Airborne Cloud Condensation Nuclei Measurements during the 2006 Texas Air Quality Study

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Abstract. Airborne measurements of aerosol and cloud condensation nuclei (CCN) were conducted aboard the National Oceanic and Atmospheric Administration (NOAA) WP-3D platform during the 2006 Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMACCS). The measurements were conducted in regions influenced by industrial and urban sources. Observations show significant local variability of CCN activity (CCN/CN from 0.1 to 0.5 at \( s = 0.43\% \)); while variability is less significant across regional scales (\( \sim 100 \text{ km} \times 100 \text{ km} \), CCN/CN is \( \sim 0.1 \) at \( s = 0.43\% \)). CCN activity can increase with increasing plume age and oxygenated organic fraction. CCN measurements are compared to predictions for a number of mixing state and composition assumptions. Mixing state assumptions that assumed internally-mixed aerosol predict CCN concentrations well. Assuming organics are as hygroscopic as ammonium sulfate consistently overpredicted CCN concentrations. On average, the water-soluble organic carbon (WSOC) fraction is 60 ± 14\% of the organic aerosol. We show that CCN closure can be significantly improved by incorporating knowledge of the WSOC fraction with a prescribed organic hygroscopicity parameter (\( \kappa = 0.16 \) and effective \( \kappa \sim 0.3 \)). This implies that the hygroscopicity of organic mass is primarily a function of the WSOC fraction. The overall aerosol hygroscopicity parameter varies between 0.08 and 0.88. Furthermore, droplet activation kinetics are variable and 60\% of particles are below the threshold of rapid droplet growth.
1. Introduction

Atmospheric particles, by acting as cloud condensation nuclei (CCN), can indirectly influence climate through their impact on cloud radiative properties and the hydrological cycle [e.g., Lohmann and Feichter, 2005, and references therein]. The complexity and incomplete description of aerosol-cloud interactions in models result in large uncertainties in assessments of the anthropogenic indirect aerosol effect [e.g., Haywood and Boucher, 2000; Ramanathan et al., 2001; Lohmann and Feichter, 2005; Intergovernmental Panel on Climate Change (IPCC), 2007]. Much of this uncertainty in global climate models arises from the subgrid nature of cloud processes and the effect of poorly-constrained parameters [e.g., Intergovernmental Panel on Climate Change (IPCC), 2007] one of which is the CCN concentration. The prime factor controlling CCN concentration is the aerosol size distribution [Twomey, 1977; Dusek et al., 2006]; however the variability of aerosol composition has also been shown to play a significant role in CCN activity [Jimenez et al., 2009]. Predictions of CCN concentrations in climate models require simplifying assumptions, particularly in the description of chemical composition, and the resulting uncertainty in indirect forcing from their application need to be quantified [e.g., Sotiropoulou et al., 2006].

Each aerosol particle requires exposure to a “critical” level of water vapor supersaturation, $s_c$, before it can act as a CCN and activate into a cloud droplet. $s_c$ depends on the aerosol dry size and chemical composition, and is computed from considering solute and curvature effects on the equilibrium water vapor pressure...
“Köhler theory” remains to date the basis for linking CCN activity with aerosol thermophysical properties, and is used in all physically-based models of the indirect effect to predict CCN number concentrations from knowledge of the aerosol size distribution, chemical composition and dynamical forcing. The simpler forms of Köhler theory involve aerosol composed of an “insoluble” and completely soluble fraction, and have been successfully applied to water-soluble inorganic and low molecular-weight organic aerosol. Simple forms of the theory may be subject to uncertainty when partially soluble compounds are present or when the aerosol is a complex mixture of inorganic and organic compounds. A comprehensive theory can become quite complex, as the presence of multiple phases and all the interactions of organics and inorganics with water must be accounted for, and requires the knowledge of poorly constrained parameters. This is especially true if the aerosol contains substantial amounts of ambient water-soluble organic carbon (WSOC), which can contribute solute [Shulman et al., 1996], act as a surfactant that depresses droplet surface tension [Facchini et al., 1999; Decesari et al., 2003; Asa-Awuku et al., 2008] and, potentially affect the condensation rate of water onto growing droplets [e.g., Feingold and Chuang, 2002; Chuang, 2003; Nenes et al., 2002b; Asa-Awuku et al., 2009].

“CCN closure”, or comparison of predictions with observations of ambient CCN concentrations, has been the focus of numerous studies and is the ultimate test of Köhler theory [e.g., Liu et al., 1996; Covert et al., 1998; Ji et al., 1998; Snider and Brenguier, 2000; Cantrell et al., 2001; Dusek et al., 2003; Roberts et al., 2003; VanReken et al., 2003; Rissler et al., 2004; Broekhuizen et al., 2006; Gasparini et al., 2006; Rissman et al., 2006;}
Roberts et al., 2006; Yum et al., 2006; Chang et al., 2007; Medina et al., 2007; Stroud et al., 2007; Ervens et al., 2007; Vestin et al., 2007; Sorooshian et al., 2008; Cubison et al., 2008; Quinn et al., 2008; Lance et al., 2009; Shinozuka et al., 2009; Bougiatioti et al., 2009; Gunthe et al., 2009; Hegg et al., 2009; Murphy et al., 2009; Wang et al., 2010; Rose et al., 2010]. Most closure studies are based on ground site measurements, although the recent advent of CCN and aerosol instrumentation with very fast sampling frequency (\(\sim 1\) Hz) will ensure that airborne process-oriented studies will appear more frequently in the literature. Apart from establishing the applicability of Köhler theory, closure studies can be used to quantify the CCN prediction uncertainty associated with simplifying assumptions commonly used in models regarding aerosol mixing state, variation of composition with size and affinity of carbonaceous material with water.

For example, Broekhuizen et al. [2006] and Stroud et al. [2007] found that omitting size-resolved composition and treating the organics as insoluble leads to a 30-50\% CCN prediction bias. Ervens et al. [2007] found that neglecting the hygroscopicity of the organic fraction (i.e. treating the organic as insoluble) had little effect on CCN closure for aerosol sampled at Chebogue Point during the ICARTT 2004 campaign. Based on CCN measurements obtained at Thompson Farm during ICARTT 2004, Medina et al. [2007] found that usage of size-averaged chemical composition can lead to significant CCN concentration overpredictions. Sotiropoulou et al. [2006] and Sotiropoulou et al. [2007] further processed the Medina et al. [2007] data set and propagated the CCN prediction error in a global model simulation of the indirect effect; they concluded that simplified implementations of Köhler theory could introduce a 30\% uncertainty in
global annual average CCN concentrations that results in a 20-40% uncertainty in the model-derived indirect forcing of -1 W m$^{-2}$. Cubison et al. [2008] found that omission of size-resolved composition and aerosol mixing state information in a polluted urban site (Riverside, California) may bias calculated CCN concentrations by a factor of two. Quinn et al. [2008] found that changes in composition can account for a 40% difference in CCN activity of boundary layer marine aerosol in the Gulf of Mexico, Texas. In the same region, Lance et al. [2009] found that different assumptions concerning the internally-mixed chemical composition result in average CCN overprediction ranging from 3% to 36%; it is hypothesized that the externally-mixed fraction of the aerosol contributes much of the CCN closure scatter, while the internally-mixed fraction largely controls the overprediction bias. Bougiatioti et al. [2009] found particles in the Eastern Mediterranean were significantly aged, mostly activating at $\sim 0.6\%$ supersaturation; organic solubility assumptions improved CCN closure. Gunthe et al. [2009] observed CCN properties in pristine tropical rainforest air in Amazonia and observe good agreement (to within $\sim 20\%$ deviation) by including both hygroscopicity and organic fraction data into their predictions which were consistent with biogenic SOA. Rose et al. [2010] measured CCN in polluted air and biomass burning smoke at a rural site $\sim 60$ km northwest of the mega-city Guangzhou in southeastern China. The inferred hygroscopicity parameters ranged from 0.1 to 0.5 for their measurements. Rose et al. [2010] then used a constant average hygroscopicity parameter equal to 0.3 and variable size distributions for closure studies and deviations were on average less than 20%. Wang et al. [2010] at a ground-site in Mexico City, Mexico observe significant changes
in CCN activity and aerosol mixing during the daytime. For their closure, Wang et al. [2010] showed during daytime, and for a few tens of kilometers away from anthropogenic sources, CCN concentrations may be derived with sufficient accuracy by assuming an internal mixture and using bulk chemical composition.

Another important and poorly-constrained aspect of cloud droplet formation is the kinetics of CCN activation. In cloud physics studies, droplet growth is largely controlled by the water vapor mass transfer to the condensed phase. It has been hypothesized that organics could dissolve slowly and form films that retard the uptake of water vapor molecules the droplet surface [e.g., Feingold and Chuang, 2002; Chuang, 2003]; this could then reduce the rate of condensation, with important impacts on the droplet number that forms in ambient clouds [Nenes et al., 2002a; Feingold and Chuang, 2002; Lance et al., 2004].

Delays in the activation kinetics are often expressed as changes in the effective water vapor uptake coefficients, $\alpha$ (defined as the fraction of water molecules that are incorporated into a droplet upon collision with it). Values of $\alpha \sim 0.042$ were used in earlier cloud modeling studies for inorganic aerosol [Lance et al., 2004]; McFiggans et al. [2006] reports a range of $\alpha$ from 0.04 to 1. Conant et al. [2004], Meskhidze et al. [2005], and Fountoukis et al. [2007] conducted aerosol-cloud droplet closure using in-situ observations of cumuliform and stratiform clouds formed in polluted and clean air masses; both studies achieved closure for $\alpha$ between 0.03 and 1.0, with optimum estimates (i.e., both average error and standard deviation within experimental uncertainty) between 0.03 and 0.06. Stroud et al. [2007], using a static diffusion
chamber combined with a model of the instrument estimated $\alpha=0.07$ for ambient
anthropogenically-influenced biogenic CCN sampled during the CELTIC experiment.

Ruehl et al. [2008] observed a wide range of growth kinetics for ambient aerosol sampled
in sites across the Northern United States, and Ruehl et al. [2009] observed evidence of
distinct activation kinetics associated with aerosol from outside the marine boundary
layer. Recently, Shantz et al. [2010] also observed reduced droplet growth of aerosol
particles containing anthropogenic organic components in Egbert, Ontario, Canada.

This study further expands upon published work and uses airborne measurements
of CCN concentration, aerosol size distribution and chemical composition measured
in Houston, Texas during the Texas Air Quality Study 2006 (TexAQS II 2006) to
determine $i$) the error in predicted CCN concentrations associated with simplifying
assumptions of the chemical composition and mixing state of CCN, $ii$) the effects of
ageing and mixing processes on CCN activity, and, $iii$) the impact of organics on CCN
activity, hygroscopicity and the condensational growth of activated droplets. This study
complements the work of Quinn et al. [2008] and Lance et al. [2009], who during the
same campaign sampled CCN aboard the NOAA ship Ronald H. Brown and the Center
for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter aircraft,
respectively.
2. Observational data set and instrumentation

2.1. Study location and flight trajectories

The Texas Air Quality Study (TexAQS) and Gulf of Mexico Climate Change Study (GoMACCS) were conducted using several platforms (e.g., ground based, airborne, ship, and satellite overpasses) in August through October of 2006. The goals of the combined studies were to observe the spatiotemporal distribution of atmospheric constituents, understand the transport of pollutants in the Eastern Texas and Northern Gulf of Mexico region, and, characterize their impacts on air quality and regional climate [Parrish et al., 2009]. The data in this study were obtained aboard the National Oceanic and Atmospheric Administration (NOAA) WP-3D aircraft from September to October, 2006. Table 1 reports the 10 research flights for which CCN data were collected.

Ambient aerosol was sampled by the WP-3D using a low turbulence inlet (LTI) [Huebert et al., 2004; Wilson et al., 2004], during which a laminar deceleration of the airstream ensured minimal particle losses for submicron aerosol (hence CCN) [Wilson et al., 2004; Brock et al., 2008].

The studied region is characterized by strong and diverse urban and industrial pollution sources. The Houston ship channel hosts many petrochemical refineries and there are several large coal-fired power plants in the east Texas region (e.g., Parrish, Big Brown, Limestone). The fine particulate mass in urban environments tends to be dominated by sulfates and organics (e.g., Zappoli et al. [1999]), this was found to be true for Houston as well.
2.2. Aerosol size distribution measurements

A white-light Optical Particle Counter (OPC), an UltraHigh Sensitivity Aerosol Size spectrometer (UHSAS) and a Nucleation Mode Aerosol Size Spectrometer (NMASS) were used to measure the aerosol dry size distribution from 0.003 to 8.3 µm diameter at a 1 Hz frequency. Other than UHSAS data, the particle size distribution measurement and analysis techniques are similar to that used aboard the WP-3D during the 2004 New England Air Quality Study (NEAQS) [Brock et al., 2008]. Ultrafine particles (diameter < 0.1 µm) were measured using five condensation particle counters (CPCs), set to measure particle concentrations down to 0.004, 0.008, 0.015, 0.030, and 0.055 µm diameter with a 50% detection efficiency at these sizes. Size distributions were derived from the observed concentrations in the five size classes, coupled with a nonlinear inversion algorithm [Markowski, 1987]. A complete description of the instrument methodology and data analysis is provided in Brock et al. [2008].

2.3. CCN measurements

A Droplet Measurement Technologies Continuous-Flow Streamwise Thermal Gradient Chamber (CFSTGC) [Roberts and Nenes, 2005; Lance et al., 2006] was used to measure CCN concentrations. A constant temperature gradient is applied across the internal wetted wall of the instrument flow chamber; the difference in the radial diffusive flux of water vapor and heat generates a supersaturation, $s$, which is maximum at the centerline [Roberts and Nenes, 2005; Lance et al., 2006]. Aerosol is introduced along the centerline of the flow chamber and exposed to $s$. The fraction
whose “critical” supersaturation, $s_c$, is less then $s$ activate into cloud droplets and an optical particle counter at the exit of the flow chamber then detects the concentration and size distribution of activated droplets. $s$ in the CFSTGC is a function of pressure, flow rate and temperature gradient in the flow chamber. $s$ is calibrated for a given set of chamber conditions using the procedure of Asa-Awuku et al. [2009]. This includes determining the minimum diameter, $d$, of calibration $(\text{NH}_4)_2\text{SO}_4$ aerosol (generated by atomization of an aqueous $(\text{NH}_4)_2\text{SO}_4$ solution with a Collison-type atomizer, which is subsequently dried and classified with a differential mobility analyzer) that activates in the instrument. $d$ is then related to $s$ by applying Köhler theory using an effective van’t Hoff factor computed using the ion-interaction approach of Pitzer and Mayorga [1973] with parameters obtained from Clegg and Brimblecombe [1988]. The effective van’t Hoff factor was computed at the molality corresponding to the critical diameter of the CCN. This procedure is repeated over a wide range of temperature and pressures. Bilinear interpolation of the calibrations to the pressure and temperature conditions occurring in-flight is used to determine the instrument $s$ during the measurements.

The CFSTGC sampled aerosol from the LTI at a flow rate of 1000 cm$^3$ min$^{-1}$, over a supersaturation range of 0.1% to 0.6%. The instrument was operated in a “temperature-stepping mode” during which flow and temperature conditions are maintained constant during the measurement interval. The instrument pressure varied with altitude and was approximately equal to the ambient pressure. During the first two flights, the temperature difference across the column, $\Delta T$, was set to 4.2±0.1°K, corresponding to a $s$ equal to 0.3±0.05%. In the remaining research flights, $\Delta T$
was cycled over 3-minute intervals between 5.2 and 7°C, varying $s$ from 0.42±0.05% to 0.74±0.05%. The reported variability accounts for the measured fluctuations in temperature gradient and instrument pressure. Data collected during shifts in instrument temperature (e.g., due to cabin temperature, pressure, or supersaturation changes) and pressure (during altitude changes) are filtered, as described in Sect. 3.

2.4. Chemical composition measurements

An Aerodyne aerosol mass spectrometer (AMS) measured size-resolved mass distributions and total mass loadings of non-refractory chemical species in submicron aerosol. During TeXAQS, a compact time-of-flight AMS (C-ToF-AMS) with a pressure controlled inlet was used [DeCarlo et al., 2006; Drewnick et al., 2005; Canagaratna et al., 2007; Bahreini et al., 2008]. Within the instrument, the sampled particles are focused into a beam and impact on a vaporizer located within the electron ionization source region of a mass spectrometer. When operated in the “particle time of flight” (pTof) mode, mass distributions of non-refractory species are obtained by interrupting the particle beam with a chopper and measuring the time particles take to traverse the vacuum chamber before detection. When operated in the “mass spectrum” mode, spectra with a mass-to-charge ratio ($m/z$) of 1 to 220 are collected from multiple particles with good time resolution (~10 s) at the expense of size-dependence. From characteristic mass spectral ion signals, quantitative concentrations for sulfate, nitrate, ammonium, organic mass and inferred oxygenated content are obtained [Jimenez et al., 2003; Allan et al., 2003, 2004; Bahreini et al., 2003; Schneider et al., 2004].
Analysis of specific m/z signals provides information about the degree to which
the organic species are oxidized. For example, the organic signal at m/z 44 (mostly
CO$_2^+$) is strongly correlated with the amount of oxygenated organic aerosol (OOA), a
surrogate for SOA [Zhang et al., 2005; Aiken et al., 2009]. The organic ion signal from
C$_4$H$_7^+$, which can be estimated as the total signal at m/z 57 minus a correction of 5% of the m/z 44 (to account for the contribution of C$_3$H$_5$O$^+$, an OOA fragment to m/z 57) is strongly correlated with hydrocarbon-like organic aerosol (HOA), a surrogate for primary combustion OA in urban areas [Zhang et al., 2005; Aiken et al., 2009].

A Particle-into-Liquid sampler (PILS) captured ambient particles and dissolved them into ultra-purified water [Orsini et al., 2003]. The stream containing soluble materials was then filtered and measured with a Total Organic Carbon (TOC) Analyzer to quantify the WSOC concentration. Additional information about the WSOC measurement, analysis, and calibration can be found in Orsini et al. [2003] and Sullivan and Weber [2006].

3. Data analysis and CCN prediction

CCN closure calculations were carried out using 30 second averages of CCN, aerosol size distribution and chemical composition measurements. Prior to the averaging, data from the CCN counter were filtered to remove temperature transients (during supersaturation changes) and pressure transients (during rapid altitude changes). At a given time, $t$, data is averaged over a 30 second window centered around $t$; averages for which pressure fluctuates more than $\pm$ 0.5% from the mean, and, temperatures more
than ± 0.05°K about its average are removed from the analysis.

### 3.1. Predicting CCN concentrations

The measured aerosol size distributions and chemical compositions were used to predict CCN concentrations with Köhler theory. CCN activity is characterized by the critical dry diameter, \( d_c \), defined as the minimum particle size (of a given composition) that activates at the instrument supersaturation, \( s \); particles are then classified as CCN if their physical diameter is larger than \( d_c \) (this is equivalent to stating that particles have an \( s_c \) less than the instrument supersaturation, \( s \)). \( s_c \) was calculated by applying Köhler theory, assuming that the aerosol is composed of a mixture of soluble and insoluble fractions [Medina et al., 2007; Seinfeld and Pandis, 2006],

\[
d_c = \left( \frac{s^2}{256} \left( \frac{\rho_w RT}{M_w \sigma} \right)^3 \left( \frac{M_w}{\rho_w} \sum \frac{\rho_s}{M_s} \nu_s \varepsilon_s \right) \right)^{-1/3}
\]

(1)

where \( R \) is the universal gas constant, \( T \) is the average temperature across the CFSTGC flow column, \( \sigma \) is the droplet surface tension at the point of activation (calculated at \( T \)), \( M_s \) is the molar mass of each solute, \( M_w \) is the molar mass of water, \( \rho_w \) is the density of water, and \( \nu_s \) is the effective van’t Hoff factor of the solute. \( \varepsilon_s \) is the volume fraction of each solute, computed assuming volume additivity as,

\[
\varepsilon_s = \frac{m_s}{\sum_j \frac{m_j}{\rho_j}}
\]

(2)

where \( m_j \) and \( \rho_j \) are the mass fraction and density, respectively, of aerosol component “\( j \)” (which includes all soluble and insoluble compounds).
The density of the organic fraction was assumed to be 1270 kg m\(^{-3}\) \cite{Cross2007}. Ammonium and sulfate dominate the inorganic aerosol dry mass, indicative of ammonium-sulfate salts, the speciation of which depends on the molar ratio of ammonium to sulfate ions, \(R_{SO_4}\) \cite{Nenes1998}, as follows: 

\(i\) \(R_{SO_4} < 1\), the soluble fraction is a mixture of sulfuric acid (\(M_s = 0.098\) kg mol\(^{-1}\), \(\rho_s = 1841\) kg m\(^{-3}\)) and ammonium bisulfate (\(M_s = 0.115\) kg mol\(^{-1}\), \(\rho_s = 1780\) kg m\(^{-3}\)), as determined from the mass balance,  

\(ii\) \(1 < R_{SO_4} < 2\), the soluble fraction is a mixture of ammonium bisulfate and ammonium sulfate (\(M_s = 0.132\) kg mol\(^{-1}\), \(\rho_s = 1760\) kg m\(^{-3}\)), as determined from the mass balance, and  

\(iii\) \(R_{SO_4} > 2\), the soluble fraction is composed of pure ammonium sulfate. \(R_{SO_4}\) was almost never below unity (i.e. free H\(_2\)SO\(_4\) was not present in the aerosol), as is typical for measurements over continental boundary layers where sources of ammonia are relatively strong \cite{Zhang2007, Salcedo2006}. The relative humidity of the sampled aerosol was less than 10%. Therefore, residual water can be assumed to be negligible in the dry aerosol sampled onboard the aircraft \cite{Murphy2009}.

Consistent with the level of acidity in the particles, nitrate salts constitute a minor fraction of the soluble ions (<5% of the total), but are included in the CCN activity calculations. The effective van’t Hoff factor applied for each of the salts during calculation of \(d_c\) was computed using the parameterized Pitzer water activity correlations \cite{Pitzer1973, Clegg1988} at the molality corresponding to the critical diameter of the CCN.

Non-refractory material, such as black carbon (also measured aboard the aircraft by
a Single-Particle Soot Photometer \cite{Schwarz2006}, did not contribute significant particulate mass \((< 2\% \text{ mass fraction})\) and was therefore not considered in the different CCN schemes. This is consistent with Lance et al. \cite{Lance2009}, who found that BC is a minor aerosol constituent, except for flights in the ship channel where neglecting its mixing state could lead to large CCN overpredictions. Since transmission of particles in the AMS inlet drops below 50\% for particles with physical diameter smaller than 50nm and larger than 640 nm, the measured aerosol composition outside this range is limited \cite{Bahreini2009}. The composition of the smallest particles detected by the AMS was hence uniformly applied to aerosol smaller than 50 nm (physical diameter). On average, this assumption impacts \(< \sim 15\%\) of the total particles that may become CCN.

Six compositional schemes were employed in this study for CCN closure calculations:

- **INORG**: Inorganic- the aerosol volume is composed of an inorganic solute mixture consistent with the inorganic portion of the AMS bulk composition data. This scheme represents an upper limit of CCN activity, as the organic fraction is implicitly assumed to have the same hygroscopic properties as the inorganic fraction.

- **BK-EX**: Bulk Composition Externally Mixed - the aerosol is an external mixture of two populations (i.e., soluble, “inorganic-only” particles and insoluble, “organic-only” particles), the relative amounts of which are determined from the bulk AMS composition measurements. The “organic-only” particles are assumed non-hygroscopic and do not contribute CCN; the “inorganic-only” particles are
composed of a mixture of salts, as determined by the AMS compositional data. The composition is assumed uniform across the entire size distribution.

- **BK-INT**: Bulk Composition Internally Mixed - aerosol is an internal mixture of insoluble organic and inorganic salts, as determined by the AMS bulk compositional data. The composition is uniform across the size distribution.

- **SR-EX**: Size-Resolved Composition Externally Mixed - aerosol is an external mixture of “organic-only” and “inorganic-only” particles. Again, the “organic-only” particles are assumed non-hygroscopic. In contrast to the **BK-EX** scheme, size-resolved composition data from the AMS is applied, meaning that the relative concentration of each population varied with size.

- **SR-INT**: Size-Resolved Composition Internally Mixed - aerosol is an internal mixture of organic and inorganic salts, as determined by the size-resolved AMS bulk compositional data.

- **BK-INT-SOL**: Bulk Composition Internally Mixed Soluble Fraction - similar to the **BK-INT** scheme, except now organics are hygroscopic. The aerosol is an internal mixture of organic and ammoniated sulfate salts, as determined by the AMS bulk compositional data. The composition is assumed to be uniform across the entire size distribution. A fraction of the organic mass, equal to the ratio of PILS WSOC to AMS organic mass, is assumed soluble with a molar volume of \( \frac{M}{\rho} = 1.48 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \), effective van’t Hoff factor of \( \nu=1 \), and 10% surface
tension depression with respect to pure water. In this study, the WSOC/OC is converted to WSOC/OM by a factor of 1.5 [Wolff et al., 1991; Seinfeld and Pandis, 2006]. For aerosol containing mostly OOA, this value may be higher [\sim1.8 to 2.1 Turpin and Lim, 2001; Aiken et al., 2008]. The lower factor limit is used to account for less oxygenated organic aerosol found near emission sources. For significantly oxygenated organics a factor of 1.5 will contribute up to -20% error in our soluble fraction estimates. The WSOC properties represent average values for WSOC obtained from biomass burning aerosol, cycloheptene, methylcycloheptene, terpinolene, monoterpenes and $\beta$-caryophyllene SOA [Asa-Awuku et al., 2010, 2008; Engelhart et al., 2008; Asa-Awuku et al., 2009] and is consistent with the CCN properties of SOA from Mexico City aerosol [Padró et al., 2010]. Analysis of the inferred hygroscopicity parameter (Sec. 4.5) confirms that the assumed WSOC molar volume used here is a reasonable choice.

Only bulk WSOC measurements were available, hence it was not possible to relax the bulk composition assumption by employing a size-resolved, internally-mixed, soluble (SR-INT-SOL) scheme. In schemes other than BK-INT-SOL, organics do not contribute solute nor affect surface tension. $\sigma$ for pure water in all schemes is computed at the average column temperature of the CFSTGC, which ranges between 30 and 45°C. In the closure studies of Chang et al. [2007] and Lance et al. [2009], some contribution of organic solute and/or surface tension reduction was necessary to improve CCN predictions and minimize bias; BK-INT-SOL goes beyond these studies in that measured
WSOC/OC is used as a predictor of hygroscopicity for the organic fraction.

3.2. Evaluating predictions against observations

CCN predictions are compared to observed concentrations for the schemes described above. Results were summarized in terms of the slope, $S$, and variance, $R^2$, between predicted and measured data (assuming a linear fit between the two, with an intercept of zero). Deviation greater than 10% from $S = 1$ was assumed to show disagreement in closure; $S > 1$ (CCN overprediction) and $S < 1$ (underprediction) are potentially due to an over or underestimation of soluble and surface active materials, respectively. $R^2$ values close to unity suggest that errors from unaccounted compositional and size distribution variation, random errors and spatiotemporal fluctuations below the averaging timescale were small. We also represent closure in terms of the Normalized Mean Error ($NME$) and the Normalized Mean Bias ($NMB$),

$$NME = \frac{1}{n} \sum_{i} |P_i - O_i| \quad \text{and} \quad NMB = \frac{1}{n} \sum_{i} \left( \frac{P_i - O_i}{O_i} \right)$$

where $n$ is the number of measurements available; $P_i$ and $O_i$ are the predicted and observed CCN concentration, respectively. The $NME$ indicates the degree of scatter between predictions and observations (small values suggest little scatter), and $NMB$ reflects the degree of systematic errors (biases) between the predicted and measured values; a negative $NMB$ is consistent with under prediction and vice versa. Other more comprehensive nonlinear error metrics could be used [Cantrell, 2008], but the differences between closure schemes are large enough so that the linear metrics presented
here are sufficient for determining the better scheme. Large NME and NMB values derived from closure schemes are indicative of poorly assumed correlations and or parameterizations for CCN predictions. Hence the CCN prediction scheme that provides the best closure also has NME and NMB values close to zero.

3.3. Hygroscopicity Parameter \( \kappa \) Calculations

The composition-dependence of CCN activity may be expressed in terms of a single hygroscopicity parameter, \( \kappa \) [Petters and Kreidenweis, 2007]:

\[
\kappa = \frac{4A^3}{27d^3ln^2s}
\]

where \( A = \frac{4\sigma_wM_w}{RT\rho_w} \); using the same symbols, Eq. 4 is derived from Eq. 1. As prescribed in Petters and Kreidenweis [2007], \( \sigma_w \) is the surface tension of water at average instrument temperature. If organics depress surface tension, to a value \( \sigma \) at the point of activation, application of Eq. 4 overestimates \( \kappa \) by a factor of \((1 - \frac{\sigma_w - \sigma}{\sigma_w})^{-3} \) [Asa-Awuku et al., 2010].

For insoluble, wettable materials that do not impact water activity nor adsorption [Kumar et al., 2009], \( \kappa = 0 \), and increases with the addition of soluble compounds [Petters and Kreidenweis, 2007]. For (NH_4)_2SO_4, the most abundant inorganic compound observed during TEXAQS, \( \kappa = 0.6 \). The \( \kappa \) value prescribing the values of WSOC from BK-INT-SOL = 0.16 with an effective \( \kappa \sim 0.3 \), assuming \( \sigma = \sigma_{\text{water}} \).

The effective \( \kappa \) value is within previously reported range of oxidized (hygroscopic) carbonaceous material [e.g., Prenni et al., 2007; Engelhart et al., 2008; Jurányi et al., 2009; Jimenez et al., 2009; Asa-Awuku et al., 2010]. \( \kappa \) values are presented in Sect. 4.5.
for the most robust CCN prediction scheme presented here that accounts for changing particle chemistry.

### 3.4. Droplet Growth and Kinetics Analysis

When exposed to the same $s$ profile (that exceeds their $s_c$) two CCN will activate and grow to cloud droplets of similar wet diameter, $D_p$, provided that their critical supersaturation and mass transfer coefficient of water vapor to the growing droplets is the same [Nenes et al., 2001; Roberts and Nenes, 2005]. The CCN instrument measures the droplet size distribution after CCN activation, which can be used to explore the impact of aerosol composition on the droplet growth kinetics using the method of Threshold Droplet Growth Analysis (TDGA). TDGA compares the droplet sizes of activated ambient particles against a standard of rapid activation kinetics. The standard used in this study is the droplet size, $D_r$, of calibration $(\text{NH}_4)_2\text{SO}_4$ aerosol with $s_c = s$, being the minimum size droplet of rapidly activating CCN (e.g, an effective uptake coefficient, $\alpha \sim 0.1 - 1$). Ambient particles, if also growing fast, will yield droplet sizes equal or larger than $D_r$ (because of the polydispersity of the ambient sample), and vice versa. As presented here, TDGA can only detect the presence of slowly activating CCN. Parameterizing delays in terms of $\alpha$ requires the use of a model [Asa-Awuku et al., 2009; Ruehl et al., 2008, 2009]. TDGA has been successfully applied in numerous studies [Engelhart et al., 2008; Moore et al., 2008; Sorooshian et al., 2008; Bougiatioti et al., 2009; Murphy et al., 2009; Lance et al., 2009; Asa-Awuku et al., 2010, 2008, 2009], and shown that hygroscopic CCN tend to exhibit activation kinetics similar to $(\text{NH}_4)_2\text{SO}_4$;
less hygroscopic CCN however can activate into droplet more slowly. A focus of this study is to explore the impact of composition on the activation kinetics of Houston aerosol. For large CCN concentrations in the instrument column (> 6000 cm\(^{-3}\)) supersaturation depletion will occur in the CCN counter \cite{Lathem and Nenes, 2011}; the droplet sizes have been corrected using the approach of \textit{Lathem and Nenes} [2011].

Droplet growth sizes of CCN concentrations greater than 5000 cm\(^{-3}\) have been excluded from the data set and the predicted \(s_c\) as prescribed in \textit{Lathem and Nenes} [2011] is presented in TDGA.

4. Results and discussion

Plumes within the Houston area quickly mix with background (regional) air. The “background” regional air is itself not uniform, but rather a mixture of aged air masses and plumes from various sources. Quantitatively following the ageing of aerosol thus becomes quite challenging; the exception is when the wind direction remains constant during a flight, and a plume is transected at different locations downwind of its source. Assuming that the nature of emissions did not vary throughout the transects, “plume age” could be determined from the distance from the source “epicenter” (Ship Channel or Downtown centers) and the wind speed. A detailed explanation of the calculation and process used to distinguish plumes from background air with gas phase tracers is found in \textit{Bahreini et al.} [2009]. In the following sections, we discuss CCN behavior and predictions on regional and local scales for selected flights of interest during TexAQS/GOMACCS II 2006.
4.1. CCN characteristics of mixed Houston plume sources

The research flight on September 20 was a 6.5 hour mission that focused on the daytime urban atmospheric chemistry and the Houston area environment. The WP-3D departed in the eastward direction, transecting different plumes by traveling westward in a “zig-zag” flight pattern across industrial areas in the region. The aircraft transected two areas of concentrated plumes (CN concentrations > $5 \times 10^4$ cm$^{-3}$); organics dominated the aerosol volume fraction ($\sim 0.7$ to 0.9, Fig. A4a). The largest CN concentrations were observed near the ship channel and downtown areas. The aerosols were from different sources and had varied chemical compositions (Fig. A1).

Particle characteristics changed substantially during the flight (varying one order of magnitude in number concentration, $\sim 10^4$ to $\sim 10^5$ cm$^{-3}$, Figs. A1 and A4a) as the aircraft sampled fresh emissions in downtown Houston and the ship channel, and more aged aerosol south and west of the urban center. Since most of the particles were $< 50$ nm in diameter (smaller than the $d_e$ required for their activation), only a small fraction were activated and measured as CCN. BK-INT-SOL and INORG schemes achieved the best closure for the September 20 flight (e.g., best closure $S, R^2 \sim 1$ and $NME$ and $NMB \sim 0$; Table 2). For INORG, when CN counts increased, closure agreement shifted from strong overprediction at lower CCN concentrations ($< 3000$ cm$^{-3}$) to a mostly unbiased scatter at higher concentrations (reflected in the relatively weak correlation between predictions and observations, $R^2 \sim 0.65$; Table 2). Most of the INORG overprediction was observed in regions with relatively lower CN concentrations and high
organic volume fraction (~0.9; Fig. 1). Assuming that organics were insoluble (BK-INT and BK-EXT schemes) resulted in considerable underprediction of CCN concentrations and increased scatter (NMB and NME > 30%, Table 2), with BK-EXT giving the worst closure of all. All the above suggests that the aerosol tended to be internally mixed, with a partially-soluble organic fraction that was less hygroscopic than sulfate salts, and with thermodynamic properties consistent with previous WSOC CCN studies. The INORG scheme gave much better closure within “polluted” (CN > 50×10^3 cm^{-3} on September 20) than “non-polluted” regions (Fig. 1); this indicates that sulfate aerosol is the largest contributor to CCN concentrations in the most polluted areas sampled during TEXAQS. Although size-resolved composition measurements were not available to confirm this, the rapid changes in gas-phase concentrations of SO_2 in these regions are consistent with this view (Fig. A5a). Nevertheless, organics are expected to be present in CCN-relevant sizes; their lower hygroscopicity (compared to inorganic sulfate and nitrate) may be partially compensated by surface tension depression [Asa-Awuku et al., 2008, 2010; Padró et al., 2007]. Hence results from September 20 also suggest that in the absence of compositional information, one can assume properties of (NH_4)_2SO_4 when computing CCN near strong SO_2 pollution sources.

The research flight on September 21 2006 characterized urban and ship channel particle sources and their evolution while being advected northward (Fig. A2). The flight on September 21 was of particular interest because a shift in CCN behavior was observed in different locations within the metropolitan area, downwind of the urban and industrial centers after 19:00 UTC (Fig. A4b). Anthropogenic particles are a
convolution of plumes from several aged sources hence separating the contribution from individual plumes is very challenging. Therefore, analysis for this flight was limited to changes in CCN with latitude, north of downtown (Fig. 2). (A plume evolution analysis for distinct sources is found in Sect. 4.3). Near downtown Houston, CCN concentrations remained fairly insensitive to fluctuations in total CN (Fig. A4b, before 18:30 UTC), which are mostly from particles too small to activate in the range of s considered. The activated ratio (CCN/CN), size and organic fraction increased as particulate concentrations decreased (Figs. 2 and A4b). This trend is consistent with changes in particle composition, as it is accompanied by a (slight) increase in the ratio of oxygenated to non-oxygenated organic AMS markers (m/z 44/57; Fig. 2). As on September 20, despite changes in aerosol composition and flight location, the average activated droplet size in the CFSTGC throughout the flight (2.05 ± 0.45 µm) was similar to droplet sizes from activation of calibration (NH₄)₂SO₄ (2.06 ± 0.2 µm, Fig. A5b). The droplet size distribution from activation of ambient CCN in the CFSTGC are much broader than those from calibration aerosol, and reflect the polydispersity of the former.

The BK-INT-SOL closure scheme was best for September 21 (S = 0.93, R² = 0.8, NMB = −2%, Table 2 and Fig. A6b), followed by INORG (S = 1.13, R² = 0.84, NMB = 15%, Table 2 and Fig. A6a). Other schemes that assumed an insoluble organic component gave considerably worse closure (Table 2). In contrast to September 20 CCN predictions, September 21 INORG showed greater deviation from closure with decreasing organic fractions. Lance et al. [2009] observed the same type of overprediction error over the ship channel, and attributed those findings to the presence of an externally-mixed
aerosol strongly linked to the black carbon source. At low CCN concentrations and low organic fractions ($< 1500 \text{ cm}^{-3}$ and $< 0.4$, respectively), predictions agreed well using any of size-invariant composition schemes (INORG, BK-INT-SOL, BK-INT, and BK-EXT; Table 2 and Fig. A6). At larger organic fractions and CCN concentrations, BK-INT and BK-EXT underpredict CCN concentrations, while BK-INT-SOL scheme gave good closure. The results of September 20 and 21 emphasize that organics in background aerosol are partially soluble, and highlight the need for constraining the WSOC fraction, especially when organics constitute a large fraction of the aerosol mass.

4.2. Comparison of two metropolitan environments

On September 25, the WP-3D aircraft headed north to Dallas and then traversed south towards the Houston metropolitan area. The daytime flight probed the mid-morning aerosol in the Dallas metropolitan area, emissions from the larger powerplants in the area (Big Brown and Limestone) and the afternoon aerosol composition in the Houston metropolitan region. During this (and subsequent) flights, the CFSTGC was operated at multiple supersaturations. CCN concentrations measured throughout the day tracked the changes in total aerosol concentration; much of the aerosol were in the CCN-relevant size range, and similar to Houston were mostly composed of organics and sulfates (Fig. A7). CCN predictions were calculated when AMS and/or PILS data where available, which for September 25 occurred during the flight leg just south of the Dallas area (between 16:30 and 19:30 UTC).

BK-INT-SOL and INORG schemes gave the best CCN closure for both Houston
and Dallas regions. INORG overpredicted CCN concentrations by 35% at the higher
supersaturation \((s = 0.71\%, \, S = 1.352)\), and 4.5% at \(s = 0.43\%\) (Table 2). The
BK-INT-SOL underpredicted for all \(s\), but was best at the higher \(s\). Relatively low \(R^2\)
suggest that either the CCN frequently deviates from a size-invariant, internally-mixed
composition or the size distribution varies substantially during the 40 second averaging
window. BK-EXT shows substantially less scatter \((R^2=0.89)\) than the INT schemes,
but systematically underpredicts CCN concentration by a factor of 3. One can infer the
nature of the aerosol mixing state from the variation in scatter \((R^2)\) of closure agreement
schemes. On September 25, the closure schemes of this day suggest the aerosol is often
externally mixed, with a size-dependent composition for each CCN population.

Table 3 compares the CCN behavior of different air masses measured in the Dallas
and Houston Metropolitan area on September 25. Both regions show considerable
variation in CN number yet the organic fraction in Dallas is similar to that measured
in Houston (e.g., September 20 and 21; no aerosol composition data is available in the
Houston Region on September 25). Less than 30% of the particles at the measured \(s\)
act as CCN, consistent with the large number concentration of particles with diameter
less than 50nm.

4.3. CCN Characteristics of distinct plumes

**Ship channel and Houston urban plumes.** Urban and industrial plumes most
often readily mix with "background" aerosol and quickly dissipate. On occasion however,
plumes are distinguishable far from their source; this occurred during September 26, 27,
and October 5 (Fig. 4) for emissions from downtown Houston and the ship channel. September 27 is characterized by the mixing of fresh urban emissions with recirculated air masses over western Houston, hence it is possible that the fresh urban plume on this day mixed with the previous day’s plumes and thus appears to be more aged than the plumes originating on September 27 from the Ship Channel. The plume age and transport time was determined by the distance from ship channel and downtown center co-ordinates (29.776 N, 95.102 W), and, (29.759 N, 95.363 W), respectively.

On all three days, CN concentrations varied substantially within the first five hours from emission for the ship channel center, but remained fairly constant for the downtown plume (Fig. 4). Despite the difference in particle number, the organic volume fractions measured on September 26 and 27 varied between 0.7 to 0.9. The organic fraction on October 5 was less (0.5 to 0.65) which led INORG to give good closure ($S = 1.004, R^2 = 0.885$ for $s = 0.43\%$, and $S = 1.089, R^2 = 0.819$ for $s = 0.71\%$, respectively; Table 2), better than September 26 and 27. The October 5 closure improvement was likely due to the reduced compositional variability (organic fraction) in the plumes. Including organic soluble data (BK-INT-SOL) produced similar closure results as INORG but with stronger correlation (Table 2).

Organic fraction decreased with plume age on September 26 and October 5 but did not on September 27 (Fig. 4). The ratio of oxygenated to less oxygenated organic aerosol on September 26 increased considerably as organic fraction decreased in the ship channel plume. This trend was consistent with an increase in CCN activation ratio, being a result of both a higher salt fraction, and larger hygroscopicity of the organic
fraction (i.e., WSOC/OC). Average droplet size of activated CCN in the CFSTGC remained fairly constant throughout the measurement period (2 µm, and similar to (NH₄)₂SO₄ calibration droplet size). Fig. 4 suggests that despite the almost immediate changes in composition and number, significant time is required (∼4 hours) for these changes to affect CCN concentrations in the plumes. These CCN changes can be attributed to shifts of the particle size distribution toward larger sizes, and, increases in aerosol hygroscopicity.

**Powerplant plumes.** During research flights on September 26 and 27, the WP-3D aircraft sampled air masses in the vicinity of the Parrish powerplant. On September 27, southwesterly winds blew over the powerplant towards downtown; on September 26, northeasterly winds from downtown blew over the powerplant. Hence the composition of the air mass that forms the plume may be influenced by background and urban emissions, or the combination thereof. As such, the first transect on September 26 was influenced by fresh urban emissions, whereas particulates measured in plume transects on September 27 were not (Figs. A10 and A9). Assuming the aerosol is internally mixed on September 26 resulted in the best CCN closure (Table 2). INORG lead to significant overprediction (NMB ≥ 20%) which is not surprising, considering that sulfates composed ∼30% of the aerosol volume fraction. September 27 results showed a similar trend, with SR-INT and BK-INT giving good and comparable closure (Table 2). On both days, the CCN closure schemes suggest that internal mixing of aerosols occurs over short spatial scales, i.e., the scale of the Houston metropolitan area (Fig. A8 and Table 2).
4.4. Overall CCN closure

Fig. 5 presents the CCN closure for all flights combined; by far, the best closure is obtained with the INORG and BK-INT-SOL schemes (Table 2). In the absence of WSOC data, INORG provides closure within 25%, with a tendency for overprediction (average $S = 1.09 \pm 0.13$ and $NMB = 11.6 \pm 9.0\%$). The other schemes underpredicted CCN (Table 2). The variance, $R^2$, for the different composition schemes ranged from 0.1 to 0.5, reflective of the large variation in aerosol chemical composition, size distribution and mixing state in the data set. The sensitivity of error metrics to the closure scheme confirms that chemical composition needs to be fairly well constrained for satisfactory CCN concentration predictions. Using size-resolved and size-averaged (“bulk”) chemical assumptions did equally well in obtaining closure; the internal mixing assumption gave much better closure than the external mixture model (Table 2). When organic solubility was accounted for using WSOC data and averaged thermodynamic properties, closure improved significantly compared to other organic schemes (BK-INT-SOL, average $S = 0.94 \pm 0.10$ and $NMB = -3.6 \pm 7.7\%$).

The performance of BK-INT-SOL compared to the other schemes confirm the expectation that organics affect CCN activity (by depressing surface tension and contributing solute) but not as effectively as inorganic salts. The good degree of closure for the BK-INT-SOL also suggests that WSOC can be described reasonably well with a single set of hygroscopic parameters ($\frac{M}{\rho} = 1.48 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, effective van’t Hoff factor $\nu=1$, and 10% surface tension depression with respect to pure water.
hence $\kappa = 0.16$ or an effective hygroscopicity parameter of $\kappa \sim 0.3$ that assumes $\sigma = \sigma_{\text{water}}$, and knowledge of WSOC/OC is a good proxy of organic soluble fraction (hence hygroscopicity).

4.5. Hygroscopicity Parameter, $\kappa$, Analysis

The generally good closure with the BK-INT-SOL scheme indicates that accounting for the partial solubility of the organic aerosol component is important. Figure 6 shows BK-INT-SOL scheme translated into the the hygroscopicity parameter, $\kappa$, and plotted as a function of the organic fraction. Here, $\kappa$ is obtained from the BK-INT-SOL predicted $d_c$ values using Equation 4. Our reported $\kappa$ dependence is consistent with the previously reported values shown in Shinozuka et al. [2009] and Gunthe et al. [2009] during the MILAGRO/INTEX-B campaign over Central Mexico and the United States west coast and the AMAZE campaign, in Amazonia, Brazil, respectively. As the organic mass fraction and the insoluble mass increases, $\kappa$ decreases. The prescribed values of $\kappa$ are $= 0.6$ and $0.16$ for $(\text{NH}_4)_2\text{SO}_4$ and the WSOC from BK-INT-SOL, respectively. Again, $\kappa = 0.16$ for WSOC accounts for the $10\% \sigma$ depression and is comparable to effective $\kappa \sim 0.3$ that assumes $\sigma = \sigma_{\text{water}}$. An upper $\kappa$ limit exists for this data set ($\kappa=0.88$) and is characterized by aerosol that is soluble like $(\text{NH}_4)_2\text{SO}_4$ but can depress surface tension up to $12\%$ from the effect of organic surfactants. $\kappa \sim 0.88$ is also the value for sulfuric acid. The variability is consistent with previously reported effective $\kappa$ parameter uncertainty [Jurányi et al., 2009]. Effective $\kappa \sim 0.3$ has been suggested for continental aerosol hygroscopicity [e.g., Rose et al., 2010; Pringle et al., 2010]. The
range of $\kappa$ reported here expresses an average $\kappa \sim 0.3$ but with significant variability due to changes in WSOC and inorganic aerosol properties.

4.6. CCN droplet growth analysis

Figure 7 shows the size of activated CCN in the CFSTGC, as a function of instrument $s$. Using TDGA, most particles in the region showed similar kinetics to $(\text{NH}_4)_2\text{SO}_4$, with moderate growth inhibition present in only a few cases. Particles that appear to grow larger than $(\text{NH}_4)_2\text{SO}_4$ reflect the polydispersity of the aerosol size distributions. At a ground site location in Houston, Ruehl et al. [2008] found that up to 62% of the sampled aerosol exhibited no change in growth kinetics relative to ammonium sulfate. During the GoMACCS airborne study, Lance et al. [2009] found that the majority of particles activated as rapidly as $(\text{NH}_4)_2\text{SO}_4$. Our data is similar to Ruehl et al. [2008] as 60% of droplets are below the threshold of rapid kinetics (Fig. 7). Deconvolution of the size distribution of composition contribution to the droplet size shifts cannot be assessed solely with TDGA and will be the subject of future study.

5. Summary and implications

The aerosol in eastern Texas and the Gulf of Mexico region is primarily composed of a mixture of sulfate salts and organics whose concentration and hygroscopicity change considerably with time and location. In computing CCN concentrations, assuming the aerosol is internally mixed and that a fraction of organics are soluble gives good closure; assuming that organics are completely insoluble or externally mixed with sulfates
substantially worsens predictions. The closure tests considered confirm the expectation that organics are not as hygroscopic as sulfates; assuming that they are tends to overpredict CCN by as much as a factor of two. The closure scheme that performed the best accounted for organic partial solubility and surface tension depression.

Much of the aerosol contain organics in CCN relevant-sizes and assuming an internal mixture gives much better closure than assuming organics are externally mixed. Close to source regions, closure error is more consistent with a less oxygenated (less hygroscopic) organic, which becomes more hygroscopic with ageing. Delays in cloud droplet growth can also be important close to source regions when organics of limited solubility constitute a substantial fraction of the aerosol volume. Quantifying and parameterizing these impacts requires a model-based deconvolution that considers CCN concentration, size polydispersity and chemical variability; this will be the subject of a future study.

The average WSOC fraction is $60 \pm 14\%$ of the organic aerosol for this data set. Including the contribution of water-soluble organics to CCN activity (using the observed WSOC/OC to define the water-soluble fraction of organics with one set of WSOC hygroscopic properties obtained from independent studies) gives the best CCN closure. We postulate that the large variation in observed $\kappa$ for organic species in the atmosphere can, to first order, be explained in terms of the soluble fraction in the material. Because of this, the possibility for a mechanistic, physically based prediction of hygroscopic properties of carbonaceous aerosol (namely the hygroscopicity parameter, $\kappa$) is feasible in global model assessments of the aerosol indirect effect. Given the
recent and substantial amounts of available WSOC/OC data, and the treatment of
the conversion process in models, it is likely that this novel set would comprehensively
address the issue of predicting hygroscopic properties for organic matter in predictions
of CCN.

In terms of the implications of this study for global models of the aerosol indirect
effect, we have shown that the assumption of internal mixture is by far the most
satisfactory for computing CCN concentrations away from sources; this is because the
spatial scales associated with aerosol mixing processes is at most the spatial scale of one
typical global climate model grid cell (\(\sim 100\)km). The simplest possible assumption of
chemical composition, that the material in the aerosol has the same CCN activity as
sulfate salts has a tendency for overprediction that can be as much as a factor of two.
This level of uncertainty can lead to large uncertainty in indirect forcing assessments
[Sotiropoulou et al., 2007], especially since the largest overprediction is mostly associated
with air masses where the aerosol contains a significant fraction of partially soluble
organics. Unequivocally size determines particle activation more than chemistry
[Twomey, 1977; Dusek et al., 2006], but this study (amongst others) shows that chemical
composition needs to be carefully considered as well, especially when organics constitute
a large fraction of the aerosol mass. As a result, knowledge of the size-resolved soluble
composition gives the best closure, in terms of bias and scatter. Finally, the degree
of closure error reported here for the “best” scenario (\(\sim 25\%\)) is consistent with other
published studies on CCN closure in diverse environments (e.g., Medina et al. [2007];
Lance et al. [2009]; Quinn et al. [2008]; Gunthe et al. [2009]; Shinozuka et al. [2009]),
suggesting that the CCN prediction error in closure studies available to date may be representative of the regional character of CCN in the North American continent.

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Figure Captions

**Figure 1.** CCN closure plot for research Flight #1 (September 20), for (a) INORG (where symbols are colored by organic volume fraction), and (b) BK-INT-SOL schemes. Dashed lines represent 1:1 perfect agreement (center) and 50% uncertainty.
Figure 2. Research flight #2 (September 21) measurements. (a) Marker sizes reflect CN concentrations, and color corresponds to latitude of aircraft position. The separation of plumes from distinct sources is challenging hence (b) CN concentrations, AMS spectral data, average droplet size and activated ratio (CCN/CN) are presented for selected latitudes. Colors correspond to locations shown in (a).
**Figure 3.** CCN closure plots for collected during research flight #3 (September 25), using (a) INORG, (b) BK-INT-SOL, (c) SR-INT, (d) SR-EXT, (e) BK-INT, and (f) BK-EXT schemes. Dashed lines represent 1:1 line and ±50% prediction error. Data for $s = 0.43\%$ are represented by closed symbols with a solid grey best fit line, and, $s = 0.71\%$ are indicated with open symbols with a solid black best fit line.
Figure 4. Urban and industrial ship channel plume analysis for September 26 (a-f), 27 (g-l) and October 5 (m-r). Emissions from downtown (open symbols) and the ship channel (closed symbols) are plotted as a function of plume age (gray scale coloring from dark to light corresponds to increasing age). Location of measurements and source centers are plotted for flights (a, g, l). CN concentrations (b, h, n), organic fraction (c, i, o), average droplet size (e, k, q), activated ratio (CCN/CN) at $s \sim 0.4\%$ (f, l, r) and oxygenated to less oxygenated organic AMS ratio (d, j, p) are plotted as a function of average plume age.
Figure 5. CCN Closure for all flights using the (a) INORG and (b) BK-INT-SOL schemes. The black solid line is the 1:1 fit and the dashed lines represent ±50% prediction error. The solid red line represents the cumulative fit with $S = 1.11 \pm 0.09$ and $S = 0.96 \pm 0.07$ for INORG and BK-INT-SOL, respectively.
Figure 6. Inferred $\kappa$ as a function (a) organic mass fraction (b) insoluble aerosol fraction.
Figure 7. Droplet size data for TEXAQS 2006. Droplet size as a function of instrument. Lines represent \((\text{NH}_4)_2\text{SO}_4\) calibration measurements at different pressures, 1000mb (black line) and 700mb (grey line). The grey shaded area indicates the region of \((\text{NH}_4)_2\text{SO}_4\) droplet size variability at 1000mb.
### Table 1. Research Flights during TexAQS 2006.

<table>
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<th>Flight</th>
<th>Date</th>
<th>Flight and Source Characteristics</th>
<th>Wind Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9/21</td>
<td>Texas City, Houston Urban Plume</td>
<td>Southerlies</td>
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<tr>
<td>3</td>
<td>9/25</td>
<td>Dallas, Houston Urban Plume, Big Brown and Limestone powerplants emission characterization and chemical processing</td>
<td>Northerlies</td>
</tr>
<tr>
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<td>9/26</td>
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<td>Northerlies</td>
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<td>South Westerlies</td>
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<td>Light winds, switching between Easterlies and Southerlies</td>
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<td>Light winds, North Easterlies</td>
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<td>North Easterlies</td>
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<td>10/08</td>
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<td>10/10</td>
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<td>Northerlies to North Westerlies</td>
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### Table 2. Closure Analysis for TexAQS 2006 Data Set

$S$ is the slope of the fit of the data and $R^2$ is the correlation coefficient. $S$ and $R^2$ values $\approx 0.9$ indicate good closure and agreement. The Normal Mean Error, NME, indicates the degree of scatter and Normal Mean Bias, NMB, reflects the degree of systematic errors from perfect closure agreement.

<table>
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<th>Flight</th>
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<th>INORG</th>
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<th>SR-EXT</th>
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<td>NAMS</td>
<td>NAMS</td>
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<td>18.7 (11.6)</td>
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<td>NAMS</td>
<td>NAMS</td>
<td>0.77 (0.76)</td>
<td>0.35 (0.62)</td>
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<td>NME (NMB) (%)</td>
<td>17.9 (-21.1)</td>
<td>24.4 (15.3)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>23.5 (-18.4)</td>
<td>60.6 (-60.0)</td>
</tr>
<tr>
<td>#3</td>
<td>9/25</td>
<td>0.43%</td>
<td>$S(R^2)$</td>
<td>0.66 (0.87)</td>
<td>0.73 (0.73)</td>
<td>0.45 (0.02)</td>
<td>0.28 (0.80)</td>
<td>0.44 (0.69)</td>
<td>0.35 (0.92)</td>
</tr>
<tr>
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<td>NME (NMB) (%)</td>
<td>26.9 (-21.2)</td>
<td>27.2 (-1.8)</td>
<td>34.5 (-28.8)</td>
<td>64.9 (-64.9)</td>
<td>40.1 (-39.8)</td>
<td>70.9 (-70.9)</td>
</tr>
<tr>
<td>#4</td>
<td>9/26</td>
<td>0.44%</td>
<td>$S(R^2)$</td>
<td>0.85 (0.74)</td>
<td>1.35 (0.88)</td>
<td>0.69 (0.19)</td>
<td>0.34 (0.18)</td>
<td>0.57 (0.19)</td>
<td>0.37 (0.85)</td>
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<td>NME (NMB) (%)</td>
<td>16.4 (-10.2)</td>
<td>38.6 (33.2)</td>
<td>31.4 (-22.9)</td>
<td>64.7 (-63.2)</td>
<td>36.9 (-36.6)</td>
<td>65.0 (-65.0)</td>
</tr>
<tr>
<td>#5</td>
<td>9/27</td>
<td>0.44%</td>
<td>$S(R^2)$</td>
<td>1.20 (0.63)</td>
<td>0.921 (0.64)</td>
<td>0.45 (0.62)</td>
<td>0.83 (0.65)</td>
<td>0.43 (0.63)</td>
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<td></td>
<td>NME (NMB) (%)</td>
<td>NPILS</td>
<td>32.6 (28.4)</td>
<td>22.1 (-1.4)</td>
<td>55.5 (-54.5)</td>
<td>23.5 (-11.9)</td>
<td>59.7 (-58.7)</td>
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<tr>
<td>#6</td>
<td>9/29</td>
<td>0.44%</td>
<td>$S(R^2)$</td>
<td>1.03 (0.93)</td>
<td>1.20 (0.88)</td>
<td>0.99 (0.88)</td>
<td>0.48 (0.76)</td>
<td>0.88 (0.90)</td>
<td>0.44 (0.60)</td>
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<td>NME (NMB) (%)</td>
<td>7.5 (2.7)</td>
<td>16.7 (15.2)</td>
<td>12.5 (-3.1)</td>
<td>52.4 (-52.4)</td>
<td>12.5 (-10.7)</td>
<td>54.3 (-54.3)</td>
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<tr>
<td>#7</td>
<td>10/05</td>
<td>0.43%</td>
<td>$S(R^2)$</td>
<td>1.02 (0.97)</td>
<td>1.15 (0.93)</td>
<td>0.90 (0.92)</td>
<td>0.44 (0.85)</td>
<td>0.89 (0.98)</td>
<td>0.41 (0.79)</td>
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<td>NME (NMB) (%)</td>
<td>7.2 (0.9)</td>
<td>14.0 (10.6)</td>
<td>13.3 (-10.9)</td>
<td>56.7 (-56.7)</td>
<td>11.0 (-10.5)</td>
<td>57.4 (-57.4)</td>
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<tr>
<td>#8</td>
<td>10/06</td>
<td>0.43%</td>
<td>$S(R^2)$</td>
<td>0.95 (0.90)</td>
<td>1.00 (0.89)</td>
<td>0.83 (0.83)</td>
<td>0.44 (0.87)</td>
<td>0.84 (0.86)</td>
<td>0.49 (0.89)</td>
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<td>NME (NMB) (%)</td>
<td>11.5 (-2.8)</td>
<td>12.4 (2.8)</td>
<td>16.9 (-12.6)</td>
<td>56.4 (-56.4)</td>
<td>15.7 (-11.9)</td>
<td>52.4 (-52.4)</td>
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<tr>
<td>#9</td>
<td>10/08</td>
<td>0.43%</td>
<td>$S(R^2)$</td>
<td>1.00 (0.88)</td>
<td>1.08 (0.82)</td>
<td>0.82 (0.76)</td>
<td>0.40 (0.62)</td>
<td>0.89 (0.90)</td>
<td>0.49 (0.80)</td>
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<tr>
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<td>NME (NMB) (%)</td>
<td>10.0 (0.2)</td>
<td>13.9 (7.7)</td>
<td>17.4 (-15.7)</td>
<td>59.6 (-59.6)</td>
<td>12.6 (-10.8)</td>
<td>51.7 (-51.7)</td>
</tr>
<tr>
<td>#10</td>
<td>10/10</td>
<td>0.42%</td>
<td>$S(R^2)$</td>
<td>1.01 (0.92)</td>
<td>1.17 (0.90)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>0.85 (0.92)</td>
<td>0.42 (0.80)</td>
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<td>NME (NMB) (%)</td>
<td>11.5 (-0.5)</td>
<td>18.5 (14.6)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>17.6 (-14.5)</td>
<td>61.3 (-61.3)</td>
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<tr>
<td>#10</td>
<td>10/10</td>
<td>0.42%</td>
<td>$S(R^2)$</td>
<td>0.94 (0.42)</td>
<td>1.02 (0.47)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>0.85 (0.35)</td>
<td>0.38 (0.46)</td>
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<td></td>
<td>NME (NMB) (%)</td>
<td>12.4 (-3.5)</td>
<td>10.4 (4.3)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>19.0 (-13.4)</td>
<td>61.5 (-61.5)</td>
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<tr>
<td>#10</td>
<td>10/10</td>
<td>0.42%</td>
<td>$S(R^2)$</td>
<td>0.90 (0.85)</td>
<td>0.95 (0.79)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>0.85 (0.84)</td>
<td>0.35 (0.79)</td>
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<td>NME (NMB) (%)</td>
<td>10.1 (-3.8)</td>
<td>7.2 (-3.9)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>15.4 (-14.8)</td>
<td>65.4 (-65.4)</td>
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<tr>
<td>#10</td>
<td>10/06</td>
<td>0.42%</td>
<td>$S(R^2)$</td>
<td>1.06 (0.15)</td>
<td>1.15 (0.05)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>0.96 (0.25)</td>
<td>0.43 (-0.81)</td>
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<tr>
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<td></td>
<td>NME (NMB) (%)</td>
<td>13.1 (10.3)</td>
<td>19.0 (18.3)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>11.4 (-1.2)</td>
<td>55.0 (-54.4)</td>
</tr>
<tr>
<td>#10</td>
<td>10/10</td>
<td>0.65%</td>
<td>$S(R^2)$</td>
<td>1.04 (0.63)</td>
<td>1.08 (0.56)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>0.95 (0.79)</td>
<td>0.43 (-0.54)</td>
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<tr>
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<td></td>
<td></td>
<td>NME (NMB) (%)</td>
<td>8.3 (4.9)</td>
<td>10.4 (9.5)</td>
<td>NAMS</td>
<td>NAMS</td>
<td>7.9 (-4.7)</td>
<td>55.8 (-55.8)</td>
</tr>
<tr>
<td>All Flights</td>
<td>all s</td>
<td>S</td>
<td>0.94±0.10</td>
<td>1.09±0.13</td>
<td>0.82±0.15</td>
<td>0.42±0.07</td>
<td>0.84±0.13</td>
<td>0.40±0.06</td>
<td></td>
</tr>
</tbody>
</table>

NAMS = no size-resolved AMS measurements applied  
NPILS = no PILS-WSOC measurements available

$NMB$ (%) = -3.6±7.7 11.6±9.3 -13.1±8.4 -57.7±4.3 -16.1±10.0 -60.9±6.4
### Table 3. September 25 Average Metropolitan Regional Comparison

<table>
<thead>
<tr>
<th>Region Studied</th>
<th>Dallas</th>
<th>Houston</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Total Particle Conc. (# cm(^{-3}))</td>
<td>15139 ± 14450</td>
<td>20753 ± 16280</td>
</tr>
<tr>
<td>Avg. Organic Fraction</td>
<td>0.79 ± 0.04</td>
<td>NAMS</td>
</tr>
<tr>
<td>Activated Fraction (CCN/CN) at s=0.43%</td>
<td>0.14 ± 0.10</td>
<td>0.15 ± 0.12</td>
</tr>
<tr>
<td>Activated Fraction (CCN/CN) at s=0.71%</td>
<td>0.20 ± 0.14</td>
<td>0.24 ± 0.15</td>
</tr>
<tr>
<td>Avg. Droplet Size at s=0.43%, (µm)</td>
<td>1.99 ± 0.21</td>
<td>1.80 ± 0.26</td>
</tr>
<tr>
<td>Avg. Droplet Size at s=0.71%, (µm)</td>
<td>2.44 ± 0.29</td>
<td>2.29 ± 0.24</td>
</tr>
</tbody>
</table>

NAMS = no AMS measurements applied
Appendix A: Auxiliary Materials
**Figure A1.** Flight track for research flight #1 (September 20). Marker size and color correspond to time of sampling, and total concentration (CN), respectively.
Figure A2. Similar to Fig. A1, but for research flight #2 (September 21).
Figure A3. Same as Fig. A1, but for research flight #3 (September 25). Locations of large powerplants (e.g., Big Brown, Limestone) are shown.
Figure A4. Measured CN and CCN concentrations, aerosol composition, and size distributions are plotted as a function of UTC Time for (a) research flight #1 (September 20) and (b) flight #2 (September 21).
Figure A5. Aircraft altitude, gas-phase species, average activated droplet size are plotted as a function of UTC Time for research (a) flight #1 (September 20) and (b) flight #2 (September 21).
Figure A6. CCN closure plots for data collected during research flight #2 (September 21) using the (a) INORG (markers colored by organic volume fraction), (b) BK-INT-SOL, (c) BK-INT, and (d) BK-EXT schemes. Black dashed lines represent perfect agreement (center) and 50% error. The solid black line represents the best fit as reported in Table 2.
Figure A7. Aircraft altitude, gas-phase species, average activated droplet size, measured CN and CCN concentrations, aerosol composition, and size distributions are plotted as a function of UTC Time for research flight #3 (September 25).
Figure A8. CCN closure plots for data collected during research flight #4 (September 26) using the (a) INORG, (b) SR-INT, (c) SR-EXT, (d) BK-INT, and, (e) BK-EXT scheme. Results are shown for $s = 0.44\%$ (closed symbols with a solid grey best fit line) and $s = 0.73\%$ (open symbols with a solid black best fit line). Dashed lines represent 1:1 line and ±50% prediction error.
Figure A9. Location of plume transects measured during research flights (a) 4 and (b) 5 on September 26 and 27, respectively.
Figure A10. Average AMS Mass distribution data collected on September 26 (a-c) and 27 (d-f) in the labeled regions of Fig. A9.