

**Mixing state and
compositional effects
on CCN activity**

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This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Mixing state and compositional effects on CCN activity and droplet growth kinetics of size-resolved CCN in an urban environment

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Received: 22 September 2011 – Accepted: 28 October 2011 – Published: 12 December 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Aerosol composition and mixing state near anthropogenic sources can be highly variable and can challenge predictions of cloud condensation nuclei (CCN). We present in-situ size-resolved CCN measurements to quantify this predictive uncertainty, which were carried out during the 2008 summertime August Mini Intensive Gas and Aerosol Study (AMIGAS) campaign in Atlanta, GA. Aerosol chemical composition was measured by two particle-into-liquid samplers measuring water-soluble inorganic ions and total water-soluble organic carbon. Size-resolved CCN data were collected using the Scanning Mobility CCN Analysis (SMCA) method and were used to obtain characteristic aerosol hygroscopicity distributions, whose breadth reflects the aerosol compositional variability and mixing state. We find that knowledge of aerosol mixing state is important for accurate predictions of CCN concentrations and that the influence of an externally-mixed, non-CCN-active aerosol fraction varies with size from 31 % for particle diameters less than 40 nm to 93 % for accumulation mode aerosol during the day. This is likely indicative of the interactions between biogenic and anthropogenic emissions which contribute to the formation and transformation of aerosols in this heterogeneous environment. Assuming size-dependent aerosol mixing state and size-invariant chemical composition decreased the average CCN concentration overprediction from greater than 50–200 % to less than 20 %. CCN activity was parameterized using a single hygroscopicity parameter, κ , which averaged 0.16 ± 0.07 for 80 nm particles and exhibited considerable variability (range: 0.03–0.48) throughout the study period.

1 Introduction

The ability of aerosol particles to act as cloud condensation nuclei (CCN) depends on their size and composition (e.g., Twomey, 1977; Dusek et al., 2006; Wang, 2007). Chemical composition can have an important effect on CCN, especially in environments where the aerosol is externally mixed (e.g., Cubison et al., 2008; Furutani et al.,

ACPD

11, 32723–32768, 2011

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2008). Köhler theory (Köhler, 1936) has been shown to adequately describe the size and compositional dependence of CCN composed of inorganic and soluble organic compounds (e.g., Cruz and Pandis, 1997; Padró et al., 2007). CCN containing higher molecular weight organic compounds can readily form cloud droplets but may exhibit more complex interactions with water, owing to their partial solubility in water, and ability to depress surface tension and exhibit lattice effects on water activity (e.g., Li et al., 1998; Facchini et al., 1999; Corrigan and Novakov, 1999; Raymond and Pandis, 2002; Hartz et al., 2006; Petters et al., 2009). Despite this complexity, simple assumptions on the chemical composition of aerosols is often employed in modeling CCN. The ultimate test of these simplified models are CCN closure studies, where measured CCN concentrations and predictions from Köhler theory are directly compared, where closure is deemed successful when agreement is found to be within the measurement uncertainty (typically 10–20 %).

Over the past decades, numerous closure studies have been carried out at a number of ground sites (e.g., Bigg, 1986; Liu et al., 1996; Covert et al., 1998; Cantrell et al., 2001; Roberts et al., 2002; Dusek et al., 2003; Roberts et al., 2003; Snider et al., 2003; Rissler et al., 2004; Broekhuizen et al., 2006; Chang et al., 2007; Ervens et al., 2007; Medina et al., 2007; Stroud et al., 2007; Vestin et al., 2007; Yum et al., 2007; Cubison et al., 2008; Kuwata et al., 2008; Bougiatioti et al., 2009; Gunthe et al., 2009; Chang et al., 2010; Kammermann et al., 2010; Rose et al., 2010; Wang et al., 2010; Rose et al., 2011), ships (e.g., Zhou et al., 2001, Quinn et al., 2008), and airborne platforms (e.g., Chuang et al., 2000; VanReken et al., 2003; Rissman et al., 2006; Roberts et al., 2006, 2010; Wang et al., 2008; Lance et al., 2009; Murphy et al., 2009; Asa-Awuku et al., 2011; Moore et al., 2011) throughout the world to address the effects of chemical composition and mixing state on CCN activity. Chemical composition data for CCN closures have been obtained from filters (Liu et al., 1996; Chuang et al., 2000), MOUDI (Micro Orifice Uniform Deposit Impactor) cascade impactors (Cantrell et al., 2001; Roberts et al., 2002, 2003; Bougiatioti et al., 2009), inferred from hygroscopic growth measurements (Covert et al., 1998; Zhou et al., 2001; Rissler et al., 2004;

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Ervens et al., 2007; Vestin et al., 2007), Particle-Into-Liquid-Samplers (PILS; Kuwata et al., 2008) and aerosol mass spectrometers (AMS; Broekhuizen et al., 2006; Medina et al., 2007; Stroud et al., 2007; Cubison et al., 2008; Lance et al., 2009; Murphy et al., 2009; Gunthe et al., 2009). CCN closure utilizing AMS measurements tend to be more successful (typically within 20–50 %), due to its fast time resolution (~ 0.1 Hz) and ability to resolve size-dependant composition. CCN closure in remote environments that use filter-based methods have nevertheless given exceptionally good closure (on the order of a few percent; Bougiatioti et al., 2009, 2011).

Although introducing size-dependent chemical composition (Medina et al., 2007; Stroud et al., 2007; Cubison et al., 2008; Gunthe et al., 2009; Murphy et al., 2009) and accounting for the aerosol mixing state (Broekhuizen et al., 2006; Cubison et al., 2008; Lance et al., 2009) have been found to improve CCN closure, it is still unclear the extent of error associated with ignoring such information in simulations of the aerosol indirect effect. For example, Ervens et al. (2007) found that knowing the mixing state of the aerosol is more important to achieve closure than the size-dependent aerosol chemical composition; while other studies (e.g., Medina et al., 2007; Lance et al., 2009; Asa-Awuku et al., 2011) have found that knowledge of both chemical composition and mixing state are required to achieve closure to within 10–20 %. The treatment of organics in Köhler theory can be described with single-parameter approaches (e.g., Petters and Kreidenweis, 2007), but will nevertheless be subject to some uncertainty and possibly contribute to the discrepancy between measurements and predictions when organics dominate the aerosol mass fraction (e.g., Moore et al., 2011). Rissman et al. (2004) and Sotiropoulou et al. (2007), have shown that even when CCN prediction errors are large, the uncertainty in cloud droplet number associated with these errors is substantially reduced by at least 50 %. When the CCN prediction error is on the order of 20 % as suggested in recent studies (Medina et al., 2007) it does not contribute a significant source of error in the assessment of the aerosol indirect effect (Sotiropoulou et al., 2007). However in regions where aerosol is externally mixed, the CCN prediction can be high enough to have an important regional uncertainty.

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Another uncertain aspect of cloud droplet formation is the potential impact of slowly-dissolving compounds, droplet surface forming films and aerosol amorphous states on the activation kinetics of CCN. If present, kinetic activation delays could have an important impact on cloud droplet number and size distribution (e.g., Chuang et al., 1997; Nenes et al., 2001; Feingold and Chuang, 2002; Lance et al., 2004). To test whether such limitations exist, in-situ field studies compare the size of the activated droplets from the CCN being studied against those obtained from calibration salt aerosol known to exhibit rapid activation kinetics (e.g., Sorooshian et al., 2008; Bougiatioti et al., 2009, 2011; Lance et al., 2009; Murphy et al., 2009; Padró et al., 2010; Cerully et al., 2011). The difference in droplet sizes can reveal whether the compounds present in the aerosol retard droplet growth (i.e., show kinetic limitations). When combined with a computational fluid dynamics model of the CCN instrument (Lance et al., 2006), changes in growth kinetics can be parameterized in terms of an uptake coefficient (Asa-Awuku et al., 2009; Engelhart et al., 2008; Ruehl et al., 2008, 2009). Many studies using this method of Threshold Droplet Growth Analysis (TDGA) have found little or no evidence of slow droplet growth kinetics (e.g., Bougiatioti et al., 2009, 2011; Lance et al., 2009; Padró et al., 2010; Cerully et al., 2011), although others have detected the occurrence of slow kinetics for organic-rich aerosol (e.g., Sorooshian et al., 2008; Murphy et al., 2009).

This paper presents size-resolved CCN and droplet growth kinetic measurements obtained during a ground site study in Atlanta, Georgia, during August and September of 2008. The site was chosen to reflect an urban environment that interacts with biogenic emissions from forested areas prevalent throughout the southeastern United States. This work complements an emerging number of studies that use size-resolved CCN measurements to infer the compositional dispersion and the processes that affect aerosol hygroscopicity (e.g., Lance, 2007; Gunthe et al., 2009; Rose et al., 2010; Mochida et al., 2010; Irwin et al., 2011; Bougiatioti et al., 2011; Su et al., 2011; Cerully et al., 2011). In-situ CCN concentrations are compared to predicted concentrations (from size distributions and chemical composition at constant supersaturation) to

quantify the predictive uncertainty associated with simplifying compositional and mixing state assumptions used in the estimation of CCN concentrations. We characterize the droplet growth kinetics of the urban aerosols by comparing the droplet size of the atmospheric CCN to those of $(\text{NH}_4)_2\text{SO}_4$ calibration aerosol. Finally, we present the trend in aerosol mixing state during the entire study.

2 Data set description

2.1 Measurement site

The main objective of the 2008 August Mini Intensive Gas and Aerosol Study (AMI-GAS) campaign was to study the interactions between biogenic and anthropogenic emissions and how these impact secondary organic aerosol (SOA) formation. Atlanta was chosen for the study site since it represents a typical urban environment, but with strong biogenic influences (Weber et al., 2003). The major components of PM mass in Atlanta aerosol are sulfate and organic carbon (OC) with mostly OC in the ultrafine particle size mode (Butler et al., 2003; Rhoads et al., 2003; Solomon et al., 2003). When aerosol composition is dominated by OC, formation mechanisms are most likely due to local sources; while periods when the particles are dominated by sulfate result from the photochemical production from sources outside of Atlanta such as power plants (Weber et al., 2003).

The measurements presented in this study were obtained during 1 August 2008 – 15 September 2008 at the Jefferson Street site (JST) in downtown Atlanta (33.777°N , 84.416°W), which is affected by fresh urban and regional emissions. Measurements were performed during the summer season since it is the period where SOA is more abundant and mostly formed from biogenic precursors (Lim and Turpin, 2002; Weber et al., 2007; Hennigan et al., 2009).

HYSPLIT back-trajectories (www.arl.noaa.gov/ready/hysplit4.html) were used to determine the characteristics and origin of the air masses affecting JST throughout the

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campaign. Two characteristic periods with different air mass types were identified (Fig. 1). Period A is affected by “polluted” air masses that originate from the continental United States (1–23 August and 28 August–15 September); while Period B is influenced by “cleaner” air masses that originate either from the Atlantic Ocean or the Gulf of Mexico (24–27 August). Period B was also characterized by precipitation events that considerably reduced particle concentrations through wet deposition processes. Although some rain events from rain events also occurred during Period A, these were not as strong and widespread as those observed in Period B. The effect of different air masses and precipitation events on JST site is evident in the total particle (condensation nuclei, CN) and CCN concentrations, (Fig. 2a) which both decrease during Period B.

2.2 Chemical composition measurements

Coarse size aerosols (2.5 μm aerodynamic diameter and above) were removed from the sample air stream with a cyclone. Two particle-into-liquid-samplers were used to study aerosol composition; one for real-time measurement of ionic composition (using ion chromatography; IC), and one for water-soluble organic carbon (WSOC). In each PILS, the aerosols are exposed to supersaturated water vapor and nucleate droplets that are subsequently collected on a plate via inertial impaction. A purified water stream flows over the plate and the solution stream is then sent to the analytical instrumentation. The PILS-IC (Weber et al., 2001) uses a dual channel Ion Chromatograph (Dionex Model 300DX), which allows the detection of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , NH_4^+ , NO_3^- , NO_2^- , SO_4^{2-} , formate, and oxalate ions integrated over roughly 3 minutes of sampling with measurements repeated every 20 min. The PILS-WSOC (Sullivan et al., 2004) uses a Sievers Model 800 Turbo Total Organic Carbon (TOC) Analyzer to obtain the aerosol WSOC mass. Before the WSOC measurements are performed, the sample stream is filtered to remove any large insoluble particles. The PILS-WSOC reports the soluble organic concentration by integrating over 10-min.

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2.3 Size-resolved CCN and particle concentrations

A Scanning Mobility Particle Sizer (SMPS) was used to measure the particle size distribution for particles having electrical mobility diameters (d_m) ranging from 7 to 500 nm. The SMPS consists of a Differential Mobility Analyzer (DMA; TSI Model 3081) running in series with a Condensation Particle Counter (CPC; TSI Model 3022A or TSI Model 3010). Prior to classification, aerosols are passed through a Kr-85 bipolar charger to acquire an equilibrium charge distribution. The charged particles are then classified by the DMA, and sent to a CPC to measure the total aerosol number concentration, and a Continuous-Flow Streamwise Thermal Gradient CCN Chamber (CFSTGC; Roberts and Nenes, 2005; Lance et al., 2006) to measure the number of particles that act as CCN (discussed in Sect. 2.4). By scanning the DMA voltage, a complete particle size distribution is obtained in two minutes. During the course of the study, two different CPCs and DMA sheath-to-aerosol ratios were used. The first CPC (TSI Model 3022A) was replaced on 26 August with a TSI Model 3010 due to an equipment malfunction. Adjustment of the DMA sheath-to-aerosol flow from 10:1 to 5:1 was made on 8 August in order to improve aerosol counting statistics from a broader DMA transfer function. Overall, three SMPS setups (Fig. 3) were employed to optimize counting statistics with the new flow rates. Setups A1 and A2 have a CPC 3022A and sheath-to-aerosol ratios of 10:1 and 5:1, respectively; while setup B has a CPC 3010 and a 5:1 sheath-to-aerosol ratio. Particles sampled were assumed to be spherical, which is supported by previous aerosol measurements in Atlanta (McMurry et al., 2002).

An intercomparison between the 3022 and 3010 CPCs was carried out by comparing the total CN concentration measured by each instrument for data collected between 15 August and 26 August (Fig. 3; Setup A2). As both CPCs have different particle size detection limits (7 nm and 10 nm for the CPC 3022 and CPC 3010, respectively), the particle size distribution obtained from the SMPS (that used the 3022 as a particle detector) was integrated above 10 nm to match the size range of the CPC 3010. The data were filtered to include only scans for which aerosol modes are fully resolved within the

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dynamic range of the scan, and, where the total CN remains constant throughout the scan (within 15 % of average CN concentration). Furthermore, periods of exceptionally high total CN concentrations ($>10^4$ particles cm^{-3}), were removed from the data to avoid coincidence errors associated with the CPC 3010. Based on the measurements, the integrated size distributions with the CPC 3022 were found to be about 25 % lower than the CN concentration from the CPC 3010 (Fig. 4). About 15 % of this bias could be attributed to instrument-dependent bias (determined by sampling the same air mass with both instruments). The absolute bias varied approximately linearly with concentration, while the relative bias remained constant. The total CN concentrations (measured and predicted) obtained for Setups A1 and A2 were corrected for this bias before the CCN closure analysis was performed. The total CN time-series (after correction) is shown in Fig. 2. Throughout the campaign the CCN was found to correlate well with the CN concentration and increased with supersaturation (Fig. 2a).

The total aerosol concentration was measured continuously with a CPC with a minimum diameter of 10 nm (TSI model 3010) from 15 August to 26 August. Apart from providing a consistency check the separate CPC was used to detect small intense plumes that may occasionally pass over the site that could not be resolved with the 120s scantime of the SMPS.

2.4 CCN activity and growth kinetic measurements

Prior to measurement, the sampled air stream was dried from ambient relative humidity (RH) to ~ 21 % RH to minimize residual water, as this can affect the inference of aerosol CCN activity, especially for very acidic aerosol (e.g., Murphy et al., 2009). The classified aerosol was sent to the CFSTGC chamber, where some particles activate to form droplets, which are counted and sized by an optical particle counter (OPC) at the end of the growth chamber. The OPC detects the droplet size distribution ranging from ~ 0.7 to $10 \mu\text{m}$ with a resolution of $0.5 \mu\text{m}$.

In this work, size-dependant CCN activity data is obtained using Scanning Mobility CCN Analysis (SMCA; Moore et al., 2010). In SMCA, the DMA voltage is exponentially

scanned over time (120 s upscan, 15 s downscan) to continuously sample particles across the size distribution. The time-series of CCN and CN counts are then inverted to obtain size-resolved CCN concentration and activated droplet size. The aerosol size, analyzed for this study, ranged from 10 to 500 nm, depending on the sheath-to-aerosol ratio used in the DMA (10:1 or 5:1). A total of five supersaturations (s) were run in the following order: 0.2, 0.6, 1.0, 0.8, and 0.4 % supersaturation, allowing sufficient time (6 min) for the instrumentation to reach steady state following a supersaturation change. Instrument supersaturation was calibrated with classified $(\text{NH}_4)_2\text{SO}_4$ particles using a similar procedure to that of Rose et al. (2008) and Padró et al. (2010). The resulting calibration curve was then used to determine the temperature gradient required to generate the desired instrument supersaturation.

3 Experimental analysis

The CCN activity of the aerosol is characterized at each supersaturation by determining the “critical” dry particle diameter, $d_{p,c}$, above which particles activate to form droplets. Operationally this is defined as the dry diameter for which the CCN to CN ratio equals 0.50 (assuming all CN are CCN active). As shown in Fig. 5a, the sigmoidal activation curve can be used to infer the $d_{p,c}$. From this size-resolved data, the mixing state and hygroscopicity parameter distribution are determined (Sect. 3.1).

CCN activation kinetics are determined from the CCN measurements by monitoring the change in droplet size measured by the OPC for all supersaturations and dry particle diameters considered, and by comparing these sizes to those for $(\text{NH}_4)_2\text{SO}_4$ calibration particles with the same critical supersaturation.

3.1 Analysis of SMCA data

Each DMA size scan was screened for fluctuations in the CFSTGC chamber temperature gradient, OPC temperature, and stability of the flows. Data exhibiting maximum

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temperature or flow deviations of more than 15% from the setpoint were discarded. The size-dependent activation ratio function, $R_a(d_p, s)$, was determined by computing the CCN to CN ratio as a function of dry particle diameter, d_p , at supersaturation, s . $R_a(d_p, s)$ was fit to a sigmoidal curve:

$$R_a(d_p, s) = \frac{N_{\text{CCN}}(d_p, s)}{N_{\text{CN}}(d_p)} = \frac{E}{1 + \left(\frac{d_{p,c}}{d_p}\right)^C} \quad (1)$$

where N_{CCN} is the total CCN number concentration, N_{CN} is the total aerosol number concentration, E is the asymptote of $R_a(d_p, s)$ at large particle sizes, $d_{p,c}$ is the characteristic dry diameter for which most particles are CCN and corresponds to the inflection point of the sigmoid, and C is an empirical coefficient that captures the slope of the sigmoidal function (Fig. 5a). Overall, we found Eq. (1) to describe the size-resolved CCN well (e.g., Fig. 5a). However, in some cases integrating the fitted sigmoids did not reproduce the measured CCN concentration within 15% and therefore were removed from the analysis.

$R_a(d_p, s)$ can be used to study the size-dependent hygroscopicity and mixing state by evaluating the function at different diameters (in this study, at 30, 40, 50, 60, 70, 80, 90, and 100 nm) for all sigmoids within a supersaturation cycle. The supersaturation-dependant activation ratio function, $R_a(s, d_p)$, (the fraction of particles of size d_p that are CCN at s) is subsequently determined and fit to a new sigmoidal function (Bougiatioti et al., 2011):

$$R_a(s, d_p) = \frac{N_{\text{CCN}}(s, d_p = \text{const})}{N_{\text{CN}}(d_p = \text{const})} = \frac{E^*}{1 + \left(\frac{s}{s^*}\right)^{C^*}} \quad (2)$$

where E^* is the asymptotic activated fraction at large supersaturations, s^* is the characteristic critical supersaturation of particles with diameter d_p , and C^* is a fitting constant that captures the slope of the fitting function (which is related to aerosol chemical heterogeneity). Figure 5b shows a typical example of $R_a(s, d_p)$ for 80 nm particles obtained on 14 August.

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As described by Lance (2007), Bougiatioti et al. (2011), and Cerully et al. (2011), $R_a(s, d_p)$ mostly reflects the cumulative distribution of the “characteristic” critical supersaturation for particles of constant d_p , and can be expressed as a cumulative distribution of hygroscopicity, $R_a(\kappa)$, as follows. Assuming that $R_a(\kappa)$ is driven solely by the chemical composition variance and using the definition of κ (if $\kappa > 0.1$; Petters and Kreidenweis, 2007),

$$\kappa = \frac{4A^3}{27d_{50}^3} s^{-2} \quad (3)$$

where $A = \frac{4M_w\sigma_w}{RT\rho_w}$ (Petters and Kreidenweis, 2007), R is the ideal gas constant, T is the temperature and M_w , σ_w , ρ_w are the molar mass, surface tension, and density of water, respectively. For every s^* there is a corresponding “characteristic” hygroscopicity parameter, κ^* , so that (s/s^*) can be expressed as $(\kappa/\kappa^*)^{-1/2}$. Substituting this into Eq. (2) gives $R_a(\kappa)$, which is the fraction of particles of size d_p that are CCN as a function of κ :

$$R_a(\kappa) = \frac{E^*}{1 + \left(\frac{\kappa}{\kappa^*}\right)^{c^*/2}} \quad (4)$$

Differentiating and normalizing Eq. (4) gives the probability distribution of κ , $\rho(\kappa)$, for particles of constant size (Lance, 2007; Bougiatioti et al., 2011; Cerully et al., 2011),

$$\rho(\kappa) = \frac{1}{E^*} \frac{dR_a(\kappa)}{d\kappa} = \frac{c^*}{2\kappa^*} \frac{\left(\frac{\kappa}{\kappa^*}\right)^{\frac{c^*}{2}-1}}{\left(1 + \left(\frac{\kappa}{\kappa^*}\right)^{\frac{c^*}{2}}\right)^2} \quad (5)$$

from which one can compute the variance of the distribution function, which represents

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the extent of aerosol chemical heterogeneity within the CCN-active aerosol fraction,

$$\sigma_{\kappa}^2 = \frac{\int_0^1 (\kappa - \kappa_*)^2 p(\kappa) d\kappa}{\int_0^1 p(\kappa) d\kappa} \quad (6)$$

The upper limit of hygroscopicity in the integrals is operationally set to unity, which captures the upper limit of atmospheric κ values in the absence of sea salt (Cerully et al., 2011). κ and σ_{κ} are obtained for all diameters and supersaturations considered.

3.2 CCN distribution

Since the size-resolved aerosols are sent simultaneously to the CPC and CCN counter for CN and CCN measurements, the CCN distribution can be obtained by multiplying the particle size distribution with the $R_a(d_p, s)$ ratio. The CCN distribution at a given supersaturation, $\frac{dN_{CCN}}{d\log D_p}$, is defined as:

$$\frac{N_{CCN}}{d\log D_p} = R_a(d_p, s) n(d\log D_p) \quad (7)$$

where $n(d_p)$ is the particle size distribution. Substituting Eq. (1) into Eq. (7) gives:

$$\frac{dN_{CCN}}{d\log D_p} = \frac{E}{1 + (d_{p50}^*/d)} n(d_p) \quad (8)$$

Integrating Eq. (8) for all sizes gives the total CCN concentration (N_{CCN}) in cm^{-3} :

$$N_{CCN} = \int_0^{\infty} \frac{dN_{CCN}}{d\log D_p} d\log D_p. \quad (9)$$

3.3 CCN closure and mixing state

CCN closure is defined as a comparison between measured and predicted CCN concentrations. CCN closures are performed to determine how well Köhler theory can predict CCN formation when the chemical composition and mixing state of the aerosol are known. To predict CCN concentrations, the supersaturation, the aerosol size distribution, and aerosol chemical composition (bulk or size resolved) are needed. CCN predictions were made using the measured CN size distributions (120 s resolution) and particle chemical composition information from the PILS-IC (20 min resolution) and PILS-TOC (620 s resolution). The chemical composition data was binned to match the SMCA time series as shown in Fig. 6 to account for the diversity of measurement frequency of each instrument.

The predicted CCN concentration at each supersaturation was determined by calculating the minimum aerosol diameter that acts as a CCN, termed “activation diameter”, $d_{p,c}$, from Köhler theory (Köhler, 1936):

$$d_{p,c} = \left(\frac{256M_w^3\sigma^3}{27R^3T^3\rho_w^3} \right)^{1/3} \left[\sum_i \left(\frac{M_w}{\rho_w} \right) \left(\frac{\rho_i}{M_i} \right) \varepsilon_i \nu_i \right]^{-1/3} S^{-2/3} \quad (10)$$

where σ is the surface tension of the CCN at the point of activation (here assumed to be equal to σ_w) and ρ_i , ε_i , ν_i , and M_i are the density, volume fraction, effective van't Hoff factor and molar mass of the solute i (sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic species). The volume fraction of solute i in the dry particle, ε_i , is related to the mass fraction of i , x_i , as:

$$\varepsilon_i = \frac{x_i/\rho_i}{\sum_j (x/\rho)_j} \quad (11)$$

For the closure, the effective van't Hoff factor of organic species was assumed to be 1, while the Pitzer activity coefficient model (Pitzer and Mayorga, 1973; Pilinis and Seinfeld, 1987; Clegg and Brimblecombe 1988) was used to calculate the effective van't

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Hoff factor of all inorganic salts present in the sample, at the concentration corresponding to the critical wet droplet diameter of the CCN. Following Nenes et al. (1998), the sulfate molar ratio, $R_{\text{SO}_4} = [\text{NH}_4^+]/[\text{SO}_4^{2-}]$, was used to determine the SO_4^{2-} speciation in the aerosol phase. When $R_{\text{SO}_4} \leq 1$, the sulfate and ammonium are present as a mixture of H_2SO_4 and NH_4HSO_4 , when $1 < R_{\text{SO}_4} < 2$, the sulfate and ammonium are present as a mixture of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ and when $R_{\text{SO}_4} \geq 2$, the sulfate and ammonium are present as $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 (if NH_4^+ is in excess).

Two different CCN closure schemes were assessed based on assumptions related to the chemical composition and mixing state of the aerosol (i.e., the maximum activated fraction, E , obtained from the CCN spectrum):

Internal Mixture (INT) – all particles have the same composition.

External Mixture (EXT) – two types of particles are present: soluble particles and insoluble particles. Only the soluble particle fraction is considered to contribute to CCN, and the relative number fractions of each type of particle are determined from the CCN sigmoidal fit parameter, E , with E soluble particles and $(1 - E)$ insoluble particles.

In addition to the different aerosol mixing states a number of different chemical composition and surface tension assumptions are explored for the soluble fraction:

Ammonium Sulfate (AS) – the aerosol is assumed to be composed of pure $(\text{NH}_4)_2\text{SO}_4$.

Soluble Salts, Insoluble Organics (SALTS) – here, soluble inorganic salts are only considered to contribute solute (as determined from the PILS IC and PILS WSOC measurements). This scenario underestimates aerosol hygroscopicity because the organics are known to contain water-soluble compounds based on the PILS sampling technique; however, this case is still instructive as neglecting organic hygroscopicity is a common model assumption.

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Soluble Salts, Soluble Organics (ALLSOL) – the aerosol is composed of soluble inorganic salts and soluble organics, as determined from the PILS measurements. Contrary to the SALTS scenario, in this case all components are treated as soluble (i.e., $\nu_{\text{org}}, M_{\text{org}} = 250 \text{ g mol}^{-1}$, $\rho_{\text{org}} = 1.4 \text{ g cm}^{-3}$).

5 *Soluble Salts, Soluble and Surface-Active Organics (ALLSOL-ST)* – the aerosol is composed of soluble inorganic salts and soluble organics, as determined from the PILS measurements. In this case, all components are treated as soluble (i.e., $\nu_{\text{org}}, M_{\text{org}} = 250 \text{ g mol}^{-1}$, $\rho_{\text{org}} = 1.4 \text{ g cm}^{-3}$) and the organic species present are assumed to be surface active and to reduce the surface tension of the solution droplet to 75 % that of pure water.

The ammonium sulfate compositional case was only applied to the internal mixture case, while the other compositional assumptions were applied to both cases for a total of seven closure scenarios considered. Hereafter, the scenarios are referenced by combining the acronyms of the mixing state and composition scenario (e.g., *INT-AS* is internally-mixed aerosol composed only of ammonium sulfate).

15 The total CCN predicted from the seven CCN closure scenarios explained above are compared to the total CCN obtained from SMCA. The CCN closure agreement between predicted and observed values is performed by a least-squares linear fit. Besides the correlation that can be obtained from the linear fit, the closure agreement is assessed in terms of two error metrics: the Normalized Mean Error (NME) and the Normalized Mean Bias (NMB),

$$\text{NME} = \frac{\sum_i^n |P_i - O_i|}{\sum_i^n O_i} \quad (12)$$

and

$$\text{NMB} = \frac{\sum_i^n P_i - O_i}{\sum_i^n O_i} \quad (13)$$

where P and O are the predicted and measured “critical” dry particle diameter or total CCN number concentrations averaged over each SMPS scan, i . These metrics provide additional information regarding the accuracy and bias of the theoretical predictions.

4 Results and discussion

4.1 CCN closure

Since the SMCA technique and the sigmoidal fit (Eq. 1) provide us with the characteristic activation diameter, a comparison between the measured and predicted $d_{p,c}$ can be performed. For the internal mixture case, a diameter comparison was done for the four chemical composition and surface tension scenarios (Table 1; Fig. 7a). For all scenarios considered, theory predicts a smaller diameter, $d_{p,c}$, is predicted than the observed. From all the internal mixture scenarios, *INT-SALTS* and *INT-ALLSOL* provide the best closure although, $d_{p,c}$ is still underpredicted by 26 and 30 %, respectively. For the external mixture cases, a comparison was done for the *EXT-ALLSOL* and *EXT-ALLSOL-ST* cases still with an underprediction bias; better closure was achieved for the *EXT-ALLSOL* case ($d_{p,c}$ is underpredicted by 35 %; Fig. 7b). Of the mixing state scenarios, the best agreement was achieved when the aerosol was assumed to be internally mixed and only the salts were soluble (*INT-SALTS*).

The predicted $d_{p,c}$ for each case was then used to determine the theoretical CCN concentration and compared to that measured. As expected from the activation diameter results (Fig. 7), a discrepancy between the predicted and measured CCN concentration was observed for all scenarios within the internal and external mixture cases (Table 2, Fig. 8). The best CCN closure was achieved for the *EXT-SOL* where the predicted CCN concentration was found to be ~40 % greater than the measured CCN concentration. For all other mixing state and chemical composition scenarios, the predicted CCN was approximately twofold greater than measured (Fig. 8). Based on the closure results (Table 2), it is likely that organics contribute some solute and possibly

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depress surface tension (less than the assumed 25 %) in Atlanta. It is also likely that better closure would be achieved if size-resolved chemical composition were available (Medina et al., 2007). For all the CCN closure analyses performed, a uniform external mixture fraction ($1 - E$ at diameter >200 nm) was assumed to perform the external CCN closure scenarios. This constitutes an “upper limit” as larger particles tend to be more internally mixed (have a lower $1 - E$; Fig. 9: see Sect. 4.2). The CCN closure for the external mixture scenarios, *EXT-ALLSOL* and *EXT-ALLSOL-ST*, lead to an overestimation and greater discrepancy than their internal mixture counterpart (e.g., *INT-ALLSOL* and *INT-ALLSOL-ST*). This analysis suggests that a more precise knowledge of mixing state (as function of size) as well as chemical composition (size-resolved) is needed in order to achieve closure for complex urban aerosol such as those seen in Atlanta.

To assess the impact of size-resolved mixing state on the CCN closure, an additional size-resolved external mixture (*SR-EXT*) scenario was assessed using the mixing state obtained from the fitted CCN activity spectrum over a range of dry diameters (Fig. 9). For *SR-EXT*, the activated or internal mixture fraction (E^*) of the aerosol was assumed to be completely soluble with compositions obtained from the PILS measurements (similar to the *ALLSOL* case above). $N_{\text{CCN,predicted}}$ is obtained by applying a modified form of Eq. (9) to find the total CCN concentration at each size bin scaled by the soluble particle fraction (E^*):

$$N_{\text{CCN}} = \int_{d_c}^{\infty} \frac{dN_{\text{CCN}}}{d \log D_p} E^* d \log D_p \quad (14)$$

where $E_{d_p}^*$ is the internal mixture fraction at each diameter. Compared to the internal and external closure scenarios previously discussed, introducing size-resolved mixing state information significantly improves CCN closure (average overprediction = 10 %; Fig. 10), which is approaching the level seen for very aged aerosol (e.g., Bougiatioti et al., 2011). The remaining error is likely due to the assumption of size-averaged composition.

4.2 Mixing state and hygroscopicity time-series

Figure 11 shows the time-series of the sigmoidal fit parameters (E^* , s^* , and C^* in Eq. 2) obtained from fitting the CCN activity spectrum as a function of supersaturation for the 80 nm particles over the entire AMIGAS campaign. The air mass periods discussed in Sect. 2.1 are indicated on the plot. There is no clear correlation between the different periods and fit parameters (Fig. 11); however, there is a slight increase in the non-CCN-active aerosol fraction ($1 - E^*$) after 27 August (2nd A Period; Fig. 11a) and a decrease in the characteristic supersaturation (s^* ; Fig. 11b). The slight decrease in the s^* (regardless of the increase in the externally mixed aerosol) suggest that the internally mixed particles at the end of the campaign (after 24 August) were slightly more hygroscopic than those observed at the beginning. The increase in the aerosol hygroscopicity may be due to organic compounds reacting in the aqueous phase; therefore increasing the water soluble organic carbon (WSOC) fraction present in the particle phase. This observation is consistent with recent studies (e.g., Hennigan et al., 2008) in Atlanta that found the fraction of the total WSOC in the particle phase to have a strong dependence with RH above 70 % as is the case in this study. As for the chemical heterogeneity of the activated particles (Fig. 11c), the particles have the same chemical variability regardless of the air mass sampled.

κ is calculated using the surface tension of water evaluated at the median column temperature (Petters and Kreidenweis, 2007). However, the surface tension of the CCN can be different from water if surfactants are present (Kiss et al., 2005; Dinar et al., 2007), which can introduce uncertainty in κ calculations (Padró et al., 2010). The κ time-series for the whole AMIGAS campaign for 80 nm particles is shown in Fig. 12, and typically ranged between 0.03–0.48 (mean of 0.16 ± 0.07). These values of κ are consistent with mixtures of soluble salts and organic species (Carrico et al., 2008; Koehler et al., 2009; Petters and Kreidenweis, 2007; Shantz et al., 2008). As for the chemical heterogeneity of the particles, there is no clear correlation between the particle hygroscopicity and air mass sampled.

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4.3 Droplet activation kinetics

The measured CCN droplet sizes were used to assess the effect of organics on activation kinetics. In Fig. 13, the droplet size at the point of activation (D_p corresponding to $d_{p,c}$) for a subset of the ambient data is plotted against the instrument supersaturation. The droplet sizes for ambient aerosol are compared to the droplet sizes from $(\text{NH}_4)_2\text{SO}_4$ calibration aerosol at the same supersaturation. If the droplets formed from ambient CCN are smaller than those from the calibrations, this may indicate that the CCN experience slow growth kinetics from the presence of organics. Special attention should be given to the CCN concentration, as if high enough, it can deplete the water supersaturation in the CFSTGC chamber and explain the reduced droplet sizes (Latham and Nenes, 2011). Thus, while threshold growth analysis can rule out the presence of slowly-growing particles, it cannot always unambiguously identify slowly-activating particles. Rather, a detailed numerical model is required to account for the various droplet growth dependencies and numerically constrain kinetic growth parameters.

During AMIGAS, Atlanta aerosol exhibit similar activation kinetics to $(\text{NH}_4)_2\text{SO}_4$ (Fig. 13); however, an increase in the number of particles that exhibit smaller droplet sizes was observed at higher supersaturations. The quantity of outliers was shown to increase with supersaturation (e.g., lower activation diameters) from 4% (at 0.2% supersaturation) to 9% (at 1.0% supersaturation) of the total data points. Of these, some points were found to lie within the variability of the average droplet diameter, especially for the lower supersaturations. A detailed assessment of the few particles that produced small CCN droplet sizes will be the focus of future work.

5 Conclusions

Size-resolved CCN measurements were performed during the AMIGAS campaign, which took place in Atlanta, GA, from 1 August until 15 September 2008. Size-resolved

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CCN activation ratio (CCN/CN) were obtained with SMCA and used to parameterize the aerosol mixing state (e.g., CCN activation fraction), hygroscopicity, and activation characteristics (CCN droplet sizes). Additionally, the SMCA data (particle size distribution and CCN measurements) were compared to predictions based on size distribution and chemical composition measurements to perform CCN closures, in which four different chemical composition and two different mixing state assumption scenarios were considered.

Of all the cases considered, the best closure was achieved for the size-resolved mixing state scenario (~10% overprediction). It is possible that the CCN closure would further improve with detailed size-resolved chemical composition. The results of the CCN closure scenarios considered here indicate the importance of knowing the chemical composition and mixing state of aerosols to predict CCN concentrations more accurately. As for the activated CCN, most of the aerosols sampled during the campaign experienced growth similar to $(\text{NH}_4)_2\text{SO}_4$.

Acknowledgements. This research was supported in part by a NASA Earth System Science Fellowship, a DOE GCEP Graduate Research Environmental Fellowship, the Electrical Power Research Institute, a NSF-CAREER award and NOAA grants.

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Table 1. “Critical” dry particle diameter closure analysis error metrics for entire AMIGAS campaign.

Description of CCN Closure Scenario	Linear Fit Slope (R^2)	Normalized Mean Error	Normalized Mean Bias
Internal Mixture – $(\text{NH}_4)_2\text{SO}_4$ (<i>INT-AS</i>)	0.57 (0.70)	0.428	–0.428
Internal Mixture – Only Salts Soluble (<i>INT-SALTS</i>)	0.74 (0.70)	0.273	–0.261
Internal Mixture – All Soluble (<i>INT-ALLSOL</i>)	0.70 (0.73)	0.307	–0.302
Internal Mixture – All Soluble and Surface Active (<i>INT-ALLSOL-ST</i>)	0.53 (0.73)	0.477	–0.477
External Mixture – $(\text{NH}_4)_2\text{SO}_4$ (<i>EXT-SOL</i>)	N/A	N/A	N/A
External Mixture – All Soluble (<i>EXT-ALLSOL</i>)	0.65 (0.71)	0.349	–0.346
External Mixture – All Soluble and Surface Active (<i>EXT-ALLSOL-ST</i>)	0.49 (0.71)	0.509	–0.509
Size-Resolved – External Mixture (<i>SR-EXT</i>)	N/A	N/A	N/A

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Table 2. CCN closure analysis error metrics for entire AMIGAS campaign.

Description of CCN Closure Scenario	Linear Fit Slope (R^2)	Normalized Mean Error	Normalized Mean Bias
Internal Mixture – $(\text{NH}_4)_2\text{SO}_4$ (<i>INT-AS</i>)	2.23 (0.32)	1.937	1.937
Internal Mixture – Only Salts Soluble (<i>INT-SALTS</i>)	1.96 (0.53)	1.462	1.462
Internal Mixture – All Soluble (<i>INT-ALLSOL</i>)	2.02 (0.48)	1.567	1.567
Internal Mixture – All Soluble and Surface Active (<i>INT-ALLSOL-ST</i>)	2.34 (0.33)	2.065	2.065
External Mixture – $(\text{NH}_4)_2\text{SO}_4$ (<i>EXT-SOL</i>)	1.17 (0.64)	0.489	0.401
External Mixture – All Soluble (<i>EXT-ALLSOL</i>)	2.09 (0.41)	1.692	1.692
External Mixture – All Soluble and Surface Active (<i>EXT-ALLSOL-ST</i>)	2.39 (0.26)	2.179	2.179
Size-Resolved – External Mixture (<i>SR-EXT</i>)	1.10 (0.95)	0.172	0.159

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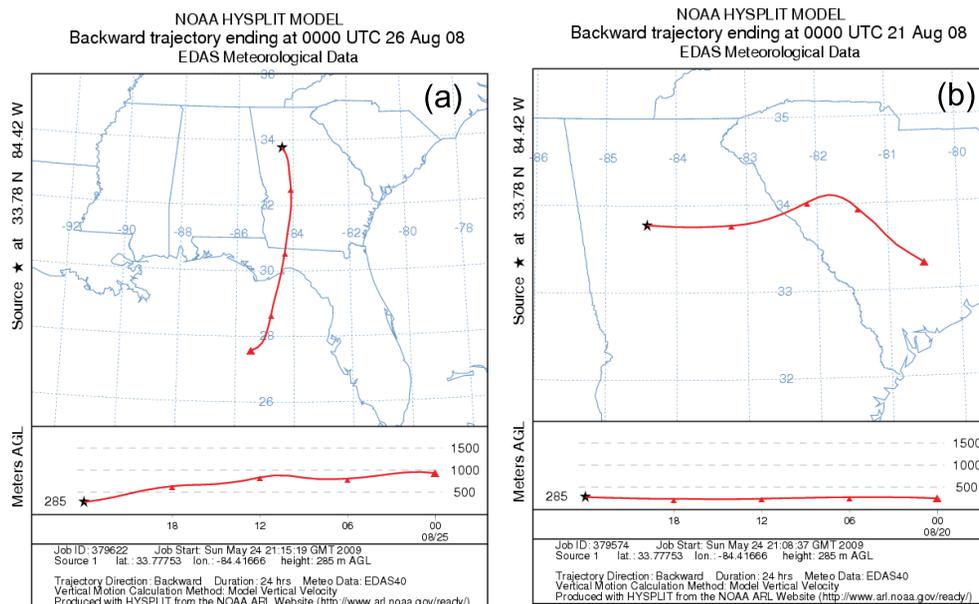


Fig. 1. HYSPLIT one day back-trajectories representative of the air masses sampled in JST during the AMIGAS campaign. Plot (a) represents a “cleaner” air mass originating from the Gulf of Mexico; while plot (b) represents a “polluted” air mass which originated from the continental US. During 24 August till the 27th, the air masses originated either from the Atlantic Ocean or the Gulf of Mexico.

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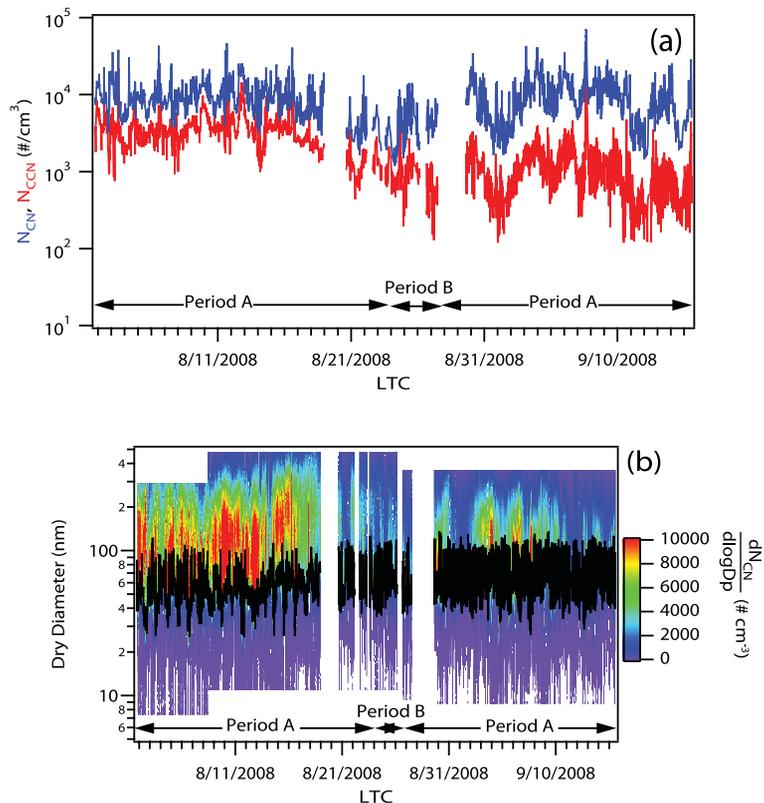


Fig. 2. (a) Total CN and CCN time-series (for all five supersaturations studied during the AMIGAS campaign) for whole AMIGAS campaign. (b) Particle size distribution time-series with characteristic dry diameter, $d_{p,c}$ (black line). Period A correspond to “polluted” air masses originating from the continental US; while period B corresponds to “cleaner” air masses originating from either the Atlantic Ocean or Gulf of Mexico. Gaps in data are a result of instrument outage.

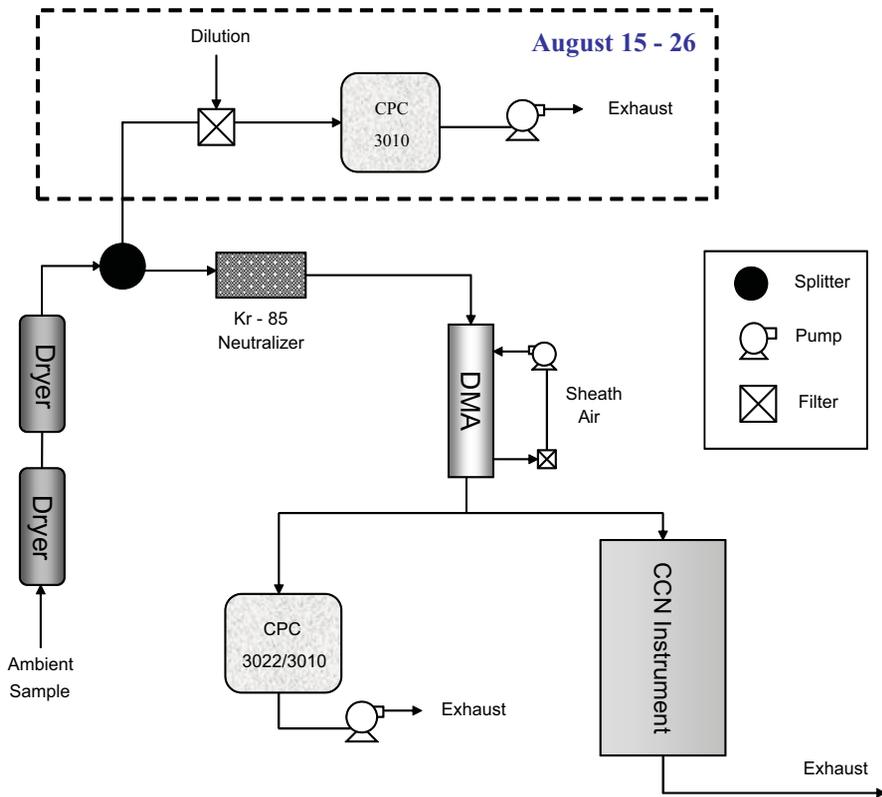


Fig. 3. AMIGAS experimental set up. From 1 till 26 August, the CPC 3022A was used for the SMPS; while the CPC 3010 was used from 26 August till the end of the campaign (15 September). The sheath-to-aerosol ratio in the DMA was run at 10:1 (1 till 8 August; Setup A1) and 5:1 (8 August till 15 September; Setup A2 and B). The dotted box highlights the total CN measurement which was done from 15 till 26 August with the CPC3010.

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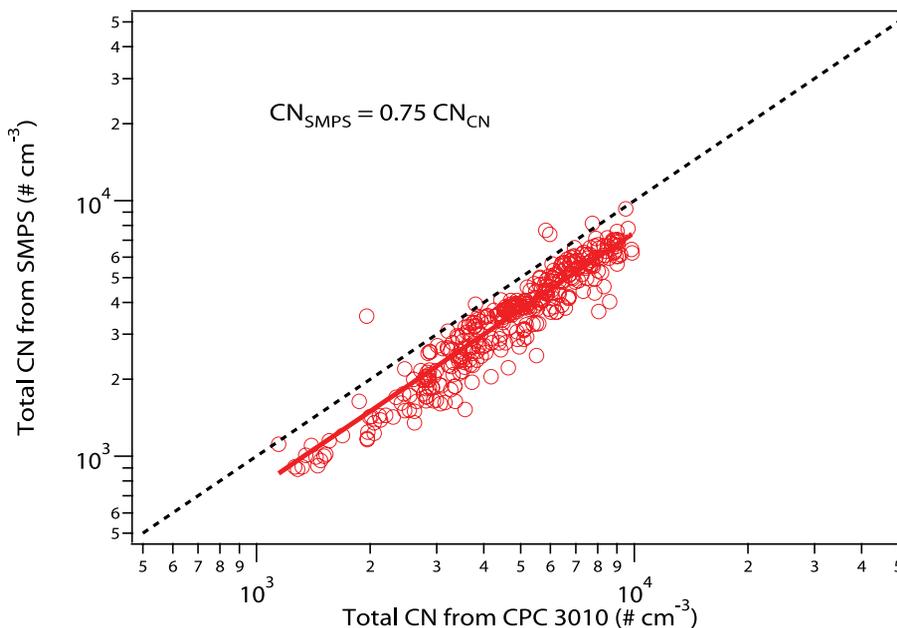


Fig. 4. Scatter plot of total CN obtained from integration of the SMPS distribution (CPC 3022) versus that measured by the CPC (3010).

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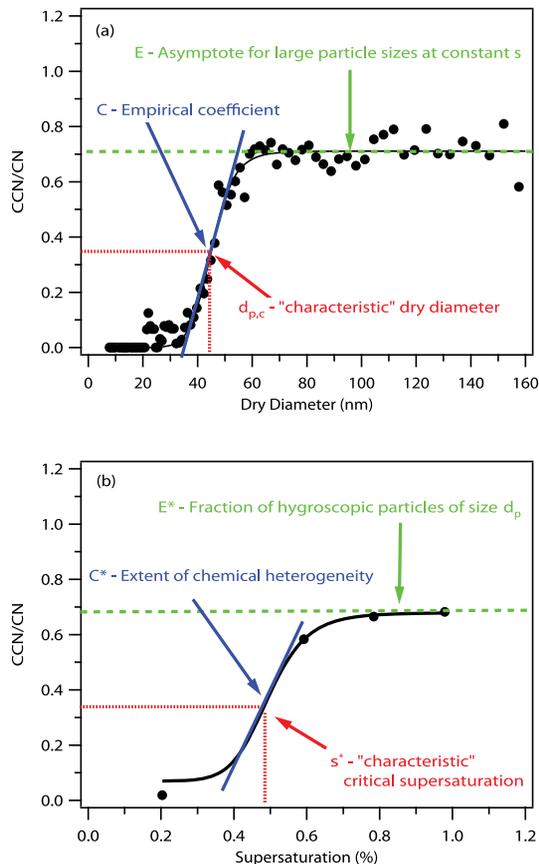
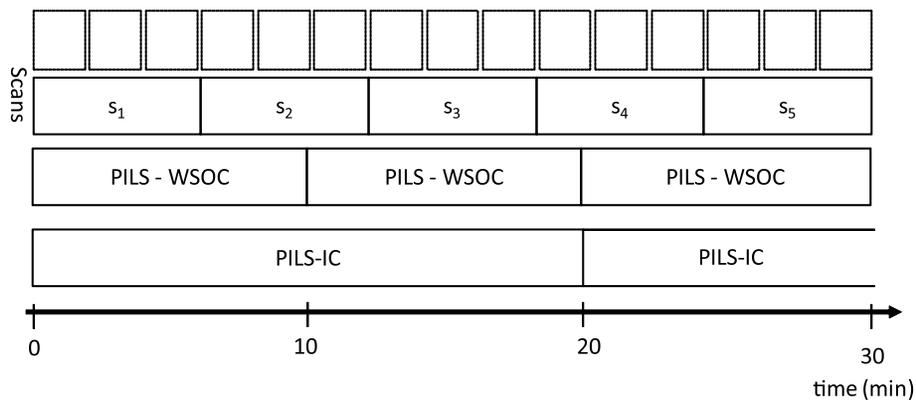


Fig. 5. (a) Example of the CCN-to-CN activation ratio as a function of dry diameter (for $s = 0.98\%$ on 2 August 2008 at 01:30 a.m.) with sigmoid fit and its defined parameters. **(b)** Example of CCN-to-CN activation ratio as a function of supersaturation for a 80 nm dry particle (sample collected on 14 August 2008 at 01:00 p.m.) as derived from the SMCA with sigmoid fit and its defined parameters data.

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**Fig. 6.** Coordination of measurements used in this study for each 30 min measurement cycle.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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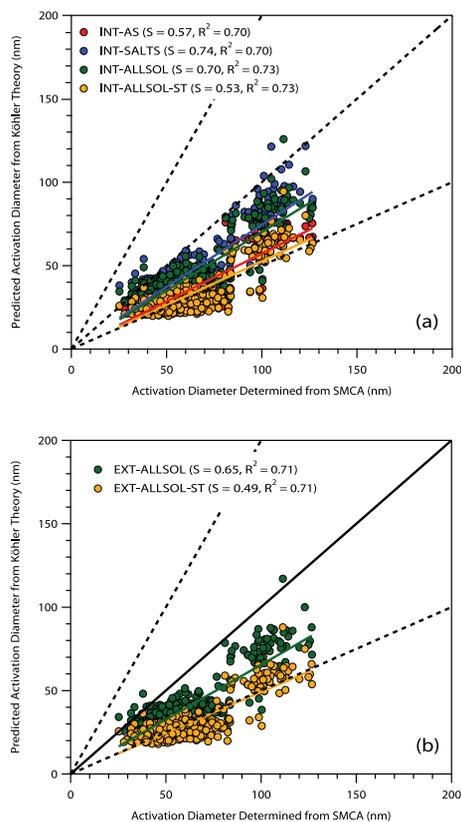


Fig. 7. (a) $d_{p,c}$ closure for the internal mixture (INT) scenarios. The red, blue, green, and yellow circles correspond to the INT-AS, INT-SALTS, INT-ALLSOL, and INT-ALLSOL-ST cases (Table 1), respectively. (b) $d_{p,c}$ closure for the external mixture (EXT) scenarios. The green and yellow circles correspond to the EXT-ALLSOL, and EXT-ALLSOL-ST cases (Table 1), respectively. Dashed lines represent 1:1, 1:2, and 2:1 prediction error.

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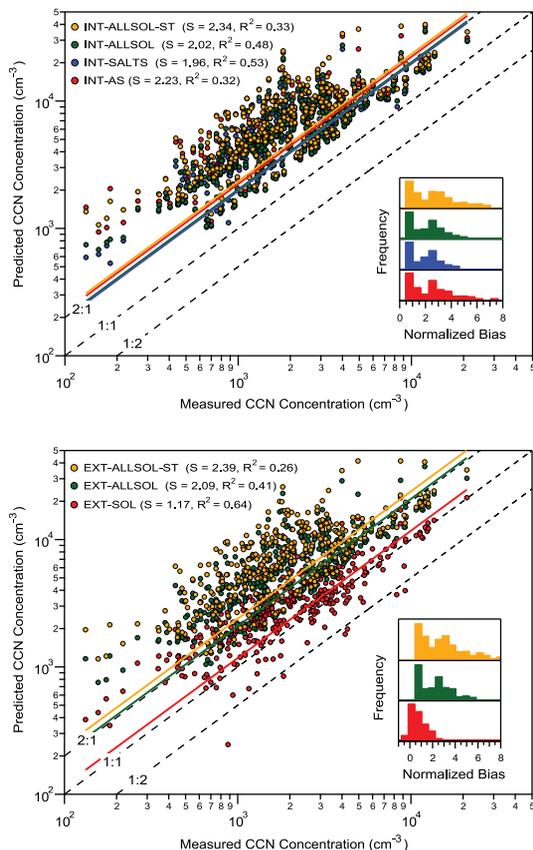


Fig. 8. (a) CCN closure plot for the internal mixture (INT) scenarios. The red, blue, green, and yellow circles correspond to the INT-AS, INT-SALTS, INT-ALLSOL, and INT-ALLSOL-ST cases (Table 1), respectively. (b) CCN closure plot for the external mixture (EXT) scenarios. The red, green, and yellow circles correspond to the EXT-SOL, EXT-ALLSOL, and EXT-ALLSOL-ST cases, respectively. Inset plots show the observed frequency distribution of the normalized mean bias = $(P_i - O_i)/O_i$.

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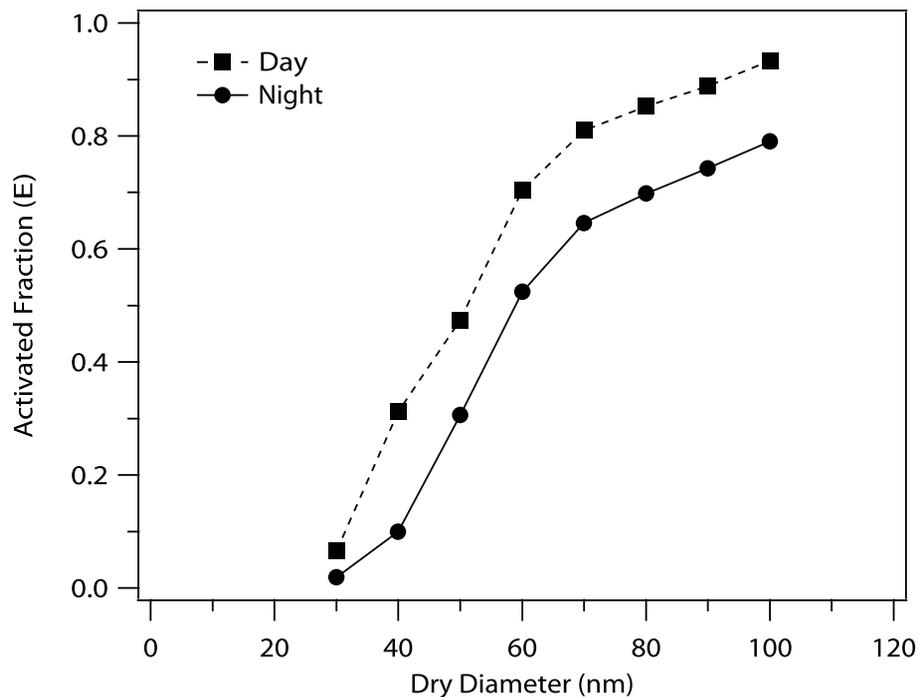


Fig. 9. Example of activation fraction as function of particle size for a day (square) and night (circle) sample. The smaller the particles the more externally mixed they become (smaller E).

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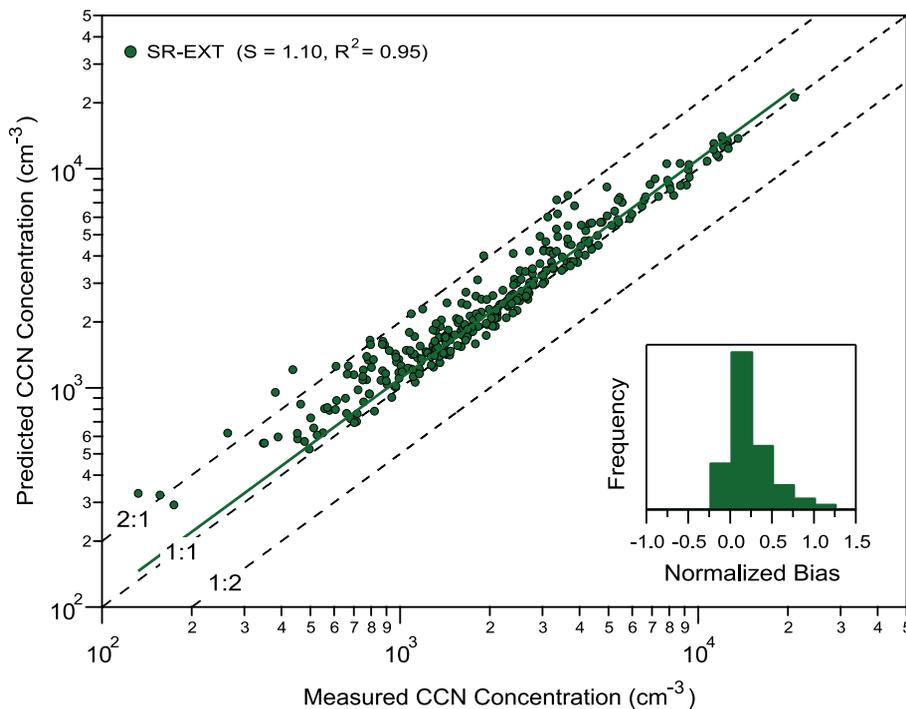


Fig. 10. CCN closure plot for the size-resolved external mixture (SR-EXT) scenario. Inset plot shows the observed frequency distribution of the normalized mean bias = $(P_i - O_i)/O_i$.

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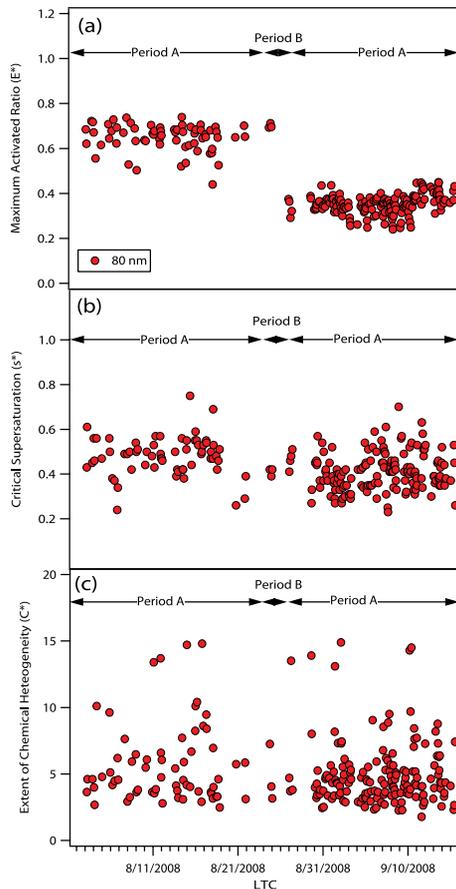


Fig. 11. Time-series of **(a)** maximum activated ratio, **(b)** characteristic critical supersaturation, and **(c)** extent of chemical heterogeneity for 80 nm particles. Period A correspond to “polluted” air masses originating from the continental US; while period B corresponds to “cleaner” air masses originating from either the Atlantic Ocean or Gulf of Mexico.

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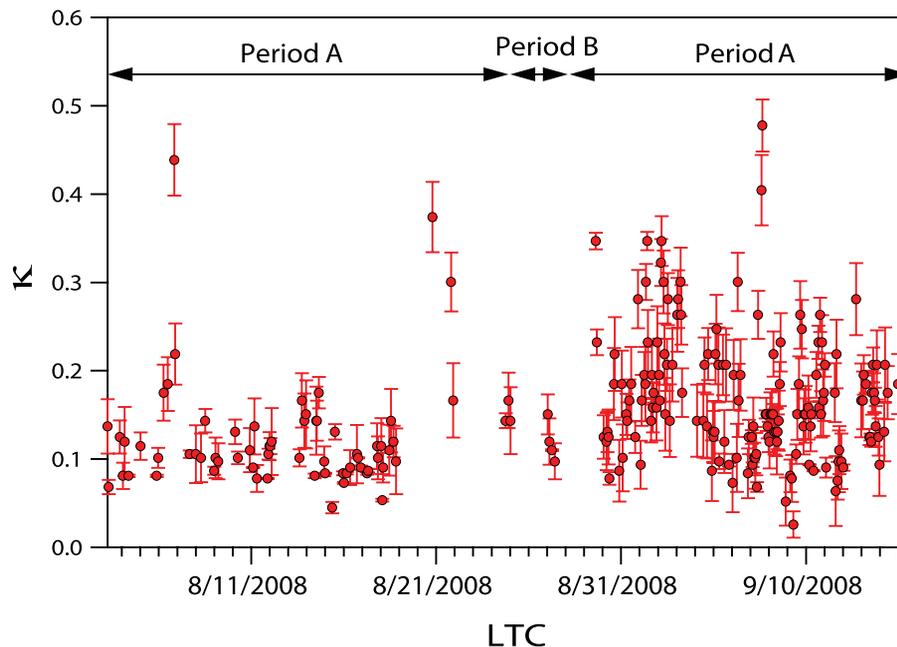


Fig. 12. Time-series of the characteristic hygroscopicity parameter (κ^* ; red circles) and its variability (error bars represented by σ_κ) for 80 nm particles. Period A correspond to “polluted” air masses originating from the continental US; while period B corresponds to “cleaner” air masses originating from either the Atlantic Ocean or Gulf of Mexico. Gaps in data are a result of power outage or instrument problems.

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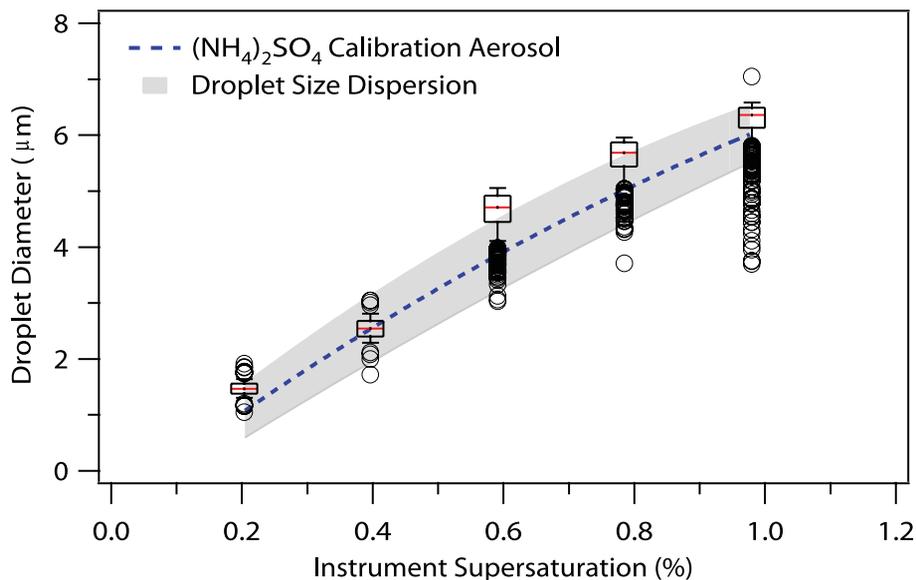


Fig. 13. Droplet growth kinetics study analysis. Box plots for ambient droplet sizes at the point of activation by supersaturation. The whiskers represent the 10th and 90th percentile; therefore capturing 90 % of the points. Outliers shown as open circles represent those points that are 1.5 times the interquartile range (box width). The dashed blue line corresponds to the $(\text{NH}_4)_2\text{SO}_4$ calibration droplet size at activation at the same supersaturation. The grey band represents the variability in the average calibration $(\text{NH}_4)_2\text{SO}_4$ droplet distribution.

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