

REPORT SERIES IN AEROSOL SCIENCE

N:o 214 (2018)

DEVELOPING EXPERIMENTAL METHODS TO  
UNDERSTAND 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 A111, Exactum,  
Gustaf Hällströmin katu 2 B, on November 2nd, 2018, at 14 o'clock.*

**Helsinki 2018**

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ISBN 978-952-7276-09-9 (printed version)  
ISSN 0784-3496  
Helsinki 2018  
Unigrafia Oy

ISBN 978-952-7276-10-5 (pdf version)  
<http://ethesis.helsinki.fi>  
Helsinki 2018  
Helsingin yliopiston verkkojulkaisut

## Acknowledgements

The largest part of this thesis work has been conducted at the Institute of Atmospheric and Earth System Research (INAR) at the Department of Science of the University of Helsinki. I would like to thank Prof. Markku Kulmala for the support both in providing the facilities, and also for great scientific as well as non-scientific discussions over the years. I would also like to thank Prof. Tuukka Petäjä for great guidance in the thesis work and very honest and helpful comments. Part of my thesis work is conducted at the Finnish Meteorological institute, and I would like to thank my supervisors Heikki Lihavainen and Antti-Pekka Hyvärinen for the help in the beginning of my scientific career. Their guidance in basic aerosol instrumentation helped me to start my own instrument development work. I would like to thank Associate Professor Nonne Prisle and Associate Professor Chris Hogan for reviewing my thesis.

The whole INAR group deserves a special acknowledgement. I have had the chance to travel and see many research groups all over the world, and this has made me appreciate the working culture and overall spirit of this group more and more. I was privileged to spin-off a company out of this group and I truly appreciate the scientific background, contacts and help I have gotten throughout these years. Especially I would like to thank Professor Mikko Sipilä, Associate professor Katrianne Lehtipalo, Jyri Mikkilä and Erkki Siivola for the great co-operation in the first years of Particle Size Magnifier development that eventually lead to the formation of the company Airmodus Ltd. A special thanks also to Pasi Aalto who has helped me with all of my questions about aerosol instrumentation throughout the years.

Also, I would like to thank my co-workers at Airmodus, where I still get to do science with our customers and co-operators every day. I feel very privileged to work in such a great team. In addition, I would like to thank Harri Joy for helping us to make real products out of scientific findings.

None of my studies would have been possible without the great support by my parents and I will be forever thankful for that. And finally, I want to thank my wife Hanni Vanhanen and our beloved daughter Joanna Vanhanen for all the love and understanding during this thesis work.

## **Developing experimental methods to understand atmospheric nucleation**

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University of Helsinki, 2018

### **Abstract**

The effects of human civilization on Earth's climate are undeniable. Some are due to emissions of greenhouse gases, some are due to atmospheric aerosol particles. In this thesis, the focus is on the aerosols. The complexity of the effects of the aerosol particles on the climate arise from high dynamics of the aerosol populations. A fraction of the aerosol particles are formed in the atmosphere by secondary particle formation, but the particles are also emitted to the atmosphere as primary emission for example from engine exhaust or from sea spray. The particles can grow by condensation and coagulation and get lost by deposition due to gravity and wet deposition. All of the processes mentioned lead to a particle population with a highly varying chemical composition. The climatic effects of the aerosol particles can be either direct, by scattering of light by the particles or indirect through cloud formation. In addition to the climatic effects of the aerosol particles, they can have adverse effects on human health. The smallest particles are capable of, not only penetrating deep into the respiratory tract and lungs, but also translocate from the nasal surfaces straight into human brain and thus penetrating the blood-brain barrier. This work concentrates on measurement methods of the very smallest particles and how they form in the atmosphere, but also touches upon the size range that is highly relevant with respect to the cloud formation.

Gas to particulate phase transitions and interactions play crucial role in climate and are still quite poorly understood. The particles in the atmosphere provide a large surface area that can act as catalyst for gas phase chemistry and contribute to the cloud formation as this typically requires presence of aerosol particles. Majority of the aerosol particles are formed in the atmosphere due to a combination of natural, and anthropogenic precursor gases. In order to understand the climatic effects of these particles, their formation and growth toward larger sizes needs to be investigated.

During this thesis work, several new instrumentation methods were developed. First one is a surface tension measurement apparatus that was used to measure the surface tension of atmospherically relevant aqueous mixture of organic acid and inorganic salt. Using a modelling approach, it was discovered that the surface tension had a slight effect on aerosol activation and cloud droplet formation in warm clouds. The second instrument is a new particle measurement system that is capable of counting the particles as small as 1 nm in diameter, making it possible to measure atmospheric new particle formation and their growth as it happens, particle per particle. The work illustrated that the particle counter needs to be able to detect the particles when they are formed in order to get correct information on the formation and growth rates relevant for the atmospheric aerosol population.

**Keywords:** surface tension, nucleation, cloud condensation nuclei, instrument calibration, particle size magnifier, atmospheric aerosols, gas-to-particle conversion.

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## List of publications

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

- I **J. Vanhanen**, A.-P. Hyvärinen, T. Anttila, H. Lihavainen and Y. Viisanen. Ternary solution of sodium chloride, succinic acid and water – surface tension and its influence on cloud droplet activation, *Atmospheric Chemistry and Physics*, 8, 4595-4604, 2008. Reprinted under Creative Commons licence.
- II S.-L. Sihto, J. Mikkilä, **J. Vanhanen**, M. Ehn, L. Liao, K. Lehtipalo, P. P. Aalto, J. Duplissy, T. Petäjä, V.-M. Kerminen and M. Kulmala. Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest, *Atmospheric Chemistry and Physics*, 11, 13269-13285, 2011. Reprinted under Creative Commons licence.
- III **J. Vanhanen**, J. Mikkilä, K. Lehtipalo, M. Sipilä, H. E. Manninen, E. Siivola, T. Petäjä, and M. Kulmala, Particle Size Magnifier for nano-CN Detection, *Aerosol Science and Technology*, 45, 533-542, 2011. Copyright 2018. Mount Laurel, NJ. Reprinted with permission.
- IV J. Kangasluoma, H. Junninen, K. Lehtipalo, J. Mikkilä, **J. Vanhanen**, M. Attoui, M. Sipilä, D. Worsnop, M. Kulmala and T. Petäjä, Remarks on ion generation for CPC detection efficiency studies in sub 3 nm size range, *Aerosol Science and Technology*, 47:5, 556-563, 2013. Copyright 2018. Mount Laurel, NJ. Reprinted with permission.
- V M. Sipilä, T. Berndt, T. Petäjä, D. Brus, **J. Vanhanen**, F. Stratmann, J. Patokoski, R. L. Mauldin, III, A.-P. Hyvärinen, H. Lihavainen, and M. Kulmala, The role of sulfuric acid in atmospheric nucleation, *Science* 327, 1234-1246, 2010. Reprinted with permission.

# 1 Introduction

Aerosol is defined as a mixture of carrier gas and particles that can be liquid, solid or a mixture of these phases. In the atmosphere aerosol particle number concentration can vary from  $10$  to  $10^2 \text{ cm}^{-3}$  at remote regions like Antarctica (e.g. Koponen *et al.* 2003) or Finnish Lapland (e.g. Vana *et al.* 2016) to  $10^4$  to  $10^5 \text{ cm}^{-3}$  at urban megacities like Beijing or New Delhi (e.g. Mönkkönen *et al.* 2004 and Mönkkönen *et al.* 2005, Sarangi *et al.* 2016). The smallest particles are in the size range of 1-2 nm (e.g. Kulmala *et al.* 2007b, Kulmala *et al.* 2013, Rönkkö *et al.* 2017) and the largest ones up to  $100 \mu\text{m}$  in diameter (Pruppacher, Klett and Pao, 1998). Also, the chemical composition, electrical charge state as well as morphology of the particles can be different in different environments. This variety of both physical and chemical properties poses a challenge for the instrumentation that is used to characterize these particles. To resolve these properties and their variation, a suite of aerosol instruments is needed (McMurry, 2000).

One important reason for measuring the aerosol particles is their effect on human health. Especially the ultrafine fraction (diameter below 100 nm) has been shown to have adverse health effects (e.g. Oberdörster *et al.* 1995, Seaton *et al.* 1995, Heinzerling *et al.* 2016). Also, epidemiological evidence has been shown already by Peters *et al.* 1997. Inhaled ultrafine particles are shown to cause inflammatory effects and for example elevated heart rate (Peters *et al.* 2015). Recently Maher *et al.* 2016 showed that nanoparticles containing magnetite can find their way into the human brain by directly translocating through olfactory nerve. The source of these metallic particles is combustion and they may be hazardous to human health due to their magnetic behavior and high redox activity.

Aerosol particles affect the climate. Radiative forcing of aerosol particles can be divided into two categories: Effective Radiative Forcing (ERF) through Aerosol Radiation Interaction (ARI) and through Aerosol Cloud Interaction (ACI). The ARI accounts for the direct effect such as scattering and absorption of light by the aerosol particles. The net ERF for this effect is estimated to be warming due to absorption of light especially by the soot particles that consist mainly elemental or brown carbon. The second effect (ACI) is due to the ability of the aerosol particles to act as condensation nuclei for cloud droplets. To form a cloud droplet in a warm cloud, oversaturated water vapor is needed. In the troposphere, the saturation ratio of water is almost never high enough for the water vapor to create cloud droplets via homogeneous nucleation. Therefore, all the cloud droplets in the atmosphere are formed on top of the aerosol particles by heterogeneous nucleation of water vapor. ACI is a combination of cloud albedo effect, that is caused by the scattering of radiation back to space by the cloud cover and the effect of aerosol particles to the lifetime of clouds. More aerosol particles mean more and smaller cloud droplets, which increases the lifetime of clouds (Ding *et al.* 2013). Also increased cloud droplet number increases the amount of radiation scattered by the cloud. This effect is called the Twomey effect (Twomey, 1977). The net ERF for the ACI estimated to be cooling (IPCC, 2014). To understand the net effect, both of these processes need to be well understood. Still today, the aerosol particles are the

least understood part of the climate change puzzle (IPCC, 2014). In this thesis the climatic effects of aerosol particles are studied through cloud droplet activation. Both the size of the particle and the chemical composition affect its capability to act as a Cloud Condensation Nucleus (CCN). The chemical composition changes the affinity of the particle to absorb water vapor, and it affects for example the surface tension of the activating and growing cloud droplet, finally altering the cloud droplet concentration and lifetime of the cloud.

The aerosol particles are divided into primary and secondary particles. The primary particles are particles that are emitted straight to the atmosphere as particles, such as Saharan dust, sea spray or soot from combustion engines. The secondary particles are formed in the atmosphere from clustering of gaseous precursor compounds (Kulmala *et al.* 2007b, Kulmala *et al.* 2013, Kulmala *et al.* 2014). These gaseous compounds are usually oxidized in the atmosphere resulting in low vapor pressure products (e.g. Ehn *et al.* 2014) contribution to the formation and growth of the secondary aerosols (Almeida *et al.* 2011, Tröstl *et al.*, 2013, Riccobono *et al.* 2013, Kulmala *et al.* 2013). Furthermore, a recent study by Rönkkö *et al.* 2017 suggests that there is an aerosol production process in between the primary and secondary particles. These particles are formed right after the combustion or emission processes, for example after the tailpipe of a car, but the formation process itself does not require oxidation in the atmosphere like in the case of secondary aerosol formation. These particles are called delayed primary particles.

New particle formation has been found to happen regularly in the atmosphere almost everywhere in the world (e.g. Kulmala *et al.* 2004b, Kontkanen *et al.* 2017, Kerminen *et al.* 2018). The most intensively studied environment is boreal forest. At the Station for Measuring Ecosystem – Atmosphere Relations (SMEAR II) station in Hyytiälä, Finland, these formation events were first discovered by Mäkelä *et al.* 1997. Similar events were also discovered for example in Hawaii (Weber *et al.* 1996) and in Macquarie island (Weber *et al.* 1998). At that time, the newly formed particles were found in the particle sizes starting at about 3 nm due to the limitations of the instrumentation. Already then sulfuric acid was proposed to be the gas compound that plays a key role in triggering the clustering process in many environments (e.g. Weber *et al.* 1996, Weber *et al.* 1998, Sihto *et al.* 2006). To further understand the atmospheric particle formation, laboratory studies on nucleation have been conducted using the same gaseous compounds that are thought to be responsible of the atmospheric new particle formation. First laboratory studies were focused on sulfuric acid and water nucleation (e.g. Viisanen *et al.* 1997, Ball *et al.* 1999, Berndt *et al.* 2005). Now it is known that even though sulfuric acid is one of the most important molecules in the first steps, other compounds are needed to carry on the growth and to stabilize the clusters (Kirkby *et al.* 2011, Almeida *et al.* 2013). These compounds are organics and especially so called highly oxidized molecules (HOMs) formed in the atmosphere by oxidation of volatile organic compounds (VOCs) are found to be important in the first steps of the particle growth (Ehn *et al.* 2014, Tröstl *et al.* 2016).

Before starting to work on this thesis, instruments capable of detecting single aerosol particles in the sub 3 nm size range were not commercially available. There were available only laboratory instruments that were not suitable for long-term measurements. To understand



the gas to particulate phase transition in the atmosphere, continuous measurements in this size range are needed to really understand the formation of particles. For this work, this need was the key driver to develop measurement instrument that is capable of measuring down to 1 nm in diameter. Furthermore, the instrument also needed to work in long term measurements 24/7 with only minor maintenance requirements. Only through the continuous measurements, the formation processes and dynamics of the smallest particles can be understood.

This thesis concentrates on understanding the atmospheric nucleation by developing and using new experimental methods. Two instruments were developed during this thesis work; capillary rise surface tension measurement device and Particle Size Magnifier for cluster – size particle counting. The thesis consists of both laboratory and field studies. Some modelling work was conducted to better understand the global impacts of the experimental results from laboratory measurements.

The main research questions of this thesis are:

- How does the surface tension affect the cloud droplet activation?
- Does the new particle formation affect the CCN concentration in boreal forest environment?
- How to correctly measure atmospheric particle formation and growth using particle counters?
- How to calibrate the particle counters in the sub 3 nm size range?
- What are the aerosol parameters affecting the detection efficiency in the size range below 3 nm?

## 2 Methods

Throughout this thesis the main phenomena I am concentrating is related to activation and condensation of vapors in presence of aerosol particles; cloud droplet formation in the atmosphere through uptake of water and detection of small nanoparticles using condensation of diethylene glycol and n-butanol. In case of the cloud droplet formation, an equation that describes the saturation ratio  $S$  for water that is needed for a cloud droplet with a diameter of  $d_{wet}$  not to evaporate is so-called Köhler equation (Köhler, 1936):

$$S = a_w \exp\left(\frac{4M_w\sigma}{RT\rho d_{wet}}\right), \quad (1)$$

where  $a_w$  is the activity of water in the solution,  $M_w$  is the molar mass of water,  $\sigma$  is the surface tension of the solution,  $R$  is the universal gas constant,  $T$  is the temperature and  $\rho$  is the density of the solution. In this equation the activity of water, or so-called Raoult term, is the ratio of vapor pressure of the solution divided by the vapor pressure of pure water. More solute in the solution, the lower is the saturation ratio needed for the equilibrium. The remaining exponent term in the Köhler equation is so-called Kelvin term. It accounts for the curvature of the droplet. When looking at the Kelvin term, it can be seen that by decreasing the size of the droplet, the saturation ratio needed to have the droplet in equilibrium is increasing. So, for small particle / droplet, it is much easier to lose a molecule than it is for a bigger one or for a flat surface. Also, from the equation it can be seen that the supersaturation is dependent on the surface tension  $\sigma$  of the droplet. The equilibrium saturation ratio is higher for solutions with higher surface tensions. This effect is investigated in the **Paper I**.

In Figure 1 the saturation ratio of water is plotted as a function of droplet diameter in the case of a pure ammonium sulfate particles with dry diameter of 50 nm. This figure is called the Köhler curve. For simplicity, the surface tension of pure water is assumed throughout the droplet size range.

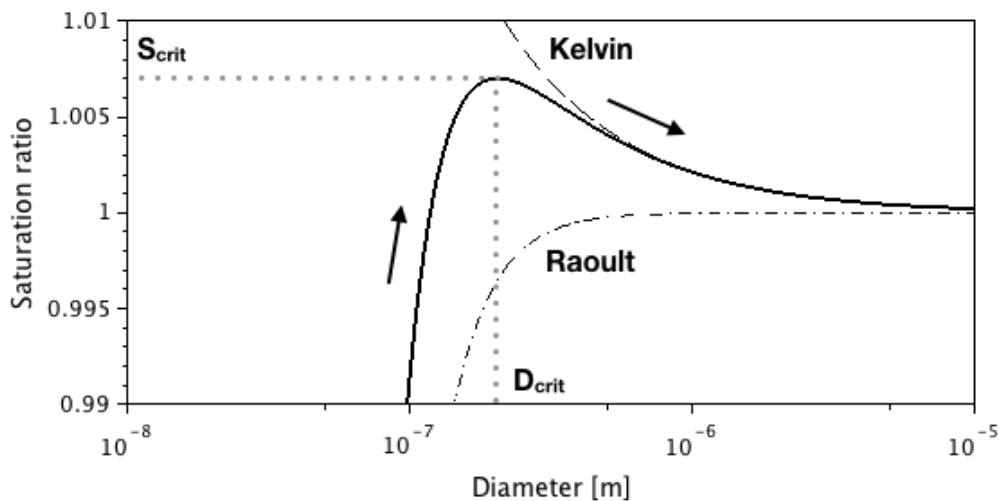


Figure 1. Saturation ratio as a function of droplet diameter according to Köhler theory.

The Köhler curve has a maximum that is called the critical point. The corresponding diameter is called the critical diameter  $d_{crit}$  and the saturation ratio is so-called critical saturation  $S_{crit}$ . Particles can grow by water uptake in sub-saturated conditions. This growth is controlled by the hygroscopicity of the particle. If the saturation ratio is decreased, the droplet will shrink to reach the equilibrium. When the critical point is crossed the particle starts to grow through condensation of water, and if the saturation ratio of water is kept above 1, the droplet can grow without limits.

The Köhler equation describes the cloud droplet formation in the low supersaturation range for particles in the cloud condensation nucleus (CCN) size range of about larger than 50 nm in diameter (e.g. Nenes *et al.* 2002, Pajunoja *et al.* 2015, **Paper II**). When considering the working principle of a Condensation Particle Counter (CPC), the Kelvin term can be used to give the first estimate of the critical supersaturation that is required for a given vapor to activate and grow aerosol particle of a given size. This assumption is quite accurate for the particles with diameter above 10 nm if the aerosol particle is not soluble to the working fluid. Below 10 nm one must take the heterogeneous nucleation probability into account (Kulmala *et al.* 2007). Figure 2 shows the critical diameter as a function of saturation ratio for diethylene glycol both according to the Kelvin equation and when accounting for the heterogeneous nucleation probability (**Paper III**). It can be seen that the critical diameter is overestimated in the sub – 10 nm region by the Kelvin equation. This has been shown already by Winkler *et al.* 2008. This makes it possible to activate, grow and eventually count particles down very small sizes as shown in the **Paper III**.

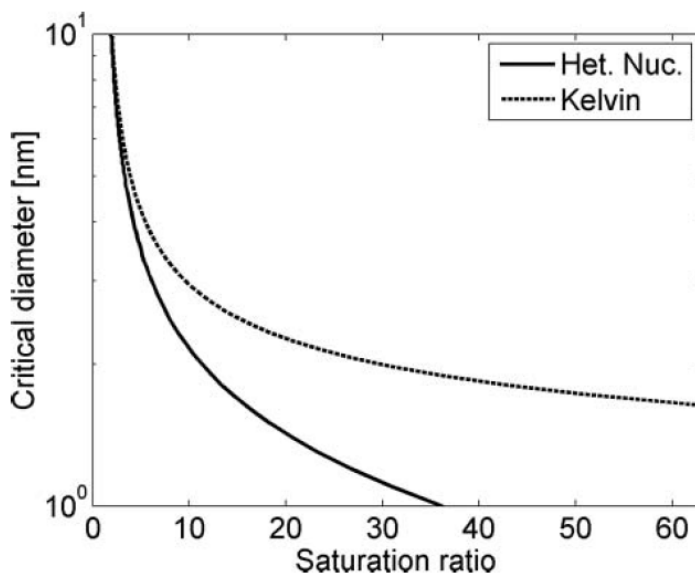


Figure 2 The critical diameter as a function of saturation ratio calculated using the Kelvin equation and heterogeneous nucleation theory (Kulmala *et al.* 2007a).

## 2.1 Surface tension measurement of aqueous solutions using capillary rise technique

In **Paper I** we investigated the effect of surface tension to the cloud droplet formation. A solution of succinic acid, sodium chloride and water was chosen as a model mixture. Sodium chloride is commonly found in atmospheric aerosol originating from sea spray (e.g. Dusek *et al.* 2006, McFiggans *et al.* 2006). In addition to salt, in coastal region the aerosol can have a notable amount of organic acids that is transferred to the aerosol phase through condensation of oxidation products of organic gases (e.g. Kulmala *et al.* 2004a, Tunved *et al.* 2007). The surface tensions were measured using a capillary rise technique. The solution inside a thin capillary rises due to capillary force. The surface tension can be calculated from the height by using following a formula (Bikerman, 1947):

$$\sigma = \frac{1}{2} \rho g r \left( h_0 + \frac{r}{3} \right), \quad (2)$$

where  $\rho$  is the density of the solution,  $g$  is the acceleration due to gravity,  $r$  is the radius of the capillary tube and  $h_0$  is the height of the solution column inside the capillary tube. A simple apparatus was designed and build to measure capillary rise of the chosen solution, using two different capillary tubes with a known radius and a modified caliper that was used to measure the height of the solution column. The whole apparatus was temperature controlled using a thermostatically controlled liquid reservoir (Lauda RC6 CS). To test the instrument, first binary solutions of both water and succinic acid and water and sodium chloride were measured and the results were compared to the literature values. In both cases, a good agreement was found. In Figure 3, the surface tension measurements are plotted as a function of mole fraction of sodium chloride ( $x_3$ ), and mole fraction of succinic acid ( $x_2$ ) at 25°C. It can be seen that sodium chloride increases the surface tension linearly and the succinic acid decreases it already in very dilute solutions.

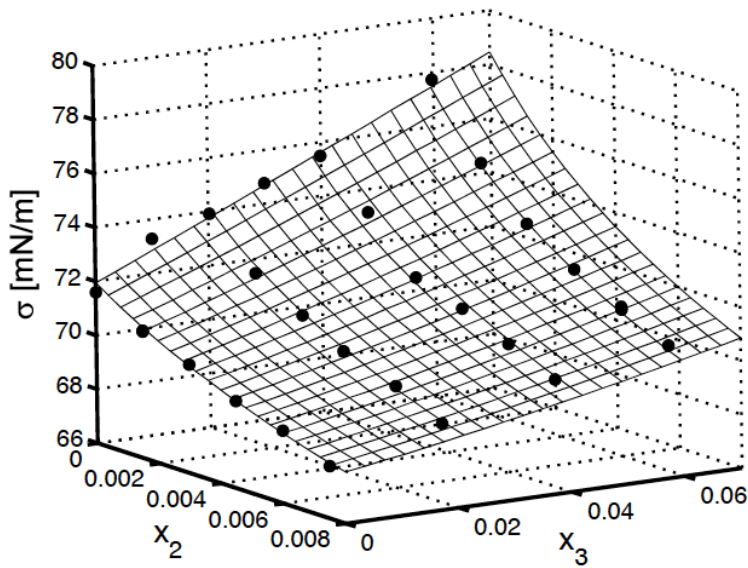


Figure 3. Surface tension of ternary solution of succinic acid, sodium chloride and water. The fitted parametrization is plotted as a mesh surface.

To make the usage of these results easier, a parametrization was made using the surface tension measurement data. The fit was interpolated to the surface tensions of pure sodium chloride and succinic acid that can be found from the literature. This was done by using the equation in Chunxi *et al.* 2000, relating the surface tension to the interaction energies between the solution molecules. In this work, this parametrization was used to investigate the effect of surface tension on cloud droplet formation utilizing a numerical cloud model. We found out that the surface tension effect was the highest with high updraft velocities in warm clouds.

## 2.2 Cloud Condensation Nucleus counter and Hygroscopicity Tandem Differential Mobility Analyzer

The effect of aerosol particles on cloud formation is still one of the largest uncertainties in the estimations on the effects of anthropogenic sources on the changing climate. This is why the cloud droplet activation of the aerosol particles need to be understood better. The activation of aerosol particles to cloud droplets can be measured using a cloud condensation nucleus counter (CCN counter) (e.g. Leitch and Megaw, 1982), where the aerosol is introduced into a controlled supersaturation of water vapor. This condition mimics the environment, which the aerosol particles face, when warm liquid cloud forms. The CCN counter used in this study was a diffusion type counter developed by Droplet Measurement Technologies Inc. (Roberts and Nenes, 2005). Inside the CCN counter the aerosol is led through

a column where walls are constantly saturated with water and there is a continuous increasing temperature gradient in direction of the flow. This creates a constant supersaturation in the centerline of the column (Roberts and Nenes, 2005). After the column, the activated droplets are counted with an optical particle counter. The particles that are activated and grown to cloud droplets are the ones that had initially diameter above the critical diameter  $d_{\text{crit}}$  shown in the Figure 1.

In the **Paper II**, we used the CCN counter to investigate activation of the aerosol particles in boreal forest environment in Hyytiälä, Finland. The measured CCN concentrations were compared with the total particulate concentrations in order to determine the activated fraction. The measurements were also compared with the aerosol size distribution data in the size range from 3 nm to 1  $\mu\text{m}$  detected using a Differential Mobility Particle Sizer (DMPS, Aalto *et al.*, 2001). By assuming that the activation probability of the particles behaves like a step function as a function of particle size, the critical diameter ( $d_{\text{crit}}$ ) can be calculated. However, this assumption isn't completely accurate due to differences in the chemical composition of the particle population. Therefore, in the same size channel, you can have both particles that are highly hygroscopic or hydrophilic based on their chemical composition. This information can also be used to probe the chemical composition of the particles, as shown in Cerully *et al.* 2011.

In this study, a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) was used to measure the hygroscopicity (ie. the affinity of material to uptake water) of the particles in sub-saturated conditions. In the HTDMA monodisperse particles, selected using an aerosol neutralizer and a DMA in RH% below 20%, are introduced to a controlled sub-saturated water vapor (Liu *et al.* 1978; Hämeri *et al.* 2001, Ehn *et al.* 2007). The hygroscopic growth of the particles in that environment is then measured by using another DMA. The second DMA was kept in the same elevated RH% to ensure that the particles don't shrink inside the classification region. The hygroscopic growth of the particles can be used to estimate also the chemical composition of the particles. For example, the aerosol particles formed from sea spray consist mainly of sodium chloride and thus grow easily due to water vapor uptake compared to for example particles that consist mainly of organic compounds (Nenes *et al.* 2002, Duplissy *et al.* 2008). The hygroscopicity can also be used to study the aging of the atmospheric particles. The aged particles that have already experienced variety of humidity conditions and oxidation in the atmosphere are more hygroscopic than freshly formed aerosol particles and their hygroscopicity is higher than for a freshly formed particle (e.g. Asa-Awuku *et al.* 2009, Pajunoja *et al.* 2015).

The critical diameter can be estimated according to the  $\kappa$  - Köhler theory (Petters and Kreidenweiss, 2007). In the  $\kappa$  - Köhler theory the hygroscopicity of the particle is expressed using  $\kappa$ , that is related to the water activity in Köhler equation (Equation 1) as follows:

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w}, \quad (3)$$

where  $V_s$  is the volume of the dry particle and  $V_w$  is the volume of the wet particle. In  $\kappa$  - Köhler theory the surface tension of pure water is used as suggested by Petters and Kreidenweiss (2007). This means that basically all the effects that are due to the chemical composition of the original dry particle is considered to be accounted with the single  $\kappa$  value. Using the Equation 1 and replacing the water activity according to Equation 3, for a known  $\kappa$  value, the critical point can be estimated. In this study, four different dry sizes were used in the HTDMA measurements; 110 nm, 75 nm, 50 nm and 35 nm. The relative humidity was kept constant  $90 \pm 1.5\%$  at constant temperature  $19 \pm 0.5^\circ\text{C}$ . For each dry size, the  $\kappa$  value can be different and in the analysis of the critical diameter the  $\kappa$  value of the measurement point nearest to the critical value was chosen.

### 2.3 Particle Size Magnifier

In order to understand gas to particulate phase transition, the freshly formed aerosol particles need to be detected. The size of these particles is in the range of 1-2 nm in diameter (Kulmala *et al.* 2007b). Before starting to work on this thesis the lowest limit for commercial particle detectors was 3 nm in particle diameter for electrically neutral particles (Stolzenburg and McMurry, 1991). For electrically charged particles, a Faraday cup electrometer can be used to measure the particles down to 1nm in diameter (e.g. Flagan, 1998, Hirsikko *et al.* 2011). The challenge with that technology is linked to the charging of the particles; most of the particles in the sub-3nm size range are not naturally charged in the atmosphere and their charging probability is very small (e.g. Wiedensohler, 1988). Some work was already done in order to tune the commercial condensation particle counters to measure also smaller particles, e.g. Sipilä *et al.* 2009 and Lehtipalo *et al.* 2009. Also, expansion type condensation particle counters capable of detecting particles in the sub-3nm size range were introduced by Wagner *et al.* 2003. In **Paper III** a Particle Size Magnifier (PSM) was introduced to tackle this measurement challenge.

However, the development towards the PSM presented in **Paper I** did not start from scratch. The first PSMs were introduced already by Kogan and Burnasheva in 1960 and Okuyama *et al.* in 1984, and further developed by Seto *et al.* (1997), Gamero-Castaño & de la Mora (2000) and Sgro *et al.* (2004). They used a mixing type design to grow particles with condensation. Inside the mixing section, highly saturated and heated aerosol-free flow is mixed with the sample flow. The mixing was supposed to be turbulent. The main benefit with the mixing type design is that the saturation ratio of the working fluid can be changed quickly by changing the mixing ratio of the saturated flow and the sample flow. This changes the critical diameter. The mixing inside the PSM is turbulent and the inlet flow rate is elevated compared to a conventional CPCs, reducing the diffusional losses of the smallest particles. The turbulent mixing is usually assumed to be adiabatic in the theoretical calculations of saturation ratios inside the PSM. A conventional butanol based laminar flow CPC can be used after the PSM to further grow and count the particles (**Paper III**).

The condensing fluid used inside any CPC defines the smallest size that can be activated and grown into detectable sizes. For this work, we also chose diethylene glycol (DEG) as the working fluid based on works by Magnusson *et al.* 2003 and Iida *et al.* 2009. The main properties that Iida *et al.* 2009 optimized were the surface tension and the vapor pressure of the working fluid. The relatively high surface tension and low vapor pressure of DEG are beneficial for heterogeneous nucleation. The effect of surface tension can also be understood from the Kelvin equation (**Eq. 1**); two different sized particles can activate with the same supersaturation, if the surface tension is higher for the smaller particle. Even though DEG can grow really small particles without homogeneous background, the low vapor pressure prevents the particles to grow to optical sizes with reasonable growth time. Thus, we chose a dual stage condensation design, first with DEG where PSM can grow the particles up to about 90 nm is diameter (**Paper III**), followed by n-butanol CPC that grows particles up to optical sizes very rapidly.

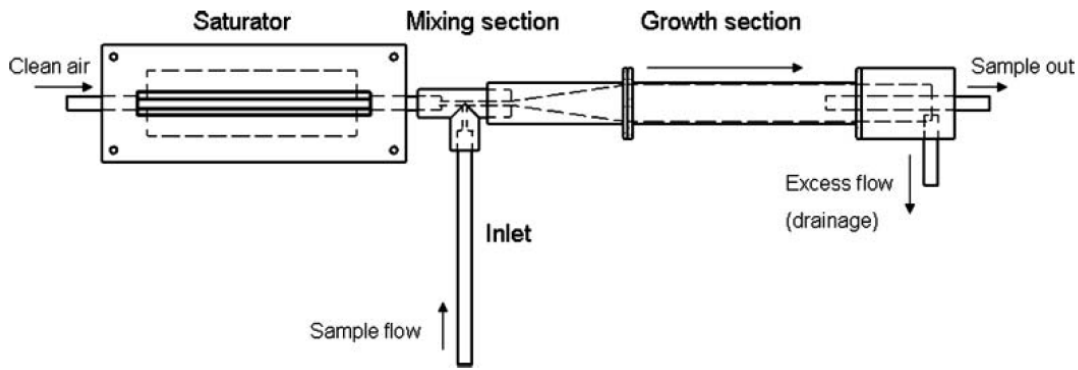


Figure 4. A schematic view of the particle size magnifier developed in this thesis (**Paper III**).

When designing the PSM we aimed for adiabatic turbulent mixing. The Péclet ( $Pe$ ) number describes the ratio of advective transport and diffusive transport.  $Pe$  inside the mixing section is between 1549 and 1128 and it shows that the heat conduction can be neglected, when calculating the saturation fields. At the same time the Reynolds ( $Re$ ) number, describing the ratio of inertial forces and viscous forces in the flow, is between 5587 and 3835 showing that the flow is turbulent. However, Gamaro-Castaño (1999) already showed that the assumption of turbulent mixing is not true with low flow rates. This makes the saturated vapor to cool before the turbulent mixing and thus can favor homogeneous nucleation of the working fluid. Also, the behavior of the DEG saturation ratio doesn't act like in a similar manner in the PSM as it does in a truly mixing type CPC. Kangasluoma (2016) showed in his thesis that the highest saturation ratio is actually achieved inside the growth tube of the PSM and thus higher saturated flow rate always results in lower cut-off diameters (consequently higher saturation ratios). In principle, this is the reason why also in previous studies the



growth section needed to be heat regulated and cooled (Gamero-Castaño *et al.* 2000, Seto *et al.* 1997, Sgro *et al.* 2004).

In the present commercial version of the PSM (Airmodus A10) the inlet temperature is slightly heated up to 40°C in order to favor the activation inside the growth tube of the PSM. The saturation ratio behaves in a much more controlled way as a function of the saturator flow rate inside the growth tube compared to the mixing section than in the version presented in **Paper III**. The saturator temperature is in the range of 75°C and the growth tube is at 3°C. In the Paper III the saturator temperature was set to 75.5°C. Also, the saturator flow rate now ranges from 0.1 to 1.3 lpm for a wider detected particle size range.

## 2.4 Calibrating particle counters for particle size range of 1-3nm

Aerosol particle counters need to be calibrated and validated to properly interpret the measurement results (Stolzenburg & McMurry, 1991, McMurry, 2000, Owen *et al.* 2012, Kangasluoma *et al.* 2014 and Kangasluoma, 2016). This holds true for the response to different size and chemical composition of the particles, number concentration or even sample gas conditions and composition. In the case of atmospheric measurements, the aim is to validate the counting behavior of the instrument with different particle composition in particle sizes ranging from 1 nm to 1000 nm and particle concentrations ranging from 1 #/cm<sup>3</sup> to about 100 000 #/cm<sup>3</sup>.

In **Paper III** we concentrated on production of sub 3 nm ions that were used for calibration of the particle counters. The ions were chosen due to lack of size classification instrumentation for electrically neutral particles. For sub 3 nm particle generation, there are multiple suitable methods for example evaporation condensation method, hotwire generator, electrospray, flame combustion and spark discharge (Ude and de la Mora 2005, Peineke *et al.* 2006, Scheibel and Porstendorfer 1983, Wang *et al.* 2016). The main challenges in the producing such small particles are to keep them from growing too quickly and to have their chemical composition homogeneous and well known. Contamination from the generation or classification system can alter the detection behavior of the instrument under calibration. To give a perspective for contaminant levels, for example 5.0 nitrogen gas can be already be considered as pure with a purity of 99.999%, but in that impurities can be present with a mixing ratio of 1 ppt, which consist of e.g. sulfur dioxide (SO<sub>2</sub>) in measurable quantity (<http://www.praxair.com/-/media/documents/specification-sheets-and-brochures/gases/nitrogen/nitrogen-n2-spec-sheet-ss-p4631.pdf?la=en>). In normal atmospheric conditions one ppt is still about 3\*10<sup>7</sup> SO<sub>2</sub> molecules in cm<sup>-3</sup>. This can be considered as high amount of contaminant, if SO<sub>2</sub> is converted to sulfuric acid and eventually to 1-2 nm clusters / particles during the particle production process, where the nitrogen is considered to be inert carrier gas.

Particle counter calibration is conducted using monodisperse aerosol particles / clusters (Ude & de la Mora, 2005, Attoui *et al.* 2013, Meisser *et al.* 2015a). The monodisperse

particles are produced by selecting mono-mobile ions using a high - resolution differential mobility analyzer (DMA) with resolving power of about 20 (Ude & de la Mora, 2005, **Paper IV**). Here the resolving power is defined as the ratio of peak mobility and full width at half maximum of a truly mono-mobile sample, like a single molecule. To reduce the effects of the contaminants the DMA was operated in a closed loop configuration with a heat exchanger and a High Efficiency Particulate grade filter in the loop. The High flow DMA uses sheath flow rates in the order of  $10^2$  liters per minute, and thus the flow rate monitoring is quite difficult. Because of this, the DMA is calibrated for every calibration measurement using mobility standards with well-known mobilities such as molecules and clusters from tetraheptyl ammonium bromide (THAB) (Ude & De la Mora, 2005). To verify the cleanliness of the sample for THAB, the measured mobility spectrum was compared to the one reported by Ude & De la Mora (2005). To verify the chemical composition of the produced particles, an Atmospheric Pressure Interface Time Of Flight Mass Spectrometer (API-TOF) was used (Junninen *et al.* 2010). It can be used to measure the mass spectrum (mass to charge spectra) of the calibration clusters in size range from 1 – 2 nm in mobility equivalent diameter (about 100 to 2000 m/z) in atmospheric pressure.

## 3 Results

### 3.1 The effect of the surface tension on CCN activation

The effect of surface tension of atmospherically relevant mixture of succinic acid, sodium chloride and water on cloud droplet formation was studied using a cloud model. In the surface tension measurements, succinic acid was found to lower and sodium chloride to increase the surface tension of the aqueous solution as expected. A parametrization with an extrapolation to pure succinic acid and sodium chloride surface tensions was developed using the measurement data. The model used was a box model simulating interactions of aerosol population and water vapor in an adiabatically rising air parcel (Anttila *et al.* 2002). The comparison was done between the simulations using the surface tension of pure water and the surface tension of the ternary solution under investigation. The aerosol size distribution used in the simulations was bimodal consisting of Aitken mode with a mean diameter of 45 nm and an accumulation mode with a mean diameter of 170 nm. The size distribution was a typical distribution found in marine environment (Heintzenberg *et al.*, 2000). The aerosol population was assumed to be internally mixed inside the parcel. It was also assumed that the aerosol particles were already been under a variety of humidity conditions in the air and thus solubility of the substances in water was neglected. In this study, the focus was on warm clouds and ice nucleation was not taken into account. For example, in latitudes of the northern Europe most of the clouds form through ice nucleation due to the low temperatures in the upper troposphere and stratosphere (Rosenfeld *et al.* 2014).

In Figure 5, activated fraction for three different updraft velocities are presented as a function of succinic acid mole fraction. It can be seen that the difference in activated fraction between model runs with surface tension of pure water versus model runs with the surface tension parametrization developed in this study is the highest with high updraft velocities and with high succinic acid mole fractions. The effect of updraft velocity can be explained by the decreasing activated dry size with increasing updraft velocity. This increases the Kelvin effect, which takes into account the surface tension. The effect of increased succinic acid is due to decrease in surface tension of the droplet. With the lowest updraft velocity of 0.1 m/s there is no clear difference between the activated fraction simulated using the surface tension of water and the surface tension of the ternary mixture of succinic acid, sodium chloride and water. With the low updraft velocity, only low supersaturation with respect to water is achieved and thus only the bigger particles get activated. For the bigger particles the Kelvin term, that accounts for surface tension, is smaller.

The results show that the surface tension starts to affect the cloud droplet activation with the updraft velocities above 0.5 m/s. The updraft velocities above 0.5 m/s are typical in convective clouds and thus the result suggest that the surface tension effect needs to be taken into account in cloud droplet activation calculations. Also, in marine environment, the clouds have usually lower number of cloud droplets and thus they are more sensitive to changes in cloud droplet concentration (Nenes *et al.* 2002). As a summary, this study shows that the

chemical composition of the seed particle affecting the surface tension of the droplet can have an effect on cloud formation in marine environment, and eventually affecting the radiative forcing through aerosol-cloud interactions.

It has to be mentioned that in the cloud model, no surface partitioning in the droplet was accounted for. This might lead to underestimation of critical supersaturation shown for example in Prisle *et al.* (2008). Furthermore, Ruehl *et al.* (2016) showed that even the surface partitioning models in some cases fail to estimate the droplet activation when there are organic species in the particle, and that a new interfacial mechanism is needed to explain the surface tension depression. Rather surprisingly, assuming the surface tension of pure water for the mixture results almost similar critical supersaturations for the particles consisting of a surfactant, when compared to results when accounting for both bulk surface tension of the mixture and the partitioning. So, in most cases just using Köhler theory with the surface tension of pure water might give accurate enough critical supersaturations. In our model mixture, there are no surfactants and thus this assumption might not be valid.

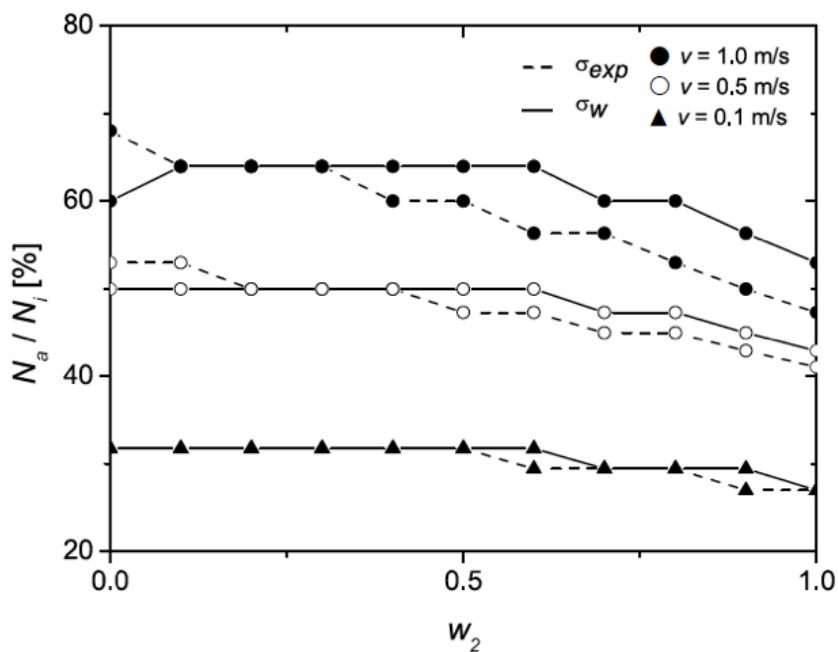


Figure 5. Activated fraction of aerosol particles as a function of the molar mass fraction of succinic acid for three different updraft velocities.

### 3.2 Atmospheric measurements of CCN in boreal forest

The CCN concentrations were measured at SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations, Hari and Kulmala 2005) station in Hyytiälä central Finland (61°51'N, 24°17'E, 181m above sea level). The environment is boreal coniferous forest. The SMEAR II station has been operational from 1990s, and there are hundreds of different measurement instruments recording data continuously. It is one of the most comprehensive atmospheric measurement stations in the world.

The CCN counter and HTDMA measurement were conducted between July 2008 and June 2009. In Figure 6, critical diameters from both measurement methods are plotted as a function of the supersaturation of water. It can be seen that the values measured with the CCN counter and the HTDMA agree surprisingly well. According to the k-theory, the activation behavior of the particles can be estimated by using single k value. In this study, the mean k-value was 0.18. In the same figure, laboratory measurements by Duplissy *et al.* (2008) for pure alpha-pinene and trimethylbenzene particles are plotted for comparison. It can be seen that for both of these pure substances the critical diameters for any given supersaturation are higher compared to our measurements. For the lower supersaturations, the critical diameter values get closer to the theoretical value for ammonium sulfate but for the higher supersaturations the critical diameters are clearly higher indicating that for the smaller particles, the fraction of organic substances in the particles might be higher. This has been shown for the Aitken mode particles for example by Hämeri *et al.* 2001, Petäjä *et al.* 2005 and Ehn *et al.* 2007. The increased fraction of organics in the Aitken mode was also shown by Allan *et al.* 2005 using aerosol mass spectrometry. This goes well in line with the minimum and maximum k values measured from ozonolysis of different mixtures of monoterpenes by Engelhart *et al.* (2008) measured in laboratory.

Massoli *et al.* 2010 and Pajunoja *et al.* 2015 presented laboratory measurements using the CCN counter and HTDMA for secondary organic aerosol (SOA) particles with different oxidation states. SOA particles are formed in the atmosphere through oxidation of organic vapors. They both showed that  $\kappa$  - values achieved from measurements in sub- and supersaturated water vapor agree nicely, when oxidation state of the SOA particle is high, but when measuring particles with low O:C ratio the HTDMA measurements give lower  $\kappa$  values compared to the CCN counter. This discrepancy between CCN counter and HTDMA measurements was already shown by for example Petters and Kreidenweis, 2007 and Duplissy *et al.* 2008. Based on this knowledge, the measurements in **Paper II** indicate that the fraction of organics is high and the oxidation state of the particles is high, but when looking at the monthly averages of critical diameters at 0.4% supersaturation in **Figure 7** it can be seen that there are discrepancies between critical diameters achieved using CCN counter and HTDMA. Especially when looking at the critical diameters during spring and summer, the critical diameters estimated from HTDMA and size distribution measurement data give higher values. This indicates that during the period, when emissions of organic vapors from vegetation are high, the oxidation state might be lower and thus hygroscopicity of the particles is lower in sub-saturated water vapor. Similar results were also measured in laboratory

study for organosulfate derived from limonene by Hansen *et al.* 2015, where they found that  $\kappa$  – values achieved with CCNC were higher compared to values calculated from the HTDMA data. The comparison between the CCN counter and the HTDMA data is not perfect in this study due to measurement gaps of the HTDMA, but shows that also HTDMA data can be used to estimate the CCN concentrations.

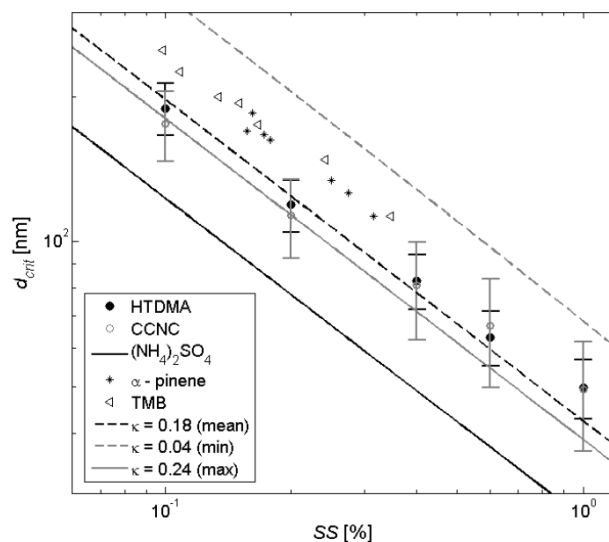


Figure 6. Yearly averages of the critical diameters measured with the CCN counter and the HTDMA compared to literature data of sulfuric acid, alpha-pinene and trimethylbenzene (TMB) are plotted as a function of supersaturation %. Also, theoretical values according to the k-Köhler theory are given for k values 0.18 (the mean value from this study), and for minimum (0.04) and maximum (0.24) values for organic aerosol form the literature (Engelhart *et al.* 2008).

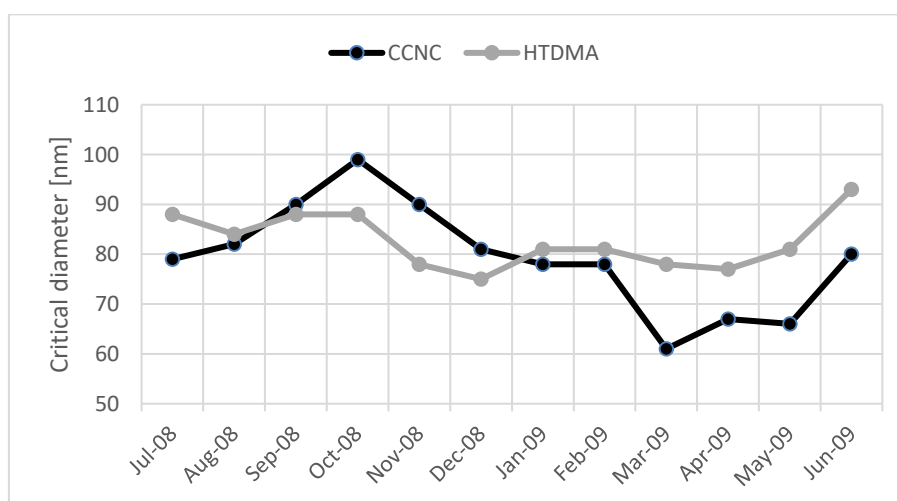


Figure 7. Monthly averages of critical diameters achieved using CCN counter and HTDMA corresponding to 0.4% supersaturation.

At the SMEAR II station, new particle formation events have been recorded around every fourth day of the year, with maximum frequency during the spring time (Kulmala *et al.* 2001, Dal Maso *et al.* 2005, Vana *et al.* 2016). Some of these particles can grow to sizes where they can act as cloud condensation nuclei (Kerminen *et al.* 2012, Paramonov *et al.* 2015). One of the aims of this thesis was to investigate the effect of these events to the CCN concentrations. In the Figure 7 the diurnal variations of mean CCN concentrations during two consecutive days are plotted for each measured supersaturation for both event and non-event days. During an event day, a clear new particle formation and growth is observed and during non-event day no particle formation or growth is observed. In this study, the event day cases are the ones when during the first day, a new particle formation event occurred. For low supersaturations, ie. large critical diameters, the diurnal trend of the mean CCN concentration for both event and non-event days is about the same. In the case of supersaturation of 0.1% the absolute concentration for event days is lower indicating that during an event day the concentration of larger particles is lower. This is an indication of lower condensation and coagulation sink that has been shown to enhance the new particle formation event probability (Hyvönen *et al.* 2005; Dal Maso *et al.* 2007). For the higher supersaturations, the diurnal variation of CCN mean concentration during event day can clearly be seen. There is an increasing trend in the concentration indicating that the particles produced during the new particle formation event grow to sizes where they can act as CCN. This implies that the new particle formation events can produce particles at ground level that have an effect to the climate through cloud formation, when transported aloft. Also, recent study by Fan *et al.* (2018) showed that ultrafine particles already in the sub 50 nm size range can significantly boost convection and precipitation in storm clouds showing that new particle formation can have an effect on clouds already quite early in their growth to CCN sizes.

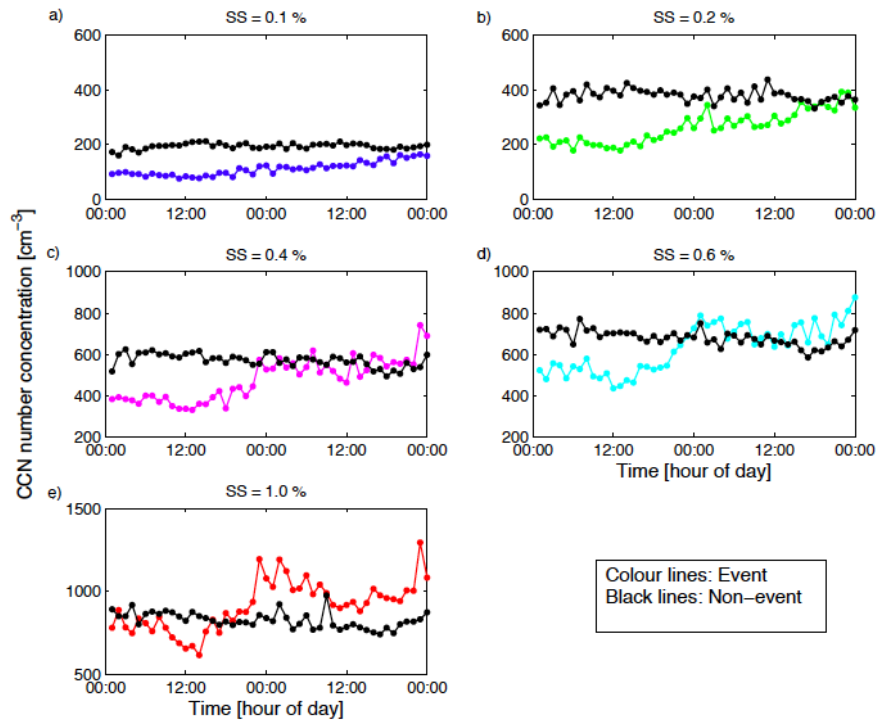


Figure 8. Mean CCN number concentration for different supersaturations calculated from data of two consecutive day classified to event and non-event cases. The event case is when during the first day, a new particle formation event was observed.



### 3.3 Condensation Particle Counter calibrations in sub 3 nm size range

Figure 9 presents an example of a PSM calibration measurement result, where PSM efficiency for a given mono-mobile particle is plotted against the PSM saturator flow rate, which indicates the supersaturation inside the instrument. The PSM efficiency consists of four terms: 1) the activation efficiency and 2) penetration efficiency of the PSM, and the same efficiencies of the CPC used in the final counting. Inside the PSM, the particles are grown up to almost 100 nm in diameter (**Paper IV**) and thus it can be assumed that the CPC counts the grown DEG droplets with its maximum counting efficiency with very low diffusion losses. The lower cut-off for the CPC used in these measurements were about 6 nm. Maximum counting efficiency of a typical laminar flow CPC is in the range of 90 to 100 % (Yli-Ojanperä *et al.* 2012). Therefore, the overall counting efficiency is dominated by the activation and efficiency and the transport efficiency of the PSM.

The efficiency here is applicable only for the particle composition used; in this case NiCr-oxide. In **Paper IV** we investigated how the PSM behaves with different types of particles.

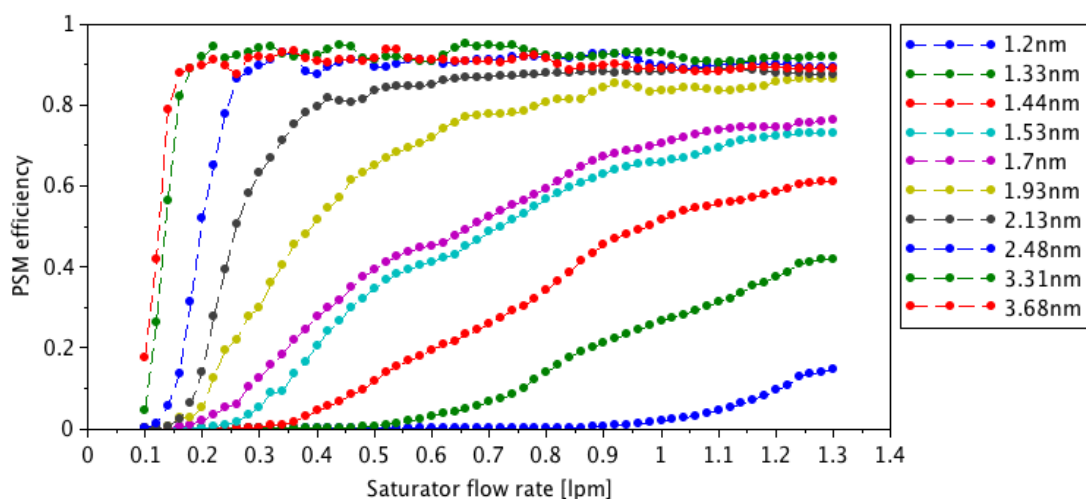


Figure 9. PSM efficiency for different size of monodisperse NiCr-oxide particles as a function of the saturator flow rate.

The PSM efficiency data can be used to invert PSM data to a size distribution in the range of about 1 to 4 nm in diameter when the PSM is used in constant scanning mode, where the saturator flow rate of the PSM is changed constantly (Lehtipalo *et al.* 2014). In Figure 10 **Figure 10**, size distribution of a laboratory test measurement is presented as a function of time. In this data, the PSM is challenged with different size of monodisperse particles and also with small air ions produced by a radioactive Americium source. The data is inverted to 10 size bins according to the step-wise inversion method (Lehtipalo *et al.* 2014). With this specific instrument and calibration, the PSM is capable of measuring particle size distribution from about 1.3 nm up to 4.3 nm in diameter. Above 3-4 nm the sizing accuracy of

the PSM decreases rapidly. The reason for that can be seen in Figure 9, where the two biggest particles are almost out of the instruments dynamic size classification range. The sizing accuracy of a scanning PSM was also studied by Kangasluoma *et al.* 2015. They found good agreement between the size distribution achieved using the simple step-wise inversion and measured using a high flow DMA and electrometer system in the size range from 1.2 to 2.8 nm. This scanning function of the PSM is already widely used in the literature (for example, Kirkby *et al.* 2011, Kulmala *et al.* 2013, Kontkanen *et al.* 2017 and Wang *et al.* 2017). The main benefit compared to other size distribution measurement methods is the high sensitivity for both electrically neutral and charged particles (Kangasluoma *et al.* 2015).

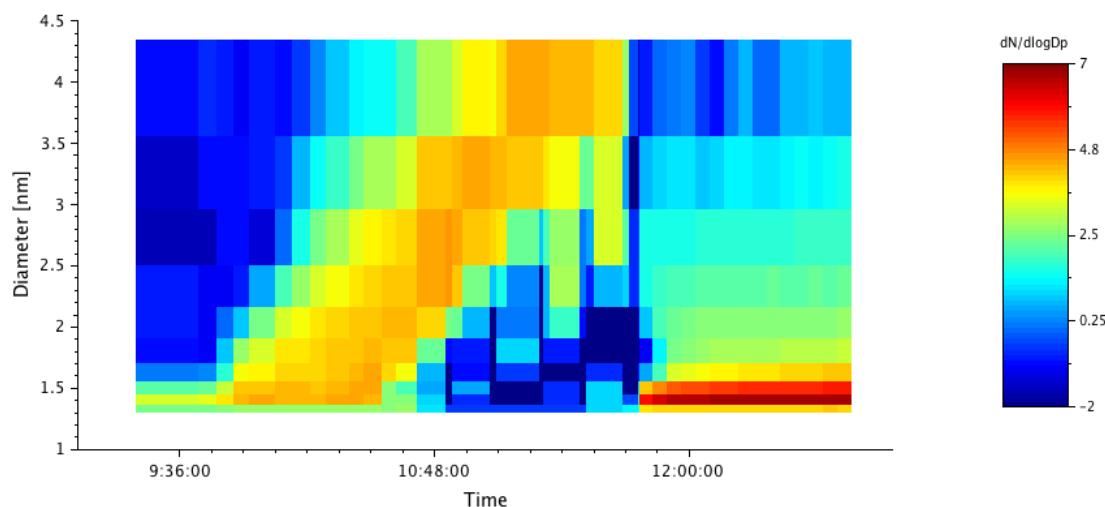


Figure 10. An example pf time series of aerosol particle size spectra in the range of 1.3 to 4.3 nm measured using a combination of PSM and butanol CPC.

In Figure 11, the measured detection efficiency is presented for particles with different chemical composition and electrical charge state. In this case both, the PSM efficiency and the detection efficiency of the CPC downstream is taken into account. Also, it has to be noted that the measurements go only up to 2.5 nm and thus the total detection efficiency is lower than for a typical PSM + CPC system. The PSM settings are kept the same for all measurements. Both chemical composition and the sign of the charge clearly affect the detection efficiency of the PSM. The effect of the chemical composition on CPC detection efficiency has also been reported for example in Petäjä *et al.* (2006), Kulmala *et al.* (2007a), Giechaskiel *et al.* (2011) and Mamakos *et al.* (2013). This effect is known to be dependent on the working fluid used by the CPC. For example, water CPCs are more capable of activating and detecting particles that are water soluble (Petäjä *et al.* 2006). Positively charged particles seem to activate with similar saturator flow rates, also reported by Winkler *et al.* (2008) and Kangasluoma *et al.* (2015). For negatively charged there is much more difference in the onset of activation, although they activate with lower saturator flow rates, ie. saturation ratios of DEG than the positively charged. In the recent studies for example by Steiner *et al.* 2014, Meisser *et al.* 2015b, Kangasluoma *et al.* 2015 and Li *et al.* 2017, they

show that the chemical composition of charged particles depends on the sign of the charge. This indicates that the apparent effect of charge to the detection efficiency of the PSM might actually not be due to the sign of the charge but the chemical composition. Positively charged particles are charged by charge carriers that is likely to be an organic compound and organic compounds are shown to activate poorly using DEG as condensing fluid (Kangasluoma *et al.* 2014).

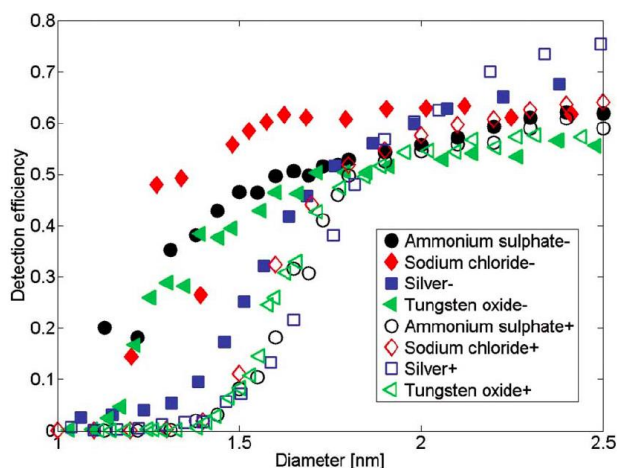


Figure 11. The PSM efficiency curve for a set of monodisperse NiCr – oxide particles as a function of the PSM saturator flow rate.

Relative humidity was found to have an effect on the activation efficiency of the PSM (**Paper IV**). With increasing relative humidity, the detection efficiency of the PSM increased. It can be argued that the losses inside the PSM will not be affected by the relative humidity and thus the measured effect is due to enhanced activation of the particles. However, the process is not yet well understood, and the role of contaminants introduced by the added water vapor needs to be further investigated.

Lauri Ahonen investigated the effect of water vapor to the PSM activation efficiency in his master’s thesis (Ahonen, 2016). He found out that adding water to the DEG used as the working fluid also enhanced the activation efficiency of the PSM up to mass fraction of 40% for water. This positive effect on activation seems not to have anything to do with water solubility of the particle and is valid for both hygroscopic and hydrophilic particles. The final outcome of the study by Ahonen (2016) was that the relative humidity enhanced the activation efficiency of the PSM up to 0.5 nm when relative humidity ranged from 0-40%. Above 40% the effect seems to level off. The measurements of the activation efficiencies as a function of water content of the sample gas are extremely challenging due to contaminations that the added water vapor will create. In the future, also direct measurements with a mass spectrometer need to be done in parallel.

Figure 12 show aerosol number size spectra together with mass spectra for three different aerosols; ammonium sulfate, sodium chloride and tungsten oxide. The aerosols were produced using tube furnace and in the case of tungsten oxide, with the hot wire generator. The

mass spectra were matched with the size spectra by assuming constant densities for each particle composition. This assumption is quite bold in this size range but serves as a good estimate when comparing these two different measurement methods (Ehn *et al.*, 2011). It can be seen that the mobility diameters and mass peaks coincide nicely, especially in the case of ammonium sulfate. This means that the peaks in the mobility diameter spectrum correspond to a distinct cluster. For ammonium sulfate it was found that the clusters were constructed of series of  $(\text{HSO}_4)_x(\text{NH}_3)_y\text{SO}_4^-$ , where the  $\text{SO}_4^-$  served as the charge carrier. These clusters serve as a very suitable monodisperse calibration particles with a known chemical composition for the any instrument capable of measuring particle in the sub - 3 nm size range.

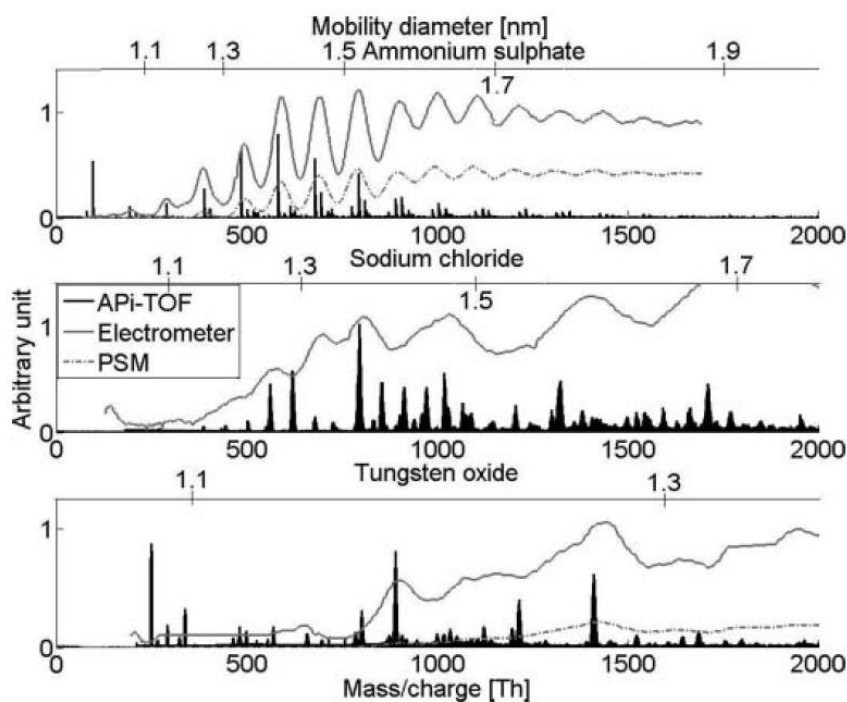


Figure 12. The mass spectra of negative ammonium sulfate, sodium chloride and tungsten oxide presented together with the measured mobility spectra.

### 3.4 Measuring sulfuric acid nucleation using the Particle Size Magnifier

Sulfuric acid is one of the key components of the early steps of atmospheric particle nucleation. It has been shown that the atmospheric particle nucleation rates are dependent on the sulfuric acid concentration (Weber *et al.* 1996; Sihto *et al.* 2006, Riipinen *et al.* 2007, **Paper V**). Sulfuric acid is formed in the atmosphere by the oxidation of SO<sub>2</sub>, which is released in the air for example by different anthropogenic combustion sources, but also natural sources like volcanoes. This makes it an important factor when considering the effects of human actions on the climate. Sulfuric acid nucleation has been studied in laboratory using for example laminar flow tubes (e.g. Viisanen *et al.* 1997, Ball *et al.* 1999 and Berndt *et al.* 2005).

In the atmosphere particle formation rates are measured to be either directly proportional  $J \sim [\text{H}_2\text{SO}_4]$  or proportional to the square of the sulfuric acid concentration  $J \sim [\text{H}_2\text{SO}_4]^2$  (Sihto *et al.* 2006, Kuang *et al.* 2008). The slope  $\text{dln}J / \text{dln}[\text{H}_2\text{SO}_4]$ , in these cases either 1 or 2, defines the number of sulfuric acid molecules needed for a particle to form. In the previous laboratory experiments the slope has been measured to be above 2, all the way up to 21. In the **Paper V** we investigated this clear disagreement between atmospheric data and laboratory experiments.

The growth rate of freshly formed particles in typical atmospheric sulfuric acid concentration of about  $10^7$  molecules in  $\text{cm}^3$  is around 1.5 nm/h (Lehtinen *et al.* 2003). This already indicates that in order to measure nucleation of sulfuric acid in such conditions with a particle counter that has a cut-off around 3 nm or even higher requires measurements with sufficient growth times.

We conducted sulfuric acid nucleation measurements in a laminar flow tube using three different particle counters to detect the nucleated particles; TSI-3025 A with lower cut-off diameter at around 2.5 nm, a Pulse Height Analysis Ultrafine Condensation Particle Counter (PHA-UCPC) with lower cut – off diameter of < 2nm and with the Particle Size Magnifier capable of measuring particles as small as 1.3 to 1.5 nm in diameter (Marti *et al.* 1996, Sipilä *et al.* 2009, **Paper III**). The measurements were conducted in two different laminar flow tubes; at Leibniz Institute for Tropospheric Research (e.g. Berndt *et al.* 2005) and at Finnish Meteorological Institute (Brus *et al.* 2010). The sulfuric acid was produced both in-situ with photolysis and also using liquid samples.

Figure 13 shows the measured particle concentrations within atmospherically relevant sulfuric acid concentration range using the in-situ sulfuric acid production, where the sulfuric acid is formed inside the flow tube by oxidation of SO<sub>2</sub> using UV lamps. The figure shows how the slope is different with different counters. This difference is produced by the different counting efficiencies of the particle counters. Sulfuric acid concentrations of  $10^6$  to  $10^8$  molecules/ $\text{cm}^3$  are too low to grow the particles up to the detection limit of some of the counters and thus the measured slope is too steep. With the PSM a slope of 1.9 was measured agreeing well with atmospheric data. This result underlines the importance of using a

particle counter that is capable of detecting the particles right when they are formed in the size range of 1-2 nm.

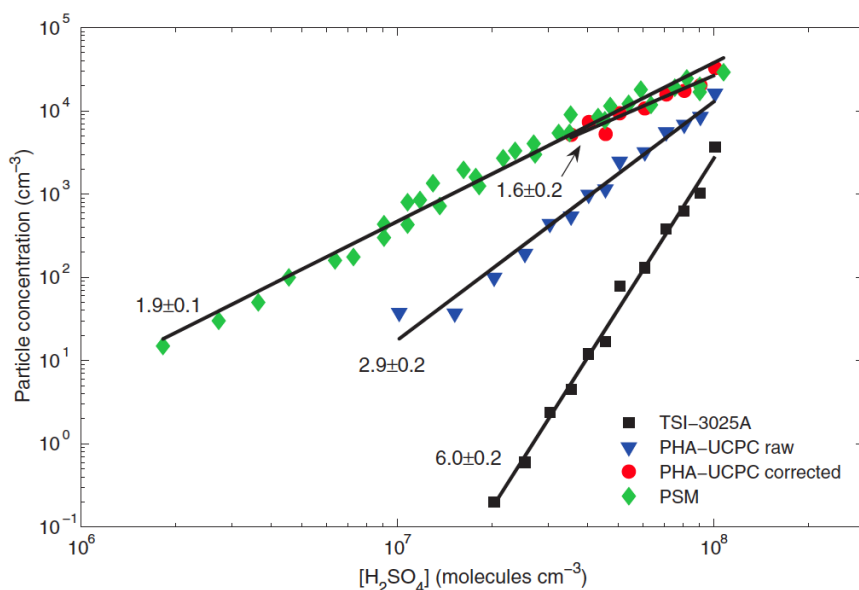


Figure 13. Particle concentrations measured from the tube reactor using three different particle counters with different cut-off diameters as a function of gas phase sulfuric acid concentration.

Due to the lack of direct measurement of particle nucleation in the atmosphere, several different methods to achieve particle growth rates in the sub 3 nm size range have been developed (Kontkanen *et al.* 2016). For example, in some cases the growth rate of sub 3 nm particles has been estimated from the time lag between the rise of sulfuric acid concentration and increase of 3 nm particle concentration (e.g. Sihto *et al.* 2006). Some methods rely on estimating the condensational growth by using the measured concentrations of the condensing vapors (Nieminen *et al.* 2010). Kontkanen *et al.* (2016) showed that by comparing different methods to estimate these sub 3 nm growth rates give quite different results depending on the atmospheric conditions. One obvious reason being the fact that the condensing vapor is not always known. Also, cluster – cluster collisions have significant effect on cluster growth in some conditions (Lehtipalo *et al.* 2016). This discrepancy between the different methods to estimate the growth rates produces high uncertainty to the estimated formation rates, highlighting the need for direct measurement of the particle formation in the atmosphere using instrumentation capable of measuring particles down to about 1 – 2 nm in diameter.

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

**Paper I** presents surface tension measurements of atmospherically relevant ternary mixture of water, sodium chloride and succinic acid. The measurements were conducted using a self-made capillary rise apparatus that was designed and constructed for this work. A parametrization based on the measured surface tensions and literature data was derived and utilized in a cloud model. The results show that especially in convective cloud formation in the case of high updraft velocities, surface tension can have an effect on cloud droplet activation. In this paper, I developed the measurement apparatus, made the surface tension measurements and the parametrization and also ran the cloud parcel model. Most of the paper was written by me.

**Paper II**, CCN concentrations were measured using CCN counter and HTDMA in SMEAR II boreal forest site in Hyytiälä, central Finland. In this paper I was responsible for the CCN counter measurements, part of the data analysis and interpretations as well as contributed to the writing of the paper.

**Paper III** introduces a new Particle Size Magnifier system capable of detecting particles down to molecular sizes. Detection efficiency of the PSM was shown for several different sizes of monomobile particles and a long-term field measurement was conducted. In this paper, I was responsible of the design, construction, calibration as well as the field measurement using the PSM. I also wrote most of the article.

**Paper IV** concentrates to ion production in the sub-3nm size range for particle counter calibration. The PSM, introduced in Paper II, was calibrated using particles with different chemical composition, charge state and with different sample relative humidities. The measurements with the PSM were also compared with mass spectrometer measurements to verify the accurate chemical composition of the particles. In this paper, I participated to the data interpretation and also to the writing of the manuscript.

**Paper V** reports sulfuric acid nucleation experiments in a laminar flow tube using the Particle Size Magnifier and the butanol CPC as the detector. This study investigated the discrepancy between nucleation of sulfuric acid in laboratory experiments and atmospheric data. We successfully showed that critical cluster size (based on classical nucleation theorem) in sulfuric acid nucleation is around 1.2nm in mobility diameter (0.9 in geometric diameter) and how the measurements need to be conducted with particle detectors capable of measuring below 2 nm particle to get the real nucleation rate as a function of sulfuric acid concentration. In this paper, I was responsible of conducting the particle detection measurements using the PSM.

## 5 Conclusions and outlook

In this PhD thesis, the main focus was on activation behavior of atmospheric aerosol particles, both in size range relevant for new particle formation and also in cloud formation. Both of these phenomena have a crucial role in climate through radiative balance. Two different measurement instruments were developed during this work; surface tension measurement apparatus and particle detector system capable of measuring particles in the size range where they are formed from gas to particle conversion. Both of them were utilized to better understand atmospheric new particle formation and its effect on cloud formation.

The surface tension of an atmospherically relevant model solution was measured using a new measurement instrument and a parametrization based on literature data and the measurements was developed (**Paper I**). That parametrization was used in a cloud model in order to understand the effect of surface tension on cloud droplet activation in warm clouds. The biggest effect was found when the updraft velocity was high, with only minor effects for lower velocities. The reduction of surface tension of the solution as a function of the mole fraction of succinic acid enhanced the cloud droplet activation. The parametrization was based on an equation by Chunxi *et al.* 2000, where the fitting parameters are interaction energies of the molecules in the solution. With the high computational power of modern computers, these energies can be calculated using quantum chemistry. For the future studies, fixing some or even all the parameters according to calculated energies and a comparison to the fitted parametrization would give more insight on the phenomena. This computational approach could also give tools for the atmospheric modelers, who need to run models also with particle compositions for which not all the thermodynamic properties are known. In this study, the partitioning of the compound in the droplets surface was neglected, which might lead to overestimation of the surface tension effect (Prisle *et al.* 2010), although for succinic acid and sodium chloride no significant partitioning can be expected.

**Paper II** on this work studied the cloud condensation nucleus activation even further by empirical means. CCN concentration was measured with both the CCN counter and the HTDMA and the data was compared with aerosol particle number size distribution measurements. The main idea was to understand, how new particle formation events affect the CCN concentrations in boreal forest environment. A clear increase on total CCN concentration was found due to new particle formation events. As the growth was slow, the effect was examined during the event day and the day after it. Size segregated CCN measurements show that the effect was first visible in the highest supersaturations (corresponding to the smallest CCN sizes) as could be expected. We also found that in the case of event days, the total particle concentration was lower compared to non-event days. This indicates that the increased condensation and coagulation sink due to pre-existing particles could actually hinder new particle formation like already reported by Hyvönen *et al.* 2005 and Dal Maso *et al.* 2007.

Before the work on this thesis was started, there were no practical means to measure aerosol particle formation as it happened. The particle counters and size classifiers were able to



measure starting from 3 nm, and theoretical estimations were needed to achieve nucleation rates and growth rates during the first steps of the growth (Kontkanen *et al.* 2016). In **Paper III** we developed, build and tested a new particle counter system including Particle Size Magnifier with a conventional butanol - based CPC. The PSM was shown to be capable of activating and growing particles as small as 1.1 nm in electrical mobility diameter. This was also the first time PSM was able to measure continuously in the field conditions. First atmospheric measurements showed good correlation with pre-existing particle detectors, but no significant number of sub 3 nm particles, although these particles are currently monitored all around the world with the same instrument (Kontkanen *et al.* 2017).

The PSM's mixing type design allows measurement of the activation diameter of the particles. For this a thorough calibration for several different particles sizes is needed. In **Paper IV**, the PSM was characterized in laboratory with charged particles with varying chemical composition. The measurements showed that in order to understand the measurement results of the PSM, some knowledge on the chemical composition of the particle is needed and also the relative humidity of the sample air needs to be known. Later it was shown that this also applied to other condensation particle counters capable of measuring in sub 3 nm size range (Kangasluoma *et al.* 2014).

The last paper (**Paper V**) in this thesis reports the first measurements of particle formation in a flow reactor, where the particles are detected as they form. The measurements were conducted for sulfuric acid and compared to the atmospheric data and previous literature data from laboratory measurements. The measurement of particles starting from almost 1 nm in diameter allowed direct measurement of growth rates in the sub 3 nm size range. It could be concluded that in order to grow the formed particles in the size range of conventional particle counters, having cut-off at about 3 nm, the growth time needs to be very long. This is why measurements starting from almost 1 nm are needed to understand the real formation and growth rates. This explains the discrepancy between the measured atmospheric and laboratory nucleation rates reported in literature.

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