STUDIES OF HYGROSCOPIC PROPERTIES OF NUCLEATION MODE AEROSOL PARTICLES

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Academic dissertation

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in the D101 auditorium, Gustav Hällstömin katu 2 on March 6th, 2002, at 12 o'clock noon.

Helsinki 2002

Acknowledgements

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Abstract

During the recent years new particle formation events have been observed in several locations ranging from rural and remote sites to urban environments. The behaviour and fate of the atmospheric nucleation mode aerosol particles are largely dictated by their composition. The small mass of the nucleated particles makes a chemical analysis extremely difficult. The sampling times have to be long and thus important temporal information might be lost.

The hygroscopic properties of particles are composition specific. This fact has been utilised in the Ultrafine Tandem Differential Mobility Analyser (UFTDMA) measurements, with which an indication of the particle composition can be gained with a reasonably high time resolution, in just few minutes. The principle idea of the UFTDMA is to study changes in particle size: first particles of certain size are selected, and further the effect of humidification on the size of these particles is studied.

This thesis introduces some of the observations of the atmospheric nucleation events, and aims to describe the functionality and benefits of the UFTDMA measurements of the nucleation mode particles. Also selected results of field measurements are presented.

The field measurements with the UFTDMA, in general, first of all proved that nucleation mode particles are present in large enough concentrations to be detected with this kind of instrumentation. Secondly, all of the measurement campaigns revealed temporal variations in the hygroscopic properties of the nucleation mode particles, thus stressing the importance of measurement systems with high time resolution. Thirdly, these measurements showed that also the nucleation mode particles, even in the remote areas, are occasionally externally mixed. It was further shown that the nucleation mode particles can be characterised with four hygroscopicity classes: non-hygroscopic (growth factor = 1), less-hygroscopic (gf = 1.05-1.2), more hygroscopic (gf = 1.2-1.4), and sea salt (gf > 1.4).

Keywords: Hygroscopicity, aerosol particles, nucleation mode, UFTDMA, growth factor

Contents

List of Publications

This thesis consists of an introductory review part, followed by five research articles. Papers are reproduced with the kind permission of the journals concerned.

I Kaarle Hämeri, Minna Väkevä, Hans-Christen Hansson, and Ari Laaksonen (2000). Hygroscopic growth of ultrafine ammonium sulphate aerosol measured using an ultrafine tandem differential mobility analyzer. *J. Geophys. Res.*, 105, 22231-22242.

II Minna Väkevä, Kaarle Hämeri, Timo Puhakka, E. Douglas Nilsson, Harri Hohti, and Jyrki M. Mäkelä (2000). Effects of meteorological processes on aerosol particle size distribution in an urban background area, *J. Geophys. Res.*, 105, 9807-9821.

III Kaarle Hämeri, Minna Väkevä, Pasi Aalto, Markku Kulmala, Erik Swietlicki, Jingchuan Zhou, Winfried Seidl, Edo Becker, and Colin D. O'Dowd (2001). Hygroscopic and CCN properties of aerosol particles in boreal forest. *Tellus*, 53B, 359-379.

IV Minna Väkevä, Kaarle Hämeri, and Pasi Aalto (2002). Hygroscopic properties of nucleation mode and Aitken mode particles during and outside nucleation bursts in west coast of Ireland, *J. Geophys. Res.*, in print.

V Minna Väkevä, Markku Kulmala, Frank Stratmann, and Kaarle Hämeri (2002). Field measurements of hygroscopic properties and state of mixing of nucleation mode particles. *Atmospheric Chemistry and Physics Discussions*, 1, 379-409.

www.atmos-chem-phys.org/acpd/1/379/

1 Introduction

Atmospheric aerosol particles have a considerable effect on earth's radiation balance, directly by reflecting, absorbing, and emitting electromagnetic radiation, and indirectly via their effect on clouds. Hence they obviously affect our climate. Further, aerosol particles have an observable impact on the everyday lives of all of us: airborne particles affect air quality and visibility, deposition of acidic and other corrosive particles deteriorates buildings and statues, and causes acidification of surface waters and forests [See e.g. Twomey 1991; Seinfeld and Pandis, 1998]. One noteworthy thing, that still puzzles researchers, is the effect of aerosol particles on human health. Particles are undeniably a health hazard, but what is actually their most dangerous property: Total number of particles? The size of the particles? Their composition? Or do all the mentioned aspects together dictate the seriousness of exposure? [See e.g. Seinfeld 1975; Dockery and Pope, 1994]

The number and composition of atmospheric aerosol particles vary in time and location. Particles are observed in sizes ranging from a few nanometers to up to 100 microns. The size of particles affects their life time and their physical and chemical properties. Usually atmospheric particles are characterised with four size modes. Particles smaller than few tens of nanometers are often referred to as nucleation mode particles. These particles are formed through gas-to-particle conversion, and consequently grow by condensation and coagulation into Aitken (about 20–100 nm) and further into Accumulation mode particles (100 nm - 1 μm). Particles larger than 1 μm are usually referred to as the coarse mode. These particles are mostly formed mechanically through e.g. soil erosion, bubble burst, volcano eruptions and human activities. Residence times of particles within the troposphere vary from a few days in the boundary layer to several weeks in the free troposphere [Seinfeld and Pandis, 1998].

During the recent years especially the nucleation mode particles have received a growing amount of attention. New particle formation events have been observed in several locations ranging from rural and remote sites to urban environments. The events have been detected to take place at the sea level, several tens of meters above ground, and numerous observations have been made while conducting aircraft measurements at the free troposphere [see e.g. Kulmala *et al*. 2001b; O'Dowd *et al*. 2002b; Weber *et al.* 1997; and Shröder and Ström, 1997].

The behaviour and fate of atmospheric nucleation mode particles is largely dictated by their composition. There is, however, no straightforward way to define what these particles consist of. The small mass of the particles makes a chemical analysis extremely difficult. Sampling times have to be long and thus important temporal information might be lost. Also, the gas phase species disturb the aerosol particle sampling. For example Viidanoja et al. [2002] demonstrate this with impactor studies. They used two impactors of which one was ran with sample air from which all particles had been removed. Analysis of the impactor plates revealed a noteworthy amount of organic carbon collected with the "particle free" impactor.

There are a few studies in which charged nucleation mode particles have been sampled on grids and new information has been gained [see e.g. Mäkelä *et al.*, 2002]. These studies are however time consuming and only give information of individual particles that might have been present any time during the sampling period.

Hygroscopic properties of particles, i.e. the way they uptake water, are composition specific. This fact has been utilised in the hygroscopic Tandem Differential Mobility Analyser (TDMA) measurements, with which an indication of particle composition can be gained with a reasonably high time resolution, in just few minutes. The principle idea of a TDMA is to study changes in particle size: first particles of a certain size are selected, and then the effect of humidification on the size of these particles is studied [see e.g. Rader and McMurry, 1986]. The TDMA has been used in several field campaigns to study atmospheric Aitken and accumulation mode particles [e.g. Svenningsson *et al.* 1992; McMurry *et al.* 1996; Swietlicki *et al.* 1999], but only during the last few years has the technique been utilised also in the determination of the properties of nucleation mode particles [Papers in this thesis, Zhou 2001]. In addition to the indirect information about particle composition, also valuable knowledge is gained about the dynamics of ambient particles. The results of TDMA measurements can be used in several different models that include chemistry and physics involving nucleation mode particles.

The aim of this work was to study hygroscopic properties of nucleation mode particles with a focus on a) the development of the Ultrafine TDMA (UFTDMA) system, b) evaluation of the system by performing laboratory and field measurements, and c) conducting field measurements of ambient nucleation mode particles in different environments.

This thesis consists of the following parts: In Chapter 2 some selected observations of nucleation mode aerosol particles are discussed. The focus of Chapter 3 is on introducing the UFTDMA system through highlighting features specific for studies of nucleation mode

particles, and Chapter 4 gives a short summary of observations during field measurements performed with the instrument.

2 Observations of new particle formation

Several researchers have reported observations of atmospheric nucleation mode aerosol particles. These studies together with theoretical ones have brought up some possible triggering or controlling factors of nucleation: low concentration of pre-existing aerosol particles, solar radiation, low temperature, changes in the structure of the boundary layer, just to mention some.

Wiedensohler et al. [1994] compared four measurement techniques used to study the size distribution of ultrafine particles. They concluded that provided the number concentration is large enough (~100 cm^{-3}), a Differential Mobility Particle Sizer (DMPS) gives the best size distribution data. The DMPS system basically consists of a Differential Mobility Analyser (DMA) to select a narrow fraction of an ambient aerosol and a Condensation Particle Counter (CPC). On the other hand, the best indication about the presence of nucleation mode particles was gained using a pulse height CPC. The other two studied instruments were a diffusion battery specially constructed for studies of ultrafine particles and a CPC with varying condenser temperature (the condenser temperature directly influences the cut size of the instrument). All the field measurements discussed in this thesis, have been conducted using either a DMPS system or systems consisting of one or several CPCs.

Nucleation has been proven to take place in the free troposphere, where temperatures are low as is the number of pre-existing aerosol particles, and thus the surface area for condensation. However, Schröder and Ström [1997] state based on their aircraft measurements that the production process does not necessarily require low values of pre-existing aerosol surface area.

Raes *et al.* [1997] measured size distributions of ultrafine aerosol particles on Tenerife, Canary Islands. They used two measurement sites, one located in the free troposphere (2367 m asl), the other in marine boundary layer. At the free troposheric site a strong daytime mode of ultrafine particles was observed, interpreted as being a result of photo-induced nucleation in up-slope winds, which were perturbed by anthropogenic and biogenic emissions on the island. No nucleation bursts were observed within the marine boundary layer. However, other researchers have found evidence of marine boundary layer nucleation events, see for e.g. Hoppel *et al.* [1994] or O'Dowd *et al.* [1998, 1999, 2002a and b].

Aalto *et al*. [2001] performed an extensive study of characteristics (e.g. number concentration and size distribution, vertical profiles etc.) of nucleation mode particles in a boreal forest [see also Mäkelä *et al,* 1997, and Kulmala *et al.* 2001a and 2001b]. They studied aerosol particles from 3 nm up to 20 microns in diameter, and showed evidence that the particles formed in the morning or early afternoon grew up to accumulation sizes during the course of a day, and that the particles continued to grow during the following day. Their studies, just as the previously mentioned study in Tenerife, showed that nucleation required photochemistry: events usually happened during sunny days and the presence of clouds seemed to suppress the particle production efficiently. They also saw that during the formation episodes the concentration of ultrafine particles increased above the canopy earlier than within the forest, which could be an indication about the importance of the changes of the structure of boundary layer to the nucleation event [see also Nilsson *et al.*, 2001a and 2001b]. Furthermore, it was found that during the event days the surface area and volume of pre-existing particles were lower than average, suggesting that in the forest environment particle surface area could be one of the triggering factors for nucleation.

In Paper II of this thesis the observations of new particle formation in an urban background area in Southern Finland are presented. A comparison to other simultaneous measurements [Mäkelä *et al*., 1998] revealed that new particle formation took place also in downtown Helsinki and at a forest site that are some 200 km apart from each other. This led to the assumption that these nucleation events were synoptic or meso scale phenomena. And once again the detected event at the urban site seems to question the crucial importance of a low surface area of pre-existing particles.

It has been shown that meteorological conditions play a major role in atmospheric new particle formation, but what are the actual chemical species taking part in the process? Several researchers have theoretically shown possible nucleation paths, but field evidence supporting any particular path is still missing. For example Korhonen *et al.* [1999] have shown that ternary nucleation involving water-H_2SO_4 and NH_3 is one likely particle formation mechanism. In several field studies, however, even though this could have been the path originally triggering the formation of particles, still the concentrations of measured vapours have not been large enough to further grow the particles to detectable sizes [Kulmala *et al.*, 2001a and b]. Thus a question remains – what is then the vapour responsible for the particle growth?

O'Dowd *et al.* [1998, 1999, 2002a, 2000b] have measured and modelled new particle formation in a coastal environment in Ireland. They state that a species, X, is emitted during low tide, and

this compound X is the vapour involved in nucleating and, or just, in growing the particles to detectable sizes. What this compound is, remains unknown. As opposed to the previously mentioned measurements in the rural area of Finland, the observed nucleation events in the clean marine air at the coastal site showed abrupt appearance and sudden disappearance of the newly formed particles. During several of the events the mode of the nucleated particles did not significantly increase in size. What is noteworthy, is that during the reported campaigns [O'Dowd and Hämeri, 2000; O'Dowd *et al.*, 2002a and b], at the coastal site in question, particle formation also happened (though rarely) at times when solar radiation was very low. Despite these few incidents solar radiation was named to be one of the crucial factors for nucleation at the site.

In many of the above mentioned cases investigation of the composition of the newly formed particles (~1 nm in diameter) would be the only certain way of finding out what are the processes forming (nucleating) the particles. But due to the small size and mass of the particles such measurements are extremely difficult.

3   UFTDMA

To understand the formation mechanisms and dynamics of nucleation mode aerosol particles, some information about their composition is needed. Due to the small mass and often very low concentration of these particles, the investigation of their chemical composition is very difficult. A Hygroscopic Tandem Differential Mobility Analyser (HTDMA) has been successfully used by several researchers to study the properties of sub-micron aerosol particles, both laboratory generated and ambient (see e.g. Svenningsson *et al.* 1992; McMurry *et al.* 1996; Swietlicki *et al.* 1999; and Virkkula *et al.* 1999). Selected results of ambient HTDMA measurements are presented on page 15. The most often used TDMA systems are not, however, ideal for the measurement of nucleation mode particles. Thus an ultrafine TDMA has been developed [Paper I].

3.1   Instrument

The HTDMA is used to detect changes in aerosol particle size when taken from a dry state to a controlled humidified state [see e.g. Rader and McMurry, 1986]. It consists of the following main parts: a) a DMA to select a narrow size fraction of a polydisperse aerosol particle population, b) a conditioner in which the selected particles are humidified in a well defined

relative humidity, and c) an another DMA followed by a condensation particle counter to detect changes in the size of the humidified particles.

Ambient concentrations of ultrafine particles are often low, and, furthermore, only a small fraction of nucleation mode particles is charged. For example, only 5% of 10 nm (in diameter) are negatively charged (single charged) in equilibrium. The TDMA measurements are based on the detection of charged particles, and since the fraction of negatively charged particles of a given size exceeds that of positively charged particles [Wiedensohler and Fissan, 1991] a positive voltage was used on the center rod of the DMAs of the UFTDMA.

To further make sure that as many as possible of the particles leaving DMA1 are detected, the following conditions were fulfilled:

1) All aerosol lines inside the instrument were constructed as short as possible.

2) The aerosol sample was humidified prior to entering DMA2 in a "diffusion" humidifier, i.e. the sample air passed through a short (< 3 cm) micro porous (GoreTex[®]) tube which was in a water bath. The tube let through only water vapour keeping liquid water outside.

3) Short (center rod length 11 cm) Vienna type DMAs were used with 1:10 aerosol (1 lpm) to sheath flow (10 lpm) ratio in order to minimise particle losses inside the DMA. A high sheath air flow rate reduces the diffusional broadening during the passage of the particles through the DMA [Stoltzenburg, 1988] and thus affects the penetration of particles.

4) A CPC 3010 (TSI, Inc.) was used as the particle counting instrument. The model 3010 was selected rather than the model 3025, which otherwise is capable of detecting smaller particles, to avoid the effect of dilution of sample aerosol. That way one can ensure the highest possible sensitivity in concentration measurements. The cut size of 3010 was brought down to 7-8 nm by increasing the temperature difference between the CPC saturator and the condenser to 25°C.

Since the studied particles were small, also changes in the particle size were expected to be small and thus a high sensitivity was required also for the detection of size. This was gained using the previously mentioned short Vienna type DMA, a dense measurement grid (voltage steps) and by making sure that the flows of the system were stable and accurate. The maintenance of the instrument is discussed further in Chapter 4.3.

3.2 Data analysis

The result of a TDMA measurement is usually described with a growth factor, *GF*

$$GF = Diameter\ at\ increased\ relative\ humidity\ /\ Diameter\ at\ dry\ air \qquad (1)$$

The data presented in this study have been analysed using two different techniques

a) A sophisticated data inversion procedure developed by Strattman and co-workers [e.g. Stratmann et al, 1997, Yuskiewicz et al, 1998]. The data inversion procedure is needed, to determine the mobility distribution in front of DMA2. From this mobility distribution, the changes in particle mobility and consequently the growth factors can be determined [Paper V].

b) A simplified but also a less accurate procedure (described in Paper V).

The more sophisticated algorithm was only used for randomly selected spectra to make sure that the simple approach was trustworthy within the error limits of the measurement system. This approach was taken to decrease the time needed for data analysis.

The uncertainty in the growth factors measured with an UF-TDMA is less than 5% for the particle sizes discussed in this work. The uncertainty consists of errors caused by the measurement system itself and by the data analysis [Paper I].

The overall detection efficiency of the system is determined by the detection efficiency of the CPC and the diffusion losses inside the system. The highest uncertainty stems from the stability and determination of the relative humidity. Already small changes in the temperature or flows inside the system might cause substantial errors in relative humidities and further lead to miss-interpreted data. Also the detection of the dry size used to calculate the growth factors is one factor possibly causing uncertainties.

3.3 Theoretical aspects and laboratory measurements of the hygroscopic properties of nucleation mode sized particles

At low relative humidities atmospheric aerosol particles containing inorganic salts are solid. When humidity increases over a threshold value, known as the deliquescence relative humidity, that is characteristic for the aerosol composition, the particles spontaneously absorb water, producing a saturated aqueous solution droplet. At the deliquescence relative humidity the humidity of the surrounding air is equal to the water activity of the saturated solution. A further

increase of relative humidity leads to additional water condensation onto the droplet to maintain thermodynamic equilibrium [see e.g. Tang, 2000].

Also compounds other than inorganic salts absorb water, and some species do not exhibit deliquescence: e.g. the water content of H_2SO_4 droplets changes smoothly as the relative humidity increases [see e.g. Seinfeld and Pandis, 1998; Tang, 2000], this is also true for several water soluble organic salts [Peng and Chan, 2001].

Relative humidity (RH) at a given temperature is $\frac{p_w}{p_{ws}} * 100$ i.e. the ratio of water vapour pressure (p_w) to the saturation vapour pressure (p_{ws}). The equilibrium between water vapour and an aqueous droplet at a given relative humidity can be expressed with

$$\frac{RH}{100} = a_w \exp(\frac{4\sigma v_w}{RTd}),\qquad(2)$$

where a_w is the activity of water in a salt solution (which describes the reduction of water vapour pressure due to dissolved material.), σ is the surface tension, v_w is the partial molar volume of water in the solution, R is the gas constant, T is the temperature, and d is the diameter of the particle [see e.g. Hämeri et $al.$, 2001]. The exponential part of the equation is due to the curvature of the droplet surface, which is discussed further in section 3.3.1.

The growth factor (GF), described in (1), defines the ratio with which a particle of a known composition and dry size will grow at the prevailing relative humidity. This quantity can be measured with the UFTDA. For completely soluble particles the growth factor can be expressed as [Swietlicki et $al.$, 1999]

$$GF = \frac{\rho_s}{\rho_{sol}} \left[1 + \frac{1}{mM_s} \right]^{\frac{1}{3}},\qquad(3)$$

where ρ_s is the density of the dry salt particle, ρ_{sol} is the density of the solution droplet, m is the molality of the solution and M_s is the molar weight of the salt.

3.3.1   Kelvin effect and laboratory measurements of salt particles

In studies of hygroscopic properties of nucleation mode sized particles the Kelvin effect plays a major role. The Kelvin effect means that the vapour pressure over a curved surface always exceeds that of the same substance over a flat surface [see e.g. Seinfeld and Pandis, 1998]. That

is, the smaller the particle the larger the Kelvin effect, resulting in a lower relative growth in the same humidity conditions.

The theoretical expression for the Kelvin effect is usually referred to as the *Kelvin equation*

$$p_A = p_A^0 \exp(\frac{4\sigma v_w}{RTd}), \qquad (4)$$

where p_A^0 is the vapour pressure of pure species A over a flat surface, and p_A is the actual equilibrium vapour pressure over the liquid. Thus Kelvin effect depends on the droplet diameter, d, temperature, T, the surface tension, σ, and the partial molar volume of water in the solution, v_w.

The magnitude of the Kelvin effect for nucleation mode sized particles is often difficult to determine, since thermodynamical data on e.g. surface tensions is sparse.

In Table 1, the growth factors at 90% relative humidity of laboratory generated $(NH_4)_2SO_4$ and NaCl particles are shown to demonstrate the magnitude of the Kelvin effect. The particle sizes in the table are given as mobility diameters, as are all UFTDMA data presented in this work. The results of laboratory studies with the UFTDMA are presented in more detail in Paper I and in paper by Hämeri et al. (2001). The growth factors of 100 nm particles have been taken from the reports of work conducted by the university of Lund (Svenningsson 1997; Swietlicki *et al.* 2000).

Table 1. Growth factors of laboratory generated $(NH_4)_2SO_4$ and NaCl particles in 90% relative humidity.

Salt / diameter	8 nm	10 nm	15 nm	20 nm	50 nm	100 nm
$(NH_4)_2SO_4$	1.34	1.38		1.52	1.66	1.8
NaCl	1.72	1.78	1.92		2.2	2.4

Both $(NH_4)_2SO_4$ and NaCl are compounds that have been detected in ambient particles. NaCl is an interesting salt also since even though it is considered well known, and in many cases used as a reference aerosol, the structure of NaCl particles is not evident. This issue has been addressed for accumulation sized particles (~400 nm) by Weis and Ewing [1999]. An interesting observation about how the structure of nucleation mode sized particles affect their hygroscopic properties was made in UFTDMA laboratory studies with ultrafine NaCl particles generated

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with an evaporation and condensation technique. When particles of 14 nm in diameter were selected with DMA1 and humidified (< 50% RH), their size decreased to 10 nm. The decrease of the particle size is explained by a restructuring process that the particles undergo when in touch with water vapour. Most likely the initial particles are rather loose aggregates of very small primary crystals, and these aggregates collapse into more compact objects due to cohesion forces between adsorbed water molecules as the relative humidity is increased [Hämeri *et al.,* 2001; see also Krämer *et al.,* 2001]. When the relative humidity was further increased these particles behaved similarly to 10 nm particles generated using an atomiser.

3.3.2 Size dependent deliquescence and adsorption

Not only the magnitude of the growth but also the deliquescence relative humidity of ultrafine particles differs from larger particles (>100 nm). This aspect has been discussed and studied by Djikaev and colleagues [Djikaev *et al.* 2001]. The deliquescence of nucleation mode sized particles is more gradual than that of particles with diameter of 100 nm and above, for which the deliquescence happens very abruptly. This gradual start of hygroscopic growth can be seen in Figure 1, where growth curves for 10 nm $(NH_4)_2SO_4$, NaCl, and silver particles are plotted. The deliquescence relative humidity of micron sized particles of $(NH_4)_2SO_4$ is 80% and for NaCl 75% respectively [Tang and Munkelwitz, 1994; Tang 1980].

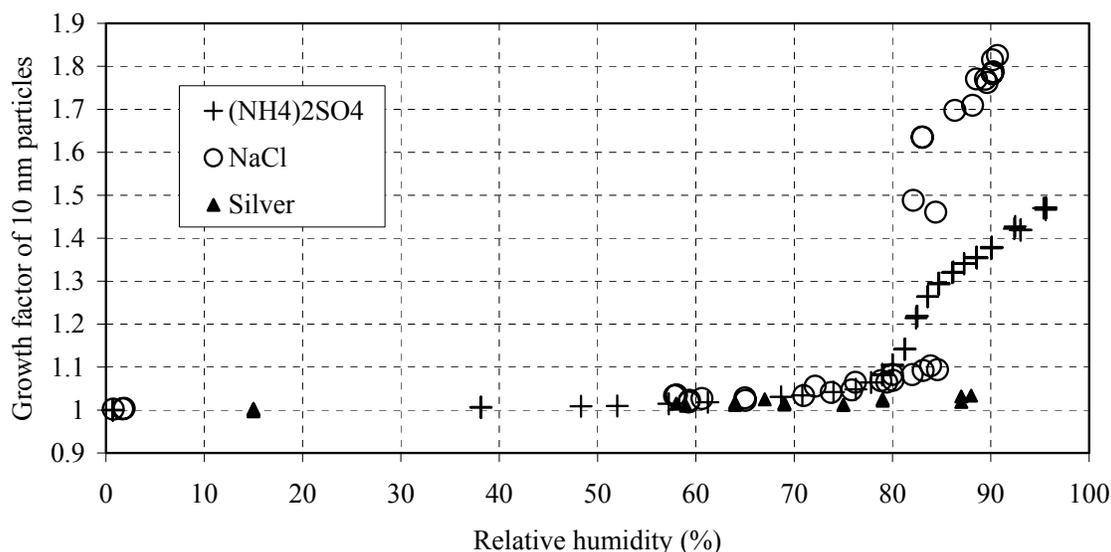**Figure 1.** Growth factors versus relative humidity of 10 nm $(NH_4)_2SO_4$, NaCl, and silver particles measured with the UFTDMA. The salt particles were generated using an atomiser and the silver particles with a furnace. Please note that the hysteresis behaviour of the salt particles is omitted from this plot.

As can be seen in Figure 1. also non-hygroscopic silver particles exhibit a response to an increasing humidity. This is explained by adsorption. The extent of adsorption is composition specific, and depends on the chemical properties and the structure of a particle surface (for more details see Paper I and Romakanniemi *et al.,* 2001).

In ambient UFTDMA measurements growth factors slightly exceeding than 1 are occasionally observed. Due to the previously mentioned reasons these observations are very difficult to interpret without further evidence about the composition of particles. Based only on UFTDMA data, this could be interpreted a) as adsorption, b) with a composition of some slightly hygroscopic material (that might actually be more clearly hygroscopic when larger particles would be studied), or c) with a growth caused by a small volume fraction of some soluble species within the particle.

4   UFTDMA field measurements

4.1   Hygroscopicity TDMA field observations

The hygroscopic properties of a particle influence its ability to act as a cloud condensation nucleus, its chemical reactivity, the way it scatters light, and its atmospheric lifetime [see e.g. Seinfeld and Pandis, 1998].

HTDMA systems have been used in several environments to study hygroscopic properties of particles, usually larger than 30 nm in dry mobility diameter. The observed ambient hygroscopic growth factors of submicron particles are often categorised into four groups [see e.g. Swietlicki *et al.* 2000 and Paper IV]:   **1)** Non-hygroscopic particles. These particles do not exhibit any growth when put to a humid environment, **2)** Less hygroscopic particles which grow when humidified, but not to the extent of common salts, **3)** More hygroscopic particles, and **4)** Sea salt particles.

Swietlicki *et al.* [1999] measured particles with diameters from 35 to 265 nm in Great Dun Fell, in northern England, and observed average growth factors of 1.11-1.15 for less hygroscopic particles, 1.38-1.69 for more hygroscopic particles and 2.08-2.21 for sea spray particles.

In several studies of continental aerosols two distinct growth modes have been observed. For example McMurry and Stoltzenburg [1989] measured 0.05-0.5 μm (at ambient relative humidity) particles in Los Angeles, and saw non-hygroscopic and less hygroscopic growth

modes. Svenningsson *et al.* [1992] found less hygroscopic and more hygroscopic growth modes in studies conducted in Po Valley (Italy) for 30-200 nm particles, as was also the case for 20-264 nm forest aerosol particles in Southern Finland [Paper III].

In the Arctic all the four growth categories have been detected. Zhou *et al.* [2001] observed less and more hygroscopic and also sea-salt growth modes for 35-65 nm particles. The more hygroscopic growth mode was, however, observed most frequently. Covert and Heintzenberg [1993] reported observations of mainly more hygroscopic Arctic particles, but also saw a growth mode with average growth factor 1.05 when there was a strong air mass transport from Europe.

Cocker e*t al.* [2001] measured hygroscopic properties of urban (Pasadena, CA) aerosol particles of 50 nm and 150 nm in dry diameter. They occasionally observed up to 6 simultaneous hygroscopic growth modes, i.e. one sampled dry size consisted of particles with six different compositions with respect to hygroscopic properties. Average growth factors at 89% relative humidity ranged between 1.0 and 1.6 for the two studied sizes.

Dick *et al.* [2000] studied the influence of organic carbon compounds on aerosol hygroscopicity. Their data from Great Smoky Mountain National Park, Tennessee, and also calculations suggest that organic compounds contribute to the amount of excess water in ambient aerosol particles. Their analysis of dry particle sizes in the range 0.05 to 0.4 μm showed that, on a volume basis, the organic-associated water content is considerably less than that of sulphate compounds at a high relative humidity, but comparable or greater at a low relative humidity. Also Saxena *et al.* [1995] studied the effect of organics on hygroscopic behaviour of aerosol particles. They analysed HTDMA and impactor observations from non-urban (Grand Canyon) and urban (Los Angeles) environments, and found that the organic fraction in freshly produced aerosol particles (urban) diminishes the hygroscopic growth, while in aged (nonurban) air masses organics add to the water absorption of inorganics.

In general, hygroscopicity studies of Aitken and accumulation mode aerosol particles indicate that in background marine air less hygroscopic particles are rarely observed and the growth factors of the more hygroscopic mode are higher than for many continental sites [see e.g. Svenningsson 1997]. Furthermore, the polluted sites usually have a larger fraction of less hygroscopic particles than the remote sites.

4.2 The UFTDMA measurement campaigns

UFTDMA measurements of 8-30 nm particles have, during the recent years, been performed by the University of Helsinki (partnered by the Institute of Applied Environmental Research, Sweden) in several different environments:

In 1996 the instrument was used as part of studies of Arctic air [Zhou *et al.* 2001].

In 1997 several field campaigns were undertaken. In spring urban background air was studied on a site close to Helsinki, Finland [Paper II] and forest air was studied at a measurement station in Hyytiälä, Finland, as a pre-study for the BIOFOR campaign (Biogenic Aerosol Formation in the Boreal Forest). During summer nucleation mode particles were studied in Tenerife as a part of ACE-2 (Southern Hemisphere Marine Aerosol Characterization Experiment). The ACE-2 UFTDMA measurements were performed at a mountain platform site 2360 meters above the sea level [Swietlicki *et al.* 2000].

In 1998 the actual BIOFOR campaigns started [Kulmala *et al.* 2001b; Kulmala and Hämeri, 2000], and measurements were performed over two periods in April-May and in September. Also the PARFORCE campaigns (New particle formation and fate in the coastal environment) started in September in Mace Head on the west coast of Ireland [O'Dowd and Hämeri, 2000; O'Dowd *et al.* 2002b].

In 1999 both BIOFOR [see Paper III] and PARFORCE [Paper IV] campaigns continued.

During all this time urban air was studied occasionally also in downtown Helsinki, i.e. air was sampled from the out side of the physics department (see e.g. Paper V).

4.3 Description of the measurement routines

During the field studies the performance of the instrument was regularly controlled. The flows of the measurement system were checked at least once a day using a bubble flow meter. The stability of the instrument was also checked by performing humid and dry calibrations. In the humid calibrations a calibration aerosol was used to gain a growth factor of a known salt at the relative humidity used for ambient measurements. During the dry calibrations both of the DMAs were run with dry sheath air and a calibration aerosol was used in order to make sure that the instrument settings were valid.

In all of the field campaigns discussed in this thesis $(NH_4)_2SO_4$ was used as the calibration aerosol. The calibration aerosol was produced using an atomiser. Humid calibrations were

performed at least once a day, and in many cases two to three times, since the calibration runs take only a few minutes. The dry calibrations were performed every one to two days. The drying of the system was also crucial for maintaining the high detection efficiency needed in the studies of nucleation mode particles. The cut size of a CPC rapidly falls if the butanol, used to grow the particles to optically detectable sizes, is considerably diluted by water (problems encountered when using CPCs in field campaigns have been addressed by Maring and Schwartze, 1994). Thus, in addition to the drying of the system, the butanol of the CPC was drained at least once a week. The losses of particles also increase and the humidity control is disturbed if any water condenses inside the tubing, which further increased the importance of regularly drying the system. The condensation of water in sheath air tubing could not be completely avoided in some of the measurement sites. For example, in Hyytiälä forest in 1998 the temperature inside the mobile laboratory varied from 17 to 30°C during the course of one day, thus setting extreme demands for the temperature controlling system of the instrument.

For most of the field campaigns a relative humidity of 90% was selected as the nominal humidity. This humidity is the highest possible with the current UFTDMA set up – a higher relative humidity causes almost unavoidably condensation to some part of the measurement system at field conditions. The relative humidity of the sheath air of DMA1 was kept well below 10% (usually below 5%). This was also the case for the DMA2 relative humidity when performing dry measurements.

4.4   Summary of UFTDMA observations

The field measurements with the UFTDMA first of all proved that nucleation mode sized particles are present in large enough concentrations to be detected with this kind of instrumentation.

Secondly, all of the measurement campaigns revealed temporal variations in the hygroscopic properties of nucleation mode particles (see Figures 2 and 3, and discussion later in Chapter 4.4.1), thus stressing the importance of having measurement systems with a high time resolution.

Thirdly, these measurements have shown that also nucleation mode particles even in remote areas occasionally are externally mixed. This means that the particle population contains particles of two or more different compositions.   Whether, for example in the coastal environment, the particles really were formed through different nucleation paths, or whether they are originally formed the same way but grown to detectable sizes by condensation of

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different vapours, can not be determined using UFTDMA data only. The BIOFOR campaign in spring 1999 was the only campaign with simultaneous hygroscopicity measurements of particles ranging from 10 to 264 nm in diameter. This measurement period revealed that at this particular site the fraction of externally mixed particles increased with increasing particle size; e.g. in 1999 the 10 nm particles were externally mixed in 4 %, the 20 nm particles in 25%, the 50 nm in 40% and the 109 nm in 83% of all observations [Paper III]. In many of the campaigns the air mass history seemed to have an effect on the state of mixing of the particles. In the coastal environment, externally mixed nucleation mode particles were observed in polluted air masses [Papers IV and V]. At the forest site in Finland, air masses originating from Europe or Great Britain often contained particles with two kinds of hygroscopic properties. On the other hand, the wintertime 10 and 20 nm particles in Helsinki were externally mixed no matter what the air mass history [Paper V].

The earlier mentioned growth categories can also be applied for UFTDMA results, given here are the relevant growth factors of 10 nm particles: **1)** Non-hygroscopic particles, GF = 1; **2)** Less hygroscopic particles, GF = 1.05-1.2; **3)** More hygroscopic particles, GF = 1.2-1.4; and **4)** Sea salt particles, GF > 1.4.

4.4.1 Nucleation event particles

The nucleation events detected at all of the measurement sites can be roughly characterised with two types of hygroscopic behaviour of nucleation mode particles: 1) an appearance and disappearance of low hygroscopicity particles, or 2) a gradual increase of the growth factors followed by a gradual decrease of hygroscopicity. At the coastal site in western Ireland, when the nucleation was observed in clean marine air with only one low-tide region in between the measurement site and the sea, nucleation mode particles that belonged to the "newly" born mode were non-or less-hygroscopic, i.e. showed very little growth in the UFTDMA (Figure 2). On the other hand, during a particle formation event at the forest site in Finland the growth factors of nucleation mode particles had a temporal pattern (Figures 3 and 4). The growth factors started to increase a few hours before noon, reached their maximum in the afternoon, and decreased again in early evening. It should be noted, though, that this kind of a pattern was occasionally seen also on days when nucleation was not detected.

Also, at the coastal site, the growth factors showed temporal variations similar to the forest measurements when air masses arrived to the site over several source regions and were possibly affected by other natural or anthropogenic sources (see Papers III-V for more details)
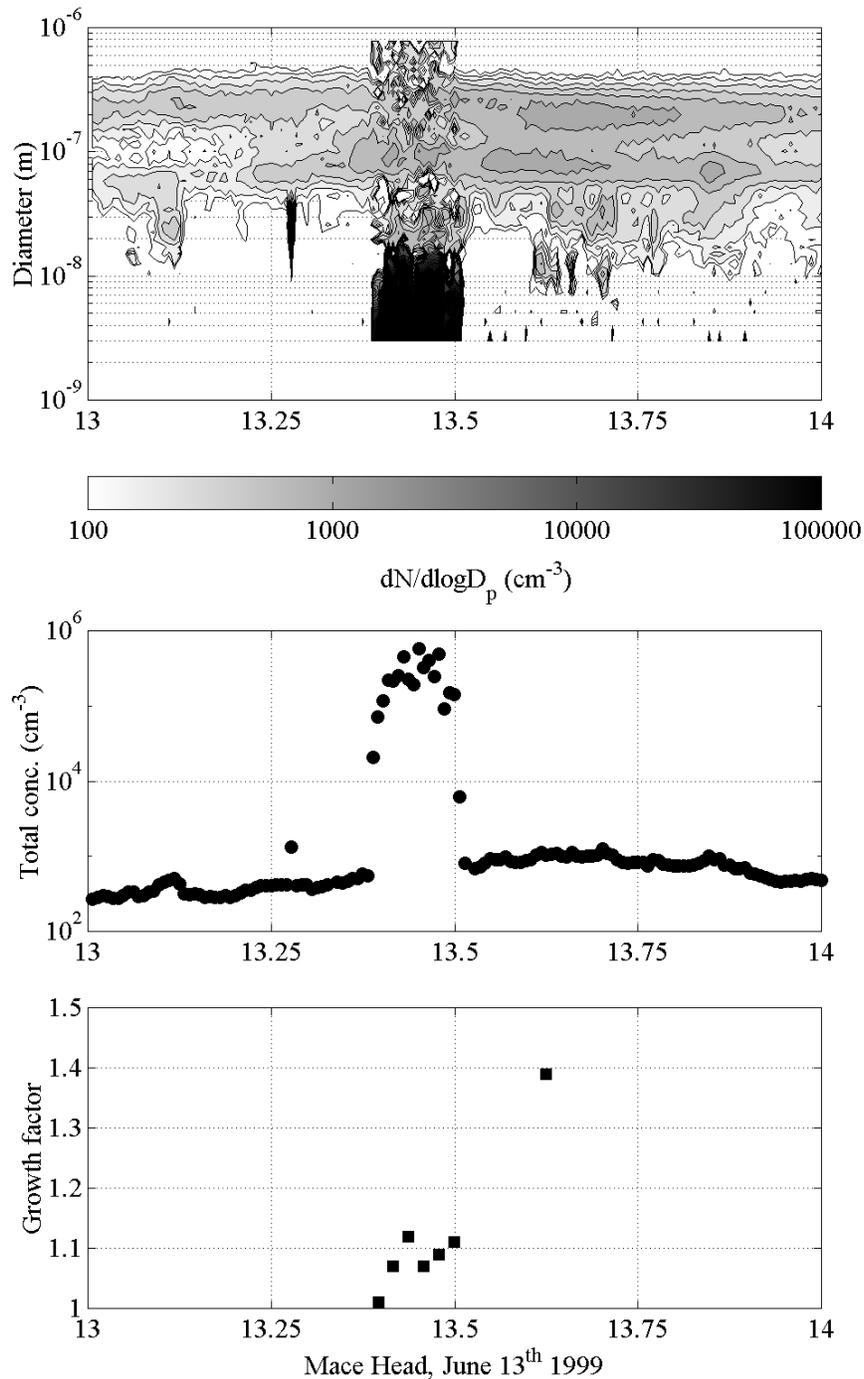
Figure 2. Nucleation event day in Mace Head Ireland – the coastal site. At the top a DMPS contour plot showing the number size distribution of submicron particles, below that the total number concentration (cm^{-3}) calculated using the DMPS data, and at the bottom the growth factors of 10 nm particles measured with the UFTDMA.
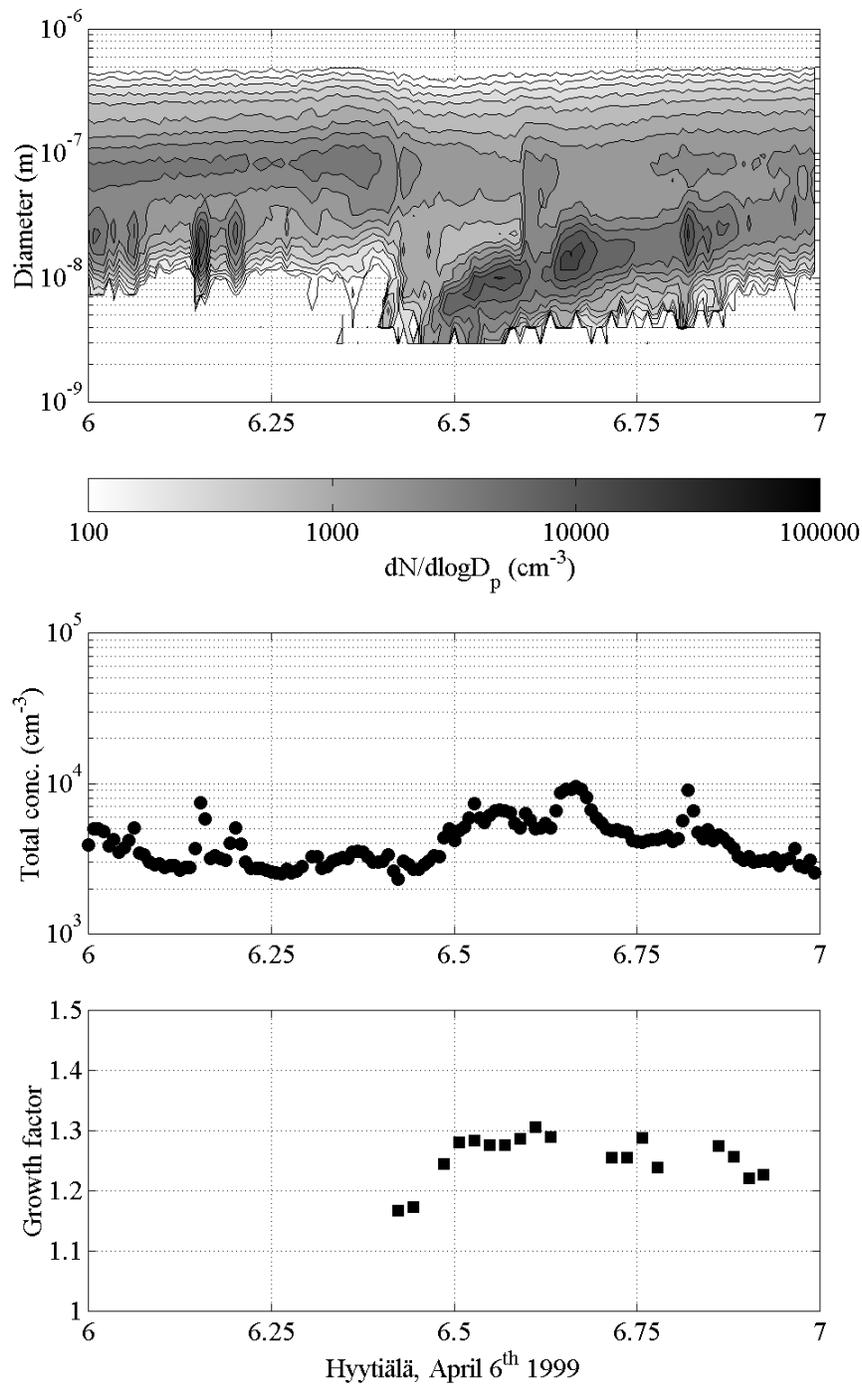
Figure 3. Nucleation event day in Hyytiälä Finland – the forest site. At the top a DMPS contour plot showing the number size distribution of submicron particles, below that the total number concentration calculated using the DMPS data (cm^{-3}), and at the bottom the growth factors of 10 nm particles measured with the UFTDMA.

4.4.2 Aitken mode particles vs. nucleation mode particles

In the above mentioned nucleation "types", differences were also seen between the hygroscopic properties of 10 nm or smaller particles and those of 20 nm particles. At the forest site, both sizes often were within the same mode (based on DMPS studies) and also the hygroscopic properties of both sizes resembled each other. An example day is presented in Figure 4. On the other hand, at the coastal site the 20 nm particles during and after the event periods clearly were of different composition than the nucleation mode particles, as can be seen in Figure 5. The background 10 nm particles were, however, often similar in hygroscopic properties as the 20 nm particles. Also, at the urban site in Helsinki, Finland, the wintertime measurements showed that 10 and 20 nm particles were very similar with respect to the hygroscopicity [Paper V]. These results show that, for instance, impactor data with the lowest cut size around 50 nm, should not be used to interpret composition of nucleation mode particles.

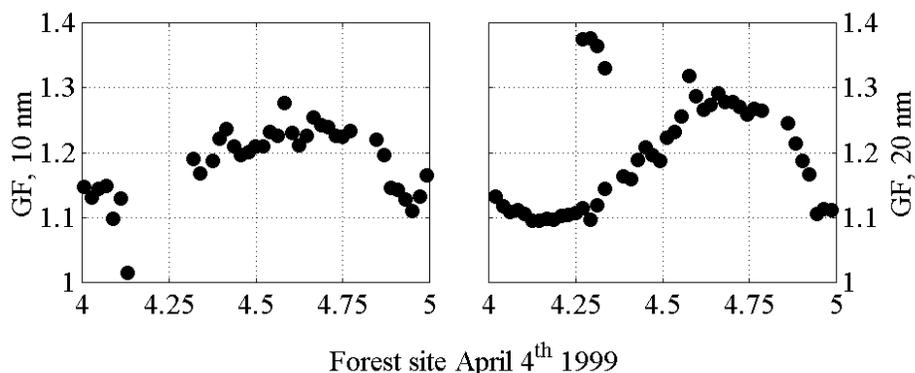

Figure 4. UFTDMA growth factors at 90% relative humidity of 10 nm and 20 nm particles measured in Hyytiälä, Finland.
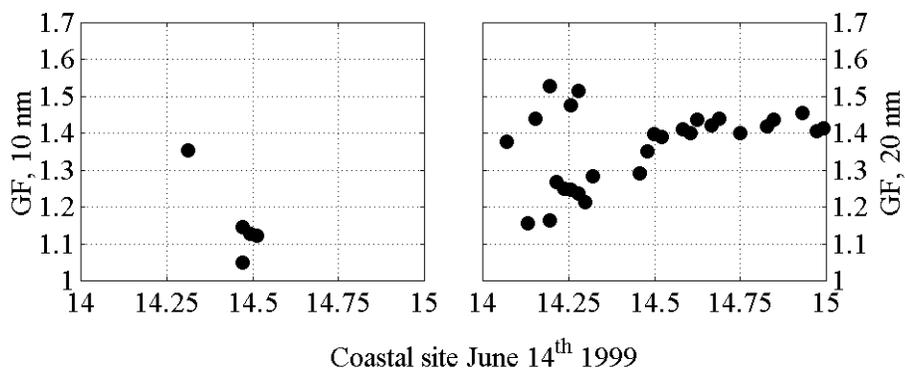

Figure 5. UFTDMA growth factors at 90% relative humidity of 10 nm and 20 nm particles measured in Mace Head, Ireland.

5 Review of the papers

All of the papers describe empirical studies concentrating on submicron and especially nucleation mode particles. Paper I introduces the UFTDMA system, and Papers II-V discuss field campaigns where the system has been used. The focus of all the reported campaigns, but particularly of those presented in Papers III-V, was to study nucleation mode particles in different environments.

Paper I introduces the ultrafine tandem differential mobility analyser (UFTDMA). The system was developed for measurements of the hygroscopicity of ultrafine aerosol particles, between 8 nm and 30 nm in mobility diameter. In the paper, the main operation features of the device are presented along with a detailed evaluation of the limits of its operation. Also hygroscopic growth data is presented for ammonium sulphate particles.

Paper II presents a measurement campaign where the number size distribution of submicron (8-450 nm in mobility diameter) and the hygroscopic properties of nucleation mode sized particles (10 nm in mobility diameter) were studied with respect to the effect of local weather parameters, transportation from an urban area, structure of the boundary layer, and precipitation. The few occurrences of new particle formation events that were observed seemed to be connected with changes in the structure of the boundary layer.

Paper III describes hygroscopic and cloud condensation properties of submicron and super-micron aerosol particles in a boreal forest during the BIOFOR campaigns in 1998 and 1999. The section relevant to this thesis presents studies conducted using two TDMA systems (one to study 20-264 nm particles and a UFTDMA to study 10-30 nm particles), and a cloud condensation nucleus counter (CCNC). It was shown that the solubility of submicron particles exhibits a diurnal pattern. The lowest growth factors were detected at night time and highest during noon-afternoon. The nucleation mode particles had the highest soluble fraction of the sizes studied.

Paper IV presents hygroscopicity data obtained during the PARFORCE field campaigns in September 1998 and in June 1999. An UFTDMA was used for monitoring of hygroscopic diameter growth factors of aerosol particles with dry mobility diameters 8, 10 and 20 nm. Also a CCN counter was used to study the activation of aerosol particles, when exposed to supersaturated conditions (dry diameters 15-150 nm). It was seen that in clean marine air masses during the observed particle formation events, the newly formed nucleation mode particles (8 and 10 nm) most often had low growth factors (about 1.1) resulting from low solubility. This

indicates that the nucleation mode particles consisted of non- or weakly soluble species, possibly accompanied by a small soluble part. When nucleation mode particles were observed outside the event periods, the growth factors were higher (about 1.3 - 1.4). The 20 nm particles usually clearly belonged to the Aitken mode (based on number size distribution measurements) and had hygroscopic properties similar to some common salts (growth factors 1.4 - 1.5).

Paper V summarises UFTDMA data measured in an urban, an urban background, and in a forest site in Finland, and a coastal site in western Ireland. It is shown also that nucleation mode particles can be characterised with four hygroscopicity classes: non-hygroscopic (growth factor = 1), less-hygroscopic (gf = 1.05-1.2), more hygroscopic (gf = 1.2-1.4), and sea salt (gf > 1.4). In summertime urban air 10 nm particles showed varying less-hygroscopic growth behaviour, while winter time 10 nm and 20 nm particles were externally mixed with two different hygroscopic growth modes. The forest measurements revealed a diurnal behaviour of hygroscopic growth, with high growth factors at day time and lower during the night. The urban background particles had growth behaviour similar to the urban and forest measurement sites, depending on the origin of the observed particles. The coastal measurements were strongly affected by the air mass history. Both 20 nm and 10 nm particles were hygroscopic in marine background air, but the 10 nm particles, produced during the observed nucleation events, were non-hygroscopic. External mixing was occasionally observed at all the sites.

6   Discussion and Conclusions

Atmospheric nucleation events are constantly observed and yet it is not clear what are the formation mechanisms and physico-chemical properties of the nucleated particles. An ultrafine TDMA system was developed to gain indirect information about the composition of nucleation mode particles through the detection of their hygroscopic properties. In several field studies the high time resolution of the UFTDMA together with its' high detection efficiency, both with respect to size and to concentration, have been proven to be valuable. The UFTDMA hygroscopicity data alone cannot, however, be used to define the exact chemical composition of ambient particles. Additional measurements, for example volatility studies and analysis of particles with electron microscopy, have to be performed and the results of all these measurements should be analysed together.

Due to the differences in hygroscopic behaviour of particles of the same material but of different sizes (i.e. super-micron vs. ultrafine), a substantial amount of laboratory work is still needed to

gain a sufficient database to characterise the nucleation mode particles. In many cases the differences caused by the particle size are difficult to predict based on theoretical studies only. The laboratory measurements of known compounds further act as a valuable source of thermodynamical data that can be utilised in several models. More knowledge is also needed, not only of pure compounds, but also of ultrafine particles that consist of mixtures of species that are likely to exist in the ambient air.

In this work, the principle idea of an UFTDMA was presented together with an introduction of selected laboratory measurements and field data obtained during campaigns that were focused on studies of nucleation events. The field measurements with the UFTDMA proved that nucleation mode particles are present in large enough concentrations to be detected with the instrument. Also, all of the measurement campaigns revealed temporal variations in the hygroscopic properties of the nucleation mode particles, thus stressing the importance of measurement systems with high time resolution. Further more, the field measurements showed that also the nucleation mode particles occasionally are externally mixed.

7 References

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