively+positively naturally charged particles divided by the total number concentration) using the total concentration of the negative and the positive DMA are represented by blue and red crosses, respectively. The time during which the NPF event took place for each size is indicated by vertical bars.

to another, from one event to another, and within an event. The ion-induced fraction was about 6% in Hyytiälä, a remote background area, and around 1% in Helsinki, an urban and polluted area. Manninen et al. (2010) saw a similar tendency: polluted areas had lower ion-induced fractions than pristine areas. They also show that the formation rate of ions seems to stay the same in all areas, but that the formation rate of neutral particles varies widely from one place to another.

In **Paper IV**, the seasonal tendencies of ion-induced nucleation are investigated. In Hyytiälä, the fraction of ion-induced nucleation had a clear maximum in summer, and a minimum in winter (**Paper IV**, Figure 7). Most events were overcharged (78%) and happened in spring and summer. However, in Helsinki, no such tendency was found (**Paper V**) and most of the events were undercharged (95%). A comparison of the classification of event days in both places is shown in Figure 10. Because the fraction of ion-induced nucleation varies much more in Hyytiälä, it is a much better place to study the variations of the fraction of ion-induced nucleation than Helsinki, which is done in **Paper VI**.

**Paper VI** is an analysis of the factors influencing the fraction of ion-induced nucleation. The study uses 2 years and 7 months of Hyytiälä Ion-DMPS data, classified into two categories (over- and undercharged), to find the parameters favoring ion-induced nucleation over neutral nucleation, or vice-versa. This analysis relies on the fact that, in Hyytiälä, the fraction of ion-induced nucleation varies from one NPF event to another.

One of the main findings of this study was that events with higher ion-induced fractions, overcharged events, take place on days with lower vapor saturation ratios. Only sulfuric acid and water were included in the study, but both showed the same tendency. This is consistent with laboratory experiments by Winkler et al. (2008), during which they saw that negative ions, followed by positive ions, activated at smaller vapor saturation ratios than neutral particles. Moreover, in Hyytiälä, more overcharging was observed for the negative polarity than for the positive polarity (Figure 10 and **Papers IV** and **VI**). In Helsinki, the positive polarity is more often slightly overcharged because of the small ion polarity asymmetry: the concentration of positive small ions is bigger than that of negative small ions.

NPF events with a higher fraction of ion-induced nucleation also happened on warmer days, as high temperatures promote evaporation, especially for neutral particles for which the attraction is not as strong as for charged particles (Lovejoy et al., 2004). On

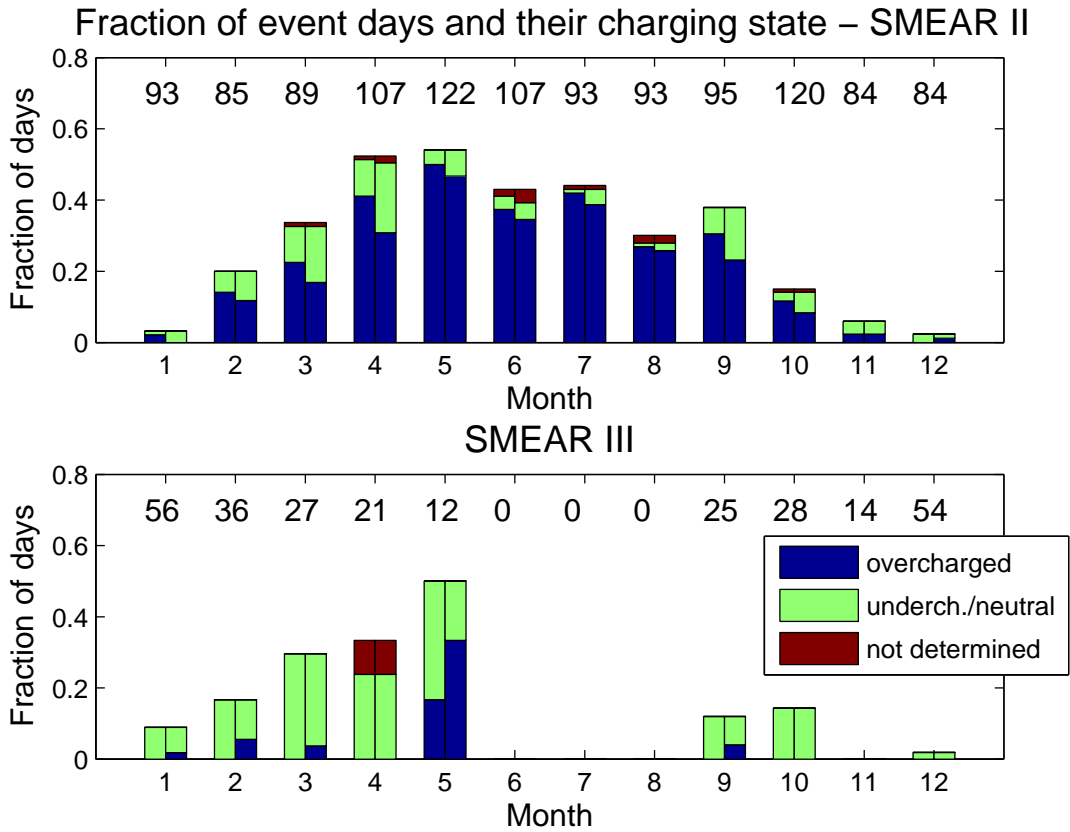


Figure 10: The fraction of measured day that were classified as event days in Hyytiälä (SMEAR II) and Helsinki (SMEAR III) for each month of the year. The charging state classification is indicated by the colors. The total number of days measured during each month is indicated on top of each month. For each month, the column on the left represents the classification of the negative polarity and the column on the right represents the positive polarity.



days where the ion-induced nucleation fraction was bigger, there was more sunlight and more important decrease in small ion concentrations during the events were noticed. According to **Paper VI**, NPF events with a smaller fraction of ion-induced nucleation were producing a larger number of particles. This agrees with the findings of Vana et al. (2006) and Manninen et al. (2010). It suggests that the ion-induced contribution does not vary much from one day to another and is limited by the ion pair production rate, while neutral nucleation is influenced by many factors and varies more from one day to another.

The fraction of ion-induced nucleation can also vary during an event. Figure 11 shows an event from Hyytiälä during which the charging state varies as a function of time. This behavior was observed only a few times a year. In this case, the core of the event is dominated by neutral nucleation, whereas in the negative polarity, the beginning and the end of the event see a more important contribution of ion-induced nucleation. During the core of the event, when neutral nucleation becomes more important, the number concentration of nucleation mode particles increases drastically.

The ion pair production rate, which influences ion-induced nucleation, is rather constant over the year, but can diminish when the ground is covered with snow or ice, or when the soil is filled with water (Hatakka et al., 1998). The snow, ice, or water acts as a lid on top of the ground that absorbs the radiation from the decay of radioactive materials in the soil. Undercharged events, with a very low ion-induced fraction, were observed more frequently in winter while no overcharged events were seen. **Paper VI** suggests that the number of particles produced through ion-induced nucleation is more or less constant (compared to the variation found for neutral nucleation) and depends on the ion pair production rate, but that neutral nucleation thrives at lower temperature and at higher vapor saturation ratio.

This can explain why higher fractions of ion-induced nucleation are observed in clean areas (low vapor concentrations) and in elevated altitudes (high ion pair production rate, Carslaw et al., 2002) and smaller fractions of ion-induced nucleation are observed in polluted areas.

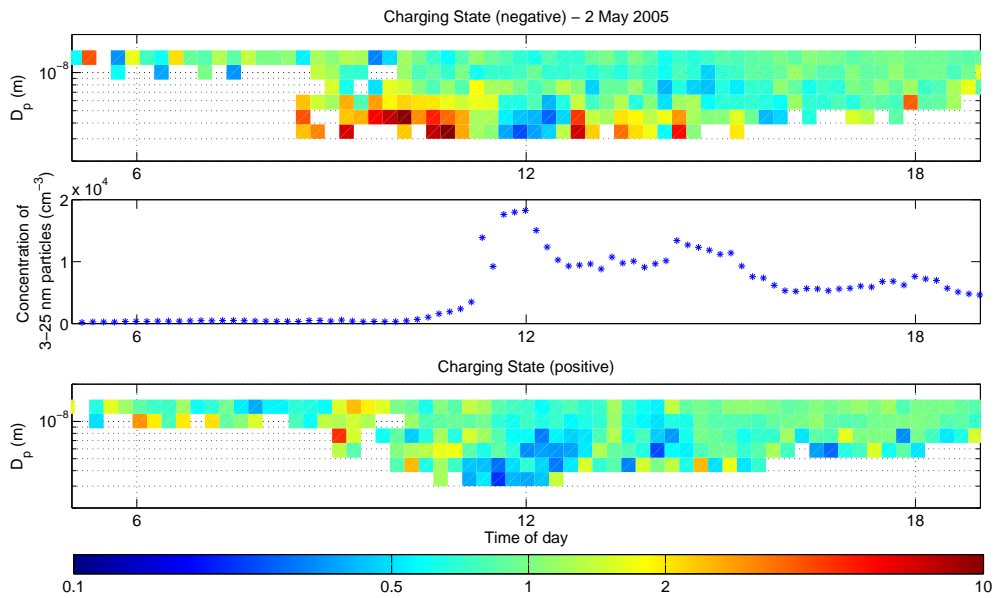


Figure 11: The charging ratio (color bar, upper and lower panels) as a function of particle diameter and time on 2 May 2005, in Hyytiälä. Red charging ratios are overcharged and blue ones are undercharged. The middle panel shows the concentration of nucleation mode particles during the event. The negative aerosol population is overcharged at the beginning and at the end of the event, while its core, and the positive aerosol population are undercharged. The concentration of particles increases at the same time as the negative aerosol population switches from overcharged to undercharged.

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

**Paper I** investigates the behavior of the charging state of a growing nucleation mode theoretically in different atmospheric conditions. After a number of simplifying assumptions, an analytical expression describing the dependence of the charging state as a function of the particle diameter is derived, based on the balance equations. Two parameters can be extracted from this analytical expression: one describing the charging state of an NPF event, and another quantifying how the aerosol population retains the memory of its charging state. This equation is used in **Papers II, IV** and **V**. In this paper, I provided the experimental basis for the development of this tool. The analytical expression was derived to describe the output of the Ion-DMPS, the data analysis of which I was responsible for.

**Paper II** describes a new instrument, the Ion-DMPS, to measure the charging state of aerosol populations. The Ion-DMPS features in all papers presented in this thesis. The calibration of the instrument as well as a 2-month sample of analyzed data was presented, using the equations derived in **Paper I**. This paper shows, for the first time based on field measurements, that ion-induced nucleation is contributing to atmospheric nucleation to a significant extent. Cases with low ion-induced participation and cases with more important ion-induced participation are presented, suggesting that the fraction of ion-induced nucleation changes from day to day, and probably also from place to place. In this paper, I performed the analysis of the Ion-DMPS data from spring 2005 and wrote a few sections, especially those related to the data analysis and its interpretation.

**Paper III** reports on the results of the second (N)AIS calibration and intercomparison workshop, where 11 ion spectrometers (5 AISs, 5 NAISs and one Airborne NAIS) were calibrated and compared to other instruments, namely a BSMA, a DMPS and an Ion-DMPS. The charged fraction of aerosol particles during an NPF event was calculated from the NAISs and from the Ion-DMPS and compared. The paper provides guidelines for analyzing (N)AIS data. In this paper, I executed some of the measurements, did most of the data analysis, and wrote most of the paper.

**Paper IV** presents one year of measurements with the Ion-DMPS, and the charging state of the aerosol population in Hyytiälä, Finland. The annual average ion-induced nucleation contribution to new particle formation is reported, and the ion-induced fraction is reported to be higher in summer. The seasonal and dynamical features of

overcharged, undercharged and steady-state charging state of new particle formation events are presented. In this paper, I analyzed the data and wrote most of the paper.

**Paper V** reports on the charging state and the ion-induced fraction of new particle formation events taking place in Helsinki, Finland. It presents a new analysis method to retrieve the charging state from Ion-DMPS data. It also introduces a new set of equations for which we do not need to assume that the concentration of small ions is the same for both polarities: polarity asymmetry. We also calculate the growth rate of new particle formation events based on the charging state, with and without assuming polarity symmetry. In this paper, I performed the measurements, and did most of the data analysis, especially the sections regarding the charging state and ion-induced nucleation. I also wrote most of the paper.

**Paper VI** investigates the atmospheric conditions and meteorological factors influencing the fraction of ion-induced nucleation participating in new particle formation events analyzing over two years of Ion-DMPS data. The new particle formation event days were divided into two groups, overcharged and undercharged, after which the characteristics of each group were investigated and compared. The ion-induced fraction was higher on warm, dry and sunny days. On days with a higher ion-induced fraction, new particle formation started earlier, less particles were nucleated and a larger dip in the small ion concentrations was observed. In this paper, I analyzed the data and wrote most of the paper.

## 7 Conclusions

The charging state and the charged fraction are proven to be useful quantities well worth measuring. Not only do they give information about the contribution of ion-induced nucleation to the particle number concentration but they can also provide insight about the dynamical features of a new particle formation event, such as the growth rate. Given the controversial nature of the role of ion-induced nucleation in the Earth's climate, it is of the utmost importance to know its contribution with accuracy, using as many methods as possible.

Several measurement techniques have been developed that enable us to measure the charging state or the charged fraction of aerosol populations. The Ion-DMPS is one of them, and was discussed in depth in this thesis. The instrument was designed with the purpose to retrieve the charging ratio as a function of the particle size and time. Its specially designed inlet system with a neutralizer that can be “on” or “off” makes it possible to have the same losses for the neutralized and ambient sample. The NAIS also allows to measure the charged fraction as a function of diameter and time, with an excellent time resolution. However, in overcharged cases, the particle operation mode, which has mostly been used so far, misestimates the charged fraction. Using the so-called alternative mode might help in that regard, and is recommended for future measurements, although this issue is still under investigation. Other techniques, such as a combination of an ion-spectrometer and a DMPS or SMPS system can also be used, although the losses can be very different from one instrument to another, and so corrections have to be made very carefully. Yet another technique, which was used in the CLOUD chamber at CERN, is a CPC-battery with a common inlet equipped with an ion precipitator. Because of the need of several CPCs, this technique can be rather costly. The use of a scanning size CPC, such as the Particle Size Magnifier (PSM, Vanhanen et al., 2011) would be more practical. Even though the loss corrections have to be done very carefully to compare one CPC to another, the ratio obtained from one individual CPC should remain the same before and after correction for losses. This technique thus has a clear advantage over a combination of independent instruments. The Ion-DMPS, however, remains the instrument of predilection to measure the charging state.

These instruments have allowed measurements in different environments, and the estimation of the ion-induced nucleation fraction. More measurements of this kind need

to be done in other environments in order to improve our understanding of nucleation and improve global climate models. Sites in high altitude, over the ocean, or in the free troposphere would be interesting places to pursue measurements of the charging state. Currently, the Ion-DMPS is probably the best instrument to measure the charging state, and similar principles should be considered for future instrumentation. Moreover, a number of theoretical tools have been developed to retrieve the fraction of ion-induced nucleation from measurements of the charging ratio as a function of the diameter. These tools have recently been improved to take into account the asymmetry between the concentration of small ions of the negative and positive polarity. The Ion-DMPS, in combination with this set of theoretically derived tools, makes for a robust analysis of the contribution of ion-induced nucleation to new particle formation.

In this thesis, instruments capable of measuring the charging state or the charged fraction of particle populations are presented (first aim of this thesis, **Paper II & III**). Theoretical tools that describe the behavior of the charging state during a new particle formation event and give us information about the fraction of ion-induced nucleation are presented and used (second aim of this thesis, **Papers I & V**). This thesis also contributes to the measurements and analysis of the charging state in two different environments: remote and urban (third aim of this thesis, **Papers IV & V**). In the boundary layer, where the Ion-DMPS was measuring, ion-induced nucleation contributes to a minor part of the observed nucleation. The median contribution of ion-induced nucleation at 2 nm during one year of measurements in the rural site of Hyttiälä was around 6.4%. In the urban site of Helsinki, the median contribution at 2 nm for a bit more than a year of measurements was around 0.8%. Ion-induced nucleation can generate a big fraction of the nucleated particles when it is difficult for neutral nucleation to occur. This behavior can even be observed within an NPF event (fifth aim of this thesis, presented in this synthesis, Figure 11): the fraction of ion-induced nucleation is rather high at the beginning of the event, but when neutral nucleation becomes more important, the number of new particles increases dramatically. In this thesis, the factors influencing the fraction of ion-induced nucleation are investigated and presented (fourth aim of this thesis, **Papers V & VI**): temperature, sulfuric acid and water vapor saturation ratio, the concentration of small ions, sunlight, external radiation (from ionizing gamma rays), particle growth rates, formation rates, condensation sink, environment, etc. were factors studied. Neutral nucleation seems to produce more nucleated particles than ion-induced nucleation in all environments where the fraction of ion-induced nucleation has been measured. However, the frac-

tion of ion-induced nucleation is larger in cleaner environments (e.g. Hyytiälä), where condensing vapors are not abundant enough for neutral nucleation to take place. The fraction of ion-induced nucleation thus varies from place to place, from day to day and also during an NPF event. Low temperatures lead to increased vapor saturation ratios and favor neutral nucleation in the boundary layer. Ion-induced nucleation requires smaller saturation ratios than neutral nucleation, but is limited by the number of ion seeds in the atmosphere.

Finally, this thesis presents robust evidence that, at least in the boundary layer, ion-induced nucleation plays a minor role in NPF. It also presents a reliable way of measuring and analyzing the charging state to retrieve the fraction of ion-induced nucleation, which could be used in other environments thought to be more favorable to ion-induced nucleation. A good example of such an environment would be the free troposphere, where the ion pair production rate is higher. Hopefully, such measurements will be done and the results will be used in global climate models to better understand the role of ions in the Earth's climate.

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