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Lance, Sara

Nenes, Athanasios

Mazzoleni, Claudio

Dubey, Manvendra

Gates, Harmony

Varutbangkul, Varuntida

Rissman, Tracey A.

Murphy, Shane M.



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2 **CCN Activity, Closure and Droplet Growth Kinetics of Houston Aerosol**3 **During the Gulf of Mexico Atmospheric Composition and Climate**4 **Study (GoMACCS)**

5

6 Sara Lance and Athanasios Nenes*, Georgia Institute of Technology;

7 Claudio Mazzoleni, Michigan Technological University; Manvendra Dubey, Los Alamos

8 National Laboratory; Harmony Gates, Varuntida Varutbangkul, Tracey A. Rissman,

9 Shane M. Murphy, Armin Sorooshian, Richard C. Flagan and John H. Seinfeld,

10 California Institute of

11 Technology; Graham Feingold, National Oceanic and Atmospheric

12 Administration; Haflidi H. Jonsson, Naval Postgraduate School

13

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22 * Corresponding author

23 **ABSTRACT**

24 In-situ Cloud Condensation Nuclei (CCN) measurements were obtained in the
25 boundary layer over Houston, TX during the 2006 Gulf of Mexico Atmospheric
26 Composition and Climate Study (GoMACCS) campaign onboard the CIRPAS Twin
27 Otter. Polluted air masses in and out of cloudy regions were sampled for a total of 22
28 flights, with CCN measurements obtained for 17 of these flights. In this paper, we focus
29 on CCN closure during two flights, within and downwind of the Houston regional plume
30 and over the Houston Ship Channel. During both flights, air was sampled with particle
31 concentrations exceeding $25,000 \text{ cm}^{-3}$ and CCN concentrations exceeding $10,000 \text{ cm}^{-3}$.
32 CCN closure was evaluated by comparing measured CCN concentrations with those
33 predicted on the basis of measured aerosol size distributions and Aerosol Mass
34 Spectrometer particle composition. Different assumptions concerning the internally-
35 mixed chemical composition result in average CCN overprediction ranging from 3% to
36 36% (based on a linear fit). It is hypothesized that the externally-mixed fraction of the
37 aerosol contributes much of the CCN closure scatter, while the internally-mixed fraction
38 largely controls the overprediction bias. Finally, based on the droplet sizes of activated
39 CCN, organics do not seem to impact, on average, the CCN activation kinetics.

40

41 ***1. Introduction***

42 In addition to human health and direct climate radiative forcing implications,
43 aerosols play an important role in the formation of clouds, as they provide the sites upon
44 which cloud droplets form. Higher aerosol concentrations generally lead to a greater
45 number of cloud droplets, but not all particles are equally efficient CCN. Each particle
46 requires exposure to a threshold water vapor concentration, termed “critical
47 supersaturation”, before acting as a cloud condensation nucleus (CCN) and
48 spontaneously activating into a cloud droplet. The complexity of aerosol-cloud
49 interactions, and, the strong impact of clouds on the planetary radiative budget leads to an
50 “aerosol indirect climate effect” that constitutes the largest source of uncertainty in
51 anthropogenic climate change predictions [IPCC, 2007].

52 The conditions under which a particle can act as a CCN depend strongly on
53 particle size [e.g., Seinfeld and Pandis, 2006] although particle composition also plays an
54 important role. The latter effects are a challenge for predictive models, as they require
55 simulating the evolution of the aerosol population as it ages and interacts with fresh
56 emissions. Dusek et al [2006] suggest that the aerosol composition has only a minor
57 effect on CCN concentrations, with variability in the size distribution alone accounting
58 for 84-96% of the variability in CCN concentrations. Wang [2007] showed that cloud
59 albedo is insensitive to particle composition. Others however have found that the mass
60 fraction of one type of chemical compounds, known as Hydrocarbon-like Organic
61 Aerosol (HOA), can explain up to 40% of the CCN concentration variability [Quinn et al,
62 2008]. Furutani et al [2008] also found that changes in aerosol composition from aging
63 processes can have an important effect on CCN activity.

64 To predict CCN concentrations for a given particle size distribution, simplifying
65 assumptions are typically made for the chemical composition of the aerosol population;
66 this is the case even when composition measurements are available, since no
67 measurement technique is capable of quantifying the full array of compounds present in
68 ambient aerosol [Saxena and Hildemann, 1996]. Solubility, density, molecular weight,
69 and surfactant properties all affect CCN activity [Saxena and Hildemann, 1996], as do
70 interactions between the organic and inorganic aerosol constituents [Shulman et al, 1996;
71 Dinar et al, 2008]. Most often, Aerodyne Aerosol Mass Spectrometer (AMS)
72 measurements are used to constrain the chemical properties of the soluble inorganic
73 fraction of ambient aerosol (nitrate, sulfate and ammonium ions) for CCN studies [e.g.,
74 Ervens et al, 2007; Medina et al, 2007]. However, AMS measurements are unable to
75 provide the refractory composition (e.g. soot) or complete speciation of the organic
76 fraction. Numerous simple approaches have been proposed, based on activation spectra
77 or hygroscopic uptake properties of carbonaceous aerosol, to characterize the impact of
78 organics on water activity and CCN activity [e.g., Petters and Kreidenweis, 2007; Vestin
79 et al, 2007; Padró et al., 2007]. Although very useful for parameterizing ambient data
80 measurements, these methods are often applied with the assumption that the organic
81 fraction is water-soluble and does not affect surface tension behavior, both of which
82 result in inferred hygroscopicity that may not reflect the properties of the water-soluble
83 carbonaceous fraction of the aerosol [e.g., Englehart et al., 2008; Asa-Awuku et al,
84 2008b].

85 Apart from the diversity of organic compounds present in ambient aerosol,
86 another important source of uncertainty in predicting CCN concentrations is the mixing-

87 state of the aerosol population, especially close to emission sources. Modeling studies
88 often assume that particles are internally-mixed (i.e., all particles of a given size have the
89 same composition); in reality, the aerosol is often an external-mixture, and chemical
90 composition varies amongst particles of the same size. Since the soluble (typically
91 inorganic) components dominate the water-uptake properties of the aerosol, the existence
92 of externally-mixed hydrophobic particles can have an important impact on CCN
93 number.

94 CCN closure studies have been performed over the last decade to evaluate the
95 predictive understanding of the aerosol-CCN link [e.g., VanReken et al, 2003; Chang et
96 al, 2007; Cantrell, 2001; Medina et al, 2007; Broekhuizen et al, 2006; Ervens et al, 2007,
97 and references therein]. These studies use measurements of the aerosol size distribution
98 and chemical composition to predict the number of CCN for a given supersaturation;
99 direct in-situ observations of CCN (obtained by exposing the ambient particles to a
100 controlled water vapor supersaturation) are then compared against these predictions.
101 Most often, CCN concentration is overpredicted on average by less than ~30%; the
102 variability however is often much larger and difficult to account for.

103 The current work focuses on CCN measurements taken onboard the Center for
104 Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS, <http://www.cirpas.org>)
105 Twin Otter during the Gulf of Mexico Atmospheric Composition and Climate Study
106 (GoMACCS) field campaign in Houston, TX from August 25-September 15, 2006
107 (<http://esrl.noaa.gov/csd/2006/>). Owing to a combination of motor vehicle traffic, close
108 proximity to large petrochemical refineries, chemical plants, waste treatment, coal-fired
109 power plants, and heavy industrial shipping via the Houston Ship Channel, measured

110 aerosol concentrations often exceeded $10,000 \text{ cm}^{-3}$. Houston, with its diverse mixture of
111 local industrial sources in combination with the local marine and biogenic emissions, is
112 an especially challenging area in which to predict the effect of aerosols on clouds. We
113 study the ability to predict CCN concentrations in a heavily polluted environment, in
114 which organic concentrations are often high, and explore the role of the particle chemical
115 composition in the variability and biases of our CCN predictions. This study is
116 complementary to the study of Quinn et al [2008], which took place over the same time
117 period onboard the NOAA ship *Ronald H. Brown*, and, the study of Asa-Awuku et al [in
118 review], which took place onboard the NOAA WP-3D airborne platform.

119

120 ***2. Dataset Description***

121 *2.1 Overview of Flights*

122 Figure 1a shows the flight tracks for the Twin Otter Research Flights (RF)
123 analyzed, each of which occurred during daylight hours. A total of 22 flights were carried
124 out, during which airmasses were sampled in the vicinity of powerplants (RF1-3, 9, 13,
125 14, 17, 19), the Houston Ship Channel (RF 4, 11), Downtown Houston (RF 11, 13, 21,
126 22) and its surrounding areas. Supersaturation in the measurements varied from 0.3 to
127 1.0%, and CCN concentrations, from 200 to $15,000 \text{ cm}^{-3}$. Table 1 shows a summary of
128 the flights, the major sources of pollution, and the dominant wind direction. Lu et al
129 [2008] describe the complete instrument payload on the Twin Otter during GoMACCS.

130

131 *2.2 CCNc Measurements*

132 CCN concentrations were measured using a Droplet Measurement Technologies
133 continuous flow streamwise thermal gradient CCN counter (CCNc; Roberts and Nenes,
134 2005; Lance et al., 2006) at 1 Hz time-resolution. CCN were sampled through a manifold
135 from which all other in-situ aerosol observations were taken (except for the particle size
136 distribution measurements, which will be discussed later). The common sampling
137 manifold was located downstream of a ball valve set to sample either from the main inlet
138 (Figure 1b) or downstream of a Counterflow Virtual Impactor [Noone et al, 1988; Ogren
139 et al, 1992], which selectively sampled droplets and large particles with diameters
140 exceeding $\sim 5 \mu\text{m}$, and was switched on during constant altitude legs in-cloud. CCN
141 measurements were obtained for the aerosol outside of cloud, and, for the cloud droplet
142 residuals.

143 The supersaturation within the CCNc is controlled by the sample and sheath flow
144 rates, column pressure, inlet temperature, and the temperature difference between the
145 bottom and top of the column. The uncertainty for each of these operating parameters is
146 summarized in Table 2. The CCNc was operated throughout the campaign with a set flow
147 rate of $\sim 1 \text{ L min}^{-1}$, consisting of sample and sheath flows with average rates of 0.092 and
148 0.909 L min^{-1} , respectively. The careful design of the Twin Otter main inlet (which
149 decelerates the air flow by a factor of ten before it enters the sampling manifold)
150 dampens most pressure oscillations; changes in attack angle of the aircraft still generate
151 high frequency (small amplitude) pressure fluctuations which are magnified by the active
152 flow control in the CCNc and create flow oscillations in the growth chamber. To address
153 this, a flow restriction upstream of the CCNc was used in most flights to dampen residual
154 pressure fluctuations in the main sampling inlet. Without a flow restrictor (RF4), the

155 sheath flow rate standard deviation increased by a factor of 4 (see Table 2). For RF7, the
156 flow restrictor was replaced with a 0.33m long, 1.9cm diameter dead volume (with an
157 added delay time of 4.4s), which resulted in flow rate fluctuations comparable to leaving
158 the flow restrictor off.

159 Hegg et al. (2005) report that the transmission efficiency of the Twin Otter main
160 inlet is close to 100% for particle diameters less than 3.5 μm . Similarly, particle losses
161 through the flow restrictor have been found to be negligible for submicron particles in the
162 range of pressures and flow rates experienced during flight. Since nearly all CCN are
163 below 300 nm, number losses for CCN in both the main inlet and in the flow restrictor
164 upstream of the CCNc are negligible.

165 In addition to pressure fluctuations, the CCNc is sensitive to low-frequency
166 pressure changes during ascents and descents owing to the finite time required for the
167 development of the temperature and supersaturation profiles within the instrument; this
168 issue was addressed by maintaining the pressure at the inlet of the CCNc at ~ 700 mb
169 using a DMT Inlet Pressure Controller (<http://www.dropletmeasurement.com>). It consists
170 of a vacuum pump with active flow control pulling downstream of the flow restrictor and
171 in parallel to the CCNc. The pressure controller flow was set to maintain the pressure at
172 the inlet of the CCNc to a constant value. The pressure controller was operated upstream
173 of the CCNc for all but RF4, RF5, RF6, RF7 and RF9.

174 The reduced pressure in the CCNc expands the sample volume and decreases the
175 CCN concentration, requiring correction of the measured concentrations back to ambient
176 concentrations, according to the ideal gas law:

$$177 \quad [CCN]_{amb} = [CCN]_{meas} \left(\frac{P_{amb}}{P_{CCN}} \right) \quad (1)$$

178 where $[CCN]_{amb}$ and $[CCN]_{meas}$ are the ambient and measured CCN concentrations, and
 179 P_{amb} and P_{CCN} are the ambient and CCNc pressures, respectively. As the inlet pressure
 180 controller was not installed until midway through the mission, supersaturation in the
 181 CCNc during RF4, RF5, RF6, RF7 and RF9 drifted with the ambient pressure. For these
 182 flights, data collected during altitude changes are not considered.

183 In addition to pressure changes, the drifting temperature of the CCNc inside the
 184 fuselage of the Twin Otter can cause changes in the CCNc supersaturation. The CCNc
 185 control software sets the column temperature at the top (T1) to a constant offset above
 186 ambient temperature for the thermal electric coolers to operate efficiently. The
 187 temperature setpoints at the middle and bottom of the column (T2 and T3, respectively)
 188 are adjusted accordingly, to maintain a constant setpoint temperature difference (T3-T1).
 189 For this study, the ambient temperature is the uncontrolled temperature within the
 190 unpressurized cabin of the aircraft, which heats up from the nearby pumps in an enclosed
 191 space and cools off as the aircraft ascends to higher altitudes. The T1 setpoint does not
 192 continuously follow ambient temperature, rather only when the ambient temperature
 193 exceeds 1°C difference from T1. Thus, the temperature setpoint increments in step
 194 changes as the ambient temperature drifts, which occasionally causes slight but abrupt
 195 changes in supersaturation.

196 Uncertainty in the temperature difference between the bottom and top of the
 197 CCNc column translates directly to uncertainty in the CCNc supersaturation. The
 198 temperature uncertainty was significantly higher in the early flights compared to later

199 flights, as shown in Table 2. Starting with the flight on September 1, 2006 (RF11), a new
200 AC/DC power supply was installed, which significantly reduced the temperature
201 fluctuations recorded by the thermistors in the CCNc, bringing the temperature variability
202 down to levels observed in laboratory experiments and ground-based studies. The high-
203 frequency variability in recorded temperatures in the earlier flights cannot be real (as the
204 thermal resistance in the flow column does not permit such high-frequency fluctuations)
205 and is likely a result of electronic noise; nevertheless, we treat the measured temperature
206 uncertainty as true, leading to significantly higher supersaturation uncertainty (Table 2).

207 For several of the research flights (RF7, RF11, RF16 and RF17) the CCNc was
208 operated at multiple supersaturations by periodically making step-changes in the vertical
209 (streamwise) temperature gradient. The temperature gradient cycling was automated and
210 was not, therefore, purposely aligned with the sampling of plumes. For flights after
211 August 31, the supersaturation was maintained at $0.5 \pm 0.03\%$ (one standard deviation).

212 The CCNc supersaturation was calibrated throughout the mission at various
213 pressures, flow rates, and temperature gradients using laboratory-generated ammonium
214 sulfate particles (following the SMCA procedure of Nenes and Medina, in review; Asa-
215 Awuku et al., 2008b). These calibrations were then used to determine the supersaturation
216 at different operating conditions during flight, interpolating between the calibrated
217 supersaturations when required using the thermal efficiency and supersaturation
218 parameterizations from Lance et al [2006]. The slope and intercept of the supersaturation
219 versus ΔT curve were accounted for in the calculations of thermal resistance, assuming a
220 van't Hoff factor of 2.5 and spherical shape for the dry ammonium sulfate calibration
221 aerosol [Rose et al, 2008; Zelenyuk et al, 2006].

222 Figure 2 shows a summary of the operating conditions and the variability therein
223 for four representative flights (RF7, RF9, RF11, RF19). The uncertainty in their operating
224 conditions can be classified in four different categories. Flights classified in Categories 1
225 and 3 (corresponding to RF7 and RF11 in Figure 2) had a changing supersaturation
226 setpoint (three different values changing every 5 min throughout the flight). The
227 uncertainty in supersaturation at each setpoint, however, is much higher for Category 1
228 flights than for Category 3 flights due to a greater uncertainty in the sheath flow rate
229 and/or column temperature gradient. Flights designated as Category 1 also had a drifting
230 pressure in the CCNc (except for RF7, where the entire flight was at constant altitude)
231 causing shifts in supersaturation, while Category 3 flights made use of the inlet pressure
232 controller. The supersaturations for the Category 3 flight shown (RF11) remain consistent
233 throughout, even as the ambient pressure changes (except when pressure drops the
234 pressure box control setting of 700 mbar). Even with the pressure control box, minor
235 supersaturation deviations still exist owing to changes in ambient temperature. Category
236 2 and 4 (represented by RF9 and RF19 in Figure 2) were set to a single supersaturation,
237 but with pressure changes, and larger uncertainty in flow and temperature uncertainty in
238 the former. Because the supersaturation was set to a constant value for the Category 2
239 and 4 flights, it is easier to see the effect of the abrupt change in the temperature setpoint
240 as the ambient temperature changed inside the cabin of the aircraft.

241 Although the variance of the calculated instrument supersaturation is low, Rose et
242 al. [2008] suggest that the relative supersaturation uncertainty (at low supersaturations)
243 can be as high as 10% due to uncertainties in the parameters used to calibrate the
244 instrument, such as water activity and nonspherical particle shape. We assume 10% as an

245 upper limit of supersaturation uncertainty for Category 3 and 4 flights, and we assume an
246 uncertainty in supersaturation of 20% for Category 1 and 2 flights. Instrument
247 supersaturation uncertainty translates to uncertainty in the predicted CCN concentrations;
248 for the levels cited here it could be important depending on the steepness of the CCN
249 spectrum (which is a convolution of aerosol size distribution, composition and mixing
250 state) at the supersaturation of interest. Although not straightforward, the sensitivity of
251 CCN concentration to supersaturation uncertainty can be evaluated from the observed
252 particle size distributions, given assumptions about the particle composition (Section
253 2.4).

254

255 *2.3 Measurements used for CCN closure*

256 Measurements used for CCN closure calculations (in addition to CCN
257 concentrations) are dry particle size distributions (with relative humidity at $21\% \pm 5\%$,
258 during all flights) measured by the Dual Automated Classified Aerosol Detector
259 (DACAD [Wang et al., 2003]), and, the aerosol chemical composition measured by an
260 Aerodyne compact time of flight aerosol mass spectrometer (C-ToF-AMS [Drewnick et
261 al, 2005; Sorooshian et al, 2008]). The CCNc and C-ToF-AMS were positioned on the
262 same aerosol sampling manifold, which was switched between “counterflow virtual
263 impactor in-cloud”, and, “main inlet out-of-cloud” modes. Since the DACAD sampled
264 continuously from the main inlet, mobility size distribution measurements of cloud
265 droplet residuals were not available, and therefore CCN closure cannot be evaluated for
266 cloud droplet residuals. In computing the size distribution, we assume that particles
267 measured in the DACAD are spherical, which is typically valid in a humid environment

268 (even when the aerosol is dried appreciably), due to depression of the efflorescence
269 point by the organic compounds present in the particle [Salcedo, 2006; Chan et al, 2008].

270 An important temporal limitation is associated with the measurement of aerosol
271 size distribution (73 seconds). For each scan, the average number concentration of CCN
272 and supersaturation within the CCNc is computed. This dataset is then filtered by
273 disregarding 73 s-segments of data when the CCNc instrument supersaturation varies by
274 20% or more (from column temperature changes or pressure fluctuations during
275 ascents/descents). To disregard aliasing biases from sampling smaller plumes that are
276 below the temporal resolution of the DACAD, we filter out points for which the standard
277 deviation of CCN exceeds 25% of the average CCN concentration. We further filter out
278 data points when the average Condensation Nuclei (CN) concentrations differ by more
279 than 50% from the total particle concentrations integrated from the measured DACAD
280 size distribution.

281 For the CCN closure analysis, we use bulk chemical composition from the C-
282 ToF-AMS measurements, unless specified otherwise. Size-resolved AMS measurements
283 have been used for several ground- and ship-based CCN closure studies [e.g., Medina et
284 al. 2007; Ervens, et al. 2007; Quinn et al. 2008], where the airmass passes at a rate of 1 to
285 10 m s^{-1} . In airborne CCN closure studies, the airspeed is 10 to 100 times greater and
286 airmass composition changes rapidly, requiring higher sensitivity and time-resolution for
287 the size-resolved composition measurements. While size-resolved measurements can be
288 obtained rapidly in high concentration plumes [e.g. Murphy et al, 2009; Sorooshian et al,
289 2008], the loadings during many portions of the flights in this study were too low to
290 obtain size-resolved composition in reasonably short time frames. As a result, size-

291 resolved data was not used for CCN closure in this paper. However, the effect of size-
292 resolved composition measurements is shown for specific cases where the signal-to-noise
293 ratio for both the sulfate and organic size distributions is high.

294 A Droplet Measurement Technologies integrated Photoacoustic and nephelometer
295 Aerosol Spectrometer (PAS) was also operated onboard the CIRPAS Twin Otter. The
296 PAS measures aerosol absorption and $\sim 5^\circ$ - 175° integrated scattering, using a laser
297 radiation source, and an acoustic resonator coupled with a microphone to detect the
298 photoacoustic signal from absorption. A Lambertian diffuser, mounted at the center of the
299 acoustic resonator, is used to measure the light scattered by the aerosol. The standard
300 laser installed by the manufacturer is a 781 nm solid state laser which failed under the
301 high temperatures experienced in the aircraft cabin during some of the flights (a
302 replacement 870 nm laser was then used for the rest of the campaign). The PAS collects
303 data at a sampling rate of ~ 0.71 Hz. Zero air (cleaned of particles by means of a HEPA
304 filter) data are automatically collected every ~ 4.7 minutes to correct for background
305 drifts. A thorough calibration of the PAS (with the 870 nm laser) was carried out at the
306 end of the campaign in the laboratory using various concentrations of strongly and
307 weakly absorbing particles. Altogether, the calibration procedure, instrumental noise and
308 high frequency changes in the background signals introduce an estimated 20-30%
309 uncertainty in the absorption measurements discussed here. A PAS prototype, developed
310 at the Desert Research Institute, Reno, NV, has been extensively tested and successfully
311 deployed in past field campaigns [Arnott, 1998; Arnott, 1999; Moosmüller, 1998; Arnott,
312 2006]. PAS observations are shown for one flight (using the 870 nm laser) to infer the
313 impact of soot on CCN concentrations.

314

315 *2.4 Prediction of CCN concentrations*

316 To predict CCN concentrations from the measured size distribution (assuming
 317 that all particles have an internally-mixed composition), we first determine the diameter
 318 of the smallest CCN-active particle (d_{50} ; where “50” signifies that a dry particle with this
 319 size has a 50% probability of activating into a cloud droplet) given the assumptions about
 320 internally-mixed particle chemistry, using the following thermodynamic relationship
 321 [Seinfeld and Pandis, 2006]:

322

$$323 \quad d_{50} = \left[\frac{27}{4} \left(\ln \left(\frac{S}{100} + 1 \right) \right)^2 \left(\frac{\rho_w TR}{4M_w \sigma} \right)^3 \frac{\rho_s M_w \varepsilon_s \nu}{M_s \rho_w} \right]^{-1/3} \quad (2)$$

324

325 where S is the average instrument supersaturation (in %), T is the mean temperature
 326 within the CCNc column, R is the ideal gas constant, σ is the droplet surface tension at
 327 the point of activation, ρ is the density and M is molecular weight of the solute
 328 (subscript s) and of water (subscript w), and ε_s and ν are the solute volume fraction
 329 and effective van't Hoff factor, respectively. Unless specified otherwise, the surface
 330 tension used in Equation 2 to predict CCN concentrations is 69.9 mN m^{-1} , which is the
 331 surface tension of pure water at the average temperature of the observations. CCN
 332 predictions are calculated by summing all particles with diameters above d_{50} , accounting
 333 for fractional activation of the DACAD size bin containing d_{50} .

334

335 For the flights where chemical composition information is used, we assume that
 the measured species are internally-mixed. Furthermore, since the solubility of organics,

336 their surfactant properties and mixing state are unknown, they are first treated as
 337 insoluble and non-surfactant (the effect of these assumptions on CCN closure is
 338 addressed with appropriate sensitivity studies). The organic volume fraction (ε_{org}) is then
 339 computed as:

$$340 \quad \varepsilon_{org} = (1 - \varepsilon_s) = \frac{m_{org} / \rho_{org}}{m_{org} / \rho_{org} + m_{AS} / \rho_{AS}} \quad (3)$$

341 where m_{org} and m_{AS} are the mass loadings of organics and ammonium sulfate (the sum
 342 of ammonium and sulfate ions) obtained from the C-ToF-AMS, respectively, ρ_{AS} is the
 343 density of ammonium sulfate (1.76 g cm⁻³; Hinds, 1999) and ρ_{org} is an average density
 344 of organics, assumed to be 1.4 g cm⁻³. The density of organics may range from 1.4 g cm⁻³
 345 to more than 1.6 g cm⁻³ [Dinar et al, 2006]; we use the lower end of the organic density
 346 range to simulate the largest effect expected from internally-mixed organics, as further
 347 explained in the following paragraph. When not including the bulk aerosol composition,
 348 we assume as a zero-order approximation that particles are composed of ammonium
 349 sulfate ($\varepsilon_s = 1.0$ in Equation 2). Following the guidance of Rose et al [2008], ν for
 350 ammonium sulfate (whether pure or internally-mixed with organics) is set to 2.5.

351 The two compositional assumptions presented above (pure ammonium sulfate vs.
 352 internally-mixed insoluble organic) represent limiting states of aerosol hygroscopicity.
 353 Ammonium sulfate is one of the most CCN-active and abundant compounds found in
 354 accumulation mode aerosol; assuming that the particles are composed purely of
 355 ammonium sulfate will thus tend to overestimate their CCN activity. Conversely,
 356 assuming organics are insoluble neglects their potentially important impacts on droplet

357 activation, thereby leading to a tendency for underpredicting CCN number. In reality, we
358 expect that the hygroscopicity of ambient particles lies somewhere between these two
359 extremes. There are many other details about the aerosol composition that may affect the
360 CCN closure (such as surfactant components, externally-mixed particles, and size-
361 varying composition), which are insufficiently constrained by the observations. We
362 therefore first apply these two common assumptions to the whole dataset to evaluate how
363 well CCN closure can be attained. We then evaluate for specific cases the impact of more
364 detailed composition information on CCN prediction accuracy.

365 The uncertainty in predicted CCN concentration is influenced by uncertainties in
366 the instrument supersaturation, particle size distribution and chemical composition.
367 Assuming an internally-mixed composition that is invariant with particle size, an estimate
368 of CCN concentration sensitivity to supersaturation uncertainty can be obtained. For a
369 period of very poor closure at ~16:15 UTC on RF22, a 10% reduction of the instrument
370 supersaturation causes a slight increase in d_{50} (from 46.4 nm to 53.0 nm), which
371 decreases the predicted CCN concentrations from 1630 cm^{-3} to 1470 cm^{-3} . Given that the
372 measured CCN concentrations are only 580 cm^{-3} during this time period, the uncertainty
373 in predicted CCN concentrations clearly cannot explain the poor closure for this example.

374

375 **3. Results**

376 *3.1 Summary of CCN observations*

377 Table 1 summarizes the range of CCN concentration and supersaturation for all
378 research flights during which the CCNc was operating. Figure 3a shows the profile of
379 1Hz CCN data from the entire GoMACCS campaign as a function of ambient pressure,

380 and colored by date. For many of the flights, CCN concentrations exceeded $10,000 \text{ cm}^{-3}$
381 (for a range of supersaturations, from 0.3 – 1.0 %). On separate days, the CCN
382 concentrations exceeded $20,000 \text{ cm}^{-3}$ (again, for a range of supersaturations, as low as
383 0.3%). Figure 3b shows the frequency distribution of CCN concentrations with different
384 supersaturation ranges over the entire GoMACCS campaign. The solid line indicates the
385 sum of the shaded regions, which is the total frequency distribution of CCN.

386

387 *3.2 CCN Closure*

388 We first evaluate the extent to which CCN closure can be achieved using the
389 measured size distribution and the assumption of pure ammonium sulfate particles.
390 Figure 4a shows a summary of this simplified CCN closure colored by flight, for all the
391 flights shown in Figure 1a. The gray lines indicate over- and under- prediction by factors
392 of two, three and four, respectively. Despite the very simple composition assumption,
393 predictions are nearly always within a factor of two greater than the measurements.
394 Figure 4b shows that the simplified CCN closure error is not correlated with
395 supersaturation, but rather with particle concentration. The overprediction (~36%) is
396 constant for CCN concentrations ranging from $1,000$ to $10,000 \text{ cm}^{-3}$. At lower CCN
397 concentrations (suggestive of a cleaner airmass), the bias is lower. At the highest
398 concentrations (above $10,000 \text{ cm}^{-3}$), the overprediction bias decreases again. Since there
399 is no clear dependence of the CCN overprediction on instrument supersaturation and
400 CCN concentration, water vapor depletion in the CCNc is unlikely the cause for the CCN
401 overprediction observed (laboratory experiments further support this, as they have shown
402 that water vapor depletion does not reduce the maximum supersaturation in the CCNc for

403 CCN concentrations up to at least $10,000 \text{ cm}^{-3}$). Instead, the composition of the aerosol
404 population is expected to play a role.

405

406 *3.3 CCN Closure with Chemical Analysis*

407 Figure 5 shows the CCN closure for all flights to which bulk aerosol chemical
408 composition from C-ToF-AMS data is applied. In both Figure 5a and 5b, the colored
409 data points correspond to CCN closure calculations assuming that organics are internally-
410 mixed with sulfate for all particles. Figure 5a shows the CCN closure colored by flight
411 and Figure 5b is colored by the instrument supersaturation. The black “+” symbols show
412 the CCN closure assuming pure ammonium sulfate aerosol. A linear regression of
413 predicted versus observed CCN concentrations, when forced through the origin, gives a
414 slope of 1.365 ± 0.007 for the assumption of ammonium sulfate particles (with an R^2
415 value of 0.906) and a slope of 1.026 ± 0.006 for the assumption of internally-mixed,
416 insoluble organics (with an R^2 value of 0.907). The linear regression was forced through
417 the origin because a statistically significant linear offset was not supported by the data.
418 In addition to the linear regression, we also calculate the average CCN overprediction
419 bias using a “ratio method” by fitting a Gaussian curve to histograms of the ratio of
420 predicted to measured CCN concentrations; this representation of the CCN closure
421 prevents the higher CCN concentration observations from controlling the fit. The result
422 is a more modest improvement in CCN closure from the inclusion of bulk chemical
423 information (with a decrease in the CCN overprediction bias from 34% to 20% using the
424 ratio method, as opposed to a decrease from 36% to 3% using the linear fit).
425 Furthermore, using the ratio method, the standard deviation decreases slightly from 24%

426 to 19% when including the bulk chemical information (which is a more significant
427 change than that of the linear regression coefficients). Overall, these results are
428 consistent with studies published to date [e.g., Medina et al., 2007; Chang et al. 2007;
429 Wang et al., 2008; Ervens et al, 2007], which show that CCN concentrations can be more
430 accurately predicted assuming that the measured organics are insoluble.

431 Organics can also lower the surface tension of deliquesced CCN, facilitating
432 activation (potentially making the particles even more CCN-active than ammonium
433 sulfate; Asa-Awuku et al, 2008a). Figure 5a presents the impact of reducing surface
434 tension by 15 mN m^{-1} on CCN closure (grey “+” symbols), using the same composition
435 information as the colored data points. This degree of surface tension reduction is typical
436 for organic-rich ambient particles [e.g., Facchini et al, 2000; Decesari et al, 2005; Mircea
437 et al, 2005; Asa-Awuku et al, 2008a]. The modest surface tension depression may
438 reconcile the CCN underprediction bias, even for cases where the aerosol is mostly
439 composed of ammonium sulfate.

440 Although simply adding the assumed internally-mixed organic fraction to the
441 CCN closure analysis reduces the overprediction bias, it cannot be established if the
442 improved CCN closure occurs for the right reasons. It may be hypothesized that the CCN
443 overprediction bias is controlled by the internally-mixed aerosol composition (as
444 measured by the C-ToF-AMS), whereas the variability in the CCN closure is governed by
445 the externally-mixed hydrophobic fraction (assuming that a significant fraction of the
446 externally-mixed hydrophobic aerosol mass is undetected by the C-ToF-AMS, such as
447 soot and dust); this would be consistent with the reduced bias resulting from the
448 internally-mixed assumption without a large reduction in the variability (since the

449 mixing-state is unknown). Without particle-by-particle information or measurements of
450 the aerosol mixing-state, it is not possible to verify this hypothesis. Hygroscopicity
451 measurements (especially with high temporal resolution, e.g. the DASH [Sorooshian et
452 al, 2008b]), or single-particle mass spectra measurements in the size range 40-200nm,
453 may be needed to adequately address the affect of aerosol composition on CCN closure.

454 In the following sections, we examine specific flights and the CCN closure in
455 relation to specific aerosol sources, in an attempt to evaluate the chemical factors
456 influencing the observed CCN concentrations.

457

458 *3.4 Research Flight 7 (Aug 28, 2006)*

459 During RF7, backtrajectories computed with the Flexpart model
460 (<http://zardozi.nilu.no/~andreas/TEXAQS/>) suggest the wind blew consistently out of the
461 Gulf of Mexico and then curved towards the northeast over the city of Houston. The
462 consistent meteorology provided an opportunity to examine the evolution of emissions
463 from specific chemical plants and refineries along the Houston Ship Channel as the
464 emissions traveled downwind. Figure 6a shows the flight track for RF7, colored by the
465 time of day, first starting at Ellington Field southeast of downtown Houston, followed by
466 transects of the Houston plume downwind, then followed by approaches toward and
467 away from specific point sources previously identified. The plumes identified by particle
468 concentrations in excess of $10,000 \text{ cm}^{-3}$ (colored in grey) appear to be correlated with
469 specific point sources identified in the 2004 EPA NO_x emission inventory. Figure 6b
470 presents the flight track colored by the organic volume fraction (calculated from Equation
471 3), which ranges between 0 and 0.3 for this flight, with the higher values at roughly the

472 same locations as those of elevated particle concentrations. The maps (Figures 6a,b) also
473 show the location of the Houston city limit, major roadways and airports, the Houston
474 Ship Channel, and several of the largest point sources for NO_x, including petrochemical
475 refineries (Ref), chemical plants (Chem P) and power plants (PP).

476 Figure 7a shows the time series of all the measurements relevant for CCN closure
477 including the distribution of dry particle size (d_p), the C-ToF-AMS measured aerosol
478 chemical composition and the CCNc supersaturation (blue bars). Also shown are the
479 average measured (open circles) and predicted (solid circles) CCN concentrations
480 assuming that the particles are composed of *i*) pure ammonium sulfate (blue), and, *ii*) a
481 size-independent internal mixture of insoluble organics and ammonium sulfate (orange),
482 filtered by supersaturation and concentration fluctuations and discrepancies as described
483 earlier in the text. Particle concentrations above 10 nm measured with a TSI 3010
484 condensation nuclei counter are plotted (grey line) along with particle concentrations
485 integrated from the particle size distribution measurements (blue horizontal lines). The
486 pressure trace (black line) indicates that the whole flight occurred at a single low altitude.
487 At the top of Figure 7a, the distribution of droplet size (D_p) is shown, which clearly
488 shows the effect of changing supersaturation on the droplet size at the exit of the CCNc.

489 The particle concentration spikes observed in the first half of the flight correspond
490 to plume transects. Starting around 2:30 PM UTC, the in-plume legs began. Two
491 sections are highlighted with blue and pink shaded areas and correspond to when the
492 Twin Otter first flew from and towards two point sources along the Ship Channel; Figure
493 7b presents these sections in higher resolution. The blue shaded area corresponds to the
494 plume labeled “1” in Figure 6a while the pink shaded area corresponds to plume “2”. For

495 both plumes, the overprediction is greater when sampling closer to the point source, and
496 cannot be attributed to the specific internally-mixed composition assumption (since the
497 blue and the orange points lie almost on top of each other, consistent with the low volume
498 fraction of organics for this flight). Thus, we expect that the overprediction originates
499 from unresolved mixing state and composition variation with size. The improvement in
500 CCN closure further from specific point sources may imply that the aerosol composition
501 changes rapidly downwind of the aerosol source. However, the CCNc supersaturation
502 was also coincidentally higher as we sampled nearer to the point sources for these two
503 cases. It may be that the CCN closure is improved at low supersaturations
504 (corresponding to a larger d_{50}) because most of the CCN are internally-mixed, whereas
505 at higher supersaturations (corresponding to a smaller d_{50}) there are more externally-
506 mixed particles. Since the aerosol mass is weighted strongly by the particle size, another
507 possibility is that the bulk aerosol composition measured by the C-ToF-AMS does not
508 adequately represent the smaller particles, which could then have a higher organic mass
509 fraction and act less efficiently as CCN. For most of this flight, the size-resolved C-ToF-
510 AMS measurements were unable to show conclusively whether the size distribution of
511 organics is different from the sulfate size distribution (which could then be used as
512 evidence for an externally-mixed aerosol), since the organic mass loadings were quite
513 low (average for flight = $0.65 \pm 0.26 \mu\text{g m}^{-3}$).

514 Figure 8 shows that the CCN closure for the duration of RF7 is much better at
515 lower supersaturations. The color of the open circles indicates the CCNc supersaturation,
516 while the size of the markers is proportional to the concentration of particles. The
517 vertical error bars represent the effect of a 20% uncertainty in the instrument

518 supersaturation, assuming an internally-mixed composition. Ervens et al [2007] also
519 found a supersaturation-dependent overprediction bias for CCN closure at Chebogue
520 Point, Nova Scotia, attributed to undercounting in the CCNc from using a higher than
521 recommended flow rate in the CCNc. An even higher flow rate is used in this study;
522 however, the observed droplet size distribution in Figure 7b shows that the particles are
523 all above 2 μm (hence efficiently counted), demonstrating that the flow rate
524 recommendations for prevention of undercounting in the CCNc suggested by Lance et al
525 [2006] are conservative. Furthermore, in this study, CCN closure was better at low
526 supersaturations, opposite to what was seen in Ervens et al. [2007]. Thus, size-varying
527 composition (and not instrument artifacts) is likely responsible for the trend in CCN
528 prediction bias with supersaturation.

529

530 *3.5 Research Flight 22 (Sept 15, 2006)*

531 We now examine data from a flight in which sampling was carried out farther
532 from emission sources. During RF 22, backtrajectories computed with the Flexpart
533 model suggest a prevailing wind originating from the Gulf of Mexico and flowing
534 northwest over Houston; closer analysis of the trajectories (not shown) suggest the wind
535 direction changed throughout the flight, at times picking up biomass burning emissions
536 from central Texas and Louisiana. Figure 9a shows the flight track for RF22 (with marker
537 size reflecting the ambient pressure, and color, the time of day); the Twin Otter first flew
538 along the highly industrialized Ship Channel, followed by a low pass over downtown
539 Houston and several transects of the Houston plume downwind of the city. Marked on the
540 flight track are segments where particle concentrations exceed $10,000\text{ cm}^{-3}$ (indicating the

541 regions of highest concentrations), which occur inside the city of Houston and downwind
542 thereof. Figure 9b is similar to Figure 9a, but colored by the organic volume fraction,
543 which varies between 10% and 70% (much higher than in RF7). Figure 9b shows that
544 the organic fraction is higher downwind of Houston; the 2004 emission inventory does
545 not show any large sources for primary organic aerosol in this region, hence the organic
546 fraction increase may be associated with secondary photochemical production from urban
547 precursor emissions or mixing of regional biomass burning aerosol from central Texas.
548 The fact that the location of high organics is intersected at least three different times
549 between 7 PM and 8 PM UTC suggests a persistent feature consistent with the dominant
550 wind direction.

551 Similar to Figure 7, Figure 10 shows the time series during RF22 of measured and
552 predicted CCN concentrations for two particle chemical composition assumptions, the
553 measured aerosol size distribution, and, the measured particle composition. Compared to
554 RF7, the aerosol mass and organic volume fraction in RF22 is substantially higher.
555 Figure 10 also presents an estimate of soot mass based on the photoacoustic absorption
556 measurements. For this, the absorption coefficient (Mm^{-1}) is divided by the mass-
557 absorption efficiency ($2.33 \text{ m}^2 \text{ g}^{-1}$ at 870 nm) extrapolated from a relation in Moosmuller
558 et al. [1998], assuming that all absorbing material is externally-mixed soot. This
559 approach in general would overestimate soot mass, since *i*) absorption can be enhanced
560 when internally-mixed with non-absorbing compounds [e.g., Mikhailove et al, 2006],
561 and, *ii*) a variety of organic compounds other than soot can be absorbing. However,
562 measurements from a single particle soot photometer during the concurrent TexAQS
563 campaign suggest soot loadings as high as $2 \mu\text{g m}^{-3}$ in the Houston plume and a mixing-

564 state that is strongly external [Schwarz et al, 2008]. The urban soot particles observed
565 during TexAQS also show a size distribution centered around 60 nm [Schwarz et al,
566 2008], which is very close to the average d_{50} we calculate for the particles during
567 GoMACCS. Altogether, this suggests that a significant fraction of particles may be
568 externally-mixed soot that would not readily act as CCN.

569 Figure 11 shows the particle size distribution during a period of very poor CCN
570 closure (1630 cm^{-3} predicted CCN, and only 630 cm^{-3} measured CCN) on RF22 at 16:14-
571 16:18 UTC. Using the photoacoustic absorption measurement to estimate the soot mass
572 concentration as explained previously ($0.7 \mu\text{g m}^{-3}$ for this time period), and assuming that
573 the local maximum in the particle size distribution at 65 nm is due to an external mixture
574 of soot (consistent with the TexAQS observations), we infer a lognormal distribution of
575 soot particles (with geometric standard deviation of 1.2). Assuming that this soot
576 distribution does not contribute CCN, predicted CCN concentration drops to 720 cm^{-3} ,
577 which is only a 14% overprediction (as opposed to an almost 160% overprediction when
578 assuming an internal mixture without any contribution from soot). An internal-mixture
579 of soot with the other aerosol species could also decrease the number of predicted CCN
580 by reducing ε_s in the particles (i.e., increasing d_{50}). However, to explain the observed
581 CCN concentration, ε_s would need to decrease from 0.57 to 0.09 (i.e., an increase in d_{50}
582 from 50.8 nm to 94.6 nm), which is not consistent with the composition measurements
583 (with $\sim 1 \mu\text{g m}^{-3}$ sulfate and $0.8 \mu\text{g m}^{-3}$ organics measured by the C-ToF-AMS at that
584 time, a lower estimate for ε_s would be ~ 0.38 , assuming a soot density of 2 g cm^{-3} [Slowik
585 et al, 2004]). Since soot aerosol in Houston was found to be most often externally-mixed
586 by Schwarz et al [2008], and since the photoacoustic observations onboard the Twin

587 Otter show significant absorption consistent with a large soot number concentration, we
588 are confident that an external mixture of nonhygroscopic soot aerosol is contributing to
589 the extreme CCN overprediction for this example. As the Twin Otter was sampling
590 directly downwind of the Houston Ship Channel during that time, an external mixture
591 with soot is not unexpected. However, when looking at Figure 10, there are clearly times
592 when absorption is even higher, and yet the CCN closure is good (for example, at 16:08-
593 16:11 UTC); this may result from the fact that the absorption measurements do not
594 provide the mixing-state or size distribution of the particle composition and the fact that
595 other compounds such as dust and organics can also contribute to the observed
596 absorption.

597 Due to the high mass loadings of both organics and sulfate for much of RF 22, the
598 size-resolved particle composition measurements may also provide important insight for
599 this flight. Figure 12a shows the size-resolved C-ToF-AMS measurements for the period
600 of extremely poor closure (160% CCN overprediction) at 16:14-16:17 UTC on RF 22.
601 These measurements, although noisy, confirm that the organic mass (like the soot mass)
602 is likely externally-mixed with sulfate since the size distributions of organic and sulfate
603 mass are quite dissimilar. During another period of poor closure on RF 22 (76% CCN
604 overprediction) at 16:47-16:50 UTC, the major bulk of the sulfate and organic mass
605 follow similar size distributions (Figure 12b) and the assumption of an internal mixture
606 appears to be reasonable (at least for particles larger than about 200 nm). In addition, the
607 expected soot mass during this time period is very low (the absorption is just above the
608 detection limit of the photoacoustic measurements). Both time periods shown in Figure
609 12 have similar bulk organic to sulfate ratios (0.74 ± 0.12 for period 12a and 0.87 ± 0.16

610 for period 12b). However, the CCN overprediction is much lower for the second time
611 period, and the mechanisms responsible for CCN overprediction may be different. Since
612 the aerosol appears to be internally-mixed, perhaps the effect of size-varying composition
613 is controlling the CCN overprediction for the second time period. For particles smaller
614 than about 200 nm (where many of the CCN occur), the ratio of organics to sulfate
615 appears to be much higher than for particles larger than 200 nm (where most of the mass
616 occurs); therefore, the soluble volume fraction derived from bulk composition may be
617 biased high for the majority of particles smaller than 200 nm. In order to explain the
618 number of observed CCN, the smaller particles (< 200 nm) would need to be highly
619 enriched in organics. The other possibility is that the smaller particles are much more
620 externally-mixed, which is not unexpected since many primary aerosol emission sources
621 produce extremely fine particulates. Unfortunately, it is not possible to unambiguously
622 verify the extent to which either of these mechanisms is affecting the CCN closure, since
623 the signal-to-noise ratio of the size-resolved C-TOF-AMS measurements at CCN relevant
624 sizes (between about 50 to 200 nm) is very low.

625 The CCN closure for RF 22 is shown in Figure 13, where vertical error bars
626 represent the effect of a 10% uncertainty in the instrument supersaturation on an
627 internally-mixed aerosol population. Figure 13 shows that CCN are, on average,
628 overpredicted when assuming pure ammonium sulfate aerosol (not always by the same
629 amount). On average, the closure is not better than for RF7, although the uncertainty in
630 the CCNc supersaturation is certainly lower. CCN closure improves when assuming that
631 the measured bulk organic fraction is insoluble and internally-mixed with sulfate. Under
632 more polluted conditions (higher particle concentrations), assuming the organic fraction

633 is internally-mixed results in CCN underprediction; this suggests that the organics are
634 either partially soluble or they depress droplet surface tension (thereby facilitating droplet
635 activation and increasing CCN concentrations).

636 The underlying message is that the details of particle composition (e.g. size-
637 resolved chemical composition, surfactant properties and mixing-state) are fundamental
638 for successful CCN closure in close proximity to emission sources, especially for such a
639 complex environment as Houston.

640

641 *3.6 Kinetics of Droplet Growth*

642 Figure 14 shows the average droplet diameter at the exit of the CCNc column for
643 all flights as a function of the CCNc supersaturation. For comparison, we show the
644 average droplet diameter for classified ammonium sulfate particles exposed to a range of
645 supersaturations in the laboratory at 1 L min^{-1} total flow rate (dashed line in Figure 13).
646 We vary the dry ammonium sulfate particle size from 10 nm to over 200 nm during the
647 calibration to obtain the range of droplet sizes expected for a given supersaturation (grey
648 shaded region in Figure 13). On average, the droplet diameter from ambient
649 measurements is above the lower limit established by the calibration aerosol. Since the
650 critical supersaturation of the ambient particles is unknown, the droplet size cannot be
651 unambiguously related to the growth rate. The droplet growth rate is driven by the
652 difference between the instrument supersaturation and the particle equilibrium
653 supersaturation, and is also proportional to the amount of time the droplets are given to
654 grow upon activation. Particles that activate at a lower supersaturation than the
655 instrument supersaturation will have both a higher driving force for condensational

656 growth and more time to grow (as they will activate even before supersaturation has fully
657 developed in the instrument). Another factor influencing the droplet growth rate is the
658 number of CCN present in the column, which can deplete the water vapor at very high
659 particle concentrations. The ammonium sulfate calibrations supplied no greater than 600
660 cm^{-3} CCN at any given time; therefore, we expect that comparisons with ambient
661 measurements having much higher CCN concentrations (and, therefore, potentially
662 smaller droplet sizes) may bias our assessment of the droplet growth rate. However,
663 Figure 13 supports that all droplets formed from ambient aerosol are, on average, larger
664 than the droplet formed from calibration aerosol. This comparison, termed “Threshold
665 Droplet Growth Analysis”, suggests that significant water vapor depletion does not occur
666 within the CCNc, even with CCN concentrations up to 10,000 cm^{-3} . Furthermore,
667 droplets on average do not grow more slowly than activated ammonium sulfate particles,
668 which suggests that the presence of organics, for the range of supersaturations
669 considered, does not substantially delay the activation kinetics of CCN. This is contrary
670 to the findings of Ruehl et al [2008] who report up to 62% of the particles having
671 moderate kinetic inhibition to condensational growth at a ground-based site in Houston
672 during GoMACCS, using a Phase Doppler Interferometer to monitor the droplet size in
673 another continuous-flow streamwise thermal gradient CCN chamber. The apparent
674 discrepancy between this study and Ruehl et al [2008] motivates future side-by-side
675 comparisons of the instruments to establish whether observed differences arise from
676 differences in sampled particle phase state, or artifacts from the optical detection or
677 thermal processing of the aerosol in either of the instruments [Asa-Awuku et al., 2008b].
678

679 **4. Conclusions**

680 This study provides an airborne CCN closure analysis in a heavily polluted
681 environment. Average CCN concentrations ranged from 100 cm^{-3} to more than 10,000
682 cm^{-3} , and organic volume fraction in the aerosol were as high as 70%. The results show
683 that CCN closure is overall attainable with an average overprediction bias of 36%, by
684 simply assuming it to be composed of pure ammonium sulfate. Accounting for the
685 internally-mixed particle soluble volume fraction, estimated from the sulfate and organic
686 mass loadings, reduces the average overprediction bias to 3%. Even when the first-order
687 behavior of CCN is well constrained by simple volume fraction assumptions, the scatter
688 between predicted and observed CCN concentrations remains large. Simultaneous
689 measurements of size-resolved composition and mixing-state as well as surfactant
690 properties of the aerosol are required to reduce the uncertainty in CCN closure for such a
691 heterogeneous mix of pollution sources. Contrary to ground-based measurements in the
692 Houston area, the activation kinetics of the CCN are always similar to ammonium sulfate,
693 and do not suggest delays from the presence of organics.

694

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869 **Table 1.** Twin Otter Science Flights During GoMACCS. Note CCN data in first 3

870 Flights are not available.

871

Flight	Date	Mission Description	Wind Direction (from)	AMS Data Used?	Super-Saturation Range [%]	CCN Concentration Range [cm ⁻³]
RF 1	8/21	Parish coal PP	E-SE	No	-	-
RF 2	8/22	Parish coal PP	E	No	-	-
RF 3	8/23	Parish coal PP	E	No	-	-
RF 4	8/25	Ship Channel	S-SE, NE	No	0.35-0.7	250-5,000
RF 5	8/26	Conroe	S, N-NE	No	0.4-0.7	200-800
RF 6	8/27	Beaumont	S-SE	Yes	0.3-0.5	200-1,000
RF 7	8/28	Baytown	SW	Yes	0.5-1.0	500-5,000
RF 8	8/28		S	No	-	-
RF 9	8/29	Parish coal PP	W-NW	No	0.55-1.0	200-3,000
RF 10	8/31		N-NW	No	0.5-0.55	600-6,000
RF 11	9/1	Houston, Ship Channel	N	No	0.35-0.85	250-10,000
RF 12	9/2	Local BB	N-NE	Yes	0.5-0.55	600-9,000
RF 13	9/3	Houston, Parish coal PP	NE	No	0.45-0.5	1,500-15,000
RF 14	9/4	Parish coal PP	NE, NW	Yes	0.5-0.55	400-3,000
RF 15	9/6	Waste Treatment	N-NE	Yes	0.5-0.6	200-5,000
RF 16	9/7	Galveston	NE	Yes	0.35-0.9	200-6,000
RF 17	9/8	Parish coal PP	E-NE, W	No	0.4-0.9	250-9,000
RF 18	9/10		S	No	-	-
RF 19	9/11	Fayette coal PP	S, NW	No	0.45-0.55	150-1,000
RF 20	9/13	Conroe	N	No		350-7,000
RF 21	9/14	Houston, Parish	E-NE	Yes	0.45-0.55	200-15,000
RF 22	9/15	Houston	S-SE	Yes	0.45-0.55	300-8,000

872

PP = Power Plant

873

BB = Biomass Burning

874

875 **Table 2.** Summary of CCNc operation characteristics. Refer to explanation of “Flight
876 Category” in text.

Flight	IPC On?	Flow- Restrictor Present?	Flight Category	ΔT variance [°C]	Q_{sh} variance [cc min⁻¹]	P variance [mbar]	SS variance [%]
RF 4	No	No	2	0.50	19.4128	1.226	0.064
RF 5	No	Yes	2	0.34	5.90161	1.657	0.052
RF 6	No	Yes	2	0.06	4.71778	1.735	0.008
RF 7	No	No	1	0.73	19.6443	1.068	0.095
RF 9	No	Yes	2	0.76	3.51723	1.003	0.087
RF 10	Yes	Yes	4	0.01	5.46324	1.906	0.003
RF 11	Yes	Yes	3	0.01	5.44902	0.201	0.002
RF 12	Yes	Yes	4	0.01	5.06662	1.669	0.002
RF 13	Yes	Yes	4	0.01	5.61638	0.263	0.003
RF 14	Yes	Yes	4	0.01	5.15539	1.639	0.003
RF 15	Yes	Yes	4	0.01	4.43912	1.800	0.003
RF 16	Yes	Yes	3	0.01	5.55128	0.909	0.003
RF 17	Yes	Yes	3	0.01	4.88951	1.040	0.004
RF 19	Yes	Yes	4	0.01	4.84348	1.514	0.003
RF 20	Yes	Yes	4	0.01	4.94734	2.042	0.003
RF 21	Yes	Yes	4	0.01	4.07664	1.886	0.003
RF 22	Yes	Yes	4	0.01	4.31556	1.600	0.003

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878

879 **Figure Captions**

880 **Figure 1.** (a) Flight tracks for the Twin Otter research flights (RF) during which CCN
881 measurements were available. (b) Photograph of the Twin Otter (with the main inlet and
882 CVI inlet indicated), over a photograph of the industries along the Houston Ship Channel.

883 **Figure 2.** CCNc operating conditions (pressure, temperature and supersaturation) for four
884 representative flights.

885 **Figure 3.** 1Hz CCN observations obtained during this study plotted as a (a) function of
886 ambient pressure and time (exposed to a range of supersaturations, from 0.3% to 1.0%),
887 and, (b) supersaturation range histogram. Total CCN are plotted as the solid black line.

888 **Figure 4.** CCN closure for all flights, assuming pure ammonium sulfate aerosol. The
889 thick solid line shows the 1:1 relationship, and the grey bands indicate over- and under-
890 prediction by factors of 2-4. Symbols are colored with respect to research flight number
891 (top panel, a), and instrument supersaturation (lower panel, b). The dashed line in the
892 lower panel shows the best fit relationship with the given equation.

893 **Figure 5.** CCN closure for select flights, using bulk particle composition from the C-
894 ToF-AMS. Symbols indicate the particle composition assumption in the CCN
895 concentration calculation; black “+” symbols correspond to pure ammonium sulfate,
896 colored points assume an internal mixture of sulfate and insoluble organic with 1.4 g cm^{-3}
897 density and surface tension of pure water, grey “+” symbols indicate the same
898 assumptions about organic mass and also a 15 mN m^{-1} reduction in surface tension.
899 Symbols are colored by flight number (top panel, a), and instrument supersaturation
900 (lower panel, b). The dashed line in the lower panel gives the linear best fit slope (with
901 zero offset) assuming ammonium sulfate for all flights, while the red solid line gives the
902 linear best fit slope (with zero offset) assuming an internal mixture based on the bulk
903 composition for the flights listed in 5a.

904 **Figure 6.** Flight track for RF7. Aircraft position colored by (a) flight time; sections with
905 particle concentrations (with diameter larger than 10nm) greater than $10,000 \text{ cm}^{-3}$ are
906 shown in greyscale, and, (b) aerosol organic volume fraction (calculated as explained in
907 the text). Map scale is approximately 50 miles across.

908 **Figure 7.** Time-series for RF7 of measured and predicted CCN concentrations, particle
 909 concentrations with $d_p > 10\text{nm}$, ambient pressure and AMS measured mass loadings of
 910 sulfate, organic, nitrate and ammonium ions. At the top are image plots of dry particle
 911 diameter (d_p) and droplet diameter (D_p) size distributions, colored by the bin-normalized
 912 concentrations (colorbar not shown). The CCNc supersaturation is plotted as bars. Blue
 913 and pink shaded areas depict regions of interest, as described in the text. Results shown
 914 for the whole flight (top panel, a), and, for data collected between 2:55 PM and 3:23 PM
 915 (bottom panel, b)

916 **Figure 8.** CCN closure for RF7 with different assumptions about particle chemistry.
 917 Colors represent the CCNc supersaturation and marker size reflects the ambient particle
 918 concentrations. Vertical error bars are based on a supersaturation uncertainty of 20%.
 919 Dashed lines indicate under- and over-prediction by 100%.

920 **Figure 9.** Flight track for RF22. Aircraft position colored by (a) flight time, with line
 921 thickness proportional to the ambient pressure (lower altitude legs have a thicker line);
 922 sections when particle concentrations (with diameter larger than 10nm) are greater than
 923 $10,000\text{ cm}^{-3}$ are shown in grayscale, and, (b) organic volume fraction, calculated as
 924 described in the text. Map scale is approximately 50 miles across.

925 **Figure 10.** Time-series for RF22 of measured and predicted CCN concentrations,
 926 particle concentrations with $d_p > 10\text{ nm}$, ambient pressure and AMS measured mass
 927 loadings of sulfate, organic, nitrate and ammonium ions. Also shown is the soot mass
 928 estimated from the photoacoustic absorption measurements. At the top are image plots of
 929 dry particle diameter (d_p) and droplet diameter (D_p) size distributions, colored by the bin-
 930 normalized concentrations (colorbar not shown). The CCNc supersaturation is plotted as
 931 bars. Vertical gray bars indicate time periods when the counterflow virtual impactor was
 932 turned on.

933 **Figure 11.** Particle size distribution (red bars) during a period of very high CCN
 934 overprediction on RF22 (at 16:10-16:18 UTC). Soot size distribution (blue bars)
 935 assuming a lognormal distribution with mean diameter of 65 nm, with particle number
 936 concentration constrained using estimated soot mass concentrations from photoacoustic
 937 absorption measurements. Vertical solid line indicates the smallest particle size expected

938 to activate, d_{50} , given the assumptions of internally-mixed aerosol composition. The
939 horizontal error bar shows the effect of a 10% supersaturation uncertainty on d_{50} under
940 the same assumptions.

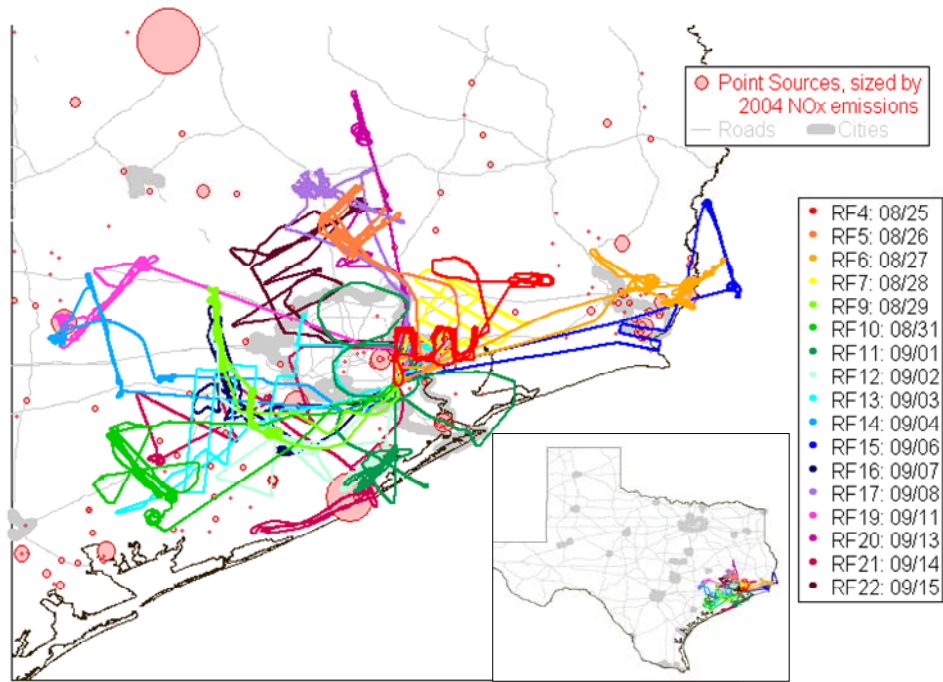
941 **Figure 12.** Size-resolved chemical composition measured by the C-TOF-AMS during
942 RF 22, a) at 16:14-16:18 UTC (160% CCN overprediction), and b) at 16:47-16:50 UTC
943 (76% CCN overprediction). $dM/d\log D_{va}$ is the observed mass for each size bin
944 normalized by the bin width (in log-space) of vacuum aerodynamic diameter.

945 **Figure 13.** CCN closure for RF22 with different assumptions for particle composition.
946 Higher organic volume fractions (represented by redder markers) are correlated with
947 higher CCN and particle concentrations. Vertical error bars are based on a
948 supersaturation uncertainty of 10%. Dashed lines indicate under- and over-prediction by
949 100%.

950 **Figure 14.** Average droplet diameter at the exit of the CCNc as a function of the
951 instrument supersaturation for all ambient CCN measurements during the campaign. The
952 gray shaded area indicates one standard deviation of the calibrations with ammonium
953 sulfate aerosol.

954

955 **Figure 1.**
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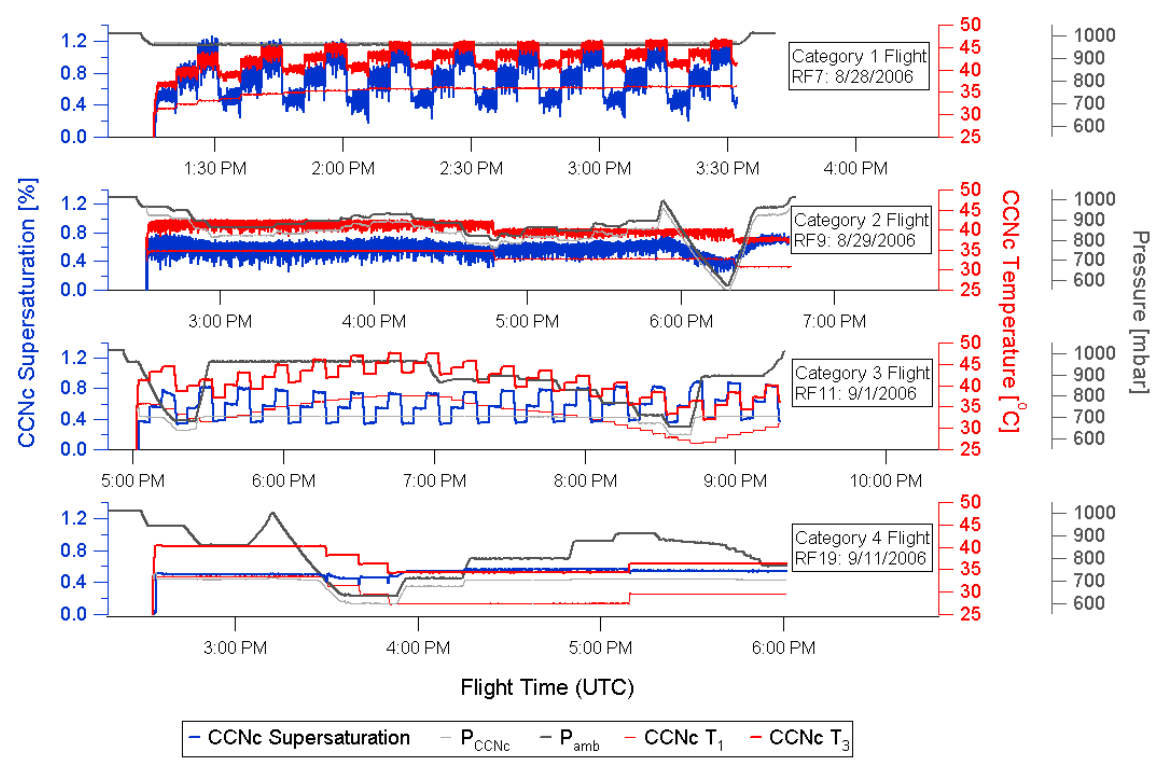
(a)



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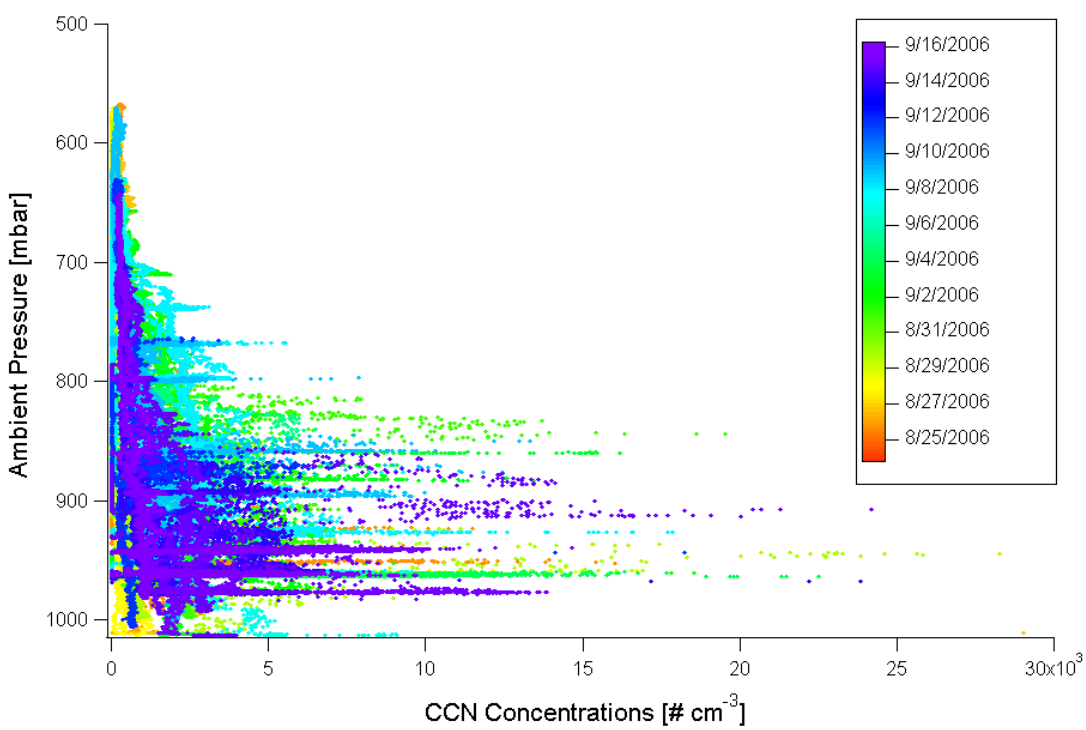
(b)

964 **Figure 2.**
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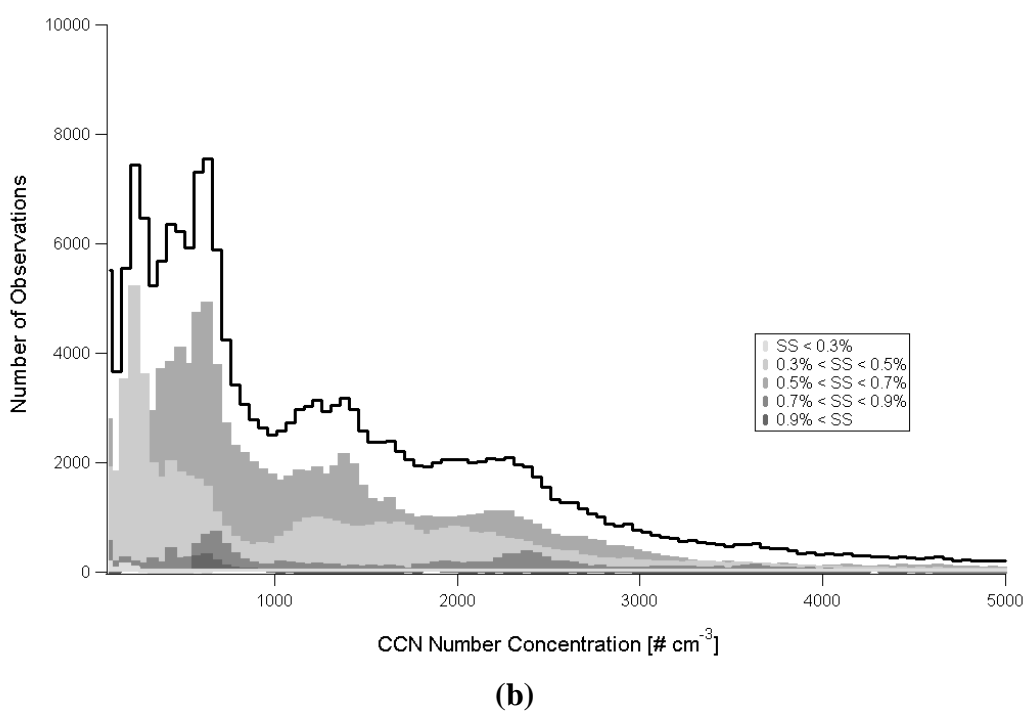


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967 **Figure 3.**
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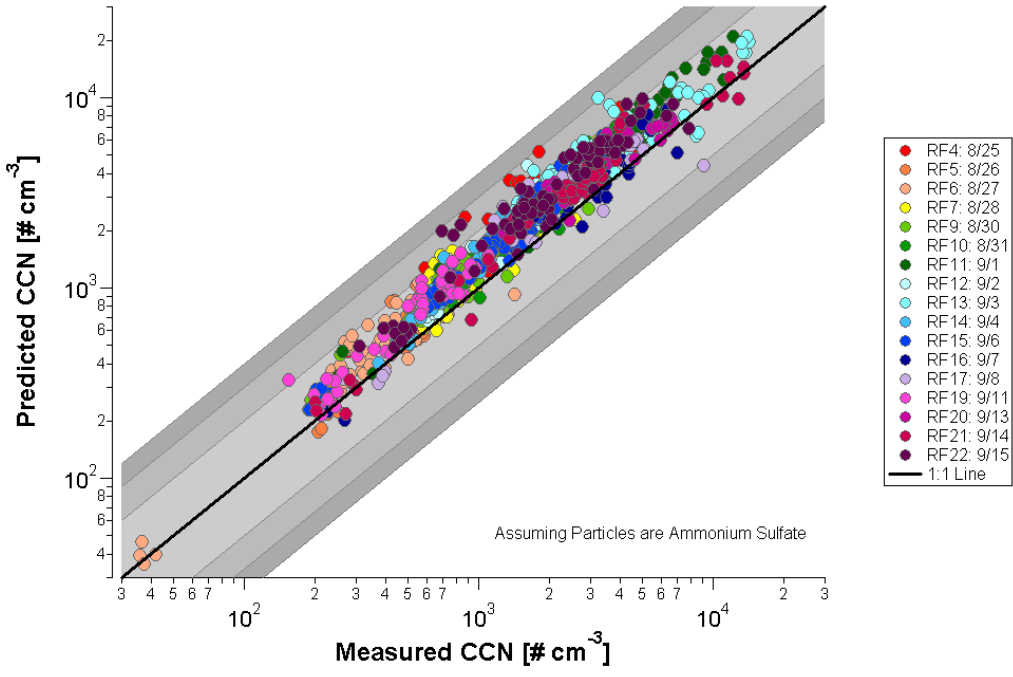


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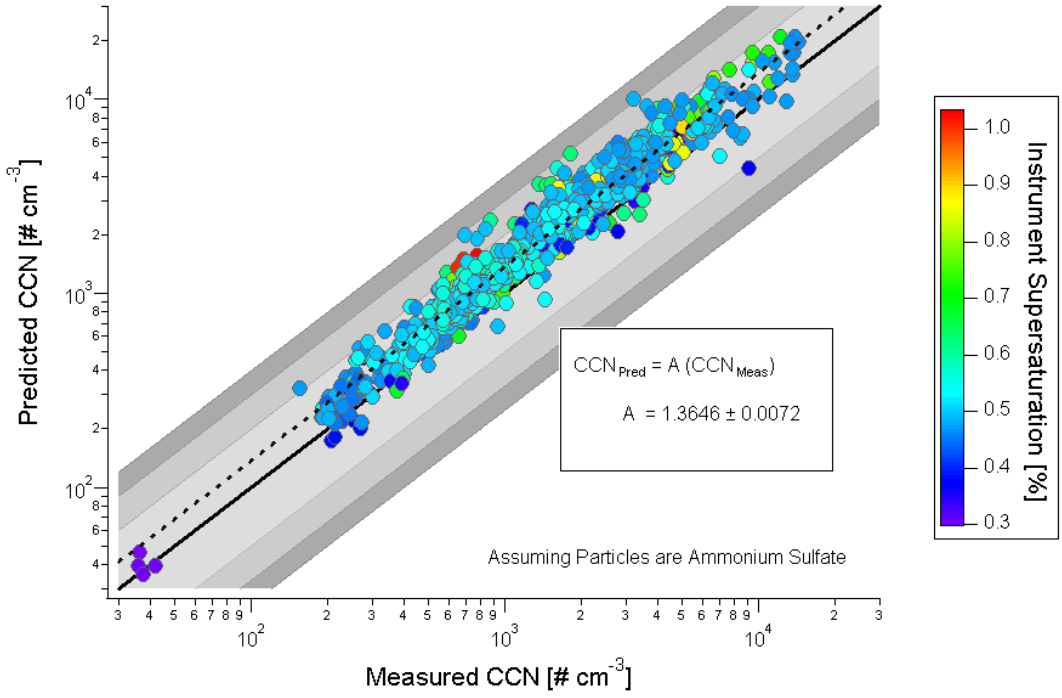
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975 **Figure 4.**
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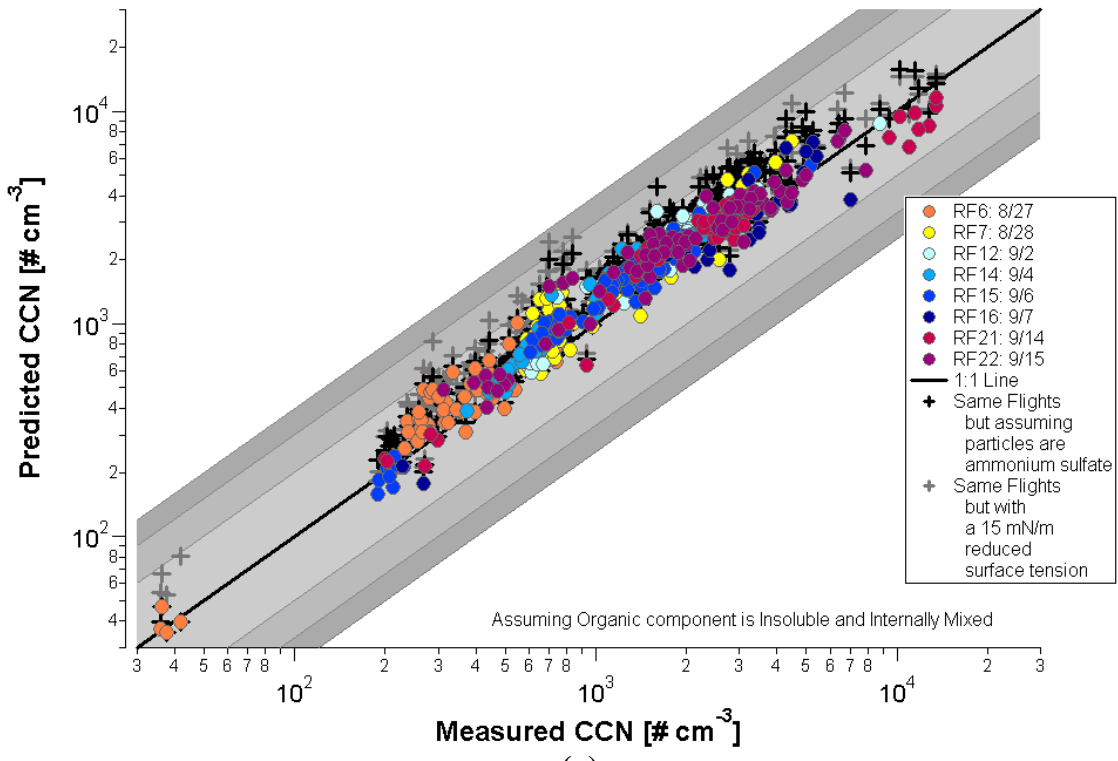
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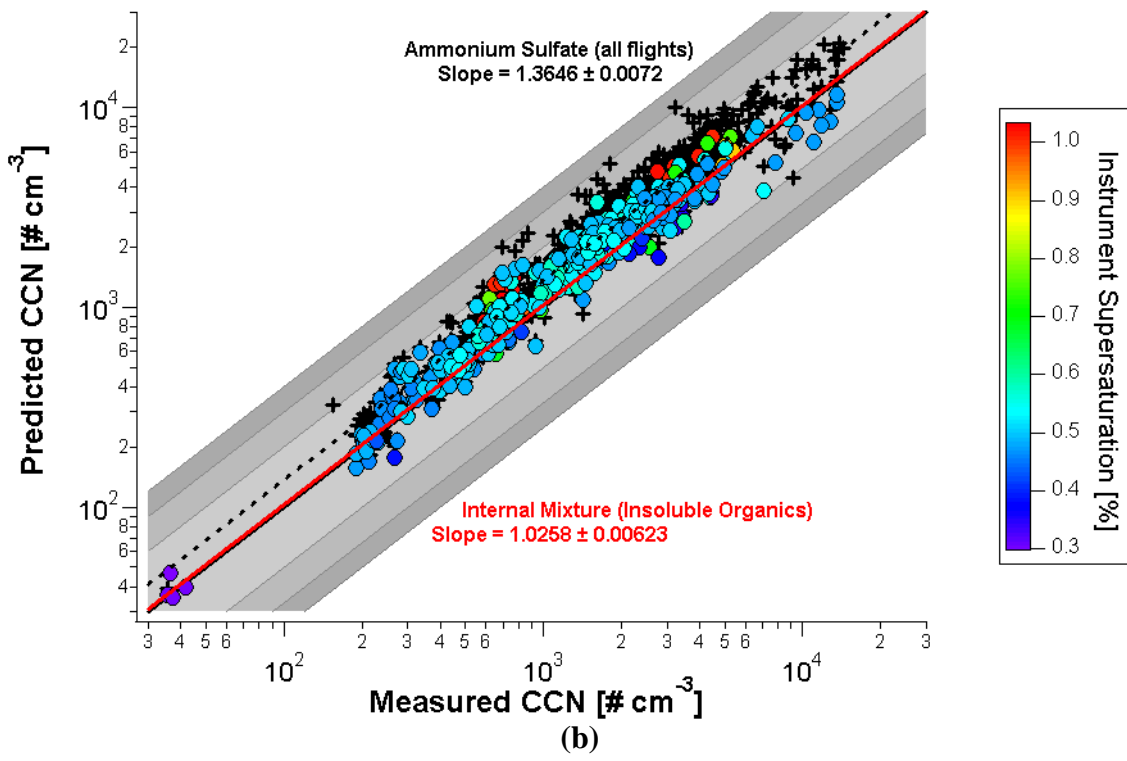
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986 **Figure 5.**
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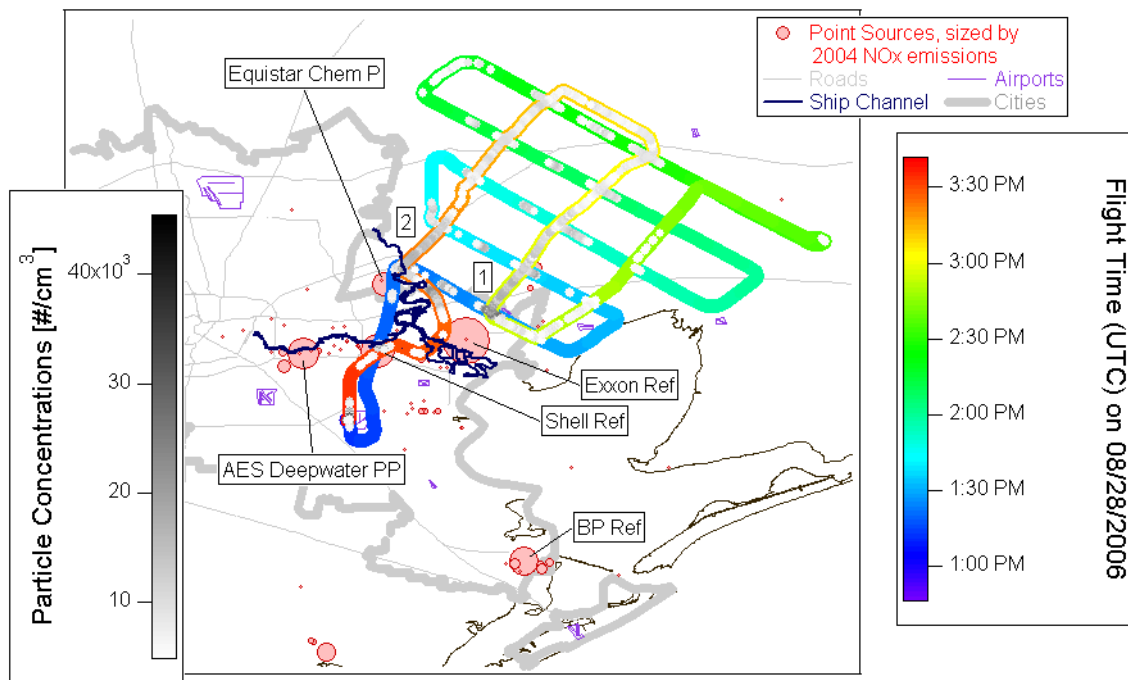


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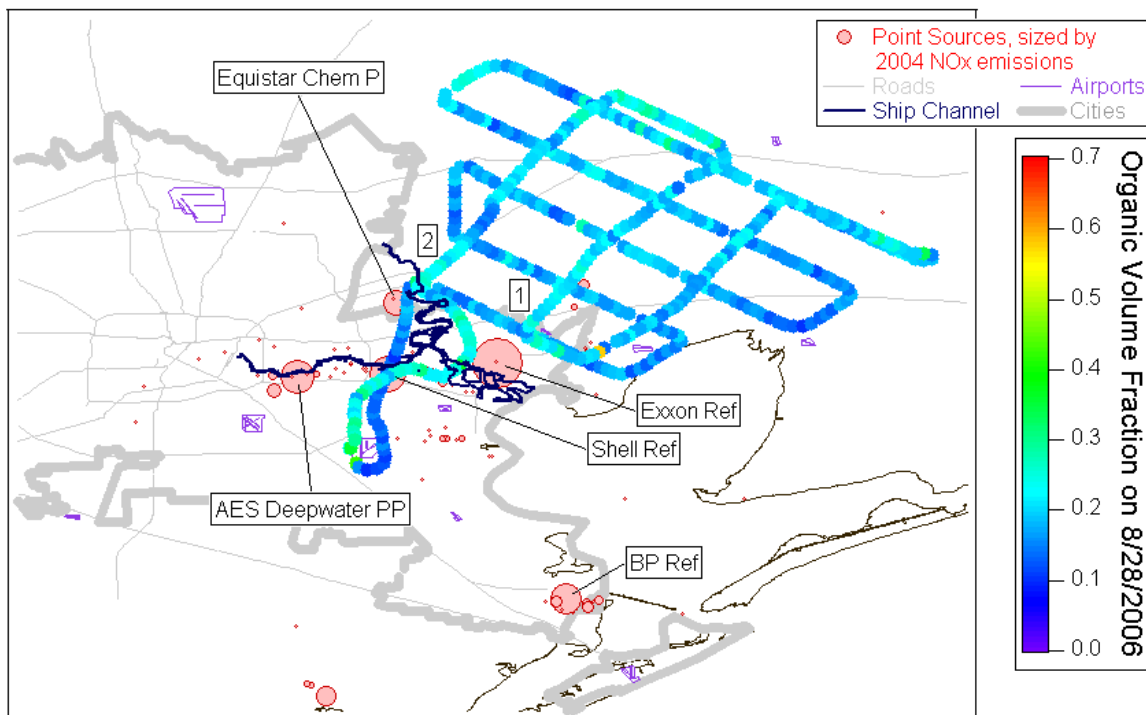
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994 **Figure 6.**



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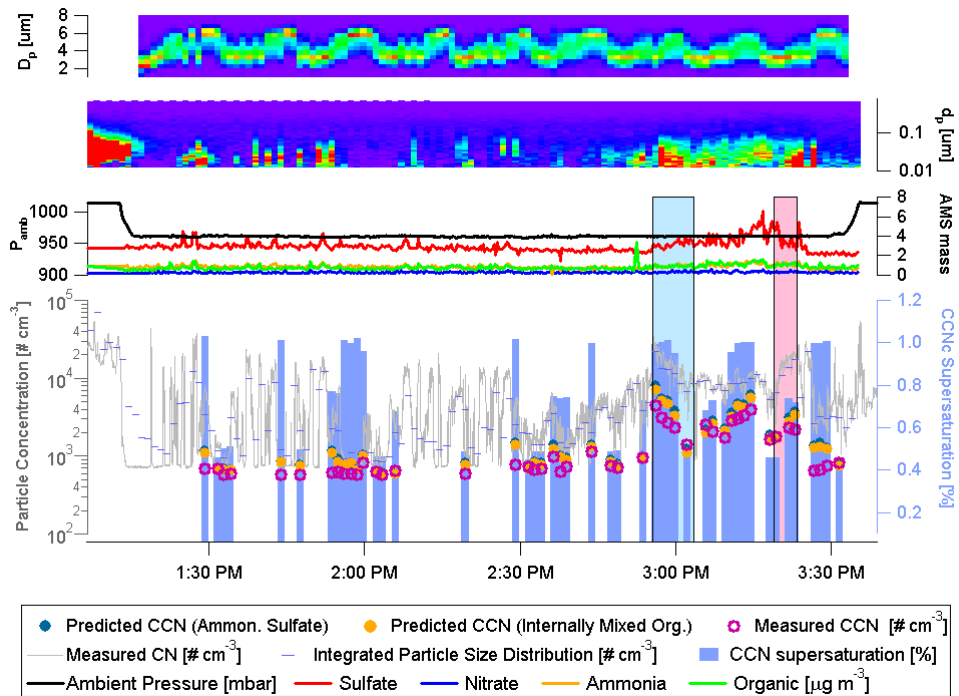
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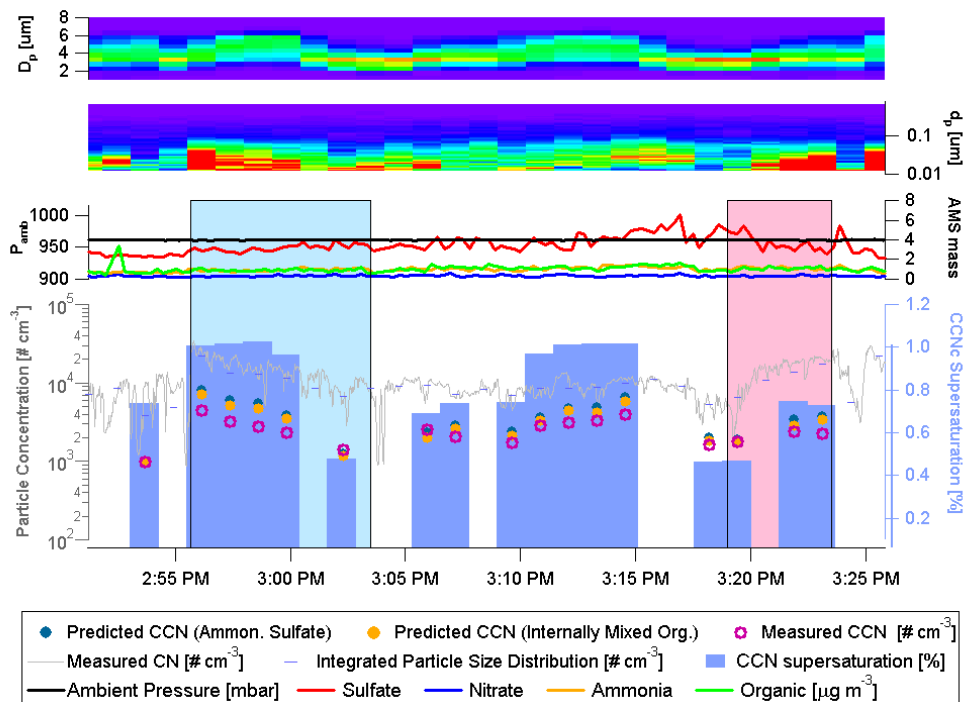
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(b)

1000 **Figure 7.**
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(a)

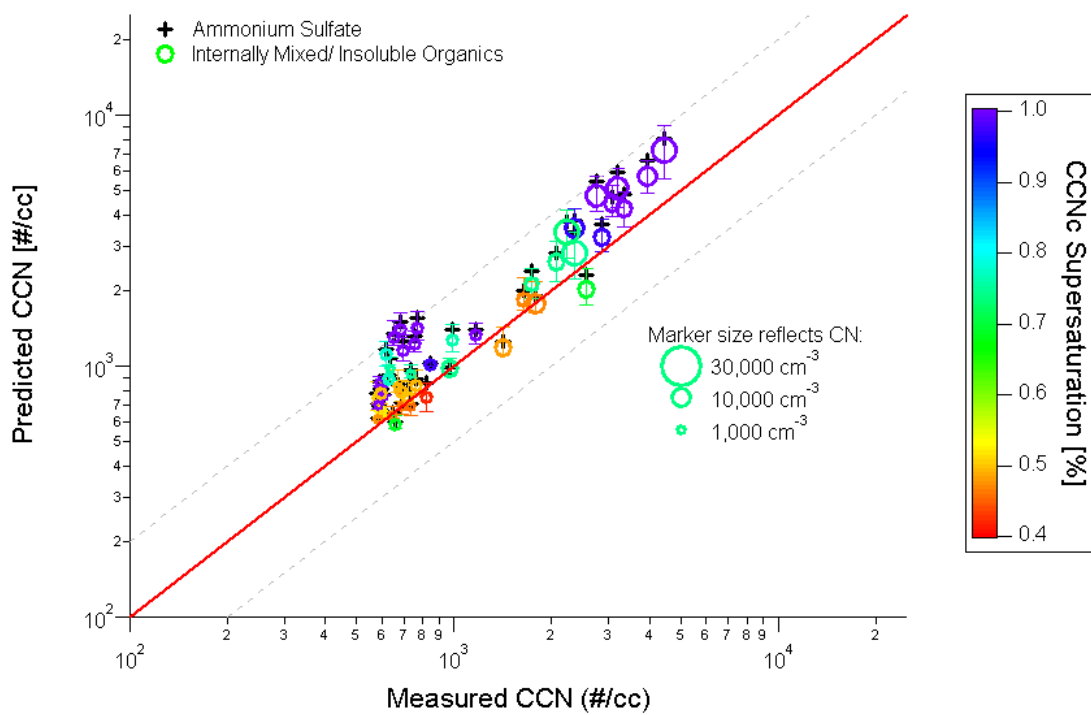


(b)

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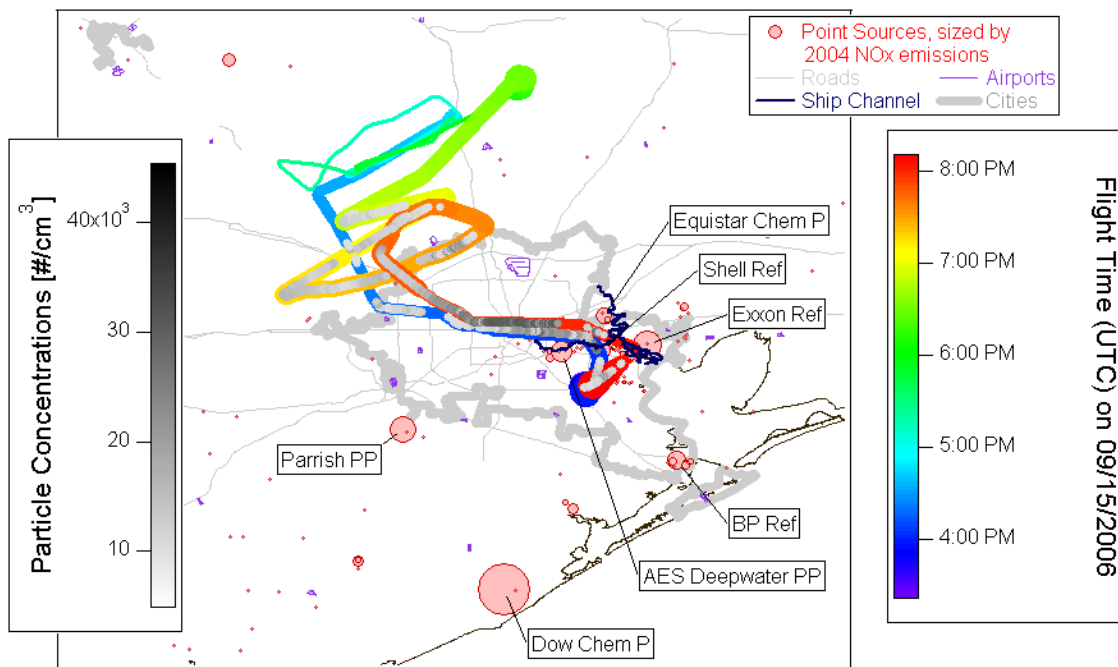
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1009 **Figure 8.**
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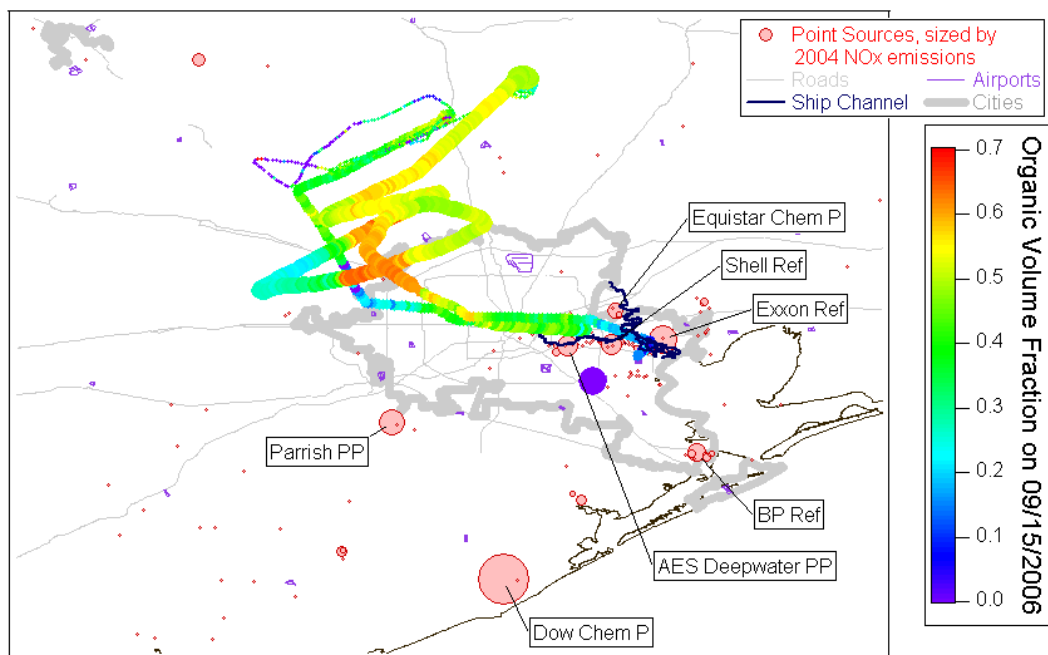
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1013 **Figure 9.**
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(a)

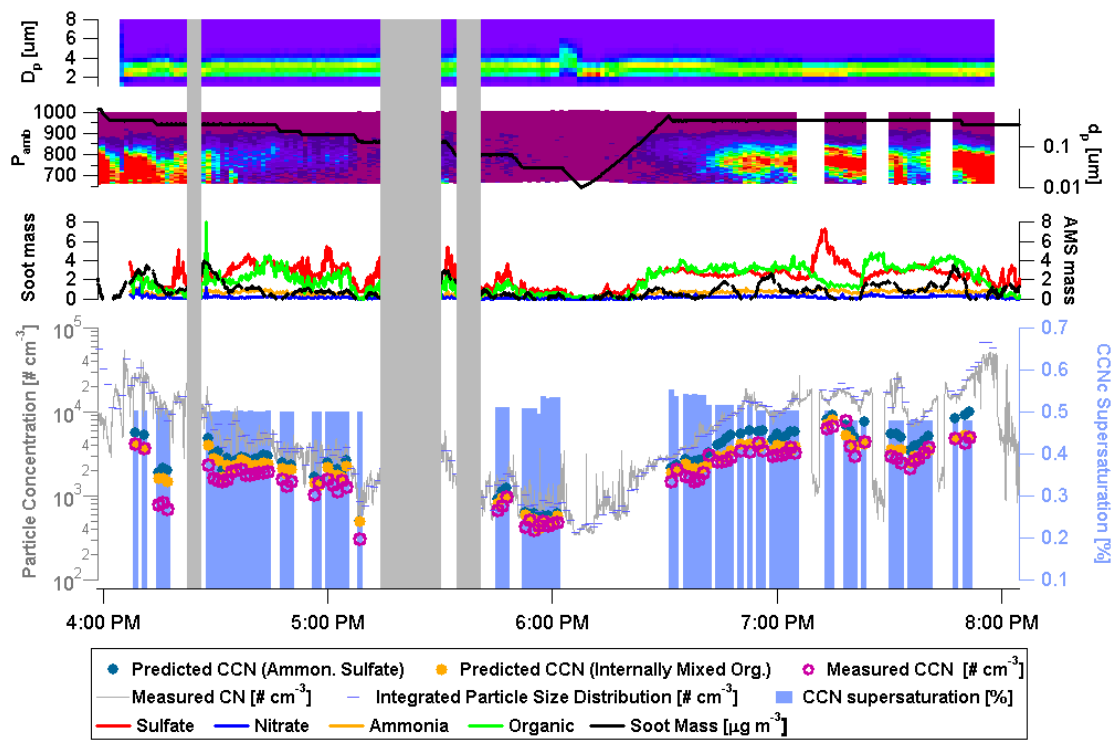
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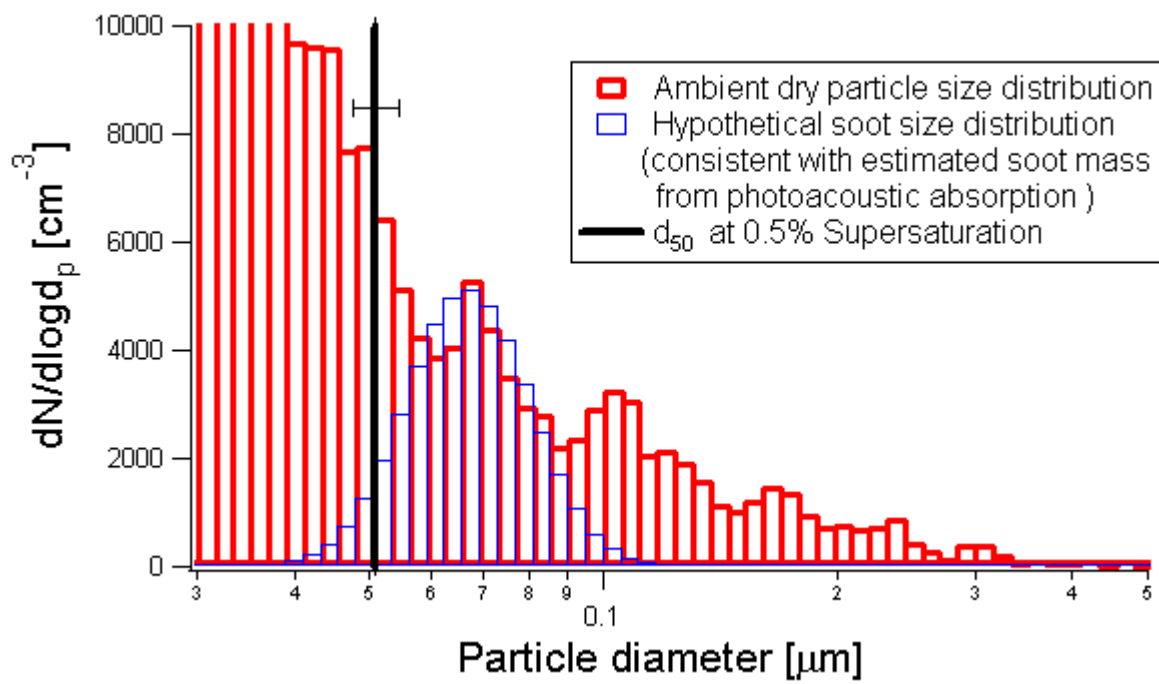
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1021 **Figure 10.**



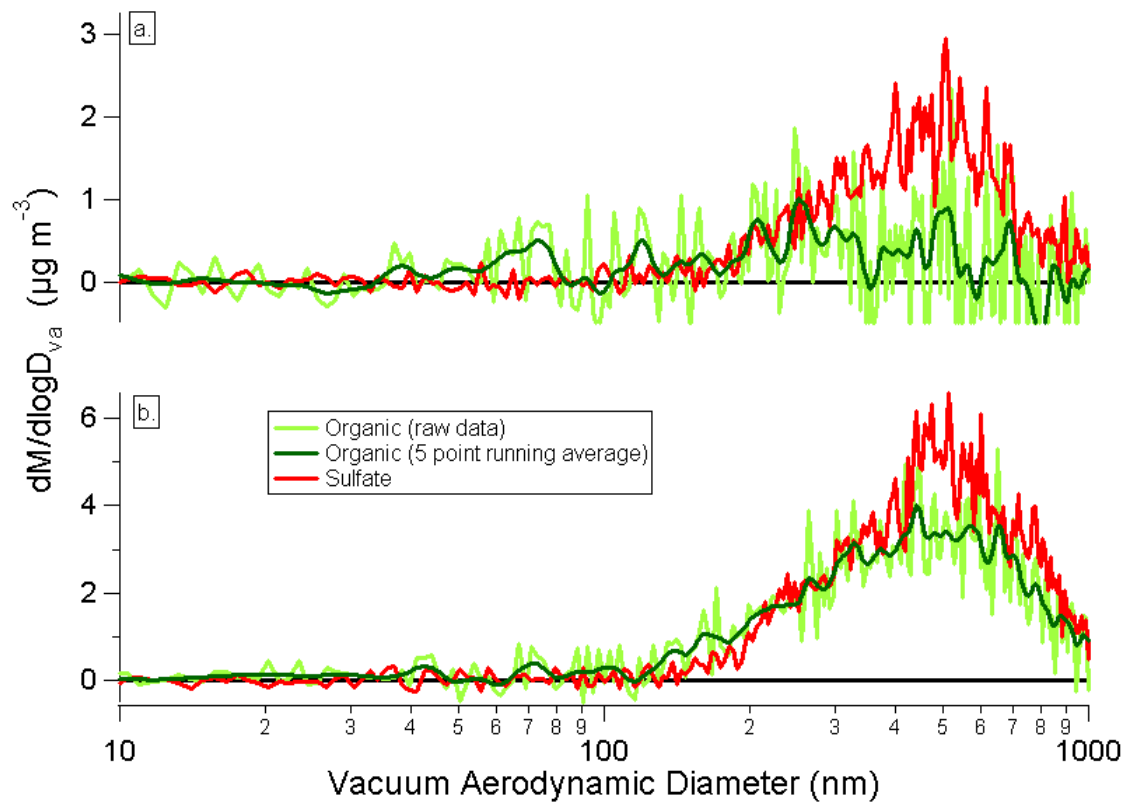
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1023 **Figure 11.**
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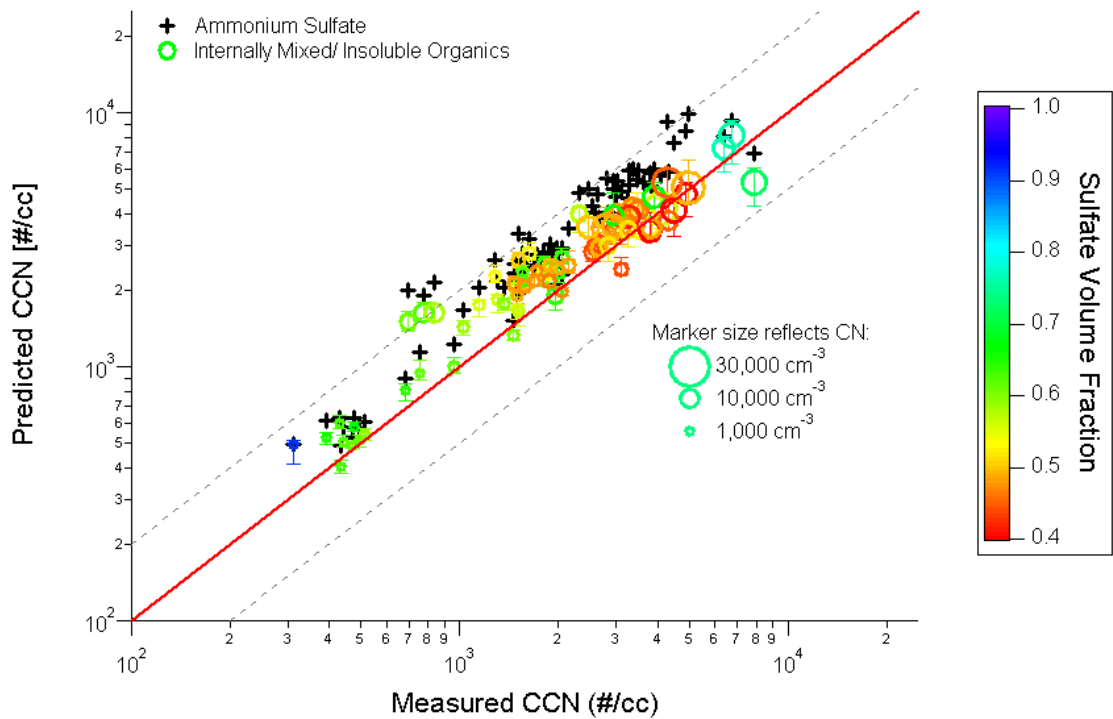
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1027 **Figure 12.**
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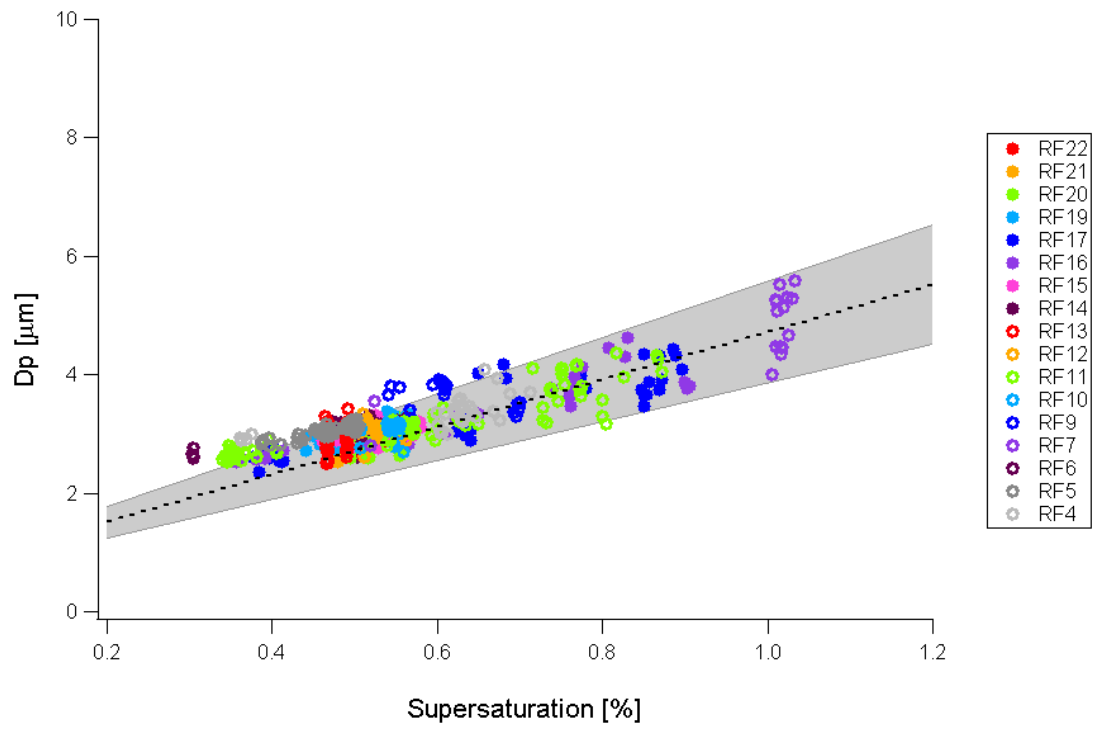


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1030 **Figure 13.**
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1033 **Figure 14.**

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