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Hygroscopic and CCN properties of aerosol particles in boreal forests

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ABSTRACT

The measurements of the hygroscopic and cloud condensation nuclei (CCN) properties of submicrometer atmospheric aerosol particles were performed with two tandem differential mobility analysers (TDMA) and a CCN counter at the Hyytiälä forest field station in south-central Finland during the BIOFOR campaign. The TDMAs were used to measure hygroscopic diameter growth factors of individual aerosol particles in the dry particle diameter range 10–365 nm when taken from the dry state (relative humidity $RH < 5\%$) to $RH = 90\%$. The CCN counter was used to study the activation of aerosol particles when exposed to supersaturated conditions. The measurements show clear diurnal pattern of particle solubility. The pattern was strongest for particles in nucleation and Aitken modes. The lowest growth factor (soluble fraction) values were detected during late evening and early morning and the maximum was observed during noon–afternoon. The highest soluble fractions were determined for nucleation mode particles. The response of hygroscopic growth to changes of relative humidity suggests that the soluble compounds are either fully soluble or deliquescent well before 70% RH. The hygroscopic growth was investigated additionally by a detailed model using the size-resolved composition from the impactor samples. The comparison between different instruments shows good consistency. We found good agreement for the 20 nm growth factors measured with two TDMAs, not only on average but also regarding the temporal variation. The similar conclusion was drawn for comparison of TDMA with CCNC for Aitken mode particles with dry sizes 50 and 73 nm. Differences between wet and dry spectra measured using APS and CSASP spectrometer probes were used to derive growth factors for coarse mode particles. Growth factors for coarse mode particles (D_p ca. 2 μm) ranged between 1.0 and 1.6. Agreement between the evolution of growth factors with time for both accumulation and coarse modes was observed regularly. However, similar portions of the data set also indicated clear differences and consequently different chemical compositions between both modes. When the differences between both modes were observed, the coarse mode always behaved in a less hygroscopic manner, with growth factors near one.

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1. Introduction

1.1. *The rôle of hygroscopicity investigations during BIOFOR*

Formation of new atmospheric aerosols has gained focused attention during recent years. Aerosol particles scatter incoming short-wave solar radiation and contribute to the radiative balance of earth. There is experimental evidence that a fraction of the new particles survive to grow to sizes which are optically active and, thus, have the potential to contribute directly to climate forcing (Mäkelä et al., 1997). The likely sources of new particles that have been identified include free troposphere, remote continental regions, boreal forests and coastal regions of marine boundary layer (Aalto et al., 1995; Hämeri et al., 1996; Mäkelä et al., 1998; O'Dowd et al., 1998; Schröder and Ström, 1997; Väkevä et al., 2000; Weber et al., 1997 and Wiedensohler et al., 1993). At the moment, several research projects focus on better understanding of the relative importance of each of these regions. The systematic measurements of nucleation mode particles during recent years, indicates that the nucleation might play an important rôle in controlling the budget of submicrometer aerosol particles in the atmosphere (Mäkelä et al., 1998; O'Dowd et al., 1998). In spite of intense studies, the detailed particle formation mechanisms are still not known.

Deeper examination of the references mentioned above indicates that the compounds and conditions leading to formation of new particles probably vary between various locations. Focussing on the boreal forest environment, the rôle of atmospheric monoterpenes and their oxidation products seems important. It is widely accepted that the oxidation of monoterpenes leads to condensable species which by gas-to-particle conversion contributes to the atmospheric aerosol (Janson et al., 2001 and references therein). The ability of oxidation products of monoterpenes to produce new particles by homogeneous nucleation has been demonstrated in laboratory studies (Hoffmann et al., 1997). However, whether or not this is the case in atmospheric conditions in forest environments is not clear (Kavouras et al., 1998; Leaitch et al., 1999; Marti et al., 1997).

The hygroscopic properties of aerosol particles determine the interaction with water vapour in the surrounding air. The amount of condensed water both determines the size of the particles and influences strongly the optical properties of aerosol particles, both through the effect on size distribution and on the refractive index (Tang and Munkelwitz, 1994). The phase of the particles is also important in aerosol dynamics, including the aqueous phase chemistry within the particles (Pandis et al., 1995). The amount of hygroscopic material in particles influences which particles can act as cloud condensation nuclei (CCN) and in turn has an indirect effect on radiative balance through cloud properties (Twomey, 1977).

Regarding the general objectives of the BIOFOR project, the measurements of hygroscopic properties of aerosol particles give essential information on particle composition. Although the information about chemical composition is indirect, the main result being the fraction of water soluble material in aerosol particles, this information can be used in studies concerning the formation and growth of particles. New information related to the rôle of oxidation products of monoterpenes in nucleation and condensation processes is especially obtained. In addition, this information is essential in investigations of the climatic importance of the aerosol population. The focus of this paper is to put together the various measurements of hygroscopic and CCN properties of aerosol particles during the campaign. The general features are presented and the quality and reliability of the data is analysed by comparing the different methods. The hygroscopic properties are additionally studied using the size-resolved ionic concentration from impactor samples (Mäkelä et al., 2001). The calculated aerosol hygroscopic properties are compared with the experimental observations.

During the BIOFOR campaigns, the hygroscopic properties have been examined using 2 methods that study the size-resolved response of aerosol particles to changes in the relative humidity of the environment: the tandem differential mobility analyser (TDMA) and the cloud condensation nucleus (CCN) counter. The TDMA measurements were performed using 2 set-ups, one sampling inside the forest and the other above the forest. The combined size range of the 2 instruments covered nucleation, Aitken- and accumulation-mode particles. The CCN counter was placed inside the forest and the data are applied to investigate the soluble fraction of Aitken-mode particles. The data can be further used in various closure studies, for instance mass-number closure, gravimetric mass-chemical mass closure, hygroscopic closure, and CCN closure. The observed hygroscopic properties of aerosol particles can be used as a sensitive indicator for the ability of aerosol dynamics models to account for the aerosol evolution.

1.2. TDMA investigations

One possibility to determine the chemical characteristics of the aerosol particles is to measure the hygroscopic properties of individual particles. The widely used method to determine the hygroscopic response of individual aerosol particles is the tandem differential mobility analyser (TDMA). This method gives indirect information on the size-resolved chemical composition of aerosol particles, it has good time response and can be used even with rather low concentrations. The measurements also provide in-situ information on the extent of external/internal mixing of the aerosol. This information is very difficult to obtain by other means of analysis, especially for nucleation and Aitken mode particles.

During the BIOFOR campaigns, 2 TDMAs were used: we name them UF-TDMA (UF standing for ultrafine) and H-TDMA (H standing for humidity). The main difference here is that the UF-TDMA was developed for studies of nucleation mode particles (dry diameter 10 nm–30 nm) while the H-TDMA was used to study the Aitken- and accumulation-mode particles (20 nm–365 nm).

Previous studies of ambient aerosol particle hygroscopic properties using TDMA instruments were performed in several locations by a number of groups (McMurry and Stoltzenburg, 1989; Svennigsson et al., 1992, 1994; Zhang et al., 1993, Swietlicki et al., 1999, Väkevä et al., 2000). These studies have shown that sub-micrometer atmospheric aerosol particles exhibit a modal hygroscopic structure, in the sense that a continuum of hygroscopic growth factors (relative particle diameter increase from dry to humidified state) is not observed. Instead, 1, 2 or even more modes of hygroscopic growth have been observed to appear simultaneously. The atmospheric aerosol is therefore in many cases externally mixed regarding its hygroscopic properties and hence also chemically. In continental-polluted aerosols, the particles generally separate into a less- and a more-hygroscopic group. The more-hygroscopic particles show diameter growth factors (dry to $\mathrm{RH} = 90\%$) in the range between 1.2 (nucleation-mode particles) and 1.8 (accumulation mode particles). This growth is in general less than the growth expected for pure salts of the major ions making up the aerosol particles, indicating that even the particles in this more-hygroscopic group consist of both water-soluble and insoluble or slightly soluble material with the less soluble fraction as large as half of the mass (based on the assumption that the soluble part consists of inorganic ions). Nearly-hydrophobic particles have also been observed on numerous occasions when the sampling sites were influenced by fresh combustion aerosol. In marine air masses, externally mixed sea salt particles with growth factors somewhat lower than those of pure NaCl (2.4 at $\mathrm{RH} = 90\%$) appear at wind speeds $>$ about 10 ms^{-1}.

While the hygroscopic properties of major inorganic salts are widely investigated, the hygroscopic properties of organic species are often not known. This fact deserves special attention here as the organic compounds are likely to play an important rôle in forest areas. The hygroscopic influence of the organic fraction of ambient aerosol particles has been studied earlier by Saxena et al. (1995). They analysed aerosol sampled at Grand Canyon AZ, a non-urban site, and Los Angeles CA, an urban site and observed that organic compounds at the non-urban location enhanced the hygroscopicity of the inorganic compounds, whereas the organic compounds at the urban location reduced hygroscopicity of the aerosol particles. Recently, Dick et al. (2000) investigated the amount of water associated with organic carbon compounds during the Southeastern Aerosol and Visibility Study. They studied the water activity of the organic fraction of the aerosol over a wide range of relative humidity (5–85%), and concluded that organic-associated water content is considerably less than that of sulphate compounds for high RH, but comparable or greater for low RH.

Few laboratory studies concerning the hygroscopic properties of organic compounds that are commonly found in atmosphere are available in the literature. Hansson et al. (1998) investigated the effect of organic coatings on hygroscopic properties of laboratory generated NaCl aerosol particles. Hämeri et al. (1998) investigated the rôle of slightly soluble organic compounds on the hygroscopic behaviour in mixtures with ammonium sulphate. Important measurements from the point of view of this paper were presented by Virkkula et al. (1999). They investigated the hygroscopic properties of aerosols formed by oxidation of 3 monoterpenes. They found that aerosol particles formed by oxidation of terpenes proved to be slightly hygroscopic, with diameter growth factor close to 1.10 at relative humidity of about 84%.

The importance of hygroscopicity, particularly soluble volume (mass) fractions, on the cloud droplet formation has been shown in model studies (Kulmala et al., 1996). It has been shown that the formation and growth of cloud droplet vary as a function of particle size and soluble mass fraction. In some cases the more hygroscopic Aitken mode particles can activate more easily than less-hygroscopic accumulation mode particles.

1.3. CCN counter investigations

The CCN counter was used to determine the concentration of aerosol particles which can act as cloud condensation nuclei in the atmosphere. These particles play an important rôle in the atmosphere because cloud droplets are formed on them. Understanding the chemistry and physics of the aerosol that controls cloud droplet formation is important in radiative transfer and climate modeling. The CCN property is controlled by both size and composition of the particles, and data obtained can also be used in studies of the chemical characteristics of the aerosol size fraction in question.

The previous studies of atmospheric CCN spectra show overall agreement with direct measurements and calculations based on aerosol number size distribution (Hoppel, 1979; Bigg, 1986; Covert et al., 1998). Nevertheless, measurements of CCN properties are very sensitive to both the composition of the particles and the structure of the particle size distribution, and therefore discrepancies up to factor 2 to 4 are not uncommon. The measurements by Rivera-Caprio et al. (1996) show good agreement between the measured CCN concentrations and the concentrations calculated based on the simultaneous measurements of aerosol number-size distribution and impactor-derived mass-size distributions. Their measurements suggest that the carbonaceous fraction of the aerosol would be similarly activated as sulphate (at 0.5% supersaturation). This observation indicates that at least a fraction of the organic aerosol mass in forest environment could be clearly water soluble.

Typically, cloud droplets are formed in the atmosphere when water supersaturation is between 0.1 and 1%. The measurements during the BIOFOR campaign were done for Aitken- and accumulation-mode particles scanning the supersaturation between 0.3 and 0.8%. This was thought to be a most efficient strategy, providing the information both size resolved and for a range of supersaturations. Hoppel et al. (1996) estimated the effective super-saturations in tropical MBL clouds to be typically between 0.15 and 0.25%. Assuming similar values also for boundary-layer cloud cover over the boreal forest zone, the CCN measurements appear relevant for estimation of the aerosol-cloud-interactions.

The investigations of boreal aerosol particle CCN properties provide an additional data set that can also be used in determination of the soluble fraction of the particles.

1.4. Focus of this study

The primary focus of this paper is to characterise the hygroscopic properties of the whole aerosol size distribution in a boreal forest site. Special attention is paid to the properties of the newly formed particles. The comparison between various data sets as well as model calculations was done, determining the size resolved soluble fraction. This quantity is obtained using a number of assumptions. The validity of these assumptions is discussed.

The experimental data of soluble fractions based on TDMA and CCN counter measurements is compared with model calculations. These calculations are done using an independent data set, and therefore the investigations form a closure study that can be used for determining both the quality of the measurements and validity of the assumptions.

2. Experimental

2.1. Measurement sites

For a more detailed description of the BIOFOR campaign sites at SMEAR II station see Kulmala et al. 2001a). The measurements of hygroscopicity and CCN properties were performed in 2 locations: (i) The UF-TDMA was located in the SMEAR II station and the instrument was placed in a mobile laboratory. The sampling of air was done from the height of 67 m (ca. 50 m above the canopy top). (ii) The H-TDMA and CCN counter were placed in Tapiola house, some 520 m from the station. The sampling of air was done within the canopy at the height of ca. 2 m. The vertical difference between the 2 sampling points was ca. 90 m.

2.2. *Description of TDMA principle and operation*

TDMA is an instrument system that can be used to study processes leading to changes in particle size. The instrument characteristics for both TDMA systems are presented elsewhere (Hämeri et al., 2000; Swietlicki et al., 1999) and only a short overview is given here. The TDMAs used in the campaign determine, in-situ, the hygroscopic growth of individual aerosol particles in terms of a change in their diameter when taken from low relative humidity ($RH < 5\%$) to controlled higher RH, nominally 90%. Two types of TDMA systems were used: UF-TDMA (University of Helsinki) covering the nucleation mode and the lower Aitken mode sizes (10–30 nm dry diameter) and H-TDMA (University of Lund) covering the nucleation (20 nm), Aitken (35, 50, 73 nm) and accumulation (109, 166, 264, 365 nm) mode size ranges. The UF-TDMA and H-TDMA instruments thus had one overlapping particle dry size (20 nm) which enabled a direct comparison of independent data sets to be made.

The primary components of the TDMA systems include a DMA1, an aerosol flow RH conditioner, DMA2, a DMA2 sheath air RH conditioner, and a condensation particle counter (CPC, TSI model 3010). DMA1 is used to select a narrow, quasi-monodisperse size range out of the full atmospheric aerosol size distribution at low RH. The humidity of the flow after DMA1 containing monodisperse aerosol is adjusted to a selected value in aerosol conditioner. The aerosol conditioner is a Gore tex tube that allows the water vapour to diffuse into the aerosol flow; the residence time in the conditioner is only about 0.1 s. In this study, the aerosol flow humidity was kept typically 3–5% lower than the humidity of sheath air of DMA2. This ensured that no accidental deliquescence occurred in the aerosol line before entering DMA2. The nominal value for RH in DMA2 was 90%. In addition to that, some scans with other humidities were undertaken in order to study the response of the aerosol to changes in RH. The DMA2 of both the instruments was actively temperature-controlled. The dew point temperature of the excess air exitting DMA2 was continuously measured with a dew point hygrometer. The RH inside DMA2 was calculated using the dew point temperature and the temperature on the surface of the DMA2. The resulting particle size was measured with DMA2 and the particles were detected with a CPC.

The calibrations were performed at regular time intervals using $(NH_4)_2SO_4$ aerosol. These calibrations were used to check that the DMA2 RH was correctly estimated and that the data sets obtained for both instruments were comparable. In addition, the calibrations were used in studies concerning the soluble fraction of the particles. The soluble (volume) fraction was calculated using the equation

$$\varepsilon = \frac{V_{\mathrm{sol}}}{V_{\mathrm{tot}}} = \frac{g_{\mathrm{a}}^{2} - 1}{g_{\mathrm{sol}}^{3} - 1} \qquad (1)$$

(Pitchford and McMurry, 1994; Swietlicki et al., 1999). Here V_{sol} and V_{tot} are the volume of the soluble components and total volume of a particle, correspondingly. The g_{a} is the growth factor of the ambient particle and g_{sol} is the growth factor of a fully soluble particle with the same humid diameter as the ambient particle. The use of ammonium sulphate as reference aerosol is essentially based on the assumption that the ambient aerosol is a mixture of ammonium sulphate and insoluble material. The ambient aerosol is most probably a much more complicated mixture of both soluble and insoluble compounds and this approach is used mainly in order to compare the different data sets of this study as well as to provide data for later (model) use (Kulmala et al., 2001b). This approach simplifies the aerosol properties, but is widely used in connection with TDMA studies.

All flows were checked daily with an electronic piston-type or bubble flow meter. The measurement routines were different during the 3 campaign periods. The main focus of this paper was to study the hygroscopic properties of aerosol particles during nucleation events. These events were most numerous during the Biofor III period (Aalto et al., 2001), and the following description refers to conditions during that period.

2.2.1. UF-TDMA characteristics. The measurements were performed at 3 dry sizes (10, 15 and 20 nm) in order to characterise the particles during the burst and subsequent growth. The measurements were performed at nominal RH = 90%. Each particle size took ca. 10 min to measure and the whole cycle was measured every 30 min. In addition, the dry diameter and $(NH_4)_2SO_4$ calibration was done each day during the campaign.

The primary parameters obtained from UF-TDMA data reduction processes were: (i) the diameter growth factor (GF) for each hygroscopic mode and (ii) the relative fraction of particles in the growth modes. The error of the growth factor is estimated to be ±0.05 in relative units. The inaccuracy comes mostly in uncertainties of the true values of the DMA flows as well as from temperature and RH fluctuations inside the DMA2.

2.2.2. H-TDMA characteristics. The standard measurement routine of the H-TDMA was that the growth factors were determined at RH = 90%, while every 6th hour, the growth factors at 50 and 166 nm were also measured at RH = 70% for the duration of one full hour. During days with new particle formation, the 70% scanning was disabled. Occasionally, RH scanning at 50 and 166 nm dry sizes was performed from RH = 60% to RH = 90% in steps of 5%. One DMA2 scan at a given particle dry size took about 5–10 minutes to complete and a full series of scans lasted about 50 min.

The primary parameters measured by the H-TDMA and estimated by the data inversion routine for each group of particles showing similar hygroscopic growth are: (i) arithmetic mean diameter growth factor; (ii) diameter growth dispersion factor, and; (iii) number fraction of particles in each hygroscopic particle group.

The error in measured growth factor by the H-TDMA is estimated to be ±3% or ±0.05 relative units for a growth factor of 1.8. This is a result of humidity fluctuations and humidity gradients in DMA2 and errors in modal values from counting and curve fitting uncertainty. The smallest detectable number fraction of an externally mixed hygroscopic particle group is about 5%, for the case when the growth factor peaks are well separated.

2.2.3. Growth factor correction. During the operation of the TDMA systems, effort was taken to ensure stability of the system. Main attention was paid to temperature stability of the instruments. The evaluation of the data showed that the conditions were stable most of the time and RH stayed close to the nominal value. In order to make an intercomparison between different data sets, all the accepted data were calculated to correspond to the nominal RH = 90% value.

The correction of hygroscopic growth factors was made assuming an ammonium sulphate soluble particle fraction. All the data used in this calculation was quality controlled and only data with an RH between 88% and 92% were accepted. The correction made is therefore relatively small and depends only slightly on the assumption of ionic compound. The decision to use ammonium sulhate as the soluble part was estimated to make a maximum error of 1% compared with using other major inorganic salts.

The thermodynamic data needed for the growth factor correction were water activity and density of the solution droplet. These quantities are measured using an electrodynamic balance and are reported in the literature (Tang and Munkelwitz, 1994). The surface tension was taken from parameterisation by Korhonen et al. (1998).

The main idea of the growth factor correction was presented by Swietlicki et al. (2000). In summary, first the soluble fraction of the particle was calculated assuming the particle consisting of ammonium sulphate salt and additional insoluble mass. Once this quantity was obtained, the growth factor of this composition was calculated for nominal RH = 90%. The growth factor for nucleation mode particles at 90% RH was scaled to agree with more precise calibrations made under laboratory conditions. This is essential, since the theoretical calculation are made for particle sizes when the Kelvin correction is negligible (Hämeri et al., 2000).

2.3. *Principle of CCNC operation*

The CCN counter is a thermal gradient diffusion cloud chamber with horizontal flow direction and vertical parallel walls (Aalto and Kulmala, 2000). Typical supersaturations used with the chamber are between 0.2 and 1.0%. Total flow rate through the chamber is 3 LPM and the aerosol flow rate 0.5 LPM. Droplets that are formed inside the chamber are counted from outside the chamber, with an optical particle counter (Climet 7300). Droplets larger than 1 μm are considered to be activated as we focus on a study of the dry diameters of 50 nm and 73 nm. The whole measurement system contains an ordinary DMPS-system (differential mobility particle sizer), including particle neutraliser, Hauke-type differential mobility analyser (DMA) and particle (CN) counter (CPC, TSI model 3010). The CCN counter is used in parallel with the particle counter. The instrument is calibrated using ammonium sulphate aerosol.

The CCN counter can be used with different configurations. In all configurations, atmospheric aerosol is sampled with constant flow rate, one monodisperse size fraction is selected from the total sample with the DMA, and the concentration of this fraction (CN) is measured with a particle counter. The same sample is fed into the CCN counter where water supersaturation is between 0.2 and 1.0%. The supersaturation can be selected to be any value between these limits. A fraction of the aerosol sample grows inside the chamber. Concentration of this activated fraction (CCN) is measured with an optical particle counter. This concentration is compared against total particle concentration, and using the calibration, the ratio CCN/CN is calculated. This is the primary data of the device.

In principle, the chamber should work, so that when the particle diameter is below the critical diameter, the particles are not activated, and after the critical diameter, all the particles are activated and detected. Because of mixing and particle deposition inside the chamber, the CCN/CN ratio increases smoothly as a function of particle size and does not reach unity for large particles. Detection efficiency for large particles is typically around 40%. Estimations for the measurement errors can be made with the calibrations done during the campaign. During the measurement campaign, the instrument was calibrated once a day. Typical variation in the critical diameter during the campaign was ±10% and in maximum CCN/CN-ratio ±20%. Variation especially in the CCN/CN-ratio is considered large and the unstable ambient aerosol concentration makes the situation even worse. High error estimates in critical diameters also leads to high errors in calculated soluble fractions. We have estimated that the error of the soluble fraction determination is ±20%.

During the BIOFOR III period, the system was operated so that 3 particle diameters were selected (50, 73 and 109 nm) and 5 supersaturations between 0.3 and 0.8% were scanned. The CCN/CN ratio was calculated for all 3 particle diameters with given supersaturation. A soluble fraction was calculated assuming that all the soluble material is ammonium sulphate as in calibration. Critical supersaturations were determined both from calibrations and ambient measurements for 50- and 73-nm particles. Soluble fractions were calculated using the equation:

$$\varepsilon = (\ln S_s / \ln S_a)^2 \tag{2}$$

(Aalto and Kulmala, 2000), where S_s and S_a are critical supersaturations for calibration aerosol and ambient aerosol. The use of ammonium sulphate as the reference aerosol has the same problems as in the case of TDMA measurements. However, bearing this limitation in mind, the soluble fractions presented should not be taken as absolute values, but rather as a way to make a comparison, and further analysis possible.

2.4. *Coarse mode investigations*

The coarse mode particle (between 1–15 μm diameter) response in relative humidity was studied using 2 instruments, a TSI aerodynamic particle sizer (APS) and a PMS classical scattering spectrometer probe (CSASP). The CSASP probe samples wet-ambient particles in situ and thus provides measurements of ambient hydrated aerosol size distributions as a function of ambient relative humidity. By comparison, the APS samples dry-size distributions and are consequently independent of relative humidity. Comparison of both spectra leads to the ability to derive growth factors for the coarse mode (Liu et al., 1996). This information completes the analysis of the growth factors as a function of dry particle size. However, the growth factors derived using this method cannot separate the various growth modes, but give instead one average value characterising the size class.

To determine the growth factors for the coarse particles, we used the dn/d log r spectra of the APS probe (which are considered to be completely dry) with the spectra of the CSASP probe, sampled in-situ at a high flow rate, hence at ambient conditions. Over almost the complete campaign, the CSASP-spectrum is shifted towards larger particle sizes, especially at high humidity conditions. We therefore tried to match both spectra at an interval of 10 min by shifting each channel of the APS spectra until it matched a number of the CSASP spectrum. The growth factor calculated by this intercomparison is for the ambient relative humidity and has to be normalised to 90% relative humidity in order to compare it with the growth factors derived from the H-TDMA measurements. We used a rather simple approach by solving the GERBER equation for the most varying constant (Gerber, 1988). Inserting this constant in the GERBER equation with a relative humidity of 90% allows us to then calculate the growth factor for each channel of the APS spectrum.

3. Detailed model for the calculation of growth factors

In this study, the water soluble mass fractions of the aerosol particles are usually determined from the measured growth factors by a method which assumes ammonium sulfate to be the only hygroscopic compound. However, for the BIOFOR campaigns, the aerosol chemical composition is known in more detail. For the impactor samples, the ionic concentrations have been determined by ion chromatography (Mäkelä et al., 2001). Therefore, also a more detailed growth model based on the theory of Hänel (1976, 1984) was used to calculate the water soluble mass fractions. In the following section, this model will be described in brief.

The model is applicable to particles of mixed composition including a variety of electrolytes. It uses a mixing rule, which is based on the osmotic coefficient ϕ_i as a correction factor for concentrated solutions. In equilibrium, the relative humidity RH above the droplet surface is equal to the ambient relative humidity. RH is given by

$$\mathrm{RH} = \exp\left(\frac{2\sigma}{\rho_\mathrm{w} R_\mathrm{w} T r} - \frac{\dfrac{\rho_0}{\rho_\mathrm{w}} M_\mathrm{w} \sum_i \phi_i \dfrac{v_i m_{\mathrm{s}i}}{M_{\mathrm{s}i} m_0}}{(r/r_0)^3 - 1} \right), \quad (3)$$

with M_w molecular weight of water, $M_{\mathrm{s}i}$ molecular weight of electrolyte i, R_w specific gas constant of water, T absolute temperature, m_0 total dry mass, $m_{\mathrm{s}i}$ partial mass of electrolyte i, r radius of wet particle, r_0 equivalent radius of dry particle, v_i number of ions in electrolyte i, ρ_0 density of dry particulate material, ρ_w density of water, and σ surface tension. The first term describes the curvature correction of the humidity above the particle surface due to the Kelvin effect, the second term the water activity a_w. The osmotic coefficient ϕ_i of the electrolyte i is a function of the water activity and is approximated by empirical functions

$$\phi = a + b a_\mathrm{w} + c a_\mathrm{w}^2 + d a_\mathrm{w}^3 + e \exp[f(1 - a_\mathrm{w})^g], \quad (4)$$

with a, b, c, d, e, f and g compound-specific constants. They have been obtained by regression from various measurement data. The particle radius r at the relative humidity RH is calculated from eq. (3) by iteration. The growth factor then corresponds to the ratio r/r_0. Currently, the model describes 303 salts and acids; however, 127 of them are practically water insoluble as they have a deliquescence humidity above 99%. In cases where the temperature dependence is known, the deliquescence humidity is described as a function of the temperature.

From the ion chromatography analysis of the impactor samples, the concentrations of ions are known. For the application of eq. (3), the ions have to be apportioned to salts and acids. This is done according to the deliquescence humidity of the compounds. The ions are apportioned first to compounds with low solubility and high deliquescence humidities, e.g., calcium sulphate. The remaining ions are apportioned then to other compounds in order of decreasing deliquescence humidity. This procedure simulates an evaporating drop (Seidl and Dlugi, 1991).

The water-soluble mass fractions are obtained by adding additional water insoluble material to the concentrations of the ions, i.e., by increasing m_0 in eq. (3). This is done, until the calculated ratio r/r_0 is equal to the measured growth factor. The water soluble mass fractions calculated in this way are compared to those obtained by the method using ammonium sulphate as only hygroscopic compound. In Subsection 4.5, some results for the measurement campaign BIOFOR III are presented.

4. Results

The hygroscopic and CCN properties of aerosol particles had different behaviours in different size classes. In this Section, we present the characteristic data obtained using different instruments, and the various methods determining the soluble fraction of the particles is compared. We will focus on the BIOFOR III campaign, Spring 1999. During that period, most of the nucleation events were detected. In addition, the instrumentation was more complete during that period, and the performance of the instruments was slightly different from the previous campaigns.

The result that is commonly reported in studies concerning the ambient aerosol hygroscopic behaviour is the type of mixing. This can vary from a completely internal mixture, where all the particles are similar in chemical composition (and therefore also hygroscopic properties), to an external mixture, where individual particles differ from each other in chemical composition. The TDMA method is capable of proving external mixing (more than one growth factor detected). It has to be noted, however, that if only one growth factor is detected, the aerosol is not necessarily internally mixed, but also external mixture with similar growth characteristics is possible. In other measurements reported in the literature (see references in the introduction section), often between 1 and 4 different hygroscopic growth modes are observed. The occurence of externally mixed aerosol in various size classes during the BIOFOR III period is presented in Fig. 1. The frequency of observations showing externally mixed aerosol is plotted as a function of particle size. The differences between various size modes is clearly seen. One observes that the nucleation mode, which is strongly influenced by newly formed particles, is most of the time internally mixed, i.e., all the particles show most of the time the same hygroscopic growth factor. The accumulation mode on the other hand is ca. 90% of the time externally mixed, having either 2 or 3 growth modes. The Aitken mode particles are both internally and externally mixed, depending strongly on the origin of the air masses.

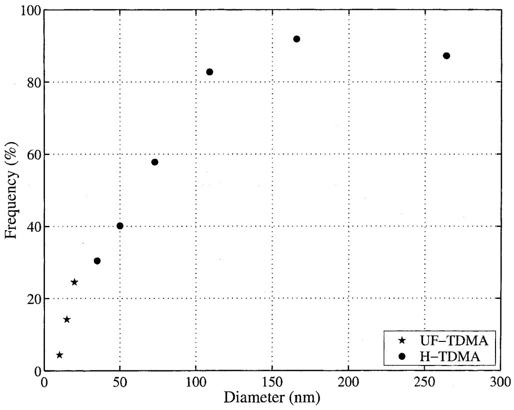

Fig. 1. The frequency of occurrence of externally-mixed aerosol as a function of particle size, based on the UF-TDMA and H-TDMA measurements. The discontinuity between 20 nm and 35 nm is most likely explained by different time periods included in the analysis. While UF-TDMA data is analysed for the whole period, the H-TDMA analysis is mostly concentrated in nucleation periods. Note also that UF-TDMA took the sample ca. 50 m above the canopy top while H-TDMA sampled within the forest.

The properties of aerosol particles in different hygroscopic growth modes during the periods of externally mixed aerosol are characterised in the Table 1. The particle number fractions in the growth modes are shown together with characteristic growth factors. The characteristic values for accumulation and Aitken-mode particles can be taken as typical for the area, as the aerosol is most of the time externally mixed. In contrast, as the nucleation mode is most of the time internally mixed, the values in Table 1 apply only to a minor part of the time. The hygroscopic characteristics of each particle size class are examined in more detail in the following.

4.1. *Nucleation mode particles*

The nucleation mode particles were measured continuously with the UF-TDMA for 3 dry particle sizes: 10 nm, 15 nm and 20 nm at nominal 90% RH. The measurement cycle from the 67 m

Table 1. *The characteristics of the different hygroscopic growth modes during the periods of externally mixed aerosol; the results are expressed as average growth factors (particle diameter at RH = 90% divided by dry particle diameter); external mixing observed refers to number of observations*

	Dry particle diameter (nm)								
Growth at 90% RH	10	15	20	35	50	73	109	166	264
external mixing observed (%)	4.4	14.2	24.5	30.4	40.1	57.8	82.8	91.9	87.3
Less hygroscopic particles									
growth factor	1.16	1.15	1.12	1.16	1.15	1.17	1.17	1.15	1.14
(average ±1 std)	0.07	0.07	0.06	0.07	0.07	0.07	0.06	0.05	0.07
% of concentration of externally mixed particles	62.5	61.5	57.2	39.8	38.7	46.1	53.5	38.3	28.0
Intermediate particles									
growth factor	—	1.31	1.25	1.22	1.24	1.32	1.36	1.32	1.46
(average ±1 std)	—	0.07	0.03	0.04	0.07	0.07	0.08	0.06	0.15
% of concentration of externally mixed particles	—	0.9	0.7	1.9	2.1	3.0	1.2	0.5	0.4
More hygroscopic particles									
growth factor	1.35	1.38	1.32	1.36	1.32	1.37	1.46	1.53	1.59
(average ±1 std)	0.11	0.14	0.11	0.11	0.11	0.09	0.07	0.05	0.06
% of concentration of externally mixed particles	37.5	37.6	42.1	58.3	59.2	50.9	45.3	61.2	71.6

height was 30 min, i.e., each size was measured twice per hour. This was thought to be the most efficient way of determining both the growth factor of each of the sizes as a function of time and the growth factor development of the nucleation mode particle population as they grow to larger sizes. The 20-nm dry size was additionally measured in the Tapiola site using the H-TDMA. These measurements were done ca. every 50 min.

During the BIOFOR III period, several nucleation event days were detected, and most of the results concerning the nucleation burst aerosol are from this period. The growth factors (and soluble fractions) during the nucleation days of each of the dry sizes show a diurnal behaviour. At night time, GF was lowest, on the average about 1.13 for all sizes, and was highest in the afternoon. The DMPS data during nucleation days show that there is usually systematic growth of particles during the day. Therefore, the growing nucleation mode appears (and disappears) later for larger particle sizes. Despite this shift in time of appearance with particle size, the diurnal variation of the hygroscopic growth factors is nearly identical for the 10, 15 and 20 nm particles.

It was typical that the growth factor of nucleation mode particles already starts increasing some hours before the DMPS system observes significant numbers of nucleation-mode particles. The actual time when the growth factors start increasing is supposed to vary according to meteorological factors (air mass history, radiation, temperature, boundary layer structure) or chemical properties of the air mass (diurnal behaviour of organics, OH, O_3, H_2O, etc.). The median growth factors and soluble fractions during the nucleation event days are plotted in Fig. 2. The median values are calculated every hour separately for each dry particle diameter. The dates included in the calculations are: 30 March, 2, 4, 5, 6, 8, 10, 12, 13, and 14 April. One can see the diurnal behaviour clearly, with the minimum of the median GFs of ca. 1.12–1.13 during night time. The maximum values are obtained between 13:00 and 16:00. Clear dependence on the particle dry diameter also can be seen from Fig. 2, the maximum median GF for 20-nm dry size reaching up to ca. 1.28 and for 10 nm dry size 1.26. In Fig. 2, the starting time of the nucleation event estimated using DMPS and CPC data for the same dates is also plotted. The mean time and the earliest and latest observed values are indicated as vertical lines. It appears

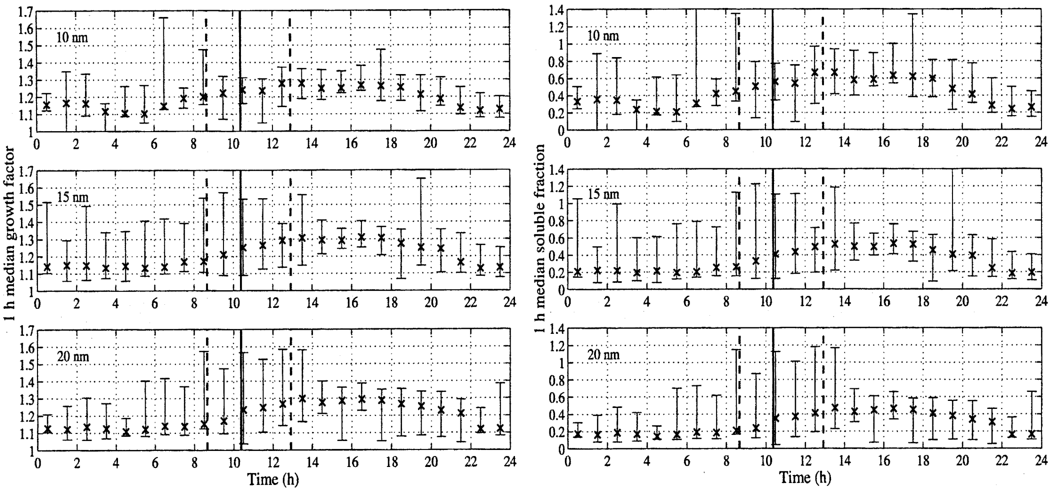

Fig. 2. The median growth factors and soluble fractions for 10, 15 and 20 nm particles during nucleation event days (30 March; 2, 4, 5, 6, 8, 10, 12, 13, and 14 April 1999) from the UF-TDMA data (sampled 50 m above the canopy). Also shown are the mean (solid line) and earliest and latest (dashed line) observed start times of nucleation event based on CPC and DMPS data.

clear, that the increase (on average) of the growth factors of all the dry sizes starts well before the nucleation mode particles are detected. It was seen that this observation applies not only for the average data but also for all of the individual nucleation days separately. Nevertheless, while the diurnal pattern is typical and can be detected during all of the nucleation days, differencies concerning the soluble fraction and the time of maximum growth are seen for individual days.

As a comparison, the diurnal behaviour was calculated for the BIOFOR II data set (August 1998). During this period no nucleation bursts were detected, and also the 20-nm particle soluble fraction remained low during the whole day (Fig. 3.). This result is possibly an indication of differences of condensable gas properties during and outside nucleation periods. This is difficult to quantify, but as the environmental conditions differ between March–April and August (temperature, radiation, etc.), the processes leading to condensation of (organic) vapours are likely to differ as well.

The quality of the TDMA measurements is investigated using simultaneous measurements of both the instruments. The 20 nm growth factors were determined with both TDMA setups, and therefore direct comparison can be made. The H-TDMA seems to detect values that are systematicly somewhat lower to those from UF-TDMA. The comparison for the whole BIOFOR III period is shown as a scatter plot in Fig. 4, where the growth factors within a 30 min time-window are plotted against each other. The reason for the systematically higher values in UF-TDMA might be either real differences between the aerosol properties in the 2 sampling sites, or perhaps more likely some systematic differences in the operation of the 2 instruments. Unfortunately, the instruments were newer compared side-by-side. We should mention here that while the UF-TDMA was measuring clearly within the usual measurement range, the H-TDMA (with, e.g., longer DMA columns and larger high voltage ranges) was operating at the very lower limit of the typical measurement range. Both data sets were corrected to nominal RH = 90% and the ammonium sulphate calibrations both during the field campaign and in the laboratory were taken as a reference size. Despite the systematic differences detected, we could conclude that the differences are well within the experimental inaccuracy.

4.1.1. Case: 5–6 April 1999. In order to highlight the features of nucleation event days, a case study concerning 2 typical nucleation days is presented here. The weather during 5–6 April 1999 was characterised with Arctic air masses and the cold

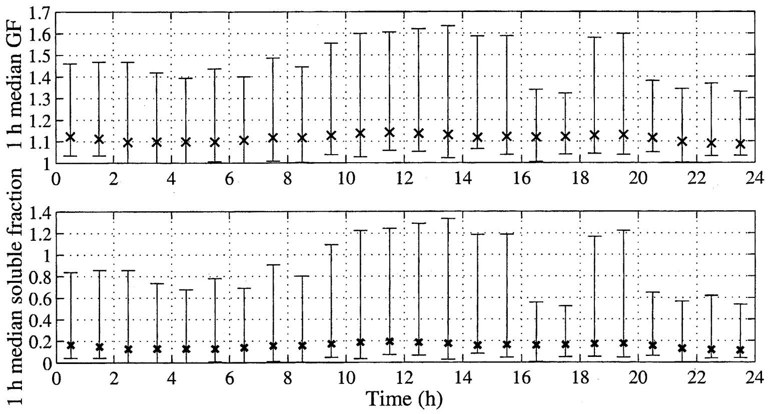

Fig. 3. The median growth factor and soluble fraction for 20-nm particles during BIOFOR II (August 1998). No nucleation was observed during this period.

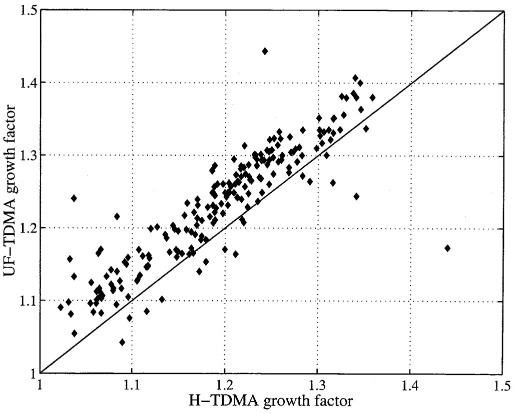

Fig. 4. The comparison for 20 nm growth factors obtained with 2 TDMA setups during the BIOFOR III period (March–April 1999). The growth factors determined within a 30 min time window are plotted against each other.

air advection (Nilsson et al., 2001). The back trajectories originated from Greenland over the north Atlantic Ocean. This type of weather is characteristic for nucleation bursts, which were detected during both days.

The maximum growth factors were obtained during the noon–afternoon, and even though the values were rather similar for all the dry sizes (GF approx. 1.30–1.36) due to the Kelvin correction, the composition differs remarkably. The calculated soluble fractions were between 50–60% (20 nm particles) and 70–80% (10 nm particles). The minimum GFs were obtained night time and corresponded to soluble fractions of ca. 10% (20 nm particles) and 20–30% (10 nm particles).

In addition to systematic diurnal behaviour of GF varying between less and more hygroscopic values, some clearly higher GFs were also obtained. These growth factors correspond to soluble fractions that exceed unity and imply that there are compounds in aerosol particles that are even more soluble than ammonium-sulphate electrolytes in various degrees of acid neutralisation. Particles with these high GFs are in earlier studies typically found in larger particle sizes, and they are commonly interpreted to originate from sea spray (Swietlicki et al., 2000). In connection with forest areas and nucleation mode particles, it seems unlikely that the particles with high GFs would originate from sea spray, but that there could be other sources producing highly soluble compounds.

The simultaneous measurements for the 20 nm dry size are presented in Fig. 5. As a main conclusion, the values obtained with the H-TDMA agreed very well with those measured with the UF-TDMA for the same dry size, not only on average but also regarding the temporal variation. This result is somewhat surprising, considering that the other instrument was sampling well above the canopy top and the other one inside the canopy.

During 5 April, the nucleation starts between 9:00 and 10:00 and the total particle concentration shows a minimum at ca. 11:00 and increases again. The same structure is also seen from the growth

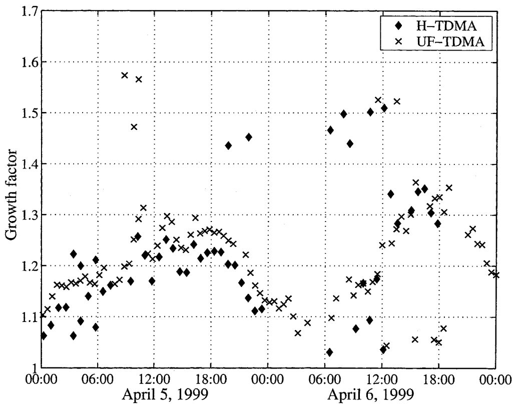

Fig. 5. The growth factors for 20 nm particles during the case study, 5–6 April 1999, sampled 50 m above the canopy (UF-TDMA) and within the canopy (H-TDMA).

factor data, but with a short time lag of ca. 1 h (Fig. 5). Even if the growth factors of nucleation mode particles starts increasing before nucleation is observed, there seems to be a clear connection in the fine structure of the total concentration and growth factors. The nucleation always starts before the particles are detected due to limitations of the instruments in the smallest particle sizes. This fact supports the connection between the change in growth factors and particle concentrations.

During 6 April, the nucleation takes place later, starting at ca. 12:00. The total particle concentration increases, levels off and shows a maximum at ca. 16:00. Once again, the growth factors follow similar trends with the maximum values within 1 h from the concentration maximum. The high number seems to be well connected with high solubility of the particles.

4.1.2. RH response of nucleation mode particles. The response of the nucleation mode particles on changing RH was studied during a nucleation event day 19 April 1999. The RH was varied between 70% and 90%. The particles already appeared hygroscopic at RH = 70%, showing no deliquescence. The GF at RH = 70% was ca. 1.1. which excludes the possibility that the soluble fraction of the particle consists of ammonium sulphate only. There are basically 2 possibilities: (i) the soluble component of the particles is a species that undergoes deliquescence well before 70% RH. This would be the case, for instance, for ammonium bisulfate or sulphuric acid. The other possibility is that (ii) the soluble fraction of the particles is a mixture of several chemical components with combined deliquescence below 70% (Dick et al., 2000).

4.2. *Aitken mode particles*

The Aitken mode particles (35, 50 and 73 nm) were measured with both the H-TDMA and CCN counters. These instruments we located at the Tapiola sampling site within the forest canopy, and thus they were sampling the same aerosol.

4.2.1. H-TDMA. The H-TDMA data imply that it is essentially the less-hygroscopic particle group that is linked to particle formation and growth, not the more-hygroscopic particles. During the nucleation events, the less-hygroscopic particle group totally dominates the 35-, 50- and 73-nm particle concentrations. The less-hygroscopic particles have growth factors between 1.0–1.4. This is much less than the growth factors for particles consisting of pure ammonium and sulphate salts, but of the same magnitude as those of many organic compounds including monoterpene oxidation products (Virkkula et al., 1999).

Similarly to the nucleation mode particles, the Aitken mode less-hygroscopic growth factors also exhibit a diurnal pattern during nucleation days and the diurnal variation of the hygroscopic growth factors is nearly identical for all the particle sizes. All these growth factors start increasing at ca. 06:00, from a low value around 1.1 to 1.2–1.4 at 12:00. Then, the growth factors are relatively constant until 20:00–21:00, when they decrease again.

The interpretation of this behaviour is that all particle sizes (nucleation and Aitken mode) are affected by condensation of the same vapours. In this way, particles of larger sizes that were not formed in the nucleation event but remained as a background aerosol from previous days, also increase their volume fraction of the condensate. The volume fraction of the condensate is expected to increase less as the particle size increases (Aitken mode), since the original "core" particle is considerably larger.

4.2.2. CCN counter. The soluble fraction obtained from the CCN data was always found to be quite low. Minimum values found were around 0.2 and maximum close to 0.4. The data showed clear diurnal variation in solubility. The activation efficiency was lower during the daytime than during the night, indicating the possibility of occurrence of internally mixed aerosol during the daytime. The particles start to activate when particle diameter is around 70 nm.

The soluble mass fraction obtained from CCN measurements can be compared with those from H-TDMA data. The lower two particle sizes (50 and 73 nm) were used in comparison. In order to compare the H-TDMA data showing external mixture (more than one soluble fraction) with CCNC data (always only one soluble fraction), the H-TDMA values were first calculated to concentration weighed average values of the soluble fraction. The largest particle size was shown to activate efficiently, even in the lowest supersaturation, and therefore no activation threshold was obtained. The comparisons between H-TDMA and CCN counter results are shown in Fig. 6. The overall agreement between the 2 independent data sets seems good, considering the various assumptions done for both data sets (e.g., assumption of particles consisting of ammonium sulphate and insoluble fraction, assumption that the aerosol is homogeneous over measurement cycle, and instrument and data analysis characteristics as described in Section 2.). Not only the average values, but also the diurnal behaviour is shown to agree well. As the measurements were not synchronised, we used values that were within a 30 min time window. Even though the amplitude of the diurnal variation (low values night time, high values day time) seems smaller for the CCN data than H-TDMA data, the agreement seems surprisingly good. This is especially so, when considering that the soluble fraction was determined in 2 different RH values: H-TDMA data based on solubility at RH = 90%, and CCN counter data at water supersaturation. This result is additionally supported by model calculations (see Subsection 4.5) using the impactor data. The model calculations show little difference for the soluble fraction, whether obtained at RH = 90% or at water supersaturation.

4.3. Accumulation mode particles

The hygroscopic properties of particles in the accumulation mode size range (about 80 nm or more in diameter) are likely to be less affected by the condensation and coagulation processes that shape the smaller particles. The accumulation mode particles are more representative of the regional background aerosol, and are not necessarily of boreal origin. Consequently, the particle hygroscopic properties were seen to differ clearly between accumulation mode particle and smaller particles.

The accumulation mode is characterised by 2 commonly observed growth modes (dry particle sizes 109, 166, 264 and 365 nm). More hygroscopic

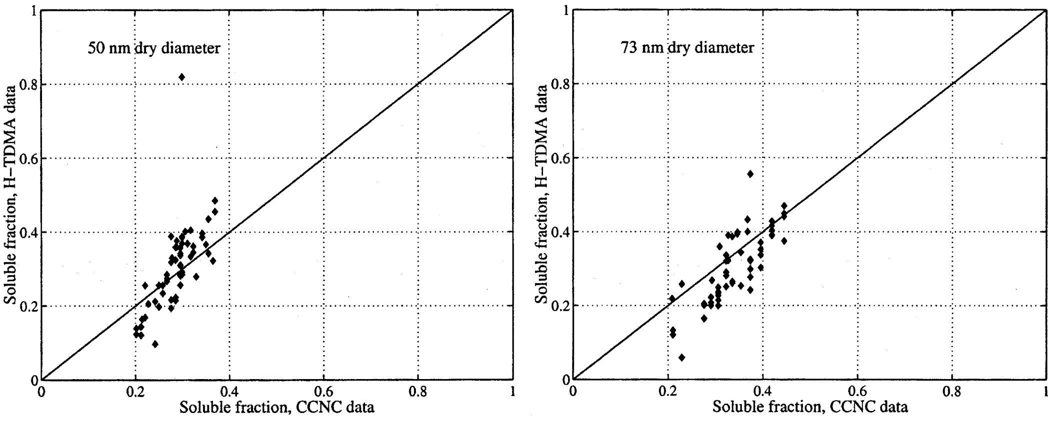

Fig. 6. The comparisons between soluble fractions obtained from the H-TDMA and CCN counter results during BIOFOR III period. The comparison is made with values within a 30 min time window for 50 nm and 73 nm dry particles.

particles with GF ca. 1.6 have been detected during 95% of the measurements and the less hygroscopic particles GF ca. 1.1 during approximately 85% of the measurements. Typical examples of data are shown for the case study period (5–6 April) for 264-nm particles in Fig. 7.

The accumulation mode particle properties are supposed to be much less affected by the condensation of vapours than the smaller particle properties. According to measurements, this hypothesis is valid. Nevertheless, the diurnal behaviour that was observed for nucleation and Aitken mode particles is visible even in accumulation mode only with much smaller amplitude.

4.4. *Coarse mode particles*

The coarse mode particle growth factors were determined comparing simultaneous dry and wet-ambient size distributions. The growth factors are derived for periods of moderately high to high relative humidities (50–100%), through comparison of the wet and dry distributions, since for lower humidities, there can be little or no difference between the wet and dry distributions. When the growth factor is derived for dry to ambient humidity, the growth factor is then normalised to 90% relative humidity for comparison with TDMA growth factor measurements.

For comparison with the accumulation mode growth factors, the largest size data from the H-TDMA (0.365 µm) is compared to 1.8 µm growth factors derived from the APS/CSASP data normalised to 90%. For the H-TDMA data, normally 2 growth factor modes are encountered: a less-hygroscopic and a more-hygroscopic mode. The relative contribution of each solubility mode is weighted, to derive a combined effective growth factor for comparison with the APS/CSASP data, since these instruments can not differentiate between individual growth-factor modes.

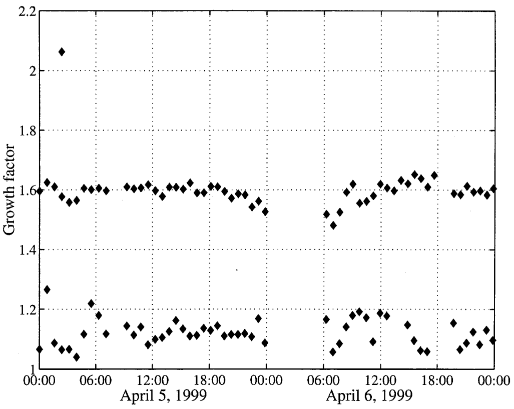

Fig. 7. The growth factors for 264-nm particles during 5–6 April 1999, from the H-TDMA data set (sampled within the canopy).

Comparison of data for 10 days during the BIOFOR III campaign, illustrates periods where the coarse mode exhibits similar growth factors to the accumulation mode along with periods where noticeable differences are also encountered. Fig. 8a illustrates one day (2 April) where very similar growth factors are encountered in both modes, with values of approximately 1.6 around noon, decreasing to approximately 1.1 later in the evening, and then rising back to 1.5 towards midnight.

By comparison, significantly different growth factors between both modes are observed on, e.g., 13 April. A consistent difference is observed throughout the day with accumulation mode growth factors of the order of 1.4–1.6, while coarse-mode growth factors remain between 1–1.3 (Fig. 8b). It should be noted that some values of 0.9 are observed for the coarse mode, however, this is an indication of the error in the method used.

In summary, similar growth factors were encountered approximately 50% of the time (taking 10 days into account) suggesting that coarse-mode particles possess different hygroscopic properties, and composition, from accumulation-mode properties for a significant fraction of the time. When deviations occur between accumulation-mode and coarse-mode growth factors, the coarse mode is always less soluble than the accumulation mode.

4.5. *Comparison between measured and modelled soluble fractions*

The soluble fraction was usually calculated from the experimental growth factor, using the assumption that the soluble part of the particle consisted of ammonium sulphate salt only. The method relies on the correctness of this assumption. Nevertheless, this method is widely used and does not need any supporting data, though the calibration value for the ammonium sulphate response

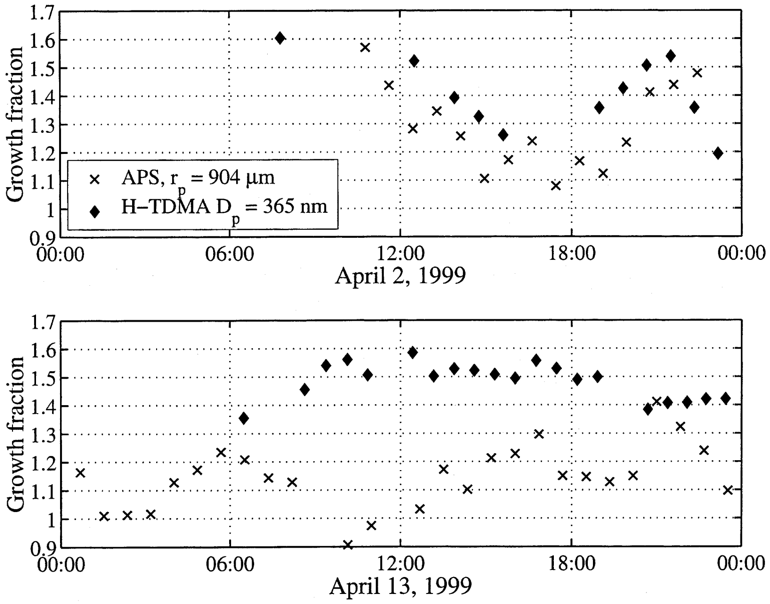

Fig. 8. The coarse mode particle growth factors for 2 example days, 2 April and 30 March, are presented, together with accumulation mode average growth factor. The coarse-mode growth factor is obtained using simultaneous dry and ambient size distributions (see text for details).

of the instruments at the conditions where ambient aerosol, is measured. As the focus of the BIOFOR campaign is to investigate the formation of new particles, the analysis here is also presented for the smallest particle size possible, 20 nm. The soluble fraction for UF-TDMA 20 nm data set is presented in Fig. 9 for days 5 and 6 April. These days overlap the "event impactor sample 2" (sampling dates: 2, 4, 5, 6, 8, 10 April during the event periods, see also Mäkelä et al. (2001)).

To check the simplified method, the more detailed growth model presented in Section 3 was applied to the ionic concentrations from the "event impactor sample 2". The ions analysed are presented elsewhere in Mäkelä et al. (2001). The mass fractions of the soluble material for the single growth factor measurements have been estimated under the assumption that the individual particle soluble part has the same composition as the impactor sample (i.e., internal mixture). Here, it must be emphasised that the time scales of the impactor-sampling and the growth-factor measurements are different. While the impactor sample has been taken over 6 days with nucleation events (only the hours when nucleation mode particles

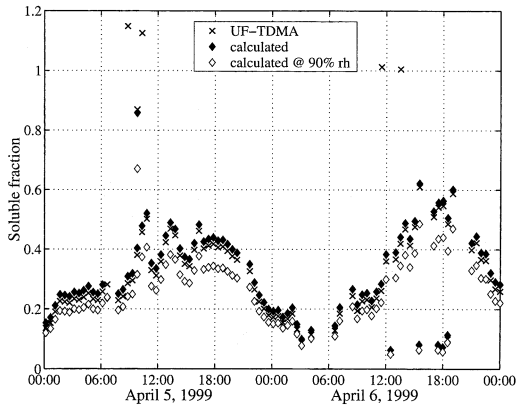

Fig. 9. The soluble mass fractions for 20-nm dry particles, obtained from the model based on ionic composition of the impactor sample and the assumption of ammonium sulphate, are compared for the case study period, 5–6 April 1999. 2 different values based on the impactor sample are shown. The other value shows the soluble fraction in RH = 90%, which is directly comparable with the TDMA measurements. The other value is calculated for supersaturated conditions, where nearly all salts and acids are dissolved, and represents the situation in cloud formation processes (see text for more details).

were present), the growth factor measurements are integrated over a few minutes only. As the ionic concentrations vary with time, the composition of the water soluble material during one growth factor measurement can differ from the impactor sample. Based on better information about the chemical composition than the assumption of pure ammonium sulphate only, nonetheless also the more detailed growth model gives only an estimate of the water soluble mass fraction. In Fig. 9, the soluble mass fractions obtained from the more detailed model and the assumption of ammonium sulphate are compared. The soluble fractions are shown to agree well for both methods used. In the impactor sample, ammonium bisulphate, ammonium sulphate and sodium sulphate have been the major salts. The soluble fractions for 90% relative humidity obtained by using the measured ionic concentration, are shown to be on average 85% of those based on the assumption of ammonium sulphate aerosol.

From the composition of the impactor sample 2 values for the soluble mass fractions have been calculated. The first value is typical for conditions in cloud water, where nearly all salts and acids are dissolved. Only calcium sulphate is considered as insoluble here. Using the concentrations of the measured ions only, this gives a soluble mass fraction of 0.975 (the rest is calcium and sulphate considered as calcium sulphate). Then, insoluble material (e.g., part of the organic material, soil dust) is added to match the measured growth factor. The second value of the soluble mass fraction is for 90% relative humidity. Here sodium sulphate, potassium sulphate, magnesium sulphate, calcium sulphate and oxalic acid are considered as not dissolved, as they have higher deliquescence humidities than 90%. This decreases the soluble mass fractions by approximately 25%.

The diurnal cycle of the growth factors can be explained by varying soluble mass fractions. In Fig. 9, the particles show a drastic change of their composition during the day. During noontime, the soluble mass fraction of the 20 nm particles is around 50% whereas during the night it is around 10%.

The diurnal behaviour explained here is based on the assumption that the relative ionic composition stays constant over the whole impactor sample with no time dependent behaviour other than the absolute concentration. In addition, we point out here that the soluble fraction shown in Fig. 9. is based on the values obtained from the TDMA measurements. Completely independent values for the soluble fraction would require the impactor total mass versus ionic mass data, which was not available for this study.

5. Discussion

The main finding of the measurements concerning the hygroscopic and CCN properties of aerosol particles during formation and growth events in boreal forest sites was the diurnal pattern of particle growth-factor and solubility. The pattern was strongest for particles in nucleation and Aitken mode. The lowest growth factors were detected during late evening and early morning and the maximum was observed during noon–afternoon. The highest soluble fractions were determined for nucleation-mode particles. The response of hygroscopic growth to changes of relative humidity suggest that the soluble compounds are either fully soluble or deliquescent well before 70% RH.

The growth factors started to increase systematically 2–4 h before the nucleation burst was observed. The increase in growth factors correlates with both the increase of sulphuric acid and the day-time oxidation products of organic gases (Janson et al., 2001). Obviously, the condensable species were present in air before the new particles were detected with the DMPS, and the condensation took place onto the surfaces of the pre-existing particles of the nucleation mode. However, it has to be noticed that the aerosol instrumentation is only capable of determining particle sizes larger than about 3 nm, and therefore the nucleation happened some time before the number concentration started to increase.

The origin of the new particles is the main question related to the observations presented in this paper. The nucleation and condensation could be coupled in such a way that the nucleating vapour also condenses onto the surfaces of the pre-existing aerosol particles, or there could be different vapours responsible for the nucleation and condensation. The key species could be emitted from the forest and therefore have biogenic origin, or they may be transported with the air masses to the measurement site. Most likely, both sources are important in the process of particle formation and growth.

The most discussed compounds in the literature are sulphuric acid and monoterpene oxidation products. The sulphuric acid is probably the most traditional candidate for nucleating species. Recently, Korhonen et al. (1999) studied the ternary nucleation of sulphuric acid–water–ammonia. The sulphuric acid concentrations during a nucleation burst are high enough for ternary homogeneous nucleation to take place (Kulmala et al., 2001a). Similar conclusion is presented by Janson et al. (2001), based on their SO_2 measurements during the campaigns. However, as they point out, the sulphuric acid concentrations are not high enough to explain the growth of particles to observable sizes. Janson et al. (2001) also present the source term for sulphuric acid, which has a similar daily pattern that we observe for the hygroscopic growth factors, supporting the idea that ternary nucleation is followed by (multicomponent) condensation including sulphuric acid.

Another compound worth mentioning is dimethylamine (Mäkelä et al., 2001). It is a volatile organic base which behaves much like atmospheric ammonia. The dimethylamine was observed in the particulate phase only during particle formation event days. This observation also supports the hypothesis that nucleation is caused by sulphuric acid, possibly with ammonia and/or dimethylamine as neutralising compound.

The rôle of monoterpenes and their oxidation products is clearly much more complicated. The monoterpenes had higher concentrations during August (no nucleation) compared with March–April, when the nucleation events were observed (Janson et al., 2001). In addition, the concentration had maximum during the night time. However, the temperatures at the onset of the nucleation events were typically between -3 and $+7$°C, which are relatively low temperatures, indicating that even though the monoterpene emissions were also relatively low, the nucleation and condensation of the monoterpene oxidation products were favored. After careful examination of the monoterpene emissions, concentrations or oxidation-product source terms, Janson et al. (2001) concluded that there is no indication that the monoterpenes were connected to the nucleation events.

Even if the monoterpenes were not responsible for the nucleation itself, the concentrations were high enough to cause significant condensation of the monoterpene oxidation products (Janson et al., 2001). As the monoterpenes are in general oxidized by various compounds (OH radical, ozone, nitrate radical) which dominate during different times of a day, the oxidation process (as well as concentrations) has probably a diurnal pattern. This is also noticed by Leaitch et al. (1999), who concluded that a significant mass of fine aerosol during a particle formation event in a forest was associated with variations in isoprene and products from the oxidation of α- and β-pinene. The monoterpene oxidation products probably became more soluble before and during the start of the nucleation event due to oxidation by OH radical (Saxena and Hildemann, 1996), coinciding with the increase of sulphuric acid source term. As a matter of fact, the behaviour of growth factor was seen to follow the diurnal pattern even during several days with no clear nucleation detected (e.g., 24 and 29 March; 3, 18, 20 and 21 April), indicating that the total of condensable species (e.g., organics, sulphuric acid) had a diurnal pattern independent of nucleation phenomenon. Janson et al. (2001) also discussed other factors that connect the diurnal pattern of growth factors with the observations of the precursor gases.

The rapid decrease of the growth factor during the late afternoon, which was the case despite that the nucleation mode particles were present in continuous manner, cannot be explained quantitatively using the available data. Based on the results of Janson et al. (2001) and Mäkelä et al. (2001), it is possible that organic compounds are involved in the process, as the decrease of growth factor correlates with the source term of the monoterpene oxidation products, by nitrate radical and ozone. However, this speculation needs to be verified in future investigations.

6. Summary and conclusions

This study presents the hygroscopic and CCN properties of the whole size distribution during the BIOFOR campaigns in the boreal forest. The main finding was the diurnal pattern of particle growth factor and solubility. The pattern was strongest for particles in the nucleation and Aitken modes. The lowest growth factors were detected during the night-time and early morning, and the maximum was observed during noon–afternoon.

The accumulation mode in a boreal forest site is characterised by 2 commonly observed growth modes. More hygroscopic particles with GF ca. 1.6 have been detected during 95% of the measurements and the less hygroscopic particles GF ca. 1.1, approximately during 85% of the measurements. The diurnal behaviour that was observed for nucleation and Aitken mode particles is also visible in the accumulation mode only with a much smaller amplitude.

Differences between wet and dry spectra measured using APS and CSASP spectrometer probes were used to derive growth factors for coarse mode particle sizes. Growth factors for coarse mode particles ranged between 1.0 and 1.6. There is no specific reason to expect the coarse mode particle properties to be connected with those of particles in other size modes. Nevertheless, agreement between the evolution of growth factors with time for accumulation and coarse modes was regularly observed. However, similar portions of the data set also indicated clear differences, and consequently different chemical compositions between the modes. When these clear differences between both modes were observed, the coarse mode always behaved in a less hygroscopic manner with growth factors near one.

The data obtained was used in analysis, focussing on the rôle of monoterpene emissions as well as other condensable species in the particle formation events. The hygroscopic growth factors as an indicator of chemical composition, show clearly that there is a strong diurnal cycle during event days. This variation can also be seen at non-event days. At the studied days, the variation is correlated with the gas-phase concentrations of inorganic and organic components. Qualitatively, the soluble fraction seems to correlate with the presence of sulphuric acid and monoterpene oxidation products. However, the sulphuric acid concentrations appear too low to explain the main part of the hygroscopic growth. A deeper understanding of both nucleation and condensation growth processes can most likely be gained when these observations are compared with the predictions from an aerosol dynamics model.

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REFERENCES

Aalto, P., Kulmala, M. and Nilsson, E. D. 1995. Nucleation events on the Värriö environmental measurement station. *J. Aerosol Sci.* **26S**, 411–412.

Aalto, P. and Kulmala, M. 2000. Using a cloud condensation nuclei counter to study CCN properties and concentrations. *Boreal Environment Research* **5**, 349–359.

Aalto, P., Hämeri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J., Hoell, C., O'Dowd, C., Karlsson, H., Hansson, H.-C., Väkevä, M., Koponen, I. and Kulmala, M. 2001. Physical characterization of aerosol particles during nucleation events. *Tellus* **53B**, 344–358.

Bigg, E. K. 1986. Discrepancy between observation and prediction of concentrations of cloud condensation nuclei. *Atmos. Res.* **20**, 82–86.

Covert, D. S., Gras, J. L., Wiedensohler, A. and Stratmann, F. 1998. Comparison of directly measured CCN with CCN modeled from the number-size distribution in the marine boundary layer during ACE 1 at Cape Grim, Tasmania. *J. Geophys. Res.* **103**, 16,597–16,608.

Dick, W. D., Saxena, P. and McMurry, P. H. 2000. Estimation of water uptake by organic compounds in submicron aerosols measured during the Southeastern Aerosol and Visibility Study. *J. Geophys. Res.* **105**, 1471–1479.

Gerber, H. 1988. Relative humidity parameterization of the lognormal size distribution of ambient aerosols. In: *Lecture notes in physics* **309** (Eds. Paul E. Wagner and Gabor Vali). Springer Verlag, Berlin, pp. 237–238.

Hämeri, K., Kulmala, M., Aalto, P., Leszynski, K., Visuri, R. and Hämekoski, K. 1996. The investigations of aerosol particle formation in urban background area of Helsinki. *Atmos. Res.* **41**, 281–298.

Hämeri, K., Charlson, R. J., Hansson, H.-C. and Jacobson, M. 1998. Hygroscopic properties of ammonium sulfate aerosol particles mixed with slightly soluble organic compound. *J. Aerosol Sci.* **29S**, 587–588.

Hämeri K., Väkevä M., Hansson H.-C. and Laaksonen A. 2000. Hygroscopic growth of ultrafine ammonium sulphate aerosol measured using an ultrafine tandem differential mobility analyser. *J. Geophys. Res.* **105**, 22,231–22,242.

Hänel, G. 1976. The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air. *Advances in Geophysics* **19**, 73–188.

Hänel, G. 1984. The physical chemistry of atmospheric particles. In: *Hygroscopic aerosols* (eds. L. H. Ruhnke and A. Deepak). A. Deepak Publishing, Hampton, VA, 1–20.

Hansson, H.-C., Rood, M. J., Koloutsou-Vakakis, S., Hämeri, K., Orsini, D. and Wiedensohler, A. 1998. NaCl aerosol particle hygroscopicity dependence on mixing with organic compounds. *J. Atmos. Chem.* **31**, 321–346.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C. and Seinfeld, J. H. 1997. Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem.* **26**, 189–222.

Hoppel, W. A. 1979. Measurement of the size distribution and CCN supersaturation spectrum of submicron aerosols over the ocean. *J. Atmos. Sci.* **36**, 2006–2014.

Hoppel, W. A., Frick, G. M. and Fitzgerald, J. W. 1996. Deducing droplet concentration and supersaturation in marine boundary layer clouds from surface aerosol measurements. *J. Geophys. Res.* **101**, D21, 26,553–26,565.

Janson, R., Rosman, K., Karlsson, A. and Hansson, H.-C. 2001. Biogenic emissions and gaseous precursors to the forest aerosol. *Tellus* **53B**, 423–440.

Kavouras, I. G., Mihalopoulos, N. and Stephanou, E. G. 1998. Formation of atmospheric particles from organic acids produced by forests. *Nature* **395**, 683–686.

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R. and Seinfeld, J. H. 1999. Ternary nucleation of H_2SO_4, NH_3 and H_2O in the atmosphere. *J. Geophys. Res.* **104**, 26,349–26,353.

Korhonen, P., Laaksonen, A., Batris, E. and Viisanen, Y. 1998. Thermodynamics for highly concentrated water — ammonium sulfate solutions. *J. Aerosol Sci.* **29S**, 379–380.

Kulmala M., Korhonen P., Vesala T., Hansson H.-C., Noone K. and Svenningsson B. 1996. The effect of hygroscopicity on cloud droplet formation *Tellus* **48B**, 347–360.

Kulmala, M., Hämeri, K., Aalto, P. P., Mäkelä, J. M., Pirjola, L., Nilsson, E. D., Buzorius, G., Rannik, Ü., Dal Maso, M., Seidl, W., Hoffmann, T., Janson, R., Hansson, H.-C., Viisanen, Y., Laaksonen, A. and O'Dowd, C. D. 2001a. Overview of the international project on Biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* **53B**, 327–343.

Kulmala, M., Dal Maso, M., Mäkelä, J. M., Pirjola, L., Väkevä, M., Aalto, P., Miikkulainen, P., Hämeri, K. and O'Dowd, C. D. 2001b. On the Formation, growth and composition of nucleation mode particles. *Tellus* **53B**, 479–490.

Leaitch, W. R., Bottenheim, J. W., Biesenthal, T. A., Li, S. M., Liu, P. S.K., Asalian, K., Dryfhout-Clark, H., Hopper, F. and Brechtel, F. 1999. A case study of gas-to-particle conversion in an eastern Canadian forest. *J. Geophys. Res.* **104**, 8095–8111.

Liu, P. S.K., Leaitch, W. R. and Banie, C. M. 1996. Comparisons between hydrated and dehydrated aerosol particle size distributions. In: *Nucleation and atmospheric aerosols 1996*, Kulmala, M. and Wagner, P. E. (eds.): Proceedings of the 14th International Conference on Nucleation and atmospheric aerosols. Elsevier Science Limited.

McMurry, P. H. and Stolzenburg, M. R. 1989. On the sensitivity of particle size to relative humidity for Los Angeles aerosols. *Atmos. Environ.* **23**, 497–507.

Mäkelä, J. M., Aalto, P., Jokinen, V., Pohja, T., Nissinen, A., Palmroth, S., Markkanen, T., Seitsonen, K., Lihavainen, H. and Kulmala, M. 1997. Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys. Res. Lett.* **24**, 1219–1222.

Mäkelä, J. M., Hämeri, K., Väkevä, M., Aalto, P., Laakso, L., Kulmala, M. and Charlson, R. J. 1998. On the spatial scale of new aerosol particle formation in southern Finland. *J. Aerosol Sci.* **29S**, 215–216.

Mäkelä, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinilä, K., Sillanpää, M., Koponen, I. K., Paatero, J., Rosman, K. and Hämeri, K. 2001. Chemical composition of aerosol during particle formation events in Boreal forest. *Tellus* **53B**, 380–393.

Marti, J. J., Weber, R. J., McMurry, P. H., Eisele, F., Tanner, D. and Jefferson, A. 1997. New particle formation at a remote continental site: Assessing the contributions of SO_2 and organic precursors. *J. Geophys. Res.* **102**, 6331–6339.

Nilsson, E. D. Paatero, J. and Boy, M. 2001. Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer. *Tellus* **53B**, 462–478.

O'Dowd, C. D., Geever, M., Hill, M. K., Smith, M. H. and Jennings S. G. 1998. New particle formation: Nucleation rates and spatial scales in the clean marine coastal environment. *Geophys. Res. Lett.* **25**, 1661–1664.

Pandis, S. N., Wexler, A. S. and Seinfeld, J. H. 1995. Dynamics of tropospheric aerosols. *J. Phys. Chem. Res.* **99**, 9646–9659.

Pitchford, M. L. and McMurry, P. H. 1994. Relationship between measured water vapor growth and chemistry of atmospheric aerosol for Grand Canyon, Arizona, in winter 1990. *Atmos. Environ.* **28**, 827–839.

Rivera-Caprio, C. A., Corrigan, C. E., Novakov, T., Penner, J. E., Rogers, C. F. and Chow, J. C. 1996. Derivation of contributions of sulfate and carbonaceous aerosols to cloud condensation nuclei from mass size distributions. *J. Geophys. Res.* **101**, 19,483–19,493.

Saxena, P. and Hildemann, L. M. 1996 Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. *J. Atm. Chemistry* **24**, 57–109.

Saxena, P., Hildemann, L. M., McMurry, P. H. and

Seinfeld, J. H. 1995. Organics alter hygroscopic behavior of atmospheric particles. *J. Geophys. Res.* **100**, 18,755–18,770.

Schröder, F. and Ström, J. 1997. Aircraft measurements of sub micrometer aerosol particles (> 7 nm) in the midlatitude free troposphere and tropopause region. *Atmos. Res.* **44**, 333–356.

Seidl, W. and Dlugi, R. 1991. Modelling of ionic concentrations and sulfate production in cloud droplets: Use of published aerosol data. *Fresenius J. Anal. Chem.* **340**, 598–604.

Svenningsson, I. B., Hansson, H.-C., Wiedensohler, A., Ogren, J. A., Noone, K. J. and Hallberg, A. 1992. Hygroscopic Growth of Aerosol Particles in the Po-Valley. *Tellus* **44B**, 556 - 569.

Svenningsson, I. B., Hansson, H.-C., Wiedensohler, A., Noone, K., Ogren, J., Hallberg, A. and Colville, R. 1994. Hygroscopic Growth of Aerosol Particles and its Influence on Nucleation Scavenging in Cloud: Experimental Results from Kleiner Feldberg. *J. Atm. Chemistry* **19**, 129–153.

Swietlicki, E., Zhou, J., Berg, O. H., Martinsson, B. G., Frank, G., Cederfelt, S.-I., Dusek, U., Berner, A., Birmili, W., Wiedensohler, A., Yuskiewicz, B. and Bower, K. N. 1999. A closure study of sub-micrometer aerosol particle hygroscopic behaviour. *Atm. Res.* **50**, 205–240.

Swietlicki, E., Zhou, J., Covert, D. S., Hämeri, K., Busch, B., Väkevä, M., Dusek, U., Berg, O. H., Wiedensohler, A., Aalto, P., Mäkelä, J., Martinsson, B. G., Papaspiropoulos, G., Mentes, B., Frank, G. and Stratmann, F. 2000. Hygroscopic properties of aerosol particles in the north-eastern Atlantic during ACE-2. *Tellus* **52B**, 201–227.

Tang, I. N. and Munkelwitz, H. R. 1994. Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. *J. Geophys. Res.* **99**, 18,801–18,808.

Twomey, S. 1977. *Atmospheric aerosols*, Elsevier, New York.

Virkkula, A., Van Dingenen, R., Raes, F. and Hjorth, J. 1999. Hygroscopic properties of aerosol formed by oxidation of limonene, α-pinene, and β-pinene. *J. Geophys. Res.* **104**, 3569–3579.

Väkevä M., Hämeri K., Puhakka T., Nilsson D., Hohti H. and Mäkelä, J. M. 2000. Effects of meteorological processes on aerosol particle size distribution in an urban background area. *J. Geophys. Res.* **105**, 9807–9821.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J. and Jefferson, A. 1997. Measurements of new particle formation and ultrafine particle growth rates at a clean continental site. *J. Geophys. Res.* **102**, 4376–4385.

Wiedensohler, A., Aalto, P., Covert, D., Heintzenberg, J. and McMurry, P. 1993. Intercomparison of tree methods to determine size distributions of ultrafine aerosols with low number concentrations. *J. Aerosol Sci.* **4**, 551–554.

Zhang, X. Q., McMurry, P. H., Hering, S. V. and Casuccio, G. S. 1993. Mixing Characteristics and Water Content of Submicron Aerosols Measured in Los Angeles and at the Grand Canyon. *Atmos. Environ.* **27A**, 1593–1607.