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Aerosol hygroscopicity and CCN activation kinetics in a boreal forest environment during the 2007 EUCAARI campaign

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Abstract

Measurements of size-resolved cloud condensation nuclei (CCN), subsaturated hygroscopic growth, size distribution, and chemical composition were collected from March through May, 2007, in the remote Boreal forests of Hyytiälä, Finland, as part of the European Integrated project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) campaign. Hygroscopicity parameter, κ, distributions were derived independently from Continuous Flow-Streamwise Thermal Gradient CCN Chamber (CFSTGC) and Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) measurements. CFSTGC-derived κ values for 40, 60, and 80 nm particles range mostly between 0.10 and 0.40 with an average of 0.20 ± 0.10; this is characteristic of highly oxidized organics and reflect their dominant influence in this environment. HTDMA-derived κ were generally 30 % lower. Diurnal trends of κ show a minimum at sunrise and a maximum in the late afternoon; this trend covaries with inorganic mass fraction and the *m/z* 44 organic mass fraction given by a quadrupole aerosol mass spectrometer, further illustrating the importance of ageing on aerosol hygroscopicity. The chemical dispersion inferred from the observed κ distributions indicates that while 60 and 80 nm dispersion increases around midday, 40 nm dispersion remains constant. Additionally, 80 nm particles show a markedly higher level of chemical dispersion than both 40 and 60 nm particles. An analysis of droplet activation kinetics for the sizes considered indicates that the CCN activate as rapidly as $(NH_4)_2SO_4$ calibration aerosol.

1 Introduction

Atmospheric aerosols are known to have a direct effect on climate through scattering and absorbing incoming solar radiation (IPCC, 2007). They also indirectly affect climate by acting as cloud condensation nuclei (CCN), and modifying cloud forcing and the hydrological cycle (Twomey, 1974, 1977). While it is generally thought that aerosols produce an overall cooling effect, the indirect effect remains a large source of

ACPD

11, 15029–15074, 2011

uncertainty in predictions of anthropogenic climate change (e.g., IPCC, 2007). For this reason, the study of aerosol and their CCN properties is necessary for an improved understanding of aerosol-cloud-climate interactions.

The ability of an aerosol particle to act as CCN depends on both its size and composition (Köhler, 1936; Seinfeld and Pandis, 2006). Köhler theory uses thermodynamic arguments to describe how changes in curvature (known as the Kelvin effect) and the amount of solute (known as the Raoult effect) impact the equilibrium vapor pressure of a droplet. Using this theory, the critical supersaturation, above which an aerosol particle "activates" spontaneously into a cloud droplet, can be predicted. While originally developed for inorganic salts, Köhler theory can be extended to include effects of organics through their contribution of solute and surface tension depression (e.g., Shulman et al., 1996; Li et al., 1998; Raymond and Pandis, 2002). κ-Köhler theory (Petters and Kreidenweis, 2007) parameterizes solute contribution in terms of a single hygroscopicity parameter, κ, that represents a "scaled" volume fraction of soluble material in the particle (Lance, 2007; Padró et al., 2010). Typical soluble salts found in the atmosphere such as ammonium sulfate or sodium chloride have values of $\kappa \approx 0.6$ and $\kappa \approx 1.25$, respectively (Petters and Kreidenweis, 2007), while $\kappa = 0$ corresponds to a completely insoluble, wettable particle that does not affect water activity via adsorption (Kumar et al., 2011). Lab and field studies show that κ of secondary organic aerosol (SOA) typically ranges between 0.1 and 0.2 (e.g., Prenni et al., 2007; Gunthe et al., 2009; Dusek et al., 2010; Engelhart et al., 2008, 2011; Asa-Awuku et al., 2009; Sihto et al., 2010), although the water-soluble fraction extracted from a range of SOA systems and biomass burning exhibits $\kappa \approx 0.3$ (Asa-Awuku et al., 2010; Padró et al., 2010; Engelhart et al., 2008, 2011). For many locations, on average, κ values for continental and marine aerosols have been typically found to be 0.3 ± 0.2 and 0.7 ± 0.2, respectively (e.g., Andreae and Rosenfeld, 2008; Pringle et al., 2010); however, assuming a constant κ can introduce a sizeable uncertainty in CCN number predictions (e.g., Chang et al., 2010; Pöschl, 2011).

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Size-resolved CCN measurements offer unique insight on compositional dispersion and the processes that affect aerosol hygroscopicity (e.g., Lance, 2007; Padró et al., 2007, 2010; Gunthe et al., 2009; Petters et al., 2009; Rose et al., 2010; Asa-Awuku et al., 2009, 2010; Mochida et al., 2010; Irwin et al., 2011; Bougiatioti et al., 2011). Petters et al. (2009) found that κ from emissions of fresh biomass burning generally decreased with particle size, although varying κ distributions and several hygroscopic modes may occur. During the AMAZE-08 Campaign at a remote site in Brazil, Aitken mode particles (50 nm) had κ of 0.1, characteristic of the hygroscopicity of biogenic SOA, while accumulation mode (200 nm) particles had an increased κ of 0.2, correlating with a 10 % increase in sulfate (Gunthe et al, 2009; Pöschl et al., 2010). In Finokalia, Crete, however, Bougiatioti et al. (2011) found that smaller particles (40 nm) generally had κ about 0.1 units greater than that of larger particles (100 nm). While the previous studies showed size-dependent hygroscopicity, Mochida et al. (2010) found that, for 34 particle sizes ranging from 24.1 to 359 nm sampled in Cape Hedo, Okinawa, Japan, the particles typically showed unimodal, high hygroscopicity likely from internal mixing with ammonium sulfate.

Bulk and size-resolved measurements of aerosol composition are important for further deconvolving the effects of composition on CCN properties and behavior. In a study of CCN closure, Lance et al. (2009) showed that average CCN overprediction bias during the GoMACCS field mission in Houston, Texas, was reduced from 36 % to 3 % when bulk aerosol chemical composition from an Aerosol Mass Spectrometer (AMS) was included. Bougiatioti et al. (2009, 2011) obtained underprediction bias as low as 0.6 ± 9 % when including bulk composition measurements from analysis of PTFE and quartz filter samples in the Eastern Mediterranean during the FAME07 campaign. While certain conditions or environments allow for a reasonable comparison of bulk composition data with smaller aerosol particles, this may not always be the case. Medina et al. (2007) overpredicted CCN by 35.8 ± 28.5 % in a CCN closure study when using AMS size-averaged chemical composition, but only 17.4 ± 27.0 % when using size-dependent composition during the ICARTT 2004 campaign at a rural site in New Hampshire. Gunthe et al. (2009) also found for a pristine tropical rainforest environment that the high bias in predicted CCN to measured CCN was a result of using bulk rather than size-resolved AMS data. Beyond CCN closure, composition measurements are able to elucidate the physicochemical processes occurring in the atmosphere. For AMS measurements, in particular, while it is not possible to identify individual organic aerosol (OA) compounds from the measured mass spectra, an estimate of oxidation state can be derived from the mass fraction of the *m/z* 44 peak (CO_2^+) in the organic aerosol signal, f_{44}, (originating mainly from decomposition of carboxyl groups during the ionization step in the AMS). f_{44} has been shown to correlate with O/C ratio in aerosol particles (Aiken et al., 2008) and the hygroscopicity of SOA-dominated aerosol (e.g., Jimenez et al., 2009; Raatikainen et al., 2010; Massoli et al., 2010). One can attribute the correlation between f_{44} and hygroscopicity to an increase of the water-soluble fraction of organic aerosol (Bougiatioti et al., 2009; Padró et al., 2010; Asa-Awuku et al., 2010, 2011).

Another uncertain aspect of cloud droplet formation is the impact of slowly-dissolving compounds, droplet surface films and aerosol amorphous states on the activation kinetics of CCN. If present, kinetic inhibitions could have an important impact on cloud droplet number and size distribution (e.g., Jensen and Charlson, 1984; Kulmala et al., 1993; Chuang et al., 1997; Nenes et al., 2001, 2002; Lance et al., 2004). Studies often detect the presence of CCN experiencing kinetic limitations by comparing the size of activated droplets against a standard of rapid activation (e.g., calibration salt CCN). Many studies have found little evidence of kinetic limitations (e.g., Chuang, 2003; Engelhart et al., 2008, 2011; Lance et al., 2009; Bougiatioti et al., 2009, 2011; Asa-Awuku et al., 2010; Padró et al., 2010), although others detected kinetic limitations when the aerosol originated from above the boundary layer or contained a large fraction of hydrophobic organics (e.g., Sorooshian et al., 2008; Ruehl et al., 2008, 2009; Asa-Awuku et al., 2009, 2011). Padró et al. (2010) showed that the water-soluble organics in Mexico City during the MILAGRO campaign did not affect droplet growth rates. Asa-Awuku et al. (2009) showed that droplet growth kinetics were strongly anticorrelated with the water-soluble organic carbon fraction for β-caryophyllene SOA. Murphy et al. (2009) detected kinetic limitations for organic-rich aerosol freshly emitted from a cargo ship. Lance et al. (2009) found that activation kinetics in the boundary layer were not greatly depressed over Houston, Texas, during the GoMACCS campaign, while Ruehl et al. (2008) and Asa-Awuku et al. (2011) found during the same campaign (but different location and time periods) that up to 30 % of the CCN exhibit some degree of delayed condensational growth. Bougiatioti et al. (2009, 2011) found that aged carbonaceous aerosol sampled at a remote marine site in the Eastern Mediterranean during the 2007 Finokalia Aerosol Measurement Experiment (FAME07) did not exhibit kinetically limited droplet growth rates. Ruehl et al. (2009) found strong kinetic limitations above the marine boundary layer near the California coast. These studies encompass a large range of environments and conditions; however the prevalence of kinetic limitations varies even for similar environments, suggesting the need for further investigation.

Boreal forests, such as the one considered in this study, offer a unique and climatically-important environment for study as they cover 8 % of the earth's surface (Sihto et al., 2010). Remote forests generally represent clean, "background" environments with strong interactions between the soil, ecosystem, and atmosphere (Hari and Kulmala, 2005; Barth et al., 2005; Kanakidou et al., 2005). Aerosol in such systems are dominated by biogenic SOA (Boy et al., 2004; Kulmala et al., 2004), The frequent occurrence of nucleation events in boreal forests influences the aerosol properties of different size modes (Hämeri et al., 2001). CCN studies for this type of environment have investigated the diurnal variation of critical activation diameter, hygroscopicity, solubility and the properties of characteristic particle sizes and modes (e.g., Aalto and Kulmala, 2000; Hämeri et al., 2001; Sihto et al., 2010). It is expected that the influence of particle formation events and secondary organic aerosol (SOA) production give rise to CCN rich in carbonaceous material, but with a small fraction of inorganic salts that further augments their hygroscopicity (Sihto et al., 2010). Few studies to date examine the CCN activation kinetics of boreal forest aerosol.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Size-resolved CCN concentrations, subsaturated hygroscopic growth, size distribution, and chemical composition were measured at Hyytiälä, Finland, during March through May, 2007, as part of the EUCAARI campaign (see Kulmala et al., 2009). The current study utilizes these measurements to investigate the time and size-dependent hygroscopicity, mixing state, and CCN activation kinetics of aerosol in a boreal forest environment.

2 Data collection

2.1 Measurement site

Data were collected from a comprehensive suite of aerosol instrumentation at the SMEAR II station (61° 51′ N, 24° 17′ E) located in a boreal forest in Hyytiälä, Finland, from 25 March through 15 May 2007. This site is described in detail in Kulmala et al. (2001) and Hari and Kulmala (2005). In addition to size-resolved CCN, subsaturated hygroscopic growth, size distribution, and chemical composition, measurements of temperature, wind direction, gas phase species concentrations, and particle size distributions were also collected.

Hyytiälä receives air masses from a variety of sources and locations. The SMEAR II station sees both “clean” and “polluted” air masses which are often, but not always, characterized by low particle concentrations transported from the Arctic Ocean and Northern Scandinavia and high particle concentrations transported from Central and Eastern Europe, respectively. NOAA HYSPLIT backtrajectories (http://ready.arl.noaa.gov/HYSPLIT.php) characterizing clean and polluted air masses are shown in Fig. 1.

2.2 Instrument setup

A “stepping mode” setup for supersaturation and size (Lance, 2007; Moore et al., 2010) is used to obtain size-resolved CCN activity data. First, an ambient sample is introduced into a Differential Mobility Analyzer (DMA, TSI 3085). The classified aerosol stream is then split to a Condensation Particle Counter (CPC, TSI 3760A), giving the total number of particles (or condensation nuclei, CN), and to a Continuous Flow-Streamwise Thermal Gradient CCN Chamber (CFSTGC) (Roberts and Nenes, 2005; Lance et al., 2006) manufactured by Droplet Measurement Technologies, Inc. While supersaturation is held constant in the CFSTGC, the mobility diameter in the DMA is “stepped” to obtain measurements of CCN and CN concentration at several particle sizes. For each particle size, the ratio of CCN to CN concentration, known as the “activation ratio,” is computed. This procedure is then repeated for another supersaturation to characterize the size-dependent CCN activity of particles.

During this study, the supersaturation, *s*, in the CFSTGC is held constant over a period of 3 min, during which particles sizes of 20, 40, 60, 80, and 100 nm were selected by the DMA (e.g, Fig. 2). Data collected up to 20 s after a change in DMA-selected particle size is discarded, and the activation ratio is measured over a period of 16 s. The 20 nm and 100 nm data were discarded, because activation spectra were not fully detected at the selected instrument supersaturation range and also as the instrument transients had an effect on the 20 nm data. Instrument supersaturation was stepped in increments of 0.2 % ranging from 0.1 % to 1.8 % for each particle size. This setup allowed for obtaining a cycle of size and supersaturation resolved CCN activity about every 30 min. The DMA was operated with a nominal aerosol flow rate of about 1 l min^{-1} and a sheath-to-aerosol flow rate ratio of 4.5 : 1 while the CFSTGC was operated at a total flow rate of approximately 1 l min^{-1} with a sheath-to-aerosol flow rate ratio of 10 : 1. Supersaturation in the instrument was calibrated with laboratory-generated ammonium sulfate particles using the Scanning Mobility CCN Analysis (SMCA) method described by Moore et al. (2010).

The Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) measures the hygroscopic growth of size-classified particles exposed to a selected relative humidity (RH) below 100 % (e.g., Liu et al., 1978; Rader and McMurry, 1986; Swietlicki et al., 2008). The HTDMA used in the current study is fully described in Ehn et al. (2007), so only a brief description is given here. A first DMA unit is used to select a narrow size range from dried ambient particles. Then, the selected particles are exposed to a selected RH and the average growth of the humidified particles is measured by the second DMA unit and a CPC. A mean value representing average humid aerosol size is calculated from the humidified size distributions and is divided by the corresponding dry size to yield the hygroscopic growth factor (GF). The dry particle sizes of 10, 20, 30, and 50 nm, were selected by the first DMA in the HTDMA. These four particle sizes were stepped through over the course of approximately 30 min giving a single GF for each size every 30 min. Only the 30 and 50 nm data are shown for this study as they fall within the measured CCN data size range. For measurements collected up to 1 May, aerosol hygroscopic growth was measured at 90 % RH. From 3 May through the end of the study, the RH was cycled between 71 % and 87 % each half hour (e.g., Fig. 2).

Aerosol chemical composition was measured by an Aerodyne AMS (e.g., Jayne et al., 2000; Allan et al., 2003, 2004; Jimenez et al., 2003; Alfarra et al., 2004; Canagaratna et al., 2007). Briefly, the instrument is capable of detecting mass concentrations of non-refractory species from sub-micron aerosol with a time resolution of about 10 min (Jimenez et al., 2003; Canagaratna et al., 2007). "Non-refractory" refers to species that volatilize rapidly at 600 °C, which means that crustal material, sea-salt, or black carbon aerosol cannot be detected. In practice, the AMS measures mass concentrations of non-sea-salt chloride, sulfate, nitrate, ammonium and organics (μg m^{-3}). Initially, the AMS was operated by altering between particle time of flight (pTOF) and mass spectrum (MS) modes (e.g., Jimenez et al., 2003), saving data every 10 min. On 4 April, the AMS was turned off and prepared for flux measurements (e.g., Nemitz et al., 2008). Starting from 6 April, the first 30 min of every hour was used for the flux measurements, and during the second 30 min period the AMS was alternating between pTOF, MS, and jump mass spectrum (JMS) modes (e.g., Crosier et al., 2007). In addition, averaging time was decreased to 5 min from the original value of 10 min. Mass concentrations were noisy due to the short averaging time, so the AMS mass concentration (MS mode) data was averaged for each 30 min CCN measurement period (e.g., Fig. 2). The data coverage for the 30 min time base is 47 %. Most of the missing data points (42 % of all data points) are due to the flux measurements, but some data points (11 % of all data points) are missing due to routine maintenance and hardware failures.

3 Methodology

The CFSTGC and HTDMA provide hygroscopicity measurements under supersaturated and subsaturated conditions, respectively; each dataset can independently be used to derive κ distributions. Petters and Kreidenweis (2007) found that agreement between CCN-derived κ and HTDMA-derived κ is within 30 % for most compounds considered in their study. Slight differences may occur between subsaturated and supersaturated κ values, as droplet solutions of activated particles in the CFSTGC are typically more dilute than if measured at subsaturated conditions (e.g., Petters and Kreidenweis, 2007). For κ obtained at subsaturated conditions, solution non-ideality, phase separation, and partial solubility of constituents may be more pronounced and affect (mostly decrease) the observed κ. Therefore, the HTDMA and CFSTGC provide two independent measures of hygroscopicity under very different water activity conditions; together, these measurements are often used to test and confirm the validity of experimental methods (e.g., Aalto and Kulmala, 2000; Good et al., 2010; Petters et al., 2009; Sihto et al., 2010; Irwin et al., 2011).

From subsaturated HTDMA GF data, κ values were predicted using

$$\kappa = (\mathrm{GF}^3 - 1)\left(\frac{\exp\left(\frac{A}{\mathrm{GF}d_\mathrm{p}}\right)}{\frac{\mathrm{RH}}{100\%}} - 1\right) \tag{1}$$

where $A = (4M_w\sigma_w)/(RT\rho_w)$, M_w is the molar mass of water, σ_w is the surface tension of water, R is the universal gas constant, T is temperature, ρ_w is the density of water (Petters and Kreidenweis, 2007). Some GF values were removed from the analysis due to limited counting statistics at low particle concentrations based on an approximated background noise. The total percentage of GFs filtered from the analysis for the 30 and 50 nm datasets are 14 % and 10 %, respectively.

From the CCN data, the supersaturation-resolved activation ratio function, $R_a(s)$, for a given size particle is fit to a sigmoid with the form

$$R_a(s) = \frac{E}{1 + \left(\frac{s}{s^*}\right)^C} \tag{2}$$

where E is the maximum fraction of particles that activate at high supersaturations, s is the instrument supersaturation, s^* is the characteristic critical supersaturation of the sigmoid, the supersaturation at which half of the size-resolved CCN activate (i.e. $R_a(s) = 0.5\,E$). C is a coefficient that is a measure of the slope of $R_a(s)$ and is affected by the chemical heterogeneity of the activated particles (Fig. 3).

Before fitting to Eq. (2), data was filtered for low CCN concentrations to avoid biases from insufficient counting statistics. This is done by applying Poisson statistics to describe the relative counting uncertainty as the inverse square root of the number concentration (Moore et al., 2010). Using the flow through the instrument during each 16 s measurement period, this number can be converted to a minimum acceptable concentration value. For the instrument setup used in this campaign, a relative uncertainty of 15 % resulted in a minimum detection limit of 4 cm^{-3}, below which data were discarded. Eq. (2) was then fit to a spectra of activated ratios at a number of supersaturations (e.g., Fig. 3) to determine E, C, and s^* for each particle size during a supersaturation cycle. Resulting fits were then filtered to assure reasonable fit values with the criteria that $0.2 < E < 1.2$ and $-15 < C < -2$; values of $C > -2$ no longer provide a physically realistic sigmoid (Appendix A) and values of $C < -15$ are limited by instrument resolution (Lance, 2007; Appendix A). χ^2 values, a measure of the goodness of the fit, are obtained, and the highest 5 % are filtered to remove the outliers. Using these filter criteria, the percentage of discarded fits for 40, 60, and 80 nm data are 14 %, 10 %, and 16 %, respectively.

$R_\mathrm{a}(s)$ represents a cumulative distribution of critical supersaturation for particles with dry diameter d_p. Assuming that this variability is driven solely by variance in chemical composition, we can transform $R_\mathrm{a}(s)$ into a cumulative distribution of hygroscopicity, $R_a(\kappa)$, using the definition of κ (if $\kappa \gtrsim 0.1$),

$$\kappa = \frac{4A^3}{27d_\mathrm{p}^3}s^{-2} \tag{3}$$

where d_p is the dry diameter of the particle (Petters and Kreidenweis, 2007).

For every s^* there is a corresponding characteristic hygroscopicity parameter, κ^*, so that (s/s^*) can be expressed as $(\kappa/\kappa^*)^{-1/2}$. From this and Eq. (2), the complement of $R_\mathrm{a}(s)$, can be written as

$$R_\mathrm{a}(\kappa) = E - \frac{E}{1+\left(\frac{\kappa}{\kappa^*}\right)^{-\frac{C}{2}}} = \frac{E}{1+\left(\frac{\kappa}{\kappa^*}\right)^{\frac{C}{2}}} \tag{4}$$

The probability distribution function (PDF) for κ, $p^s(\kappa)$ can be found by differentiating Eq. (4) with respect to κ and normalizing over the integral of possible κ values.

$$p^s(\kappa) = \frac{1}{E}\frac{dR_\mathrm{a}(\kappa)}{d\kappa} = -\frac{\frac{C}{\kappa^*2}\left(\frac{\kappa}{\kappa^*}\right)^{\frac{C}{2}-1}}{\left(1+\left(\frac{\kappa}{\kappa^*}\right)^{\frac{C}{2}}\right)^2} \tag{5}$$

Analysis of $p^s(\kappa)$ can provide the chemical dispersion, which describes the degree of chemical heterogeneity of the CCN population. As described in Lance (2007), the chemical dispersion, $\sigma(\kappa)$, of particles of size d_p can be found by computing the square root of variance about κ^* (assuming a Gaussian distribution where the average κ is equal to κ^*)

$$\sigma^2(\kappa) = \frac{\int_0^1 (\kappa - \kappa^*)^2 \, p^s(\kappa) d\kappa}{\int_0^1 p^s(\kappa) d\kappa} \tag{6}$$

so that the chemical heterogeneity of the CCN population can be approximated by $\kappa^* \pm \sigma(\kappa)$. Thus, the chemical dispersion is described by the spread in the distribution of measured κ values, illustrating the degree of heterogeneity in particle chemistry. Further explanation of this method, including a discussion on the integration limits of Eq. (6) and the contribution of instrument operation on $\sigma(\kappa)$ are discussed in Appendix A.

4 Results

Temporal variation of HTDMA-derived and CFSTGC-derived κ values, total particle concentration, and AMS mass concentrations throughout the campaign are shown in Fig. 4. CN concentrations are typically below 200 particles cm^{-3} for 40, 60, and 80 nm particles, and AMS total mass ranges from 0 to 10 µg m^{-3}. While during some periods these quantities show similar trends (e.g., 9 April 2007 to 11 April 2007 and 1 May 2007 to 11 May 2007), correlation of these parameters with κ variability is weak. The trend in κ values derived from HTDMA and CFSTGC measurements correlate well (as discussed in the following). General trends of κ values for different size particles are very similar, although specific differences between sizes will be presented in the following analysis. Average CFSTGC-derived κ values for 40, 60, and 80 nm particle are 0.20 ± 0.06, 0.19 ± 0.06, and 0.22 ± 0.06, respectively, while average HTDMA-derived κ values for 30 and 50 nm particles are 0.15 ± 0.06 and 0.14 ± 0.05, respectively. As droplet solutions in the HTDMA are more concentrated than those in the CFSTGC, it is not surprising that HTDMA-derived κ averages are generally lower. Also, the CCN counter detects only those particles that are activated (as indicated by parameter E

for large supersaturations), but the HTDMA also detects non-hygroscopic particles which invariably decreases the inferred value of κ. However, as E is almost always > 0.9, the contribution of non-hygroscopic particles to the HTDMA-derived κ is small. A likely reason for the differences seen is that a larger fraction of the commonly less soluble organic material is dissolved in the dilute droplets present in the CFSTGC. HTDMA-derived κ values from this study are in agreement with the HTDMA-derived average $\kappa = 0.18$ for 35, 50, 75, and 110 nm particles reported for this region by Sihto et al. (2010) for July 2008 to June 2009. The slight discrepancy between our results and those reported by Sihto et al. (2010) may result from the fact that particle hygroscopicity in this region is dependent on particle size (e.g., Birmili et al., 2009) and larger particles typically show increased hygroscopicity (also shown by the higher average CFSTGC-derived κ for 80 nm particles compared to that of 60 and 40 nm particles discussed in Sect. 4.2).

Comparison of κ values from 60 nm CCN data against 50 nm HTDMA data for the entire campaign is presented in Fig. 5. The higher magnitude of CFSTGC-derived over HTDMA-derived κ values is again seen in this comparison with most of the values consistent within ± 30 %. These differences are well within the range of uncertainty often seen for differences in HTDMA and CFSTGC-derived κ values (e.g., Petters and Kreidenweis, 2007; Prenni et al., 2007; Petters et al., 2009; Massoli et al., 2010). For simplicity, κ values derived from CFSTGC data will be used throughout the rest of this study.

4.1 Diurnal variability of CCN properties

Diurnal variation in CCN maximum activated fraction (E) and characteristic critical supersaturation (s^*) are shown for 40, 60, and 80 nm particles (Fig. 6a,b). While the 60 and 80 nm particles show rather constant values of E, 40 nm data seem to display an decrease in E the from late morning through evening (Fig. 6a). This daytime decrease in maximum activated fraction, however, is the result of not reaching the asymptote for 40 nm spectra at the highest supersaturation measured (s_{max}). If calculations are repeated using $R_{\mathrm{a}}(s_{\mathrm{max}})$ instead of the asymptote $E = R_{\mathrm{a}}(\infty)$, this diurnal cycle is no longer apparent. Thus, it is expected that the true diurnal variation of E for 40 nm particles is analogous to that of the 60 and 80 nm particles. Not reaching the asymptote, however, has negligible effects, if any, on the C and s^* fit parameters. As expected, 40 nm particles have the highest characteristic critical supersaturations of the particle sizes sampled in this study and reach their critical supersaturation well below the highest instrument supersaturation (1.8 %) (Fig. 6b). Diurnal trends in total particle concentration are similar for all measured sizes (Fig. 6c).

4.2 Diurnal variability of κ

Diurnal trends in CFSTGC-derived κ values are seen for all particle sizes sampled with minimum κ values occuring in the early morning (near sunrise) and maximum κ values occurring in the afternoon (Fig. 7a). This diurnal trend corresponds well with those found by previous studies at the Hyytiälä site (e.g., Hämeri et al., 2001; Väkevä et al., 2002; Boy et al., 2004; Ehn et al., 2007). CFSTGC-derived κ values covary with AMS-derived inorganic volume fraction, daily temperature trends, and AMS f_{44} data. As f_{44} increases linearly with O/C ratio (Aiken et al., 2008) and organics in the atmosphere typically become more oxidized as they age, this suggests that aerosol hygroscopicity is also determined by the aging of those organics. This is consistent with the view of oxidation state correlating with hygroscopicity presented by Jimenez et al. (2009) and Massoli et al. (2010).

As reported by Boy et al. (2004), GF (related to κ by Eq. 1) is more variable during the daytime than the early morning period. This is also observed in our study as there is typically a clear peak in normalized κ frequency in the early morning while there is a wide spread of κ values with no clear peak in the afternoon (Fig. 7b). The clear size-dependence shown by Boy et al. (2004) is also seen in our diurnal κ trend, as larger particles display larger κ values than the smaller particles (Fig. 7c). Our observations confirm the different hygroscopic modes reported by Hämeri et al. (2001) where Aitken mode particles (35, 50, and 73 nm) show distinctly different hygroscopic behavior than the larger accumulation mode particles (about 80 nm or larger).

The chemical dispersion, $\sigma(\kappa)$, describing the degree of heterogeneity in particle chemistry, for 40, 60, and 80 nm particles is shown in Fig. 8. 60 and 80 nm particles show a potential diurnal trend in chemical dispersion, similar to that of diurnal κ. Chemical dispersion of 40 nm particles, however, remains rather steady and does not show the same increase just before noon as observed for the other sizes. The composition of nucleation and Aitken mode particles are influenced by nucleation events (Hämeri et al., 2001); it is therefore possible that 40 nm particles do not experience the afternoon increased chemical dispersion since new particle formation events often occur around noon (Nieminen et al., 2009). This means that while the chemical dispersion of larger particles changes, these 40 nm particles still reflect the composition of newly formed particles originating in the boreal forest. As 60 nm particles exhibit a similar diurnal κ trend (Fig. 7c), one might initially expect similar chemical dispersion. However, 60 nm particles (and larger) would have had more time to be affected by SOA condensation, coagulation, and long range transport; thus, they may exhibit a larger degree of chemical heterogeneity than 40 nm particles. This is in agreement with Petäjä et al. (2005) whom showed considerable variability in the Aitken mode hygroscopicity (associated with air mass transport and possibly aging) while, on the other hand, the nucleation mode hygroscopicity was quite constant due to relatively homogeneous surroundings. This is also consistent with Hämeri et al. (2001) whom also saw that external mixing increases with increasing particle size in Hyytiälä.

4.3 On κ closure with AMS data

κ, which represents the overall aerosol hygroscopicity, is the sum of contributions from each aerosol constituent

$$\kappa = \sum_j \kappa_j \varepsilon_j \tag{7}$$

where ε_j and κ_j are the volume fraction and hygroscopicity parameter, respectively, of aerosol component j (Petters and Kreidenweis, 2007). Based on AMS data, the components can include organic components and inorganic salts calculated from the measured ion concentrations (e.g., Raatikainen et al., 2010). When there are no significant variations in the composition of the organic and inorganic fractions (as seems to be the case in this data set) only the inorganic and organic fraction are needed for a reasonably good prediction

$$\kappa = \varepsilon_i \kappa_i + \varepsilon_o \kappa_o \tag{8}$$

where ε_i, ε_o, and κ_i, κ_o, are the volume fraction and hygroscopicity parameters of inorganics and organics, respectively. Fits were also tested for a three component model that includes inorganic ions as one group as well as the more and less oxidized organic groups. This model was shown to be superior during a previous campaign in 2005 (Raatikainen et al., 2010), but in the current campaign the average organic mass fraction is lower and there are much less variations in organic oxidation state. As a result, predictions for the three component approach provided similar results to the two component model, which will be used in this study. The relevant inorganic ions detected by the AMS include ammonium, nitrate, and sulfate. ε_i and ε_o were computed based on their observed mass fraction and density; ammonium sulfate volume fractions were used for the inorganic fraction as it dominated the inorganic mass (density $1.77\,\mathrm{g\,cm^{-3}}$; Lance et al., 2009). Organic properties were calculated using a density of $1.4\,\mathrm{g\,cm^{-3}}$ (Lance et al., 2009) and measured mass concentrations. 60 nm CFSTGC-derived κ values as a function of AMS measured organic volume fraction are shown in Fig. 9. Typical expected κ values for a pure inorganic compound (i.e., ammonium sulfate) as well as pure SOA are shown by the sulfate-SOA mixing line.

Fitted κ_i and κ_o for 40, 60, and 80 nm particles are shown in Table 1. The higher magnitude of both of these values for 80 nm data is expected as the general magnitude of hygroscopicity is greater for this size than for 40 and 60 nm particles (Fig. 7c). Still, while these values correspond well with the κ_o value of 0.1 used in Sihto et al. (2010)

and proposed by Gunthe et al. (2009), κ_i values are too low for typical inorganic compounds as the hygroscopicity of ammonium sulfate is 0.6 (Petters and Kreidenweis, 2007). Bulk mass concentrations measured by the AMS during the campaign were dominated by particles with diameter typically ranging from about 300–400 nm (mean volume diameter 380 nm), much greater than those sampled by the CFSTGC. Since large particles have been shown to differ in hygroscopicity and chemical dispersion from smaller particles and the organic mass fraction in Aitken particles has been shown to be significantly higher than in larger particles (Allan et al., 2006), bulk composition measurements (in this case from AMS) may overestimate the inorganic mass fraction used to describe the 40, 60, and 80 nm particles in this study. These results illustrate that bulk composition measurements should be used with caution as they may sometimes be inadequate when applied to the study of particles of CCN-relevant sizes.

4.4 CCN activation kinetics

The droplet diameter of a given particle exposed to a constant supersaturation in the CFSTGC is described by (Lance et al., 2006; Lathem and Nenes, 2011),

$$D_p{}^2 = D_o{}^{*2} + 2G\int_{t_{\mathrm{act}}}^{t_{\mathrm{out}}} s\mathrm{d}t \tag{9}$$

where D_p is the droplet diameter exiting the CFSTGC, D_o^* is the diameter of the CCN when exposed to its critical supersaturation, s_c, t_act is the time (after entrance in the growth chamber) when the supersaturation in the instrument becomes equal to s_c, and, t_out is the time when droplets exit the growth column. G is a coefficient that encompasses mass and heat transfer properties of the particle (Roberts and Nenes, 2005; Lance et al., 2006). From Eq. (9), droplet diameter tends to increase with increasing s. This is shown by the range of 80 nm particle droplet diameters throughout the study in Fig. 10a, where droplet diameters are color-coded by instrument supersaturation. The second term dominates over the first term for particles of low s_c, so that the droplet size at the exit of the instrument is insensitive to its s_c. This effect is shown in Fig. 10b for all size-selected particle sizes, each with a respective s^*, where droplet diameters become increasing similar at the highest supersaturations. This also means that droplet size distributions narrow at increasing supersaturations as illustrated by the vertical error bars, representing the standard deviation in droplet diameter, in Fig. 10b, and the narrowed droplet size distribution at high supersaturations in Fig. 10a. However, the asymptotic size reached by the particles at high supersaturation (Fig. 10b) is a result of the compensating effects between a higher supersaturation and a larger entry length required for its development (i.e., t_{act} approaches t_{out} as instrument s increases; Lance et al., 2006).

Threshold Droplet Growth Analysis, or TDGA, is a method used to investigate shifts in droplet growth kinetics for ambient (Bougiatioti et al., 2009, 2011; Lance et al., 2009; Padró et al., 2010) and laboratory (Engelhart et al., 2008; Asa-Awuku et al., 2009, 2010, 2011) aerosol. Using this method, the average droplet diameter of particles exiting the CFSTGC is measured and compared to corresponding droplet size from calibration aerosol (typically ammonium sulfate or sodium chloride) with s_{c} equal to the instrument supersaturation. Calibration aerosol represents an upper limit of rapid activation kinetics, as the material is deliquesced before it activates (thus does not require time to dissolve), and the water vapor uptake coefficient is very high (maximizing the water vapor transfer coefficient to the growing droplet). Therefore, if ambient aerosol experiences rapid activation kinetics, the droplet sizes of ambient and calibration particles should be similar. Provisions should be taken to avoid high CCN concentrations in the instrument that would result in supersaturation depletion, with implications on droplet size and CCN concentrations (Lathem and Nenes, 2011).

The calibration of the CFSTGC in this study was carried out with SMCA. In addition to a highly accurate calibration curve, the method also provides wet droplet diameter, D_p, for a wide range of particle sizes and s^*. Figure 10c shows 40, 60, and 80 nm ambient particle wet diameters at $s = s^*$ and lines based on average droplet size of calibration aerosol. As the instrument did not sample particles directly at their s^* but rather for set steps on instrument supersaturation, the two supersaturation values and wet diameters closest to s^* were used in interpolating the droplet diameter at s^*. Droplet sizes from ambient aerosol are comparable to those of calibration aerosol. This means that the organics present at Hyytiälä do not cause retardations in activation kinetics.

5 Conclusions

The size-resolved hygroscopicity and activation kinetics were investigated for particles sampled at the SMEAR II boreal forest station in Hyytiälä, Finland, from March to May, 2007. CCN data show similar values for 60 and 80 nm maximum activated fraction and remain close to unity. Though results of maximum activated fraction of 40 nm particles were impacted by the range of supersaturations measured in this study, these particles are expected to show variation similar to that of 60 and 80 nm particles.

Overall, κ values are mainly found between 0.10 and 0.40 for all sizes with an average of 0.20 ± 0.06, 0.19 ± 0.06, and 0.22 ± 0.06 for 40, 60, and 80 nm particles, respectively. These low values reflect the dominant role of organics on CCN activity. The diurnal trend of κ with inorganic volume fraction and f_{44} suggests that κ variability may be partly explained by the diurnal variability of organics in the atmosphere and particle aging. This suggests that the trend in organic composition and oxidation state of both small CCN-relevant particles and larger particles sampled in bulk measurements is the same and also that more aged (oxidized) particles have higher hygroscopicities than less oxidized organics.

The diurnal trend in κ displays maximum values in the afternoon and minimum values in the early morning as has been seen in previous studies by Hämeri et al. (2001), Väkevä et al. (2002), Boy et al. (2004), and Ehn et al. (2007). The high variability of afternoon κ values and the general increase in κ observed for larger particles confirms the results of these earlier studies. 60 and 80 nm particles show a slight diurnal trend in chemical dispersion while 40 nm dispersion remains rather stable. This could be representative of the effect of new particle formation on the chemical composition of 40 nm particles and also the effect of increased external mixing with size.

Hygroscopicity of the aerosol organic and inorganic fractions were predicted from bulk composition (using an AMS) and CCN-derived aerosol hygroscopicity. Hygroscopicity of the inorganic fraction was considerably lower than expected, which indicates that bulk measurements should be used with caution for representing characteristics of small mode particles. Due to the high number of nucleation events at the SMEAR II station, the composition of small particles (which contribute significantly to CCN concentrations) differs from that of large particles (which are more closely represented by measurements of bulk composition).

Analysis of droplet growth kinetics shows that ambient particles activate and grow as rapidly as calibration aerosol, adding to an emerging body of evidence that highly oxidized organics (even if they constitute the majority of the aerosol volume) do not inhibit the rate of water uptake. If this is representative of other locations and seasons, it will substantially simplify the description of CCN activation kinetics in atmospheric models of aerosol-cloud-climate interactions.

Appendix A

There are several assumptions made in using and analyzing results from the PDF in Eq. (5) as in order to arrive at appropriate, meaningful results for $\sigma(\kappa)$. An important issue regards the sigmoidal fit function, as it can yield non-negligible probability for atmospherically irrelevant κ (Fig. A.1). For example, in Eq. (5), when κ is ten times greater than κ^* and $C = -2$, $R_\mathrm{a}(\kappa) = 0.9\,E$, which means that there is a 10 % probability that $\kappa > 10\,\kappa^*$. This is unrealistic for ambient data collected during the campaign. We have filtered the data to exclude distributions for which $C > -2$. On the other hand, values of $C < -15$ were filtered, as it means that $R_\mathrm{a}(\kappa)$ cannot be resolved with a supersaturation step size of 0.2 %. This also happens to be the practical limit for the lowest observed C from instrument calibration experiments where higher resolution can be used. A small fraction of the data are subject to these issues and have a minimal impact on the results. We have also chosen to implement a constant upper limit for integration of $\kappa = 1$ as this is the upper limit of atmospherically-relevant κ values (except for sea salt, whose $\kappa \approx 1.2$, Petters and Kreidenweis, 2007) and well above those seen in Hyytiälä during this campaign.

Instrument operation also induces some broadening of $R_a(s)$ and $R_a(\kappa)$ and contributes to $\sigma(\kappa)$. An ideal instrument sampling a chemically homogenous mixture of monodisperse particles would result in $R_a(\kappa)$ being a step function with $\sigma(\kappa) = 0$ and $C = -\infty$. In reality, the finite width of the DMA transfer function (Wang and Flagan, 1990) and a corresponding transfer function in the CFSTGC from exposure to a finite range of supersaturations, the assumption of particle sphericity, and fluctuations in instrument operation (i.e., flow rate and temperature) all induce a broadening of the response to give a finite, but still steep slope for $R_a(s)$.

In practice, the inferred $\sigma(\kappa)$ contains a fairly constant instrument offset and a strongly time-dependent component that represents the actual chemical variability. In Hyytiälä, most of the observed $\sigma(\kappa)/\kappa$ values are between 0.25 and 1.3, so the instrument offset (0.25) is rather small compared to the effect of chemical variability. As the first step to explain the instrument offset for $\sigma(\kappa)/\kappa$ (0.25) we have estimated the magnitude of instrument supersaturation fluctuations. For example, the upper limit for instrument supersaturation fluctuations due to variations in CFSTGC temperatures was found to be $\sigma(s)/s = 0.01$. Based on Eq. (3), $\sigma(\kappa) = (\mathrm{d}\kappa/\mathrm{d}s)\sigma(\mathrm{s}) = 2\kappa/s\sigma(s)$, which means that $\sigma(\kappa)/\kappa = 0.02$. This is a small value compared with the lowest observed value of 0.25, and under normal operation supersaturation fluctuations can be considered as a second order effect. Several other possibilities such as fluctuations in pressure and inlet RH were also considered, but these are found to have even smaller contribution to the instrument $\sigma(\kappa)$.

As shown by Lance (2007), the DMA transfer function results in significant spread to the activation spectrum. For example, the relative width of the DMA transfer function (Wang and Flagan, 1990) for 4.5 : 1 sheath-to-aerosol flow ratio is roughly $\sigma(D_p)/D_p = 0.053$. Again, an order of magnitude approximation based on Eq. (3) shows that $\sigma(\kappa)/\kappa = 3 \cdot 0.053 = 0.16$. Another important contribution to the spread in the activation spectrum comes from multiply charged particles as these larger particles activate at lower supersaturations. There are no simple ways to estimate this effect, because the fraction of multiply charged particles depends on charging probability and size distribution at the charger, which is not always known and hardly ever constant. When expecting uniform particle distribution at the charger, accounting for multiply charged particles (Gunn, 1956; Wiedensohler and Fissan, 1988) and DMA transfer function effects (Wang and Flagan, 1990) increases $\sigma(\kappa)/\kappa$ for 80 nm particles to about 0.2, but the effect is negligible for 40 nm particles. As a result, the DMA transfer function explains 64–80 % of the observed $\sigma(\kappa)$ offset. The unexplainable fraction of the $\sigma(\kappa)$ offset is caused by a combination of several second order effects such as CFSTGC transfer function, diffusion widening of the size distributions, and using the simplified hygroscopicity approach (Eq. 3).

Figure A1 shows an example of a typical measured activation curve based on ambient observations and calculated activation curves for different $\sigma(\kappa)/\kappa$ values mentioned above. It can be seen that the steepest detected distributions ($\sigma(\kappa)/\kappa = 0.25$) are similar to the distribution based only on the DMA transfer function ($\sigma(\kappa)/\kappa = 0.16$). In addition, ambient distributions can usually be clearly distinguished from the instrument limit ($\sigma(\kappa)/\kappa = 0.25$).

To conclude, the $\sigma(\kappa)$ values include various effects of normal operation uncertainties, dominated by the DMA transfer function. With the exception of the multiply charged particles, these effects are practically time and size invariant. This means that calculated $\sigma(\kappa)$ values contain a fairly constant instrument offset (roughly 0.25 in the current data), but the remaining much larger variations (from 0.25 to well above 1) can be related to chemical variability. More comprehensive methods exist for separating variability in particle size and composition (e.g., Lance, 2007), but the current method is a very good approximation.

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Table 1. κ_o and κ_i values for 40, 60, and 80 nm particles.

Particle size (nm)	κ_o	κ_i
40	0.12	0.30
60	0.12	0.30
80	0.14	0.35

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

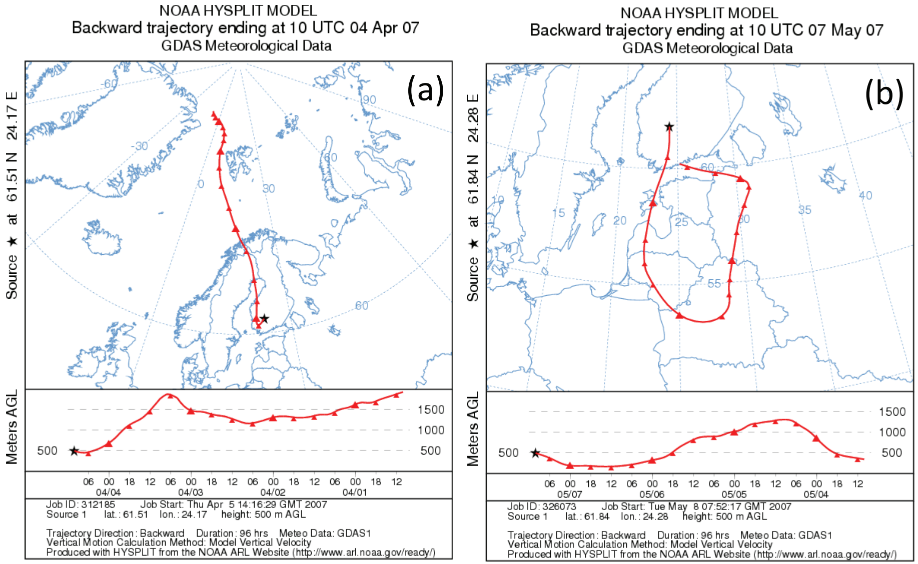

Fig. 1. HYSPLIT backtrajectories for **(a)** clean and **(b)** polluted air masses.

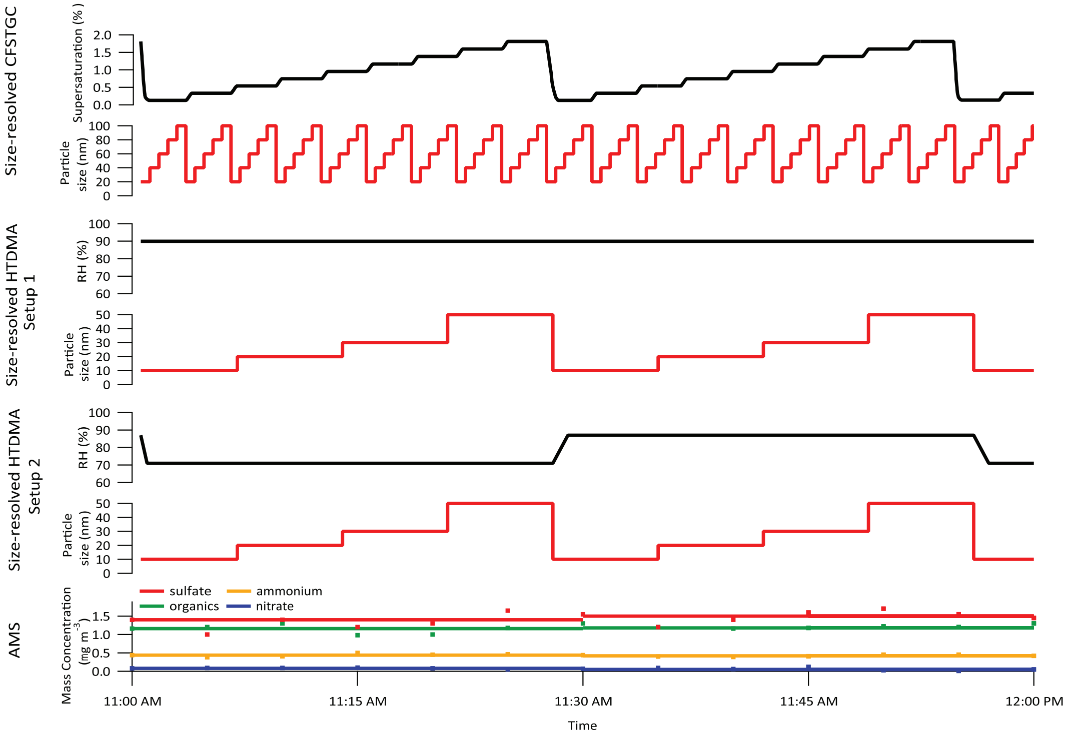

Fig. 2. Example of the operation schedule for CFSTGC, HTDMA, and AMS measurements. A schematic of the HTDMA measurement schedules for data collected up to 1 May and after 3 May are indicated as Setup 1 and Setup 2, respectively. An example of actual data collected by AMS is represented by circles, while lines represent 30 min averages used for this study.

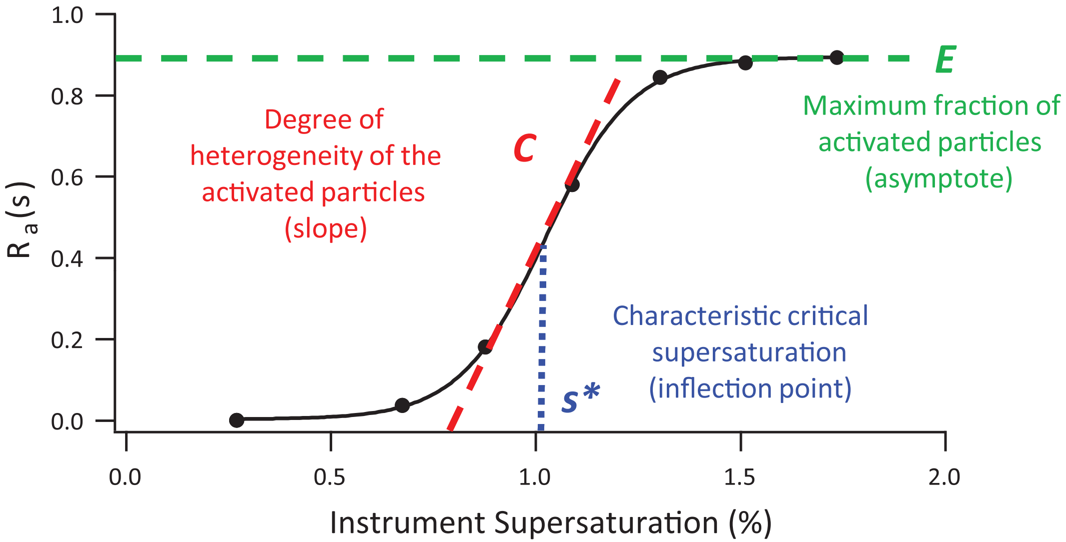

Fig. 3. Example of an activation spectra and fitted parameters.

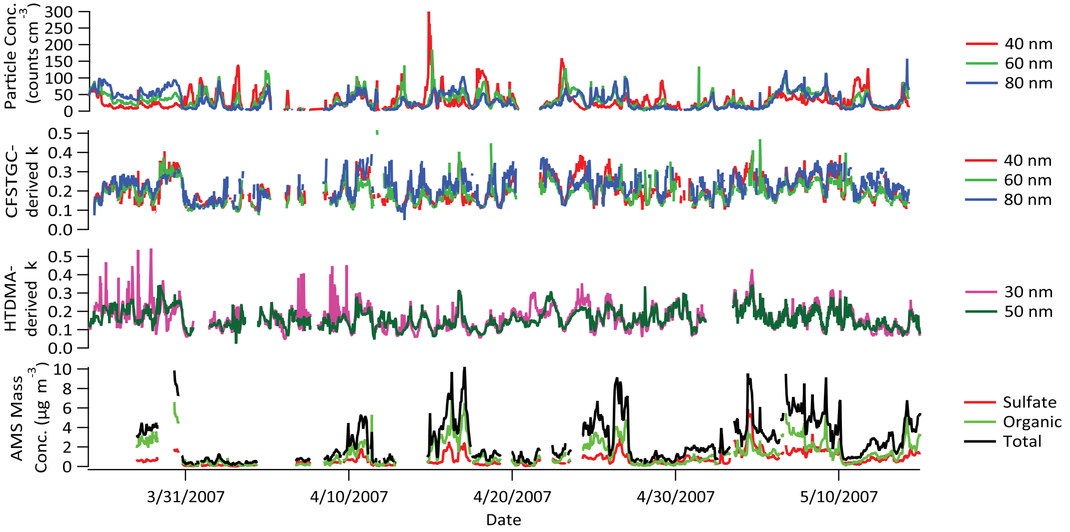

Fig. 4. Temporal variation of HTDMA-derived and CCN-derived κ values, total particle concentration, and AMS mass concentration throughout the campaign.

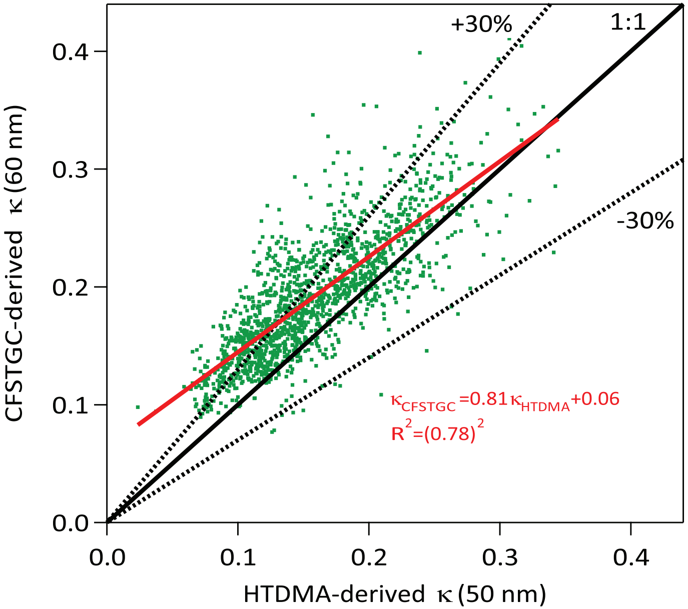

Fig. 5. CFSTGC-derived κ values for 60 nm diameter particles against HTDMA-derived κ values for 50 nm diameter particles. Shown is a best fit line (red), 1 : 1 line (black, solid), and lines of ± 30 % deviation (black, dotted).

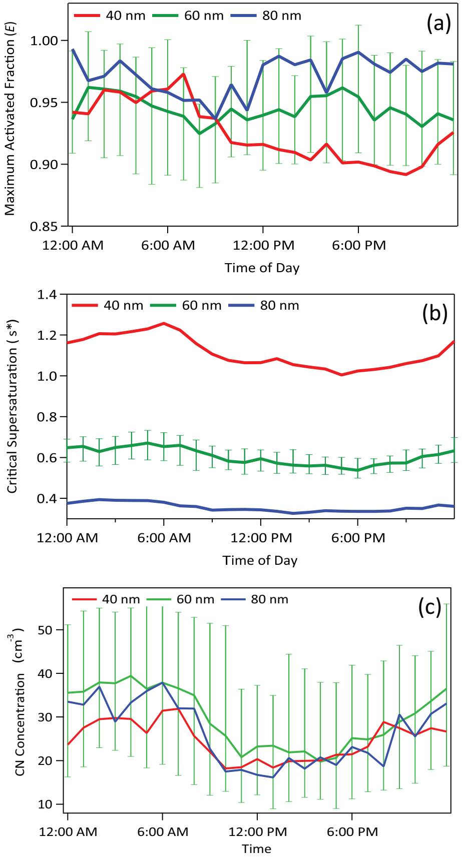

Fig. 6. Diurnal variation of the **(a)** CCN maximum activated fraction, **(b)** critical supersaturation, and **(c)** CN concentration for 40, 60, and 80 nm particles. Solid lines represent median values. Bars representing the 25th and 75th percentile values are shown for 60 nm data.

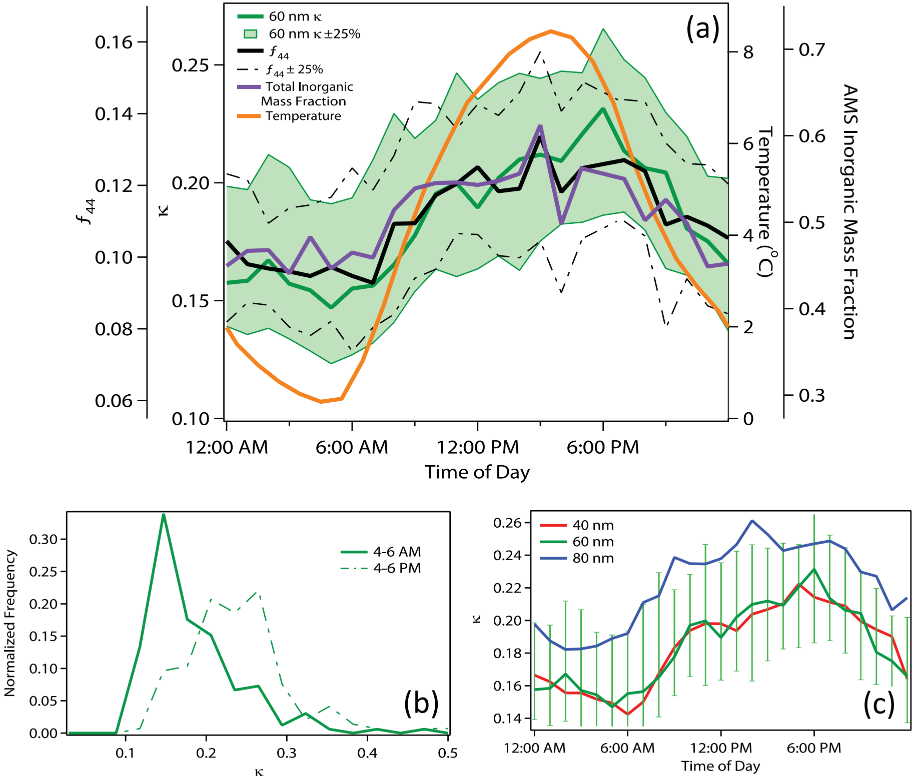

Fig. 7. (a) Diurnal trend of 60 nm median κ trend (green line) with 25th and 75th percentiles shaded in green. Also shown are average temperature (orange line), median f_{44} given by AMS (black line) with 25th and 75th percentiles shown by dotted black lines, and median inorganic mass fraction (purple line). **(b)** Frequency distributions for times of minimum (solid line) and maximum (dotted line) κ values. **(c)** Diurnal distributions for 40, 60, and 80 nm particles. Bars representing the 25th and 75th percentile values are shown for 60 nm data.

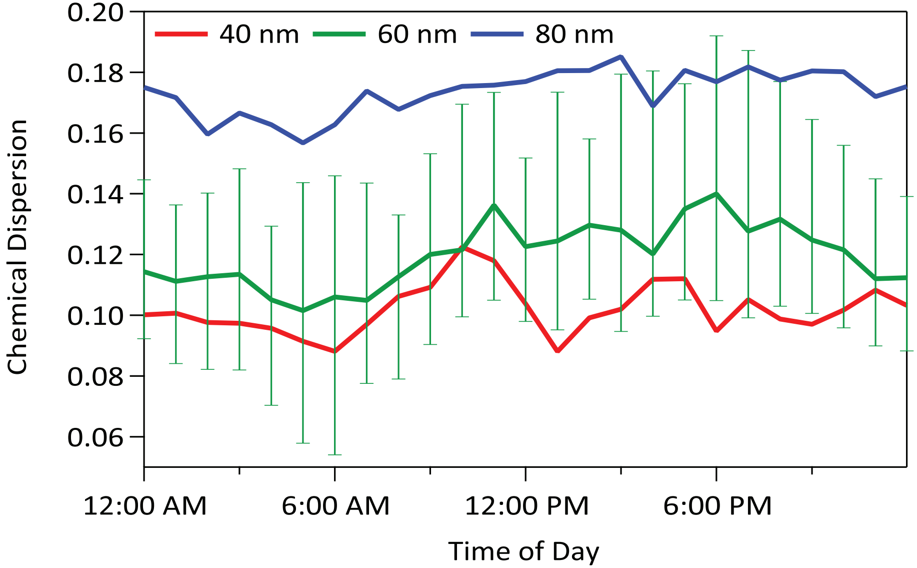

Fig. 8. Diurnal variation of $\sigma(\kappa)$ for 40, 60, and 80 nm particles.

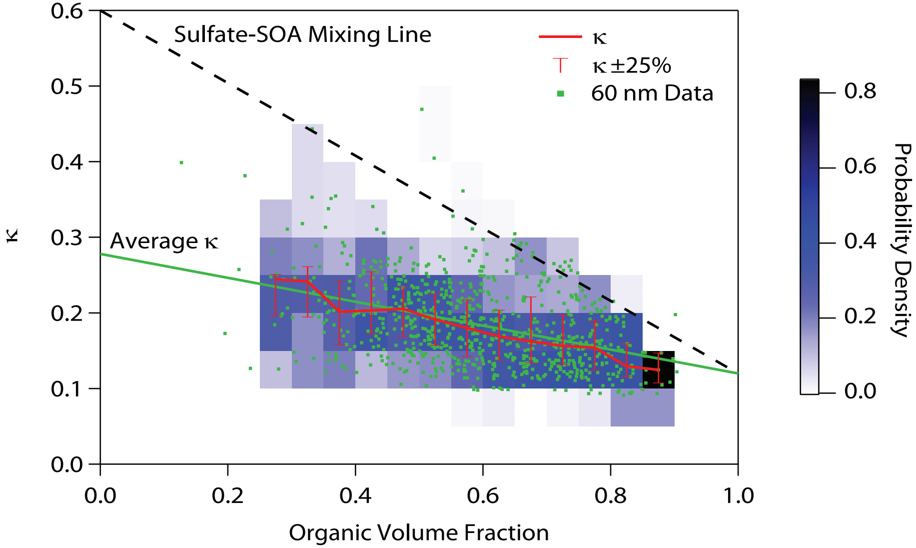

Fig. 9. 60 nm κ median values (red line) with bars showing 25th and 75th percentiles. Actual κ values shown by green circles. Probability density is indicated by the blue shading. The black dashed line indicates the sulfate-SOA mixing line. The green line shows the average value of κ as predicted by AMS closure.

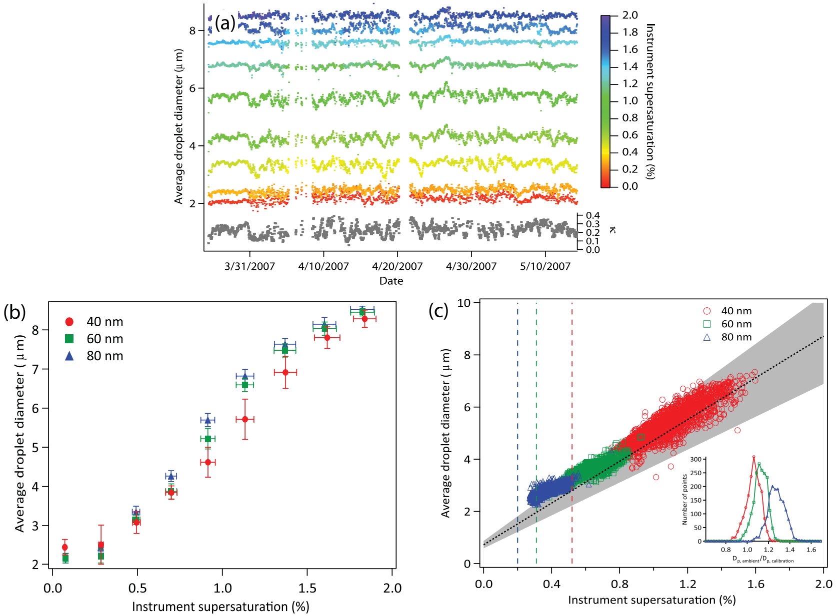

Fig. 10. **(a)** Temporal variation of droplet size for ambient 80 nm particles color-coded by instrument supersaturation. κ values are shown in grey (right-hand scale). **(b)** Average droplet diameters for 40 (red circles), 60 (green squares), and 80 nm (blue triangles). Vertical and horizontal error bars represent the standard deviation of measured droplet sizes and supersaturation, respectively. **(c)** Activated droplet sizes for 40 (red circles), 60 (green squares), and 80 nm (blue triangles) ambient particles measured at supersaturations closest to the critical supersaturation of ammonium sulfate particles of the same respective size. The calibration curve is shown by a black dotted line while the grey area indicates the sizing uncertainty for the ammonium sulfate particles. Critical supersaturations for 40, 60, and 80 nm ammonium sulfate particles are given by red, green, and blue dashed lines, respectively. Inset are histograms for each size particle indicating the occurrence of ratios of ambient wet droplet size to calibration wet droplet size.

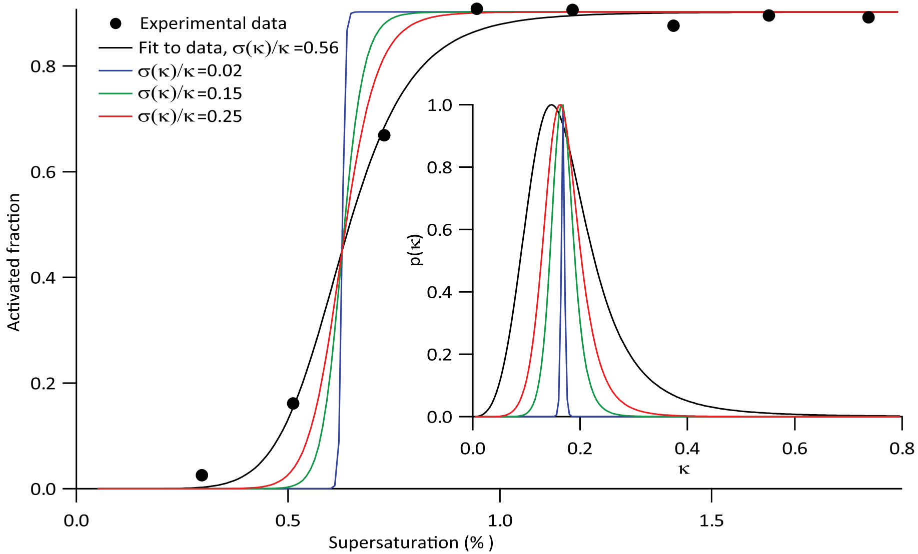

Fig. A1. An example of measured and fitted activation spectrum (60 nm dry size, 14 April 2007 18:55:00 local time) and three examples of activation spectra with different $\sigma(\kappa)$ values. Corresponding κ distributions are shown in the inset.