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LIFE CYCLE OF A CLOUD CONDENSATION NUCLEUS,
CCN

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Academic dissertation

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Life cycle of a cloud condensation nucleus, CCN

Mikhail Paramonov

University of Helsinki, 2015

Abstract

The research conducted and presented herein concentrates primarily on the life cycle of a cloud condensation nucleus CCN. The primary motivation of the work is the importance of CCN in the global aerosol-cloud-climate system, and focus is placed on the production of CCN, their behaviour in the atmosphere and their properties with respect to CCN activation, as well as the removal pathways. The work presented in this thesis covers measurements performed at 16 locations around the world.

The results further corroborated the notion that atmospheric new particle formation NPF is an important and widespread source of CCN in the atmosphere. The number of newly formed CCN from NPF depends on many factors, including, but not limited to, biogenic and anthropogenic emissions, frequency of NPF events, nucleation and growth rates and pre-existing CCN concentrations; method of calculation also affects the estimate of NPF contribution to CCN budgets. Highest relative increase in CCN as a result of NPF was observed at a clean remote location in Northern Finland, where in the summer the number concentration of particles above 50 nm in diameter N_{50} can increase by as much as 800%. Highest absolute increases in N_{CCN} as a result of NPF (up to 3500 particles cm^{-3} for N_{50}) were found at a dry savannah location of Botsalano in South Africa. In Hyytiälä Type I nucleation events were found to always, at the very least, double N_{CCN} concentrations.

It was found that in many environments around the world a rather similar fraction of aerosols activated into cloud droplets at any given level of supersaturation S , and a simple linear parameterisation is provided for an easy calculation of annual mean CCN concentration N_{CCN} based only on total number concentration N_{CN} and the desired S . At the majority of studied locations hygroscopicity was found to increase with size, with accumulation mode hygroscopicity parameter κ values being significantly larger than Aitken mode κ at some locations. Depending on the focus and desired accuracy, the use of κ values as a function of particle dry size rather than the assumption of a size-independent κ should preferably be considered. The photochemistry, aging processes, atmospheric NPF and other atmospheric processes occurring on a diurnal scale were found to affect the CCN activation and hygroscopic properties of Aitken mode aerosol only. The hygroscopicity of the accumulation mode aerosol is more affected by processes occurring on a time scale of a few days to months, e.g. long range transport and seasonal variation in vegetation activity.

Below-cloud scavenging by snow was found to be an inefficient mechanism of CCN removal from the atmosphere compared to, e.g., in-cloud scavenging. Additionally, nucleation and Aitken mode particles are scavenged by snow more efficiently than CCN-sized aerosol. No apparent difference in the scavenging efficiency of snow was observed between a rural and an urban site in Southern Finland. Ambient relative humidity was found to correlate positively with the scavenging efficiency of snow, and a new parameterisation for calculating snow scavenging coefficients based on both particle dry size and relative humidity is presented.

A reconsideration of the purpose, the focus and the motivation for the cloud condensation nuclei counter CCNC measurements at the SMEAR II is needed if they are to be continued with reasonable, interesting and exciting output.

Keywords: atmospheric aerosol, cloud condensation nuclei, particle formation, CCN activation, hygroscopicity, snow scavenging

Contents

List of publications	6
Abbreviations	7
Nomenclature	8
1. Introduction	9
2. CCN dynamics	11
2.1 Primary and secondary CCN and their aging	11
2.2 CCN activation into cloud droplets and the κ -Köhler theory	13
2.3 CCN removal mechanisms	15
3. Methodology	17
3.1 Instrumentation	17
3.1.1 Cloud Condensation Nuclei Counter CCNC	17
3.1.2 Differential Mobility Analyser DMA	18
3.1.3 Condensation Particle Counter CPC/Optical Particle Counter OPC	19
3.2 Measurement locations	19
4. Results and discussion	21
4.1 Production of atmospheric CCN	21
4.1.1 The effect of NPF on CCN number concentration	21
4.1.2 The effect of NPF on CCN activation and hygroscopic properties	23
4.2 CCN activation and hygroscopic properties	24
4.2.1 CCN activation properties	24
4.2.2 CCN hygroscopic properties	26
4.2.3 Temporal variation of CCN activation and hygroscopic properties	30
4.3 CCN removal	32
4.4 The applicability of CCNC measurements at the SMEAR II	35
5. Review of publications and author's contribution	37
6. Conclusion	38
References	39

List of publications

This thesis is composed of an introductory part and five scientific peer-reviewed research articles. In the introductory part, these research articles are referred to by the roman numerals, as shown below. **Papers I–IV** are reproduced under the Creative Commons Attribution Licence. **Paper V** is reproduced with the permission from the Boreal Environment Research Publishing.

- I. Kerminen, V.-M., Paramonov, M., Anttila, T., Riipinen, I., Fountoukis, C., Korhonen, H., Asmi, E., Laakso, L., Lihavainen, H., Swietlicki, E., Svenningsson, B., Asmi, A., Pandis, S. N., Kulmala, M., and Petäjä, T.: Cloud condensation nuclei production associated with atmospheric nucleation: a synthesis based on existing literature and new results, *Atmos. Chem. Phys.*, 12, 12037–12059, 2012.
- II. Paramonov, M., Aalto, P. P., Asmi, A., Prisle, N., Kerminen, V.-M., Kulmala, M., and Petäjä, T.: The analysis of size-segregated cloud condensation nuclei counter (CCNC) data and its implications for cloud droplet activation, *Atmos. Chem. Phys.*, 13, 10285–10301, 2013.
- III. Paramonov, M., Kerminen, V.-M., Gysel, M., Aalto, P. P., Andreae, M. O., Asmi, E., Baltensperger, U., Bougiatioti, A., Brus, D., Frank, G., Good, N., Gunthe, S. S., Hao, L., Irwin, M., Jaatinen, A., Jurányi, Z., King, S. M., Kortelainen, A., Kristensson, A., Kulmala, M., Lihavainen, H., Lohmann, U., Martin, S. T., McFiggans, G., Mihalopoulos, N., Nenes, A., O’Dowd, C. D., Ovadnevaite, J., Petäjä, T., Pöschl, U., Roberts, G. C., Rose, D., Svenningsson, B., Swietlicki, E., Weingartner, E., Whitehead, J., Wiedensohler, A., Wittbom, C., and Sierau, B.: A synthesis of cloud condensation nuclei counter (CCNC) measurements within the EUCAARI network, *Atmos. Chem. Phys.*, submitted.
- IV. Hong, J., Häkkinen, S. A. K., Paramonov, M., Äijälä, M., Hakala, J., Nieminen, T., Mikkilä, J., Prisle, N., Kulmala, M., Riipinen, I., Bilde, M., Kerminen, V.-M., and Petäjä, T.: Hygroscopicity, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010, *Atmos. Chem. Phys.*, 14, 4733–4748, 2014.
- V. Paramonov, M., Grönholm, T., and Virkkula, A.: Below-cloud scavenging of aerosol particles by snow at an urban site in Finland, *Boreal Env. Res.*, 16, 304–320, 2011.

Abbreviations

AMS	aerosol mass spectrometer
BC	black carbon
CCN	cloud condensation nuclei
CCNC	cloud condensation nuclei counter
CDNC	cloud droplet number concentration
CPC	condensation particle counter
DMA	differential mobility analyser
DMPS	differential mobility particle sizer
DMT	droplet measurement technologies
EUCAARI	european integrated project on aerosol cloud climate and air quality interactions
H-TDMA	hygroscopicity tandem differential mobility analyser
MAF	maximum activated fraction
NPF	new particle formation
OPC	optical particle counter
PBL	planetary boundary layer
RH	relative humidity
SMEAR	station for measuring ecosystem-atmosphere relations
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
TDMPS	tandem differential mobility particle sizer
UTC	coordinated universal time
VH-TDMA	volatility-hygroscopicity tandem differential mobility analyser
VOC	volatile organic compound

Nomenclature

A	activated fraction, unitless
A_{50}	effective activated fraction of particles above 50 nm in diameter, unitless
A_{100}	effective activated fraction of particles above 100 nm in diameter, unitless
c	particle concentration, cm^{-3}
D_c	critical diameter, nm
d_p	particle diameter, nm
D_s	dry particle diameter, m
D_{wet}	droplet diameter, m
κ	hygroscopicity parameter, unitless
λ_s	scavenging coefficient, s^{-1}
M_w	molar mass of water, kg mol^{-1}
N_{CCN}	number concentration of cloud condensation nuclei, cm^{-3}
N_{CN}	total particle number concentration, cm^{-3}
N_x	particle number concentration above the size of x nm, cm^{-3}
R	universal gas constant, $\text{J K}^{-1} \text{mol}^{-1}$
ρ_w	density of pure water, kg m^{-3}
S	supersaturation, %
S_c	critical supersaturation, %
S_{eff}	effective supersaturation, %
σ_{sol}	surface tension of a condensing solution, J m^{-2}
T	absolute temperature, K
t	time, s

1 Introduction

Aerosol particles are liquid or solid particles suspended in a gas (Hinds, 1999), and for all intents and purposes in the atmospheric community this gas is considered to be the atmosphere. Aerosol particles have miscellaneous sources, have a wide variety of chemical compositions, and their size can span over four orders of magnitude. Primary aerosol particles, those emitted already in the particle phase, are typically bigger; examples include sea salt and pollen. Secondary aerosol particles, those formed in the atmosphere from precursor gases, are generally smaller and have a complicated chemical footprint, frequently including organics and sulphate (Seinfeld and Pandis, 2006). Depending on the emission source, aerosol can also be classified as natural or anthropogenic. Some of the smallest atmospheric aerosol particles, on the order of a couple of nanometres, are small multi-molecular clusters formed during the initial steps of atmospheric new particle formation NPF (Kulmala et al., 2007). On the opposite end are mature cloud droplets that can be as large as several tens of micrometres in diameter (Miles et al., 2000). Several important effects pertinent to atmospheric aerosol are usually highlighted, including its effect on the visibility (e.g. Jinhuan and Liqun, 2000; Seinfeld and Pandis, 2006; Cao et al., 2012), human health (e.g. Seaton et al., 1995; Hinds, 1999; Tie et al., 2009) and climate (e.g. Twomey, 1974; Lohmann and Feichter, 2005; Paasonen et al., 2013).

From a climatic perspective atmospheric aerosol interferes with the global radiation balance both directly and indirectly. The direct effect is associated with the scattering and absorption of radiant energy (e.g. McCormick and Ludwig, 1967); a comprehensive summary of aerosol direct effect on climate can be found in Yu et al. (2006). Indirect effects of aerosols on climate deal with the interactions of aerosol particle with clouds and can be viewed in a simple form in Figure 1. Aerosol particles are known to modify the microphysical properties of clouds, such as their albedo, lifetime and precipitations patterns; it is postulated that by increasing the aerosol loading due to anthropogenic sources and, thereby, reducing the effective cloud droplet diameter, cloud albedo and lifetime increase and precipitation is suppressed (Lohmann and Feichter, 2005; Rosenfeld et al., 2008). Indirect effects of aerosol on climate, also known as the forcing by aerosol-cloud interactions, present one of the largest uncertainties in the current modelling and understanding of the aerosol climate interaction (Boucher et al., 2013).

Aerosol particles participating in cloud formation are commonly known as cloud condensation nuclei CCN, and in general terms they represent a fraction of aerosol population relevant for the formation of cloud droplets (McFiggans et al., 2006; Andreae and Rosenfeld, 2008). Being a CCN is not an inherent property; particle ability to act as CCN depends on a multitude of factors, including the ambient supersaturation S , aerosol physical and chemical properties and other micrometeorological parameters. Due to the role aerosol-cloud interactions play in the global climate system and, even more so, due to the current lack of understanding of these interactions, the life cycle of CCN, i.e. its

sources, processes and sinks, is a very important topic. The main objectives of this thesis are:

1) Quantification of the contribution of atmospheric new particle formation to regional CCN budgets. This aim includes the examination of existing and the development of new mathematical methods aimed at such quantification, the analysis of new observational data from around the world and connecting the measured and calculated data with latest modelling endeavours.

2) The examination and detailed description of CCN activation and hygroscopic properties as relevant for the CCN cloud forming potential. This aim includes the analysis of the cloud condensation nuclei counter CCNC dataset from Hyytiälä, the first long-term multi-year dataset in the world, and combining it with the CCNC measurements conducted elsewhere within the EUCAARI framework. This section specifically focuses on estimating the effect of particle size, number size distribution, aerosol hygroscopicity and its variation with size on the activation of CCN into cloud droplets.

3) Quantification of CCN removal by snow scavenging. This aim includes the estimation of the role of snow scavenging as a CCN removal mechanism and comparing its efficiency to that of other CCN removal mechanisms, specifically in-cloud scavenging by CCN activation. Part of the focus also includes the examination of various meteorological parameters on the scavenging efficiency of snow.

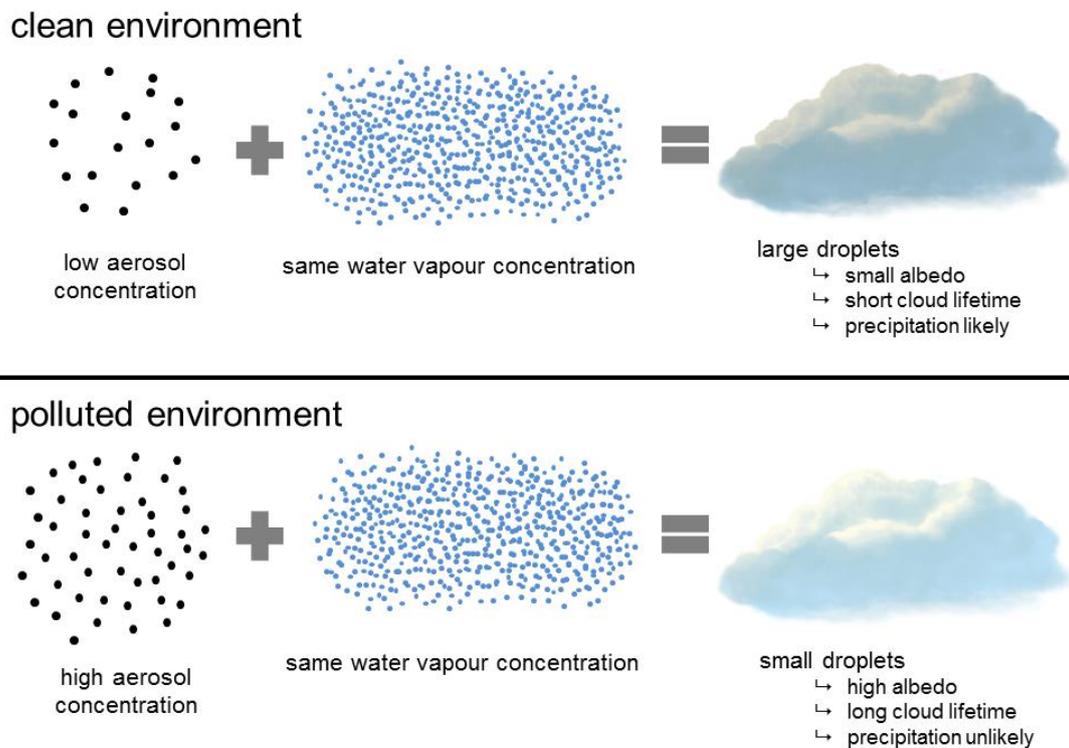


Figure 1. A simple schematic of the indirect effect of aerosols on climate.

The research presented herein is expected to significantly improve the current understanding of the CCN production associated with NPF, CCN activation and hygroscopic properties and CCN removal mechanisms.

2 CCN dynamics

In the atmosphere aerosol particles undergo a multitude of processes and have several sources and sinks (Pöschl, 2005). These are largely dependent on environment in question, as well as particle size and its chemistry. The life cycle of atmospheric CCN is a broad topic and presents a challenge in our understanding of aerosol-cloud-climate interactions (Boucher et al., 2013). This section concentrates on main points of interest of CCN life cycle as relevant to the research carried out as part of this PhD Thesis. Primary and secondary sources of atmospheric CCN are presented first, followed by the description of the κ -Köhler theory of CCN activation. The theoretical discussion ends with a brief description of deposition and scavenging processes relevant for CCN-size aerosol.

2.1 Primary and secondary CCN and their aging

Atmospheric CCN can be classified into two main groups based on their origin: primary and secondary. Primary CCN are emitted directly into the atmosphere in particle phase, while secondary CCN form from condensable gases (Pierce and Adams, 2009). Primary CCN can be emitted into the atmosphere already at CCN sizes or grow from a smaller emitted particle; examples of primary CCN are sea salt, dust particles, microbial particles and plant debris. Secondary CCN form as a result of regional NPF, and, therefore, consist of several compounds including sulphate and organics. The emissions of primary CCN and the formation of secondary CCN affect regional CCN budgets differently, as they affect CCN concentrations N_{CCN} through a variety of microphysical pathways (Adams and Seinfeld, 2003). The contribution of primary and secondary CCN to total N_{CCN} varies spatially, and while in some parts of the atmosphere NPF is a dominant source of CCN (e.g. Pirjola et al., 2002; Laaksonen et al., 2005), primary CCN prevail in the boundary layer and close to emissions sources (e.g. Spracklen et al., 2005; Pierce and Adams, 2006).

Due to the importance of atmospheric CCN in the Earth's climate system, many studies have concentrated on quantifying the atmospheric CCN production from various sources. The atmospheric budget of sea salt particles has been studied extensively due to its importance in remote marine regions (Mårtensson et al., 2003; Pierce and Adams, 2006). The impact of dust and primary sulphate on CCN has been studied as well (Manktelow et al., 2010 and Luo and Yu, 2011, respectively). The potential role of pollen (Pope, 2010), plant waxes (Kavouras et al., 1998) and fungal spores (Heald and Spracklen, 2009) as CCN has also been examined. With respect to secondary CCN, many studies have

attempted to quantify the contribution of NPF to atmospheric N_{CCN} , both on global and regional scales (e.g. Spracklen et al., 2008; Sihto et al., 2011). Closure studies, combining both primary and secondary sources of CCN, have been performed as well (Adams and Seinfeld, 2003; Pierce and Adams, 2009; Spracklen et al., 2010). The quantification of the contribution of atmospheric NPF to the CCN budget based on field observations and modelling results is one of the main goals of the current thesis, presented in **Paper I**.

One of the most important processes in the atmosphere that also affects the fate of atmospheric CCN, primary or secondary, is the ambient aging. The processes associated with aging result in an increase in particle size and changes to the chemical composition of ambient aerosol and include several aspects (Rudich et al., 2007). The most common process resulting in aging is the oxidation by OH, ozone and NO_3 . Oxidation can occur in particle phase, directly altering particle chemistry, or in gas phase resulting in the formation of gaseous compounds with low volatility and leading to their condensation on existing particles (Lelieveld et al., 2008). Oxidative aging has been shown to increase the hygroscopicity, i.e. water uptake ability, of ambient aerosol particles; aging by oxidation is especially important for organic aerosols (Furutani et al., 2008). Another process responsible for increasing hygroscopicity of atmospheric CCN is cloud processing, i.e. activation of aerosol particles into cloud droplets, chemical reactions in the aqueous phase and subsequent evaporation, which typically leads to an increase in the sulphate fraction of the aerosol mass (Hoppel et al., 1990). Oligomerisation and deliquescence/effluorescence can also modify the chemical properties of aerosols particles, although on a global scale their importance is smaller compared to oxidation and cloud processing.

Atmospheric NPF is a frequent event that has been shown to occur in a variety of environments around the world (Kulmala et al., 2004). During an NPF event new particles form in the atmosphere from condensable vapours; the fate of these newly formed particles and their potential to grow to CCN sizes initially depend chiefly on the competition between the growth by condensation and coagulation with larger particles (Kerminen et al., 2001; Pierce and Adams, 2007). As particles grow, following the initial growth and before particles reach CCN sizes, other loss processes, such as deposition, may become important. The production of these secondary CCN can be studied from both a modelling perspective and field observations; however, the exact quantification can be rather challenging. Sotiropoulou et al. (2006) showed that downwind of the NPF events N_{CCN} can increase by 40–100%. Another modelling study by Spracklen et al. (2008) has estimated that globally N_{CCN} in the planetary boundary layer (PBL) in the springtime can increase by as much as 3–20% for a supersaturation S of 0.2% and by 5–50% for S of 1.0%. Using a global aerosol microphysics model, Merikanto et al. (2009) predicted that 45% of the global low-level cloud CCN at S of 0.2% were secondary CCN resulting from NPF. Lihavainen et al. (2003) reported that particle number concentrations over 50 and 80 nm in diameter (N_{50} and N_{80} , respectively) at a clean site in Northern Finland increased by factors of 11.7 and 4.1, respectively, as a result of NPF. Kuang et al. (2009) showed that NPF increased N_{CCN} by an average factor of 3.8 at three locations around the world. Many more studies on this subject exist in the published literature; however, the examples

presented above illustrate the wide range of estimated values and the uncertainty associated with the prediction of N_{CCN} increase due to NPF. It is also clear that CCN, primary or secondary, do not carry the same or even similar chemical footprint and contain a wide variety of compounds, both soluble and insoluble.

2.2 CCN activation into cloud droplets and the κ -Köhler theory

Theoretically, the phase transition of water vapour from gas to liquid phase can proceed homogeneously or heterogeneously. Homogeneous nucleation, i.e. formation of cloud droplets from water vapour in the absence of any external material, requires levels of supersaturation S of several hundred percent and, therefore, does not occur in the atmosphere (Andreae and Rosenfeld, 2008). Aerosol particles, ubiquitous in the atmosphere, can act as nuclei for the condensation of water vapour at much lower S levels, typically only a few percent above 100% relative humidity RH. These particles, known as CCN, can be very efficient at activating into cloud droplets, and heterogeneous nucleation, as such, is the only pathway of cloud droplet formation in the atmosphere (Pruppacher and Klett, 1997). The number of these CCN can vary by several orders of magnitude depending on location, and N_{CCN} concentrations have been reported for a multitude of environments (e.g. Twomey, 1959; Hobbs et al., 1980; Wang et al., 2008; Detwiler et al., 2010). Besides aerosol particle properties, such as size and chemistry, N_{CCN} is directly related to the ambient supersaturation S with respect to water vapour. The effect of these parameters is described briefly below.

Supersaturation conditions in the atmosphere can develop through several different pathways, including the adiabatic cooling or orographic lifting of an air parcel, and the Köhler theory indicates that as S increases, so does the number of activated CCN (Köhler, 1936). In other words, as S increases, the size at which particles activate into cloud droplets decreases, leading to an increase in N_{CCN} . In the polluted PBL typical levels of S are below 0.3% (Ditas et al., 2012; Hammer et al., 2014; Hudson and Noble, 2014); however, S can reach up to 1% in intense convective updrafts (Seinfeld and Pandis, 2006). The maximum S that can be reached in the atmosphere depends on meteorological conditions, such as updraft velocities, and on aerosol properties, such as the number size distribution and the chemical composition (Snider et al., 2003; McFiggans et al., 2006; Ghan et al., 2011). The relationship between S and aerosol populations works in both directions. As mentioned already, a higher S results in a higher N_{CCN} ; however, a higher N_{CCN} limits the maximum S that can be reached by quickly depleting all available water vapour and effectively reducing S . In the research part of this thesis that explicitly dealt with the CCN activation, the effect of aerosol population on S was not considered, and it was always assumed that cloud droplet growth occurred very quickly at a constant S .

Of all the aerosol properties affecting CCN activation into cloud droplets, aerosol size and its distribution are the most important parameters (Dusek et al., 2006), and while size distribution can be typically used as is, the size of particles relevant for CCN is often expressed in terms of the critical diameter of CCN activation D_c . According to the Köhler

theory, for a polydisperse internally mixed aerosol any given S will result in the activation of a certain portion of the population above a certain size. This minimum size that divides the population into the CCN-activated particles and non-activated particles is what is typically referred to as D_c . In the atmosphere, however, aerosol populations often tend to be externally mixed, with particles of various sizes exhibiting varying chemical composition. In such cases, and therefore very frequently in practice, D_c is defined as the diameter at which 50% of the particles activate and grow to cloud droplet sizes. D_c has a negative relationship with S , with an increase in S leading to a lower D_c . D_c is not measured directly; it can be easily calculated either from size-segregated CCNC measurements (Rose et al., 2008) or from combining the size distribution data with N_{CCN} (Furutani et al., 2008). In cases where only aerosol number size distribution data are available, D_c and, therefore, N_{CCN} are frequently estimated by selecting an arbitrary diameter and calculating the total number concentration above this diameter. An example of this is the assumption that N_{CCN} is roughly equal to the total number of particles above 80 nm in diameter N_{80} (Komppula et al., 2005; Asmi et al., 2011). Assuming typical maximum S levels in the PBL of 0.3%, D_c values usually fall within the 80–100 nm size range.

Hygroscopicity, i.e. the ability and readiness of an aerosol particle to uptake and retain water, is an important parameter affecting CCN activation, albeit to a lesser degree than number size distribution (Roberts et al., 2002; Dusek et al., 2006). In the recent years several approaches have been put forward in an attempt to capture the effect of aerosol chemistry on CCN activity (Fitzgerald et al., 1982; Svenningsson et al., 1992; Rissler et al., 2006; Khvorostyanov and Curry, 2007). Most recently Petters and Kreidenweis (2007) have introduced the hygroscopicity parameter κ , a unitless value describing the hygroscopic growth the activity of the CCN. κ can vary between zero and just above unity, with values close to zero indicating a non-hygroscopic aerosol (e.g. freshly emitted soot particles; Pringle et al., 2010) and values close to unity indicating a very hygroscopic substance (e.g. sea salt; Good et al., 2010). Hygroscopicity parameter κ for ambient aerosol can be measured using aerosol-water interactions in supersaturated regime using a CCNC (e.g. Gunthe et al., 2009), in sub-saturated regime using a Hygroscopicity Tandem Differential Mobility Analyser H-TDMA (e.g. Carrico et al., 2008), as well as estimated from measurements of aerosol chemistry performed by e.g. Aerosol Mass Spectrometer AMS (e.g. Chang et al., 2010). For the measurements in the supersaturated regime, which is one of main foci of the research presented herein, κ can be calculated using the effective hygroscopicity parameter (EH1) Köhler model (Rose et al., 2008) using the following equation:

$$S = \frac{D_{wet}^3 - D_s^3}{D_{wet}^3 - D_s^3(1-\kappa)} \exp\left(\frac{4\sigma_{sol}M_w}{RT\rho_w D_{wet}}\right), \quad (1)$$

where S is water vapour saturation ratio, D_{wet} is the droplet diameter, D_s is the dry particle diameter, κ is hygroscopicity parameter, σ_{sol} is the surface tension of condensing solution, M_w is the molar mass of water, R is the universal gas constant, T is the absolute temperature and ρ_w is the density of pure water. As described in Rose et al. (2008), D_s can be substituted with D_c and σ_{sol} can be assumed to be that of pure water (0.072 J m^{-2}).

CCN concentration N_{CCN} , critical diameter D_c and hygroscopicity parameter κ can provide very useful information about the CCN activity of any given aerosol population of both ambient and laboratory origin. Corresponding size distribution data can also further improve the understanding of the effects of size and chemistry of CCN activity. However, these parameters, in general terms, do not describe *actual* activation into cloud droplets – they describe the aerosol with respect to its CCN potential and provide information about which aerosol properties matter more. Parallel measurements of cloud droplet number concentration CDNC are necessary to determine exactly how CCN activation and hygroscopic properties affect the formation and evolution of cloud droplets and their microphysical properties.

2.3 CCN removal mechanisms

In the aerosol deposition studies, the activation of CCN into cloud droplets is known as in-cloud scavenging, and it is considered as one of the aerosol removal mechanisms. Besides dry deposition, which is not covered in this thesis work, wet scavenging is an important pathway for aerosol removal from the atmosphere, and it describes the removal of aerosol particle by hydrometeors (cloud and fog drop, rain, snow and ice crystals) and the subsequent deposition onto the Earth's surface (Seinfeld and Pandis, 2006). Aerosol interactions with hydrometeors occur both inside the cloud and below the cloud, and they are briefly described below.

In the air parcels with supersaturated conditions and inside the already forming cloud aerosol particles can be scavenged by both nucleation (i.e. CCN activation) and impaction scavenging. Of these two processes, nucleation scavenging is the most dominant pathway of aerosol removal from the atmosphere (Pruppacher and Klett, 1997; Limbeck and Puxbaum, 2000), and it is described in detail in the previous section. Impaction scavenging occurs when the already formed cloud droplets collide with the interstitial aerosol, i.e. aerosol that has not activated into a cloud droplet. The collisions take place due to a variety of forces and interactions between the aerosol and the droplet, including Brownian diffusion, thermophoretic and diffusiophoretic forces, inertial and gravitational impaction and turbulence (Pruppacher and Klett, 1997). The incorporation of aerosol particle into cloud droplets, either by nucleation or impaction scavenging, does not necessarily have to result in deposition; in case S conditions are no longer met, droplets may evaporate completely leaving the aerosol residual behind. This process is called cloud processing, and it is known to modify aerosol chemical composition (section 2.1).

Below-cloud scavenging describes the process by which already formed hydrometeors remove aerosol particles below the cloud during a precipitation event (Pruppacher and Klett, 1997), and many studies have attempted to determine the efficiency of various mechanisms of below-cloud scavenging (Andronache et al., 2006; Byrne and Jennings, 1993; Laakso et al., 2003; Henzing et al., 2006; Croft et al., 2009; Kyrö et al., 2009). This efficiency depends on aerosol particle size, precipitation type and rate, hydrometeor size, as well as several micrometeorological parameters. Since particles of different sizes are scavenged with varying degrees of efficiency, the response of an aerosol population subjected to the precipitation event depends on the size distribution. Particles in the nucleation and Aitken modes are scavenged efficiently due to their Brownian motion, meanwhile coarse particles are easily scavenged due to their inertia (Andronache et al., 2006). Accumulation mode particles do not have an efficient removal mechanism, resulting in what is known as the Greenfield gap – the aerosol size range exhibiting the minimum scavenging efficiency (Greenfield, 1957). The size limits of the Greenfield gap vary among numerous studies, and have been reported to range from 0.01 to 2 μm (Andronache et al., 2006; Henzing et al., 2006). These size limits indicate that particles of CCN sizes are not very efficiently scavenged below the cloud, and that exact quantification of scavenging efficiency of various precipitation types is required in order to estimate the effect of below-cloud scavenging on CCN budgets.

One way to mathematically describe the scavenging efficiency of precipitation is by using the concept of scavenging coefficient λ_s , which, due to the abovementioned variation of scavenging efficiency with particle size d_p , is usually presented as a function of size $\lambda_s(d_p)$. The mathematical approach for determining $\lambda_s(d_p)$ is described in detail in Sperber and Hameed (1986) and has been previously used by, e.g. Laakso et al. (2003) and Kyrö et al. (2009).

$$\lambda_s(d_p) = -\frac{1}{t_1-t_0} \ln \left[\frac{c_1(d_p)}{c_0(d_p)} \right], \quad (2)$$

where $\lambda_s(d_p)$ is the scavenging coefficient of particles with a diameter d_p per unit time, t_1 and t_0 are end time and start time of the examined interval, respectively, and $c_1(d_p)$ and $c_0(d_p)$ are end and start concentrations of particles with a diameter d_p , respectively. The quantity $\lambda_s(d_p)$ represents the fraction of the aerosol of a certain diameter d_p that is removed due to the precipitation in any given volume in a unit time (Henzing et al., 2006). By using strict selection criteria for precipitation events, the effects of other processes resulting in changes in aerosol concentration, e.g. turbulence, coagulation advection etc., can be minimised. Therefore, Eq. 2 is applicable only for cases where scavenging by precipitation is the only mechanism affecting aerosol concentrations (Kyrö et al., 2009). Since the aerosol concentrations can still fluctuate during a precipitation event, $\lambda_s(d_p)$ can have both positive and negative values.

Due to the fairly uniform shapes and sizes of liquid precipitation, rain scavenging has been studied more extensively than snow scavenging (Radke et al., 1980; Laakso et al., 2003; Henzing et al., 2006). However, wet scavenging of aerosol particles by snow is an important mechanism of aerosol removal from the atmosphere in cold, mid-latitude, Polar and mountainous regions. The complexity of wet scavenging is associated with a great diversity of frozen precipitation types and their physical properties, as snowflakes, ice grains and ice pellets all have different sizes and cross-sectional areas, affecting their terminal velocity and scavenging ability (Pruppacher and Klett, 1997). Several studies have examined the scavenging efficiency of snow (Magono et al., 1975; Jylhä, 2000; Feng, 2009), with most of them reporting that snow scavenges aerosol particles more efficiently than rain per equivalent water content (Graedel and Franey, 1975; Kyrö et al., 2009). Published literature on snow scavenging indicates a large variability in $\lambda_s(d_p)$, with values spanning over two orders of magnitude from $\sim 10^{-6}$ to $\sim 10^{-4} \text{ s}^{-1}$ (Kerker and Hampl, 1974; Miller et al., 1990). Since the effects of climate change are expected to be more pronounced in the high-latitude and Arctic areas where snow is a dominant form of precipitation at least during a large part of the year (Boucher et al., 2013), estimating the effect of scavenging efficiency of snow on CCN budget in these areas is of great importance.

3 Methodology

3.1. Instrumentation

3.1.1 Cloud Condensation Nuclei Counter CCNC

The CCNC is at the centre of all instrumentation used for the research presented herein, and the CCNC measurements have been analysed in this thesis extensively (**Papers I–IV**). A CCNC is an instrument typically used for studying cloud droplet activation of aerosol particles, and the setup is a multi-component system, consisting of the CCNC chamber itself connected to an optical particle counter (OPC), condensation particle counter (CPC) and, possibly, a differential mobility analyser (DMA). The CCNC is a commercially available instrument, distributed by the Droplet Measurement Technologies (DMT), Inc., and its main component is a continuous-flow streamwise thermal-gradient diffusion chamber. The basic principles of CCNC operation are described below; a more detailed description can be found in Roberts and Nenes (2005) and Rose et al. (2008).

Ambient aerosol enters the measurement setup through an inlet and it is first dried (with, e.g. Nafion drier) and charge-neutralised (with, e.g. 370 MBq ^{14}C radioactive source) in order to obtain an equilibrium charge distribution; these are only performed for size-resolved measurements. Following these steps, the aerosol sample flow is split into two lines, with the first line leading to a CPC, which determines the total number concentration of aerosol particles in a sample, a quantity frequently denoted as N_{CN} . The second line

feeds the sample aerosol into the CCNC chamber itself, where the conditions of supersaturation S with respect to water are established. The chamber is typically a vertical flow tube of cylindrical shape, inside which the aerosol flows from top to bottom surrounded by the sheath flow; the aerosol flow occurs under laminar conditions and near-ambient pressure. The near-linear positive temperature gradient inside the chamber establishes the transport of the heat and water vapour from the inner walls of the chamber to the centreline, thus creating the conditions of supersaturation with respect to water S_{eff} . Any CCNC typically operates at several S_{eff} levels which can be selected by the user; most commonly the S_{eff} levels vary from 0.1 to 1.0%. As the particles enter the chamber, those with a critical supersaturation S_c below S_{eff} will activate and quickly grow by the condensation of water vapour into droplets. Inside the CCNC chamber the residence time of ~ 10 sec ensures that all activated particles grow to ~ 1 μm in size, large enough to be easily detected due to their optical properties. The droplets are counted by the OPC, providing the number concentration of activated aerosol particles, a quantity commonly referred to as CCN number concentration N_{CCN} . N_{CN} and N_{CCN} are the two main parameters directly measured by the CCNC. The described setup is representative of polydisperse, i.e. non size-resolved measurements. The inclusion of a drier, charge neutraliser and a DMA before the splitting of the sample flow into two sample lines can provide monodisperse, i.e. size-resolved measurements across several size channels. Such measurements can be conducted either by changing the particle size at a constant S_{eff} (D -scan) or by changing S_{eff} at a constant particle size (S -scan). A monodisperse setup, while more complex, yields activation spectra and allows for a direct calculation of the critical dry diameter of droplet activation D_c (in case of the D -scan) or the critical supersaturation S_c (in case of the S -scan). For data quality assurance, a CCNC is calibrated using an aerosol with known properties, such as nebulised, dried, charge-equilibrated and size-segregated ammonium sulphate aerosol. One such sample calibration procedure is explained in detail in Rose et al. (2008).

3.1.2 Differential Mobility Analyser DMA

The DMA is a common instrument frequently used for measuring aerosol number size distributions. The basic principle of any DMA is sorting the particles based on their electrical mobility, which, when using the voltage data, can be converted to particle size (Stolzenburg et al., 1988; Aalto, 2004). A DMA can have several configurations; however, most often it is a cylindrical chamber with a high voltage rod in the centre of the chamber, which creates an electrical field in the surrounding air. By varying the electrical field, charge-neutralised particles are sorted only according to their physical size, providing the opportunity to scan across all particle sizes. A DMA efficiently measures ultrafine particles, those from ~ 10 nm to ~ 1 μm in diameter (Stolzenburg et al., 1988), and coupling a DMA to a particle counter, such as a CPC, yields a complete number size distribution of particles in the sample air. The number of size bins used in DMA size classification can be specified by the user and can go up to several dozens. A system comprised of a DMA and a particle counter is commonly known as a Differential Mobility

Particle Sizer DMPS. In order to cover a wide particle size range, it is frequently necessary to use two DMA systems in parallel, resulting in what is known as the tandem DMPS (TDMPS). Measurements performed by the DMA are discussed in all papers presented in this thesis (**Papers I–V**).

3.1.3 Condensation Particle Counter CPC/Optical Particle Counter OPC

One of the most basic instruments in atmospheric aerosol measurements is a particle counter. It is normally used in conjunction with other measurement systems (e.g. Wang and Flagan, 1990), and simply provides the particle number concentration above a certain size. Similarly to the CCNC chamber, a CPC/OPC subjects the aerosol particles to the conditions of supersaturation with respect to water or alcohol vapour (e.g. butanol). Such conditions are achieved by the presence of the vapour and the lowering of temperature; under these conditions particles grow by condensation to several μm in diameter. When large enough, the droplets can be detected due to their optical properties and counted using either light transmission measurements or single-particle optical counters (McMurry, 2000). Measurements performed by the CPC/OPC are discussed in all papers presented in this thesis (**Papers I–V**).

3.2 Measurement locations

Data from a total of 16 locations have been used and analysed in this thesis work (Table 1, Fig. 2). Besides what is presented in Table 1, the description of the majority of locations can be found in **Paper III** and references therein; the description of locations in Botsalano, South Africa and Helsinki, Finland can be found in **Paper I** and **Paper V**, respectively. Of all stations, Hyytiälä Forestry Field Station is the most represented in this thesis; the Hyytiälä measurement data are discussed in all but one scientific article (**Papers I–IV**). Hyytiälä is the site of the Station for Measuring Ecosystem-Atmosphere Relations SMEAR II, a site with some of the most comprehensive network of aerosol- and meteorology-related measurements in Europe. It is also the site with the longest CCNC and DMPS dataset used in the analysis. Its detailed description can be found in Hari and Kumlala (2005).

Table 1. Names, location and a brief description of all measurement sites presented in the thesis work.

Name of station or campaign	Location	Geographic coordinates	Elevation (m a.m.s.l.)	Site description	Vegetation type
Hyttiälä	southern Finland	61°51' N, 24°17' E	181	rural background	boreal
Vavihill	southern Sweden	56°01' N, 13°09' E	172	rural background	grasslands
Jungfraujoch / CLACE-6	Swiss Alps	46°33' N, 07°59' E	3580	free troposphere	Alpine
Mace Head	west coast of Ireland	53°19' N, 09°54' W	0	coastal background	coastal
Pallas	northern Finland	67°58' N, 24°07' E	560	remote background	boreal
Finokalia	northern Crete	35°20' N, 25°40' E	250	remote coastal	coastal
Cabauw	central Netherlands	51°58' N, 04°56' E	-1	rural background	agricultural
K-Pusza	central Hungary	46°58' N, 19°33' E	125	rural	forested
Chilbolton	southern United Kingdom	51°09' N, 01°26' W	78	continental background	agricultural
Helsinki	southern Finland	60°12' N, 24°58' E	26	urban	mixed
Botsalano	South Africa	25°32' S, 25°45' E	1424	continental background	dry savannah
COPS	south-west Germany	48°36' N, 08°12' E	1156	continental background	forested
RHaMBLe	tropical North Atlantic	~21° N, 20° W	0	remote marine	ocean
<i>Pride-PRD2006</i>	southern China	23°33' N, 113°04' E	28	rural background	agricultural
<i>AMAZE-08</i>	northern Brazil	02°36' S, 60°13' W	108	remote background	rainforest
<i>CARE-Beijing2006</i>	northern China	39°31' N, 116°18' E	30	suburban	mixed

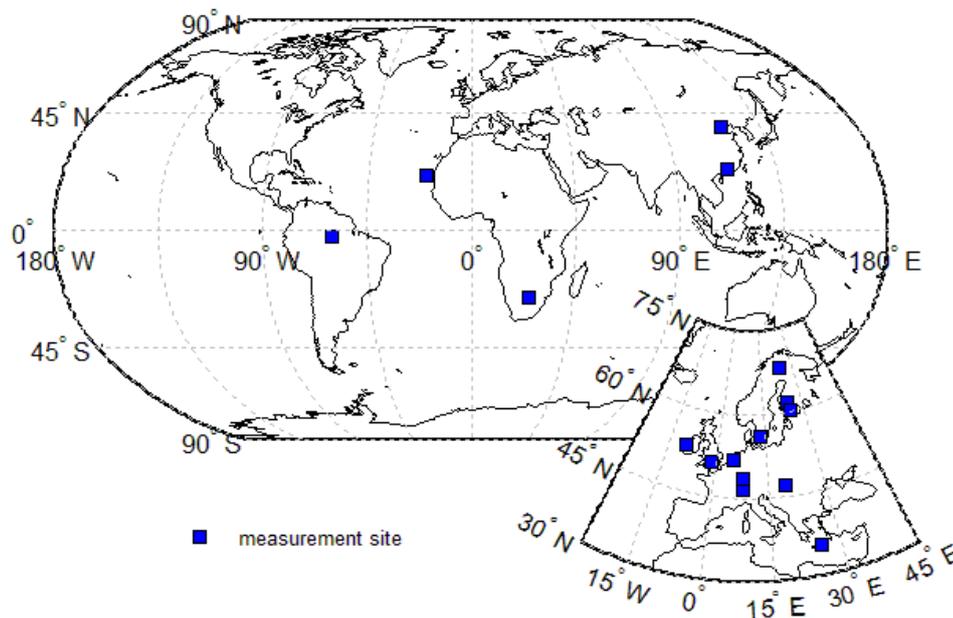


Figure 2. The location of all measurement sites discussed in this thesis.

4 Results and discussion

4.1 Production of atmospheric CCN

As discussed previously, one of the most important sources of the atmospheric CCN production is the regional atmospheric nucleation events, also known as NPF events. **Paper I** concentrated on bridging the gap between atmospheric NPF and CCN formation, from both experimental and modelling perspectives. In particular, the paper aimed at describing quantitatively the effect of NPF events on the regional CCN budget at several locations around the world, as well as raised the issue of a significant effect of computational methodology on the outcomes of such quantification. Meanwhile, **Paper II** examined the potential effect of NPF on the CCN chemistry. In summary, NPF has a noticeable effect on CCN number concentrations and, depending on the location and season, can increase N_{CCN} by as much as several hundred percent. However, the activation and hygroscopic properties of CCN formed by NPF are indistinguishable from those of pre-existing CCN-sized aerosol.

4.1.1 The effect of NPF on CCN number concentration

The contribution of NPF events to the total atmospheric CCN budget was examined using long-term DMPS and additional CCNC data at two boreal sites in Finland (Hyytiälä and Pallas), a continental background site in Southern Sweden (Vavihill) and a dry savannah site in South Africa (Botsalano). Datasets for the two Finnish stations were both over ten years in duration, with Vavihill and Botsalano datasets being 36 and 18 months long, respectively. For Pallas and Botsalano, previous studies already attempted to quantify the effect of NPF on CCN budget using different techniques (Asmi et al., 2011; Laakso et al., 2012, respectively); **Paper I**, however, added data from Hyytiälä and Vavihill and harmonized the methodology for a more comprehensive overview. Total particle number concentrations above 50 nm, 80 nm, 100 nm and 150 nm were calculated from the DMPS data, denoted as N_{50} , N_{80} , N_{100} and N_{150} , respectively – these were meant to represent potential CCN concentrations at various ambient S levels. For each NPF event and for each concentration mentioned above the method compared a one-hour average particle concentration immediately before the appearance of the newly formed nucleation mode particles and a maximum corresponding concentration during an NPF event. These were compared in both absolute and relative terms. For a subset of NPF events in Hyytiälä the results were compared to those calculated using methods presented in Asmi et al. (2011) and Laakso et al. (2012).

Figure 3 shows a typical Type I nucleation event (Dal Maso et al., 2005) in Hyytiälä with corresponding DMPS and CCNC time series. During this event newly formed particles grew to CCN sizes, which can be seen in peaks of N_{50} and N_{100} concentrations 8 and 10.5 hours after the beginning of the event, respectively. These peaks represent an increase of 317% and 202% in corresponding N_{50} and N_{100} concentrations compared to those just

before the event. It is clear that CCN concentrations approximated from the DMPS data match well with those directly measured by the CCNC at a given supersaturation, illustrating that N_{CCN} can be reliably estimated for a given S from size distribution measurements alone.

Nucleation events were found to increase N_{CCN} at all locations and for all seasons. Pallas exhibited the highest relative increase in N_{CCN} due to NPF, with an average increase in N_{50} of 360% and over 800% throughout the year and in the summer only, respectively. This is a direct consequence of very low absolute particle number concentrations in Pallas compared to other sites (Dal Maso et al., 2007; Kristensson et al., 2008; Laakso et al., 2008; Asmi et al., 2011). Botsalano also had high relative increases in N_{CCN} , especially during the local summer; during this season N_{80} can increase by as much as 400% due to NPF events. Laakso et al. (2012) reported that such high increase may be contributed to high growth rates and generally cleaner air. Smallest relative increase in N_{CCN} was observed in Vavihill for all N_{CCN} concentrations almost for all seasons. Proximity to more urbanised environment compared to Hyytiälä is likely the reason for higher background concentrations and, therefore, lower relative increases. In Hyytiälä Type I nucleation events always at the very least double N_{CCN} concentrations with no particular seasonal pattern. The highest absolute increase in N_{CCN} was in Botsalano for almost all N_{CCN} concentrations and seasons, with N_{50} during the local summer increasing by as much as 3500 particles cm^{-3} . If one takes into account high background aerosol concentrations at this site (Laakso et al., 2008), such behaviour must be due to very intense nucleation events. Indeed, both Laakso et al. (2008) and Vakkari et al. (2011) reported growth rates in Botsalano to be considerably higher than at the three other sites. High absolute N_{CCN} contribution and, therefore, fairly intense NPF events were also observed in Vavihill. The smallest absolute effect of NPF on N_{CCN} was observed in Pallas, illustrating comparatively low nucleation rates compared to other sites. Besides pre-existing particle number concentrations, the magnitude of the contribution of NPF events to the CCN budget depends strongly on the biogenic and anthropogenic emissions, frequency of nucleation events and the nucleation and growth rates.

While the general pattern of N_{CCN} response to NPF is similar when using different methods of quantification, the exact values in both relative and absolute terms are notably different. Both Asmi et al. (2011) and Laakso et al. (2012) used a slightly different method than in **Paper I**, resulting in smaller additions to N_{CCN} budgets. This is logical since the analysis in **Paper I** utilised the maximum N_{CCN} during an event. All three studies highlighted the difficulty in differentiating between the primary pre-existing CCN and the CCN introduced solely by the NPF events, a challenge than none of the three methods resolved well. Besides standardising the procedure for the calculation, a more rigorous analysis including non-event and undefined nucleation event days supplemented with the model simulations would be highly useful and desirable for a more accurate determination of the contribution of NPF to atmospheric CCN budget.

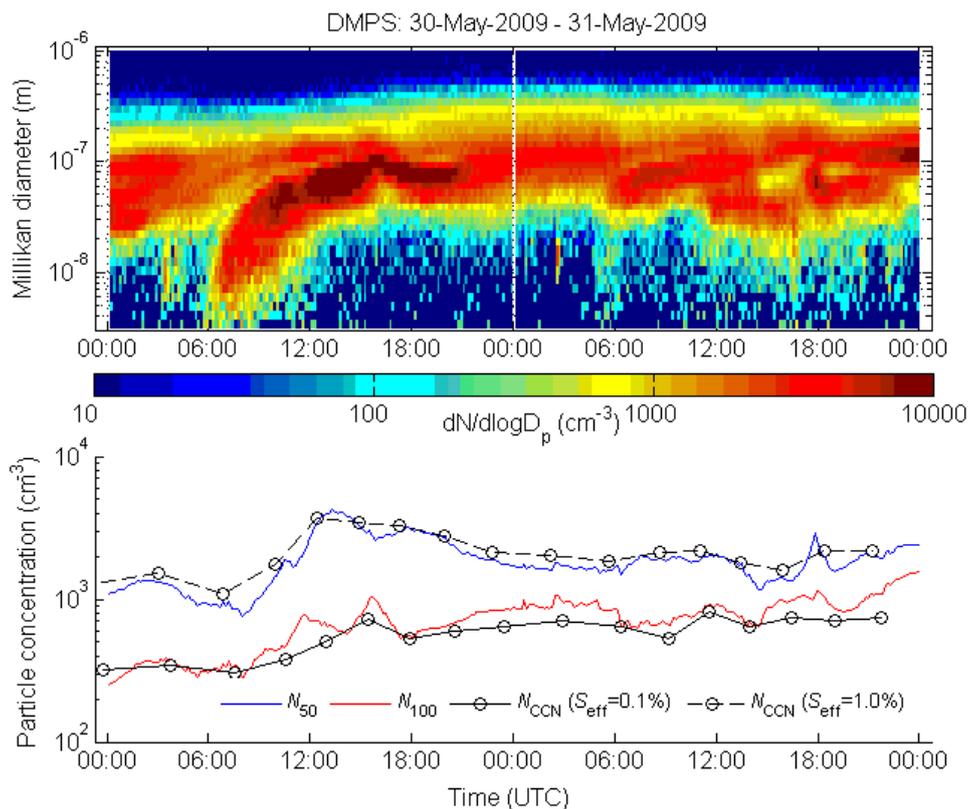


Figure 3. An example of a nucleation event in Hyytiälä station on May 30, 2009. The top panel depicts the time series of particle number size distribution. The bottom panel shows the corresponding time series of two DMPS-derived CCN concentrations (N_{50} and N_{100}) and two CCN concentrations N_{CCN} measured by the CCNC at two supersaturation (S_{eff}) levels of 0.1% and 1.0%. Adapted from **Paper I**.

4.1.2 The effect of NPF on CCN activation and hygroscopic properties

Of special interest also is the effect of NPF on CCN from a chemical perspective. The chemical precursors and the process of atmospheric nucleation have been studied extensively (e.g. Kurtén et al., 2008; Kirkby et al., 2011; Kulmala et al., 2014), bearing the question of chemical composition of CCN produced by the NPF. **Paper II** attempted to determine whether there was a noticeable difference in the CCN activation and hygroscopic properties caused by NPF. Considering typical growth rates in Hyytiälä (Dal Maso et al., 2005; **Paper I**), newly formed particles are, on average, expected to grow to ~ 50 nm by late evening of the same day/midnight/early morning of the next day. CCN activation and hygroscopic properties, namely D_c and κ , were examined on a diurnal basis for a subset of spring Type I nucleation events and non-events. The comparison revealed that there is no significant difference between the chemical composition of CCN produced by NPF versus pre-existing CCN, a claim previously reported by Ehn et al. (2007) and Sihto et al. (2011). This demonstrates that by the time newly formed particles grow to ~ 50 nm in diameter (approximately 15 hours in Hyytiälä; **Paper I**), their chemical composition

is indistinguishable from that of the pre-existing ~50 nm aerosol. Same is true for the larger, accumulation mode aerosol. As previously reported by Fierce et al. (2013), photochemical reactions, atmospheric oxidation and other aging processes seem to affect CCN activation and hygroscopic properties more than the original source of CCN in a way that by the time newly formed particles grow to CCN sizes, their NPF chemical footprint is no longer identifiable.

4.2 CCN activation and hygroscopic properties

The analysis of CCN activation and hygroscopic properties comprises the bulk of the research presented in this thesis. A detailed analysis of the first multi-year CCNC dataset (**Paper II**) is complimented by the comprehensive overview of CCN properties at 14 different locations within the European Integrated project on Aerosol Cloud Climate and Air Quality interactions EUCAARI framework (**Paper III**). Several long-term datasets allowed for a careful seasonal analysis of CCN activation and hygroscopic properties, and the ability to compare data from more than a dozen locations around the world led to some interesting conclusions that are important potentially on a global scale (**Paper III**). **Paper IV** also compared the CCNC-derived CCN parameters with those derived by the Volatility-Hygroscopicity Tandem Differential Mobility Analyser (VH-TDMA). Two main conclusions applicable to the majority of locations around the world were achieved. It was found that a) a similar fraction of aerosol activated at any given S and a simple linear approximation of annual mean N_{CCN} as a function of S_{eff} is given; b) CCN chemical composition varies with size significantly enough to warrant certain implications of the current use of hygroscopicity parameter κ in CCN studies.

4.2.1 CCN activation properties

CCN activated fraction is one of the simplest parameters that can be derived from both size-segregated and non size-segregated CCNC measurements; it can, however, provide an insight into the effect of aerosol size distribution and its chemical composition on the activation of CCN into cloud droplets. Figure 4 presents the activated fraction A as a function of supersaturation S_{eff} for a subset of EUCAARI locations, the figure also includes the overall fit based on all locations except for Finokalia, COPS, Jungfraujoch and Pallas A, B and C.

It is immediately visible that the majority of activation curves in figure are similarly placed and have similar slopes, indicating that there is little difference in how S_{eff} affects annual mean A at the majority of locations, something that was previously reported by Andreae (2009). Of the four locations that have clearly different activation curves, aerosol in Finokalia is expected to be hygroscopic due to its marine origin, Aitken mode during the COPS campaign was more hygroscopic than accumulation mode and aerosol in Pallas and Jungfraujoch had low concentrations and, depending on the season, low hygroscopicity (Figs. 4 and 5). The locations presented in Fig. 4 are rather different with

respect to the aerosol properties, and, therefore, the similarity of activation curves for most of the locations is an interesting result. For example, an order of magnitude difference in N_{CCN} , a substantial difference in κ and at least some presumed difference in the shape of size distribution between the RHaMBLe cruise and the PRIDE-PRD2006 campaign seem to result in no apparent difference in the fraction of the aerosol that activates into cloud drops at any given S_{eff} . Reasons for such behaviour are hidden in the thermodynamics of the aerosol-water vapour interactions, different ambient S , N_{CN} and their chemistry, droplet growth kinetics etc.; however, total number concentration N_{CN} alone is sufficient to make a fairly accurate prediction of annual mean N_{CCN} at any given S_{eff} . **Paper III** suggested a simple linear fit for an easy calculation of annual mean N_{CCN} at any given S_{eff} based on N_{CN} alone:

$$N_{CCN} = N_{CN} \times (0.22 \times \ln(S_{eff}) + 0.69), \quad (3)$$

where S_{eff} is in percent and N_{CN} and N_{CCN} are in particles per cm^3 .

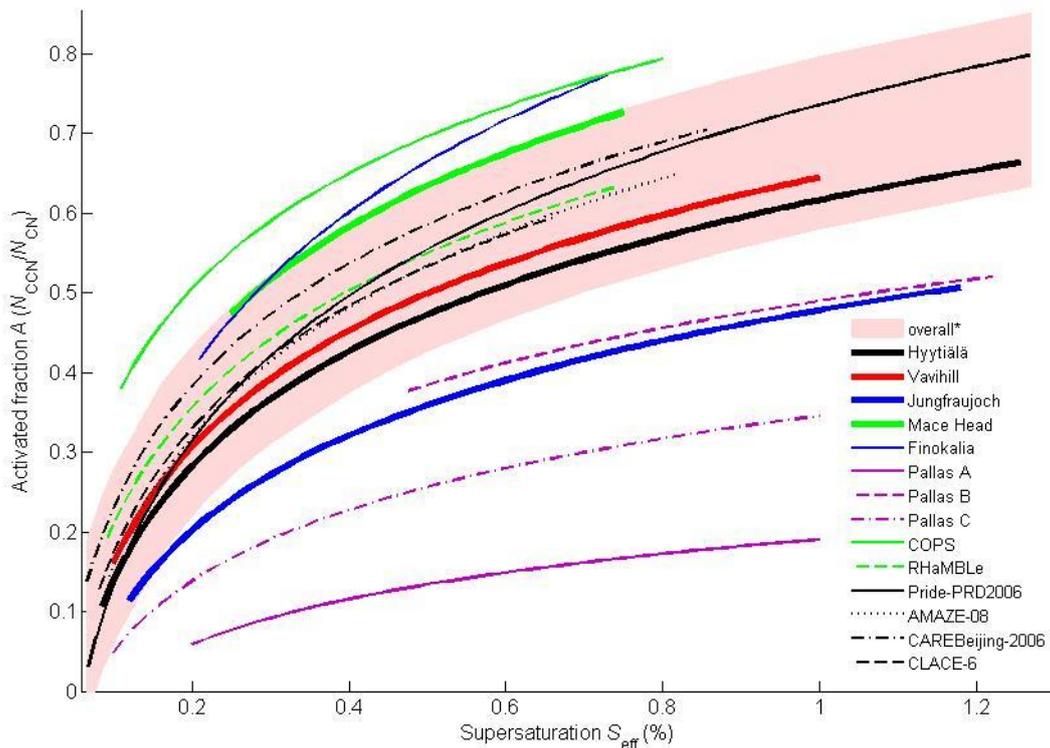


Figure 4. Average activated fraction A as a function of supersaturation S_{eff} for all available datasets. Shown are the linear fits in the form $A = a \times \ln(S_{eff}) + b$. Also shown is the overall fit based on all data points (*Finokalia, COPS, Jungfraujoch and Pallas A, B and C datasets excluded). The shading of the overall fit represents the prediction bounds of the fit with a confidence level of 95%. Adapted from **Paper III**.

The overall fit in Figure 4, on which Eq. 3 is based, produced an excellent correlation coefficient r of 0.96, demonstrating the accuracy of potential application. Care should be taken when using this parameterisation, as it might not provide the best results for certain marine locations, free tropospheric sites and locations with exceptionally low particle number concentrations.

The examination of effective activated fractions, calculated using particle number concentrations above 50 nm and 100 nm in diameter (N_{50} and N_{100} , respectively) instead of N_{CCN} , revealed that, when used together with normally-derived A values, they can provide additional information about the size distribution of the aerosol population and its effect on the aerosol activation efficiency.

Besides the activated fraction presented above, which is typically calculated from total N_{CCN} and N_{CN} concentrations, activation spectra resulting from size-segregated measurements yield another useful parameter, maximum activated fraction MAF. Using the non-normalised fitting (**Paper II**), MAF gives an idea about the fraction of CCN-sized aerosol population that does not activate into cloud droplets no matter how large the particles are or high the S_{eff} inside the CCNC chamber is. Therefore, for every size-segregated measurement spectrum MAF represents the CCN-active fraction and $1 - \text{MAF}$ represents the CCN-inactive fraction of aerosol population of $\sim 75\text{--}300$ nm in diameter. In Hyytiälä the median CCN-inactive fraction comprised 5% of the total aerosol population of the CCN size. The length of the Hyytiälä dataset made it possible to also examine the seasonal variation of the CCN-inactive fraction, and a seasonal pattern was, indeed, discovered. The smallest CCN-inactive fraction was observed in May, June and July, with a median value of 0.2%. During the rest of the year a much larger CCN-inactive fraction was present, with a median value of 6.6%. In the CCN studies, the aerosol species that are CCN-inactive are typically assumed to be insoluble and refractory species, such as mineral dust and black carbon (BC) (Gunthe et al., 2009). The observed seasonal pattern of the CCN-inactive pattern in Hyytiälä matches well with that of BC. The highest and lowest absorption coefficients in Hyytiälä are observed in February and July, respectively (Virkkula et al., 2011). At the same site both Hyvärinen et al. (2011) and Häkkinen et al. (2012) reported the lowest BC concentrations in the summer time. The near-absence of CCN-inactive fraction during the summer may also indicate that, on average, the aerosol in the $\sim 75\text{--}300$ nm size range in Hyytiälä is close to being internally mixed in May, June and July.

4.2.2 CCN hygroscopic properties

CCNC-derived critical diameters D_c and hygroscopicity parameters κ were examined for a dozen locations around the world (**Paper III**), were the backbone of the first multi-year dataset of CCN activation and hygroscopic properties (**Paper II**), and were compared to those derived from the VH-TDMA measurements in Hyytiälä (**Paper IV**). The resulting amalgamation of outcomes provided a useful and interesting insight into the spatial

variability of CCN hygroscopic properties, as well as its dependence on particle size and method of measurement and derivation.

One of the most interesting results presented in this thesis is the variation of κ with size. As initially postulated by Petters and Kreidenweis (2007), hygroscopicity parameter κ is independent of the particle size and relative humidity and is solely related to chemical composition of a CCN. Figure 5 presents the variation of κ with particle dry size for 11 locations around the world, some being short-term campaigns, others being sites of long-term CCNC measurements. The figure is split into four panels for a better visual representation. For almost all datasets the observed κ values are between 0.1 and 0.5; exception to this is the RHaMBLe campaign in the tropical North Atlantic, during which κ values for all studied sizes were just below unity. Figure 5 clearly shows that at the majority of presented locations κ increases with size, indicating that the large accumulation mode particles are frequently more hygroscopic than the Aitken mode particles. Such trends have been reported for most of these locations in published literature. It is usually assumed that accumulation mode particles have already activated into cloud droplets at least once, with the fraction of soluble material increasing in the particle mass after the reactions in the aqueous phase and subsequent evaporation. Such sequence of events, known as cloud processing, has been shown to increase particle hygroscopicity (e.g. Crumeyrolle et al., 2008). The increase of κ with particle dry size is observed for 8 out of 11 locations. In fact, for all datasets depicted in both upper panels of the Figure 5 (except Pallas B), the Mann-Whitney U test (Mann and Whitney, 1947) for two populations that are not normally distributed (below and above 100 nm of dry size; **Paper II**) revealed that the difference in κ is statistically significant at the 5% significance level, i.e. the median values of κ of Aitken and accumulation mode particles are significantly different. During the COPS campaign (Figure 5, lower left panel) aerosol exhibited a decrease of hygroscopicity with particle dry size. While Irwin et al. (2011) did report that accumulation mode particles at the mountainous location of the south-west Germany were less hygroscopic than the Aitken mode aerosol, the same study showed that κ derived from H-TDMA in a sub-saturated regime did increase with size. No particular trend in the variation of κ with particle size was observed during a research cruise in the North Atlantic (RHaMBLe) and during a campaign at the K-pusztá site in central Hungary. It can be said that at these sites aerosol chemical composition seems to have no particular size dependence across the whole measured size range. The implications of the variation of κ with size are discussed below.

The examination of κ distributions in Hyytiälä at different S_{eff} levels also revealed an interesting pattern (**Paper II**). At the S_{eff} above 0.4% the distributions are similar, close to log-normal and narrow, with all three median κ values for S_{eff} of 0.4%, 0.6% and 1.0% being approximately 0.2. As the S_{eff} decreases below 0.4%, the distributions become much wider, illustrating a larger scatter of κ values at low S_{eff} levels; the median κ increases to 0.4 for S_{eff} levels of 0.1% and 0.2%. A larger variability of κ may be due to larger instrumental uncertainties at smaller S_{eff} (Rose et al., 2008); additionally, larger particles are expected to have a greater degree of variability of their chemical composition, as they

have been in the atmosphere for longer times, subject to a variety of atmospheric processes. Nevertheless, κ distributions also point out the apparent difference of chemical composition of accumulation and Aitken mode aerosol particles.

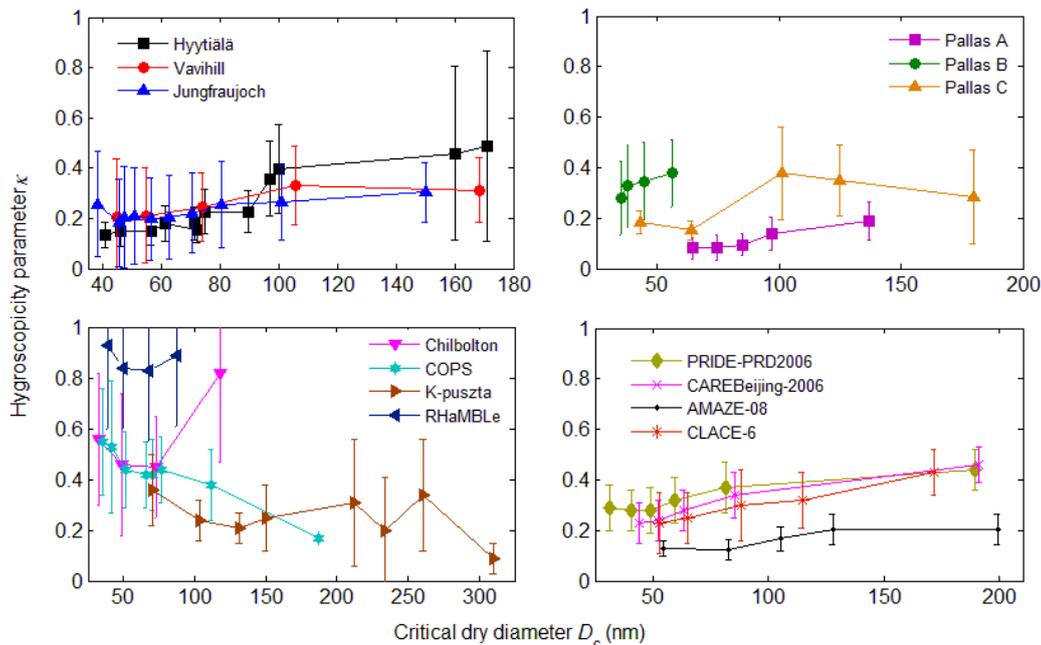


Figure 5. Mean hygroscopicity parameter κ as a function of critical dry diameter D_c for selected locations. Figure split in four for more detail. Shown with one standard deviation. Adapted from **Paper III**.

The variation of κ and its distribution with size in Hyytiälä and elsewhere (**Paper II**, **Paper III**) intuitively leads to two conclusions. First, it is clear that using one single, mean or median, value for describing the hygroscopicity of the whole aerosol population is incorrect and leads to a loss of important size-segregated information about hygroscopicity distribution. The hygroscopicity of an aerosol population should preferably be presented either as a function of size, e.g. with separate κ values for Aitken or accumulation mode, or by using hygroscopicity distribution functions which can also describe the external mixing effects (Lance, 2007; Su et al., 2010). Chemistry of aerosol particles can be deduced using a variety of aerosol instrumentation, e.g. AMS, and hygroscopicity parameter κ can be calculated from these measurements as well (Petters and Kreidenweis, 2007; Chang et al., 2010). Depending on location, if such measurements are representative of particles in the accumulation mode, the second conclusion is that the chemistry derived from such measurements should be extended down to the Aitken mode size with caution. The effect of the extension of accumulation mode κ to the Aitken mode aerosol was investigated for Hyytiälä. By assuming the same κ for Aitken mode as for the accumulation mode, the N_{CCN} concentration is overestimated on average by 16% and

13.5% for the S_{eff} of 0.6% and 1.0%, respectively. Overestimation of such magnitude is not trivial, and the exact use of κ for predicting N_{CCN} is dependent on the desired output accuracy of N_{CCN} .

Paper IV investigated aerosol hygroscopic properties in Hyytiälä during the summer of 2010 using VH-TDMA under the sub-saturated conditions and compared the results to those derived from the corresponding CCNC measurements. VH-TDMA-derived κ values were found to increase with size, similar to those derived from the CCNC. This was attributed to the presence of the varying amounts of organics and sulphate in the particle mass. However, the absolute κ values in sub-saturated regime were notably lower than in the supersaturated regime (Figure 6). VH-TDMA-derived κ was 0.12 and 0.15 for Aitken and accumulation modes, respectively. The observed difference may be due to organics having different dissolution degrees under sub- and supersaturated conditions (Prenni et al., 2007), the dependence of hygroscopicity on RH stemming from particle mixing state and potential phase separation (Zardini et al., 2008) or the exact aerosol composition (Good et al., 2010).

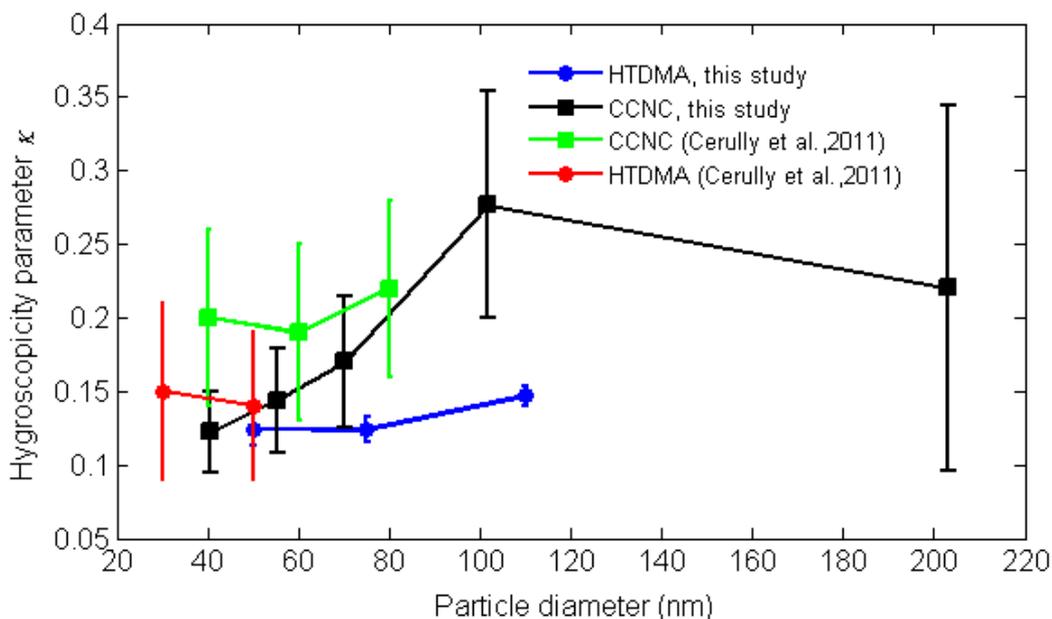


Figure 6. Median hygroscopicity parameter κ values derived from measurements in sub-saturated (H-TDMA) and supersaturated (CCNC) regimes as a function of particle dry size. Shown also are values from a study by Cerully et al. (2011) at the same location. Error bars are 25th and 75th percentiles. Adapted from **Paper IV**.

4.2.3 Temporal variation of CCN activation and hygroscopic properties

Paper II and **Paper III** presented the first of its kind seasonal analysis of the CCN activation and hygroscopic properties. The datasets from Hyytiälä, Vavihill and Jungfraujoch, being 47, 25 and 23 months in duration, respectively, allowed for the examination of both seasonal patterns and spatial differences among sites. Now over six years long, the dataset from Hyytiälä remains the longest dataset of size-segregated CCNC measurements in the world. **Paper III** reported that at the three locations discussed below, the particles measured at the S_{eff} of 0.1% can be said to be representative of the accumulation mode (D_c between 120 and 200 nm in diameter) and those measured at the S_{eff} of 1.0% are representative of the Aitken mode (D_c between 40 and 50 nm in diameter).

The inspection of the seasonal variation of aerosol hygroscopic properties at three long-term sites revealed no particular pattern at any of the sites. The hygroscopicity of Aitken, ~50 nm aerosol is fairly constant throughout the year and rather similar for all three locations. The absence of spatial difference further solidifies the claim made in section 4.1.2 that the effect of new particle formation on hygroscopicity is indistinguishable from those of other atmospheric processes. The absence of any seasonal pattern was also seen for accumulation mode particles in Vavihill and Jungfraujoch. The only obvious annual pattern of aerosol hygroscopicity was observed in Hyytiälä for accumulation mode (120–200 nm in diameter) aerosol, reported both in **Paper II** and **Paper III**. In the boreal environment of Southern Finland accumulation mode aerosol is most hygroscopic in February and least hygroscopic in July. A similar trend has been previously reported for the same site by Sihto et al. (2011) and for sites in Germany and Colorado by Pringle et al. (2010) and Levin et al. (2012), respectively. In Hyytiälä the low aerosol hygroscopicity in the summer can be explained by the higher vegetation activity and higher emissions of volatile organic compounds (VOCs). These emissions lead to a more active formation of secondary organic aerosol (SOA) and increase the organic fraction in the aerosol. An increase in the hygroscopicity of the accumulation mode aerosol in the winter can be attributed to the higher sulphate fraction, more intense aerosol oxidation and probably other aging processes. The fact that ambient supersaturation levels in the atmosphere typically remain below 0.3% (Ditas et al., 2012; Hammer et al., 2014; Hudson and Noble, 2014) means that particles most frequently participating in the cloud droplet formation are in the accumulation mode. Therefore, their chemical composition and its observed variation throughout the year play an important role in the cloud formation in Hyytiälä.

Another parameter that could be compared seasonally is the rate of the increase of aerosol hygroscopicity with size in Hyytiälä, i.e. the slope of a potential linear fit in the Figure 5. It was found that such rate is highest in the winter and lowest in the summer, similar to the variation of absolute κ values of the accumulation mode aerosol (**Paper II**). In the winter, as mentioned previously, larger aerosol is expected to contain a larger sulphate fraction and be subjected to stronger oxidation. Additionally, aerosol growth is slower in the winter due to lower concentrations of condensable vapours, allowing for longer oxidation and

aging times. Similarly, the lowest rate of increase of hygroscopicity with size in the summer is possibly due to higher aerosol organic fraction and more active SOA formation.

While the examination of seasonal variation of aerosol hygroscopic properties can reveal something about the effect of temperature and vegetation activity, the diurnal profiles are indicative of the potential effects of photochemistry and solar radiation. Aerosol hygroscopic properties were examined on a diurnal basis for Hyytiälä, Vavihill and Jungfraujoch. The diurnal variation of aerosol hygroscopicity for the larger, accumulation mode aerosol revealed no particular patterns for any of the three locations; same can be said if the diurnal trends are separated by seasons. Photochemistry and other atmospheric processes governed by the presence/absence of the solar radiation have no effect on the hygroscopicity of the accumulation mode aerosol. When Aitken mode aerosol is examined, the situation becomes slightly more complex; hourly variation of the hygroscopicity of the Aitken mode aerosol was examined on a seasonal basis (Fig. 7). During the winter no particular diurnal pattern exists for any of the examined stations; logically, the diminished solar activity in the winter is likely responsible for the observed behaviour. In the spring and continuing into the summer, both Hyytiälä and Vavihill exhibited a diurnal pattern of increased hygroscopicity of around noon and decreased hygroscopicity at night. **Paper II**, Sihto et al. (2011) and Cerully et al. (2011) all attributed such pattern in Hyytiälä to the influence of photochemistry and aging of the organics during the sunlight hours. A more conclusive diurnal pattern of Aitken mode aerosol hygroscopicity in summer in Hyytiälä further strengthens this notion. The environment of the Southern Sweden is not expected to be drastically different from that of Hyytiälä, with similar reasons likely being true for the observed diurnal patterns of Aitken mode aerosol in Vavihill as well. No pattern of Aitken mode aerosol hygroscopicity is observed in Hyytiälä and Vavihill in the autumn. Diurnal profiles in Jungfraujoch are clearly different from those of Hyytiälä and Vavihill (Fig. 7). As mentioned above, no pattern exists in Jungfraujoch during the winter, and same is true for the spring. During the summer and autumn Aitken mode aerosol displayed a clear decrease in hygroscopicity around 15:00 local time with an increase in the middle of the night. Kammermann et al. (2010) has previously reported that a decrease in hygroscopicity in the afternoon is due to the intrusions of air from the growing PBL. Typically, Jungfraujoch is in the free troposphere with low concentrations of fairly hygroscopic Aitken mode aerosol (Collaud Coen et al., 2011); in the summer and autumn strong thermal convection brings the more polluted air and aerosol of lower hygroscopicity up to the station (Jurányi et al., 2010; Kammermann et al., 2010; and Jurányi et al., 2011).

Overall, photochemistry, aging processes, atmospheric NPF and other atmospheric processes occurring on a diurnal scale have little to no effect on the hygroscopicity of the accumulation mode aerosol. They are, however, important to varying degrees in affecting the hygroscopicity of Aitken mode (~50 nm) aerosol. The hygroscopicity of the accumulation mode aerosol is more affected by processes occurring on a time scale of a few days to months, e.g. long range transport and seasonal variation in vegetation activity; however, the effects of these processes vary spatially quite a lot.

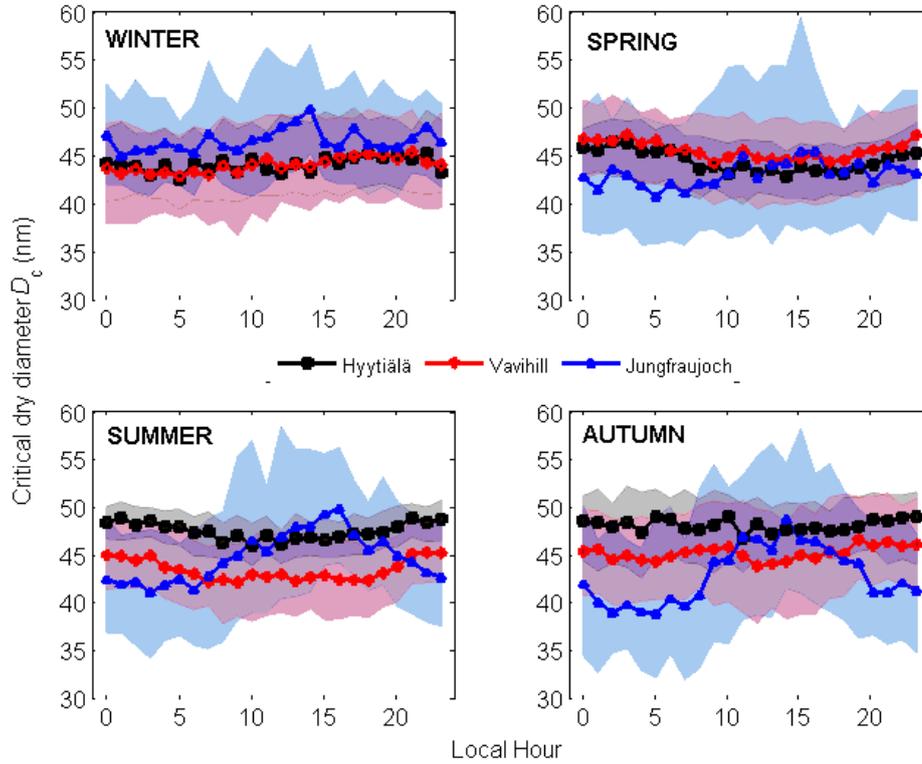


Figure 7. Hourly median critical dry diameters D_c at the S_{eff} of 1.0% for three long-term measurement locations separated by seasons. Shaded areas represent the 25th and 75th percentiles, with colours corresponding to the median data. Adapted from **Paper III**.

4.3 CCN removal

Wet scavenging of aerosol particles by snow is an important mechanism of aerosol removal from the atmosphere in cold, mid-latitude, Polar and mountainous regions. **Paper V** concentrated on the quantification of the scavenging efficiency of snow at an urban site in Helsinki, on the grounds of the Kumpula Campus of the University of Helsinki. The location is the site of the SMEAR III (System for Measuring Ecosystem-Atmosphere Relations) station (Järvi et al., 2009). The study utilised aerosol size distribution data with the range from 10 nm to 1 μm in diameter during four winters from October 2006 until April 2010 and presented size-segregated scavenging coefficients. Besides calculating scavenging coefficients and comparing them to previously published values, **Paper V** also focused on determining the effects of precipitation type and rate, ambient air temperature and relative humidity on the scavenging efficiency of snow.

Mean scavenging coefficients across the whole dataset varied between $1.87 \times 10^{-6} \text{ s}^{-1}$ and $4.20 \times 10^{-5} \text{ s}^{-1}$, with the mean and median values being $1.42 \times 10^{-5} \text{ s}^{-1}$ and $7.75 \times 10^{-6} \text{ s}^{-1}$, respectively. These values are in a fair agreement with the most recent studies by Laakso

et al. (2003) and Kyrö et al. (2009), both for Hyytiälä, although they are an order of magnitude smaller than in some earlier published literature (e.g. Graedel and Franey, 1975; Miller, 1990). Figure 8 presents the mean values of scavenging coefficients across the whole studied size range. Besides the mean values themselves, the left panel also presents the fit suggested by Laakso et al. (2003) to the dataset under investigation and two additional datasets: one for snow by Kyrö et al. (2009) and one for rain by Laakso et al. (2009). The right panel presents exactly the same except for a Pearson IV fit (Kyrö et al., 2009) used instead of that by Laakso et al. (2003). In both panels the Greenfield gap extends roughly across the particle size range of 60 to 300 nm, meaning that particles in this size range are scavenged by snow least efficiently compared to other sizes. This size range contains a large fraction of particles that are expected to potentially act as CCN, implying that snow scavenging is not a very important pathway of CCN removal from the atmosphere compared to other removal processes. No discernible difference in the scavenging efficiency of snow was found between the urban and rural sites of Southern Finland. It was, however, argued that snow might be a better scavenger of aerosol particles than rain per equivalent water content. Such argument has been presented in several previously published studies (e.g. Magono et al., 1975; Croft et al., 2009) and attributed largely to the filtering effect of cavities in the snowflake creating a flow through rather than around it (Mitra et al., 1990).

Several meteorological parameters were examined with respect to their potential effect on the scavenging efficiency of snow. It was discovered that snow mixed with other types of hydrometeors, such as raindrops and ice grains, is a more efficient particle scavenger than snow alone. Higher snowfall rate also resulted in a higher scavenging efficiency, although this pattern was pronounced only when examining very high precipitation rates. Over 80% of the examined precipitation intensity was below 0.6 mm hr^{-1} , where no dependence of scavenging coefficients on the precipitation rate was observed. Only snowfall rates over 0.6 mm hr^{-1} can lead to a discernible increase in the efficiency of snow scavenging. Scavenging of aerosol particles by snow was found to increase with increasing temperature and relative humidity, with the latter having the largest and most discernible effect on the snow scavenging efficiency. It was postulated that, when examining the scavenging only by Brownian diffusion, impaction and interception, higher RH leads to changes in the physical properties of snowflakes, which, in turn, increases their capacitance (Field et al., 2006; Westbrook et al., 2008). Similar to the expected effect of higher temperature and the presence of raindrops, higher RH is expected to make the snowflakes heavier and stickier, increasing their cross-sectional area and terminal velocity and, therefore, their scavenging efficiency. **Paper V** presented a new parameterisation equation for the determination of scavenging efficiency of snow based on both particle diameter and RH.

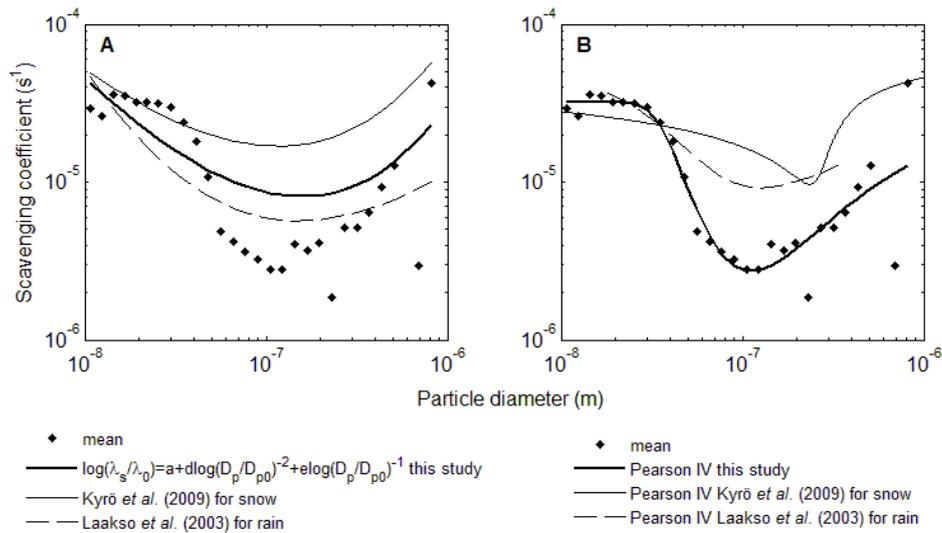


Figure 8. Mean snow scavenging coefficients λ_s shown with A) parameterisation function according to Laakso et al. (2003) and B) Pearson IV function. Included in both figures are corresponding parameterisations from two previous studies. Adapted from **Paper V**.

In all of the attempted parameterisations, the functions also reached their minima around the 100 nm particle size, implying that the effect of varying meteorological parameters is more pronounced for the scavenging of nucleation and Aitken mode particles and is minimal for the accumulation mode particles. Around 100 nm size the difference in parameterisation classes was the smallest, implying that CCN concentrations are affected by varying temperature, relative humidity and precipitation types and rates equally. Using simple assumptions it is possible, however, to roughly estimate the effect of snow scavenging on N_{CCN} .

It is known that the ambient supersaturation S in the PBL usually remains below 0.3%; **Paper II** reported that in Hyytiälä D_c at the S_{eff} of 0.3% is 85 nm, meaning that at the S_{eff} of 0.3% all particles above 85 nm in diameter N_{85} will activate into cloud droplets. The first assumption here is that N_{CCN} is equal to N_{85} . In Helsinki the average scavenging coefficient for the size range of 85 nm to 1 μm is $7.59 \times 10^{-6} \text{ s}^{-1}$. Since **Paper V** reported no significant difference in the scavenging efficiency of snow between Helsinki and Hyytiälä, it is reasonable to assume the abovementioned value to be applicable for Hyytiälä data as well. Assuming a constant snowfall lasting one hour with 0.2 mm hr^{-1} intensity, the fraction of aerosol removed from any given volume over this time is 0.027. This means that for any given N_{CCN} in any given volume of air in Hyytiälä, a typical and constant snowfall of one hour will remove only 2.7% of the initial N_{CCN} . Even if one further assumes that snowfalls in Hyytiälä are longer in duration and of higher intensity than in Helsinki, the expected effect on N_{CCN} is very small, meaning that wet scavenging by snow is not an important removal pathway of CCN in the boreal environment of Hyytiälä. In-cloud scavenging, i.e. activation of CCN into cloud droplets and impaction

scavenging, is a much more efficient and important pathway of CCN removal from the atmosphere.

4.4 The applicability of CCNC measurements at the SMEAR II

Indirect effects of aerosols on climate frequently serve as an important motivation for the ambient CCN and aerosol hygroscopicity studies. Such is the case for three publications in this thesis (**Papers I–III**), and, at least partially, in **Paper IV**. Amongst various effects, CCN activation into cloud droplets has been described and is understood better than ice nucleation (Boucher et al., 2013; DeMott et al., 2011), and two of the three first-author articles in this thesis closely concentrate on CCN activation and hygroscopic properties of ambient aerosol (**Paper II** and **Paper III**). Upon the conclusion of the PhD research work, several important questions, especially pertaining to the usefulness and practical applicability of the CCNC, arose.

In very broad and general terms, the chain of events resulting in the indirect effects of aerosol on climate can be described as follows. Atmospheric NPF produces new particles (Kulmala et al., 2004), which, after growth by coagulation, condensation and other processes, grow to CCN sizes and significantly increase local CCN concentrations (**Paper I**). Depending on the total particle number concentration, aerosol size distribution and chemistry (**Paper II** and **Paper III**), increased N_{CCN} results in increased CDNC and decreased droplet size, leading to changes in cloud microphysical properties, such as their albedo, lifetime and precipitation patterns (Boucher et al., 2013). Since atmospheric NPF is not the main focus of this thesis, this sequence of events at the SMEAR II is examined starting from the CCN activation into cloud droplets.

It is already well-known that particle size is more important than chemistry in affecting the particle ability to act as CCN (Dusek et al., 2006; Rose et al., 2010). While it was found that at a large number of locations around the world hygroscopicity increases with particles size, extending the accumulation mode κ down to the Aitken mode in Hyytiälä results in the average overestimation of N_{CCN} by 16% and 13.5% for the S_{eff} of 0.6% and 1.0%, respectively (**Paper III**). It is expected that at the SMEAR II size distributions play a more important role in determining N_{CCN} than κ values. Additionally, for any expected S level, N_{CCN} can be easily and fairly accurately estimated using only size distribution data (**Paper I**) or even just the total particle number concentration using Eq. 3 (**Paper III**).

Even when the N_{CCN} is known using whichever method of measurement and calculation, its effect on CDNC is not as straightforward as one tends to think. A modelling study by Moore et al. (2013) reported that CDNC is fairly insensitive to the N_{CCN} over continents, with the sensitivity increasing in pristine areas. The study presented that, on average, a 4–71% change in N_{CCN} over the continents results in 1–23% change in CDNC. While within the framework of this thesis it is not possible to exactly compute such sensitivity for changing N_{CCN} in Hyytiälä, a 16% change in N_{CCN} , as computed above, is likely to result in a ~5% change in CDNC, which is very small. Using satellite observations and a cloud

model, Janssen et al. (2011) also reported the lack of a clear correlation between CDNC and N_{CCN} in Hyytiälä. Therefore, even though hygroscopicity in Hyytiälä increases with particle size, using one κ value is more than sufficient for an accurate prediction of N_{CCN} . Moreover, considering the comparative insensitivity of N_{CCN} to κ and the amount of work associated with the operation of CCNC and data processing, one single κ value for continental aerosol (e.g. 0.27, as reported by Pringle et al. (2010)) would be an appropriate approximation. If the main goal at SMEAR II is to measure N_{CCN} , CCNC measurements are not necessary. N_{CCN} can be fairly accurately estimated using one κ value for continental aerosol or hygroscopicity can be abandoned altogether, with DMPS or even CPC data being sufficient for a rough N_{CCN} estimate.

If one considers that at the SMEAR II a) N_{CCN} is fairly insensitive to κ and b) CDNC is fairly insensitive to N_{CCN} , it becomes obvious that the effect of CCN hygroscopicity on cloud droplet number at SMEAR II is minuscule. Therefore, the main motivation behind CCNC measurements needs to be reconsidered as changing CCN hygroscopic properties will not have a significant effect on cloud microphysical properties. CCNC is a complex and old-generation measurement system, the maintenance and data processing of which requires a lot of time and effort. Unfortunately, given the abovementioned, it makes no sense to continue operating CCNC at the SMEAR II unless the focus of measurements changes as described below.

Besides the presumed role of CCN hygroscopicity in the changes to cloud microphysical properties, particle hygroscopicity is important in other aspects of atmospheric science. There is, of course, the direct effect of aerosols on climate, by which particles themselves absorb and scatter incoming solar radiation. The direct radiative forcing of aerosol certainly depends on aerosol size and chemical composition (Bellouin et al., 2005), implying that particle chemistry derived from CCNC measurements can be used in estimating it. Aerosol particles are also known to affect the visibility (e.g. Jinhuan and Liqun, 2000), and particle hygroscopicity has a direct link to the aerosol light scattering potential (e.g. Liu et al., 2012); although in this case measurements in sub-saturated conditions may be more appropriate for many compounds. Additionally, CCNC-derived particle hygroscopicity can be used when studying atmospheric aqueous phase chemistry and droplet kinetics, with CCN concentrations also being useful for looking at the variability of data with a purpose of model constraints. Unless the focus of CCNC measurements and the rationale behind them shift towards any of the abovementioned topics, the current use of CCNC at the SMEAR II and the amount of work and time that goes into its maintenance and data processing is unwarranted. The author of this thesis strongly suggests a significant reduction of the resources directed at the CCNC maintenance or a reconsideration of the main motivation and scientific ideas if the CCNC measurements are to be continued.

5 Review of publications and author's contribution

Paper I discusses an important topic of the contribution of atmospheric NPF to atmospheric CCN budgets and utilised both modelling and experimental tools to aid the synthesis of results. The climate effect of the recurrent and widespread contribution of NPF to CCN concentrations in the continental boundary layer is addressed as well. The exact quantification of this contribution is complicated and spans a wide uncertainty range. Some of most important challenges here are the determination of factors governing the NPF, the differentiation of primary and secondary CCN, the coupling of observational data with modelling and quantification of the NPF effects on climate. I conducted the analysis of supplementary data of new field observations, and wrote the text and produced figures in the section 3.2.

Paper II presents the first of its kind long-term multi-year dataset of CCNC measurements, conducted at the SMEAR II station in Southern Finland. The paper describes in detail CCN activation and hygroscopic properties in a boreal environment and conducted a thorough analysis of CCNC-derived parameters. Aerosol hygroscopicity was found to be slightly below the modelled global continental average, and it was found to increase with size, with the degree of increase being dependent on the season. Due to the observed relationship between κ and particle size and due to κ distributions being log-normal, a recommendation is made to present κ as a function of particle size. Seasonal and diurnal profiles of CCN activation and hygroscopic properties varied for particle sizes and seasons. I conducted the data analysis and wrote the majority of the text of the paper.

Paper III presents a comprehensive overview of CCNC measurements at 14 locations around the world, all conducted within the EUCAARI framework. Spatial and temporal differences of CCN activation and hygroscopic properties were evaluated, and a new method for estimating annual mean CCN concentration N_{CCN} from total particle number concentrations is introduced. Even though particle hygroscopicity at the majority of locations was found to increase with size, its effect on N_{CCN} is secondary compared to total particle number concentrations. Seasonal and diurnal variation of CCN activation and hygroscopic properties was found to vary among particle sizes, locations and seasons. I conducted the data analysis and wrote the text of the paper.

Paper IV investigates CCN hygroscopic and volatility properties during a summer campaign at the SMEAR II station. The study examines particle hygroscopicity derived from VH-TDMA in sub-saturated conditions and compares it to that derived from the corresponding CCNC measurements in supersaturated regime. CCNC-derived κ values were found to be higher than those calculated from VH-TDMA data. The dependence of particle volatility on particle size is explored. Regardless of the heating temperatures, some hygroscopic material was found to always remain in the aerosol mass. This non-volatile fraction of the aerosol was found to include compounds other than black carbon. In this study I provided the necessary CCNC data and helped with the interpretation of the results.

Paper V examines the wet scavenging of aerosol particles by snow at the SMEAR III station in Helsinki, Finland. The analysis focused on particles in the 0.01–1 μm size range and snowfalls with intensities below 1.2 mm hr^{-1} . Scavenging coefficients at the urban SMEAR III station were in good agreement with those in rural SMEAR II station. A minimum in the scavenging efficiency of snow was observed for particles in the 0.06–0.3 μm size range. The effect of various meteorological parameters on snow scavenging was investigated, resulting in the discovery that relative humidity is the most important parameter affecting snow scavenging. An increase in RH leads to a clear increase in snow scavenging of particles, and a new parameterisation equation is suggested for calculating scavenging coefficients based on both particle diameter and ambient RH. I conducted the data analysis and wrote the text of the paper.

6 Conclusion

Research work carried out as part of this PhD Thesis has resulted in significant advances in the field of CCN studies, all with respect to production of atmospheric CCN, their activation and hygroscopic properties and potential removal mechanisms. The results presented herein are of great importance for the studies of the life cycle of atmospheric CCN, and have supplemented both new qualitative outcomes and new quantitative parameterisations.

Atmospheric NPF in the boundary layer has been found to greatly increase local CCN concentrations, with the exact quantification being largely dependent on selected methodology. As expected, the number of newly formed CCN from NPF depends on many factors, including, but not limited to, biogenic and anthropogenic emissions, frequency of NPF events, nucleation and growth rates and pre-existing CCN concentrations. Pallas, a remote station in Northern Finland, exhibited the highest relative increase in CCN concentration N_{CCN} as a result of NPF; in the summer the particle number concentration above 50 nm in diameter N_{50} can increase by as much as 800%. At the same location absolute increases in N_{CCN} were very small due to low nucleation rates. Highest absolute increases in N_{CCN} as a result of NPF (up to 3500 particles cm^{-3} for N_{50}) were found at a dry savannah location of Botsalano in South Africa. In Hyytiälä Type I nucleation events were found to always, at the very least, double N_{CCN} concentrations.

In many locations around the world the same fraction of aerosols activates into cloud droplets at any given supersaturation S . A simple linear parameterisation is provided for an easy calculation of annual mean N_{CCN} based only on N_{CN} and the desired S . The parameterisation should not be used in estimating N_{CCN} for certain marine locations, sites in the free troposphere, locations with exceptionally low particle number concentrations and locations where cloud droplet activation is frequently induced by orographic lifting. CCN chemical composition and particle hygroscopicity were found to vary with size significantly enough to warrant certain implications of the current use of hygroscopicity parameter κ in CCN studies. At the majority of studied locations hygroscopicity increased

with size, with accumulation mode κ values being significantly larger than Aitken mode κ at some locations. Depending on the focus and desired accuracy, the use of κ values as a function of particle dry size should preferably be considered. The photochemistry, aging processes, atmospheric NPF and other atmospheric processes occurring on a diurnal scale were found to have little to no effect on the hygroscopicity of the accumulation mode aerosol. They were, however, found to be important to varying degrees in affecting the hygroscopicity of Aitken mode (~ 50 nm) aerosol. The hygroscopicity of the accumulation mode aerosol is more affected by processes occurring on a time scale of a few days to months, e.g. long range transport and seasonal variation in vegetation activity; however, the effects of these processes vary spatially quite a lot.

CCN were found to be removed by snow scavenging inefficiently compared to other removal mechanisms and compared to nucleation and Aitken mode particles. The trough in the efficiency of snow scavenging was found for particles in the 60–300 nm size range. No apparent difference in the scavenging efficiency of snow was observed between a rural and an urban site in Southern Finland. Ambient temperature, precipitation rate and relative humidity were all found to correlate positively with the scavenging efficiency of snow. Being the most important parameter, the effect of RH was examined further and a new parameterisation for calculating snow scavenging coefficients based on both particle dry size and RH is presented.

While the research presented herein is of great importance to the CCN pool of knowledge and the community, a very important link, that to CDNC, is missing. As a big part of this thesis, the knowledge about CCN activation and hygroscopic properties in the boreal environment has been improved. It is, unfortunately, not possible to say anything about how the observed parameters and expected changes to them will affect the cloud droplet number concentration and, therefore, cloud properties. Previous studies have raised the difficult issue of connecting N_{CCN} to CDNC, and the results of the work presented here would be much more useful and interesting if the connection to CDNC would have been established, even if to a degree. Additionally to the missing link to the CDNC, the expected (Moore et al., 2013) and reported (Janssen et al., 2011) absence of a clear correlation between CDNC and N_{CCN} in Hyytiälä further imply that at the SMEAR II the usefulness of the CCNC measurements and the derived parameters alone in the aerosol-cloud-climate system is inadequate and meagre, and their applicability is compromised and questionable. A reconsideration of the purpose, the focus and the motivation for the CCNC measurements at the SMEAR II is needed if they are to be continued with reasonable, interesting and exciting output.

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