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OBSERVATIONS OF TROPOSPHERIC AEROSOL SIZE DISTRIBUTIONS

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Academic dissertation
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Ismo K. Koponen

Observations of tropospheric aerosol size distributions

Ismo Kalevi Koponen
University of Helsinki, 2003

Abstract

In this thesis, a selection of articles on atmospheric aerosol size distribution studies at different locations and environments are presented. Measurements were carried out in urban, rural, marine and remote areas. The study gives more information about the detailed structure of different aerosol size distributions and will bring us closer to distinguishing between natural and anthropogenic sources of aerosols. Also illustrative examples of dynamical aerosol processes taking place in the atmosphere were observed. Additionally, since all these field studies have been performed using quite similar apparatus, both the instrumentation and data analysis methods are discussed in two of the papers. The first one shows that it is important to test commercial instruments and verify the manufacturer's specifications before using them in field measurements. The other reveals the benefits of modal fitting when studying long term aerosol dynamics.

Northern hemisphere background aerosol has a clear modal structure and a clear seasonal variability. At a boreal forest measurement station in Hyytiälä, southern Finland, numerous new particle formation events were observed usually followed by growth of these particles to cloud condensation nuclei (CCN) size. These events occurred mostly in spring time. Over the southern hemispheric oceans we did not detect any nucleation events, however when measuring close to the coast of Antarctica a nucleation mode was observed several times. Nucleation events were also observed in the measurements in Antarctica. More detailed investigations showed that these nucleation events coincided with coastal/marine air masses. Also with onboard ship measurements we were able to follow the transformation of polluted urban air into marine backround air. This has importance when climate change related processes are studied.

It is known that atmospheric aerosols can cause negative health effects. Therefore, we investigated transportation of urban air into indoor air was investigated. Since indoor air quality is usually very dependent on outdoor air, urban air measurements can be utilized in health related studies.

In general, size distribution measurements are important because aerosol properties are highly size dependent. In this thesis we used a Differential Mobility Particle Sizer (DMPS) to perform measurements with reasonably high time and size resolution, which thereby gives information of aerosol processes in situ.

Keywords (INSPEC): aerosol size distributions, marine aerosols, urban aerosols, Antarctic aerosols

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 journal concerned.

I Kaarle Hämeri, Ismo K. Koponen, Pasi P. Aalto and Markku Kulmala, (2002). Technical Note: The particle detection efficiency of the TSI-3007 condensation particle counter. *J. Aerosol Sci.*, 33, 1463–1469.

II Ismo K. Koponen, Ari Asmi, Petri Keronen, Katri Puhto and Markku Kulmala, (2001). Indoor air measurement campaign in Helsinki, Finland 1999 - the effect of outdoor air pollution on indoor air. *Atmos. Environ.*, 35, 8, 1465–1477.

III Jyrki M. Mäkelä, Ismo K. Koponen, Pasi Aalto and Markku Kulmala, (2000). One-year data of submicron size modes of tropospheric background aerosol in Southern Finland. *J. Aerosol Sci.*, 31, 5, 595–611.

IV Ismo K. Koponen, Aki Virkkula, Risto Hillamo, Veli-Matti Kerminen and Markku Kulmala, (2002). Number size distributions and concentrations of marine aerosols : observations during a cruise between the English Channel and the coast of Antarctica. *J. Geophys. Res.*, 107, D24, 4753, 10.1029/2002JD002533.

V Ismo K. Koponen, Aki Virkkula, Risto Hillamo, Veli-Matti Kerminen and Markku Kulmala, (2003). Number size distributions andgoogle.fi/ concentrations of the continental summer aerosols in Queen Maud Land, Antarctica. *J. Geophys. Res.*, in press.

Chapter I
Introduction

The term aerosol refers to an assembly of liquid or solid particles suspended in a gaseous medium for a long enough time to be observed or measured (Baron and Willeke, 2001). In this thesis the aim of the study was to investigate atmospheric aerosol. Aerosols can be emitted to the atmosphere directly as emissions of particles. They are called primary particles. Secondary aerosol particles are formed through conversion of certain gases to particles in the atmosphere (Seinfeld and Pandis, 1998).

Health effects of aerosol particles have raised a great interest in the investigation of aerosols. Several studies have shown that exposure to air contaminants, and particularly particulate air pollution, can cause severe health effects (CEOHA, 1995). Usually particles are measured as particulate matter (PM10 and PM2.5) in the health related studies. However, the effect of the number concentration and specially the role of the ultrafine particles (<100 nm) may be even more relevant concerning health effects than mass concentrations. There are several studies, which link the effects of the ultrafine particles to respiratory symptoms (e.g. Peters *et al.*, 1997). Since people spend most of their time indoors (Jenkings *et al.*, 1992) and indoor air is highly influenced by outdoor air (Paper II), it is essential to investigate the possible indoor sources and transportation of aerosols from outdoors to indoor air.

Atmospheric aerosols play a significant role in the understanding of both global and regional climate effects. Atmospheric aerosols can effect climate through the Earth's radiation balance both directly by scattering and absorbing incoming solar radiation and indirectly by acting as cloud condensation nuclei (CCN) (Seinfeld and Pandis, 1998). According to the study of Charlson and Wigley (1994), the concentrations of natural aerosols have roughly remained the same during industrial times, but human activities have increased the concentrations of anthropogenic aerosols. The report of the International Panel of Climate Change (IPCC, 2001) claims that the effect of anthropogenic aerosols has a big uncertainty concerning their influence on the climate change.

One of the most important aerosol particle properties is the particle size, which, to a great extent, determines the behavior of aerosols. Since aerosols cover a wide range of particle sizes, it is of fundamental importance to have an understanding of the whole size distribution to be able to study their effects and behavior. The size distribution spectra give us not only information about atmospheric aerosols, but also about the origin and history of the aerosols. However, in order to explain the origin or composition of the aerosol, we also need information about the meteorology (e.g. trajectories) and the chemistry (e.g. chemical size distributions) of the aerosols. To obtain aerosol number size distributions several instruments have been developed (Baron and Willeke, 2001).

Aerosol measurements are one of the main tools used to study processes, which affect the ambient aerosol. The most relevant processes, concerning this work are nucleation, condensation and coagulation since these are the processes which determine the aerosol particle number size distribution. Basically, nucleation is a process in which, for example, vapor in a gas phase is transformed to a solid or liquid phase. One hypothesis to explain observed nucleation events in the atmosphere is the so called thermodynamically stable clusters (TSC) (Kulmala *et al.*, 2000). However, these clusters are so tiny ($d_p \sim 1$ nm) that they cannot be detected until they have grown to 3 nm in diameter. Condensation, in turn, is one of the processes, which is responsible for particle growth. In condensation, under favorable conditions vapor condensates on the surface of the particles and causes the aerosol particles to grow (Vesala *et al.*, 1997). Another essential process for particle growth is coagulation, by which due to e.g Brownian motion or turbulence, particles collide and stick to each other (Hinds, 1999).

Modal structures of submicron aerosol size distributions (3-500 nm) have been investigated in several studies (e.g. Whitby, 1978; Birmili, *et al.*, 2001). Aerosol spectra are usually divided into three main modes according to the origin and behavior of the particles. These modes are called the nucleation, Aitken and accumulation mode. Nucleation mode particles are usually under 20 nm in diameter they are recently formed or emitted directly e.g. by traffic. The Aitken mode size is between 20 to 90 nm, such particles are the result of growth of nucleation mode particles or from primary combustion particles. Both nucleation and Aitken mode particles have quite a short lifetime (Hinds, 1999). They are removed away or end up growing in the accumulation mode due to condensation. Larger Aitken particles can also serve as cloud condensation nuclei. Accumulation mode particles are from 90 to 500 nm and they include combustion particles, smog particles, grown nucleation and Aitken mode particles or they can be result of cloud processes (Hoppel *et al.*, 1986). Aerosol size spectra can also be presented as mass, surface area or ume distributions. They are more relevant, when studying supermicron particles (Hinds, 1999). For submicron modes log-normal functions have been used to parameterize distribution spectra. The reasoning behind this is to get computationally fast parameterizations for models,

and generally, to simplify data.

Over the last decade a vast number of atmospheric aerosol measurement studies have been done and those studies cover geographically a significantly area of the globe (e.g. Heintzenberg, 2000; Kulmala *et al.*, 2003). However, most measurements are still made in short campaigns and are aimed to study tropospheric aerosols in a certain area over a short period (e.g. Kulmala *et al.*, 2001; O'Dowd *et al.*, 2002). It is crucial to investigate individual aerosol processes in great detail. Usually these kind of measurements require cooperation of several laboratories and they are very expensive to perform. However, to study e.g. climate change as a whole, one have to have long term measurements. There are only a few studies of the size distribution of continental aerosol over observation periods that allow climatological conclusions to be drawn (Birmili *et al.*, 2001; Whitby, 1978; Mäkelä *et al.*, 2000). Aerosol particle size distributions play an important role in understanding both detailed aerosol processes and long term changes in the atmosphere. For an example, scattering and absorbtion of light are strongly depend of aerosol particle size. Health related studies size distribution is essential when investigating particle lung deposition. Other aerosol properties which influneces to aerosol effects are e.g. hygroscopic properties, cloud physics and chemical composition of the aerosol. Hence, it is important to report aerosol particle size distribution data and improve measurement techniques.

The aim of this thesis is to present a short overview of the Differential Mobility Particle Sizer (DMPS) system, explain the basis of DMPS data analysis, and give a brief explanation of the conducted field measurements. Based on these field measurements, the evolution of the aerosol size distribution and its dynamics have been studied. Formation and growth of the aerosol particles in different locations, meteorological conditions and origin of air masses were investigated.

This thesis consists of the following parts : **1)** in chapter two all parts of DMPS system are described individually, **2)** in chapter three data analysis is discussed, **3)** in chapter four different measurement in various environments and the results obtained are presented and **4)** in chapter five there is a short review of the papers included in this thesis.

Chapter II

Instrumentation

In this thesis a Differential Mobility Particle Sizer (DMPS) system is used to study aerosol particle size distributions in different locations and in different situations. In this chapter the operation principle and accuracy of the DMPS systems is discussed. An understanding the physical phenomena that we are able to measure is very important in interpretation of the DMPS data. The DMPS system consists of three parts: the charger, the differential mobility analyzer (DMA) and the condensation particle counter (CPC). In the following sections these parts are presented in more detail.

2.1 Particle charging

Most aerosol particles carry some electric charge. They can be positively or negatively charged and some portion of them can be neutral. When using DMA techniques to measure aerosol size distributions we are utilizing the electrical property of aerosol particles. Hence, one has to keep in mind that converting raw data to final size distribution is representative only if the bipolar charge distribution of a given aerosol sample is well known (Widensohler, 1988). The charging efficiency gives the ratio between charged and neutral particles after the pass through charging device. The DMPS measurements discussed in this thesis are made using a bipolar diffusion charger to achieve a steady state charge distribution (e.g. Liu and Pui, 1974). Another possibility is to use a unipolar charger, but for the DMPS measurements the bipolar charger is found to be better, since the charging equilibrium is more easily achieved. Diffusion charging caused by random thermal motion of ions and particles leads to collisions of ions and particles. Particles capture ions and are charged or neutralized depending of their original state. Several studies have been done to investigate charging probabilities of aerosol particles (Reischl *et al.*, 1996; Hussin *et al.*, 1983; Adachi *et al.*, 1985; Wiedensohler, 1988). However, the charging probability of particles smaller than 10 nm is still not very well known (Reischl *et al.*, 1996).

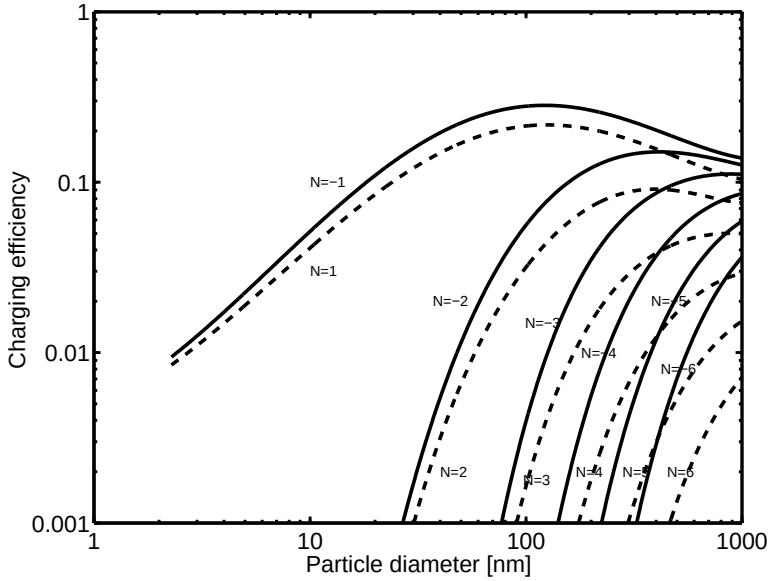

Figure 2.1: Charging efficiency of aerosol particles as a function of particle diameter, for negatively charged (solid line) and for positively charged (dashed line). N stands for number of elementary charges. Efficiencies are calculated according to Wiedensohler (1988).

In Figure 2.1 charging efficiencies for negatively and positively charged particles as a function of size are presented. The charging probability increases with increasing particle size (e.g. Kousaka *et al.*, 1983). However, increasing particle size will introduce another problem: multiply charged particles. In the same electric field multible charged particles have bigger mobility than than same size particle with single charge and therefore measurements will underestimate particle size. As can be seen in Figure 2.1 particles larger than 30 nm have a probability to carry more than one charge. However, when measuring particles larger than 100 nm multiple charging becomes more relevant and has to be taken account in the inversion of the size distributions.

In our data analysis we have used Wiedensohler's (1988) parameterization, which is valid for particles from 1 nm to 1000 nm. The parameterization agrees well with Fuchs theory and similar results were obtained by Reischl *et al.* (1996). The accuracy of the parameterization is sufficient to be applied to the DMPS measurements. According to the Wiedensohler's parameterization, the charging probability of three nanometer particles is 0.02 and 0.03 for positive and negative charge, respectively. The highest probability for single charged particle occurs in the 100 nm size, where just less than 30 % of the particles carry a negative charge and approximately 21 % are positively charged. We have to keep in mind that we only measure either negatively or positively charged particles. Hence we can draw a conclusion that the charging efficiency may give a uncertainly to the size distribution measured with the DMPS systems. However,

accurately verified chargers and meticulous data analysis give reliable results.

2.2 Differential Mobility Analyzer (DMA)

The DMA method was first described by Hewitt (1957) and in the last decades it has became the most widely used method for aerosol particle classification. Liu and Pui (1974) and Knutson and Whitby (1975) developed the DMA further in order to produce monodisperse aerosol size distributions. The theory and structure of the cylindrical DMA has been described in detail by e.g Knutson and Whitby, (1975). Here the purpose is to consider the function of the DMA technique and especially when applied to the measurement of particles under 10 nm in diameter.

The DMA is an analyzer which classifies particles according to their electrical mobility. The electrical mobility Z is related to the particle diameter as

$$Z = \frac{neC_c}{3\pi\eta d_p} \tag{2.1}$$

where n is the number of charges carried by the particle, e elementary charge, C_c is the slip correction factor, η is the gas viscosity and d_p is particle diameter. In ideal cases, DMA measurements are able to produce monodisperse aerosols. But, as it will be shown that is not always the case. In practice the DMA transfer function (Ω) should be a triangle, and the width of it is determined by the ratio of the sheath (Q_{sh}) and aerosol (Q_a) flows (e.g. Winklemayr *et al.*, 1991). The width of the transfer function increases as the ratio between the flows decreases.

The ideal size region, where the DMA method works is in the range of 20 to 200 nm where multiple charging is still quite easily taken care of in the data analysis. Multiple charging is more common for the particles larger than 200 nm, however it is still possible to correct for this in the data analysis. Particles larger than 1000 nm are carrying so many charges that data analysis is getting too complicated to do. This is because large particles with multiple charges have the same mobility as small single charged particles. For less than 10 nm particles the most severe problem is diffusion. It causes loss of particles inside the DMA due to narrow sample entrance at the top of the DMA. Due to diffusion, part of the particles inside the DMA sample flow which should, in theory, migrate to the particle free sheath flow but are either removed by the excess flow or are deposited to the central electrode. These processes cause changes in the shape of the transfer function by making it broader and decreasing the overall transport efficiency.

In Figure 2.2 the final transfer function for three different tages are presented. The charging probabilities of the particles are taken from Wiedensohler (1988) and the DMA transfer function

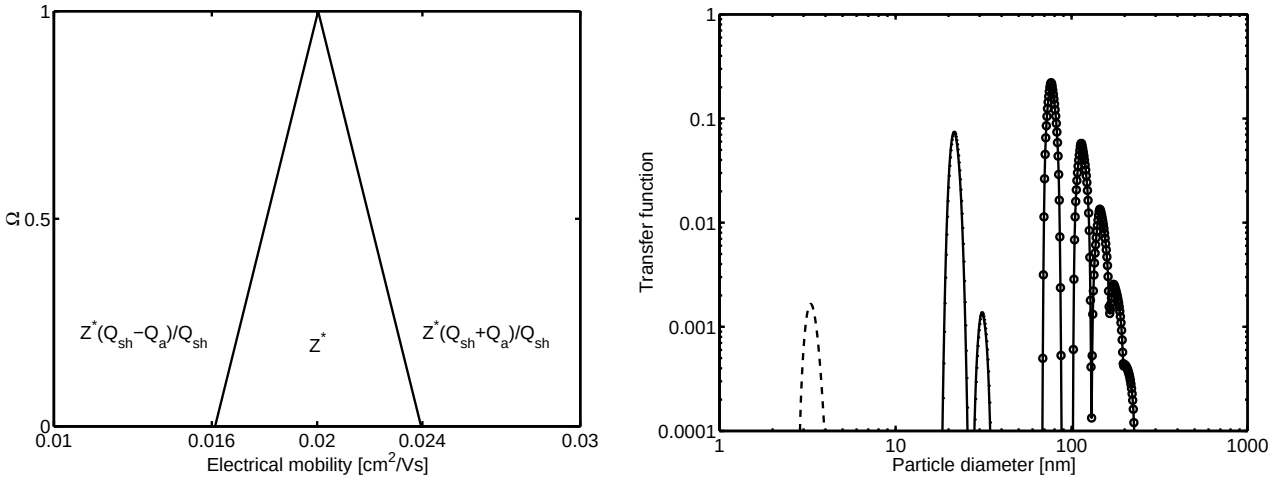

Figure 2.2: Left figure depicts the DMA transfer function as a function of electrical mobility,. Right figure describes transfer functions for three tage values which corresponds sizes 3.3 nm, 21.5 nm and 76.4 nm respectively. Effects of multiple charging and diffusion are also taken into account.

from Stolzenburg *et al.*, (1988). Figure 2.2 shows huge particles losses for 3.2 nm particle size. First multiply charged size is in 22 nm, but not yet a significant portion of the particles carry more than one charge. As can be seen from the function of the 78 nm particle multiple charged particles begin to be important factor in the data analysis.

2.3 Condensation particle counter (CPC)

Condensation particle counters are widely used to measure number concentrations of submicron aerosol particles. The principle behind the condensation technique was first introduced by John Aitken (1897). Since then the detection limit has improved remarkably and nowadays even 3 nm particles can be measured (Baron and Willeke, 2001).

Laminar flow type CPC function is based on three main processes: 1) exposure of the sample aerosol to supersaturated butanol vapor (TSI type CPCs), 2) growth by condensation of butanol vapor, and 3) detection of particles optically with a laser light and a detection unit. There are several commercial CPC models available and in the present studies a TSI 3025 (Stolzenburg and McMurry, 1991) and a TSI 3010 (Quant *et al.*, 1992) were used. In Figure 2.3 measured detection efficiency curves of CPC TSI 3010 and 3025 are presented. Since all the instruments are individuals they all have their own cut off sizes and overall detection efficiencies. It is important to verify function of all individual instruments and make sure that they are performing well for ones purpose. Therefore, one usually calibrate the CPCs before

going to the measurement campaigns. Calibration usually covers concentration calibration and verification of lower detection limit. As Figure 2.3 illustrates detection curve is a very deep in the lower end. This might cause a problem in the DMPS measurements because we already have a poor penetration for the particles smaller than 10 nm due to the loses and weak charging efficiency. Therefore there is a great interest to have valid calibration for the CPC in order to able to calculate correct concentrations and in the other hand taking that limitation of lower detectable measurement size in to account when planning the measurements. Different calibration methods are described in papers by e.g. Aalto *et al.*, (2001); Paper **I**; Hämeri *et al.*, (2002). Curves presented in Figure 2.3 have been used in the calculation of kernel matrices for the DMPS data analysis.

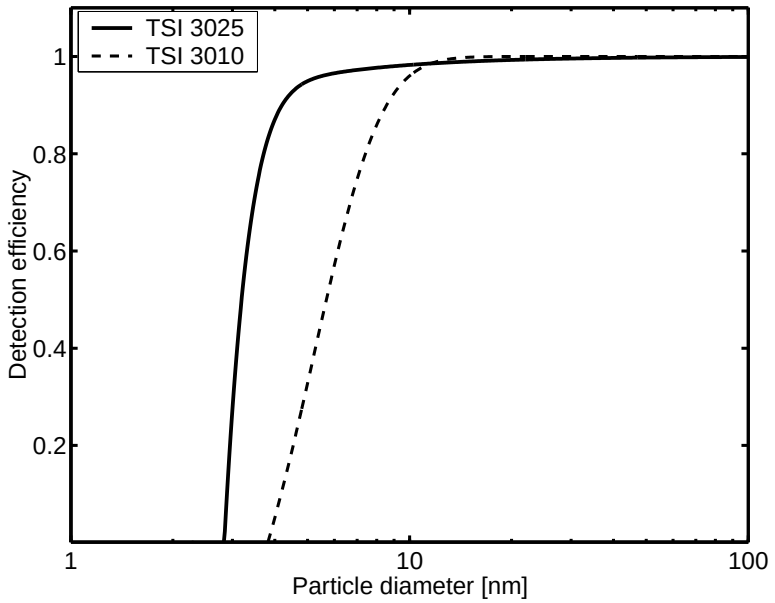

Figure 2.3: CPCs TSI 3010 and 3025 cut off curves.

2.4 Measurement setups

In the previous paragraphs the three main parts of DMPS system have been discussed. In this section measurement strategies, size ranges and time resolution will be described. In paper **I** a DMA (HAUKE type) was used to produce monodisperse size distribution for calibration. We used an aerosol flow/sheath flow ratio of 2/20 to get a sufficiently narrow transfer function for the calibration purposes. An electrometer was first used to calibrate a TSI UFCPC 3025 and later two TSI CPCs 3007 were calibrated against the 3025. In paper **II** two DMPS systems as identical as possible were constructed. Comparison measurement between the DMPS systems

were made in the laboratory before and after the measurement campaign. After taken into account all corrections from individual parts of the DMPS's, a final correction was made based on comparison measurements. In paper **III** we used data, which was measured with a DMPS system installed in Hyytiälä. The instrumentation is described in Aalto *et al.*, 2001. In papers **IV** and **V** the same system was used. Aerosol number size distributions were measured over the size range 3–800 nm using two parallel DMPS systems. The time resolution was 10 minutes and the flow ratios were approximately 1/5 which gives a wider transfer function and therefore better statistics of low concentrations. Measurements performed in the papers **I, II, IV** and **V** were dry size measurements. By drying the sheath flow aerosol sample flow were kept dry. All the CPCs and DMAs were calibrated before the campaign. The calibration method has been described in detail by Aalto *et al.*, (2001). However, in these measurements we had to transport the instruments to Antarctica and we could not be sure if the calibrations of the instruments remained unchanged. Therefore we choose to measure the total concentration with a pair of CPCs (TSI 3010 and 3025) and compare the readings with the total concentration calculated from the DMPS spectra. This was done in order to ensure quality of the DMPS measurements.

Chapter III

Data analysis

In order to interpret measurements, the raw data must be converted to the final size distribution. In our system we use an inversion method. Inversion method was applied here because aerosol size distribution is a quantity that cannot be directly observed. We calculate the kernel matrix, which includes all the information of the DMPS system. To solve the final spectra we have to invert the kernel matrix. To be able to compare different data and to make final data analysis more simple we applied log normal fitting method for aerosol distribution spectra. In the following sections those methods are briefly introduced.

3.1 Inversion of size spectra

As discussed in chapter 2 the DMPS consists of three main part: a charger, a DMA and a CPC. The DMPS measurements produce data files, which contain tages, signals from CPC and a few parameters of the conditions inside the DMA. For calculation of the kernel matrix (instrument matrix) the charging probabilities of particles are taken from Wiedensohler (1988) and DMA transfer functions from Stolzenburg (1988). The CPC and the DMA efficiencies are based on calibration results. Tube losses in sampling lines have been calculated using laminar flow diffusion theory. Inversion of the kernel matrix has been done by using pseudoinversion (*pinv*)(papers **II & III**) and in the other papers the non negative least square (*nnls*) method (MATLAB, 1998).

3.2 Fitting procedure

In order to evaluate the characteristics of a typical aerosol, we want to describe the number size distribution with a few well chosen parameters. Several papers have discussed the applicability of the lognormal distribution and the general conclusion has been positive (e.g. Whitby, 1978; Hoppel *et al.*, 1994; Heinzenberg, 1994). Since the real evolution of an aerosol distribution is

not known, a manual analysis of each individual spectrum is needed. After analyzing spectrum graphs we decided the number of modes and then fitted the sum of one to three lognormal distributions in papers **III & IV** and in paper **V** two to four lognormal distributions to the spectra. The lognormal distribution is (e.g. Seinfeld and Pandis, 1998)

$$\frac{dN}{d\log D_p} = \sum_{i=1}^{n} \frac{N_i}{(2\pi)^{1/2}\log\sigma_{g,i}} \exp\Big[-\frac{(\log D_p - \log \overline{D}_{p,i})^2}{2\log^2\sigma_{g,i}}\Big] \tag{3.1}$$

Here $\overline{D}_{p,i}$ is the geometric mean diameter (GMD), $\sigma_{g,i}$ is geometrical standard deviation (GSD), N_i is the aerosol particle number concentration in each mode and n is the number of modes. Initial values for fittings are obtained as follows : GSD's are taken from the literature, modal number concentrations are calculated from the measured values for $\frac{dN}{d\log D_p}$, and modal geometric diameters are set manually on the computer display.

The fitting procedure contains several MATLAB functions (MATLAB, 1998). In paper **III**, for a rough fitting *leastsq.m* (Quasi–Newton method) was used and for final fitting *fmins.m* (the Nelder-Mead simplex (direct search) method) was utilized. This procedure was seen to be efficient in most cases. For some simple spectra only *fmins.m* was used since one fitting was enough to obtain accurate results. In papers **IV** and **V** only *fmins.m* was used.

Chapter IV

Atmospheric aerosol number size distributions

The atmospheric aerosol number size spectrum gives information about the present situation in the atmosphere. However, when studying atmospheric processes, one spectrum measured within e.g. 10 minutes, does not provide sufficient information to draw any conclusions. In order to study aerosol dynamics there is a need to carry out continuous measurements that provide information on the eution of size spectra. A appropriate size range and time resolution has to be chosen depending on what the aim of the study is. The DMPS is the proper instrument to investigate number size distribution from 3 to 1000 nm and with temporal resolution of 5 to 10 minutes. However, if faster time response is needed a Scanning Mobility Particle Sizer (SMSP) (Wang and Flagan, 1990) is the right solution. With the SMPS system one can get size distribution from 10 to 900 nm under one minute, which is necessary in studies of rapidly changing aerosol. Other instrument which is utilizing electrical mobility to measure size spectra is the Electrical Aerosol Spectrometer (EAS). The function of EAS has been described in several papers (Mirme, 1997; Kikas *et al.*, 1996; Tammet *et al.*, 1997).

Knowledge of meteorological conditions is essential when investigating aerosol number size distribution under atmospheric conditions. Local meteorological parameters e.g. relative humidity, pressure and temperature give information on the conditions, where the measurements are conducted and are important in the data interpretation. In addition, backward trajectories show the origin of the air mass. By combining distribution spectra and meteorology, we are already able to tell quite a lot about the history and eution of the measured aerosol.

To get a better idea of the measured aerosol, several other properties are needed such as chemical composition, hygroscopic and optical properties. There is a clear spatial difference in aerosol spectra depending on the measurement site and origin of the aerosols. In the following sections these differences are discussed. Figure 4.1 shows locations which our laboratory has conducted measurements (bold letters correspond to the sites which measurements are presented in this thesis). Presented distributions are taken from the papers **II, III, IV and V** included in this

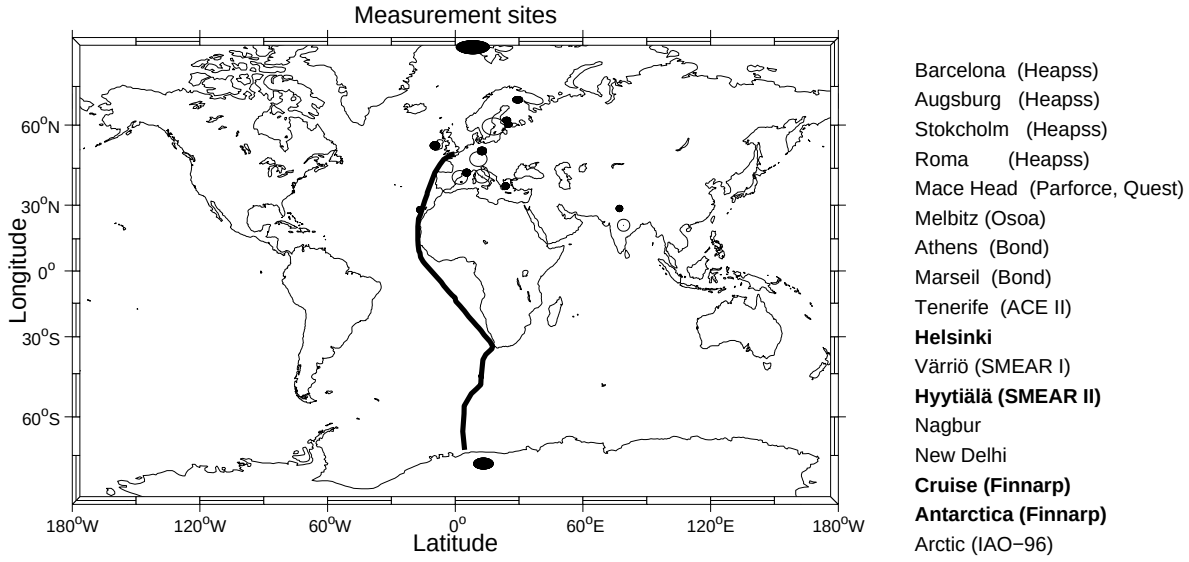

Figure 4.1: Measurements conducted by the Division of Atmospheric Sciences (corresponding projects in the parentheses) are presented. Dots correspond to locations of aerosol number size distribution measurements and circles the places where total concentration measurements have been performed.

thesis.

4.1 Outdoor and Indoor aerosols in urban areas

Aerosol particles smaller than 100 nm might have negative health effects and therefore there is a need to study urban aerosol size distributions. There is a wide selection of international and national projects and continuous measurements of aerosol number size distributions in urban air (e.g. Buzorius *et al.*, 1999; Morawska *et al.*, 1999). Also, since people are spending most of their time inside and lot of the aerosol sources are outside, it is very important to know, how effectively aerosol particles are transported from outside to indoor air (Jenkins *et al.*, 1992). Thus, filtration and air ventilation systems play a key role. Urban air number size distributions have their own nature because of multiple sources. Due to this, log-normal distribution fittings were not applied in this study to urban size distributions.

Figure 4.2a,b presents aerosol size distribution spectra in outdoors and indoors measured in the Helsinki metropolitan area on the 13th of January, 1999 (Paper **I**). Figure 4.2a was measured in the middle of the night, when traffic density was low and 4.2b during the rush hour in the afternoon. A difference can be seen in Aitken mode particles (from 20 to 90 nm) where the traffic emissions were influencing the size spectra. There was very little change in accumulation

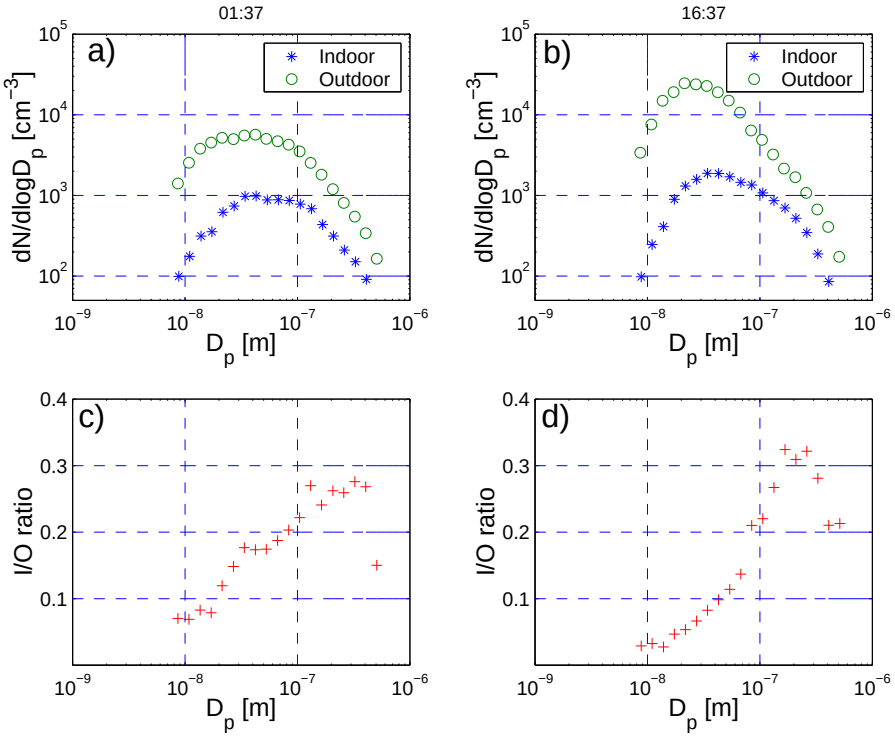

Figure 4.2: (a) and (b) are the 13 January measured spectra during two different ventilation rates. (c) and (d) presents, I/O ratios of spectra (a) and (b) with ventilation rates 0.3 and 3.7 h^{-1} respectively.

size particles (which are from 90 to 500 nm in size) which can also be transported from elsewhere due their longer lifetime compared to Aitken mode particles. Total number concentration in the Helsinki area varies approximately between 2000 to 80000 cm^{-3} and on averages 20000 cm^{-3} (Buzorius et al., 1999). However, in a bigger metropolitan like New Delhi, India, the total concentrations can reach values of 280000 cm^{-3} (Mönkkönen *et al.*, submitted). In Figure 4.2 I/O ratios from the spectra measured in Helsinki are presented (Paper **II**). Spectra measured during the night, when ventilation rate was 0.3 h^{-1} and in the afternoon 3.7 h^{-1}. The increase in the ventilation rate strongly influences the particles smaller than 100 nm. They are effectively removed by filters in the ventilation system. Accumulation mode particles, on the other hand, are too big for diffusion loss and too small for interception and gravitational settling losses to be effectively eliminated. Thus they penetrate from outside to inside independently of ventilation and filtration rate. Naturally, these observed ratios are not universal and can only be applied to similar ventilation rates and filtration system.

4.2 Rural aerosols

Examples of rural aerosol size distributions presented here are measured at the SMEAR II (Station for Measuring forest Ecosystem - Atmosphere Relations) in Hyytiälä. The station is located in central Finland in Finnish boreal forest and was built to provide a cross disciplinary co-operation between atmospheric, silvicultural, soil and forest ecological studies (Vesala *et al.*, 1998). The station is an example of long term measurements which give us an excellent opportunity to study diurnal, seasonal and even annual variability in size distributions.

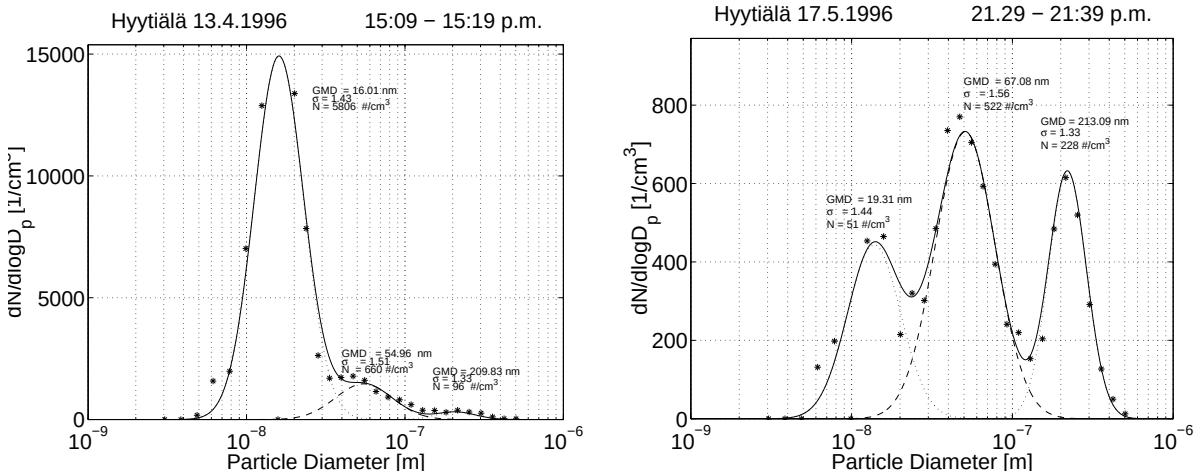

Figure 4.3: Two measured spectra (dots) accompanied by the fitting results (solid line, using lognormal distribution). The nine fitted parameters are shown in each plot.

In rural areas aerosol number size distributions are influenced by aerosols from local sources and particles from long range transport. However, we usually measure aged or very diluted aerosol, so a modal structure is apparent. Total concentrations in Hyytiälä varies between 100 to 10000 cm^{-3} depending on the origin of the air masses and whether or not there is nucleation. In Figure 4.3 two spectra measured in Hyytiälä are presented and, in addition, an example of how fitted lognormal distribution describes size spectra. New particle formation occurs in Hyytiälä approximately 50 times per year and most of these are during spring time (Mäkelä *et al.*, 1997; Kulmala *et al.*, 2001). Figure 4.3 (left) depicts the size distribution during new particle formation. The distribution is clearly tri-modal and the number concentration is dominated by nucleation mode particles (5800 cm^{-3}). However, nucleation mode particles were also observed even though 3 nm particles were not present (Figure 4.3, right) in this case. The number concentration in the nucleation mode (51 cm^{-3}) was lower than in the Aitken and accumulation mode.

4.3 Marine aerosols

A number of studies have been done of marine aerosols and several review papers have been published (Junge,1972; Fitzgerald, 1991; O'Dowd *et al.*, 1997; and Heintzenberg *et al.*, 2000). In the absence of significant transport from continental sources, marine areas provide an ideal environment to study formation and fate of natural sea-salt particles (Seinfeld and Pandis, 1998). However, continental air mass interaction between marine air and anthropogenic pollution brings up another interesting subject. As an example of this marine air size spectra measured during the cruise from the English Channel to Antarctica onboard the Russian research vessel Akademik Fedorov (Paper **V**) are presented in Figure 4.4.

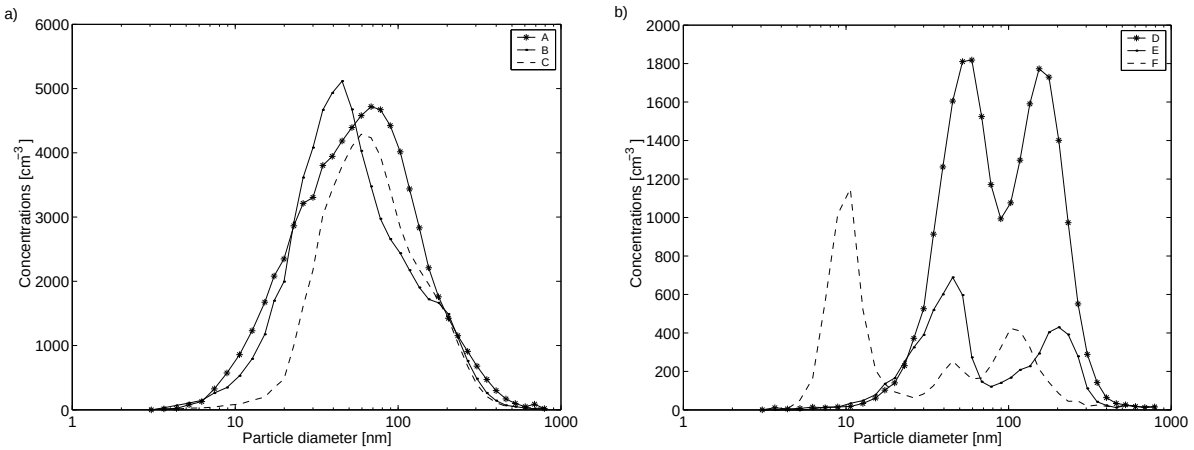

Figure 4.4: Examples of measured particle number size distributions in (a) continental and (b) marine air masses. The different spectra are measured at latitudes 50 N (the spectrum A), 35 N (B), 7 N (C), 7 S (D), 25 N (E), and 55 N (F).

Examples of aerosol number size spectra measured in polluted air masses are shown in Figure 4.4a. Two of the spectra (A and B) represent air originating from Europe and one (spectrum C) air moving along the coast of Africa. In all these spectra, the total particle number concentration is high (5000-10000 cm^{-3}), and the Aitken and accumulation modes are strongly overlapping. Both these features are common of air masses affected by fresh anthropogenic pollution (e.g. Shi *et al.*, 1999; Väkevä *et al.*, 2000).

Examples of typical marine particle number spectra are shown in Figure 4.4b. Spectrum D is bimodal with no nucleation mode and it has a total particle number concentration of about 1000 cm^{-3}. This kind of spectrum is typical for remote marine boundary layer in both the tropics and mid latitudes (Hoppel and Frick, 1990; Covert *et al.*, 1996; Jensen *et al.*, 1996; Raes *et al.*, 1997; Brechtel *et al.*, 1998). Clear separation between Aitken and accumulation modes in spectrum D

can be ascribed to cloud processing, as suggested by Hoppel et al. (1996) and confirmed later by several other investigators. Spectrum E represents a case, where the measured air comes from the European continent, but has spent at least 40 hours over the ocean. The total particle number concentration in this spectrum is much lower (300 cm^{-3}) than in the spectra displayed in Figure 4.4a. The most likely reason for this is that an originally very polluted air has been diluted into the free marine troposphere by entrainment, as demonstrated by Van Dingenen et al. (2000) in polluted marine boundary layers using a simple model approach. It is also probable that spectrum E had undergone some cloud processing, since it had already developed a clear bimodal character. Finally, spectrum F represents a case with a prominent nucleation mode (600 cm^{-3}). These kind of distributions were relatively common when approaching Antarctica.

4.4 Antarctic aerosols

Antarctica is one of the cleanest places on earth, thus it gives a great opportunity to study properties of aerosols which are not influenced by mankind (Shaw, 1988). Therefore a better understanding of Antarctic aerosols gives us an idea of the impact of human activities on atmospheric aerosols. Antarctic aerosols have been studied with regards to different characteristics e.g. chemical composition (e.g. Savoie *et al.*, 1993), total number concentrations (e.g. Samson *et al.*, 1990) or number and chemical mass size distributions (Gras *et al.*, 1993, Teinilä *et al.*, 2000). Since aerosol number spectra studies have mainly been concerned with the general characteristics of size spectra, we have provided more detailed information about the short-term variability and structure of the size distributions.

In Figure 4.5 two particle number size distributions measured for different air mass types are presented. Both spectra are averages over an hour. The spectrum in Figure 4.5 (left) is a typical example of a case when air masses come directly from inland. Both Aitken and accumulation modes are very stable during the whole day, showing a small change with respect to their mean diameter and total particle number concentration. Because of the very low size of the accumulation mode, the two modes are located very close to each other. No nucleation mode particles were observed during any of these days. In the second example (Figure 4.5, right) the air mass originates from marine/coastal areas, and as a result, a very distinct accumulation mode peaking above 100 nm is seen. On these days nucleation mode particles were also frequently observed. Figure 4.5 (right) is an example of the day, when we have a clear three modal distribution. Total aerosol particle concentrations of continental air masses ranged from 100 cm^{-3} to 400 cm^{-3} and in coastal/marine air from 300 cm^{-3} to 2000 cm^{-3}. This difference is mainly explained by the existence of nucleation mode particles.

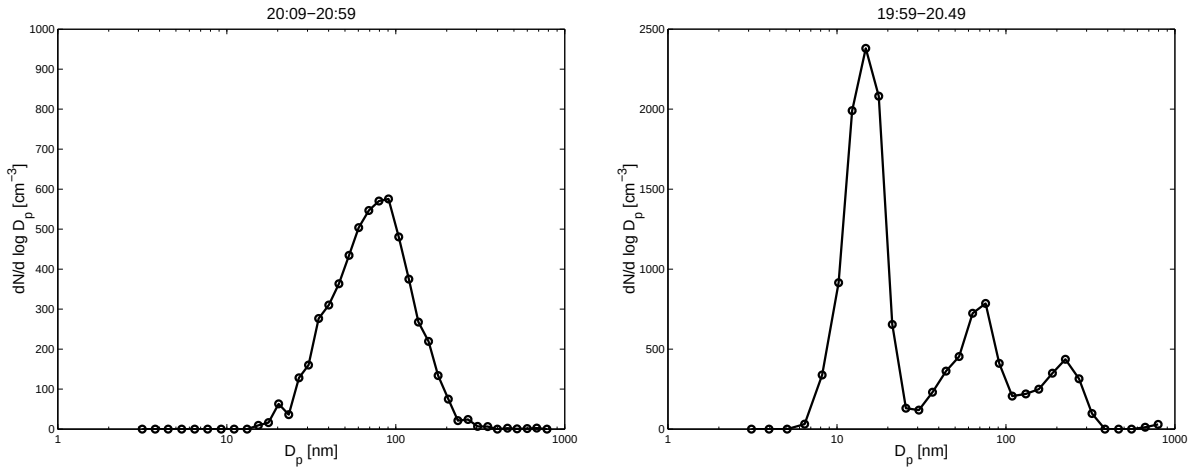

Figure 4.5: Examples of measured particle number size distributions in (left) continental and (right) marine coastal air masses.

4.5 Summary of the observed modal features

Parameters from lognormal fittings from papers **III,IV** and **V** have been presented in Table I. They represent measurements from four different locations. Since marine air and Antarctic air number spectra were strongly influenced by the origin of the air masses they were distinguished as five different types of aerosol. In addition, winter and spring time fitting parameters from the rural measurements have been presented. First of all, the number of modes depends on the location. Marine and rural air contains two to three modes and aerosol in Antarctic two to four modes. In all the spectra, accumulation and Aitken modes were detected.

Observation of nucleation modes does not necessarily indicate that particle formation had taken place near the measurement site. Continental nucleation mode GMDs are usually larger, which indicates that particles are more aged, originating from polluted air or the growth rate of the particles were bigger. According to Table 1 nucleation mode geometric average of GMD varies between 5.8 to 21.9 nm. Smallest values are obtained from the Antarctica in the case of two nucleation modes and the largest one from marine air with polluted air masses.

Least variability is found among Aitken mode parameters. However, continental marine air and rural B (spring month) GMDs are noticeably larger in these cases. For continental marine air the reason is most probably pollution plumes from Northern Africa. In Hyytiälä a large Aitken mode was the result of condensational growth of the particles. These two cases have also by far the highest Aitken mode concentrations. The difference is that sources of Aitken mode particles in Hyytiälä are originated from surrounding boreal forest and continental marine

concentrations can be attributed to human activities.

Accumulation modes were observed in every spectra. Accumulation mode GMD varies between 99 and 200 nm. Lowest mean size is found in Antarctica during the measurements influenced by continental air masses. Highest values are found in spring time rural measurements. These two are good examples of the influence of condensable trace gases.

Table 4.1: Twelve size distribution parameters obtained from the fitting procedure are presented. The geometric averages of geometric standard deviations of each quantity are given in parentheses. In the table, continental and coastal/marine indicates origin of the air masses during measurements (Paper **IV,V**). Marine A stands for measurements between the English Channel and Cape Town and marine B from Cape Town to coast of the Antarctica (Paper **IV**). Rural A stands for winter and rural B spring month measured in Hyytiälä (Paper **III**).

		Antarctica		Marine air			Rural air	
		Continental	Coastal/marine	Continental	Marine A	Marine B	Rural A	Rural B
Nuc 1	D_p [nm]	10.6(1.2)	5.8(1.4)	–	–	–	–	–
	N [cm^{-3}]	40(1.8)	216(2.7)	–	–	–	–	–
	σ	1.21(1.21)	1.32(1.13)	–	–	–	–	–
Nuc 2	D_p [nm]	18.9(1.4)	14.1(1.6)	21.9(1.5)	–	12.9(1.4)	13.6(1.35)	15.4(1.51)
	N [cm^{-3}]	140(2.3)	140(3.8)	907(3.0)	–	138.2(2.8)	306(2.9)	610(3.50)
	σ	1.31(1.09)	1.36(1.15)	1.48(1.13)	–	1.3(1.17)	1.42(1.07)	1.43(1.11)
Ait	D_p[nm]	42.5(1.2)	42.8(1.3)	51.9(1.3)	39.7(1.3)	37.9(1.2)	42.9(1.3)	53.7(1.51)
	N [cm^{-3}]	154(2.0)	222(2.0)	1470(1.1)	252(2.3)	245.9(2.1)	322(2.42)	1015(2.03)
	σ	1.50(1.13)	1.48(1.11)	1.59(1.12)	1.58(1.15)	1.50(1.14)	1.62(1.07)	1.74(1.12)
Acc	D_p[nm]	99.7(1.2)	119.8(1.3)	154.1(1.3)	175.9(1.3)	123.3 (1.22)	180(1.24)	199(1.29)
	N [cm^{-3}]	158(1.8)	105(1.8)	484(1.6)	138(2.2)	197.2 (1.6)	96(2.26)	247(2.29)
	σ	1.51(1.09)	1.47(1.10)	1.53(1.14)	1.35(1.13)	1.5 (1.17)	1.47(1.06)	1.47(1.09)

At all other locations except Antarctica we were able to describe spectra with three modes. However, data analysis by fitting is never an absolute measure. It depends strongly on how the fittings are executed. In cases of large data set automatic fitting programs are often used, but they might produce more mathematical than physical solutions. In this thesis manual fitting has been done due to the fact that it is more trustworthy way to find detailed information of modal dynamics and high resolution modal eution. Although this brings another variability to the fittings; the modal structure of spectrum depending of the person doing the fittings.

In conclusion, it can be stated that geographical differences in the parameters are smaller than the differences caused by the origin of the aerosol or local conditions. Therefore meteorological backward trajectories and synoptic scale atmospheric motions are essential for investigations of atmospheric aerosol number size distributions.

Chapter V

Review of the papers

All papers except paper one are based on aerosol number size distribution measurements and analysis of them. Paper three introduces fitting technique and fitting softwares which were applied in papers four and five. Those papers discuss how geographical and meteorological conditions influence aerosol number size distributions and fitted parameters. Paper one is an example of instruments calibration, which is an important although often underestimated part of field measurements.

Paper I presents calibration of a commercial instrument model TSI-3007 condensation particle counter(CPC). CPCs are widely used for measuring number concentrations of submicron aerosol particles. Size calibration and coincidence studies were performed to define the characteristics of the instrument. According to the measurements, the CPC was operating according to the manufacturer's specification's with respect to the lower detection limit and highest detectable concentrations. A comparison with other CPC models was conducted using urban air. The resulting differences between the concentration levels are easily explained by technical differences of the CPC models. Generally aerosol measurement instruments should be calibrated before and while using them and it should be part of the standard procedure prior to the measurement campaigns.

Paper II is a study of wintertime indoor and outdoor particle size distributions at an office building near downtown Helsinki. Particle size spectra were measured with two similar DMPS systems. Measurements were conducted simultaneously inside the office room and on the roof top of the building, where sampling was done in front of the intake of the ventilation system. We found that in this scenario indoor particles are mainly of outdoor origin and therefore ventilation had a strong influence on indoor particle and gas concentrations. I/O (indoor/outdoor) concentration ratios change as a function of particle size. Actually I/O ratios follow the deposition efficiency curve (Seinfeld and Pandis, 1998). Small particles (D_p <80 nm) deposit due to diffusion and larger ones (D_p >500 nm) are impacted and intercepted to the walls of the air

conditioning duct and to the filtration system.

Papers III presents an analysis of the annual behavior of atmospheric submicron aerosol particles using experimental field data. Data was measured using twin-DMPS system which determines aerosol size distribution from 3 to 500 nm with a temporal resolution of 10 minutes. Measurements have been performed at a forest site in Southern Finland in SMEAR II station between February 1st 1996 and January 31st, 1997 producing more than 50000 number aerosol size spectra. Data was analyzed by fitting two to three log-normal modes to each spectrum. The occurrence and eution of different size modes were described, and the seasonal variation of the modes was discussed. The Aitken and accumulation mode were observed in every spectra. The Nucleation mode occurred frequently during spring months, especially during March and April. Aerosol particle growth was detected from 3 nm up to climatically relevant CCN sizes ($D_p > 80$nm).

Paper IV describes submicron aerosol number size distributions measured onboard a research ship Akademic Fedorov during a cruise from the English Channel to the coast of Antarctica. The observed size spectra were fitted with two to three log-normal modes and the data was classified according to calculated air mass back trajectories. In marine air masses total number concentrations were mostly below 1000 cm^{-3} and between 1000 and 10000 cm^{-3} in air masses influenced by continental air. Marine air masses showed distinctive latitudinal changes. Over the tropical Atlantic no nucleation mode could be seen and the total particle number concentration usually remained below 500 cm^{-3}. In the mid and high-latitude Atlantic several episodes of elevated particle concentrations (> 1000 cm^{-3}) which were caused on the appearance of either the nucleation or Aitken mode particles. These observations indicate that there is no simple and universal relationship between total particle number concentration, submicron aerosol ume (or mass), and number of particles able to act as cloud condensation nuclei over the southern hemispheric oceans.

Paper V presents a study of total particle number concentrations and particle size distributions in the diameter range 3-800 nm measured in continental Antarctica during the austral summers 2000 and 2001. The total particle concentrations were about 200 and 2000 cm^{-3}, on average higher concentrations in marine/coastal air masses than in continental air masses were measured. Periods with higher concentrations were attributed to the presence of small (< 20 nm) nucleation mode particles. Measured size distributions were fitted with two to four log-normal modes. All spectra displayed an accumulation mode peaking at 70–150 nm and an Aitken mode peaking at 30–50 nm. The nucleation mode was present in more than half of the measured spectra, and occasionally two nucleation modes could be identified. Evidence on recent new particle formation and subsequent particle growth up to about 40 nm was observed in marine/coastal air masses only. Our measurements indicate that these recently formed parti-

cles contribute significantly to the overall particle budget of the Antarctic boundary layer, and they can be also a source of climatically important Aitken and accumulation mode particles.

Chapter VI
Discussion and Conclusions

Atmospheric aerosol particle number size distributions provide information on the origin and eution of the aerosol. To be able to distinguish the difference between aerosols formed naturally and aerosols formed due to human activities, we conducted measurements in urban, rural and polar areas. These three different environments give us an opportunity to study, what is naturally formed aerosol and what part of aerosol is a result of anthropogenic sources. Urban aerosol is in most cases polluted and influenced strongly by human activities. Rural areas give us information about more aged and mixed aerosol and therefore usually origin of air masses and environment play important roles when interpreting these measurements. Polar regions give us knowledge of aerosols, which do not suffer from the influence of human activities.

Aerosol particle size distribution measurements have been carried out by various researchers almost all over the world. Thorough knowlegde of the instrument and proper data analysis are essential in order to produce good quality measurements. Most of the measurements are performed with commercial instruments and while manufacturers give certification of performance of these instruments with time the performance may change. Therefore it is vital to check instrument function with regular intervals. Lower detection limit and highest detectable concentration calibration of the two TSI CPC 3007 showed that the instruments were operating correctly according to manufacturer's specifications. While these specific instruments were not used in the other measurements presented here, similar calibration techniques were applied to all the particle counters used in measurements presented in this work. This ensures consistently good data quality.

In this thesis atmospheric aerosol number size distribution measurements in different environments are presented. In an urban area indoor and outdoor measurements have been conducted in order to be able to study possible indoor sources and the indoor/outdoor ratio. In a boreal forest long term behavior of the aerosol size distribution, particle formation and growth are studied. Marine air aerosol measurements have been carried out from the English Channel

to the coast of the Antarctica. In these measurements the influences of different air masses were observed. Two separate measurement campaigns were performed in Antarctica, where several particle formation events were observed and the difference between continental and coastal/marine air masses was well defined.

In our measurements of indoor/outdoor relations in the urban air with mechanical ventilation showed that indoor aerosol total number concentrations were strongly related to outdoor air. The penetration of particles from outdoors to indoors was strongly size dependent with filtration being a key factor. With an effective filtration system indoor total number concentrations in urban air were 10 % of the outdoor total concentrations. This, of course, requires that there is no indoor sources. Considering the amount of time people spend indoors and the numerous known aerosol health effects it is important to perform these kind of studies to investigate the effects of different ventilation systems.

In this thesis it is shown that there is much variability in the aerosol total number concentrations depending on the location of the measurements and the origin of the air masses. Total number concentrations between clean air in Antarctica and polluted urban differ by several orders of magnitude. That can give an idea of what effect mankind has on atmospheric aerosol total concentration. Papers in this thesis present several particle formation events in Antarctica and the boreal forest. Observed growth rates in Antarctica can be ten times smaller than in the boreal forest. Indeed particle growth to CCN size can last several days in Antarctica. However, in both locations particles can grow to reach CCN size at which point they can be climatically important.

We can conclude based on this thesis that a) it is important to test commercial instruments and verify the manufacturer's specifications before using them in field measurements, b) indoor air quality is usually very dependent on outdoor air and it is very important to study indoor air in order to investigate health effects, c) northern hemisphere background aerosol has a clear modal structure and has a clear seasonal variability, d) there is no simple relationship between the total particle number concentration and the submicron aerosol ume concentration or the number of particles which are able to act as cloud condensation nuclei over the southern hemispheric oceans and e) in Antarctica newly formed particles can be observed but only in marine air masses.

Chapter VII

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