

REPORT SERIES IN AEROSOL SCIENCE

N:o 123 (2011)

HOW THE DEVELOPMENT OF CONDENSATION PARTICLE
COUNTERS IS REFORMING OUR VIEW ON
ATMOSPHERIC 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 May 13th, 2011, at 12 o'clock noon.*

Helsinki 2011

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ISBN 978-952-5822-43-4 (printed version)
ISSN 0784-3496
Helsinki 2011
Unigrafia Oy

ISBN 978-952-5822-44-1 (PDF version)
<http://ethesis.helsinki.fi/>
Helsinki 2011
Helsingin yliopiston verkkojulkaisut

Acknowledgements

The research for this thesis was carried out at the Department of Physics of the University of Helsinki. I express my gratitude to the head of the department, Prof. Juhani Keinonen, for providing me the working facilities. I'm grateful for Prof. Markku Kulmala, head of the Division of Atmospheric Sciences, who had the scientific vision and intuition that led to this thesis. I thank Prof. Kulmala for creating a hectic, inspiring and international research environment.

I thank Doc. Annele Virtanen and Prof. Markus Olin for reviewing and Dr. Matthew McGrath for proofreading this thesis. Maj and Tor Nessling foundation is acknowledged for funding a part of the research. I'm grateful to Dr. Ilona Riipinen for leading the Nessling project and mentoring me in the beginning of my doctoral studies.

I warmly thank the leader of the aerosol measurement group, Dr. Tuukka Petäjä for subtle but invaluable guidance and encouragement, and for always trying to make the world (or at least the Division) a better place.

This thesis, as it is, could not exist without Dr. Mikko Sipilä, who is truly *the king of the lab*. Mikko shared with me his enthusiasm in the search of neutral clusters, and was kind enough to leave me a lot of strange data and cryptic measurement diaries.

I thank Joonas Vanhanen and Jyri Mikkilä for fluent and fruitful collaboration. I'm greatly indebted also to Hanna Manninen, who always found the time to help me with various practical issues, as well as to share views on chick-lit and romantic comedies. Let's bring some girl power to the aerosol labs!

My career in atmospheric science started at Värriö research station, where I spent two summers carrying 12kg batteries back and forth in the forest to keep the measurements going, climbing to the top of distant fells to measure photosynthesis and fearing for thunderstorms that would kill the SMEAR-station. I'm grateful to the staff in Värriö and Hyytiälä, who taught me the basics of doing field measurements. All the numerous people participating in different measurement campaigns and field courses together with me would also deserve to be mentioned.

I warmly thank all my marvelous co-workers at the Division of Atmospheric Sciences, many of you I consider not merely as colleagues, but friends. Especially Maija, Stéphanie, Taina, Hanna, Ale, Sigi, Tuomo *et al.* have made my Friday afternoons mellifluous!

How the development of condensation particle counters is reforming our view on atmospheric nucleation

Katrianne Lehtipalo

University of Helsinki, 2011

Abstract

Aerosol particles deteriorate air quality, atmospheric visibility and our health. They affect the Earth's climate by absorbing and scattering sunlight, forming clouds, and also via several feed-back mechanisms. The net effect on the radiative balance is negative, *i.e.* cooling, which means that particles counteract the effect of greenhouse gases. However, particles are one of the poorly known pieces in the climate puzzle.

Some of the airborne particles are natural, some anthropogenic; some enter the atmosphere in particle form, while others form by gas-to-particle conversion. Unless the sources and dynamical processes shaping the particle population are quantified, they cannot be incorporated into climate models. The molecular level understanding of new particle formation is still inadequate, mainly due to the lack of suitable measurement techniques to detect the smallest particles and their precursors.

This thesis has contributed to our ability to measure newly formed particles. Three new condensation particle counter applications for measuring the concentration of nano-particles were developed. The suitability of the methods for detecting both charged and electrically neutral particles and molecular clusters as small as 1 nm in diameter was thoroughly tested both in laboratory and field conditions. It was shown that condensation particle counting has reached the size scale of individual molecules, and besides measuring the concentration they can be used for getting size information. In addition to atmospheric research, the particle counters could have various applications in other fields, especially in nanotechnology.

Using the new instruments, the first continuous time series of neutral sub-3 nm particle concentrations were measured at two field sites, which represent two different kinds of environments: the boreal forest and the Atlantic coastline, both of which are known to be hot-spots for new particle formation. The contribution of ions to the total concentrations in this size range was estimated, and it could be concluded that the fraction of ions was usually minor, especially in boreal forest conditions. Since the ionization rate is connected to the amount of cosmic rays entering the atmosphere, the relative contribution of neutral to charged nucleation mechanisms extends beyond academic interest, and links the research directly to current climate debate.

Keywords: atmospheric aerosols, clusters, nucleation, condensation particle counters

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List of publications

This thesis consists of an introductory part, followed by six research articles. In the introductory part, the articles are cited by their roman numerals. Papers I, IV and V are reprinted under the Creative Commons License.

I Sipilä, M., **Lehtipalo, K.**, Kulmala, M., Petäjä, T., Junninen, H., Aalto, P. P., Manninen, H.E., Vartiainen, E., Riipinen, I., Kyrö, E.-M., Curtius, J., Kürten, A., Borrmann, S., and O'Dowd, C. D.: Applicability of condensation particle counters to measure atmospheric clusters. *Atmos. Chem. Phys.*, 8, 4049-4060, 2008.

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1 Introduction

Air consists of gas molecules, at atmospheric pressure *c.* 2.5×10^{19} of them in one cubic centimeter. Additionally, there are always liquid or solid particles in the air, their concentrations ranging from a few up to millions per cubic centimeter. Thus, air is perhaps the most typical example of an aerosol, which is by definition a mixture of particles suspended in a carrier gas. The size of aerosol particles can vary between about a nanometer and hundreds of micrometers. The upper size limit is determined by the deposition velocity, *i.e.* the competition between gravity and drag force, and the lowest size is limited to the molecules that the particles are composed of.

The size range between molecules and particles poses a challenge for both theory and experiments. Approaching the nano-realm is like falling through the rabbit hole to Wonderland, where objects can be too small and too large at the same time, and everyday logic seems to fail. Even the smallest aerosol particles are far too complex to be treated by means of quantum mechanics. However, the theories for macroscopic particles start to fail on the molecular limit, and the thermodynamic properties of very small particles are poorly known, or badly defined. Even such a simple concept as the diameter is ambiguous at small sizes. Experimentalists can use mass spectrometers for measuring gas phase molecules and ions, but most commonly used particle counters only work for aerosol particles larger than about 3 nm. Subsequently, there is a gap of knowledge of sub-3 nm particles, just at the size range that is critical for nucleation.

Nucleation is a first-order phase transition, *i.e.* the creation of a new phase, in this context a liquid or solid aerosol particle from precursor gases. The atmospheric new particle formation process starts by nucleation followed by condensational growth of the newly formed particles. The particles formed in the atmosphere by gas-to-particle conversion are called secondary particles, whereas primary particles, *e.g.* volcanic dust, enter the atmosphere in particulate phase. It is energetically more favorable to form a particle on a pre-existing surface, which is called heterogeneous nucleation. For example a cloud droplet is always formed around an aerosol particle. Particles that can serve as seeds for cloud droplets are called cloud condensation nuclei (CCN).

Analogously molecules, clusters or nanometer-sized particles that can serve as condensation nuclei in particle counters are called nano-CN.

The terminology around the sub-3 nm atmospheric objects is ambiguous. The concept of nano-CN was first introduced in 2009, and appears in literature since 2010 (Zhao *et al.*, 2010; **V**; McMurry *et al.*, 2011; **VI**). In earlier studies, the sub-3 nm particles were often called simply clusters (Kulmala *et al.*, 2007a; **I**; **II**; **IV**). The size range of vapor molecules, clusters (of several molecules) and tiny aerosol particles is overlapping, and it is usually not possible to distinguish between them. In the following, I will mainly address the sub-3 nm objects detected by condensation technique as *nano-CN*, while the larger condensation nuclei are *particles*. The charged molecules and clusters measured with ion spectrometers are called *small ions* (sometimes referred to as cluster ions in the literature). The actual molecular clusters detected and identified by mass spectrometry are called *clusters*. When referring to literature, I will use the term the authors have chosen. However, in some places the terms nano-CN, cluster and nano-particle are used interchangeably.

Once the newly formed particles reach sizes where they can serve as CCN, they start to affect the Earth's climate by modifying cloud properties and lifetime. It has been shown by model studies that new particle formation adds to the CCN budget significantly on both regional and global scale (Spracklen *et al.*, 2006; Merikanto *et al.*, 2010; Sihto *et al.*, 2010). Additionally, particles can directly scatter and absorb solar radiation, which can be observed as deterioration of visibility when the aerosol loading is high. Adding new particle formation into climate models requires a conceptual understanding of the process, as well as both qualitative and quantitative knowledge of the precursors and other parameters affecting the process. Aerosols are the dark horse in the current climate debate, since they are relatively short-lived, extremely variable, and involved in several feed-back mechanisms (Arneeth *et al.*, 2009; Carslaw *et al.*, 2010).

In addition to their climatic effects, aerosols affect human health. A variable amount of particles enter our body every time we breathe in. Inhaled particles can lead to adverse acute and chronic health effects, a striking example being asbestosis. On a population level the exposure to anthropogenic particle

pollution have been estimated to cause an 8.6 month decrease in the life expectancy of Europeans (Amann *et al.*, 2005). The health effects of nanoparticles in particular are still very poorly known. It seems that the particle number, rather than total mass, determines the health effects (Peters *et al.*, 1997), which creates a need to be able to measure even the smallest particles.

Not all aerosols are harmful. The use of nano-materials is expanding quickly, they can already be found in various kinds of consumer products from sun screens to ties and self-cleaning windows. In many industrial applications, the functional material is in aerosol form at least during some stage of the process. Condensation particle counters could be of use in optimizing these processes and protecting workers and consumers from exposure to potentially harmful particles.

The main objectives of this PhD-thesis are to

- 1) develop, evaluate and compare methods to measure particles in the sub-3 nm size range (**papers I-VI**)
- 2) determine properties and behavior of the atmospheric nano-CN (**papers IV-VI**)
- 3) add to the understanding of new particle formation processes (**papers IV-VI**)

Thus the main goal, in one sentence, is to bridge the gap between measurements and knowledge on individual molecules and the smallest aerosol particles.

2 New particle formation

2.1 Nucleation

Nucleation is the start of a phase-transition, in which the new phase is created as tiny clusters in the surrounding medium. In atmospheric context, nucleation describes the formation of a new solid or liquid aerosol particle from precursor vapors. Nucleation, followed by condensational growth, also happens inside a condensation particle counter.

The lion's share of air molecules in the atmosphere are in the form of single monomers. Clusters of several molecules constantly form by collisions, but most of them fall apart very quickly. If the air gets saturated with a specific gas, the number of collisions between the molecules increases, and it starts to condense on surfaces, such as pre-existing aerosol particles. The aptitude of a specific gas to condense is described by its saturation vapor pressure, which is a strong function of temperature, and the gas species that are condensable are called vapors.

Lacking suitable surfaces, the vapor can become supersaturated and larger and larger clusters form until the vapor starts to nucleate. Nucleation has occurred when a cluster gets large enough, that it is energetically favorable for it to continue growing to a particle. The free energy barrier that is usually related to nucleation is caused by the need to create a surface for the new phase. A cluster that is just on the verge of becoming a particle (*i.e.* its size corresponds to a maximum in the free energy diagram) is called a critical cluster. It should be noted that the criticalness of a cluster depends on its surroundings.

For small particles the curvature of the surface is very high, and the molecules are more loosely bound than on a flat surface. The saturation ratio needed for keeping the particle from evaporating can be calculated from the Kelvin equation

$$S = \exp\left(\frac{4\sigma M}{RT\rho d_p}\right) \quad [1]$$

where S is the saturation ratio, ρ the density, σ the surface tension, M the molar mass, R the molar gas constant, T the temperature, and d_p the particle diameter. On the other hand, the Kelvin equation can be used to give the critical size at a certain saturation ratio.

When nucleation happens heterogeneously on the surface of *e.g.* an aerosol particle, the amount of new surface that needs to be created is smaller and thus the free energy barrier lower than in the case of homogenous nucleation. If the seed-particle is electrically charged, the process is called ion-induced nucleation. The charge lowers the nucleation barrier further, since it attracts polar vapor molecules. Another special case of heterogeneous nucleation is the Köhler phenomenon, which is a combination of the before mentioned Kelvin phenomenon and Raoult's law, which describes how the saturation vapor pressure depends on the mole fraction of the solute and the solvent. Therefore, if the seed particle is soluble to the nucleating vapor, the supersaturation needed for activating the particle for growth is lower. In connection to new particle formation the theory is sometimes called nano-Köhler (Kulmala *et al.*, 2004b).

Nucleation can occur when the cluster production and growth rates are high enough due to increased supersaturation of the precursor(s), or alternatively when the cluster evaporation rate is lowered due to lower temperature or a stabilizing compound. If the cluster evaporation rate is negligible compared to the collision rate of vapor molecules, there is no energy barrier for nucleation, since it is only limited by the collision rate. Formation of particles in this case is called kinetic (or barrierless) nucleation (*e.g.* McMurry 1980; Laakso *et al.*, 2004).

2.2 Current view on atmospheric new particle formation

Atmospheric new particle formation starts either by thermodynamic or kinetic nucleation to form the initial clusters, or by activation of pre-existing charged and/or neutral clusters. After the particles are formed, they need to grow by condensation before they are scavenged, in order to become observable particles. While different nucleation mechanisms are conceptually

understood (although not to detail) their relative contribution to atmospheric new particle formation is under heated debate. It is possible that different mechanisms prevail in different kind of environments (or in the same environment but different conditions), and several types of nucleation might happen simultaneously or successively.

Several compounds can be involved in the new particle formation process. Nucleation is likely to be initiated by vapors that can form relatively stable clusters, like sulphuric acid (Ehn *et al.*, 2010, Zhao *et al.*, 2010). However, once the initial clusters are formed, different compounds might get involved in the process *e.g.* as stabilizing agents in the clusters or later as condensing vapors. Also chemical reactions like oxidation, formation of salts or polymerization are possible steps in the process (Kalberer *et al.*, 2004; Smith *et al.*, 2010).

It is widely agreed that sulphuric acid is a key compound in atmospheric new particle formation (*e.g.* Weber *et al.*, 1997; Hanson & Eisele, 2002; Sihto *et al.*, 2006; Kuang *et al.*, 2008; Petäjä *et al.*, 2009; Nieminen *et al.*, 2009, Sipilä *et al.*, 2010, Ehn *et al.*, 2010). However, there are lot of studies showing that sulphuric acid and water alone cannot explain observations of new particle formation in the troposphere, and some other low-volatile vapors, like organics are needed in the process (*e.g.* Weber *et al.*, 1996, Kulmala *et al.*, 1998; Fiedler *et al.*, 2005; Boy *et al.*, 2005; Wehner *et al.*, 2005). Both quantum chemical calculations and experimental data shows that bases like ammonia or amines might be needed for stabilizing the sulphuric acid clusters (*e.g.* Hanson & Eisele, 2002; Torpo *et al.*, 2007; Kurtén *et al.*, 2008, Ehn *et al.*, 2010). Many laboratory experiments claiming binary sulphuric acid-water nucleation might also have had contamination of undetectable amounts of ammonia and/or organic vapors.

Volatile organic compounds (VOCs) have also been connected to new particle formation (*e.g.* Mentel *et al.*, 2009). VOCs are a large group of different compounds emitted both by vegetation and anthropogenic sources. Some of the VOCs get oxidized in the atmosphere creating products that are less volatile, and can thus condense to particle phase. It is not clear in which part of the process organics start to play a role. Some claim that organics affect only the growth, while some that organics already affect at the

formation step (Metzger *et al.*, 2010; Paasonen *et al.*, 2010). As the particles grow, the supersaturation needed for condensation decreases as a result of the Kelvin equation, and even vapors with higher saturation vapor pressure can start to condense. However, discerning nucleation from initial growth is hard, especially since most of the measurements until now have started at 3 nm, or even at larger sizes, when growth has already taken place. Both indirect and direct measurements of the chemical composition indicate the presence of organic compounds already in ultrafine particles (O'Dowd *et al.*, 2002a; Smith *et al.*, 2008; Riipinen *et al.*, 2009).

Marine environments are a special case regarding new particle formation. On coastal sites, like Mace Head in Ireland, nucleation is strongly connected to the biological emissions of iodine-containing compounds that are processed by photochemical reactions (O'Dowd *et al.*, 2002b; c). Several laboratory experiments have demonstrated particle formation from the oxidation products of these iodine-compounds (Hoffmann *et al.*, 2001; Jimenez *et al.*, 2003).

New particle formation can also be assisted by atmospheric small ions. So called ion-mediated particle formation pathways, which include both ion-induced nucleation and nucleation on neutral clusters formed by recombination of ions, are likely to be important when the temperature and pre-existing aerosol surface area are low, but ion and sulphuric acid concentrations high – for example in the upper troposphere (Curtius *et al.*, 2006; Yu, 2010). Since the amount of electric charges, and thus small ions in the atmosphere, is limited by the ionization rate, the relative role of ion-induced nucleation seems to decrease with increasing total particle formation rate (Gagné *et al.*, 2010; Manninen *et al.*, 2010). On average, the ion-induced fraction in the boundary layer seems to be mostly around or below 10% (Iida *et al.*, 2006; Gagné *et al.*, 2008; Manninen *et al.*, 2010; Kulmala *et al.*, 2010), even though some studies give higher estimations (Yu & Turco, 2008; Yu *et al.*, 2008). However, ions might be more important in the beginning of particle formation (Laakso *et al.*, 2007a;b).

3 Experimental methods for studying nano-particles

A variety of measurement methods based on different physical or chemical phenomena are needed for getting a complete picture of the atmospheric aerosol population. Measurements of newly formed particles or nano-CN are especially tricky due to their small size and minuscule mass. Nano-particles are extremely diffusive, meaning that a large fraction of them is always lost in the measurement system, and they do not easily take electric charge. There are basically two different techniques available for measuring nano-particles: condensation particle counting (3.1), which is the focal point of this thesis, or electrostatic methods such as ion spectrometers (3.2).

A few words on the subject of particle size are in order. It is customary in the aerosol community to express the size of particles by their diameter. However, diameter is not well defined for non-spherical particles, or when approaching molecular sizes. Since the size is usually determined indirectly, there are different definitions of diameter based on the method. The one used in this thesis, unless explicitly stated otherwise, is the electrical mobility equivalent diameter, since all of the instrument calibration methods are based on selecting the particle size by their mobility in an electric field. Another commonly used diameter is the mass diameter, which is closer to the actual geometrical diameter of the particle (Tammiet, 1995). The difference between the mass and mobility diameter in sizes below 3 nm is about 0.3 nm, which is approximately the size of an air molecule. Recently the mobility to diameter conversions has been studied experimentally by Ku & Fernandez de la Mora (2009) and Ehn *et al.* (2011).

3.1 Condensation particle counters

In the following, I will give a short summary of how the evolution of CPCs has affected our knowledge on new particle formation and what are the challenges when measuring nano-particles. The history of CPCs has been reviewed in more detail *e.g.* by McMurry (2000). Sections 3.1.1-3.1.3

introduce the three CPC applications developed and used during this research.

The working principle of a condensation particle counter (CPC; also previously often called condensation nuclei counter) is simple: the aerosol is exposed to a supersaturated vapor, which condenses on the particles making them large enough to be observed optically. The supersaturation is primarily created by three different methods, which serve as a classification of different CPC types: a) adiabatic expansion, b) thermal diffusion in a laminar flow or c) mixing two flows with different temperatures. All three different types of CPCs have been used in this thesis.

The first instruments based on water vapor condensation on the surface of aerosol particles were developed already in the late 19th century individually by Coulier and Aitken. Aitken was also the first to understand that particles can be formed as a result of photochemical processes in the atmosphere (Aitken, 1911).

Practically all early CPCs were expansion type instruments and used water as the condensing vapor. Modern condensation particle counters using different working fluids and usually single-particle counting optics have been developed since 1970s, and are now widely used in aerosol science. The continuous flow rate and fast response time made them suitable for field studies, and connectable to for example size spectrometers, such as the DMPS/SMPS (Differential/Scanning Mobility Particle Sizer).

Liu and Kim (1977) were the first to notice, that the detection efficiency of a CPC drops when approaching smaller sizes, even though ideally the counting efficiency curve would be a step function from 0 to 1 at the Kelvin diameter. The lower size limit of a CPC is described by its cut-off size. The cut-off size is defined as the lowest particle diameter at which the instrument detects at least half of the particles (Fig. 1). The cut-off diameter and the steepness of the cut-off curve are determined both by the activation probability of particles (which in turn depends both on the created supersaturation profile in the instrument and the physico-chemical properties of the particles), and by diffusion losses of particles inside the instrument.

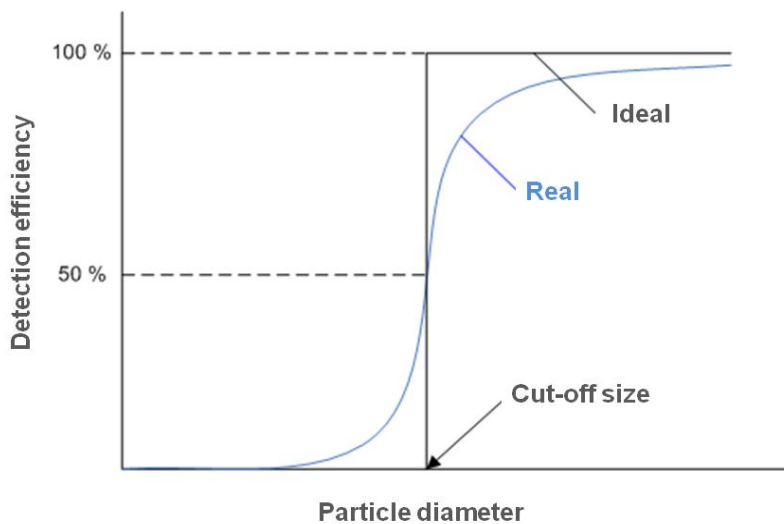


Figure 1. *The definition of the cut-off size of a condensation particle counter.*

The first CPCs designed specifically for ultrafine particles were developed in 1990s (Stolzenburg and McMurry, 1991), and are thus called ultrafine-CPCs. Since then, hundreds of articles have revealed, that new particle formation is a common phenomenon that happens almost everywhere in the troposphere (Kulmala *et al.*, 2004a). However, even at 3 nm, the measurements still did not reach the sizes where nucleation actually happens. Sipilä *et al.* (2010) showed that the usage of insufficient counters can even lead to misinterpretation of the data describing nucleation processes, or at least explains the discrepancy between field data and most previous laboratory experiments.

When this thesis work began in 2007, there were still no commercially available CPCs with cut-off sizes lower than 3 nm. A few attempts of measuring smaller particles with custom-made CPCs had been reported (Seto *et al.*, 1997; Gamero-Castaño & Fernandez de la Mora, 2000; Sgro & Fernandez de la Mora 2004; Kulmala *et al.*, 2007a). However, there was no proof of their suitability to continuous long-term field measurements.

There are two means of lowering the cut-off size of a CPC: minimizing the diffusion losses by different instrumental geometry or flow arrangements, or

increasing the supersaturation. However, if the supersaturation is too high, homogenous nucleation of the working fluid occurs leading to false counts. In this thesis, this problem has been solved with three different methods: measuring the homogenous nucleation background and subtracting it from the signal (**I**), separating the homogenous mode from activated particles by pulse-height analysis (**I**, **II**, **IV-VI**), or selection of suitable working fluid (**III**). Kulmala *et al.* (2007b) and Fernandez de la Mora (2011) reasoned that seed-particles well below the Kelvin diameter should theoretically be activated before the start of homogenous nucleation of the CPC working fluid, which is also verified experimentally (Gamero-Castaño & Fernandez de la Mora 2000; Winkler *et al.*, 2008a; b; **I**).

An important step in the recent evolution of CPCs was the work by Iida *et al.* (2009), who evaluated hundreds of different working fluids for CPCs. The selection of a working fluid with high surface tension, but low enough saturation vapor pressure seemed to enable achieving high supersaturations without considerable homogenous nucleation. Based on that study, the fluid chosen by several different research groups seem to be diethylene glycol (DEG; **III**, Jiang *et al.*, 2011a). However, all these DEG-based instruments need a second stage, a growth booster, to reach optically detectable sizes. Later, Fernandez de la Mora (2011) came to the conclusion that water in low temperatures could be even better at activating small neutral particles, even down to 0.6 nm.

The charge and chemical composition of nano-particles affect their activation probability in a CPC due to reasons explained in chapter 2.1 in connection to heterogeneous nucleation, since in principle a CPC is working as a nucleation chamber for the sampled particles. Thus the cut-off size of a CPC for material soluble in its working liquid is lower than for insoluble particles (*e.g.* Ankilov, *et al.*, 2002; Hering *et al.*, 2005; Petäjä *et al.*, 2006; Kulmala *et al.*, 2007b). According to Winkler *et al.* (2008a) negative ions are activated at smaller sizes than positive ones, and both polarities before neutral particles.

A condensation particle counter, by default, measures the total number concentration of particles above its cut-off size. The difference between the concentration readings of two CPCs with different cut-off sizes - or even better, one CPC in which the cut-off size can be quickly adjusted - can give

information about the particle concentration in the small size range between the cut-off sizes (Gamero-Castaño & Fernandez de la Mora, 2000, **III**). By cleverly exploiting the inherent properties of the condensation technique, CPCs can also be used to gain more information about the particles. For example, one can obtain indirect information of the chemical composition of nano-particles by comparing two CPCs with the same cut-off size, but different working fluid (Kulmala *et al.*, 2007b; Riipinen *et al.*, 2009), or by pulse-height analysis (O'Dowd *et al.*, 2002a; 2004).

3.1.1 Expansion CPC

In an expansion CPC the supersaturation needed for particle growth is achieved by letting the aerosol expand adiabatically. The particle concentration is then calculated from the light intensity scattered by the growing particle population, which is, according to the Mie theory, directly proportional to particle concentration and size (see *e.g.* Drake & Gordon, 1984; Wagner, 1985). The expansion CPC (E-CPC) in **paper I** is a modified version of the one described in Kürten *et al.* (2005). Both butanol and water was used as the condensing liquid in E-CPC. In laboratory calibrations (see chapter 3.3.1) the detection efficiency for butanol was observed to be slightly higher than for water.

At expansion ratios around 1.7 (for butanol) the concentration measured with the E-CPC was comparable to ultrafine CPC (Kürten *et al.*, 2005, **I**). When increasing the expansion ratio (and therefore the supersaturation), the concentration rose steadily, as smaller and smaller particles were activated. Finally, at expansion ratio around 2.3 homogenous nucleation of the condensing liquid occurred, leading to a sharp increase in the observed concentration. This was also demonstrated in laboratory calibrations (Fig. 2).

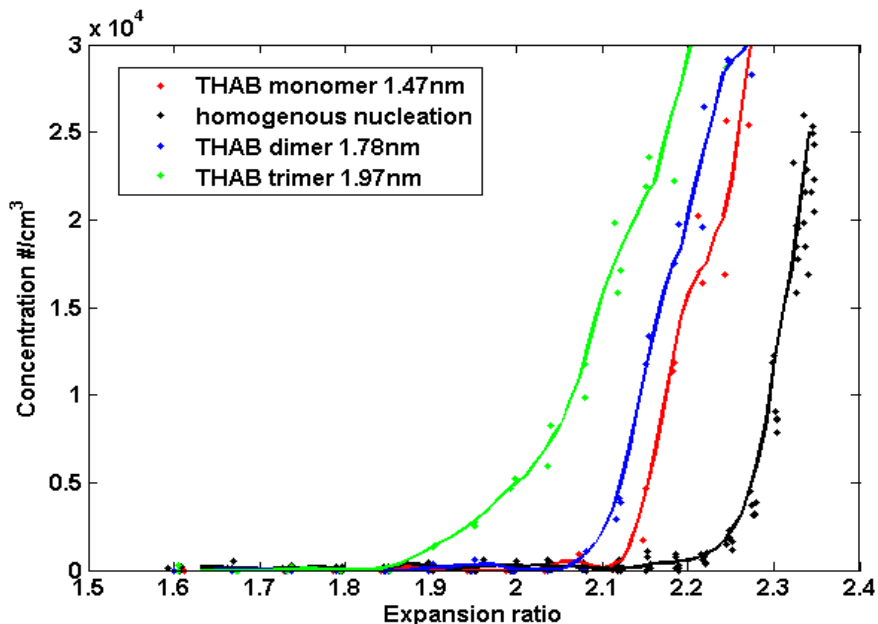


Figure 2. Calibration of the E-CPC using THAB-clusters. Butanol was used as the condensing liquid. Solid lines are moving averages over the expansion scans. Black dots were measured through a filter, describing the homogenous nucleation inside the instrument.

In the field campaign, the expansion ratio was slowly scanned until homogenous nucleation of the condensing liquid started. Every other scan was performed through a diffusion tube, which removes most of sub-3 nm particles (50 % penetration efficiency at 3.5 nm), but leaves the signal from larger particles and homogenous nucleation. A diffusion tube was used instead of a filter, since the presence of larger particles affect the start of the homogenous nucleation (Winkler *et al.*, 2008b, I). An estimation for the concentration of sub-3 nm particles was obtained from the difference between the scans with and without the diffusion tube.

As shown in figure 4 in **paper I**, ions formed inside a ^{241}Am neutralizer (mostly below 1.5 nm in size) were activated clearly before their neutral recombination products, which demonstrates the effect of charge on the activation probability. The nano-CN in field measurements were activated at

approximately the same expansion ratio as the recombination products, which supports the assumption that most of them are neutral (**I**). However, in the atmospheric measurements, no clear step between the activation of small ions clusters and neutral nano-CN was observed in the expansion ratio scans, as predicted by Kulmala *et al.*, (2007b). This is probably because of the polydispersity of the nano-CN, and the relatively low ions concentrations and because the detection efficiency of small particles increases smoothly as a function of expansion ratio.

While the expansion scan method clearly demonstrated the existence of neutral sub-3 nm particles, the concentrations obtained were largely qualitative. The time resolution of one measurement point (a scan with and without a diffusion tube) was about half-an-hour, during which the concentration might change significantly. The expansion-CPC can, however, be a powerful tool for heterogenous nucleation experiments in the laboratory, as shown especially by the Size Analyzing Nuclei Counter in Vienna (*e.g.* Wagner *et al.*, 2003; Winkler *et al.*, 2008a;b; 2011).

3.1.2 Pulse-Height CPC

The pulse height analysis technique (*e.g.* Saros *et al.*, 1996; Weber *et al.*, 1996) relies on detecting the intensity of light scattered by particles after their condensational growth in the CPC. For white light, the intensity is directly proportional to the scattering cross section of the particle, and thus to its diameter. Due to a supersaturation gradient inside the condenser, particles are activated at different axial positions depending on their size, and have different amount of time to grow before detection. The smaller the particle, the later it will be activated leading to smaller final droplet sizes. The pulse-height CPC is sensitive to size only in sizes below about 15 nm (Saros *et al.*, 1996), since all larger particles activate almost instantly leading to equal sized final droplet and their size information is lost in the growth process.

The pulse-height analysis technique has previously been used for detecting and sizing ultrafine (about 3-10 nm) particles (Weber *et al.*, 1995; 1996) and for getting information of the composition of nano-particles (O'Dowd *et al.*,

2002a). Papers in this thesis (**I**, **II**, **IV**, **V**, **VI**) are to our knowledge the first ones where pulse-height analysis has been used to separate between homogenous nucleation and activation of nano-CN, and measure the particle concentration and size below 3 nm.

The pulse height CPC (PH-CPC) used in this study comprises a TSI-3025A ultrafine CPC with modified optics (Dick *et al.*, 2000) and a multichannel analyzer. For increasing the detection efficiency of small particles, the supersaturation inside the condenser was increased from nominal until homogenous nucleation appeared, and the flow rate through the inlet capillary was increased. Figure 2 in **paper II** shows how the 1.3 nm calibration ions were clearly distinguishable from the mode formed by homogenous nucleation. In the field or during nucleation experiments, however, the signal from the nano-CN was partly overlapping with the homogenous mode (Fig. 5 in **VI**), which complicates the data analysis. During field measurements, we therefore measured the homogenous nucleation background using a diffusion tube on every second measurement cycle, and subtracted it from the data. Most of time we also applied an ion trap in front of the PH-CPC inlet for filtering charged particles and leaving only the signal of neutral particles.

The detection of small particles with pulse-height CPC is affected by the concentration of larger particles, because of a ‘dead time’ in the multichannel analyzer and because vapor consumption by the growing droplets affects the achieved supersaturation (**II**). When the background aerosol concentration was higher than about 4000-5000 cm⁻³, the homogenous nucleation of butanol was almost completely suppressed, and the detection efficiency and pulse-height for the smallest particles decreased. Thus data during strong nucleation events or pollution episodes was not considered quantitatively reliable, and was usually excluded from further analysis.

An inversion method was developed based on laboratory calibrations for retrieving the real size distribution of ~1.3-5 nm particles from the pulse-height data (**II**). The inversion takes into account the size-dependent detection efficiency of the particles. However, it should be kept in mind that the inversion is based on measurements of insoluble positive ions, whereas the atmospheric nano-CN can consist of a variety of neutral and charges

particles with different compositions. The most important uncertainties associated with the PH-CPC method (sensitivity to background aerosol concentration, calibration using ions instead of neutral particles) both tend to lower the detection efficiency, leading to underestimation of the concentration and size of particles. However the effect of composition, in particular, is difficult to quantify (Hanson *et al.*, 2002).

3.1.3 Particle Size Magnifier

In comparison workshops of different CPCs, mixing-type instruments have been reported to show very low cut-off sizes (Bartz *et al.*, 1985; Ankilov *et al.*, 2002). The work by Fernandez de la Mora and his group especially have shown the superiority of the mixing-type instruments in detecting small particles (*e.g.* Seto *et al.*, 1997; Gamero-Castaño & Fernandez de la Mora 2000). As a bonus, the saturation ratio can be changed rapidly and accurately by changing the mixing ratio of the two flow rates (Gamero-Castaño & Fernandez de la Mora, 2000; 2002; **III**).

The particle size magnifier (PSM), developed in **paper III**, is basically a mixing-type CPC without the optics part, using diethylene glycol (DEG) as the condensing liquid. The aerosol is turbulently mixed with air saturated with DEG, therefore creating a supersaturation high enough to activate even 1 nm ions (**III**), the cut-off size being about 1.5 nm. DEG can only grow the particles to about 90 nm (**III**), so they need to be grown further with *e.g.* water or alcohol before optical counting. The second stage growth and optical counting can be done using any kind of CPC. In **paper III**, the prototype version of the PSM was compared to the first commercially available instrument PSM A09 (manufactured by Airmodus Oy). Contrary to many earlier mixing-type CPCs, the stability of the PSM is good, and thus the instrument was found suitable for long-term field studies.

The PSM can be used in scanning mode, in which the mixing ratio of the saturator and inlet flow is continuously altered, changing the supersaturation and thus the cut-off size. Figure 6 in **paper III** shows the activation curves for different sized particles as a function of mixing ratio. When looking that

in a different way – the selected particle size as a function of the mixing ratio at which the activated fraction is 50% (Fig. 3), one will see that between 1 and 2 nm the activation diameter is almost linear function of the mixing ratio. Therefore information about the size distribution of sub-2 nm particles can be obtained, assuming that the sampled particles activate as the calibration ions.

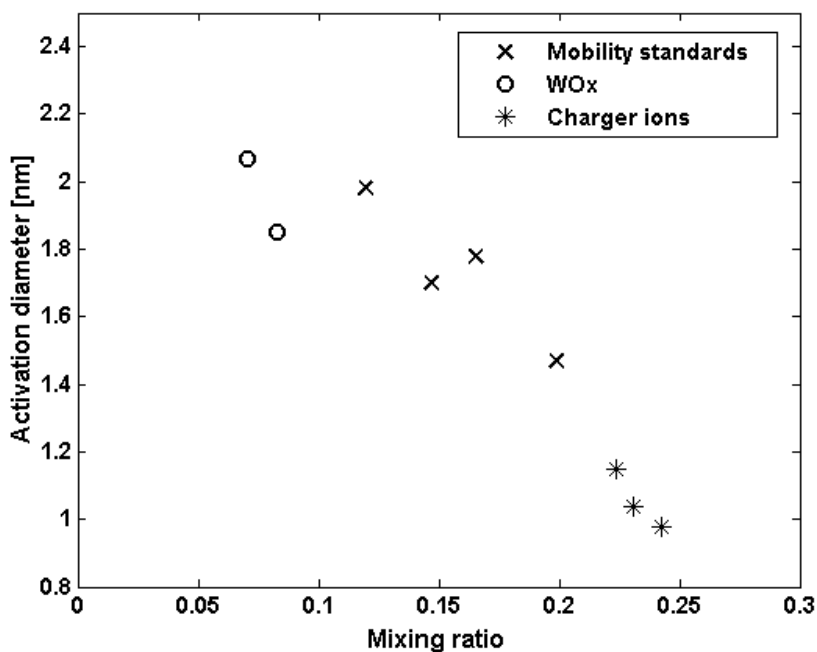


Figure 3. The mixing ratio (saturator flow / total flow) at which different sized calibration ions are activated in the PSM.

The PSM has been so far used for field measurements in Hyytiälä (III) and Mace Head, in Jülich plant chamber experiments (Dal Maso *et al.*, 2010), in the CLOUD nucleation chamber experiments at CERN (Duplissy *et al.*, 2010), and in laminar flow tube experiments in Leipzig (Sipilä *et al.*, 2010; Berndt *et al.*, 2010) and the Finnish Meteorological Institute (FMI, Brus *et al.*, 2010).

3.2 Ion spectrometers

Even the tiniest particles can be easily handled and detected if they happen to possess an electric charge (Flagan, 1998). Ion spectrometry has therefore been used for more than a century for aerosol research (*e.g.* Hirsikko *et al.*, 2011 and references therein). Ion spectrometers are instruments that use the electric charge of particles for measuring their size distribution. The size selection of the ions is usually done based on their mobility in an electric field, and the concentration can be retrieved from the current the ions carry to an electrometer. The technique is also applicable for the total particle size distribution, if it is first brought to charge equilibrium.

The ion spectrometers used in this thesis (**IV-VI**) were manufactured by Airel Ltd, based in Tartu, Estonia. The performance of the instruments was estimated in two calibration and intercomparison workshops held in Helsinki (Asmi *et al.*, 2009; Gagné *et al.*, 2011) prior to and after the ion spectrometers spent one year in field measurements as a part of the EUCAARI campaign (Kulmala *et al.*, 2009; Manninen *et al.*, 2010).

Three types of ion mobility spectrometers were used in this work:

The Balanced Scanning Mobility Analyzer (BSMA; Tammet, 2006) is a single-channel differential aspiration condenser that consists of two parallel aspiration condensers connected as a balanced capacitance bridge, which allows for continuously scan through the mobility range of $0.032\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which approximately corresponds to ion mobility diameters of 0.8–7.6 nm. Because of its very high flow rate (2400 l min^{-1}) leading to low diffusion losses of ions, the BSMA was used as a reference instrument in calibrating ion spectrometers (Asmi *et al.*, 2009, Gagné *et al.*, 2011).

The Air Ion Spectrometer (AIS; Mirme *et al.*, 2007) consists of two parallel differential mobility analyzers (DMAs) to measure the mobility distribution of positive and negative ions simultaneously. Ions are classified according to their electrical mobility and the signals they produce are recorded by 21 electrometers. The AIS measures small ions and charged particles in the $0.0013\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ mobility range (0.8–40 nm in mobility diameter).

The Neutral Cluster and Air Ion Spectrometer (NAIS; Manninen *et al.*, 2009) is similar to the AIS, except that there is an additional measurement mode for the total particle population, in which the sample is neutralized by ions from corona discharges before size selection. An electric post-filter section is used to remove the ions produced in the charger unit. The lower size limit of the NAIS in total mode is around 2-3 nm depending on the corona ions distribution and post-filtering (Asmi *et al.*, 2009, Manninen *et al.*, 2011). A second generation NAIS, the Airborne NAIS (A-NAIS) was introduced in 2010 (Mirme *et al.*, 2010), and has been used for measurements onboard an aircraft.

Mass spectrometry provides a different approach to measure atmospheric ions. The main problem in mass spectrometry of atmospheric ions is transferring them into vacuum without high losses or perturbation of ion composition. A high resolution mass spectrometer APi-TOF (Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer, manufactured by ToFwerk AG, Switzerland) was introduced in 2010, and has been used for identification of the atmospheric ion composition in Helsinki and Hyytiälä (Junninen *et al.*, 2010; Ehn *et al.*, 2010). The APi-TOF covers the mass-to-charge range up to about 2000 Da, which corresponds approximately to a diameter range from below 1 nm to 2.5 nm (Ehn *et al.*, 2011); however its transmission gets lower at higher masses. With a suitable charging mechanism, mass spectrometry can also be applied to measure selected neutral cluster species, like sulphuric acid clusters (Eisele & Hanson, 2000; Hanson & Eisele, 2002; Zhao *et al.*, 2010).

3.3 Comparison of the instruments

Since most of the instruments used in this study are still in development phase, one way to validate the results is to compare different methods. Careful laboratory calibration/verification of instruments is also vital for reliable, reproducible measurements, and when interpreting results from different instruments. Chapter 3.3.1 discusses the difficulties related to calibrating aerosol instrumentation at small sizes. Figure 4 shows the size

ranges covered by different particle or ion instruments used during this study, arranged from top to bottom according to the time they were developed.

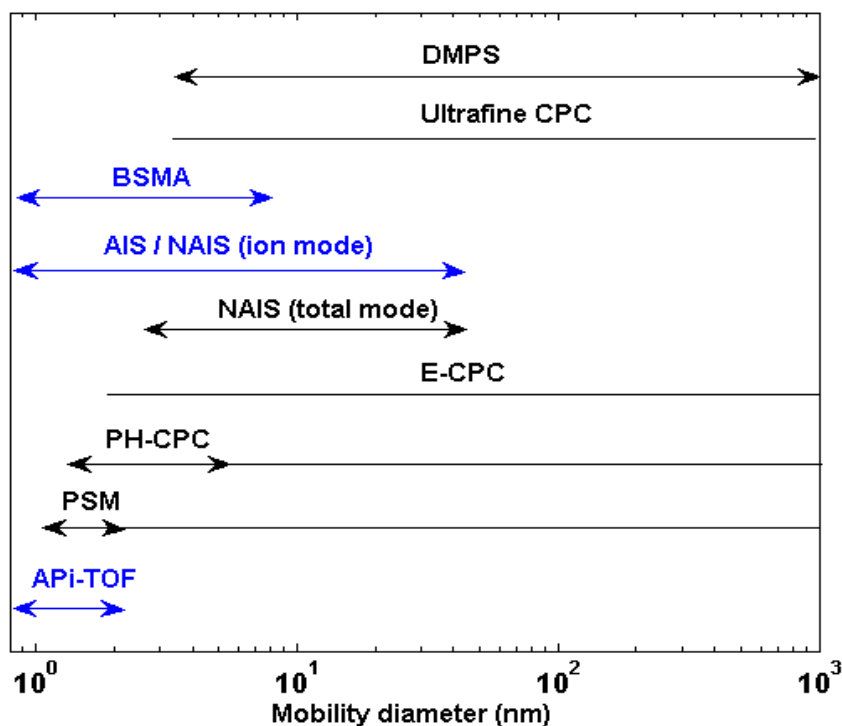


Figure 4. The measurement ranges of different particle counters and size spectrometers, arranged by the development time of the instrument. The arrow heads indicate the region, where size distribution can be retrieved. Blue lines represent ion measurements, whereas black lines represent measurements of total particle population.

The E-CPC and PH-CPC were operating in parallel during the spring of 2007, and the concentrations of nano-CN obtained from these two techniques were observed to generally be within a factor of 5 (I). The PH-CPC and PSM were measuring together in spring 2009 for a period of time. The raw signal of the PH-CPC was following closely the PSM data, while both of them sometimes showed higher concentrations than the ultrafine CPCs, which was

attributed to the presence of nano-CN (Fig. 8 in **III**). The PSM and PH-CPC have also been measuring in parallel in different laboratory experiments (Sipilä *et al.*, 2010; Dal Maso *et al.*, 2010), where their agreement was usually good.

The performance of the PH-CPC and the NAIS in total mode was compared in papers **IV** and **V**. In the size range between 3-5 nm, the instruments usually agree fairly well, but at smaller sizes clear discrepancies are seen. The PH-CPC shows much more variation in the nano-CN concentrations than the NAIS, and agreement is found only when the concentration is very high (Fig. 5). This is probably because the measurements of the total concentration with the NAIS are the most accurate at high concentrations, because then the background noise level of the electrometers and the ions created in the corona charger interfere the least (Asmi *et al.*, 2009; Gagné *et al.*, 2011). On the contrary, the PH-CPC measurements are disturbed by very high concentrations, which makes it unfavorable to compare these two instruments. One should, however, keep in mind that the PH-CPC and the ion spectrometer determine the size with completely different methods. Discrepancies might be also explained by the sensitivity of the PH-CPC to particle composition and background aerosol concentration.

The measurements with the PH-CPC and the PSM can be also compared to the small ions and ion-clusters measured with the APi-TOF. In **paper VI** the mass spectra from the APi-TOF were used to interpret the PH-CPC data. The complication in this comparison is that the APi-TOF only detects ions, whereas the CPCs measure total concentration. Ehn *et al.*, (2011) compared measurements with ion spectrometers to the APi-TOF, and found that especially above 200 Da (~1.2 nm) the BSMA and APi-TOF correlated well, whereas the AIS size channels appeared to be slightly shifted. However, in the calibration workshops (Asmi *et al.*, 2009; Gagné *et al.*, 2011) the AISs were observed to detect the mobility of calibration ions peaking at the correct channel, although the signal was broadened to several channels.

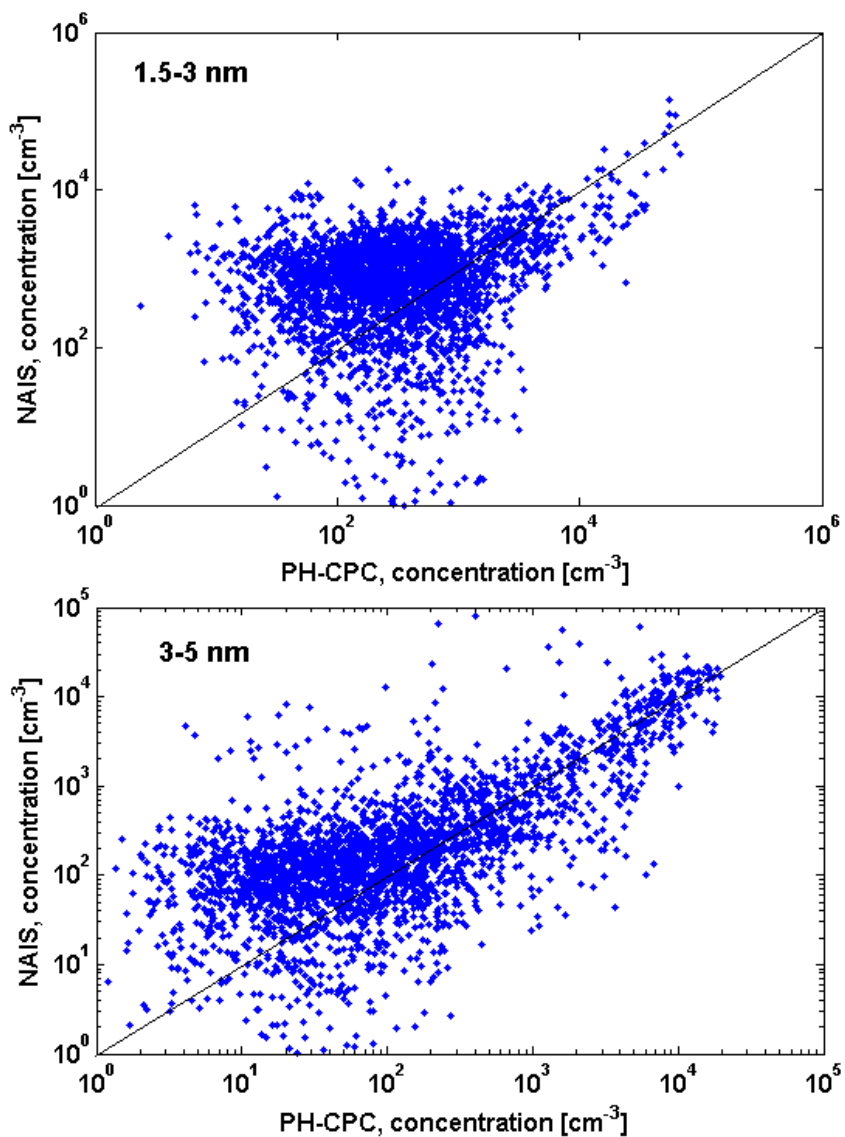


Figure 5. Particle concentrations measured at Mace Head simultaneously with the PH-CPC and the NAIS in two different size classes.

In figure 6, the median size distribution measured in Hyytiälä during the EUCAARI-campaign in spring 2007 is given for different instruments. For comparison, data points from the PSM measured in August 2010 are also shown. All the CPC-applications as well as the NAIS in total mode (negative

analyzer) give approximately similar numbers below 5 nm. A larger discrepancy was observed between the NAIS and the DMPS in sizes above 5 nm. Manninen *et al.*, (2009) and Gagné *et al.*, (2011) also observed that the NAIS seems to overestimate the concentration compared to the DMPS.

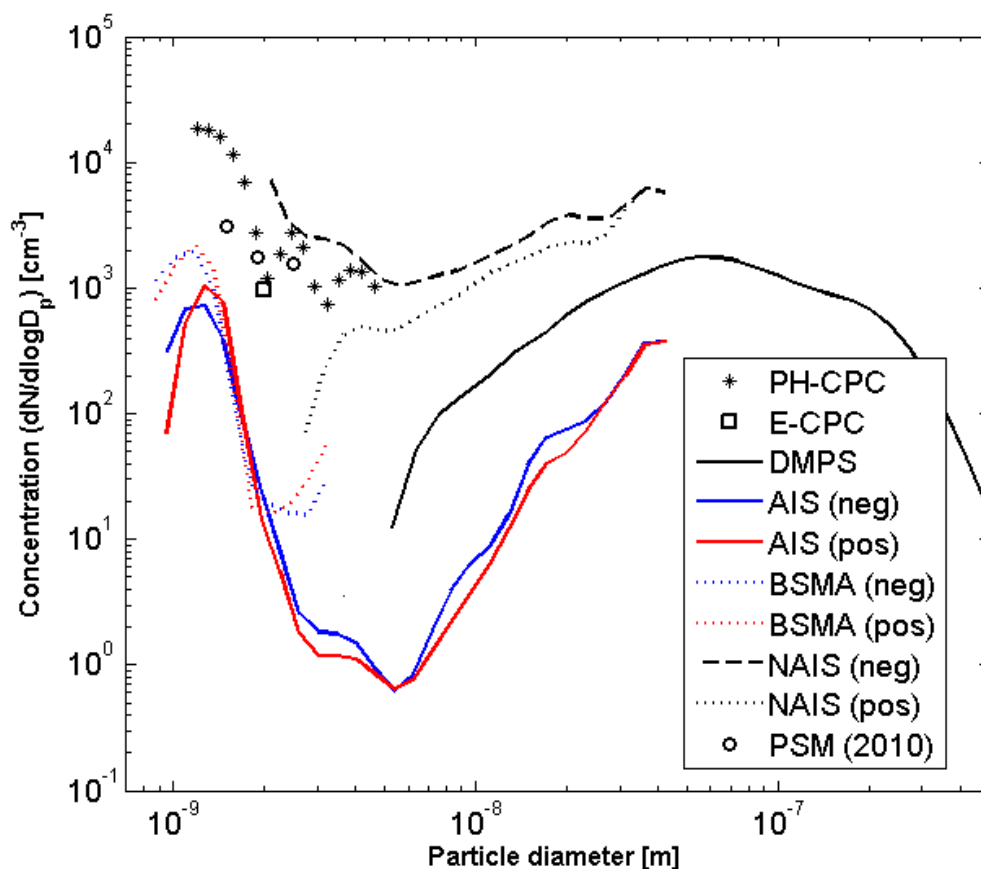


Figure 6. Median size distributions measured with different instruments during the spring 2007 EUCAARI campaign in Hyytiälä. Red and blue represent positive and negative ions, respectively, whereas black stands for the total particle size distribution. PSM data is from August 2010.

3.3.1 Remarks on instrument calibration in sizes below 3 nm

For several reasons calibrating aerosol instrumentation in the size range below 3 nm is not straightforward.

First and foremost: there is no reference instrument or size selecting method available for neutral particles. Thus, most calibration measurements are done using charged particles, and as discussed before, the charge might affect the activation probability of particles inside a CPC. Secondly, producing sufficient amounts of particles with a single charge and known composition over a wide range of sizes is not usually possible, and therefore several different types of particles and production methods need to be used. The calibration ions should not cluster, fragment, evaporate or otherwise change their nature after size selection. Impurities coming from the tubing or carrier gas could also interact with the calibration particles or be directly detected by the CPC when working at very high supersaturations. Thirdly, often most of the produced particles are initially neutral and need to be charged before size selection and detection, usually by a radioactive source. However, the source itself produces ions by ionizing air molecules, and these charger ions are overlapping with the calibration aerosol in the sizes below about 1.5 nm. Finally, a high-resolution DMA is needed for size-selecting particles especially below about 3 nm, since the transfer function of conventional DMAs broaden at smaller sizes (Winklmayr *et al.*, 1991).

In **papers II & III**, the instruments were calibrated using mobility standards, *i.e.* tetra-alkyl ammonium halide salts, which produce single positive ions in large quantities when electrosprayed from alcohol solutions (Ude & Fernandez de la Mora, 2005). For instance, tetraheptyl-ammonium-bromide (THAB) produces a monomer (A^+), dimer ($(AB)A^+$) and trimer ($(AB)_2A^+$) with mobility diameters of 1.47, 1.78 and 1.98 nm, respectively. The correct peak can be selected with a DMA. Positively and negatively charged tungsten oxide (WO_x) was produced using a tungsten oxide generator (Grimm 7860) and silver particles with a tube furnace. We also measured ions produced inside an Am^{241} charger, even though the nature of these ions is not known. All the calibration particles were size classified using a Herrmann-type high-resolution nano-DMA (Herrmann, 2000). The reference instrument was a TSI 3068B electrometer.

Detection efficiencies as a function of particle size are compared in figure 7 at the best settings for each instrument. Whereas the detection efficiency of the laminar flow ultrafine CPC (TSI 3776) approaches zero very quickly below 2.5 nm, the PH-CPC and E-CPC saw a significant fraction of mobility

standards at 1.78 and even at 1.47 nm, even though their cut-off sizes were of the same order as the ultrafine CPC. The cut-off size of the PSM is clearly lower than for the other instruments, *c.* 1.5 nm, and dominated mainly by diffusion losses in the instrument rather than activation probability (III).

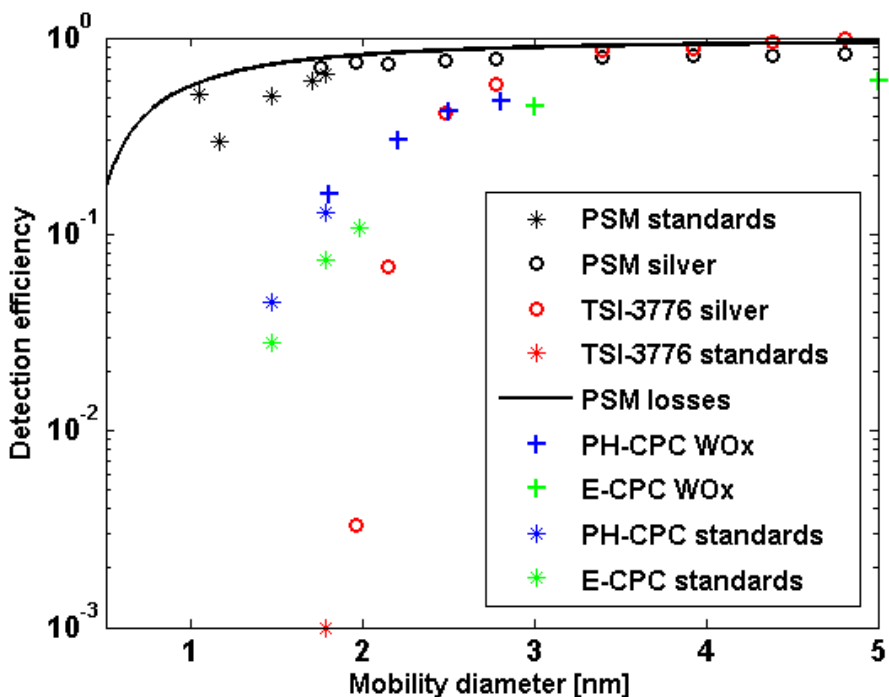


Figure 7. Detection efficiency of different CPCs at their best settings. Crosses are positively charged particles from the WO_x -generator, circles are positive silver particles, and stars mobility standards. Black line gives theoretical losses in the PSM. The condensing liquid used in the E-CPC was butanol.

From figure 7 (and Fig. 5 in **paper II**, and Fig. 5 in **paper III**), we can see that the material dependence of the calibration particles seems to be similar for DEG and butanol. For all the instruments, we activated the negative particles generated in the WO_x -generator better than the positive ones, and WO_x and silver in general easier than the mobility standards. For ions generated inside the radioactive charger, however, the polarity effect was the

opposite, the positive ions activating clearly before the negative ones both in the PH-CPC and PSM (**II** and **III**). In fact, the size did not seem to matter for positive ions below about 1.3 nm. Gamero-Castaño & Fernandez de la Mora (2002) also found that the critical supersaturation for positively charged particles below 1 nm was independent of size. However, as pointed out in papers **II** and **III**, the composition and dynamics of charger ions are not exactly known and are likely to differ according to air composition, relative humidity, impurities, *etc.*

In ion spectrometers the composition of calibration ions should not affect the detection, as long as the calibration particles are stable enough. However, even the ion spectrometers seemed to detect silver particles slightly better than mobility standards, while the size of the mobility standards were detected more accurately than the size of silver particles (Asmi *et al.*, 2009; Gagné *et al.*, 2011). The reason for this is probably the inhomogeneity of the produced silver ions, even after selection with a high-resolution DMA. Fernandez de la Mora (2011) also commented on the lack of uniformity of size-selected WO_x -particles used for heterogenous nucleation experiments, which could explain why the experimental activation curves are broader than predicted ones.

Clearly, more research on the composition and dynamics of calibration ions and improvements on the calibration methods in sub-3 nm sizes are urgently needed.

3.3.2. The advantage of CPCs over electrical techniques

Developing CPC applications which both measure the concentration and give size information is advantageous compared to electrical measurement techniques, because the CPC detects both neutral and charged particles without the need to neutralize the particle population, and without the additional diffusion losses of a size-selection unit.

The problem of any technique based on detecting charged particles is that if we want to resolve the total particle population, it needs to be brought to a

charge equilibrium before measurement. The charging efficiency of small particles is very low, about 1% at 3 nm (Hoppel & Frick, 1986), which leads to very poor counting statistics, especially when accounting for diffusion losses in the system. Also, the ions produced inside the neutralizer can extend close to 2 nm depending on polarity and air composition, which makes it impossible to separate between the signal and the charger ions in the overlapping area (*e.g.* Asmi *et al.*, 2009; Manninen *et al.*, 2011). Charging can also be selective to particle composition, since certain chemical compounds, like acids, are more prone to take the charge than others.

Even measurements with such commonly used instruments as the DMPS/SMPS show large deviations for particles below 20 nm (Wiedensohler *et al.*, 2010). New type of SMPSs using high-resolution DMAs and low cut-off CPCs are starting to emerge (Jiang *et al.*, 2011a) improving the detection of nano-particles. However, as a combined effect of low charging efficiency, losses in the sampling lines, DMA penetration efficiency and CPC detection efficiency, the counting statistics of such instruments drops drastically below 2 nm to one per ten thousand and even lower. The DEG-SMPS of Jiang *et al.* (2011a), claiming to measure down to 1 nm, is also highly sensitive to particle composition.

Condensation particle counters usually count single particles, which leads to a much better signal-to-noise ratio than what can be obtained with ion spectrometers using electrometers. In particular, when the concentration is low, the ion spectrometers show a constant background (Gagné *et al.*, 2011). However, single-particle counting can be disadvantageous in high concentrations, as the sample needs either to be diluted or the concentration corrected for coincidence. The measurements with pulse-height CPC are especially affected by large background concentrations (**I, II**).

On the other hand, the advantages of ion spectrometers are their stability and low need of maintenance, which make them very suitable for long-term field measurements (Manninen *et al.*, 2010). They also operate at a high flow rate, which considerably reduces diffusional losses.

3.4 Field measurements

Field measurements for this thesis were mainly carried out at the Hyytiälä SMEAR II station located in Juupajoki, Central Finland. SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) is equipped with comprehensive facilities for atmospheric and forest ecological measurements (Hari & Kulmala, 2005). The station is surrounded by a rather homogenous forest stand dominated by Scots pine. The distance to the nearest large city, Tampere, is about 60 km, but there is a smaller village with some industrial activity less than 10 km away from the station, and the forestry field station buildings are by a small lake *c.* 500 m from the measurement location.

The aerosol size distribution measurements with a DMPS (Aalto *et al.*, 2001) began in 1996, making it the longest time series in the world. Continuous measurements with ion spectrometers (BSMA and/or AIS) in Hyytiälä began in 2003. The different condensation particle counter applications and other state-of-art instruments were used for field measurements campaign-wise mostly in the springtime. Measurements with the E-CPC and PH-CPC were conducted in Hyytiälä in spring 2007, May 2008 and May 2009 (PH-CPC only) as a part of the EUCAARI campaign (Kulmala *et al.*, 2009). During early May 2009 the prototype version of the PSM was also measuring shortly in parallel with the PH-CPC. As supportive data sets we have also used measurements with the NAIS (available for 2007 and 2009 campaigns), APi-TOF (spring 2009) and a CPC-battery, typically consisting of two pairs of water and butanol CPCs, one ultrafine (cut-off around 3 nm) and one normal (cut-off around 7 nm). Most particle instruments were located close to each other in a small hut inside the forest canopy.

Paper V uses data from the Mace Head atmospheric research station, which is a GAW (Global Atmosphere Watch) super-site situated on the west coast of Ireland facing the North Atlantic ocean (Jennings *et al.*, 2003) The station is located 100 m from the coastline and surrounded by bare land (rocks, grass and peat bog) with no forest or trees. Few scattered single houses are located at a distance of 1 km or greater, while the nearest city (Galway, 80 000 inhabitants) is located 60 km to the east/south-east of the station.

The PH-CPC and the NAIS were measuring in Mace Head during June-August 2008. Additional data from a nano-SMPS was also available.

The occurrence of new particle formation has been studied extensively on both of the field sites. In Hyytiälä, new particle formation is observed on about 25% of days, most frequently during spring time (Dal Maso *et al.*, 2005). In Mace Head, strong particle formation bursts are frequently observed in daytime during low tide, probably due to iodine vapors emitted by the algae that are exposed to sunlight (O'Dowd *et al.* 2002c; Yoon *et al.* 2006; Vana *et al.*, 2008).

4. Observations of atmospheric nano-CN

While the continuous existence of small ions in the atmosphere has been known for at least a century, the existence of their neutral counterparts was uncertain as they could not be detected. Weber *et al.* (1995) studied the occurrence of ultrafine particles using pulse-height analysis, together with clusters measured with a chemical ionization mass spectrometer at Mauna Loa observatory in Hawaii. They found that larger clusters (5000-10 000 amu) were detected simultaneously with ultrafine particles especially during nucleation bursts. They also commented that ~3-4 nm particles were seen in low concentrations most of the time, especially in up-slope air, while nucleation bursts were rare.

By theoretical reasoning Kulmala *et al.* (2000; 2005) predicted a pool of neutral clusters as the explanation for the observed new particle formation events. In the laboratory experiments by Hanson & Eisele (2002) the concentration of neutral pre-nucleation clusters in a H₂SO₄-H₂O-NH₃ system was estimated to be of the order of 10⁶ cm⁻³. The first direct experimental evidence of neutral clusters in the atmosphere was presented in Kulmala *et al.* (2007a). They concluded that there was a constant pool of neutral clusters, the concentration ranging from 10³-10⁴ cm⁻³.

This thesis work and the following chapter focus on verifying and quantifying these observations and further analyzing the concentration and behavior of neutral nano-CN. Most of the results presented and discussed here are based on the measurements using PH-CPC, subject to the uncertainties discussed in chapter 3.1.2. The concentration of nano-CN is thus the total (inverted) concentration between about 1.3-3 nm.

4.1 Temporal and spatial variation

The measurements in both Hyytiälä and Mace Head show that neutral nano-CN are present not only before and during nucleation events, but continuously, and the concentrations seem to vary several orders of

magnitude (**I**, **IV**, **V**). The lowest concentrations, sometimes just 10^1 cm^{-3} , were found in Mace Head during nighttime, when the air masses came from the Atlantic Ocean. The largest concentrations, up to 10^5 cm^{-3} , were also measured during nighttime, but in Hyytiälä. The occurrence of increased nighttime concentrations was studied further in **paper VI**. The median concentrations in Hyytiälä and Mace Head during the 2008 campaigns were 3380 and 890 cm^{-3} , respectively. Concentrations were in general lower in Mace Head than in Hyytiälä, and still lower in marine air masses coming directly from the Atlantic Ocean (median 570 cm^{-3}). The concentration of small ions is also lower in marine air masses (Vana *et al.*, 2008, **V**). The range of observed nano-CN concentrations along with selected values from literature are summarized in table 1.

The diurnal variation of nano-CN in Hyytiälä was similar on days classified as event, non-event or undefined days regarding new particle formation (Dal Maso *et al.*, 2005; **IV**). However, as discussed in chapter 3.3.2, the concentrations measured with the PH-CPC during strong nucleation events are not reliable and were excluded from the analysis. In Mace Head, the nano-CN concentrations did not depend on the tidal cycle, which determines the occurrence of particle formation bursts. Instead, especially in marine air masses, the nano-CN concentration seemed to follow the solar elevation angle. Unfortunately, our measurements were done mostly during the spring, so seasonal variation of the nano-CN could not be studied.

The variation of nano-CN concentration is dependent on the combination of their sinks and sources. The main sinks of nano-CN are coagulation to larger particles, activation and growth to larger sizes and evaporation. Deposition is expected to be a minor sink, even though it has been shown that deposition to forest canopy is a sink for small ions (Tamm et al., 2006). Since the nano-CN pool probably consists of a variety of species, their sources can be multiple as well. Neutral nano-CN can be formed at least by nucleation and by recombination of small ions (Turco *et al.*, 1998). **Papers V** and **VI** suggest that oxidation of VOCs is a source of nano-CN, which is supported by laboratory experiments. Formation of nano-CN could also involve photochemical reactions as their concentration follow solar radiation especially in the marine air masses in Mace Head. The variation in the coagulation sink was not enough to explain the difference in concentration

levels between Hyytiälä and Mace Head (**V**). However, boundary layer dynamics also affect the measured concentrations.

Table 1. Summary of the observed atmospheric nano-CN concentrations during this study and from literature.

Location	Time	Instrument & size range	Concentration (cm ⁻³)	Charged fraction	Reference
Hyytiälä	13.3-16.5.2006	NAIS, UF-02proto* 1.8-3 nm	10 ³ -10 ⁴ (7 000-50 000 during events)	<10%	Kulmala <i>et al.</i> , 2007a
Hyytiälä	2006-2007	NAIS 1.8-3 nm	50-6 000 (median 1010 for spring 2007)	<5%	Manninen <i>et al.</i> , 2009
Hyytiälä	15.3-26.6.2007	E-CPC < 3 nm	< 50 000 (mean 10 ⁴)		Lehtipalo, 2007; I
Hyytiälä	15.3-26.6.2007	PH-CPC 1.5-3 nm	1510-31 100 (median 8060)	~1%	IV
Hyytiälä	1.5-31.5.2008	PH-CPC 1.5-3 nm	220-36 300 (median 3380)	1%	IV, V
Mace Head	13.6-25.8.2008	PH-CPC 1.5-3 nm	30-12 000 (median 890/570, all/clean sector)	18%	V
Boulder, USA	26.9.2008	DEG-CPC 1.9-2.3 nm	10 ⁴ (during event)		Zhao <i>et al.</i> , 2010

* Mordas *et al.*, 2005

4.2 Charged fraction of nano-CN

Small ions are formed when air molecules are ionized mainly by radon decay and external radiation, which consists of gamma radiation from the ground and cosmic radiation (Israël, 1970; Bazilevskaya *et al.*, 2008; Harrison & Aplin, 2001, Hirsikko *et al.* 2007b). Small ions (<1.6 nm) exist practically all the time throughout the troposphere, as evidenced by a large number of observations (*e.g.* Hirsikko *et al.*, 2011, and references therein), whereas intermediate ions (1.6-7.5 nm) are usually detected only during new-particle formation (*e.g.* Hörrak *et al.*, 1998; Hirsikko *et al.*, 2005, 2007a). Intermediate ions can be produced via ion-induced nucleation or by charging of the neutral particles. Intermediate ions can also be formed by falling hydrometeors, like in waterfalls and during rain or snowstorms (Laakso *et al.*, 2007c; Tammet, 2009; Virkkula *et al.*, 2007).

Due to differences in their chemical composition, small negative ions usually have a larger mean mobility (*i.e.* smaller size) than positive ones (Hörrak *et al.*, 1994, 2000; Harrison & Aplin, 2007). The chemical composition of small ions depends on the trace gas concentrations, and also on their age. Ehn *et al.* (2010) showed that the negative ions in Hyytiälä consisted mostly of strong organic and inorganic acids, and the positive ions of strong bases.

We compared the concentrations of neutral nano-CN to ions in corresponding size class both in Hyytiälä and Mace Head. We also calculated a maximum estimate for the concentration of neutral recombination products formed when two ions of opposite polarity collide and form a stable entity (Turco *et al.*, 1998). On average, the charged fraction in Hyytiälä was ~1%, close to the steady-state value, and recombination of ions could explain on average only about 3% of the neutral species. In Mace Head, the contribution of ions was clearly larger, the charged fraction being 18% on average, and about half of the nano-CN could be explained by recombination. The fractions were slightly higher in the marine air masses, even though the absolute ion concentrations were lower due to reduced ionization as there is no ion source from radon over the ocean (Vana *et al.*, 2008; V). During the night, when the total nano-CN concentration was low, even the majority of the neutral nano-CN could be formed by ion-ion recombination in Mace Head.

As the neutral nano-CN concentration varied much more than the concentration of small ions, the contribution of ions were the lowest during high total nano-CN concentrations. This observation is qualitatively similar to what Manninen *et al.* (2010) concluded about charged and total formation rates of 2 nm particles. When looking at the diurnal variation of the charged fraction and fraction of recombination products of all nano-CN (Fig. 5 in **paper V**), one can see that the lowest numbers were obtained during evening in Hyytiälä and midday in Mace Head, when the total nano-CN concentration were at maximum. However, the day to day variation of the contribution of ions to nano-CN concentrations was considerable.

4.3 Nano-CN and nucleation

Mass spectrometers have revealed the extreme diversity of atmospheric small ions and clusters (Ehn *et al.*, 2010; Zhao *et al.*, 2010). Some of the compounds are detected all the time, clearly not participating in new particle formation, while some can be directly connected to nucleation. Zhao *et al.*, (2010) measured neutral sulphuric acid clusters (up to four sulphuric acid molecules) during periods of new particle formation with Cluster-CIMS and concluded that their concentration were about 10^4 cm^{-3} both in an urban and a forested site. Jiang *et al.* (2011b) claimed that the sulphuric acid clusters measured by the Cluster-CIMS overlap in size with the nano-CN measured with the DEG-SMPS and the measured concentrations were in agreement during nucleation events. The cluster-CIMS also detected a high signal from unidentified large molecular weight compounds, which were probably not associated with nucleation (Zhao *et al.*, 2010; Jiang *et al.*, 2011b), and which were not observed with the DEG-SMPS. However, their DEG-CPC was very sensitive to particle composition and had much poorer detection efficiency than for example the PH-CPC or PSM (0.5% compared to 5% and 51% for THAB monomer at 1.47 nm).

A good correlation was obtained between the nano-CN concentration and the calculated concentration of monoterpene oxidation products, both in Hyytiälä and in laminar flow tube experiments in Leipzig (IfT-LFT; **VI**). However, the LFT experiments showed that while the increase in the initial concentration

of the organic compound increased the number of nano-CN detected by the PH-CPC, the nano-CN did not show any growth unless sulphuric acid was produced in the flow tube. This could explain why we do not observe new particle formation in Hyytiälä during nighttime, when there is no photochemical production of sulphuric acid, although both the concentration of small ions and nano-CN were often high (Junninen *et al.*, 2008, **VI**).

Paper VI shows that the nighttime concentrations of small ions correlated best with the large highly oxidized organic compounds that dominate the APi-TOF mass spectra during nighttime. The neutral nano-CN, however, correlated better with charged sulphuric acid clusters than with any other single compound, both during daytime and nighttime, although the concentration of sulphuric acid clusters is generally low during nighttime. This could be explained by the fact that oxidation of VOCs leads to formation of OH and thus sulphuric acid, and/or that higher sulphuric acid concentrations leads to formation of larger clusters, even nucleation in low rates, leading to higher nano-CN signal. Both the ion spectrometers and the PH-CPC showed that the nano-CN and the small ions formed during nighttime can occasionally reach about 4 nm and **paper VI** presents an example, where they are even visible in the lowest channels of the DMPS.

Not all the measured nano-CN, nor all the small ions, seem to participate in new particle formation. Clearly, the nano-CN concentration alone does not determine when new particle formation occurs. However, while most studies have highlighted the role of intense nucleation events as the source of new particles, nucleation might occur at low rates also outside the event times (Weber *et al.*, 1995), even during nights. The occurrence of nucleation events might be determined by the competition between particle growth and loss processes, rather than formation of initial clusters (Riipinen *et al.*, 2007, **IV**). In Mace Head, the observed nano-CN concentrations were much lower than the number of particles formed during nucleation bursts, so clearly the particles could not have been formed by activation of pre-existing clusters, but rather via homogenous or kinetic nucleation.

5. Review of the papers and author's contribution

Paper I introduces the pulse-height analysis technique and expansion-CPC as methods to detect atmospheric nano-CN. A set of simple laboratory experiments are used to prove their ability to detect neutral sub-3 nm particles and interpret field measurement data. A first estimate of the concentration and average size of the atmospheric nano-CN is given.

I took part in the field measurements and laboratory experiments; I analyzed the expansion-CPC data, and contributed in writing the paper.

In **paper II** the performance and sensitivity of the PH-CPC is tested in a series of laboratory experiments. Based on the calibrations, an inversion method is developed for converting the multi-channel analyzer signal to particle size distribution, and an example from field measurement data is given. Also, the limitations and error sources of the method is discussed.

I participated in the calibration and field measurements, I developed the measurement programs and the inversion method for the data, and I wrote minor parts of the paper in collaboration with the main author.

Paper III introduces the Particle Size Magnifier prototype and its commercialized version, and proves its ability to measure particles down to about 1 nm. The performance of the PSM was compared against other CPCs and its suitability for continuous field measurements is shown.

I participated in the field measurements and analyzed the field data, I did a part of the calibration measurements and helped in writing and correcting the manuscript.

In **Paper V** the first continuous time series of sub-3 nm neutral particles are presented from Hyytiälä. The field measurement data from EUCAARI 2007 and 2008 campaigns using pulse-height CPC is analyzed in detail. The concentrations are compared to measurements with ion spectrometers and theoretical predictions.

I took part in the field measurement campaigns, I performed all the data analysis, and I wrote the paper.

Paper VI compares the measured nano-CN concentrations in Hyytiälä and Mace Head during the 2008 measurement campaigns. Based on the concentrations, we speculated about the role of nano-CN in new particle formation at the two sites.

I took part in the field measurements in Hyytiälä, I analyzed all the data, and I wrote most of the paper.

Paper VII concentrates on the elevated nighttime concentrations of nano-CN that were observed in Hyytiälä. We analyze their occurrence and conditions favoring nighttime nano-CN. We also assess the plausible composition and sources of nano-CN in general, based on comparison of the PH-CPC and APi-TOF in Hyytiälä and supportive experiments in a laminar flow tube.

I took part in the field measurements, I analyzed most of the data (except for the IfT-LFT measurements), and I wrote most of the paper.

6. Conclusions

When looking at the articles that make up this thesis in chronological order (**I, II, IV, V, VI, III**) one can clearly see the progress in both methods and our conceptual understanding, which is in line with the general advancement of nucleation research (Kerminen *et al.*, 2010). This thesis work started by testing and proving the applicability of condensation particle counters for measuring particles smaller than 3 nm both in field conditions (**I**) and in the laboratory (**II**). Altogether three new methods for detecting nano-CN were developed, the third one leading to a commercially available instrument (PSM; **III**). It was shown that in addition to particle number concentration, one can also gain size information of nano-particles using these CPC-applications (**I-III**). As the instrumentation for measuring nano-particles is still in the development phase and large uncertainties regarding the methods certainly exist, the measurements were verified by calibrations and by cross-checking data from several independent instruments (**I-VI**).

Next, the newly developed instruments were applied to field conditions in order to gain information about nano-CN. The first continuous time series of sub-3 nm neutral particles were measured using the pulse height CPC in Hyytiälä (**IV-VI**) and in Mace Head (**V**). The concentrations in Hyytiälä were consistent with the theoretical predictions and earlier observations (*e.g.* Kulmala *et al.*, 2007a). This thesis shows that 1) concentrations of neutral nano-CN are much higher and vary much more than ions in the same size range, 2) concentrations in a boreal forest environment are higher than on the Atlantic coast, and this difference cannot be explained by variations in the coagulation sink alone, 3) ion-ion recombination cannot be the only source of neutral nano-CN, and 4) nano-CN concentration is not a limiting factor for the occurrence of new particle formation events (**IV, V**). The nano-CN concentrations could also be connected to oxidation products of VOCs, however, they also seemed to correlate with charged sulphuric acid clusters (**VI**). The exact chemical compounds and processes forming the nano-CN remain to be solved, but it can be speculated that the neutral nano-CN, just as with the small ions, consist of a variety of clusters and molecules, some of which can participate in new particle formation, and some that do not.

Papers III and VI, in particular, show that we have indeed reached the molecular limit with the CPCs, and can detect smaller neutral particles than is possible using electrical techniques that require neutralizing the particle population. A decrease from 3 to 1 nm in the mobility diameter of the smallest detectable particles converts to almost a 2 orders of magnitude difference in the particle mass (Ehn *et al.*, 2011). Contrary to many low cut-off instruments reported in literature, these CPCs were also found to be stable enough for long-term field studies.

The sensitivity to particles as small as 1 nm makes it possible to measure directly at the size where nucleation occurs and thus minimize the chance of bias due to particle growth and loss processes. If the growth is slow, a significant part of newly formed particles may not even reach the instrument detection limit before being lost. Sipilä *et al.* (2010) , Berndt *et al.* (2010) and Brus *et al.* (2010) all saw that in laminar flow tube experiments the nucleation rate as a function of sulphuric acid concentration gave a lower slope when the particle concentration was measured with the PSM or PH-CPC than an ultrafine CPC with a 3 nm cut-off size.

As the atmospheric ion concentration is limited by the ionization rate, the total particle formation rates vary much more between different locations than ion formation rates, the ion-induced fraction being 1-30% (Manninen *et al.*, 2010). Thus ion measurements have only limited usability in studying new particle formation. Mass spectrometers can also reveal only part of the truth, since due to different proton affinities certain compounds get charged easier than others, so the ion mass spectra will be biased in comparison to neutral species. A first attempt to compare CPC-measurements with the mass spectra from the APi-TOF is also presented in this thesis (**VI**).

The best approach for solving atmospheric nucleation is to tackle the problem simultaneously from all directions using a variety of different experimental and theoretical methods. Together with the development of ion spectrometers (Mirme *et al.*, 2009; Manninen *et al.*, 2010), the work done during this thesis is listed among the principal accomplishments of the EUCAARI project: “The most important technical achievement of the project was the development of new instruments for measuring sub-3 nm particle

populations, along with the extensive application of these instruments in both the laboratory and the field” (Kerminen *et al.*, 2010).

Our view on atmospheric nucleation, as a possibility to directly look and see what is happening in the size range of clusters and the smallest particles, has indeed been reformed by the development of condensation particle counting. We can now directly observe particles starting from molecular sizes and gain information on their size. Our view, as a way of understanding the process, has also been clarified, but detailed laboratory and field studies are still needed to gain a full understanding of the phenomenon.

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