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STUDIES ON THE CONNECTIONS BETWEEN ATMOSPHERIC
SULPHURIC ACID, NEW PARTICLE FORMATION
AND CLOUD CONDENSATION NUCLEI

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Academic dissertation

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Preface

This thesis was made during 2004–2013 at the Division of Atmospheric Sciences of University of Helsinki. I express my gratitude to Prof. Markku Kulmala, head of the division, for the opportunity to work with such an interesting subject, atmospheric science, in a motivated group. I thank the head of the Department of Physics, Prof. Juhani Keinonen, for providing the working facilities needed for the research.

While located in the Department of Physics, the research at the Division of Atmospheric Sciences is a fascinating multidisciplinary combination of physics, chemistry, meteorology and even biology. I am grateful to have been able to work in this interesting field, which in some aspects still resembles how natural sciences once started: let's go out to nature and see how it works! In our division people have mainly gone to the forest in Hyytiälä and measured how new particles are formed there. During these years, I have learned many interesting things — and many of them outside the basic physics — for example which gases trees are emitting when they are stressed and how water is transported in a tree.

I thank all my coauthors for good research co-operation. Especially I want to thank Ilona Riipinen for excellent co-operation in preparing paper II, Hannele Korhonen for giving her UHMA-code to my use, Henri Vuollekoski and Johannes Leppä for doing modelling work together, and Joonas Vanhanen and Jyri Mikkilä for co-operation in my last paper about CCN. This thesis combines modelling and analysis of field data. I personally did not participate the measurements, and therefore I want to acknowledge all researchers responsible for measurements as well as the technicians working at the field stations for providing the data used in this thesis.

I thank my supervisors Kari Lehtinen and Michael Boy for guidance during the whole path of PhD studies. Veli-Matti Kerminen deserves thanks for commenting the manuscripts and for supervision when I was finalizing this thesis. I thank my reviewers for the constructive comments to improve the introduction part as well as PhD Theo Kurtén for proofreading the thesis. Maj and Tor Nessling Foundation (project no 2008310) and Academy of Finland (Center of Excellence Program) are acknowledged for financial support.

I thank all the staff at the Division of Atmospheric Sciences for creating a nice working environment and offering good company. Being nostalgic, I want to mention the "gang" who started the doctoral studies at about the same time and/or with whom I shared a room: Ilona Riipinen, Anne Hirsikko, Lauri Laakso, Tareq Hussein, Theo Kurtén, Antti Lauri, Henri Vuollekoski, Tuomo Nieminen, Martta Toivola (Salonen), Johanna Lauros and Eija Asmi (Vartiainen). Thank you for company in research, studies, Hyytiälä courses and during conference trips, and for many many discussions both about scientific and non-scientific topics.

This period of PhD studies coincided with a difficult period in my personal life, and that certainly has affected my work too and made the period of PhD studies longer

than expected. I thank my supervisors and coauthors for patience and humane attitude — we all are simply humans and face problems from time to time.

I express my gratitude for collaboration and friendship with PhD Amar Hamed, a colleague from Kuopio, who passed away just two months ago. Thank you Amar for these years.

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In Kumpula, Helsinki, October 2013

Sanna-Liisa Sihto-Nissilä

Studies on the connections between atmospheric sulphuric acid, new particle formation and cloud condensation nuclei

Sanna-Liisa Katariina Sihto-Nissilä
University of Helsinki, 2013

Abstract

Atmospheric aerosol particles (small nm to μm sized particles floating in air) are an important part of the atmosphere and the climate system. Aerosols directly scatter sunlight and influence cloud formation, thereby causing a net cooling effect on the climate which counteracts global warming caused by greenhouse gases. Aerosols, particularly those from anthropogenic pollution, also deteriorate human health.

Aerosols originate either from direct particle emissions or are formed in the atmosphere from gas-phase vapours through nucleation. Aerosols have both anthropogenic and natural sources. In the atmosphere, particle formation occurs frequently in continental areas all around the globe, and it is an important source of aerosol particles and cloud condensation nuclei. Sulphuric acid is one of the main compounds in atmospheric particle formation, and it participates both in nucleation and particle growth.

This thesis studied the process of atmospheric particle formation and specifically its connection to gaseous sulphuric acid, based on analysis of field measurement data and modelling. New particle formation rates were observed to correlate with sulphuric acid concentration to the power between 1–2. This correlation was notably different than expected on the basis of nucleation theories. Based on the observed linear and squared correlation, new semi-empirical parameterisations for atmospheric nucleation rate were proposed: the activation and kinetic nucleation mechanism. Empirical nucleation coefficients were determined from atmospheric field data measured at two field stations in Hyytiälä, Finland, and Heidelberg, Germany.

The correlation of new particle formation with sulphuric acid and the factors affecting the correlation were further investigated by performing simulations with an aerosol dynamical model.

Atmospheric relative humidity was observed to correlate negatively with sulphuric acid concentration and particle formation rate. It was proposed that cloudiness at high relative humidities could decrease the amount of UV-radiation reaching the ground, thereby decreasing the formation of sulphuric acid through a photochemical reaction pathway.

This thesis also investigated the ability of aerosol particles in boreal forest to act as cloud condensation nuclei (CCN). New particle formation events were observed to produce significant amounts of potential CCN.

The results of this thesis provided new insights on atmospheric particle formation and its connection to sulphuric acid. The developed nucleation rate parameterisations are useful for modelling of aerosol formation in regional and global climate models. The CCN parameters determined for boreal forest environment can be applied in climate modelling to predict boreal forest aerosols' effects on climate.

Keywords: atmospheric aerosol, particle formation, nucleation, sulphuric acid, cloud condensation nuclei

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List of publications

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- I Sihto, S.-L.**, Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A. and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos. Chem. Phys.*, 6, 4079–4091, 2006.
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- IV Sihto, S.-L.**, Vuollekoski, H., Leppä, J., Riipinen, I., Kerminen, V.-M., Korhonen, H., Lehtinen, K. E. J., Boy, M., and Kulmala, M.: Aerosol dynamics simulations on the connection of sulphuric acid and new particle formation, *Atmos. Chem. Phys.*, 9, 2933–2947, 2009.
- V Vuollekoski, H., Sihto, S.-L.**, Kerminen, V.-M., Kulmala, M., and Lehtinen, K. E. J.: A numerical comparison of different methods for determining the particle formation rate, *Atmos. Chem. Phys.*, 12, 2289–2295, 2012.
- VI Sihto, S.-L.**, Mikkilä, J., Vanhanen, J., Ehn, M., Liao, L., Lehtipalo, K., Aalto, P.P., Duplissy, J., Petäjä, T., Kerminen, V.-M., Boy, M., and Kulmala, M.: Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest, *Atmos. Chem. Phys.*, 11, 13269–13285, 2011.

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1 Introduction

The air surrounding us is a mixture of gases (nitrogen, oxygen, argon, water vapour, carbon dioxide etc.) and small particles. Air is an example of an *aerosol*: a mixture of gas and small particles floating in it. The floating particles are called *aerosol particles*.

Due to their small size, in most cases aerosol particles are invisible to the human eye. However, at sufficiently big particle sizes and number concentrations the particles become visible, as seen in pollution from car exhaust pipe or from industry smokestacks, as smog in polluted cities, dust storms in desert areas or haze in a moist forest. In addition to the atmosphere, aerosols are encountered in many technical applications, for example: in deodorant spray, paints and other liquids that can be dispersed smoothly by first spraying them as aerosols to air or in inhalators used in drug delivery. This thesis deals with aerosol particles in the atmosphere, i.e. *atmospheric aerosols*.

Atmospheric aerosols originate either from direct particle emissions (primary aerosols) or are formed in the atmosphere from gases through nucleation (secondary aerosols). The direct particle emissions include soot and other particle emissions from wood and fossil fuel combustion, road dust particles, sea salt aerosols suspended to air from whitecaps on the sea surface, pollen emitted from flowering plants and trees, bacteria and viruses floating in air, and dust particles removed from Earth's surface by blowing wind (e.g. Reid et al., 2005; Engelstaedter et al., 2006; Viana et al., 2008; Hultin et al., 2011; Wang et al., 2013). These processes generate aerosol particles at all particle sizes from ~ 10 nm upto several tens of μm . In atmospheric particle formation, new particles are produced when vapour molecules collide together and form a stable cluster of 1–2 nm size (Kulmala, 2003; Kulmala et al., 2007, 2013). This process is called nucleation. In the atmosphere, sulphuric acid is considered as the most important nucleating vapour.

After being emitted to or formed in the atmosphere, aerosol particles are subject to various physical and chemical processes. Particles grow when different vapours condense onto the particle surfaces. Due to their random Brownian motion in air, aerosol particles collide with each other and stick or merge together in a process called coagulation. Chemical reactions on the particle surface or inside the liquid phase change the chemical composition of the particles. Finally, the particles are removed from the atmosphere when they deposit on any available surfaces: on the ground, ocean and lake surfaces, tree leaves, walls, windows, etc. In addition to dry deposition, particles are washed out from atmosphere by falling rain droplets or snow flakes.

Atmospheric aerosols cover a wide range of particle sizes from molecular clusters close to 1 nm to big dust or sea-salt particles of several μm in diameter. The upper size limit is set by gravity, which makes large particles fall down rapidly. The aerosol number concentration varies from a few 100 cm^{-3} in very clean Arctic areas (Koponen et al., 2003) to several $100\,000\text{ cm}^{-3}$ in polluted megacities (Mönkkönen et al., 2005; Wu et al., 2008). The large range of variation is a challenge for instrumentation, as the same instrument has to be capable of measuring three to four orders of magnitude particle size range and even five orders of magnitude concentration range.

The lifetime of an aerosol particle in the lower atmosphere is on the order of one day to one week (e.g. Williams et al., 2002). Despite their short lifetime, there is a persistent aerosol population in the atmosphere, maintained by the continuous emission and removal of aerosol particles into and out of the atmosphere. Due to different physical processes — nucleation, particle growth by condensation, collisions between particles, removal by gravitational settling or diffusion to surfaces — atmospheric aerosol has a characteristic particle size distribution. Aerosol particles tend to center around some particle sizes, thus forming different modes. Typically atmospheric aerosol has 3–4 modes: a nucleation mode around particle sizes $\sim 10\text{--}30$ nm resulting from new particle formation, an Aitken mode around $30\text{--}100$ nm (named after a pioneer aerosol scientist who first observed it), an accumulation mode around $0.1\text{--}1$ μm , and a coarse mode of large particles around $1\text{--}10$ μm . The accumulation mode results from the fact that for this size range the removal processes are slowest, making particles of this size accumulate in the atmosphere (Laakso et al., 2003; Mammarella et al., 2011). In addition, there is a persistent cluster mode at sizes $1\text{--}2.5$ nm (Kulmala et al., 2007).

Due to their short lifetime, aerosol particles travel in the troposphere (lower part of the atmosphere) typically some hundreds of kilometers, at maximum some thousands of kilometers. Thus, in contrast to long-lived greenhouse gases, tropospheric aerosols are not uniformly distributed around the globe, but are a local or regional phenomenon. However, in the stratosphere aerosol particles (e.g. those emitted from volcanic eruptions) survive much longer, having effects on weather and climate on longer time scales (Deshler, 2008).

Locally, aerosols affect air quality and deteriorate visibility (Chang et al., 2009a; Wang et al., 2010). Elevated particle mass (PM) concentrations have been observed to correlate with increased mortality in big cities (Dockery and Pope, 1994; Brunekreef and Holgate, 2002; Peters and Pope, 2002). Based on these studies, regulations for safe particle mass concentrations in size ranges < 10 μm (PM_{10}) and < 2.5 μm ($\text{PM}_{2.5}$) have been set up. Recently it has appeared more and more evidence, that especially fine particles (< 2.5 μm) have negative health effects (Pope et al., 2002). While the large (> 2.5 μm) particles deposit already in the nose and upper respiratory track, fine particles can be transported far in our respiratory system and some of the ultrafine particles (< 0.1 μm) may even enter the blood circulation system. It is expected, that in the future there will be regulations not only for the particle mass but also for the particle number concentration.

Despite their local nature, aerosols have regional and global effects on the weather and climate (Mitchell et al., 1995; Haywood and Boucher, 2000; Lohmann and Feichter, 2005; Bennartz et al., 2011). Aerosol particles directly scatter and absorb solar and infrared radiation, thereby affecting the amount of radiation reaching or escaping from the Earth’s surface (*the direct effect of aerosols*) (Yu et al., 2006). Indirectly, aerosols affect cloud formation by acting as cloud condensation nuclei (CCN) (Twomey, 1991; Penner et al., 2004). Aerosols are crucial for cloud formation, because in the Earth’s atmosphere the water vapour does not form droplets alone. Cloud droplets are formed when water vapour nucleates (condenses) heterogeneously on the surface of an aerosol particle — thus every cloud droplet has an aerosol particle inside it. The amount of

aerosol particles available for cloud droplet formation affects the cloud cover as well as the cloud properties: if there are more aerosols, there will be more but smaller cloud droplets, as the same amount of water is divided to a larger number of aerosol particles. Smaller cloud droplets reflect sunlight more efficiently i.e. make whiter clouds (*first indirect effect*). Also, smaller cloud droplets are less eager to fall down as rain, and the lifetime of the cloud will increase (*second indirect effect*).

From a climate point-of-view, the quantity of interest is the aerosols' effect on the radiative balance of the Earth (see Fig. 1). It is estimated that both the direct and indirect effect have a total negative effect on the radiative balance (negative radiative forcing): the more aerosols, the more sunlight will be reflected from aerosol particles and clouds back to space. The absorption of sunlight and infrared radiation by aerosol particles (especially black carbon aerosols) and cloud droplets (especially in high-level clouds) causes a small warming effect, but in total the aerosol effect is estimated to be cooling. The Intergovernmental Panel on Climate Change report gives an estimate -0.5 W/m^2 for the direct and -0.7 W/m^2 for the indirect effect (IPCC, 2007). Overall, the estimate for the total aerosol cooling effect (-1.2 W/m^2) is comparable to the warming effect of CO_2 (1.66 W/m^2). However, the aerosol effect is associated with the largest error bars (see Fig. 1), and the level of scientific understanding is stated to be low, in contrast to greenhouse gases, whose effect is rather well understood. The research in this thesis is one small contribution to quantify the aerosol effect more precisely, and to reduce the uncertainty related to it.

In recent 20–30 years, considerable decreases in anthropogenic aerosol emissions have happened in the Western countries, due to cleaning and filtering of the gas exhausts of industry and transport systems (Hamed et al., 2010; Asmi et al., 2013). In the future, this trend will continue, thus decreasing the man-influenced aerosol cooling effect. In view of climate change, the major environmental problem of our time (Archer and Pierrehumbert, 2011), this raises a concerning question: If the aerosol cooling effect has been large, how much will the warming be accelerated, when the aerosol cooling effect continues to decrease (Andreae et al., 2005; Arneth et al., 2009)? It is clear that aerosols need to be taken into account in climate models when making predictions on future climate change.

Measurements all around the world have shown that new particle formation seems to occur almost everywhere on the Earth's land-surface where aerosol measurement instruments have been carried to (Kulmala et al., 2004d; Kulmala and Kerminen, 2008; Vakkari et al., 2011; Kyrö et al., 2013). Sulphuric acid has been identified as a key compound in atmospheric particle formation and it participates both in nucleation and particle growth. However, equally important for natural particle formation are organic vapours, which contribute to particle condensational growth and account for the major part of atmospheric aerosol mass (Jimenez et al., 2009; Riipinen et al., 2011). The atmospheric aerosol is to some extent a self-regulating system: if there are many particles emitted from other sources, such as pollution, there are less particles produced by new particle formation; on the other hand, if the atmosphere is very clean of particles, new particle formation occurs more frequently. Thus, atmospheric particle formation maintains the aerosol particle population in the atmosphere.

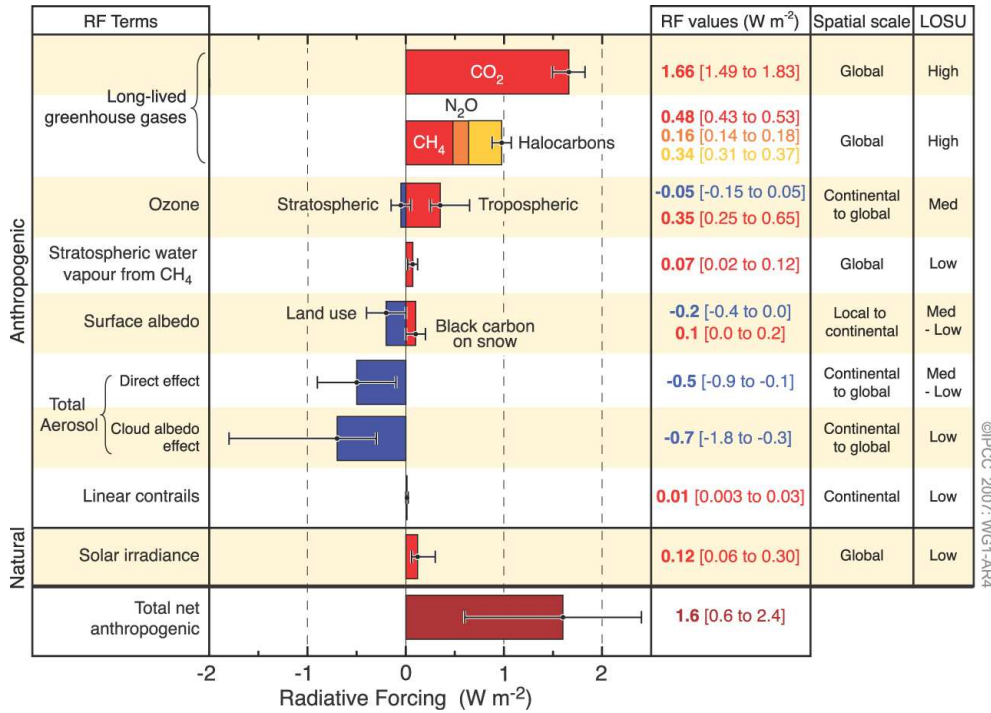


Figure 1: Estimates for radiative forcing (RF) components for year 2005 (global averages). Positive radiative forcing means a warming effect on climate and negative radiative forcing a cooling effect. From IPCC (Intergovernmental Panel on Climate Change) Fourth Assessment Report (IPCC, 2007).

In oceanic areas and in rain forests in Amazonian, new particle formation in the boundary layer occurs very rarely. There are still plenty of aerosols from other sources in these environments, such as: sea salt particles and particles transported from the upper atmosphere to the boundary layer on the oceans, biomass burning aerosols and secondary organic aerosols in the Amazonian region, as well as particles from anthropogenic emissions.

One way to characterize aerosols is whether they are of natural or anthropogenic origin. For primary aerosols, the origin is easily identified: sea salt, sand, pollen, bacteria, viruses and other micro-organisms are examples of natural aerosols while all kinds of pollution from combustion processes and biomass burning are examples of anthropogenic aerosols. For secondary aerosols, the situation is not that easy. At first sight, new particle formation could be called as natural, as it is happening "naturally" in the air — but new particle formation is to a large extent controlled by sulphuric acid, which has both natural and anthropogenic sources. Sulphuric acid is formed in the atmosphere mainly by oxidation of SO₂, for which a major source is the burning of fossil fuels. Volatile organic compounds, which condense on aerosol particles and constitute most of the secondary aerosol mass, are mainly emitted by vegetation, but have also anthropogenic sources (combustion of fossil fuels and other organic matter). Thus, natural and anthropogenic sources of particles and condensing vapours are mixed together

so that it is not fully possible to distinguish them. Also some natural primary emissions are influenced by human activity: for example desertification increases emission of mineral dust into air.

This thesis investigates atmospheric particle formation in the boreal forest environment by the methods of field data analysis and aerosol dynamical simulations. The main emphasis is on studying the correlation of new particle formation with sulphuric acid concentration. More specifically, this thesis aims to answer to the following research questions or objectives:

- How are new particle formation and gas phase sulphuric acid connected with each other?
- To develop empirical parameterisations for the nucleation rate. What are the values of the empirical nucleation coefficients in different environments and which parameters do they depend on?
- Which factors, besides the nucleation mechanism, affect the correlation of the particle formation rate with sulphuric acid?
- How accurate is the method used to calculate particle formation rate from the size distribution data?
- What is the ability of aerosol particles in the boreal forest environment to act as cloud condensation nuclei (CCN), and is new particle formation affecting the CCN concentrations?

These research questions are discussed in this introductory part and in the six articles included in this thesis.

2 Atmospheric particle formation

In atmospheric particle formation, new nm-sized particles are formed in the atmosphere from precursor vapours. The process is initiated by nucleation, in which small stable clusters, of size 1–1.5 nm in "diameter", are formed. The precursor vapours must be "condensable", i.e. they must have low saturation vapour pressures, so that the vapours are eager to nucleate and stay in the condensed phase. The surrounding inert gas is air, and air molecules do not participate in nucleation. The formed clusters grow further by condensation of different vapours, eventually reaching sizes of 100–500 nm, unless scavenged by the various aerosol removal processes. The upper size limit of aerosol particles in atmosphere is set by gravitation: particles bigger than a few tens of μm fall down rapidly due to gravitation.

Atmospheric particle formation typically occurs around midday, on sunny days with low background aerosol concentration (W. Birmili and A. Wiedensohler, 2000; Boy et al., 2003; Birmili et al., 2003; Stanier et al., 2004; Lyubovtseva et al., 2005; McMurry et al., 2005). While particle formation from gas phase compounds (gas-to-particle conversion) has been known to take place, and to be a source of new particles in the atmosphere, already for a long time, it was only in late 1990's that the whole process of atmospheric particle formation was recorded for the first time (Weber et al., 1996; Mäkelä et al., 1997). Since 1997, the continuous measurements of particle size distributions at the Hyytiälä forestry field station (SMEAR II), from 3 nm to 500 nm and with 10 min. time resolution, have shown that in boreal forest conditions new particle formation occurs frequently all around the year, on 50–120 days per year (Aalto et al., 2001; Dal Maso et al., 2005).

Figure 2 shows a typical example of a new particle formation event, measured by a Differential Mobility Particle Sizer (DMPS) at the SMEAR II station in Hyytiälä, Finland. Nucleation produces new 1–2 nm sized particles from gas-phase precursor vapours, below the detection limit (diameter 3 nm) of the DMPS. After nucleation, the clusters grow in size by condensation of vapours; these vapours can be the same or different than the nucleating vapours. Due to their random Brownian motion in air, the particles collide with each other and stick together, in a process called coagulation. Due to condensation and coagulation, the new nucleation mode shifts to larger particle sizes. When particles reach the size range > 50 nm (in diameter), they start to have effects on climate: the particles can act as cloud condensation nuclei (CCN) i.e. be seed particles for cloud droplets (Kerminen et al., 2012). The aerosol particles are subject to these dynamical processes, until they are removed from the atmosphere by gravitational settling and diffusion onto surfaces (dry deposition), or are scavenged by falling rain droplets (wet deposition).

In the atmosphere, there is always a background aerosol distribution present. Often simultaneously to or just before the start of nucleation, this background particle concentration is decreasing due to the turbulent mixing initiated by sunlight warming the ground in the morning. The onset of turbulent mixing increases the boundary layer height (boundary layer = the lowest, turbulently mixed layer of the atmosphere), thus

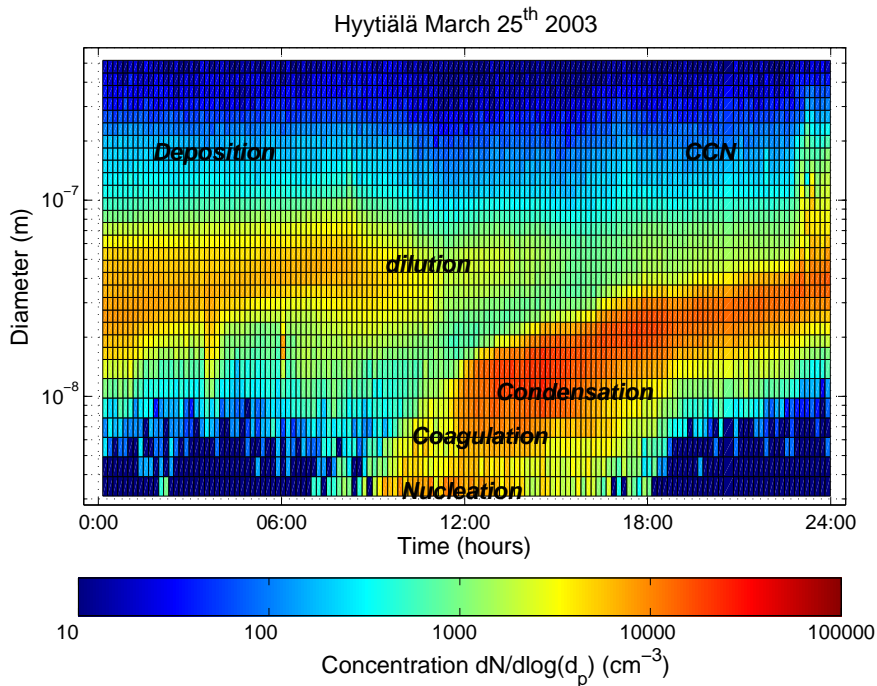


Figure 2: An example of a new particle formation event measured by DMPS (Differential Mobility Particle Sizer) at the SMEAR II station in Hyytiälä, Finland. The surface plot presents the evolution of the particle size distribution with time on the x-axis, particle diameter on the y-axis (log scale), and the normalized number concentration indicated by the colour code. The aerosol dynamical processes modifying the size distribution (at an exemplary location on diameter and time axes) are indicated.

mixing the particle-rich air mass of the boundary layer, left from the previous day, with an upper air mass having a much lower particle concentration. This results in a remarkable dilution of the particle concentrations in the morning hours (see Fig. 2). There are observations that new particle formation is enhanced in conditions of strong turbulent mixing (Nilsson et al., 2001; Lauros et al., 2007). However, it is not clear whether the enhancement is due to turbulence itself or due to the decrease of the background aerosol concentration.

In continental areas, large amount of evidence shows that sulphuric acid (H_2SO_4) participates in both formation and growth of new particles. Sulphuric acid is thought to be main nucleating compound, together with water and ammonia (see Sect. 2.2), although some organic molecules may also participate in nucleation. Of the particle growth (by condensation of vapours) sulphuric acid can explain only a minor part, while the main part is accounted for by various organic vapours present in the atmosphere. For example, in boreal forest conditions in Hyytiälä, the sulphuric acid contribution to the observed particle growth rate (determined as $GR = dd_p/dt$, where d_p is the particle diameter) is estimated to be 8–30 % (Boy et al., 2005). In polluted cities, where SO_2 and H_2SO_4 concentrations are high, the sulphuric acid contribution is higher (34–65 %), but even in those conditions it does not alone explain the particle growth (Yue et al., 2010; Gao et al., 2011).

The particle growth rates, determined from the particle size distribution measurements, show a seasonal variation according to the growth season of the vegetation, implying that organic compounds emitted by vegetation are important for particle growth (Hir-sikko et al., 2005; Yli-Juuti et al., 2011). A major source for condensable organic vapours in the atmosphere are *volatile organic compounds* (VOCs) emitted by vegetation, although anthropogenic VOC emissions also exist. The main biogenic VOC groups are isoprene, monoterpenes and sesquiterpenes. In boreal forest areas, monoterpenes (chemical formula C_5H_{10} , having several different molecular structures) emitted from coniferous trees constitute the main part of VOC emissions (Haapanala et al., 2007), while in deciduous forests isoprene is dominating (Carlton et al., 2009). The VOCs do not condense directly on particles, since they are *volatile* i.e. have a high saturation vapour pressure, but when VOCs are oxidised in the atmosphere by OH, O_3 and NO_3 , semi-volatile reaction products having a lower saturation vapour pressure are formed. The VOC oxidation chemistry is complex and the exact identities of the condensable vapours are still unknown. However, these organic compounds have recently been observed directly by in situ measurements of aerosol particle chemical composition, showing that a major part of the aerosol mass is organic (Jimenez et al., 2009; Laitinen et al., 2011; Zhang et al., 2011).

As a simple approximation, in aerosol science the formed particles are typically considered to be liquid spheres, and mostly the modelling of aerosol formation is based on this assumption. However, for very small clusters close to 1 nm one cannot accurately determine the phase and diameter, and it would rather be more correct to speak about a molecular cluster than a particle. From 3 nm upwards the number of molecules in the particle is high enough, that we can speak of a "macroscopic" particle, with a well defined diameter and phase. For particles larger than 3 nm the assumption of spherical liquid particles is usually good (excluding agglomerates of e.g. soot particles), based on the typical temperatures in atmosphere and the fact that particles are growing mainly due to condensation, thus making a liquid phase particle. However, there are new observations which indicate that the phase of the formed particles is amorphous (Virtanen et al., 2010), and it might be that the phase of aerosol particles needs to be reconsidered in more detail in future studies.

In recent years, great advances in aerosol measurement technology have been achieved, making it possible to detect the process of atmospheric nucleation directly from the nucleation size at 1–2 nm (Zhao et al., 2010; Kulmala et al., 2012, 2013). However, the details of atmospheric particle formation and particle growth are still not fully understood.

2.1 Aerosol size distribution and its dynamics

The atmospheric aerosol particle population is described by the particle concentration, size (diameter) and chemical composition. Typically, in physical studies of aerosols, the chemical composition is neglected, and the aerosol is characterized by an *aerosol size distribution function*, expressed either for the number concentration as the *particle*

number size distribution (mathematically denoted as $dN(d_p)/dd_p$ or $dN(d_p)/d\log(d_p)$) or for the mass concentration as the *particle mass size distribution* ($dm(d_p)/dd_p$). The atmospheric particle number size distribution peaks at small particle sizes, while the mass distribution peaks at larger particle sizes as mass is proportional to the particle volume ($\sim d_p^3$) (see Fig. 3). The actual number or mass concentration (for a certain size range and having units $1/\text{cm}^3$ or $\mu\text{g}/\text{cm}^3$), is obtained by integration over the desired size range.

In aerosol dynamical studies, most often we consider the number size distribution. However, in air quality studies and the regulation standards for particulate pollution, the mass concentration is used. In the following, the shortened term *particle size distribution* means the particle number size distribution and the number concentration has units $1/\text{cm}^3$. Due to the log-normal distribution with respect to particle size, number concentration is most often expressed in the normalized form $dN(d_p)/d\log(d_p)$.

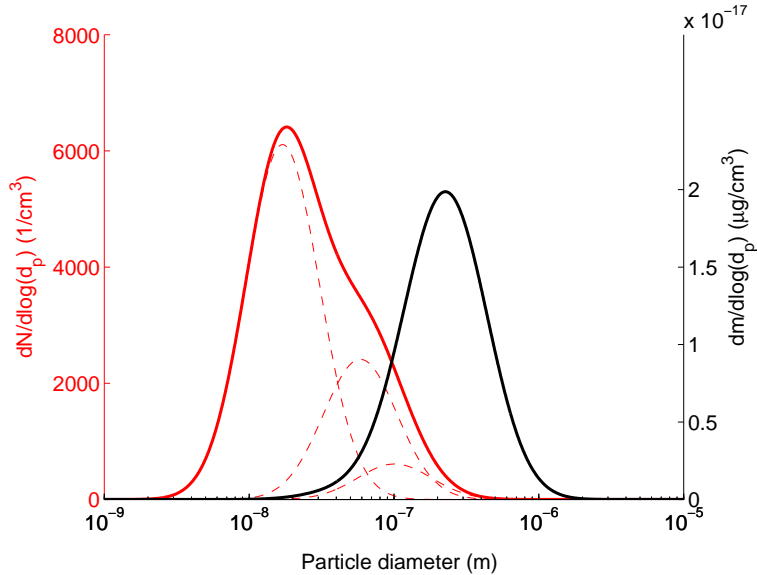


Figure 3: An average particle number size distribution (red) and the corresponding mass size distribution (black) in Kumpula, Helsinki, in springtime (Hussein et al., 2004). The number size distribution consists of three modes, which are indicated by dashed lines; for the mass distribution (assuming particle density of $1 \text{ g}/\text{cm}^3$) only the total distribution is plotted.

The atmospheric aerosol size distribution is typically composed of 2–4 log-normally distributed modes: a nucleation mode at $< 30 \text{ nm}$, an Aitken mode at $30\text{--}100 \text{ nm}$, an accumulation mode at $100 \text{ nm}\text{--}1 \mu\text{m}$ and a coarse mode at $1\text{--}10 \mu\text{m}$. Aitken and accumulation modes are always present in the atmosphere, with the accumulation mode being the most persistent, because for that size range the removal mechanisms (dry and wet deposition) are the slowest. The nucleation mode emerges on new particle formation days and the strength of the coarse mode is dependent on primary emissions of big particles, such as dust emissions. The atmospheric aerosol distributions differ in different environments: in continental areas the distribution has 3–4 modes, whereas in

marine areas, where nucleation is rare, the distribution is bi- or trimodal (e.g. Koponen et al., 2002).

The aerosol size distribution is changing all the time due to various aerosol dynamical processes, which modify particle concentrations, size and chemical composition. The particles collide with each other and stick together, forming bigger particles or agglomerates, in the process called *coagulation*. Particles grow by *condensation* of vapours onto particle surfaces or shrink by *evaporation* of molecules from particle surfaces to the gas phase. *Nucleation* inserts new, nm-sized particles into atmosphere, when condensable vapours form new stable particles. Particles are removed from atmosphere by *dry and wet deposition*: in dry deposition particles diffuse and stick to macroscopic surfaces, e.g. tree leaves, or settle down to the Earth surface by gravitation; in wet deposition particles are washed away from atmosphere as they collide with falling rain droplets or with cloud droplets.

The processes mentioned above are the main aerosol dynamical processes acting in the boundary layer. In clouds, aerosols may also undergo changes in size and chemical composition. Every cloud droplet has an aerosol particle inside it (e.g. McFiggans et al., 2006). Vapours and gases present in the cloud (such as nitric acid, sulphur dioxide, organic compounds and water) condense or dissolve to particles, and after that the compounds undergo chemical reactions in the aqueous phase. When the prevailing ambient conditions change, some amount of condensed material may evaporate from the particle, leaving the seed particle composition and size changed in comparison to the original state (e.g. Romakkaniemi et al., 2006). This is called cloud processing of aerosol particles. A special bimodal structure of aerosol size distributions, often encountered in marine boundary layer, is related to several cloud processing cycles of aerosol particles (Hoppel et al., 1996).

In addition to these physical processes, there may be surface reactions or heterogenous nucleation (nucleation on top of an existing particle) that change the particle size and composition. Chemical reactions and polymerisation processes inside the particle can modify the chemical composition and stability of the aerosol particle (aging of aerosol).

2.1.1 Condensation and coagulation

Because the size distribution of aerosol particles spans from the molecular scale (diameter of few nm) to microscopic scale (diameter of few μm), different theoretical frameworks are needed: small nm-sized particles are in the *free-molecular regime*, where particles behave similarly to gas molecules, whereas large particles are in the *continuum regime*, where particle experiences the surrounding gas as a continuous fluid. In the continuum regime, both condensation and coagulation in aerosol systems are dealt with the aid of diffusion theory. With condensation the use of diffusion theory is self-evident, but also coagulation in the continuum regime can be considered as a diffusion process: small particles in a fluid are diffusing towards a big (stationary) particle. In the free molecular regime, the kinetic gas theory applies both for condensation and

coagulation. In between these, there is a *transition regime*, in which both diffusive and free-molecular effects are important.

The condensation or evaporation flux is governed by the equilibrium vapour pressure (or concentration) prevailing at the particle surface. On the curved particle surface, the equilibrium pressure is always higher than on a planar surface of the same composition, because of weaker atomic bonding between surface molecules/atoms on a curved surface. This curvature effect on the equilibrium (saturation) vapour pressure is called the Kelvin effect and it is determined by the Kelvin equation:

$$p_{eq} = p_{sat} \exp\left(\frac{4M_v\sigma}{RT\rho d_p}\right), \quad (1)$$

where p_{sat} is the vapour saturation pressure for a planar surface, M_v is the molar mass of the vapour, σ is the surface tension of the liquid, R is the universal gas constant, T is temperature, ρ is the density of the liquid and d_p is the diameter of the liquid particle (Seinfeld and Pandis, 2006; Vehkamäki, 2006).

The difference between the vapour concentration far from the particle and the equilibrium concentration at the particle surface determines the direction and magnitude of the mass flux towards/from the particle ($I_m \propto (c_{vapour} - c_{eq})$). The Kelvin effect limits the condensation of vapours on a curved surface: the smaller the particle diameter, the more eagerly the molecules evaporate from the particle surface.

Due to the Kelvin effect, the condensation onto small, few-nm sized particles, would be extremely difficult for most of the condensable vapours (e.g. oxidation products of VOCs) present in the atmosphere. Sulphuric acid is the exception: it has a very small saturation vapour pressure ($< 10^{-4}$ Pa, Ayers et al., 1980; Marti et al., 1997), so that even with the Kelvin effect the saturation vapour pressure remains negligible, and it starts to condense on particles directly after nucleation. However, also for the smallest particles, the particle growth rate is explained only partly by sulphuric acid, and the rest of the growth is attributed to various organic compounds (Riipinen et al., 2012).

To theoretically explain the organic vapour contribution on the particle growth rates, Kulmala et al. (2004b) presented the nano-Köhler theory, which would facilitate organic vapour condensation on small ($d_p < 10$ nm) particles. Analogously to the Köhler theory of cloud formation (see Sect. 2.4), the solubility effect (Raoult effect) is assumed to act also for a semi-volatile, water-soluble organic vapour to lower its equilibrium vapour pressure on the particle surface. While the traditional Köhler theory describes the equilibrium of μm -sized cloud droplets with water vapour, nano-Köhler theory considers a nm-sized cluster, consisting of ammonium bisulphate, an organic compound and water, in equilibrium with a water-soluble organic vapour. The Raoult effect lowers the equilibrium pressure of the organic vapour, given by the equation:

$$p_{eq,org} = p_{sat,org}\gamma_{org}x_{org} \exp\left(\frac{4M_{org}\sigma}{RT\rho_{org}d_p}\right), \quad (2)$$

where $p_{sat,org}$ is the organic vapour saturation pressure, γ_{org} is the activity coefficient of the organic substance, x_{org} its molar fraction, M_{org} the molecular mass and ρ_{org} the density. This mechanism for organic vapour condensation was applied in aerosol dynamical simulations of **paper III**.

In the atmosphere, coagulation is caused by random Brownian motion of aerosol particles. Due to velocity differences, both in direction and magnitude, particles collide with each other. For aerosols, the collisions are assumed to be non-elastic, i.e. particles always stick together. Often, the collision is assumed to be between liquid spheres, making the particles merge together, thus forming a new, slightly larger spherical particle (agglomeration is not taken into account). The collision frequency function (= coagulation coefficient) can be derived from diffusion theory for the continuum regime and from kinetic gas theory for the free molecular regime particles, and it depends strongly on particle sizes. Coagulation is most efficient between particles of big size difference: the large particle surface collects the small, rapidly moving particles. Therefore, coagulation scavenging to background aerosol (at around 100–500 nm) is the main loss mechanism for small, nucleation mode particles. The coagulation coefficient is smallest and rather independent on particle size for the particles of equal size (Seinfeld and Pandis, 2006).

In addition to Brownian motion, velocity differences resulting from gradients in air flow, electrical or gravitational force field can cause collisions between particles. These processes, however, are important only at high velocity or force gradients occurring e.g. in flow tubes and are not significant coagulation processes in the atmosphere.

The theory regime for condensation and coagulation is defined by the Knudsen number, which describes the nature of the suspending fluid relative to the particle:

$$Kn = \frac{2\lambda_{air}}{d_p}, \quad (3)$$

where λ_{air} is the mean free path of air molecules (about 65 nm at $T = 298$ K and $p = 1$ atm) and d_p is the particle diameter. When $Kn \gg 1$, aerosol particles experience collisions similarly as molecules and we are in the kinetic regime. In this regime, the kinetic gas theory applies. When $Kn \ll 1$, aerosol particles see the surrounding medium as a continuous fluid, and we are in the continuum regime. In this regime, the diffusion theory holds. In the transition regime, when $Kn \sim 1$, kinetic and continuum effects have to be taken into account by special parameterisations. The most widely used are the Fuchs formulas for kinetic and transition regime correction factors, separately for condensation (Fuchs and Sutugin, 1971) and Brownian coagulation (Fuchs, 1964).

In case of condensation, the Knudsen number would in principle be $Kn = 2\lambda_{A,air}/d_p$, where $\lambda_{A,air}$ is the mean free path of vapour A molecules in air. Usually, as the concentration of A molecules is much smaller than that of air molecules and if its molecular mass is not much different from that of air molecules, the approximation $\lambda_{A,air} \approx \lambda_{air}$ is valid and Kn returns to the form of Eq. 3.

With coagulation, the quantities to be compared are the mean free path of the diffusing aerosol particle (smaller particle, λ_p) and the diameter of the absorbing particle d_p . However, the mean free path of aerosol particles is only weakly dependent on particle size, and the value is quite close to the air mean free path (λ_p varies between 10–60 nm; Seinfeld and Pandis (2006, Table 8.5)). Because of that, the same definition of Knudsen number (Eq. 3) can be used also in the case of coagulation to roughly characterize the theory regime. In exact calculations, the different equations for transition regime and free molecular coagulation coefficient use slightly different expressions for the Knudsen number (Seinfeld and Pandis, 2006). The most widely used formula for the coagulation coefficient (which is also used in this thesis) is the one by Fuchs (1964).

2.1.2 General dynamical equation

The time evolution of the particle size distribution is described by a differential equation containing terms for all aerosol dynamical processes acting on the aerosol population. The general dynamic equation (GDE), expressed in the volume space $v = \frac{1}{6}\pi d_p^3$, reads (Seinfeld and Pandis, 2006):

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} = & \frac{1}{2} \int_0^v K(v - q, q) n(v - q, t) n(q, t) dq - n(v, t) \int_0^\infty K(q, v) n(q, t) dq \\ & - \frac{\partial}{\partial v} [I(v) n(v, t)] + J_{nuc} \delta(v - v_{nuc}) + S(v) - R(v), \end{aligned} \quad (4)$$

where $n(v, t) = \partial N(v, t) / \partial v$ is the particle size distribution function, t is time and v is the particle volume, $K(v, q)$ is the coagulation coefficient between particles of volume v and q , $I(v)$ is the total volume flux of vapour molecules onto the particle due to condensation/evaporation, J_{nuc} is the nucleation rate, v_{nuc} is the volume of the nucleated particle and $\delta(v - v_{nuc})$ is the delta function, with a value of unity for $v = v_{nuc}$ and otherwise zero. The first two terms on the right hand side represent coagulation (production of v -sized particles in collisions of smaller particles and the coagulation loss of v -sized particles in collisions with background particles). The third term represents condensational growth or shrinkage due to evaporation, the fourth term represents nucleation, and S and R are possible additional source and removal terms.

In practice, the general dynamic equation is often used in a discrete form, as we deal with measured discrete spectrums or utilize models with a sectional representation for aerosol size distribution. In modal models, which express the aerosol size distribution as a superposition of continuous log-normal modes, the GDE is used in the continuous form of Eq. 4. In models, the GDE is integrated numerically to solve the particle size distribution evolution. In aerosol studies, particles are often assumed to be spherical, and the GDE can then be expressed more conveniently with the particle diameter.

2.1.3 Condensation and Coagulation sinks

Two useful quantities – the condensation sink and the coagulation sink – have been introduced to characterize the aerosol size distribution in terms of condensation and coagulation with one scalar quantity (Kulmala et al., 2001a).

The condensation sink (CS) describes the condensation rate of vapour onto the whole particle size distribution:

$$\text{vapour loss rate due to condensation} = CS \times C_v, \quad (5)$$

where C_v is the concentration of condensable vapour, i.e. the condensation sink is the *vapour condensation rate per one molecule* and has units 1/s.

The equation for the condensation sink can be derived from condensation theory. It depends on the background particle size distribution (particle surface area) and vapour diffusion properties (Kulmala et al., 2001a):

$$CS = 2\pi D_v \int_0^\infty \beta_m(d_p) d_p n(d_p) dd_p \cong 2\pi D_v \sum_i \beta_m(d_{p,i}) d_{p,i} N_i, \quad (6)$$

where D_v is the diffusion constant of the vapour, $n(d_p)$ is the particle size distribution function, d_p is the particle diameter, and the integration is performed over the whole particle size distribution. The latter form is for a discrete particle size distribution $N_i(d_{p,i})$. Because the diffusion constant is vapour-specific, the CS has to be determined for a specific vapour, typically for sulphuric acid (H_2SO_4). The parameter $\beta_m(d_p)$ is the Fuchs-Sutugin correction factor for the transition regime mass flux (Fuchs and Sutugin, 1971):

$$\beta_m = \frac{1 + Kn}{1 + \left(\frac{4}{3\alpha_m} + 0.377\right)Kn + \frac{4}{3\alpha_m}Kn^2}, \quad (7)$$

where Kn is the Knudsen number and α_m is the mass accommodation coefficient. With the Fuchs-Sutugin transitional regime correction factor, Equation 6 is valid for all particle sizes, from kinetic to continuum regime; the semi-empirical correction factor takes into account the changes in the condensation theory when particle size decreases. The mass accommodation coefficient α_m is also called "a sticking coefficient" and it describes the probability that a molecule, when hitting a particle surface, sticks onto it. There has been quite much debate about the value of α_m (Jefferson et al., 1997). In most cases, it is assumed to be unity ($\alpha_m = 1$), meaning that when a molecule hits a surface, it will be absorbed.

Analogously to the condensation sink, the coagulation sink is defined for a certain particle size as the *loss rate due to coagulation per one particle*. For a discrete size distribution this is expressed as:

Coagulation rate of particles of diameter $d_i = CoagS_{d_i} \times N_i$,

where $CoagS_{d_i}$ is the coagulation sink (unit 1/s) and N_i is the number concentration of particles in a size bin around particle diameter d_i . The formula for coagulation sink can be derived from the equation for Brownian coagulation rate, giving (Kulmala et al., 2001a):

$$CoagS(d_{p,i}, t) = \int_{d_{p,0}}^{\infty} \beta(d_{p,i}, d'_p) n(d'_p, t) dd'_p \cong \sum_j \beta(d_i, d_j) N_j, \quad (8)$$

where $\beta(d_{p,i}, d'_p)$ is the Brownian coagulation coefficient i.e. the collision frequency function between particles of diameters $d_{p,i}$ and d'_p (Seinfeld and Pandis, 2006). The sum expression on the right is the formula for discrete size distribution.

Typically the coagulation sink is calculated for small nucleation mode particles, as Brownian coagulation with the background aerosol particles is the main loss mechanism for nucleation mode particles. The coagulation rate and thus $CoagS$ is largest for the smallest particles, and decreases as the particle size increases (Dal Maso et al., 2002). For small particles of $d_p = 1$ nm the coagulation sink approaches the condensation sink, because condensation can be viewed as collisions (= coagulation) of H_2SO_4 molecules (having "diameter" below 1 nm) with background particles.

Some researchers have used the concept of Fuchs surface area instead of condensation sink:

$$A_{Fuchs} = \frac{4\pi}{3} \int_0^{\infty} Kn\beta_m(d_p) d_p^2 n(d_p) dd_p, \quad (9)$$

the meaning is analogous to the condensation sink (McMurry and Friedlander, 1978; McMurry et al., 2005). Connecting this with the equation for CS (Eq. 6) and applying $\lambda_v = 3D_v/\bar{c}_v$ for the mean free path in Kn (Seinfeld and Pandis, 2006), a relationship between the condensation sink and the Fuchs surface area A_{Fuchs} can be derived:

$$CS = \frac{1}{4} \bar{c}_v A_{Fuchs}, \quad (10)$$

where \bar{c}_v is the mean thermal velocity of the condensing vapour molecule.

The condensation and coagulation sinks are useful quantities to describe the particle size distribution with a one scalar quantity. Both are measures of total aerosol surface area, the former in the view of condensation and the latter in view of coagulation. The value of CS and $CoagS$ is determined especially by the concentration of large particles, which have a large surface area.

In new particle formation studies, CS is often used instead of CoagS, even if one actually, in a conceptual sense, is referring both to the condensation and the coagulation sink. The phrase "new particle formation events occur preferably at low CS conditions", actually means that both the CS and CoagS are low, having two effects favouring nucleation: i) there will be more vapour available for nucleation and condensational growth (low CS), and ii) the removal rate of freshly nucleated particles due to coagulation with large particles will be smaller (low CoagS).

2.2 Nucleation

2.2.1 Basic concepts of nucleation theory

By definition, nucleation is the first step of a phase transition process (Vehkamäki, 2006). All phase transitions start with nucleation. For example, freezing of water typically starts with nucleation of small ice crystals around impurities present in water (molecules, small particles). These crystals then grow in size and result in macroscopic freezing of the water, if the temperature stays below zero. Similarly, boiling of water begins with bubble formation (= nucleation of gas phase bubbles from liquid phase) around impurities dissolved in water or present on the inner surface of the stewpot. These are examples of heterogenous nucleation, in which nucleation happens on top of a foreign surface, such as the surface of a small impurity particle. In distilled water, which is free from impurities, nucleation (such as formation of ice crystals or bubbles) happens homogenously without the aid of an existing surface. Homogenous nucleation is always energetically more difficult than heterogenous nucleation; therefore freezing of distilled water requires lower temperatures and boiling happens at higher temperatures than for normal water with impurities.

In atmospheric particle formation, we consider the transition from gas phase to liquid or solid phase, i.e. the nucleation of liquid or solid phase clusters from gas-phase precursors. Typically, for simplicity, the phase of the formed cluster or particle is considered to be liquid.

As all physical processes in nature, nucleation is governed by energy. For nucleation to happen, the energy state of a nucleated, liquid phase particle must be lower than the initial state of vapour molecules. The first requirement for this is, that the vapour is supersaturated. The saturation ratio S_i (for vapour i) is defined as:

$$S_i = \frac{p_{i,v}}{p_{i,sat}}, \quad (11)$$

where $p_{i,v}$ is the partial pressure of vapour i (in air) and $p_{i,sat}$ is its saturation vapour pressure. The vapour is supersaturated when $S_i > 1$, meaning that there is an excess amount of molecules in the vapour phase and the liquid state would be energetically more favourable.

In nucleation, in between the initial (vapour) and final (nucleated cluster) energy states there is an energy barrier which needs to be crossed with the aid of thermal energy. In classical nucleation theory, the probability of crossing the barrier is given by the Boltzmann factor $e^{-\Delta G/k_B T}$ (ΔG is the height of the energy barrier, k_B is Boltzmann's constant and T is temperature), and the nucleation rate is:

$$J_{nuc} = K_{kin} e^{-\Delta G^*/k_B T}. \quad (12)$$

In this equation ΔG^* is the Gibbs free energy of the formation of the critical cluster (= height of the energy barrier) and K_{kin} is a kinetic prefactor accounting for the collision rate of vapour molecules with the cluster, which make the cluster grow. According to classical nucleation theory the Gibbs free energy (for homogenous nucleation) is (Seinfeld and Pandis, 2006; Vehkamäki, 2006):

$$\Delta G = -nk_B T \ln S + 4\pi r^2 \sigma, \quad (13)$$

where n is the number of molecules in the cluster, r is the cluster radius, S is the saturation ratio of the vapour and σ is the surface tension. The first term represents the gain in energy that is obtained in forming a liquid phase cluster, and the second term is the energy needed to create a new surface (due to surface tension). The typical form of the Gibbs free energy curve is shown in Figure 4, where the maximum of the curve represents the critical point: the smallest stable cluster i.e. *the critical cluster*, that does not tend to evaporate (radius r^* at saturation ratio S^*). The clusters bigger than r^* start to grow spontaneously by condensation, as the cluster moves downhill on the Gibbs free energy curve (provided that the saturation ratio stays the same). Typical critical cluster sizes are $\sim 1\text{--}5$ nm, number of molecules being from a few molecules to ~ 100 . In multicomponent nucleation, involving more than one compound, the Gibbs free energy becomes a surface with i dimensions, i being the number of compounds. Depending on the substances, multicomponent nucleation can be either easier or more difficult than homogenous nucleation of the participating substances.

In deriving the equation for ΔG , several approximations were made. For example, the cluster is assumed to be a liquid sphere, and it is assumed to have the properties (density, surface tension) of bulk liquid. It is clear that these approximations are very rough and do not hold very well for clusters of a couple of nanometers in diameter (Merikanto et al., 2007). Despite its deficiencies, classical nucleation theory is so far the best concise theory for nucleation and it is useful in interpretation of experimental studies on nucleation. In many cases the classical nucleation theory predicts the S -dependence right but T -dependence wrong, suggesting that the theory predicts the size of critical cluster correctly, but fails in describing the energy of the cluster (Vehkamäki, 2006). For molecular clusters, *ab initio* quantum chemical calculations provide physically and chemically more accurate description, and can give insights on the structure of nucleated clusters (Kurtén et al., 2007; Torpo et al., 2007; Kurtén et al., 2008; Ortega et al., 2012).

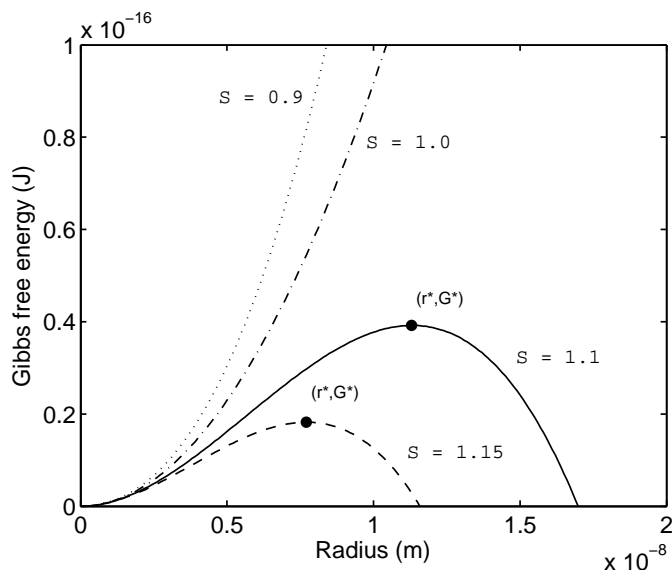


Figure 4: The Gibbs free energy curves for homogenous nucleation of water vapour at four different saturation ratios. The Gibbs free energy has a maximum and nucleation is possible when $S > 1$. The critical cluster size r^* and the corresponding energy of the critical cluster (G^*) at the maximum of the ΔG curve are indicated.

One of the most useful theoretical results for nucleation is *the nucleation theorem*. The first nucleation theorem states, that the derivative of the logarithm of nucleation rate with respect to the logarithm of saturation ratio is related to the number of molecules in the critical cluster (Vehkamäki, 2006):

$$\frac{\partial \ln J_{nuc}}{\partial \ln S_i} = n_i^* + 1 \approx n_i^*, \quad (14)$$

where J_{nuc} is the nucleation rate, S_i is the saturation ratio of the nucleating vapour, and n_i^* is the number of molecules of this substance in the critical cluster. In multi-component nucleation, the nucleation theorem applies separately for each nucleating substance.

The first nucleation theorem is a general result and not restricted to any special nucleation theory; thus it is valid more widely than the classical nucleation theory. In principle, it applies for any nucleation process which has an energy barrier associated with it. Therefore, it is very useful in interpretation of nucleation experiments. By measuring the nucleation rate (J_{nuc}) as a function of saturation ratio (S_i) of a vapour, and plotting the results on log-log axes, the slope gives the number of molecules of that vapour in the critical cluster.

Besides laboratory measurements, the nucleation theorem has been applied in connection of field measurements of atmospheric nucleation to predict the size of the critical cluster (e.g. **papers I–II**). Just recently, there are new results that indicate that the nucleation theorem may not hold in conditions in which there are local minima in the

Gibbs free energy surface (Vehkamäki et al., 2012). In that case, the conclusions on the number of molecules should not be made based on the slope of $\log(J_{nuc})$ vs. $\log(S_i)$ curve. So far, it is not known how the Gibbs free energy looks like in atmospheric nucleation. However, a local minimum would be expected in atmospheric nucleation, as a stable pre-nucleation cluster pool is observed to exist in field measurements (Kulmala et al., 2007).

Also, Malila (2013) suggests that when applying the nucleation theorem to nucleation in the presence of background aerosol (as in atmospheric measurements), the condensation sink of the background aerosol may affect the interpretation of the results.

2.2.2 Atmospheric nucleation mechanisms

A wide range of experimental and theoretical evidence shows that sulphuric acid (H_2SO_4) is involved in atmospheric particle formation. In atmospheric aerosols, sulphate is always observed, even if organic compounds often form the dominant part of the aerosol mass (e.g. Jimenez et al., 2009). Sulphuric acid has low saturation vapour pressure ($< 10^{-4}$ Pa, Ayers et al., 1980; Marti et al., 1997), which makes it eager to nucleate and stay in the condensed phase in atmospheric conditions. Sulphuric acid co-nucleates efficiently with water vapour, which is abundant in the atmosphere. Even small amounts of H_2SO_4 cause a huge increase of water nucleation rates in laboratory experiments (Doyle, 1961).

On the basis of classical nucleation theory, two mechanisms for atmospheric nucleation have been proposed: binary homogenous nucleation of sulphuric acid and water (Kulmala et al., 1998a; Vehkamäki et al., 2002) and ternary nucleation of sulphuric acid, water and ammonia (Korhonen et al., 1999; Napari et al., 2002a,b; Anttila et al., 2005; Merikanto et al., 2007). Based on the acid-base interactions between the molecules (in solution ammonia lowers the equilibrium vapour pressure of sulphuric acid), ternary $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ nucleation happens easier (i.e. at lower saturation ratios) than binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation; and both binary and ternary nucleation happen easier than homogenous nucleation of H_2SO_4 .

Binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation predicts nucleation rates well in the free troposphere (Spracklen et al., 2005), but fails to explain nucleation in the boundary layer (e.g. Spracklen et al., 2006; Chang et al., 2009b). However, lacking better nucleation theories, binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ and ternary $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ nucleation theories have been used widely to calculate nucleation rates in aerosol dynamical box models and global models. In applying the theories, sometimes a correction factor has been used in order to get the nucleation rates closer to the observed particle formation rates (Jung et al., 2008). Ternary nucleation has been shown to work reasonably well in predicting the occurrence of nucleation events in polluted cities with high concentrations of sulphuric acid and ammonia, but in terms of particle number it seems to produce too intense nucleation events (Gaydos et al., 2005; Jung et al., 2008).

It has also been proposed that atmospheric nucleation could be purely kinetic i.e.

happen without any energy barrier (McMurry and Friedlander, 1979). In that case, the nucleation rate would be determined only by the kinetic collision rate between the molecules (with $\Delta G = 0$ in Eq. 12), assuming that every collision results in the formation of a stable cluster. For example, the rate of homogenous, barrierless kinetic nucleation of sulphuric acid would equal the collision rate of H_2SO_4 molecules. The kinetic collision rate between molecules a and b is given by the equation (McMurry and Friedlander, 1980; Seinfeld and Pandis, 2006):

$$K_{kin} = \left(\frac{8k_B T}{\pi m_{ab}} \right)^{1/2} \pi (r_a + r_b)^2, \quad (15)$$

where r_a and r_b are the radii of the reactant molecules and $m_{ab} = m_a m_b / (m_a + m_b)$ is their reduced mass, T is temperature and k_B the Boltzmann's constant. The term $\left(\frac{8k_B T}{\pi m_{ab}} \right)^{1/2}$ is the relative mean thermal velocity of the molecules and $\pi (r_a + r_b)^2$ their collision cross section. For H_2SO_4 molecules at room temperature, the kinetic collision rate is about $3 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The kinetic collision frequency sets the absolute maximum for the possible nucleation rate in a system.

In atmospheric field measurements, a striking observation is that nucleation rates are observed to correlate with sulphuric acid to the power between 1–2 (Weber et al., 1996; Birmili et al., 2000; Fiedler et al., 2005; Kulmala et al., 2006, **paper I** and **II**). This is in contradiction with binary and ternary nucleation theories, which predict the correlation exponents of > 10 and 5–10, respectively (Kulmala et al., 1998a; Vehkamäki et al., 2002). In case of classical, homogenous nucleation with a simple form for the Gibbs free energy curve, the correlation exponent corresponds to the number of molecules in the critical cluster (Eq. 14, Vehkamäki et al., 2012). The slope of 2 was first observed by Weber et al. (1996) and reported also by Birmili et al. (2000), but at that time the observation did not receive wider attention. Later, by H_2SO_4 concentration measurements at the Hyytiälä SMEAR II station, this connection was rediscovered (Fiedler et al., 2005; Kulmala et al., 2006). In **papers I–II** this connection and its implications were studied in detail.

The failure of binary and ternary nucleation theories, and the observation that particle formation rates correlate simply with the first or second power of the sulphuric acid concentration ($J_{nuc} \propto [\text{H}_2\text{SO}_4]^n$, with $n = 1-2$), has led scientists to develop empirical parameterisations for the nucleation rate. These parameterisations, namely activation and kinetic nucleation, were developed in **papers I** and **II**. They have been applied quite widely in aerosol models (e.g. Spracklen et al., 2006) and been further developed by Paasonen et al. (2009, 2010).

The correlation exponent (the slope of $\log(J_{nuc})$ vs $\log([\text{H}_2\text{SO}_4])$ plot) has been taken to represent the number of molecules in the critical cluster (see Eq. 14). Thus, atmospheric observations have been interpreted so, that the critical cluster contains only few (1–2) sulphuric acid molecules (**papers I–II**). However, this is too strong a conclusion to make: as Vehkamäki et al. (2012) pointed out, if the Gibbs free energy curve has a local minima at pre-nucleation sizes, the simple form of the nucleation theorem (Eq. 14) is not valid. Thus, the correlation exponent n should not be interpreted

as the number of molecules of that kind in the critical cluster, but rather as giving information about the rate limiting step in atmospheric nucleation. According to the results of **paper I** and **II**, this rate limiting step is proportional to the sulphuric acid concentration to the power 1–2.

Ion-induced nucleation, i.e. nucleation initiated by charged clusters, and ion-mediated nucleation, including also the formation of neutral clusters by recombination of positive and negative ions, have also been proposed as possible nucleation mechanisms in the atmosphere (Yu and Turco, 2000). There is a constant charged cluster pool (of both polarities) observed to exist in the atmosphere, and ion events similar to neutral new particle formation events are observed (Kulmala et al., 2007; Hirsikko et al., 2011). Theoretically, the presence of ions should enhance nucleation by introducing a local minimum to the Gibbs free energy curve and by lowering its maximum. According to current knowledge, ion-induced nucleation is expected to have only a minor contribution to particle formation in the boundary layer, but possibly has some importance in nucleation in the mid-troposphere (Hirsikko et al., 2011; Kirkby et al., 2011); although some contradicting opinions also exist (Yu et al., 2008, 2010). In boreal forest conditions, the contribution of ions to nucleation has been estimated to be about 1–10 % (Manninen et al., 2009; Gagné et al., 2010, 2012), while in other environments the fraction has been observed to vary in the range 0.5–27 % (Manninen et al., 2010).

In coastal areas, such as Mace Head in Ireland, particle formation is observed to happen through nucleation of iodine dioxide (OIO), emitted by algae when exposed to direct sunlight (O’Dowd et al., 2002; O’Dowd and Hoffmann, 2005; Vuollekoski et al., 2009).

2.2.3 Laboratory measurements of atmospheric nucleation

In laboratory studies, performed mainly for the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system, it has been extremely difficult to observe nucleation at conditions mimicing the atmosphere (Viisanen et al., 1997; Ball et al., 1999; Young et al., 2008; Benson et al., 2008; Brus et al., 2010). Berndt et al. (2005) presented the first results of laboratory measurements, in which nucleation was observed at close to atmospheric concentrations of sulphuric acid and slopes approaching the atmospheric value of 2.

The comparison of various laboratory measurements and atmospheric measurements (QUEST II, **paper I**) is presented in Figure 5 (Brus et al. 2010). Summarizing, in the first decade of 2000’s, there were three discrepancies found in almost all laboratory studies of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation: i) The onset of nucleation requires much higher concentrations than observed in the atmosphere. ii) The slope of the $\log(J)$ vs $\log([\text{H}_2\text{SO}_4])$ plot is much higher than observed in the atmosphere, typically in the range 4–8. iii) The results are sensitive to the production method of H_2SO_4 : the nucleation rates were much higher (or onset of nucleation happened at many orders of magnitude lower concentrations) if H_2SO_4 was produced in situ by reaction of SO_2 and OH than if the H_2SO_4 was evaporized from a liquid H_2SO_4 sample. Especially the last observation (iii) of high nucleation rates for in situ production of H_2SO_4 as compared to the liquid source was considered as a big mystery (Berndt et al., 2005; Brus et al.,

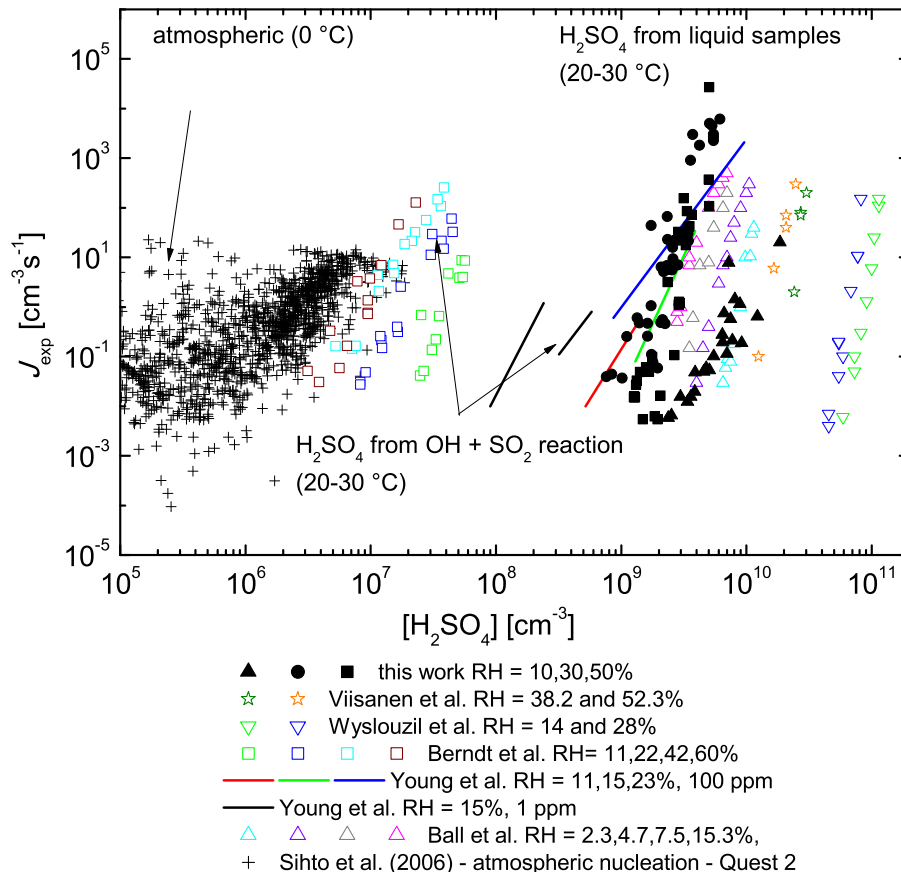


Figure 5: Homogenous nucleation rate as a function of sulphuric acid concentration for binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system, obtained from different laboratory measurements and comparison with the atmospheric data from the QUEST II campaign at the Hyytiälä, SMEAR II station (**paper I**). Reprinted by permission from Brus et al. (2010).

2010). It led scientists to propose theories, that the nucleating agent would be some other reaction product in the SO_2+OH reaction pathway (see Sect. 2.3), such as HSO_3 or HSO_5 (Berndt et al., 2008; Laaksonen et al., 2008; Salonen et al., 2009).

In 2010, all three mysteries were solved at the same time by Sipilä et al. (2010). They performed new laboratory measurements in a laminar flow tube applying novel measurement technology for detection of small particles down to ~ 1.3 nm: pulse-height-analyzing ultrafine-condensation particle counter (PHA-UCPC, Sipilä et al., 2009) and particle size magnifier (PSM, Vanhanen et al., 2011). With these instruments, nucleation of H_2SO_4 and H_2O was observed at atmospheric conditions (onset of nucleation at H_2SO_4 concentration $\sim 10^6 \text{ cm}^{-3}$) and with a slope 1.6–1.9.

The high onset H_2SO_4 concentrations for nucleation and steep slopes of the $\log(J)$ vs $\log([\text{H}_2\text{SO}_4])$ plot reported in earlier studies were explained to be caused by improper instrumentation, which was not able to measure close to 3 nm sized particles with a sufficient efficiency. The ultrafine condensation particle counter (UCPC, TSI 3025), which was used in many studies, has a steeply rising counting efficiency at 3–6 nm. This caused nucleation rates at different H_2SO_4 concentrations (having also different

particle growth rates after nucleation) to be measured with different counting efficiencies, resulting in an apparent increase of the nucleation rate with H_2SO_4 concentration and a high slope of the $\log(J)$ vs $\log([\text{H}_2\text{SO}_4])$ curve. Thus, in addition to the importance of a suitable detector, also the growth rate (determined by H_2SO_4 concentration and residence time in the flow reactor) affects the results. Many earlier experiments were performed with rather short residence times, resulting in a small growth rate, and a large fraction of particles remaining so small that they were not counted.

The difference between liquid source and production of H_2SO_4 from SO_2+OH reaction ("the sulphuric acid mystery") was explained by different concentration profiles (as a function of time) between these two cases: with a liquid, point-like instantaneous source the concentration of H_2SO_4 decreased steeply after nucleation, whereas in-situ production yielded quite constant H_2SO_4 concentration as long as the OH source (UV-light) was on. In the former case, the growth rates were smaller than in the latter case, resulting in a considerable fraction of nucleated particles not reaching a size big enough to be detected.

In summary, proper instrumentation and high enough growth rates are required in order to obtain correct results in nucleation experiments. Especially the Particle Size Magnifier (PSM), which has close-to-unity counting efficiency for small particles, has made it possible measure nucleation rates with good accuracy. It is possible that all earlier laboratory experiments of nucleation are affected by the errors sources pointed out by Sipilä et al. (2010), and therefore earlier laboratory results on sulphuric acid-water nucleation should be interpreted with care.

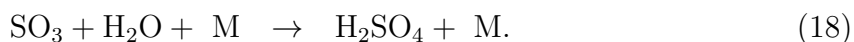
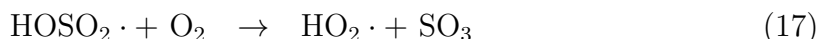
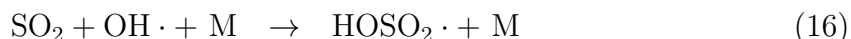
Current thinking on atmospheric particle formation is as follows (Kulmala et al., 2013). A more or less constant neutral cluster pool at 1–2 nm is observed to exist in the atmosphere (Kulmala et al., 2007). Under certain, partly yet unidentified, conditions these pre-critical clusters start to grow to bigger sizes. This happens normally during daytime, with the participation of condensable vapours produced by photo-oxidation. The most important vapour for initiation of the growth of pre-nucleation clusters seems to be sulphuric acid. Simultaneously with sulphuric acid, organic vapours start to condense, possibly with the nano-Köhler mechanism, and speed up the particle growth rate.

2.3 Formation and loss processes of sulphuric acid in the atmosphere

Gas-phase sulphuric acid is produced in the atmosphere mainly through oxidation of sulphur dioxide (SO_2) by OH radicals. The main sources of sulphur dioxide in today's atmosphere are emissions from fossil fuel burning and industry, global estimate for emissions being 70 Tg(S)/year (Seinfeld and Pandis, 2006). Naturally SO_2 is emitted from volcanic eruptions (global estimate 7–8 Tg(S)/year) and forest fires (global estimate for emissions from biomass burning 2.8 Tg(S)/year) (Seinfeld and Pandis, 2006). Over oceans, which lack extensive anthropogenic sulphur emissions, dimethylsulphide

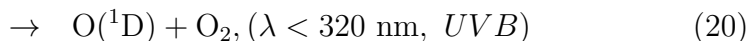
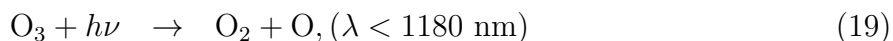
(CH₃SCH₃, DMS) is the dominant source for SO₂. DMS is produced by phytoplankton and other marine organisms in the ocean and emitted into the atmosphere, where it reacts with OH radicals and forms SO₂ (among other compounds). Altogether, DMS is the largest natural contributor to the global sulphur flux into the atmosphere with global emissions of 15–25 Tg(S)/year (Seinfeld and Pandis, 2006).

In the atmosphere, SO₂ reacts with hydroxyl radical (OH) in a sequence of reactions, eventually forming sulphuric acid (e.g. Reiner and Arnold, 1994):



Here M represents a non-reactive molecule of the surrounding gas (in air typically N₂ or O₂), which is taking the excess energy released in the reaction. According to present knowledge, this is the main mechanism for production of gas phase sulphuric acid in the atmosphere. The second and third reaction (17 and 18) are fast, so that the rate limiting step in the reaction scheme is reaction 16. Thus the formation rate of sulphuric acid is given by the rate of reaction 16: $k_{16} [\text{SO}_2][\text{OH}]$, where k_{16} is the reaction rate constant.

Hydroxyl radicals (OH·), in turn, are formed in photodissociation of ozone (O₃) molecules by ultraviolet (UV-B) radiation. The reaction mechanism is as follows:



where O(¹D) is the excited singlet state of the oxygen atom. This formation process makes the OH concentration vary according to the intensity of UV-B radiation. The formation depends also on the water vapour concentration ([H₂O]), but the effect is smaller as water vapour is abundant in the troposphere, and has less variation compared to the solar UV radiation. OH is a highly reactive radical, with a lifetime of about 1 second, which reacts with almost all chemically reactive compounds in the atmosphere. Despite the variety of loss processes for OH, the total OH concentration has been observed to follow UV radiation with a good accuracy, both on diurnal and seasonal time scales (Rohrer and Berresheim, 2006). Therefore, simply the intensity of UV radiation can be used in modelling as a proxy for OH concentration, just scaled to a proper maximum value (of the order 10⁵ cm⁻³–10⁶ cm⁻³).

Owing to the high reactivity and short lifetime of OH radicals, measurement of OH concentrations is rather difficult and requires indirect mass spectrometric techniques.

For modelling and data-analysis purposes, it is very useful that UV-B radiation can be used as a proxy for OH. If measurements of UV radiation are not available, global radiation (including all wavelengths) can be utilised in many cases, without losing too much accuracy (Petäjä et al., 2009). However, the intensity of UV-B radiation on the ground depends highly on the ozone column (the amount of O₃ in a vertical path), implying that global radiation cannot be used as a proxy for UV-B in regions, where the ozone column has strong seasonal variation.

Due to its low saturation vapour pressure, the main loss process for sulphuric acid vapour is condensation onto pre-existing aerosol particle surfaces. In addition, nucleation (if involving sulphuric acid) acts as a sink for sulphuric acid. Thus, the ambient concentration of sulphuric acid vapour in the atmosphere (C_v) is governed by the equation:

$$\frac{dC_v}{dt} = Q - CS \cdot C_v - J_{nuc} \cdot n_{sa}^*, \quad (22)$$

where Q is the source rate of H₂SO₄ (the oxidation rate of SO₂ by OH: $Q = k_{16}[SO_2][OH]$), CS is the condensation sink (see Sect. 2.1.3), J_{nuc} is the nucleation rate and n_{sa}^* is the number of H₂SO₄ molecules in the nucleating cluster.

As a loss process for H₂SO₄, the nucleation rate is of minor importance as compared to condensation, even though nucleation is important with regard to particle formation. Therefore as a first approximation the balance equation 22 can be rewritten:

$$\frac{dC_v}{dt} = Q - CS \cdot C_v \quad (23)$$

$$= k_{16} [SO_2][OH] - CS \cdot C_v. \quad (24)$$

Thus, the concentration of H₂SO₄ is affected by the variations in SO₂ and OH concentration as well as the condensation sink of the aerosol particle population. As explained above, OH varies according to sunlight (UV radiation). If the variations in SO₂ and condensation sink are small compared to the variation of the daily cycle of OH, which often is the case, then the H₂SO₄ concentration varies approximately according to OH, and thus according to sunlight.

Figure 6 shows an example of measured H₂SO₄ concentration, together with the quantities affecting its formation: OH radical concentration, solar radiation (mainly UV-B), SO₂ and water vapour concentration. The overall trend of the H₂SO₄ concentration follows roughly that of OH, but has some peaks that can be attributed to the SO₂ emission peaks from anthropogenic sources. Note that Fig. 6 shows only the quantities affecting the source rate and not the factors influencing the loss rate of H₂SO₄; the ambient H₂SO₄ concentration is of course determined by the combined effect of source and loss processes. Condensation on the background aerosol distribution is the main loss mechanism for sulphuric acid, and abrupt changes in background aerosol concentrations can cause rapid changes in the ambient H₂SO₄ concentration.

Measuring the sulphuric acid concentration in the atmosphere is rather complicated, and requires mass-spectrometric techniques (Berresheim et al., 2000, see Sect 3.1). Therefore, based on the balance equation (24), proxies for estimating sulphuric acid concentration from SO_2 concentration, UV-radiation and CS data have been developed (Petäjä et al., 2009; Mikkonen et al., 2011). The proxy sulphuric acid concentration was proven to agree reasonably well with measured H_2SO_4 concentrations. However, it should be noted that most of the proxies are constructed based on measurement data from campaigns in spring and summer time, which may reduce the reliability of the proxies in predicting the sulphuric acid concentrations during the cold season (Mikkonen et al., 2011).

In clouds, aqueous reactions of SO_2 in cloud water (inside cloud droplets) is an important source of sulphuric acid. Other sources for gas-phase sulphuric acid, in addition to oxidation of SO_2 by OH, may also exist. Just recently, Mauldin III et al. (2012) proposed a new, possibly important source of atmospheric H_2SO_4 by reaction of SO_2 with Criegee Intermediates, highly reactive atmospheric biradicals (Welz et al., 2012).

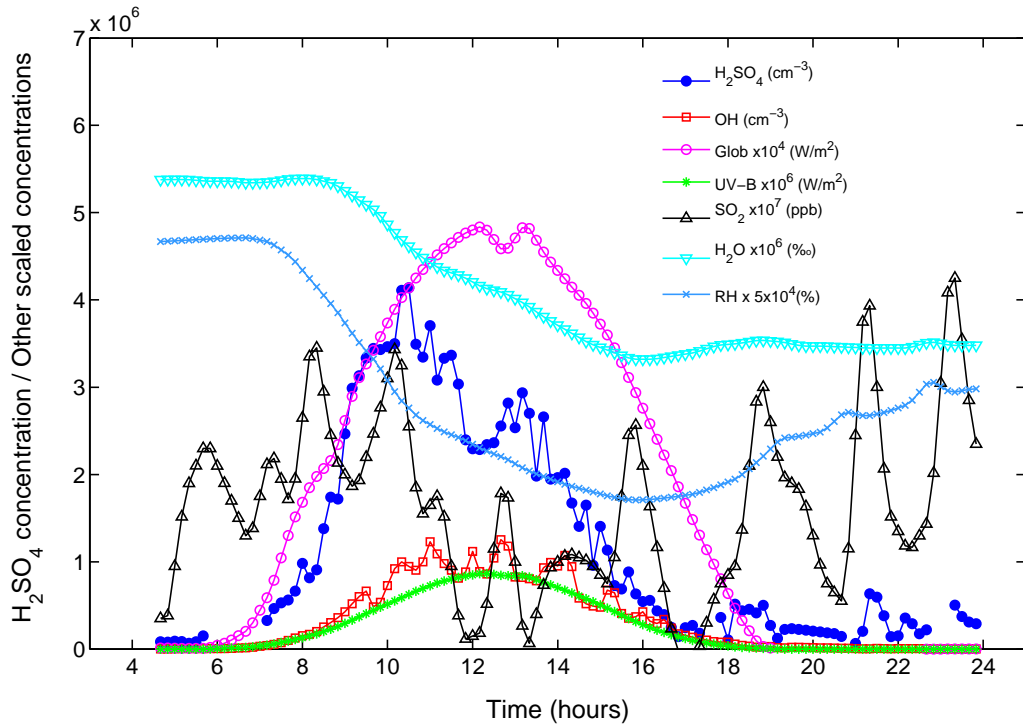


Figure 6: Example of the diurnal profile of sulphuric acid concentration (blue dots), OH concentration, global and UV-B radiation, SO_2 concentration, water vapour concentration and relative humidity (RH). The concentrations have been scaled to fit to the same axis. The data were measured on March 25th 2003 at the Hyttiälä SMEAR II station.

2.4 Activation of aerosol particles to cloud droplets

Clouds are formed in the Earth’s atmosphere when water vapour in supersaturated conditions ($RH > 100\%$) condenses on aerosol particles, thus forming cloud droplets. In atmospheric temperatures, the homogenous nucleation of water vapour, i.e. formation of water droplets without a seed aerosol particle, would require a relative humidity on the order of 400% ($S \approx 4$). These conditions are never met for water vapour in the Earth’s atmosphere, and therefore all cloud droplets are formed by heterogenous nucleation and subsequent condensation of water vapour on top of a seed aerosol particle, which happens at significantly lower saturation ratios. The supersaturated (supersaturation is defined as $SS = S - 1$ and expressed typically in $\%$) conditions required for cloud formation ($SS > 0\%$) are typically met in the upper boundary layer and in the free troposphere, where air temperature is low enough to cause a low saturation vapour pressure and a high enough water saturation ratio. The seed aerosol particles are called cloud condensation nuclei, abbreviated as CCN.

Activation of an aerosol particle means that water starts to condense irreversibly on the particle, making it grow into a cloud droplet with size on the order of μm . The critical diameter is the smallest particle size that gets activated at a certain water supersaturation. Vice versa, the critical saturation ratio is the saturation required for a certain particle size and composition in order to start irreversible water condensation (i.e. activate the particle). The equilibrium between the aerosol particle and water vapour is described with the Köhler equation:

$$S_{eq} = a_w \exp\left(\frac{4M_w\sigma}{RT\rho d_{wet}}\right), \quad (25)$$

where S_{eq} is the water equilibrium saturation ratio, a_w is the water activity of the solution ($a_w = \gamma_w x_w$, in which γ_w is the activity coefficient and x_w is the mole fraction of water in the solution), M_w is the molar mass of water, σ is the surface tension of the droplet, R is the universal gas constant, T is temperature, ρ is the density of the solution and d_{wet} is the wet particle diameter. Typically, for the surface tension and the density the values for water are used (dilute solution).

The Köhler equation combines the curvature effect (the Kelvin effect, Eq. 1), which increases the equilibrium vapour pressure of water on top of the droplet surface, and the solute effect (the Raoult effect), which decreases the equilibrium vapour pressure above a solution. As a result, a curve with one maximum is obtained. The Köhler curve is calculated for a certain dry aerosol particle. The critical saturation ratio S_{crit} (with a certain dry particle size and composition) corresponds to the maximum of the Köhler curve: at saturation ratios bigger than S_{crit} , water condenses continuously onto the particle. At a certain saturation ratio, the corresponding dry particle size can be obtained by iteratively solving the Köhler-equation: this particle size is the smallest dry particle that gets activated at the given saturation ratio. This particle size is called the *critical diameter* or *threshold diameter* for cloud droplet activation (Kerminen et al., 2012).

The critical diameter for cloud droplet activation depends on the water saturation ratio and on the chemical composition of the aerosol particle. In the atmosphere, the critical diameters are typically in the range 50–100 nm.

Particle hygroscopicity means its ability to take up water in subsaturated conditions ($S < 1$ or $RH < 100\%$) and it is described by the hygroscopic growth factor:

$$g_a = \frac{d_{wet}}{d_{dry}}, \quad (26)$$

where d_{wet} and d_{dry} are diameters of the wet (at certain RH) and dry particle, respectively. Particle hygroscopic growth factors are measured by Hygroscopic Tandem Differential Mobility Analyser (HTDMA) for a specific relative humidity (RH).

Another formulation of the Köhler equation was presented by Petters and Kreidenweis (2007), who expressed the thermodynamic properties of the particle (the solute effect described by water activity a_w) with the aid of a hygroscopicity parameter κ , determined by:

$$\frac{1}{a_w} = 1 + \kappa \frac{V_{dry}}{V_{water}}, \quad (27)$$

where V_{dry} is the volume of dry particulate matter and V_{water} is the volume of water in the solution ($V_{wet} = V_{dry} + V_{water}$). With this parametrisation for the water activity, and a couple of other assumptions, the kappa-Köhler equation can be derived:

$$S_{eq}(d_{wet}) = \frac{d_{wet}^3 - d_{dry}^3}{d_{wet}^3 - d_{dry}^3(1 - \kappa)} \exp\left(\frac{4M_w\sigma_w}{RT\rho_w d_{wet}}\right), \quad (28)$$

where ρ_w is the density of water and σ_w is the surface tension of water. Note that particle density has disappeared from the equation and all the physico-chemical properties (except the diameter) of the aerosol are captured in the κ -parameter.

The Köhler equation is typically applied at saturation ratios $S > 1$ necessary for cloud formation, even though it is valid also for $S < 1$. The idea of kappa-Köhler equation is to apply it also for $S < 1$, thus covering the full range of saturation ratios from hygroscopic growth ($S < 1$) to cloud droplet activation ($S > 1$) (Petters et al., 2009). By expressing the wet diameter with the aid of the hygroscopic growth factor ($g_a = d_{wet}/d_{dry}$), the κ -Köhler equation becomes:

$$S_{eq}(d_{dry}) = \frac{g_a^3 - 1}{g_a^3 - (1 - \kappa)} \exp\left(\frac{A}{g_a d_{dry}}\right), \quad A = \frac{4M_w\sigma_w}{RT\rho_w}. \quad (29)$$

Using HTDMA data on particle hygroscopic growth factors at subsaturated conditions with a known saturation ratio, the κ -parameter of the aerosol can be determined by

solving it from the kappa-Köhler equation. The higher the value of κ , the more hygroscopic the aerosol is. Kappa-parameters have been determined in laboratory conditions for pure organic aerosol ($\kappa_{org} = 0.1$, from α - and β -pinene) and for ammonium sulfate ($\kappa_{as} = 0.6$) as well as in field measurements at several locations (e.g. Gunthe et al., 2009; Dusek et al., 2010). For purely non-hygroscopic aerosol, such as mineral dust, $\kappa = 0.01$ – 0.08 (Koehler et al., 2009). Estimates for the global mean of κ are 0.27 ± 0.21 for continental and 0.72 ± 0.24 for marine aerosol (Pringle et al., 2010). The kappa-values can then be applied to predict the CCN activity of the studied aerosol: to estimate the critical diameter for cloud droplet activation using the kappa-Köhler equation.

3 Methods

This thesis combines analysis of field measurement data and aerosol dynamical simulations. This section describes the experimental data, the main data analysis methods and the aerosol dynamical model used in this study.

3.1 Experimental data

The data used in this thesis were measured mostly at the SMEAR II station in Hyytiälä, Finland (**papers I-III, VI**). In **paper II** also measurement data from the Heidelberg station in Germany were analyzed.

The SMEAR II (Station for Measuring forest Ecosystem-Atmosphere Relations) station is located at the Hyytiälä Forestry Field station, about 60 km north-east of the city of Tampere (<http://www.atm.helsinki.fi/SMEAR/>). The environment represents a typical Finnish rural area, with fields and large areas of mixed forest, dominated by coniferous trees (spruce and pine). The station is affected also by pollution from a nearby city (Tampere) and industrial sites. The measurement station itself is inside a roughly 40-year old Scots pine (*Pinus Sylvestris* L.) forest. The leading idea in setting up the Hyytiälä measurement station has been to measure "everything possible" related to forest and atmosphere: from soil moisture to photosynthetic gas exchange between vegetation and atmosphere, pollutant trace gases as well as aerosol particle and ion concentrations. The Hyytiälä SMEAR II station is a unique site for multi-disciplinary research with high synergetic effects arising from the possibility to combine different sources of data (Hari and Kulmala, 2005).

Particle size distribution measurements

Particle size distributions were measured by a Differential Mobility Particle Sizer (DMPS) setup. Figure 7 presents the setup operating at the Hyytiälä SMEAR II station (Aalto et al., 2001) at the present configuration; some details (for example the charger and the inlet) have changed since the measurements in 2003 reported in **paper I**.

The inlet is situated at a height of about 8 m from the ground (until 21.9.2004 the inlet was at 2 m height) and the measurement devices are located inside a cottage. The air sample is taken using a TSP-inlet (Total Suspended Particles). Particle sizing is performed using differential mobility analysers (DMA), which classify aerosol particles according to their electrical mobility. The sheath flow for the DMA is dried, so that inside the DMA aerosol is "dry" at a relative humidity $< 30\%$. For sizing with DMA the particles must be charged. This is achieved using a charger with a ^{14}C beta-source (until 14.10.2008 the charger was ^{85}Kr), in which the aerosol achieves a charge equilibrium (for this reason the charger is also called a "neutralizer"). At a certain voltage between the plates of a cylindrical DMA, a certain particle size $d_p \pm \Delta d_p$ is

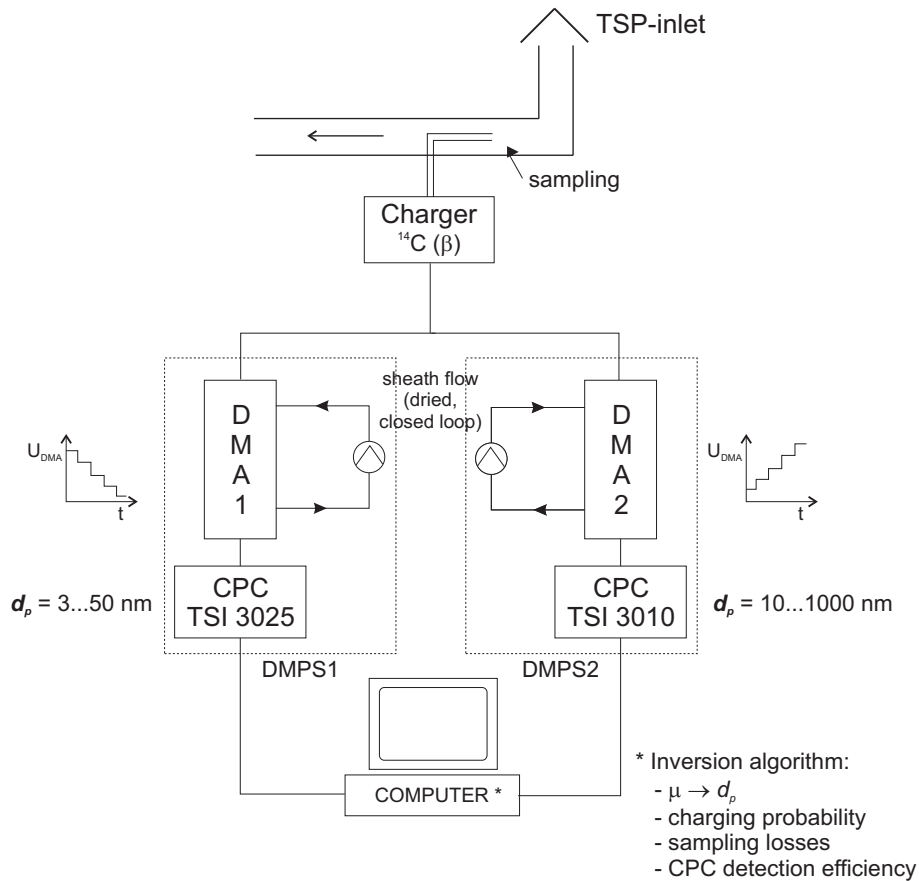


Figure 7: A schematic picture of the DMPS (Differential Mobility Particle Sizer) setup at the Hyytiälä SMEAR II station.

passing through the DMA and this concentration is measured with a condensation particle counter (CPC). By scanning the voltage of the DMA as a step function, a size spectrum is obtained. To cover the particle size range 3 nm–1 μm , two parallel DMA+CPC systems are needed (twin-DMPS): the first one measures the range 3–50 nm and the second the range 10 nm–1 μm (until 8.12.2004 the upper limit was 500 nm). The voltage scanning is performed in different directions in DMA1 (small particles) and DMA2 (bigger particles) in order to measure the overlapping part of the spectra temporally as close as possible. One scan of the whole size distribution takes about 10 min., defining the time resolution of the twin-DMPS system.

The raw output data from the DMPS is the mobility distribution of the aerosol particles, which were negatively charged after the ^{14}C -charger. By applying an inversion algorithm, the electrical mobilities are converted to particle sizes and the concentration of neutral aerosol particles (corresponding to the ambient situation before the charger) is deduced using the particle charging probabilities. The inversion algorithm takes also into account the estimated particle losses happening in the sampling lines.

The Hyytiälä DMPS system measures particle size distribution with 10 min. time intervals in 38 channels logarithmically distributed between 3 nm and 1 μm (diameter) (previously 23 size channels between 3 and 500 nm). The constant RH (about 30 %)

allows for comparison of size distributions despite of big variations in ambient RH.

Sulphuric acid concentration measurements

The gaseous sulphuric acid concentrations were measured with a Chemical Ionisation Mass Spectrometer (CIMS) (Hanke et al., 2002; Fiedler et al., 2005). The measurements during the QUEST II–IV campaigns were performed by a group from Max Planck Institute (MPI-K Heidelberg) led by Frank Arnold.

The measurement principle of CIMS is to convert sulphuric acid molecules (H_2SO_4) to ions by a chemical reaction, after which the concentration of the product ions can be measured by a mass spectrometer (Fiedler et al., 2005; Aufmhoff et al., 2011). The instrument consists of an ion source ($NO_3^-(HNO_3)_n$ -ions), a flow reactor and the quadrupole mass spectrometer, as well as a H_2SO_4 source for the calibration of the instrument. In the flow reactor, a fast ion-molecule reaction between $NO_3^-(HNO_3)_n$ -ion and H_2SO_4 happens:



The concentrations of reagent ($NO_3^-(HNO_3)_n$) and product ions ($HSO_3^-(HNO_3)_m$) are measured with the quadrupole MS. The concentration of H_2SO_4 can then be inferred from the ratio of these concentrations when the reaction rate constant is known (Berresheim et al., 2000). The detection limit for sulphuric acid was $1 \cdot 10^5 \text{ cm}^{-3}$ and the relative measurement error 30 %. The time resolution of the spectrometer was less than 1 s, but the data was averaged over 60 s in order to reduce statistical error.

The CIMS instrument has also been used to measure other atmospheric trace gases, such as volatile organic compounds (Sellegrì et al., 2005) and OH (Berresheim et al., 2000; Petäjä et al., 2009; Aufmhoff et al., 2011).

Cloud condensation nuclei and hygroscopicity measurements

The cloud condensation nuclei concentrations were measured at ground level at the SMEAR II station by a CCN-counter (CCNC, model DOC-0086 by Droplet Measurement Technologies). The CCN-counter mimics the conditions inside a cloud and measures the number of particles that are activated for cloud droplets at a certain water supersaturation. By comparing the number of activated particles (the "cloud droplets") to the total particle concentration, the activated fraction can be determined; by comparing the number of activated particles with the particle size distribution, an estimate of the critical diameter for cloud droplet activation can be obtained. The instrument operates at supersaturations from 0.07 % to 3 %, thus capturing the typical conditions prevailing in cloud formation. At the SMEAR II station the CCNC instrument operates at water supersaturations of 0.1–1.0 %.

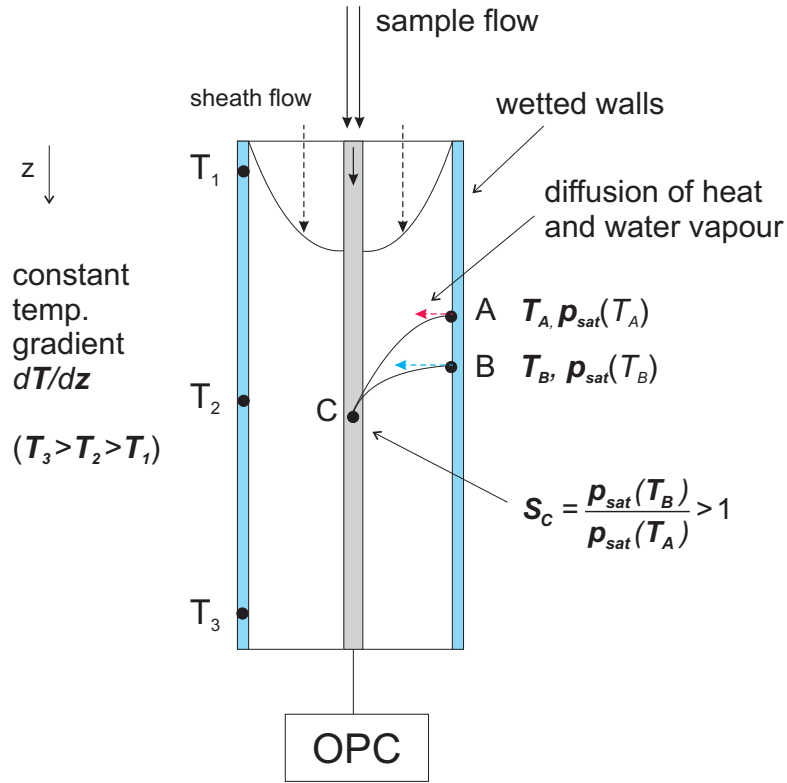


Figure 8: A schematic picture of the Cloud Condensation Nucleus Counter (CCNC).

The operation of the CCN-counter is based on the principle that diffusion of heat in air is slower than diffusion of water vapor (Roberts and Nenes, 2005; CCNC manual). Figure 8 presents a schematic of the CCN-counter. An aerosol sample is led through a cylindrical flow chamber, which has wetted walls for providing a constant water vapour source and a constant, increasing temperature gradient over the cylinder height. The water vapour (saturation concentration prevailing above the wetted walls) and heat diffuse from the outer shell inwards, to the center of the cylinder. Because water molecules diffuse more quickly than heat (due to the smaller size of a H₂O molecule in comparison to air molecules N₂ and O₂), the vapour concentration and heat (temperature) at the centerline (point C) originate from different locations on the wall (points A and B): at point C there is a concentration $p_{sat}(T_B)$ of water vapour at a temperature of T_A . Because $T_A < T_B$, the vapour is supersaturated at C: $S = p_{sat}(T_B)/p_{sat}(T_A) > 1$. Due to the constant temperature gradient, in the centerline of the cylinder there is a constant supersaturation prevailing (actually $S > 1$ almost everywhere inside the cylinder).

The supersaturation at the centerline of the flow tube, where the aerosol sample is flowing, depends on the temperature gradient between bottom and top of the cylinder, flow rate and pressure. While the flow rate and pressure are kept constants, the operating supersaturation is chosen by adjusting the temperatures T_1 , T_2 and T_3 . At a given supersaturation, particles bigger than the critical diameter activate (i.e. water starts to condense on them irreversibly) and continue to grow fast as they travel in the centerline of the flow tube (to about to some μm in diameter). The concentration

of activated cloud droplets is then counted by an optical particle counter (OPC). The OPC detects particles of size 0.75–10 μm and allows also a rough sizing of the droplets. In this work, the droplet size detection possibility of the CCNC was not utilized.

The hygroscopicity of the aerosol was measured with a Hygroscopic Tandem Differential Mobility Analyser (HTDMA) (Ehn et al., 2007). The principle of the instrument is to first select a dry aerosol particle size with a DMA, then lead the sample through a humidifier with a specified RH (RH < 100 %), and after that measure the humidified size distribution. From the humidified distribution (which may be uni- or multimodal depending on the mixing state of the aerosol) the growth factor distribution is obtained by dividing it by the original dry diameter (see Eq. 26).

Meteorological and gas data

In addition to the data described above, accompanying data of meteorological variables (T , p , RH) and common trace gases (H_2O , SO_2 etc.) were utilized in the data analysis (for the measurement methods see SMEAR webpage <http://www.atm.helsinki.fi/SMEAR/index.php/smea-ii>).

3.2 The calculation of particle formation rate

The particle formation rate J_{d_p} is defined as the *number of particles of diameter d_p formed per cm^3 per second*. In atmospheric particle formation studies, the common terminology is as follows:

- "the nucleation rate" is the formation rate of the smallest stable clusters. According to current knowledge, the size of the nucleated clusters is 1–2 nm (Kulmala et al., 2007). The nucleation rate is marked as J_{nuc} , J_1 or J_2 (subscript referring to the size in nm). The unit is $\text{particles}/(\text{cm}^3 \text{ s}) = \text{cm}^{-3} \text{ s}^{-1}$.

- "the particle formation rate" refers to the formation rate of particles at some other size than the nucleation size. Often the size of interest is set by the lower detection limit of the measurement instrument, e.g. 3 nm (in diameter) for the conventional aerosol instruments (CPC, DMPS and SMPS). The rate is marked as J_{d_p} , for example J_3 , and the unit is $\text{cm}^{-3} \text{ s}^{-1}$. Sometimes also the term "apparent particle formation rate" is used.

This distinction of the nucleation rate and the particle formation rate was first suggested by McMurry and Friedlander (1979) and has become a common convention in aerosol science.

3.2.1 Particle formation rate at 3 nm

Let us consider first a continuous particle size distribution at the diameter $d_p = 3$ nm. We can write for the number concentration at 3 nm:

$$\left. \frac{dN}{dt} \right|_3 = \left. \frac{dN}{dd_p} \right|_3 \left. \frac{dd_p}{dt} \right|_3 = n(d_p)|_3 \times GR_3 \equiv J_3, \quad (30)$$

where $n(d_p)|_3 = dN/dd_p|_3$ is the size distribution function at $d_p = 3$ nm and $GR_3 = dd_p/dt$ is the diameter growth rate of 3 nm sized particles. This is the mathematical definition of the particle formation rate at 3 nm, J_3 (provided that self-coagulation is not significant). In words, J_3 means the flux of particle concentration on the diameter axis at size $d_p = 3$ nm (see Fig. 9). In principle, if we know the size distribution and growth rate accurately at 3 nm, one could apply directly Eq. 30 to calculate J_3 , or in practice with an approximated expression (Weber et al., 1996):

$$J_3 = n(d_p)|_3 \times GR_3 \cong \left. \frac{\Delta N}{\Delta d_p} \right|_3 GR_3, \quad (31)$$

where ΔN is the particle number concentration at a narrow size range Δd_p around $d_p = 3$ nm. This expression has been used by some researchers to estimate J_3 from PHA (Pulse Height Analysis method) and nano-SMPS (Scanning Mobility Particle Sizer, similar to DMPS) data, with particle size ranges $\Delta d_p = 3\text{--}4$ nm (PHA) and $\Delta d_p = 3\text{--}6$ nm (nano-SMPS) (Weber et al., 1997; Kuang et al., 2008).

We adopt a slightly different method for the calculation of the particle formation rate, in which the particle size distribution is explicitly considered as a discrete distribution (Kulmala et al., 2001a). This corresponds to the real case of aerosol measurements, where the particle size distribution is measured as discrete channels. For one size bin at diameter $d_{p,i}$ we can write the balance equation for the number concentration N_i :

$$\frac{dN_i}{dt} = J_i - J_{i+1} - Coag. loss, \quad (32)$$

where J_i is the flux into the size bin (= formation rate of particles at the lower limit of the bin), J_{i+1} is the flux out of the size bin at the upper limit of the bin, and *Coag. loss* is the loss rate of particles due to coagulation with other (larger) particles of the size distribution. The quantities are depicted in Figure 9. This balance equation can be derived from the general dynamic equation (Eq. 4) by integrating it over the particle diameter range $\Delta d_{p,i}$ (**paper V**).

Applying Eq. 32 for the particle size range 3–6 nm and using the definition of particle formation rate (J_{d_p} , Eq. 30) we get:

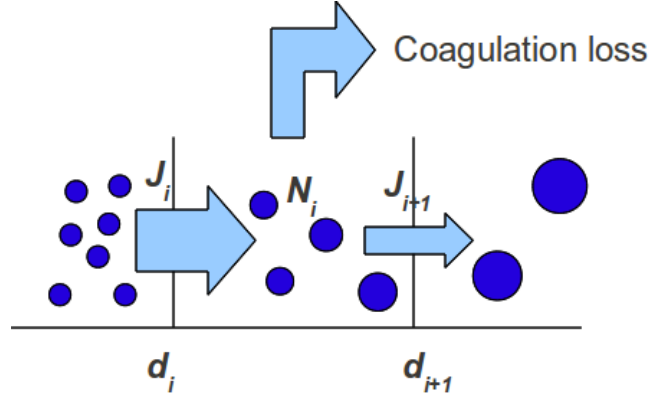


Figure 9: A schematic picture of the quantities affecting the particle concentration N_i in a size bin $d_i \dots d_{i+1}$.

$$\frac{dN_{3-6}}{dt} = J_3 - J_6 - Coag. loss \quad (33)$$

$$\approx n_3 GR_3 - n_6 GR_6 - Coag S_{d_p=4nm} N_{3-6}, \quad (34)$$

where the coagulation loss has been expressed with the aid of the coagulation sink. To simplify the calculation, the coagulation loss for 3–6 nm particles is approximated by the coagulation loss of 4 nm sized particles having the concentration N_{3-6} (4 nm is close to the geometric mean of 3 and 6 nm). The size range 3–6 nm was chosen, because it is small enough to be considered as freshly nucleated, but large enough to achieve relatively good statistics for the number concentration. In addition, the same size range has been used in earlier studies of atmospheric nucleation (Weber et al., 1997).

By solving Eq. 34 for J_3 we obtain:

$$J_3 = \frac{dN_{3-6}}{dt} + n_6 GR_6 + Coag S_{d_p=4nm} N_{3-6}. \quad (35)$$

Calculating the size distribution function from N_{3-6} as $n_6 = \Delta N_{3-6} / \Delta d_p$, using the growth rate determined from the DMPS data (for size range 3–10 nm) and approximating differentials with finite differences, we get:

$$J_3 = \frac{\Delta N_{3-6}}{\Delta t} + \frac{N_{3-6}}{(6-3) \text{ nm}} GR_{DMPS} + Coag S_{d_p=4nm} N_{3-6}. \quad (36)$$

This is the equation which is used to calculate the formation rate of 3 nm particles from the size distribution data measured with DMPS.

3.2.2 Estimation of the nucleation rate from the apparent particle formation rate

After nucleation, the newly formed particles grow by condensation and are scavenged by coagulation with the pre-existing particle size distribution. In the absence of coagulation (and other removal mechanisms) J_3 would equal the nucleation rate J_{nuc} ($J_3(t + \Delta t) = J_{nuc}(t)$), after a time delay Δt associated with the growth time from nucleated size (d_{nuc}) to 3 nm. With coagulation scavenging, which acts as a sink for particles during the growth from d_{nuc} to 3 nm, the particle formation rate at some other diameter is always smaller than the real nucleation rate: $J_3(t + \Delta t) < J_{nuc}(t)$.

In measurements, the typical lower detection limit (e.g. DMPS and SMPS instruments) for particle size is $d_p = 3\text{--}10$ nm, even though recent advances in aerosol instrumentation have pushed the detection limit down to 1–2 nm (NAIS, PSM; Asmi et al., 2009; Sipilä et al., 2009; Vanhanen et al., 2011). Anyhow, a vast majority of aerosol measurements are still done with a lower detection limit of 3 nm. For nucleation studies, it would be useful to be able to estimate the real nucleation rate at 1 nm or 1.5 nm from the observed apparent particle formation rate at some greater diameter, say 3 nm.

The original Kerminen-Kulmala formulation

Kerminen and Kulmala (2002) presented a formula connecting the apparent particle formation rate J_{d_p} at a diameter d_p with the nucleation rate J_{nuc} at diameter d_{nuc} :

$$J_{d_p}(t + \Delta t) = J_{nuc}(t) \exp\left(\gamma \frac{CS'}{GR} \left(\frac{1}{d_p} - \frac{1}{d_{nuc}}\right)\right), \quad (37)$$

where GR is the particle growth rate (in units nm/h) and nucleated size d_{nuc} and particle size d_p are expressed in meters (m). CS' (units m^{-2}) is directly proportional to the condensation sink (CS):

$$CS' = \frac{1}{2} \sum_i \beta_{m,i} d_{p,i} N_i = \frac{CS}{4\pi D_v}, \quad (38)$$

where D_v is the diffusion coefficient of the condensing vapour (assumed to be sulphuric acid). γ in Eq. 37 is a fitting parameter with an approximate value of $0.23 \text{ nm}^2 \text{ m}^2 \text{ h}^{-1}$.

Equation 37 takes into account the competition between coagulation scavenging (through the term CS') and condensational growth (through the term GR) during growth from the nucleated size d_{nuc} to a size d_p . The exponential represents the probability that a nucleated cluster of size d_{nuc} , subject to coagulation and condensational growth, will survive to the size d_p . The time delay Δt arises from the the growth time from d_{nuc} to d_p : $\Delta t = (d_p - d_{nuc})/GR$.

The Kerminen-Kulmala equation (referred to as the K-K equation) was derived under three main assumptions (Kerminen and Kulmala, 2002):

- (i) coagulation to background aerosol is the only sink for nucleated particles, i.e. self-coagulation and dry deposition are neglected. Neglecting self-coagulation is justified if concentrations are below 10^5 – 10^6 cm^{-3} .
- (ii) the particle growth rate is constant during growth from d_{nuc} to d_p .
- (iii) background aerosol (i.e. CS') stays constant during the growth from d_{nuc} to d_p .

The K-K equation was derived analytically, but it contains a fitting parameter γ , which arises from expressing the coagulation scavenging (the coagulation sink) in terms of the condensation sink. The reason behind this is that at small particle sizes, approaching the molecular size, coagulation can be thought of as condensation of nm-sized particles onto the background distribution. Also, CS is often the quantity that is calculated from measured particle size distributions, and is more straightforward to calculate than CoagS.

The Brownian coagulation coefficient of d_p -sized particles is proportional to $d_p^{-\kappa}$, where the exponent κ is in the range 1.5–2 (Kerminen and Kulmala, 2002; Seinfeld and Pandis, 2006). Kerminen and Kulmala assumed $\kappa = 2$, and thus the coagulation sink of d_p -sized particles can be expressed as:

$$CoagS_{d_p} = \gamma' \cdot CS' \left(\frac{d_{nuc}}{d_p} \right)^2 = \gamma \cdot CS' \left(\frac{1}{d_p} \right)^2. \quad (39)$$

The proportionality factors γ' and γ connect $CoagS(d_p)$ to CS' . Based on fittings to data from aerosol dynamical simulations, Kerminen and Kulmala (2002) presented a parametrisation for γ which depends weakly on many factors such as temperature and nucleated particle density. However, usually an approximate value of $0.23 \text{ nm}^2 \text{ m}^2 \text{ h}^{-1}$ is accurate enough for atmospheric particle formation studies.

In connection with aerosol measurements, the K-K equation is often used in the reverse direction, i.e. to estimate the nucleation rate from the observed particle formation rate:

$$J_{nuc}(t) = J_{d_p}(t + \Delta t) \exp \left(-\gamma \frac{CS'}{GR} \left(\frac{1}{d_p} - \frac{1}{d_{nuc}} \right) \right). \quad (40)$$

Usually the equation is used at the lower detection limit of particle size distribution measurements, i.e. at $d_p = 3$ nm, and with nucleation size in the range 1–2 nm.

The Kerminen-Kulmala equation has proved to be very useful in testing and developing nucleation theories (e.g. **papers I** and **II**). With this equation we can obtain quite reliable estimates of the actual nucleation rates, when accurate measurements of

nucleation rate at the real nucleation size (1–2 nm) are missing. Another important use of the K-K equation is in large scale atmospheric models, where it (in the form of Eq. 37) can be used to transfer nucleation rates to particle formation rates e.g. at 3 or 10 nm, without the need to model all the initial steps of particle growth in detail.

The Kerminen-Kulmala equation corresponds to a similar formula presented by McMurry and Friedlander (1979). However, the Kerminen-Kulmala equation has become more popular, most probably because it is easier to apply and uses two main quantities that are determined in new particle formation event studies, namely *GR* and *CS*. In their paper, McMurry et al. (2005) present a rigorous examination on the connections between these two similar methods to estimate nucleation rates from the apparent particle formation rate.

The revised form of the Kerminen-Kulmala equation

Afterwards, Lehtinen et al. (2007) have presented a revision for the Kerminen-Kulmala equation. In their formulation, two improvements were made: the coagulation scavenging is calculated explicitly from the coagulation sink (not through the condensation sink) and a more accurate expression for coagulation sink is used. Instead of assuming the coagulation sink to be proportional to the square of the particle diameter (Eq. 39), the exponent is kept as a free parameter:

$$\text{CoagS}(d_p) = \text{CoagS}(d_{nuc}) \cdot \left(\frac{d_p}{d_{nuc}} \right)^m, \quad (41)$$

where $\text{CoagS}(d_{nuc})$ is the coagulation sink of nucleated particles and $m = -\kappa$. By solving this, an equation for the exponent m is obtained:

$$m = \frac{\log [\text{CoagS}(d_p)/\text{CoagS}(d_{nuc})]}{\log[d_p/d_{nuc}]}. \quad (42)$$

By this equation the value of exponent m (typically in the range $[-2, -1.5]$) can be calculated directly from the particle size distributions. At the Hyytiälä SMEAR II station, m varies in the range $[-1.75, -1.5]$ with a mean value -1.7 (Lehtinen et al., 2007).

The main improvement of this approach is that we get rid of the fitting parameter γ , which in the K-K formula was adjusted based on modelling results. With the new expression for the CoagS (Eq. 41), a new equation for the apparent particle formation rate was obtained:

$$J_{d_p}(t + \Delta t) = J_{d_{nuc}}(t) \exp\left(-\gamma d_{nuc} \frac{\text{CoagS}(d_{nuc})}{GR}\right),$$

$$\text{where } \gamma = \frac{1}{m+1} \left[\left(\frac{d_p}{d_{nuc}}\right)^{m+1} - 1 \right] \quad (43)$$

Note that here the parameter γ is a dimensionless parameter, and different from the one in the original form of the K-K-equation. To get the units correct in this equation, the CoagS has to be expressed in units h^{-1} , if the GR is in nm/h .

There are a couple of advantages in the revised version of the K-K equation. First, it is conceptually more clear to use directly the coagulation sink instead of condensation sink for calculating the coagulation scavenging. Also, the dependence of the condensation sink on the diffusion properties of the condensing vapour is avoided. Second, the coagulation scavenging is calculated more accurately. Third, the varying ambient conditions are more easily taken into account, as the parameter m can be calculated explicitly from the particle size distributions.

The revised version of the K-K equation (Eq. 43) is applied as follows. First, the proper value of m is calculated from experimental particle size distribution data, to represent the conditions of the studied case. The parameter m can be determined for the average conditions of the station, or even separately for each new particle formation event. Then the particle formation rate is evaluated using Eq. 43.

In addition to the modification by Lehtinen et al. (2007), a few other improvements have been presented to the original K-K equation. Kerminen et al. (2004) presented a formulation which accounts for, in addition to sulphuric acid, an organic vapour contribution to the particle growth, and allows for a time-dependent growth rate. Anttila et al. (2010) included in their parameterisation the effects of self-coagulation of freshly nucleated particles. However, in most cases of atmospheric particle formation (when the nucleation rates are not too high and the growth rate is not varying fast), the original formulation by Kerminen and Kulmala (2002) or Lehtinen et al. (2007) is accurate enough.

In the articles included in this thesis, the original formulation of the K-K equation (Eqs. 37 and 40) was used, except in **paper III**, where the new, revised formula by Lehtinen et al. (2007, Eq. 43) was applied. In future studies, the use of the revised formula is recommended.

3.3 Evaluation of the calculation method of J_3

Equation 36 has been widely used for estimating the new particle formation rate from measured particle size distribution data. In **paper V** we studied the accuracy of this calculation method to predict the actual particle formation rate at 3 nm. The study

was based on simulations made with the University of Helsinki Multicomponent Aerosol model (UHMA; see Section 3.4 for description of the model). Using simulated data, the exact particle formation rate at 3 nm (J_3) as well as other model conditions are known, and can be compared with the estimate given by approximate equation (36).

For the evaluation study, a new particle formation event, similar to the observed new particle formation events, was produced with the UHMA model (Fig. 10). The nucleation mechanism was activation nucleation (see Sect. 4.2) at a diameter of 1.5 nm, and particle growth was caused by sulphuric acid and a non-volatile organic vapour. Both vapours had a sinusoidal-like diurnal profile, while the concentration of organic vapour was significantly higher than that of H_2SO_4 , so that particle growth was caused mostly by the organic vapour. The background particle distribution corresponded to a typical case in Hyytiälä.

From the simulated data, the particle formation rate at 3 nm was calculated by Eq. 31 (corresponding to the Eq. 3 in **paper V**):

$$J_3 = \frac{\Delta N}{\Delta d_p} \Big|_3 GR_3, \quad (44)$$

where $\Delta N/\Delta d_p|_3$ is the size distribution function and GR_3 is the growth rate at $d_p = 3$ nm. Let us denote this formation rate as "exact". This formation rate is called "exact", since we get the values of particle size distribution $\Delta N/\Delta d_p$ and the growth rate GR_3 directly from the simulated data, and the formula (Eq. 31 or 44) does not contain any approximations despite the calculation of n_3 from the discrete model data. In the simulated case we used 60 size sections (as compared to 23 size sections in the measured data), so discretization will have only a minor effect on the results. Consequently, J_3 calculated by Eq. 44 can be considered to represent the actual J_3 quite accurately.

For evaluation of the validity of the J_3 calculation methods, Eq. 36 was applied to the modelled event in the same way as for a measured particle formation event. The $\Delta N_{3-6}/\Delta t$, N_{3-6} and $CoagS_{d_p=4nm}$ were obtained directly from the simulated discrete particle size distribution. The growth rate was calculated in two ways: i) directly from the condensation rate of vapours, calculated as an average for particle sizes 3–7 nm, or ii) by estimating a constant GR from the time evolution of the nucleation mode peak diameter between 3–7 nm ($GR = \Delta d_p/\Delta t$). The first method (i) is applicable only with the simulated data and gives a time-dependent (but size-averaged) GR . The latter method (ii, denoted as "constant GR ") is the way the growth rate is determined from measured new particle size distribution data (Hirsikko et al., 2005). Thus Eq. 36 with the "constant GR "-growth rate corresponds to the measurement case for calculating J_3 .

The investigation showed that Eq. 36 (corresponds to Eq. 5 in **paper V**) gives a fairly good estimate for new particle formation rate J_3 (see Fig. 10). The equation tends to overestimate the particle formation rate J_3 , as compared to the exact values given by Eq. 44, with an error of 10–20 %. Surprisingly, the J_3 estimation is better with the

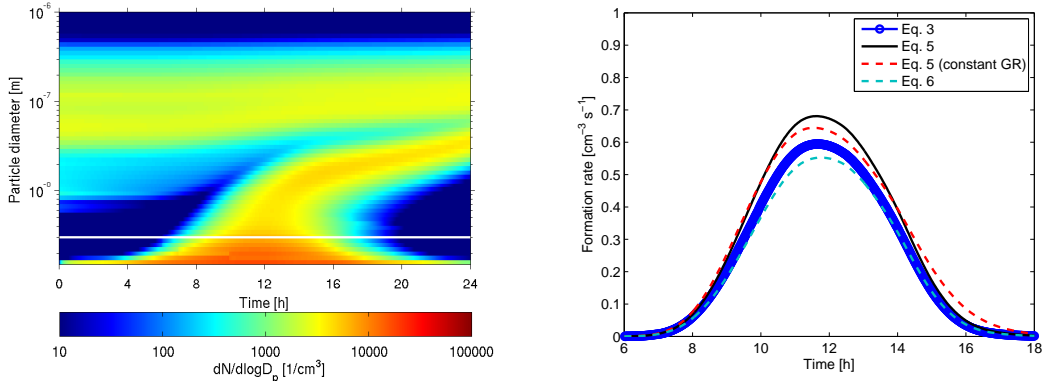


Figure 10: Simulated new particle formation event (left) and comparison of different methods to calculate the particle formation rate J_3 during this event (right) (same as Figs. 2 and 3 in **paper V**). Note that the legend refers to the equations of **paper V**.

”constant GR ” growth rate, i.e the method used in analyses of measured data, than with the more exact, time-dependent GR calculated from the simulation. This effect is most probably caused by a fortuitous error cancellation.

The sensitivity studies presented in **paper V** indicated that most of the error in J_3 calculation (Eq. 36) can be attributed to coagulation and its various effects. Between 3 and 6 nm particles experience significant coagulation scavenging to background aerosol, with the coagulation rate decreasing as particles grow larger (from 3 to 6 nm). The coagulation scavenging term $CoagS_4 \times N_{3-6}$ is only a rough approximation to the coagulation rate of 3–6 nm particles. The other main error source is the calculation of J_6 : $J_6 = n_6 GR_{3-7}$ (Eq. 31), where the size distribution function was approximated as $n_6 = N_{3-6}/(6-3)\text{nm}$. Due to decreasing coagulation rates, more particles at 3 nm are removed by coagulation than at 6 nm, and thus the mean number concentration in the size range 3–6 nm, N_{3-6} , is not the best estimate for n_6 close to upper diameter 6 nm. A better choice would be to estimate n_6 from a size range closer to 6 nm, e.g. 5–7 nm: $n_6 \approx N_{5-7}/(7-5)\text{nm}$.

Applying the more accurate calculation for n_6 improved the estimate of J_3 significantly; the error in J_3 was reduced to only 6 %.

In this study, the effect of self-coagulation was neglected, but the effect should be small at these concentrations (significant only at very high number concentrations).

With this modification to the n_6 estimation, a new formula for calculating J_3 was proposed (corresponds to Eq. 6 in **paper V**):

$$J_3 = \frac{\Delta N_{3-6}}{\Delta t} + \frac{N_{5-7}}{(7-5)\text{nm}} GR_{3-7} + CoagS_{d_p=4\text{nm}} N_{3-6}. \quad (45)$$

Because this improvement is straightforward to implement, in **paper V** we recommend this new form of J_3 equation to be used in the analyses of experimental particle formation data.

It is clear that also the growth rate GR_{3-7} , calculated from the time evolution of the nucleation mode, has inaccuracies (Leppä et al., 2011), but those errors are hard to quantify and so far no other reasonable way to estimate growth rates exists. Simulation results showed that the J_3 calculation was quite sensitive to the value of the growth rate.

This study (**paper V**) was to our knowledge the first attempt to estimate the validity of the particle formation rate calculations, which have been performed for a wide range of measurement data from different locations. It gave confidence that the method used to estimate J_3 gives generally fairly good results, and the magnitude of error is acceptable. However, the study was based on only one type of new particle formation event, although several sensitivity tests on the simulation conditions were performed. To set the results on a more solid base, a more detailed study with a variety of simulated new particle formation events would be needed in order to find out if these results are statistically valid, and what is the uncertainty in the calculation of J_3 for larger datasets.

3.4 University of Helsinki Multicomponent Aerosol model

Aerosol dynamical simulations were carried out in order to gain insight into the processes behind atmospheric particle formation (**papers III–V**). The advantage of an aerosol dynamical model is that we can track the whole process of atmospheric particle formation from nucleation size at 1–2 nm up to 500 nm under controlled conditions.

The simulations were performed using the University of Helsinki Multicomponent Aerosol model (UHMA), which has been developed at the University of Helsinki by Korhonen et al. (2004) and designed specifically for studies of new particle formation. UHMA is a box-model to simulate the dynamics of the aerosol population in a uniform "box" of air, without any advection or turbulent transport fluxes. It calculates the evolution of the aerosol size distribution under all the basic aerosol dynamical processes for clear-sky conditions: nucleation, condensation, coagulation and dry deposition.

The two main approaches in atmospheric modelling are the Eulerian and Lagrangian frameworks. In the Eulerian framework, a situation at stationary observer is modelled, whereas in the Lagrangian framework, a situation for an observer moving with the air flow is considered. In principle, as UHMA does not include advective mass transfer, it represents a Lagrangian modelling framework. The measurements e.g. at the Hyytiälä SMEAR II station, however, are done at a stationary point i.e. in an Eulerian perspective. The results from a Lagrangian box-model can be compared to measurements at a stationary station, provided that air flow at the station is from the same direction for a sufficiently long time, and no strong horizontal transport occurs (calm conditions). In that case the station is observing the same and rather homogenous air mass. This condition is often fulfilled for the class I events (Dal Maso et al., 2005; an example shown in Fig. 2). In the steady conditions of one air mass, the observed new particle formation behaves smoothly, having a steady growth without abrupt changes in the size distribution.

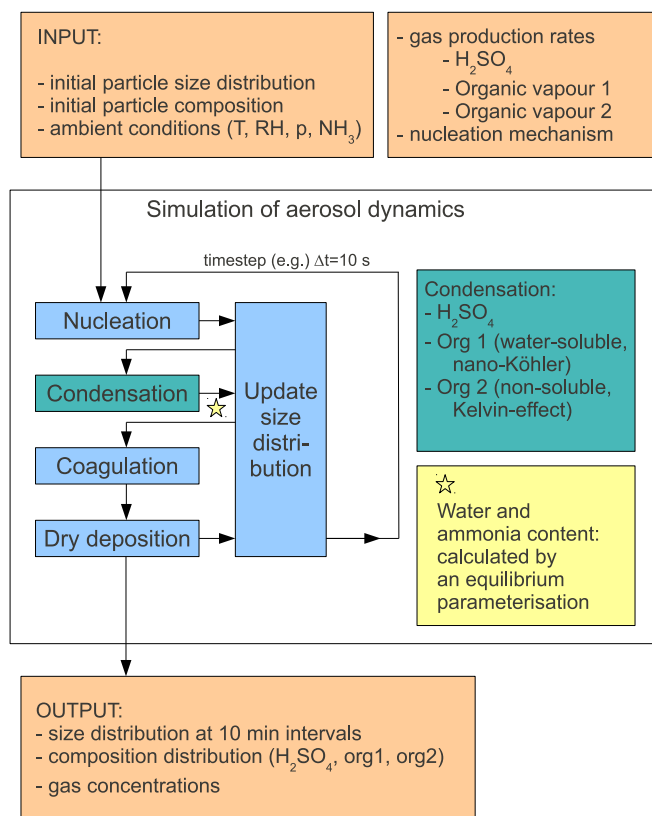


Figure 11: The structure of the UHMA (University of Helsinki Multicomponent Aerosol model). The model is a 1-dimensional box-model designed for particle formation studies.

The basic structure of the UHMA model is presented in Fig. 11. As an input, the model takes the initial particle size distribution and composition. In addition, the condensable gas production rates (or concentrations) and nucleation mechanism have to be specified. The model then calculates the dynamics of the aerosol population, subject to the four aerosol dynamical processes, according to the General Dynamic Equation (Eq. 4). In the basic version of UHMA, the integration of differential equations is performed with the simple, 1st order Euler-forward method. At chosen time intervals, e.g. 10 min., the model gives as an output the current particle size and composition distribution as well as the concentrations of condensable gases.

UHMA is a sectional model, meaning that the size distribution is divided into sections uniformly distributed on a logarithmic particle diameter axis. The number of sections can be chosen freely according to the accuracy needed in the study; typically 40–60 sections between 1–500 nm are used. Particles are assumed to be totally internally mixed within a size section, i.e. all particles in a size bin have the same composition. The particles are composed of the following "substances": sulphuric acid, 1–3 organic compounds, a possible insoluble core, ammonia and water.

Condensation is calculated using the transition-regime theory of Fuchs and Sutugin

(1971) (also in Seinfeld and Pandis, 2006), with the modification by Lehtinen and Kulmala (2003) for the molecular regime condensation flux. For condensation calculations, UHMA applies a hybrid-sectional method, in which the particle is divided into a "core particle" part including sulphuric acid, organic compound(s) and possible non-soluble core-particle, and a "non-core part" including water and ammonia. For the "core" part the condensation (or evaporation) flux and the resulting diameter increase (or decrease) is calculated explicitly from the condensation equations, whereas water and ammonia uptake are calculated through an equilibrium parameterisation, which depends on relative humidity, ammonia concentration, particle size and composition (Napari et al., 2006). One of the condensing organic compounds can be set to be a "nano-Köhler"-compound, meaning that its condensation follows the nano-Köhler-mechanism proposed by Kulmala et al. (2004a) (see Sect 2.1.1). If more than one condensable organic compounds are used, the rest are assumed to be water-insoluble and follow the normal Kelvin effect.

Coagulation is calculated according to the conventional equations by Fuchs (1964, also in Seinfeld and Pandis, 2006). Dry deposition follows a parameterisation for Hyytiälä conditions by Rannik et al. (2003). For nucleation, several different parameterisations can be used: binary, ternary, activation and kinetic nucleation mechanism. To update the model for this study, I added the subroutines for activation and kinetic nucleation mechanisms (Sect. 4.2, Eqs. 46 and 47) as well as a subroutine for sulphuric acid production rate. The sulphuric acid production rate is calculated as a chemical reaction rate of SO₂ and OH, while for OH a sinusoidal profile dependent on the zenith angle of the sun was assumed, corresponding to cloudless conditions.

In this study, the following model set-up was applied (for the base case): Particles consist of sulphuric acid, water, ammonia and one nano-Köhler-organic compound. The properties of the organic compound were chosen to correspond to a possible VOC oxidation product with a saturation vapour concentration $c_{sat} \leq 10^6 \text{ cm}^{-3}$ (c_{sat} corresponds to saturation vapour pressure via ideal gas law) (Kulmala et al., 1998b, 2001b). The sulphuric acid saturation concentration is assumed to be zero, i.e. it condenses with the maximum flux. For the activation and kinetic coefficients the mean values determined for the QUEST II campaign (Hyytiälä) were used, namely $A = 1 \times 10^{-6} \text{ s}^{-1}$ and $K = 5 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$ (**paper I**).

The UHMA model (and its modified versions) has been applied widely in studies of atmospheric aerosols and particle formation: in combination with a chemistry model for new particle formation studies (Grini et al., 2005); in a pseudo-Lagrangian way for simulating aerosol transformation during continental transport, with a simple treatment for boundary layer entrainment/detrainment (Komppula et al., 2006; Tunved et al., 2006b); in studies of iodine oxide induced nucleation in coastal, marine environment (Vuollekoski et al., 2009; Ehn et al., 2010); for investigating sea salt aerosol and its effect on marine aerosol and cloud droplet number concentrations (Mårtensson et al., 2010); and for studying cloud processing and CCN activation (Korhonen et al., 2005). Leppä et al. (2009) have developed a model version including atmospheric ions and charged particles. In addition, UHMA has been incorporated as part of a 1-dimensional columnar model MALTE (Boy et al., 2006; Lauros et al., 2011).

4 Connection between sulphuric acid and new particle formation

As described in previous sections, sulphuric acid is the key compound in atmospheric nucleation. In addition to nucleation, sulphuric acid participates in the condensational growth of particles. Due to its extremely low saturation vapour pressure, sulphuric acid starts to condense already on the smallest, freshly nucleated particles.

The main part of this thesis studies the correlation of new particle formation with sulphuric acid concentration. This correlation was studied both by analyzing field measurement data (**papers I–III**) and by conducting aerosol dynamical simulations (**paper IV**). This chapter describes the results published in **papers I–IV**.

4.1 General correlation of sulphuric acid and new particle formation in the field data

An important background to this study are the measurements by Weber et al. (1995, 1996, 1997), which reported concurrent measurements of sulphuric acid and freshly nucleated particle concentrations in the 3–4 nm size range at a marine site (Mauna Loa) and a continental site (Idaho Hill) in USA. They observed the formation rate of 3 nm particles to be correlated with the ambient sulphuric acid concentration to the power between 1–2, a much smaller power than predicted by classical nucleation theory. Their measurements indicated, that nucleation would be collision controlled (McMurry and Friedlander, 1979), but with a rate about three orders of magnitude smaller than the kinetic collision frequency of the hydrated H_2SO_4 molecules. Weber et al. (1997) speculated that this would be caused by ammonia needed to stabilize the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters.

After the studies by Weber et al., few research efforts were devoted to investigating the correlation of particle formation with H_2SO_4 , probably due to the lack, at that time, of mass spectrometric instruments needed for the measurement of sulphuric acid. The correlation between sulphuric acid and particle formation rate was "rediscovered" after the measurements of the QUEST II campaign in Hyytiälä in 2003, where the sulphuric acid concentration was measured continuously with a good time resolution using a chemical ionisation mass spectrometer (CIMS) (Fiedler et al., 2005; Kulmala et al., 2006). The QUEST II campaign was the first field campaign in Hyytiälä with continuous sulphuric acid concentration measurements.

The correlation studies presented in this thesis started from the observation, that on some days the number concentration of freshly nucleated particles (3–6 nm in diameter) follows nicely the sulphuric acid concentration after some time delay (Fig. 12). The striking similarity between these quantities strongly suggests that sulphuric acid participates in nucleation. The time delay Δt arises from the time needed for growth from the nucleation size (1–2 nm; in **papers I–II** nucleation at 1 nm was assumed) to the detection limit 3 nm of the DMPS.

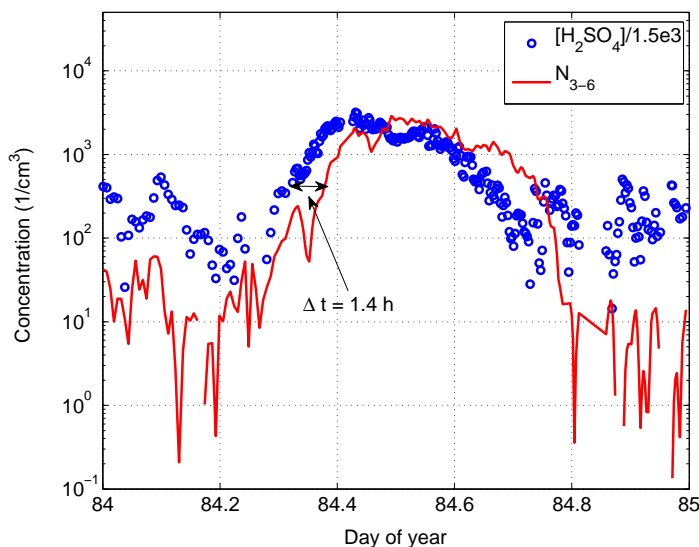


Figure 12: The number concentration of 3–6 nm particles and the concentration of gas phase sulphuric acid on 25th March (day 84), 2003, at the Hyytiälä SMEAR II station, an example of a pure ”activation day” with linear correlation between sulphuric acid and N_{3-6} . The number concentration of freshly nucleated particles follows the sulphuric acid concentration after a time delay of approximately 1.4 hours.

The correlations between new particle formation and gas-phase sulphuric acid concentration were studied in detail in **papers I** and **II**. The study was based on analysis of field data, measured during three campaigns: QUEST II campaign in 2003 in Hyytiälä, Finland (**paper I**), QUEST III campaign in 2004 in Heidelberg, Germany (**paper II**), and BACCI/QUEST IV campaign in 2005 in Hyytiälä (**paper II**). These data sets offered good material to investigate the connection between new particle formation (abbreviated hereafter as NPF) and sulphuric acid in different environments, Hyytiälä representing a rural site in boreal forest environment and Heidelberg a slightly more polluted site in Central Europe.

We studied the correlation with sulphuric acid separately for the number concentration of 3–6 nm particles (N_{3-6} , obtained from the lowest four channels of the DMPS measurements), for the formation rate of 3 nm particles (J_3 , calculated from DMPS data by Eq. 36) and for the formation rate of 1 nm particles (J_1 i.e. the nucleation rate, calculated by Eq. 40). In all data sets, both the number concentration N_{3-6} and the particle formation rates (J_3 and J_1) were observed to correlate with sulphuric acid concentration to the power of 1–2 (see Fig. 13). The correlations were very similar in all three data sets, suggesting that the nucleation mechanism is similar in both environments, Hyytiälä and Heidelberg.

To examine the correlations in more detail, we determined for each day the exponent maximizing the correlation coefficient, separately for the three relationships: $N_{3-6} \sim [\text{H}_2\text{SO}_4]^n$, $J_3 \sim [\text{H}_2\text{SO}_4]^n$ and $J_1 \sim [\text{H}_2\text{SO}_4]^n$. These ”best-fit” exponents are called here *the correlation exponents* and labelled as $n_{N_{3-6}}$, n_{J_3} and n_{J_1} . In all three data sets there

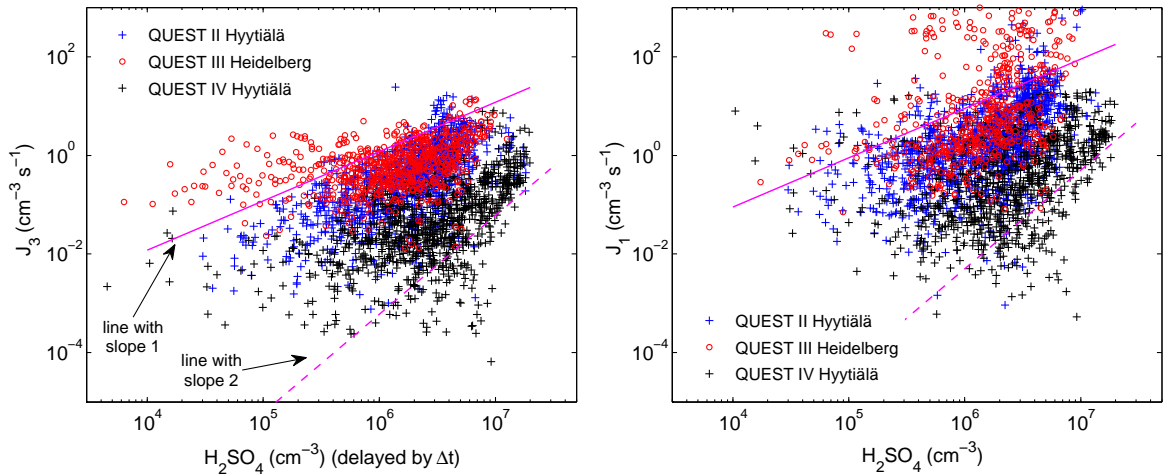


Figure 13: Formation rate of 3 nm particles (J_3) (left) and 1 nm particles (J_1) (right) versus sulphuric acid concentration during the three QUEST campaigns in Hyytiälä, Finland, and in Heidelberg, Germany. The straight lines correspond to the linear and squared relationship between J_{d_p} and $[\text{H}_2\text{SO}_4]$ (with slopes 1 and 2 on logarithmic axis).

were pure exponent $n = 1$ days (linear correlation with $[\text{H}_2\text{SO}_4]$) and pure exponent $n = 2$ days (squared correlation with $[\text{H}_2\text{SO}_4]$), as well as variants between $n = 1$ – 2 (Table 1). The correlation exponents could be different for N_{3-6} , J_3 and J_1 , typically in the order that $n_{N_{3-6}} \leq n_{J_3}$ and $n_{N_{3-6}} \leq n_{J_1}$. Based on simple theoretical calculations, the change in the correlation exponent was attributed to sulphuric acid participating in the growth of nucleated clusters (**paper II**). This conclusion was supported also by the results from aerosol dynamical simulations presented in **paper IV**.

The time delay between the rise in $[\text{H}_2\text{SO}_4]$ and N_{3-6} can be used to estimate the growth rate of nucleated clusters from the nucleation size at 1 nm to 3 nm: $GR_{1-3} = 2\text{nm}/\Delta t$ (Fiedler et al., 2005). The mean values for the initial particle growth rates were 1.2–3 nm/h in Hyytiälä and 1.3 nm/h in Heidelberg.

The strong correlation of particle formation rates and number concentration with the H_2SO_4 concentration implies that sulphuric acid is participating in nucleation and/or growth of freshly nucleated particles. However, the correlation analysis does not give ultimate proof that sulphuric acid is the nucleating compound. In principle, there are three possibilities which could produce the observed correlation between NPF and sulphuric acid:

- (i) sulphuric acid participates only in nucleation (= formation of stable clusters around 1–1.5 nm);
- (ii) sulphuric acid participates in initial particle growth, but nucleation happens by other substances (e.g. organic compounds);
- (iii) sulphuric acid participates both in nucleation and initial particle growth.

Table 1: The exponents of the correlation $N_{3-6} \sim [\text{H}_2\text{SO}_4]^n$ (R is the mean correlation coefficient) and the median values of the nucleation coefficients A and K for the QUEST II–QUEST IV campaigns (**paper II**).

| | QUEST II Mar 18–Apr 9, 2003 Hyytiälä | QUEST III Feb 28–Apr 4, 2004 Heidelberg | BACCI/QUEST IV Apr 5–May 16, 2005 Hyytiälä |
|---------------------------------|--|---|--|
| $n \approx 1$ | 6 (38%) | 6 (60%) | 9 (45%) |
| $n \approx 1.5$ | 4 (25%) | 3 (30%) | 2 (10%) |
| $n \approx 2$ | 5 (31%) | 1 (10%) | 6 (30%) |
| $n \approx 2.5-3$ | 1 (6%) | – | 3 (15%) |
| mean R | 0.85 | 0.75 | 0.82 |
| median A (1/s) | 1.0e-06 | 1.1e-05 | 2.4e-07 |
| median K (cm ³ /s) | 4.5e-13 | 3.9e-12 | 3.2e-14 |

Of these, the possibility (iii) is the most probable one. Option (i) can be ruled out, because due to its small saturation vapour pressure, sulphuric acid always condenses on particles. Therefore, if sulphuric acid participates in nucleation, it will also participate in the growth of freshly nucleated particles. Overall, the participation of organic compounds in nucleation or early growth is probable, e.g. the presence of organic acids has been observed to enhance nucleation in laboratory (Zhang et al., 2004).

4.2 Activation and kinetic nucleation mechanisms

None of the previously presented nucleation theories — classical binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ or ternary $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ nucleation — is able to explain the small correlation exponents between new particle formation rate and $[\text{H}_2\text{SO}_4]$. Classical binary and ternary nucleation theories would predict correlation exponents of $\sim 4-10$, and based on the nucleation theorem (Eq. 14) this would mean that there are 4–10 H_2SO_4 molecules in the critical cluster. The correlation exponents 1–2 observed in the field measurement data (**papers I and II**) are far below this.

To explain the observed linear relationship between new particle formation and sulphuric acid concentration, Kulmala et al. (2006) proposed a new nucleation mechanism, “*activation nucleation*”, in which the nucleation rate is directly proportional to the sulphuric acid concentration:

$$J_{act} = A [\text{H}_2\text{SO}_4]. \quad (46)$$

Here A is an empirical activation coefficient (units 1/s), which will be determined

according to measurement data.

In activation nucleation, nucleation is thought to happen via activation of small (~ 1 nm) clusters, which after activation reach the critical radius and start to grow larger by condensation of sulphuric acid and other vapours available. Two possibilities for this activation process have been suggested: (i) small clusters which contain one sulphuric acid molecule are activated via heterogenous nucleation of some other substance or by surface chemical reactions; or (ii) small clusters of unspecified composition (e.g. organic clusters) are activated when a sulphuric acid molecule hits them. These both processes would generate a linear relationship between the nucleation rate and the sulphuric acid concentration. Even though at present the theory of activation nucleation is somewhat ambiguous, it provides a simple parameterisation that can be tested and utilized in modelling nucleation. The physical and chemical details of the nucleation process are lumped together in the activation coefficient, which so far is merely an empirical coefficient.

To explain the squared relationship between new particle formation and sulphuric acid, the "*kinetic nucleation*" scheme was proposed (**paper I**), in which the nucleation rate is proportional to the square of H_2SO_4 concentration:

$$J_{kin} = K [\text{H}_2\text{SO}_4]^2, \quad (47)$$

where K is an empirical kinetic coefficient (units cm^3/s). This nucleation mechanism has the functional form of collision-limited kinetic nucleation of sulphuric acid, where stable clusters are formed by collision of two H_2SO_4 molecules (McMurry and Friedlander, 1979). However, here the prefactor K is kept as a free empirical parameter, which will be determined based on measurement data. Similarly as in activation nucleation, the kinetic coefficient K contains the details of the nucleation process: specifically the probability that a collision of two sulphuric acid containing molecules/clusters results in the formation of a stable cluster. The upper limit for K is set by the collision frequency, which is obtained from the kinetic gas theory (Eq. 15). For H_2SO_4 molecules at $T = 293\text{K}$, the kinetic collision frequency is about $3 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

In **papers I** and **II** these nucleation mechanisms were examined and the values of the nucleation coefficients A and K were determined for the first time. We fitted J_3 and J_1 with the sulphuric acid concentration and determined values for the nucleation coefficients which produced the best fit (see Figs. 5 and 6 in **paper I**). The fitting was performed separately for each day, thus obtaining a distribution of daily A and K coefficients. Due to scatter in the data, on many days it was hard to decide which nucleation mechanism (activation or kinetic) fitted better. Therefore, for every day the values of both coefficients were determined.

The median values of the activation and kinetic coefficients for each campaign are listed in Table 1. The values of the activation and kinetic coefficients showed large variation from day to day: inside one data set (each the length of a couple of months) the nucleation coefficients varied over 1–2 orders of magnitude. The values of A and K were

about an order of magnitude higher in Heidelberg as compared to Hyytiälä, probably related to Heidelberg being more affected by anthropogenic pollution such as ammonia which could enhance nucleation. The sulphuric acid concentrations were measured with the same method (CIMS, see Sect. 3.1) during all the campaigns, but the individual instruments were different. This causes some uncertainty to the comparison of the data sets, as there may be some offset between the different instruments.

The variations of the A and K coefficients during different measurement campaigns are compared in Figure 14, with also the values reported by Nieminen et al. (2009) for EUCAARI 2007 campaign in Hyytiälä and by Paasonen et al. (2009) for Hohenpeissenberg station in Germany included. The nucleation coefficients are similar in magnitude for Hyytiälä and Hohenpeissenberg, although some variations between the three Hyytiälä data sets is observed. The values of A and K are about an order of magnitude higher in Heidelberg as compared to Hyytiälä. In Hohenpeissenberg data set the variation of the coefficients is much larger than in Hyytiälä and Heidelberg: over 3 orders of magnitude for A and up to 5 orders of magnitude for K . This is probably related to the Hohenpeissenberg data set being 1.5 years long, thus covering all seasons, while measurements in Hyytiälä and Heidelberg were from spring-summertime campaigns.

In comparison with the earlier results by Weber et al. (1995, 1996, 1997), our study shows strikingly similar results. Weber et al. (1996) reported a prefactor ϕ to the kinetic collision frequency of sulphuric acid-water clusters of $\phi = 0.001$ for Mauna Loa and $\phi = 0.003$ for Idaho Hill, with which the nucleation rate would be: $J_{nuc} = \phi K_{kin} [\text{H}_2\text{SO}_4]^2$. With $K_{kin} = 3 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, Weber's prefactor (corresponding to our nucleation coefficient K) would be $3\text{--}9 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, which is in the same range with our values for the kinetic coefficient in Hyytiälä.

The physical and chemical details of the nucleation process are hidden behind the empirical activation and kinetic coefficients. The large variation in A and K implies that, besides sulphuric acid, there are other factors that affect the atmospheric nucleation rate crucially.

The existence of pure "activation days" with linear correlation (e.g. the day in Fig. 12) and pure "kinetic days" with squared correlation with $[\text{H}_2\text{SO}_4]$ (e.g. the day in Fig. 3b of **paper II**), implies that there are different (at least two) nucleation/initial growth mechanisms working on different days with varying ambient conditions. The conditions affecting the nucleation mechanism can be the level of $[\text{H}_2\text{SO}_4]$, presence of organic compounds (oxidation products of VOCs), ammonia or amine concentrations, temperature, relative humidity etc.

After **papers I and II**, a few studies on the connection of NPF with sulphuric acid have been published. Kuang et al. (2008) investigated the sulphuric acid correlations at several locations by applying somewhat different methods for J_3 calculation (Eq. 31) and correlation analysis than in this thesis. They found that kinetic nucleation (with exponent very close to 2) was explaining nucleation in all studied places. In their analysis, Kuang et al. combined the data points from different days into one data set,

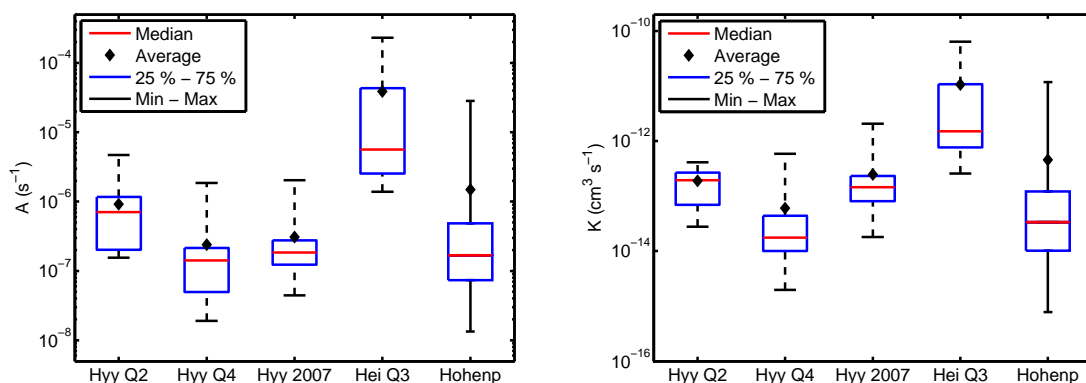


Figure 14: The values of activation (A , left) and kinetic (K , right) coefficients during five measurement campaigns: QUEST II, QUEST IV and EUCAARI 2007 (Nieminen et al., 2009) at the Hyytiälä SMEAR II station; QUEST III in Heidelberg, Germany; and HAFEX at the Hohenpeissenberg station, Germany (Paasonen et al., 2009).

for which the correlations were determined, whereas in the studies of this thesis the correlations were investigated separately for each day.

Paasonen et al. (2009, 2010) examined the effect of organic vapours in activation and kinetic nucleation mechanisms. The nucleation coefficients A and K were observed to correlate positively with monoterpene oxidation products, but no such correlation existed for the nucleation rate ($J_{1.5}$) (Paasonen et al., 2009). A comprehensive study of data from Hyytiälä, Hohenpeissenberg (Germany), Melpitz (Germany) and San Pietro Capofiume (SPC, Italy) showed that overall, kinetic sulphuric acid nucleation explains nucleation well in all other places than Hohenpeissenberg, where the effect of organics is dominant. However, even at the sulphuric acid-dominated sites (Hyytiälä, Melpitz, SPC), the inclusion of co-nucleation of organic vapour and sulphuric acid (together with kinetic nucleation of H_2SO_4) improved the nucleation rate prediction (Paasonen et al., 2010). The importance of organic vapours very probably explains the high variation for A and K in Hohenpeissenberg shown in Fig. 14.

There are indications that ammonia or amines (Petäjä et al., 2011; Zhao et al., 2011; Paasonen et al., 2012) and organic compounds (Metzger et al., 2010) could be important for atmospheric nucleation. Brus et al. (2011) have reported laboratory measurements of H_2SO_4 - H_2O nucleation, in which the correlation exponent was observed to decrease with increasing temperature (from $n = 2.2$ at 5°C to $n = 1.2$ at 25°C).

In **papers I–II** the exponent of the correlation $J_1 \sim [\text{H}_2\text{SO}_4]^n$ (the slope of the $\log(J_1)$ vs $\log([\text{H}_2\text{SO}_4])$ plot) was interpreted as the number of H_2SO_4 molecules in the critical cluster, based on the approximate version of the nucleation theorem (Eq. 14). According to current knowledge, this conclusion does not hold: if the Gibbs free energy curve has local minima, the basic nucleation theorem is not valid, and at least the approximation $n^* + 1 \approx n^*$ can not be done, when n^* is small. However, the correlation exponent can be interpreted as giving information on the rate limiting step in atmospheric NPF (cluster formation or their growth): this step seems to be proportional to the H_2SO_4

concentration to the power between 1 and 2.

When **papers I** and **II** were published, there existed a remarkable gap between atmospheric and laboratory measurements of nucleation (see Sect. 2.2.3): the slope of $\log(J_{nuc}$ vs $\log([\text{H}_2\text{SO}_4])$ curves were significantly higher in the laboratory (order of 4–10) than in the atmosphere. This discrepancy has been overcome by recent advances in measurement technologies of 1–3 nm particles, and the slopes of 1–2, as observed in atmospheric measurements, have been reproduced also in laboratory conditions (Sipilä et al., 2010).

Korhonen et al. (2010) made a computational study on the sulphuric acid correlations, investigating the accuracy of the analysis methods to determine the exponent of nucleation and the values of the nucleation coefficients (A and K). The result was that there are several uncertainties in the analysis procedure, especially in the determination of nucleation rates from the particle formation rates at 3 nm. Therefore, the correlation exponents and values of the nucleation coefficients determined with several different steps in the data analysis procedure should be interpreted with caution: at least noting that they contain significant error bars.

Despite their deficiencies (the large variation of A and K even within the same data set), the developed parameterisations for activation and kinetic nucleation have already been used quite widely in global aerosol and climate models (e.g. Spracklen et al., 2006, 2008; Makkonen et al., 2009). The parameterisations capture quite well nucleation happening in the atmospheric boundary layer.

Summarizing, the atmospheric particle formation rate is observed to depend on the sulphuric acid concentration to the power 1–2 (**papers I** and **II**). According to current knowledge, the kinetic nucleation (with exponent 2) seems to be most widely valid, together with co-nucleation of sulphuric acid and organics. In some places, nucleation may be dominated by organic compounds (Paasonen et al., 2010). Pure activation nucleation (with linear correlation with H_2SO_4) seems to be a special case, which certainly acts in some conditions, but overall it happens rather rarely. In the future, aerosol mass spectrometric measurements will probably reveal the constituents of the nucleated clusters. The final goal is to develop a parameterisation and a theoretically consistent framework that captures all important factors affecting the atmospheric nucleation rate.

4.3 The effect of relative humidity on the nucleation rate

Atmospheric new particle formation has been known to happen preferably in conditions with low relative humidity (RH) (e.g. Birmili et al., 2000; Boy and Kulmala, 2002; Hyvönen et al., 2005). This has been observed consistently in several locations, but no solid explanation for the observation has been given so far. It has been speculated, that the main reason would be the increased coagulation and condensation sink, due to background particles' diameter increase when they take up water from humid air. This leads, on one hand, to increasing coagulation scavenging of small, nucleated particles; on the other hand, increased condensation sink decreases the concentrations of condensable vapours, thereby hindering nucleation and initial particle growth. Both these effects act in the same direction, and prevent particle formation.

In contrast to atmospheric observations, in laboratory measurements of nucleation in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ or $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ -system, the nucleation rates are consistently observed to increase with relative humidity (Berndt et al., 2005; Brus et al., 2011; Benson et al., 2008, 2009). Also from a theoretical point of view this would be expected. As atmospheric particle formation is thought to happen via co-nucleation of sulphuric acid and water or via a ternary mechanism involving also ammonia, increasing water vapour concentration should enhance nucleation as the formation energy of a critical cluster is lowered when the concentration (or saturation ratio) of a nucleating substance increases (Vehkamäki et al., 2002, Merikanto et al., 2007).

In **paper III**, the reasons behind the RH-inhibition of new particle formation were examined in detail with the aid of field measurement data, theoretical calculations and aerosol dynamical simulations. A new hypothesis for RH-inhibiting effect was presented: *decreased solar radiation in humid conditions might limit sulphuric acid production and thereby lead to smaller nucleation rates*. The purpose was to find out, which of the following effects is the dominating one in preventing NPF at high RH:

- i) effect of RH on H_2SO_4 concentration via reduced OH concentration (reduced solar radiation) at high RH;
- ii) effect of RH on H_2SO_4 concentration via increased condensation sink at high RH;
or
- iii) effect of RH to J_3 through increased coagulation sink at high RH.

New hypothesis for the RH-inhibiting effect on NPF

The new hypothesis was based on the field measurement data of particle formation rates ($J_{1.5}$) and sulphuric acid concentrations presented in Fig. 15. When the points in $J_{1.5}$ vs $[\text{H}_2\text{SO}_4]$ plot were colour scaled according to relative humidity, a clear dependence on RH emerged: nucleation rates were highest when RH was lowest and vice versa. When plotted with absolute humidity (water vapour concentration), no such separation of points happened as with RH.

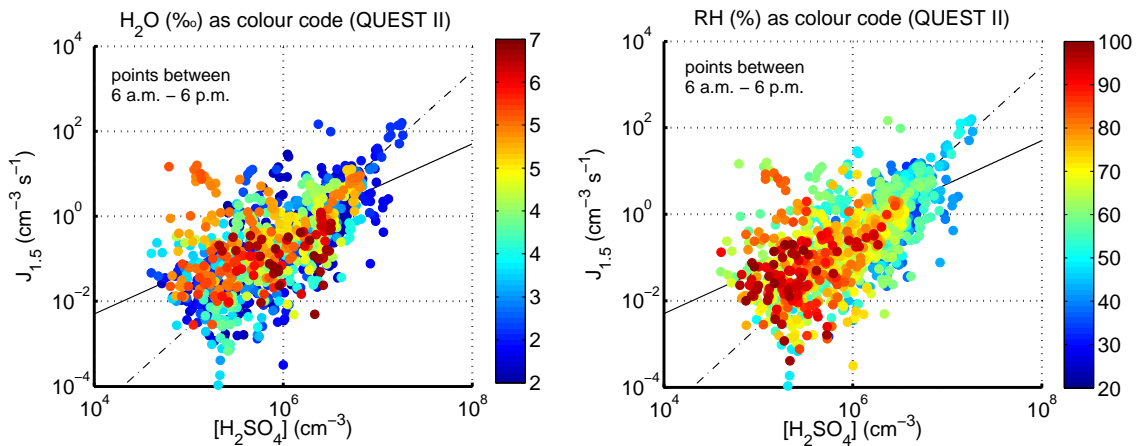


Figure 15: Nucleation rate versus sulphuric acid (in log axes), colour scaled according to absolute humidity (H_2O concentration, left) and relative humidity (RH, right) during QUEST II campaign at the Hyttiälä SMEAR II station. The lines correspond to the linear and squared correlation between $J_{1.5}$ and $[\text{H}_2\text{SO}_4]$.

The observation shown in Fig. 15 led us to present a hypothesis that the RH-effect on the nucleation rate is mediated through sulphuric acid concentration: high RH may prevent H_2SO_4 formation via decreased photochemistry due to decreased sunlight reaching the ground on hazy or partially cloudy days with high RH. Decreased solar radiation leads to decreased formation of OH radicals, which further affects the formation of H_2SO_4 through reaction of SO_2 and OH (see Sect. 2.3). As the nucleation rate is controlled by sulphuric acid (as reported in **papers I and II**), smaller sulphuric acid concentrations are directly transferred to smaller nucleation rates.

Data analysis revealed that at $\text{RH} > 60\%$ the sulphuric acid concentrations decreased with increasing RH. Especially the highest H_2SO_4 concentrations were totally missing at $\text{RH} > 60\%$ (see Fig. 1 in **paper III**). The SO_2 concentration was observed to be rather independent of RH. Instead, OH and UV showed very similar correlation with RH as H_2SO_4 : both the OH concentration and UV radiation intensity started to decrease above a RH of 60%. Taken together, this data suggests that RH limits nucleation through limiting UV-B and OH, and thereby sulphuric acid production.

The decreasing effect of RH on UV radiation can be explained as follows. At humid conditions, the probability of cloud and fog formation increases, and in the presence of clouds the UV radiation reaching the lower atmosphere (boundary layer) decreases. The relationship between cloudiness and RH was investigated using a 30-year long data set of low level clouds collected by the Finnish Meteorological Institute at the Jokioinen weather station. As expected, the amount of low level clouds was negatively correlated with RH. Interestingly, there seemed to be a threshold value of RH (about 40–60%) above which cloudiness started to increase steeply with RH, especially around midday hours (see Fig. 5 in **paper III**). A plot of global radiation versus RH in the Jokioinen data set showed a similar decreasing trend with RH as in the Hyttiälä QUEST II data set, and a mirror-like behaviour as compared to cloudiness. It is worth noting, that a

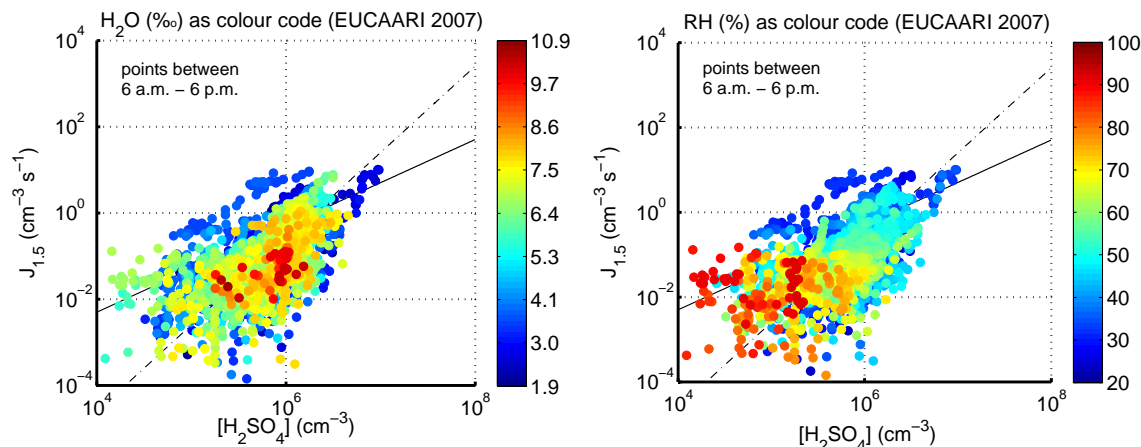


Figure 16: Nucleation rate versus sulphuric acid, colour scaled according to absolute humidity (H_2O concentration, left) and relative humidity (RH, right) during EUCAARI 2007 campaign at the Hyytiälä SMEAR II station. The lines correspond to the linear and squared correlation between $J_{1.5}$ and $[\text{H}_2\text{SO}_4]$.

similar threshold at $\text{RH} = 40\text{--}60\%$ was observed for all variables: H_2SO_4 , OH, UV, global radiation and cloudiness. The cloudiness data supports the hypothesis that the RH limits the H_2SO_4 concentration through limiting OH production, and this effect is because of decreased UV radiation reaching the ground due to cloudiness in humid conditions.

The study presented in **paper III** was based on data from the QUEST II campaign from Hyytiälä. The similar correlation of $J_{1.5}$ and H_2SO_4 with RH (but not with H_2O concentration) is seen also for QUEST IV and EUCAARI 2007 data sets (see Fig. 16) from Hyytiälä in spring 2005 and 2007, respectively. This gives confidence that the results are more generally valid, at least in conditions at the Hyytiälä SMEAR II station.

Another reason for the observed anti-correlation of OH and UV with RH could be, that these variables have opposite diurnal profiles: UV radiation (and thus OH) peaks at noon, whereas RH has minimum at noon/afternoon, when temperature and water saturation concentration are the highest. This results in an apparent anticorrelation between UV (and OH) with RH, without a necessary causal correlation between these variables. The effect of opposite diurnal variations makes it difficult to distinguish how much of the observed correlation is explained by cloudiness and how much is only due to diurnal variations. In **paper III** it is suggested that opposite diurnal cycles would be the main reason for the anticorrelation of OH and UV (and H_2SO_4) with RH, and the effect of cloudiness would be a minor effect.

Effect of increased condensation and coagulation sink

At humid conditions aerosols experience hygroscopic growth: they take up water, thereby increasing their diameter and surface area. The DMPS measures the particle size distribution as a dry distribution at about RH = 30 % prevailing inside the instrument. The hygroscopicity of particles then has to be taken into account using a parameterisation for particle wet diameter, in this case with a parameterisation by Laakso et al. (2004) for Hyytiälä conditions. As an example, from RH of 30 % to 90 % hygroscopic growth increases the condensation and coagulation sinks by about a factor of 3 (**paper III**).

The increased condensation sink (CS) increases the loss rate of sulphuric acid, leading to smaller H_2SO_4 concentrations. This is further transferred to a smaller nucleation rate and particle formation rate at 3 nm, J_3 . The increase in coagulation sink (CoagS), in turn, increases the coagulation scavenging of small clusters. The probability of a cluster surviving from the nucleation size (1–1.5 nm) to 3 nm size becomes smaller, leading to a smaller particle formation rate at 3 nm (J_3 , as described by Eq. 37 or 43).

The effect of increased coagulation sink was examined by theoretical calculations performed using the new form of the Kerminen-Kulmala equation, Eq. 43 (Lehtinen et al., 2007). We calculated how much J_3 decreases from the nucleation rate $J_{1.5}$ at different relative humidities, when wet-CoagS is calculated with the parameterisation by Laakso et al. (2004). The result was that increased CoagS could suppress new particle formation, provided that the particle growth rate is low and the coagulation sink (background aerosol concentration) is high ("extreme case" in **paper III**). In such conditions, J_3 decreased by 1–3 orders of magnitude from $J_{1.5}$ when RH increased from 10 to 90 %, indicating that at high RH CoagS could mask the new particle formation event from observation at 3 nm. However, at average conditions of typical growth rate and CoagS, the decrease from $J_{1.5}$ to J_3 was smaller, and not enough to suppress the nucleation event.

The relative importance of the effects of decreased OH production, increased CoagS and increased CS were further investigated by performing aerosol dynamical simulations. The OH concentration was assumed to decrease linearly as a function of RH for RH > 60 %, based on the observed correlation of OH with RH (Fig. 4 in **paper III**) and analysis from a chemical model (Boy et al., 2005). The modelling results showed that, of these variables, the particle formation rate J_3 was most sensitive to the reduced OH levels, as decreased OH directly leads to smaller sulphuric acid concentrations and nucleation rates. The effects of increased CS (through decreased H_2SO_4 concentration) and increased CoagS (through the coagulation scavenging of small clusters) on J_3 were similar in magnitude, but these effects were significantly smaller than that of reduced OH concentration.

In conclusion, **paper III** reports the finding that RH seems to limit the nucleation rate by limiting OH and H_2SO_4 production at high relative humidities. In comparison to OH-effect, the earlier proposed mechanisms for the RH-inhibiting effect, increased condensation and coagulation sinks, are shown to have smaller contribution in suppressing

new particle formation. The effect of RH on OH could be related to cloudiness at high RH: cloud and haze droplets increase the scattering of sunlight, leading to less radiation reaching the ground and smaller OH production rates. However, it is possible that the observed anticorrelation of H_2SO_4 and RH is mainly due to opposite diurnal profiles of UV radiation and RH. **Paper III** concludes that "even though at first glance RH appears to limit NPF, this appearance is due to its anticorrelation with solar radiation."

The study of **paper III** demonstrates how difficult it is to distinguish real reasons and causal relationships behind an observed correlation in atmospheric data, when almost all variables have a diurnal variation related to sunlight. Actually, **paper III** provokes even more questions than it answers. A continuing study would be needed, with more sophisticated data analysis methods to separate the diurnal variation from the other variations in the data. Also, it would be interesting to repeat the investigation at other sites, to find out how generally the proposed mechanism of suppression of new particle formation by reduced OH production at high RH is valid.

4.4 Modelling the connection between sulphuric acid and particle formation

In **papers I** and **II** the strong correlation between new particle formation and gas-phase sulphuric acid concentration was studied based on data measured at field stations in Hyytiälä and Heidelberg. The activation and kinetic nucleation mechanisms were proposed as explanations for the linear or squared relationship between particle formation at 3 nm and sulphuric acid concentration. In order to study in more detail this correlation, aerosol dynamical simulations were performed (**paper IV**). The purposes of the simulations were:

- (i) to find out whether other factors than the nucleation mechanism, such as condensation and coagulation, affect the correlations of J_3 and N_{3-6} with $[\text{H}_2\text{SO}_4]$;
- (ii) to examine how the correlation with $[\text{H}_2\text{SO}_4]$ changes as particles grow from nucleated size (1–2 nm) to 3 nm;
- (iii) to find the conditions which would yield the observed linear correlation (on some days) between particle number concentration N_{3-6} and sulphuric acid.

The simulations were performed with the UHMA model using three different nucleation mechanisms: activation, kinetic and ternary nucleation. The condensing vapours were sulphuric acid and an organic vapour with nano-Köhler mechanism for condensation. Sulphuric acid had a sinusoidal profile with maximum of $5-7 \cdot 10^6 \text{ cm}^{-3}$ at noon, corresponding to typical sulphuric acid concentrations in Hyytiälä, whereas the organic vapour had a constant concentration of 10^7 cm^{-3} . The relative humidity was 50 % and ammonia (NH_3) concentration 5 ppt. To investigate how the correlation of J_3 and N_{3-6}

with $[\text{H}_2\text{SO}_4]$ depends on the particle condensational growth rate and the size at which nucleation is happening (objective ii), we varied the saturation vapour concentration of the organic vapour ($c_{sat,org}$, which affects the profile of the growth rate as a function of particle diameter), and the size of the nucleated cluster (d_{nuc}), respectively. In total, a high number of sensitivity runs were performed; **paper IV** reports in more detail the results of six case studies representing the main features of the simulations (Fig. 17).

The correlations with sulphuric acid concentrations were studied separately for the nucleation rate, the particle formation rate at 3 nm and the number concentration of 3–6 nm particles. The correlation exponents were determined for $J_{nuc} \sim [\text{H}_2\text{SO}_4]^{n_{nuc}}$, $J_3 \sim [\text{H}_2\text{SO}_4]^{n_{J_3}}$ and $N_{3-6} \sim [\text{H}_2\text{SO}_4]^{n_{N_{3-6}}}$ by finding the slope of the log-log curve.

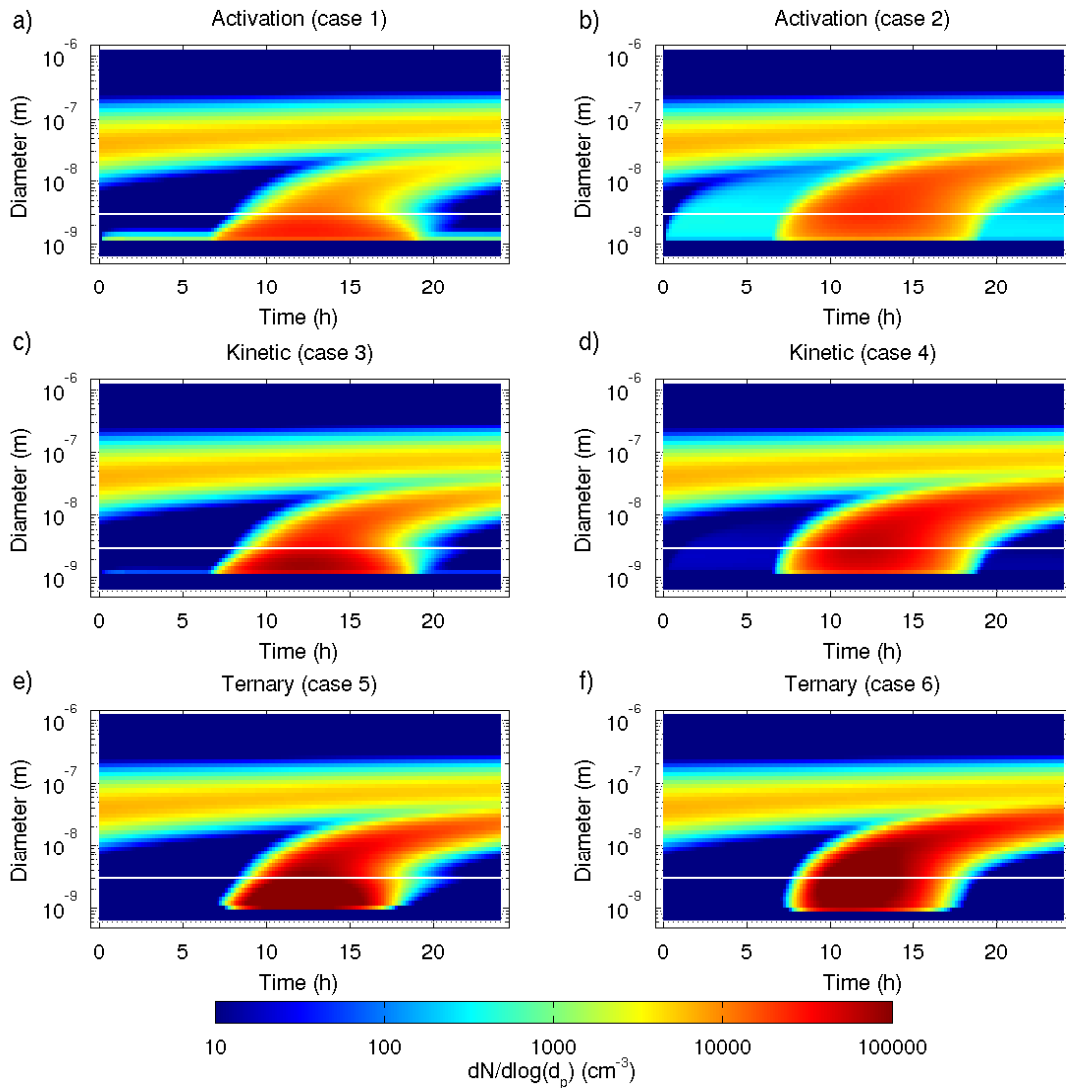


Figure 17: Simulated new particle formation events applying different nucleation mechanisms: activation (top), kinetic (middle) and ternary nucleation (bottom). The left column (a, c, e): $c_{sat,org} = 10^6 \text{ cm}^{-3}$ and nano-Köhler mechanism for the condensable organic vapour; the right column (b, d, f): $c_{sat,org} = 0 \text{ cm}^{-3}$. The white horizontal line shows the 3 nm border.

Table 2: The correlation exponents n_{J_3} and $n_{N_{3-6}}$ for $J_3 \sim [\text{H}_2\text{SO}_4]^{n_{J_3}}$ and $N_{3-6} \sim [\text{H}_2\text{SO}_4]^{n_{N_{3-6}}}$, for events simulated by the UHMA model (Fig. 17), using different nucleation mechanisms and condensing organic vapour properties. The nucleated cluster size was in all cases $d_{nuc} = 1$ nm.

| | Activation nucleation $n_{nuc} = 1$ | Kinetic nucleation $n_{nuc} = 2$ | Ternary nucleation $n_{nuc} \approx 5.6$ |
|--------------------------------------|--|--|---|
| $c_{sat,org} = 10^6 \text{ cm}^{-3}$ | $n_{J_3} = 3.2$ $n_{N_{3-6}} = 2.3$ | $n_{J_3} = 3.4$ $n_{N_{3-6}} = 2.3$ | $n_{J_3} = 5.6$ $n_{N_{3-6}} = 4.1$ |
| $c_{sat,org} = 0 \text{ cm}^{-3}$ | $n_{J_3} = 1.3$ $n_{N_{3-6}} = 1.2$ | $n_{J_3} = 2.1$ $n_{N_{3-6}} = 1.7$ | $n_{J_3} = 5.0$ $n_{N_{3-6}} = 4.0$ |

The simulations showed that the correlation with sulphuric acid can be notably different for these three quantities (Table 2). Especially with activation nucleation, which has nucleation exponent $n_{nuc} = 1$, the correlation exponent could increase by 1–2 units for J_3 and N_{3-6} . Generally, the exponent for N_{3-6} correlation was smaller than for J_3 . In case of ternary nucleation, the correlation exponent for N_{3-6} was even smaller than the nucleation exponent.

These changes in sulphuric acid correlation exponents may seem peculiar. However, they are explained by aerosol dynamical processes happening during the growth from nucleation size at 1–2 nm to 3–6 nm. The simulations revealed that most important for the change of the correlation exponent is the particle growth rate between 1–3 nm, which is both size and time dependent. The size dependence of the growth rate with different values of organic vapour saturation concentration ($c_{sat,org}$) is presented in Fig. 18. At high saturation concentration ($c_{sat,org} = 10^5\text{--}10^6 \text{ cm}^{-3}$), the growth of the smallest particles (1–1.5 nm) is solely due to sulphuric acid, and the organic vapour starts to condense gradually between 1.5–4 nm, following the nano-Köhler mechanism (see Fig. 5 in **paper IV**). When the organic saturation concentration decreases, the growth rate of small particles increases, as organic vapour starts to condense on smaller and smaller particles. At $c_{sat,org} = 0$, the organic vapour condenses with the maximum flux (not limited by the Kelvin effect).

With activation nucleation, preserving the exponent of nucleation for J_3 and N_{3-6} required either i) fast growth of the nucleated particles, or ii) nucleation happening at 2 nm size. For the first requirement, the nano-Köhler mechanism (with non-negligible saturation concentration) for organic vapour condensation was not alone sufficient to increase the growth rate of the smallest particles, but a negligible saturation ($c_{sat,org} \leq 10^2 \text{ cm}^{-3}$) concentration was required to get high enough growth rate (see Fig. 18). In both these cases, particles grow fast from nucleation size to 3–6 nm, so that also the sulphuric acid correlation "has no time to change much".

In addition to condensational growth, the coagulation loss of freshly nucleated particles affects the correlation of J_3 and N_{3-6} with sulphuric acid. This question was not addressed in the study of **paper IV**. As coagulation becomes important at high nucle-

ation rates, it was speculated that the different behaviour of the correlation exponents in case of ternary nucleation (exponent decreases from J_{nuc} to J_3 and N_{3-6}) could be caused by the effect of coagulation (the ternary mechanism causes more intense nucleation, as seen in Fig. 17).

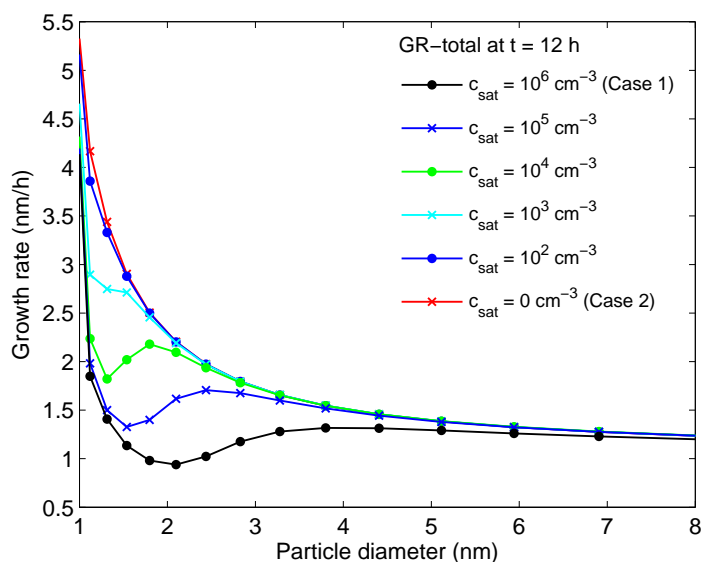


Figure 18: The particle growth rate due to condensation of sulphuric acid and organic vapour as a function of particle size in the simulations made with the UHMA model. The different curves are for the different values of the organic vapour saturation concentration ($c_{sat,org}$). The organic vapour condensation followed the nano-Köhler mechanism.

As a conclusion, the correlation with sulphuric acid can change significantly during particle growth from the nucleation size 1–1.5 nm to 3–6 nm, and therefore the correlation exponents observed for J_3 or N_{3-6} should not be interpreted directly as the exponent of nucleation. However, modelling results showed that the correlation exponent can not change very much, only by 1–2 units, and therefore ternary nucleation, having a correlation exponent 4–6, can be most probably ruled out, at least for nucleation happening in the boundary layer in boreal forest conditions. According to the results presented in this thesis, one can safely say that the nucleation mechanism seems to involve sulphuric acid and has a dependence on the sulphuric acid concentration to the power of 1–3. This result is supported also by laboratory studies with novel instrumentation (Sipilä et al., 2010; Brus et al., 2011).

5 CCN activity of boreal forest aerosols

Aerosols are needed in cloud formation as seeds for water condensation, i.e. to act as cloud condensation nuclei (CCN). An aerosol particle can act as a CCN, if its size is bigger than the critical (threshold) diameter for irreversible water condensation to happen. In the fast condensation of water, called activation, the CCN are converted to cloud droplets. The critical size depends on the physical size of the particle (diameter) and its chemical composition (solubility to water). Typically aerosol particles bigger than 50–100 nm are potential CCN. It is probable, that a considerable fraction of particles acting as CCN are produced by atmospheric nucleation events (Merikanto et al., 2009; Kerminen et al., 2012).

Aerosol climate effects through acting as CCN are called the aerosol indirect effects (Penner et al., 2004). In cloud formation, increasing CCN concentrations inside a cloud cause a larger number of cloud droplets but smaller in size to be formed, assuming that the same water amount is condensing on a bigger number of CCN. This has twofold effects on cloud characteristics: i) smaller cloud droplets scatter solar radiation more efficiently, resulting in a higher cloud albedo i.e. whiter clouds (first indirect effect) and ii) smaller cloud droplets do not precipitate as easily, making the cloud lifetime longer (second indirect effect). Thus, increasing aerosol concentrations imply whiter and longer-lasting clouds, exerting a cooling effect on the climate (see Fig. 1). In addition to these cooling effects, clouds scatter back infrared radiation coming from the Earth's surface. Also, black carbon and dust aerosols can form so called "brown clouds", which are actually thick aerosol layers and not clouds. These brown clouds, which are encountered in heavily polluted areas in Asia (India and China), absorb solar radiation and via complex effects on atmospheric temperature, may have both warming and cooling effects on the climate (semi-direct effects) (Ramanathan et al., 2007; Koch and Del Genio, 2010).

Aerosol-cloud effects are one of the poorest understood parts of the climate system. According to current knowledge, aerosols have during the past 50–100 years caused a significant net cooling effect on the climate, thus masking part of the warming by greenhouse gases (Andreae et al., 2005; Makkonen et al., 2012).

The possibility to cool the climate artificially, e.g. by inserting sulphate aerosols in to the stratosphere (where they directly scatter sunlight) or sea-salt aerosols to the marine troposphere (where they affect the formation of stratocumulus clouds), has been suggested as a possible way to counteract climate warming. This is called geo-engineering, and despite the big risks associated with it, it has become a serious path in climate research (e.g. Partanen et al. (2012)). Also for this reason, understanding the aerosol-cloud interactions is crucial.

It has been proposed that Nature itself could also have a feedback mechanism through aerosols which would decrease the climate warming (Kulmala et al., 2004c; Tunved et al., 2008; Paasonen et al., 2013). Natural aerosols are to a big extent formed on continental areas with forests and other vegetation. Formation of secondary organic aerosols could increase in the warming climate, as most of the organic vapour emissions

increase with temperature. This would increase direct scattering of solar radiation and affect cloud formation, thus having a cooling feedback effect on climate.

Boreal forest areas, covering 8 % of the Earth’s surface, are even a globally important source of secondary organic aerosol (SOA) particles (Tunved et al., 2006a), which have climatic effects at least on a regional scale (Lihavainen et al., 2009). In **paper VI** the ability of boreal forest aerosols to act as cloud condensation nuclei was investigated based on 1 year of continuous CCN concentration measurements at the Hyytiälä SMEAR II station. In addition, concurrent hygroscopicity measurements were analysed, to get more information on the CCN activity of aerosols in Hyytiälä.

5.1 Seasonal variation of CCN properties at the Hyytiälä SMEAR II station

The measured CCN concentration at a certain supersaturation is determined by the aerosol number concentration, the aerosol size distribution (whether there are more large, CCN active particles or more small, non-CCN-active particles), and the chemical composition (the hygroscopicity) of the particles. The chemical composition determines the critical diameter for cloud droplet activation.

Measured CCN concentrations were observed to have a clear seasonal variation, with highest concentrations in the summertime (Fig. 2 in **paper VI**). In June-July the CCN concentration was at least double the concentration in December-January. Also the activated fraction (calculated in this study as the total fraction of particles activated to cloud droplets, $F_{act} = N_{CCN}/N_{CN}$, where N_{CN} is the total particle number concentration) had a maximum in summertime. The seasonal variation of the critical diameter was a bit different, but it also had the smallest values during the growing season in spring-summer. These findings indicate that, on average, the aerosol particles in the summertime boreal forest are more hygroscopic and more CCN-active than aerosols in wintertime. In summertime, aerosols are expected to contain a larger fraction of oxidation products of organic substances emitted from the forest; the high CCN activity of the summertime aerosol particles in Hyytiälä suggests that these organics are highly hygroscopic.

The critical diameter (d_{crit}) for cloud droplet activation was determined in this study by two different methods. First, d_{crit} was determined from CCN concentrations and particle size distribution (DMPS) data by simply integrating the size distribution from the largest particle size towards smaller sizes, until the concentration matches the measured CCN concentration:

$$\sum_{d_i=d_{crit}}^{d_{max}} N_i = N_{CCN}, \quad (48)$$

where the lower size limit corresponds the critical diameter. In this method it is assumed that particles are internally mixed (i.e. particles of certain size have the same

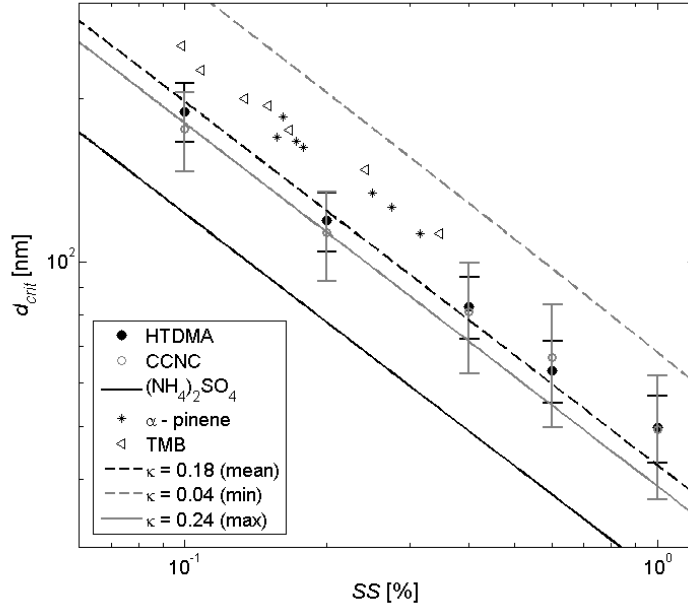


Figure 19: Average critical diameters as a function of water supersaturation for Hyytiälä aerosol, estimated from CCNC and HTDMA data (error bars indicate the standard deviations in the one year data set). Laboratory measurements for secondary organic aerosol (α -pinene and trimethylbenzene, TMB) are shown for comparison (Duplissy et al., 2008). Lines show the theoretical values from the kappa-Köhler equation for pure ammonium sulphate particles and for a range of SOA kappa values.

chemical composition), all particles larger than d_{crit} are activated (i.e. differences in chemical composition are neglected) and the activation probability behaves as a step function at d_{crit} .

Second, the critical diameter was estimated from the hygroscopicity measurements (HTDMA) using kappa-Köhler theory (see Sect. 2.4). The value of the hygroscopicity parameter κ (kappa) was determined from HTDMA-data (for conditions $S < 1$), and after that the value of the critical (dry) diameter was calculated from Eq. 29 for the supersaturations corresponding to CCN measurements ($SS = 0.1\text{--}1.0\%$).

The critical diameters determined by these two methods corresponded well to each other, the mean values being ~ 50 nm, ~ 80 nm and $150\text{--}200$ nm at SS of 1.0% , 0.4% and 0.1% , respectively. While there were differences between daily and monthly values, on average both methods produced very similar behaviour of d_{crit} as a function of supersaturation (see Fig. 19 and Table 1 in **paper VI**). The points fall nicely on the theoretical slope of $-2/3$ on the log-log plot ($d_{crit} \sim SS^{-2/3}$). The determined critical diameters are not far from the laboratory results for α -pinene secondary organic aerosol. In Hyytiälä, α -pinene is one of the main monoterpenes emitted by the forest. The presence of sulphate in Hyytiälä aerosols makes the critical diameters somewhat lower than for pure organic aerosol.

The mean kappa parameter, as determined from HTDMA measurements, was 0.18. This corresponds to estimated fractions of 84 % organics ($\kappa = 0.1$) and 16 % sulphate ($\kappa = 0.6$). These fractions are in line with other estimates of the organic fraction of Hyytiälä aerosols (Boy et al., 2005; Jimenez et al., 2009). Of course, this division to only two constituents (organics and sulphate) is very rough. There are certainly also less-hygroscopic organics (with $\kappa < 0.1$) or purely non-hygroscopic aerosols such as black carbon present in Hyytiälä aerosol. The value of 0.18 is an average over all supersaturations (0.1–1.0 %), and there are most probably differences in the κ values between different particle sizes. This is reflected also in Fig. 19: at high supersaturations the points start to deviate from the same straight line with slope $-2/3$.

The value determined for the κ -parameter ($\kappa = 0.18$) can be utilised in modelling the concentrations of potential CCN in boreal forest. To capture the seasonal variation of CCN concentrations, a seasonal profile for κ would be needed. This remains to be determined in future studies.

The comparison of the two methods for determination of the critical diameter showed, that even the simplified method of integrating the size distribution is capable of giving at least a rough estimate of the threshold diameter for CCN activation. This is in line with earlier results, which report that the particle size distribution dominates over the chemical composition in determining the CCN concentrations (Dusek et al., 2006; Quinn et al., 2008). In principle, the simplified integration method should give an upper limit to d_{crit} , because all particles larger than that size are assumed to activate, regardless their chemical composition.

5.2 Effect of new particle formation on cloud condensation nuclei

Figure 20 shows an example of a period with several new particle formation (NPF) events, together with the measured CCN concentrations, the activated fraction and critical diameter (determined from the CCN-concentration and particle size distribution data by Eq. 48). The CCN concentrations increase constantly during these NPF days, even though the total number concentration (CN) is approximately constant. This indicates that NPF events are producing significant numbers of particles to the CCN-active size range. The increase in CCN concentration is more pronounced for the three highest supersaturations ($SS \geq 0.4$ %), which (due to smaller critical diameters) are more affected by the growing nucleation mode.

The effect of new particle formation on CCN concentrations was further studied by computing the average diurnal variation of the CCN concentration, activated fraction and critical diameter separately on new particle formation event days and non-event days (see Figs. 7–9 in **paper VI**). The diurnal variation was examined for a two-day period, because the nucleation mode typically grows to CCN active sizes (to 50–100 nm) by the end of the NPF day. Nucleation events were observed to cause an increase in CCN concentrations, which started in the evening of the NPF event day and lasted

until the end of next day (Fig. 21). A moderate increase in CCN number was observable even at the smallest supersaturations, indicating that nucleation is really capable of producing CCN-active particles.

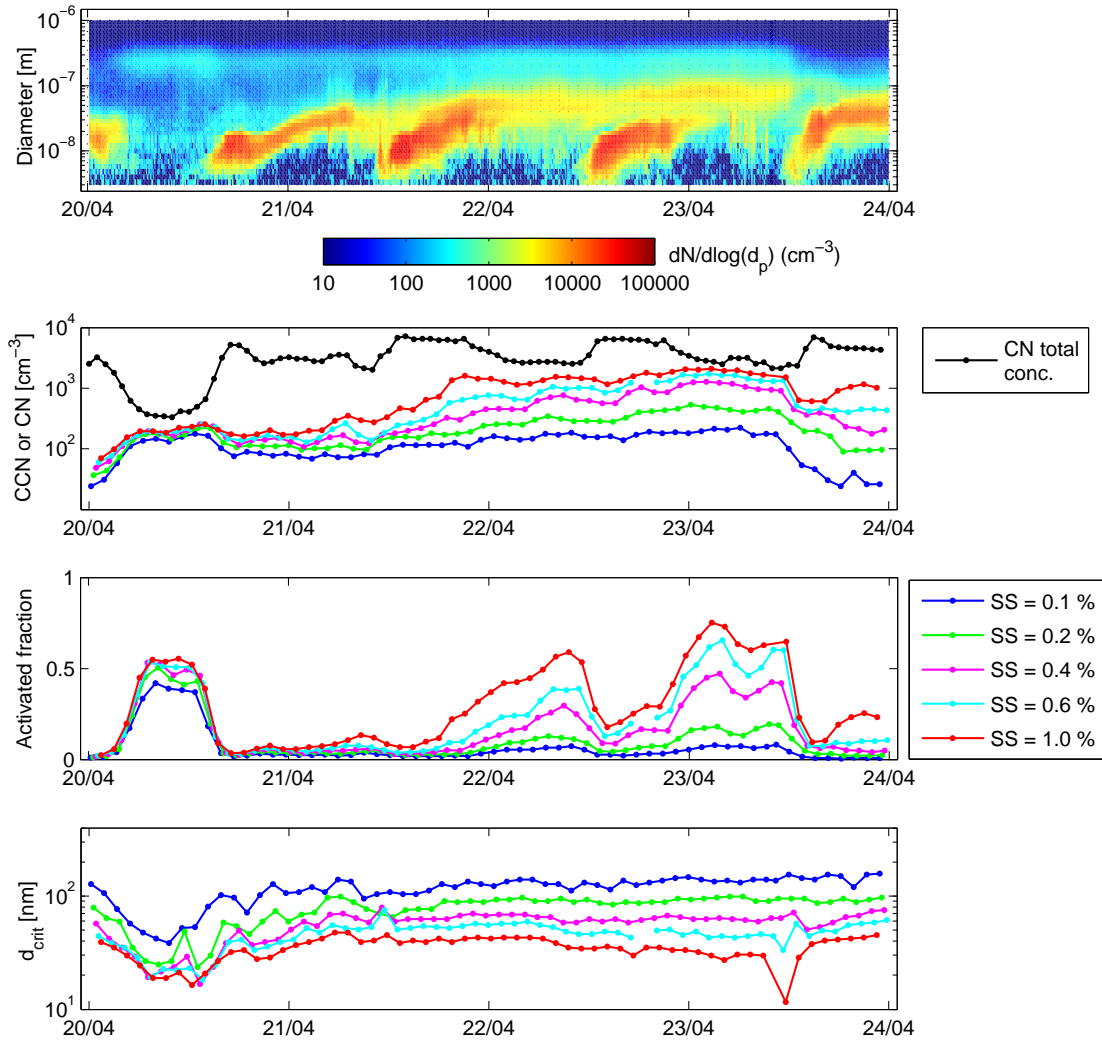


Figure 20: Comparison of the particle size distribution data and cloud condensation nuclei (CCN) data for a period with four consecutive new particle formation days in Hyytiälä (20.4.-23.4.2009). (a) The time evolution of particle size distributions, (b) CCN and total particle (CN) concentrations, (c) the activated fraction (CCN/CN), and (d) the critical diameter estimated from CCN and particle size distribution measurements.

Elevated CCN concentrations due to new particle formation events have been reported also in other studies (Lihavainen et al., 2003; Kuwata et al., 2008; Wiedensohler et al., 2009; Asmi et al., 2011).

The study of **paper VI** was based on analysing ground-based measurements. It must be noted, that the link between organic aerosols formed in the atmospheric boundary layer and clouds formed in the upper part of the troposphere is not straightforward. To really influence cloud formation, aerosols should travel from the forest up to the height of 1–2 km. Airborne measurements are needed to find out whether the CCN inside tropospheric clouds originate from the boundary layer, or are formed by in-situ nucleation in the upper troposphere.

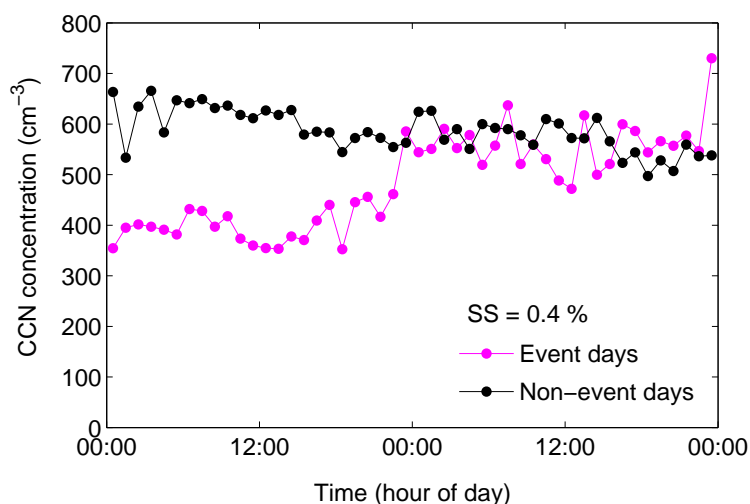


Figure 21: Mean diurnal variation of CCN concentrations on two consecutive days, compared between new particle formation event and non-event days at supersaturation $SS = 0.4 \%$ (data points are averages over 1 year data from the Hyytiälä SMEAR II station).

6 Review of papers and the author's contribution

Paper I investigates the correlation of sulphuric acid and new particle formation by analysing field data measured during the QUEST II campaign in Hyytiälä, at the SMEAR II station. The paper reports day-specific values for empirical activation and kinetic nucleation coefficients for the first time. I made all the data analysis and was responsible for writing the main parts of the article.

Paper II continues to study the correlation between sulphuric acid and new particle formation utilizing data sets from the QUEST III and IV campaigns from Heidelberg (Germany) and Hyytiälä (Finland). The methods for correlation analysis were developed further in this paper. The values for activation and kinetic coefficients in these data sets were determined. I made half of the data analysis and participated in writing the article.

Paper III studies the effect of relative humidity on atmospheric particle formation by combining data analysis and aerosol dynamical modelling. Utilizing the QUEST II data set, the paper presents an anticorrelation of sulphuric acid concentration and particle formation rate with relative humidity. Aerosol dynamical modelling is used to investigate the reasons for the observed anticorrelation, concluding that relative humidity suppresses nucleation due to decreased production of sulphuric acid. I participated in the data analysis and assisted in finalizing the manuscript.

Paper IV examines factors affecting the correlation of sulphuric acid and particle formation rate with the aid of aerosol dynamical modelling. Especially, the effect of the nucleation mechanism and condensational growth on the observed correlation at 3 nm are investigated. The paper demonstrates that the correlation with sulphuric acid can change significantly during the particle growth from nucleation size to 3 nm. I made most of the simulation runs and data processing, and was responsible for writing the article.

Paper V investigates the methods used to calculate particle formation rates from the time evolution of the particle size distribution. The study is based on the analysis of a simulated particle formation event. The paper compares different particle formation rate calculation methods and gives a recommendation of the most appropriate one. I participated in planning the paper, gave ideas for the data analysis and assisted in writing the manuscript.

Paper VI presents an analysis of one-year measurements of cloud condensation nuclei (CCN) concentrations at the SMEAR II station, combined with the hygroscopicity measurements. The critical diameters for CCN activation and the hygroscopicity parameter κ were derived from the data. The seasonal variation of CCN concentrations and critical diameters were investigated, as well as the effect of new particle formation on them. I made most of the analysis related to CCN concentration measurements and was the main author of the paper. The hygroscopicity data was analysed by other co-authors.

7 Summary and conclusions

Particle formation from gaseous precursors is a major source of new particles in the atmosphere. Due to their ability to scatter solar radiation and influence cloud formation, aerosol particles cause a net cooling effect on the Earth's climate, thus partly counteracting the climate warming caused by greenhouse gases. The understanding of atmospheric aerosol formation, their growth to climatically relevant sizes and role in cloud formation is crucial for reliable modelling of the climate system.

Atmospheric new particle formation or nucleation is a complex phenomenon to be handled both experimentally and theoretically. Sulphuric acid (together with water vapour) is assumed to be one of the key compounds in atmospheric nucleation, but the exact nucleation mechanism and the identity of other nucleating compounds, such as ammonia, amines or some oxygenated organic compounds, are still unknown.

At the start of the research made in this thesis, aerosol instrumentation was limited to measure only particles larger than 3 nm in diameter. This detection limit prevented researchers from performing direct measurements of atmospheric nucleation. One aim of examining the correlation of particle formation with sulphuric acid, the assumed main nucleating substance, was to obtain indirect information on the processes below the detection limit: for example, from the time shift analysis the growth rate of particles < 3 nm could be estimated. The gap between 3 nm and the nucleation size at 1–1.5 nm was crossed using theoretical methods to account for particle losses in between those sizes.

The main part of the research performed in this thesis was devoted to the investigation of the correlation of new particle formation with the sulphuric acid concentration (**papers I–IV**). The number concentration of freshly nucleated particles (3–6 nm in diameter) as well as the new particle formation rate were observed to correlate with the sulphuric acid concentration to the power of 1–2. Based on this correlation, new semi-empirical parameterisations for the atmospheric nucleation rate were developed: *activation nucleation* with a linear dependence and *kinetic nucleation* with a squared dependence on the sulphuric acid concentration. The values of the proportionality coefficients for these nucleation mechanisms, activation coefficient A and kinetic coefficient K , were determined for three data sets from two different environments in Finland and Germany. The determination of the empirical A and K coefficients can be considered as the most valuable result of this thesis. The developed parameterisations, especially the activation type nucleation, have been used widely by other researchers in aerosol dynamical and climate models.

The large variations in both A and K (two and three orders of magnitude, respectively), even at the same measurement site, suggest that there are other important factors affecting the nucleation process in addition to sulphuric acid. The parameterisations have been further developed by Paasonen et al. (2010) to include the possible effect of organic vapours. However, the exact physical and chemical details hidden in the empirical A and K coefficients remain still unknown. More research, especially in-situ measurements of the chemical composition of nucleated clusters, is needed to

explain the large variation of nucleation coefficients and to develop more accurate parameterisations for nucleation.

The connection between particle formation and sulphuric acid concentration was further investigated by means of aerosol dynamical modelling, applying the activation and kinetic nucleation mechanisms (**paper IV**). It was found that the correlation exponent with sulphuric acid concentration was different for the formation rate of 1.5 nm particles ($J_{1.5}$ i.e. the nucleation rate), for the formation rate of 3 nm particles (J_3), and for the number concentration of 3–6 particles (N_{3-6}). When going from $J_{1.5}$ to J_3 and N_{3-6} , the value of the correlation exponent could increase by 1–3 units, the change depending on the particle growth rate and especially its profile as a function of particle size. In order to obtain close to linear dependence for N_{3-6} , activation nucleation and a negligible saturation concentration for the condensable organics were required, i.e. the growth rate of freshly nucleated particles needed to be high.

Atmospheric new particle formation happens preferably in conditions with low relative humidity, which has been explained mainly by high condensation and coagulation sinks due to water uptake by particles at high humidities. This thesis produced a new possible hypothesis for the effect of relative humidity on new particle formation (**paper III**). The particle formation rate seems to be limited by decreased production of sulphuric acid at high relative humidities, due to decreased solar radiation reaching the ground at humid conditions (where clouds may be present). However, a clear causal relationship between the decreased solar radiation and relative humidity could not be proven, because these variables have opposite diurnal profiles, thereby creating an apparent anticorrelation between them. Aerosol dynamical modelling revealed that, in comparison to the reduced sulphuric acid effect, the previously suggested effects of increased condensation and coagulation sinks have a smaller contribution in inhibiting nucleation at high humidities.

With regard to research methods, in this thesis the methods for analysing the correlation of particle formation rate with sulphuric acid were developed (**papers I, II and IV**). Additionally, the accuracy of the conventional method to estimate particle formation rate from the particle size distribution data was evaluated and a new, slightly improved method for J_3 calculation was proposed (**paper V**).

The importance of aerosols in the climate system is primarily associated with their ability to act as cloud condensation nuclei. The potential of boreal forest aerosols to act as cloud condensation nuclei was studied based on 1 year of CCN concentration measurements and hygroscopicity measurements at ground level at the SMEAR II station (**paper VI**). The CCN concentration was found to have a seasonal variation with highest concentrations in summertime, when also the particle growth rates caused by biogenic organic vapours are the highest. New particle formation events were observed to almost double the CCN concentrations on the day following the event. Estimates for the critical diameter of cloud droplet activation and for the hygroscopicity parameter κ were determined. The values corresponded to a mixture of mainly organic aerosol, with a small fraction of inorganic sulfates, as expected in the boreal forest environment. The determined κ -values can be applied in modelling the CCN-activation of boreal forest

aerosols in climate models.

By the time this thesis was finalized, in summer-autumn 2013, huge advances in aerosol measurement technology have been achieved. Several new developed instruments — such as AIS, NAIS, PHA-CPC, PSM — have gone below the 3 nm limit, and opened up the world of aerosol science directly down to the nucleation size at 1–2 nm. This has increased our understanding of the complicated processes related to atmospheric new particle formation. Mass spectrometric techniques and the particle size magnifier (PSM) are closing the gap between molecular clusters ($\lesssim 1$ nm) and aerosol particles (> 2 –3 nm): in laboratory conditions the growth of nucleated clusters can be followed molecule by molecule (Kirkby et al., 2011; Almeida et al., 2013). Still, many things remain to be investigated, e.g.: What is the role of other substances than sulphuric acid (amines, various organic molecules/vapours) in nucleation and early growth of nucleated clusters? What is the molecular structure of nucleated and pre-nucleation clusters? In the observed cluster pool, are there different kinds of clusters, and which of them start to grow further? In the atmosphere, the variety of compounds (especially of organic compounds) is so huge, that there is certainly work also for the next generations.

Measurement data both from field and laboratory are needed to get real information on the quantities and processes under study. In atmospheric data — all processes happening under one common sun — there are many correlations, but fewer, and often complex causal relationships between the variables. Careful data-analysis and modelling can give insights on how the measurement data can be interpreted: what is the importance of a certain possible reason behind an observed phenomenon, and what can be concluded based on the data.

As an end product, research will provide useful tools, for example in the form of nucleation rate parameterisations. These can be applied in regional aerosol and global climate models, for making predictions of the future and suggestions for the actions needed to prevent climate change or to improve air quality — for the good of society and mankind.

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