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Atmospheric Measurement Techniques Discussions

External and Internal CCN Mixtures: Controlled Laboratory Studies of Varying Mixing States.

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Abstract

Particle mixing states modify CCN activity. A method of cloud condensation nuclei (CCN) data analysis for multicomponent mixtures of varying mixing states and its relationship to activation curves consisting of one or more activation points is presented. Simplified two component systems of varying solubility were generated under internal, external, and transitional mixing conditions. κ-Köhler theory predictions were calculated for different organic and inorganic mixtures and compared to experimentally derived kappa values and respective mixing states. This work

employs novel experimental methods to provide information on the shifts in CCN activation data due to external to internal particle mixing from controlled laboratory sources. Results show that activation curves consisting of single and double activation points are consistent with internal and external mixtures, respectively. In addition, the height of the plateau at the activation points are reflective of the externally mixed concentration in the mixture. The presence of a plateau indicates that CCN activation curves consisting of multiple inflection points are externally mixed aerosols of varying water-uptake properties. The plateau disappears when mixing is promoted in the flow tube. At the end of the flow tube experiment, the aerosol are internally mixed and the CCN activated fraction data can be fit with a single sigmoidal curve. The technique to mimic external to internally mixed aerosol is applied to non-hygroscopic carbonaceous aerosol with organic and inorganic components. To our knowledge, this work is the first to show controlled CCN activation of mixed non-hygroscopic black carbon with hygroscopic material as the aerosol population transitions from external to internally mixed. Results confirm that CCN activation analysis methods are robust and may be used to infer the mixing state of complex aerosol compositions of unknown origin.

1. Introduction

Atmospheric cloud condensation nuclei (CCN) are comprised of complex mixtures of organic and inorganic compounds. The chemical and physical diversity present in these complex mixtures can significantly complicate the quantification of aerosol-cloud interactions, thereby making it difficult to predict CCN activity. However, knowledge of the mixing state and the chemical composition can greatly improve CCN predictions and has been the focus of several studies (Abbatt et al., 2005; Bilde at al., 2004; Henning et al., 2005; Liu et al., 2013; Padró et al., 2012; Svenningsson et al., 2006).

It is well accepted that the water content and the point of activation is dependent on more factors than just the supersaturation and dry diameter for CCN active aerosols (Dusek et al., 2006; Petters and Kreidenweis, 2007). The droplet growth and activation of slightly soluble inorganics can be modified when internally mixed with inorganic salts that readily deliquesce (Cruz et al., 1998; Padró et al., 2002; Svenningsson et al., 2006). Although inorganic salts are well characterized, the quantification of CCN activity is complicated when they are internally mixed with a complex organic. Consequently, simple mixing rules may no longer be appropriate. It has been observed that mixed aerosols can activate at lower supersaturations than their bulk constituents and organic compounds that may not

traditionally be considered as water soluble may aid in the formation of a cloud droplet by acting as a surfactant, depressing surface tension, or simply by contributing mass (Cruz et al., 1998; Padró et al., 2007; Svenningsson et al., 2006). In addition, when there is a sufficiently large enough fraction of salt, the slightly soluble core can dissolve before activation, thus lowering the required supersaturation (Sullivan et al., 2009). Thus, the mixing state and extent of mixing can substantially influence CCN activity.

To help minimize the complexity in characterizing aerosol hygroscopic and CCN activation properties, CCN data analysis has been simplified by assuming that the aerosols share a similar or uniform hygroscopicity over a particle size distribution, the CCN mobility diameter data sets consist of few doubly charged aerosols and all CCN active aerosols readily dissolve at activation. As a result, a singular sigmoidal fit is commonly applied over the entire CCN sample. However, this method of analysis may not be fully representative of the heterogeneous mixing state occasionally present in the aerosol sample.

Previous studies have addressed aerosols with singular or internally mixed binary chemical species (Bilde et al., 2004; Broekhuizen et al., 2004; Petters and Kreidenweis, 2007; Shulman et al., 1996; Sullivan et al., 2009). However, ambient measurements indicate complex aerosol populations consisting of both external and internal mixtures (Ervens et al., 2007; Lance et al., 2012; Padró et al, 2012). By accounting for the mixing states and extent of mixing in field data sets, CCN concentration predictions can be greatly improved (Padró et al., 2012; Wex et al., 2010). However, dynamic changes in particle mixing states and subsequent treatment of CCN measurement and analysis have not been readily observed and studied in depth.

In this work, we seek to improve the experimental CCN activation analysis techniques of complex mixtures by investigating the influence of mixing state on activation curves with known aerosol composition. Theoretical postulations have been explored and applied to ambient data sets (e.g., but not limited to, Bhattu et al., 2016; Padró et al., 2012) but never before has a systematic laboratory experiment controlled and modified the extent of particle heterogeneity for CCN activation. To understand the impact of mixing state on CCN activation, simplified two component mixtures of known compounds with varying hygroscopicities are created under internal, external, and in-between (transition) mixing conditions. In addition, black carbon (BC) and BC mixing state data is presented. BC is renown for its direct radiative effects yet little is known experimentally about the contributions of BC to aerosol-cloud interactions at varied mixing states. Here, the hygroscopic properties of black carbon mixed with atmospherically relevant constituents of varying hygroscopicity are investigated. This work provides evidence on the stark differences

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between inorganic, slightly soluble, and insoluble externally and internally mixed compositions for the uptake of water, and subsequent CCN activity.

2. Experimental Methods

2.1 Aerosol Composition and Sources

The CCN activity of two component aerosol mixtures under internal, external, and combinations of mixing states are explored in this study. The components include very hygroscopic (inorganics), hygroscopic (organic acids), and non-hygroscopic (Black Carbon, BC). For known chemical compositions, a Collison-type atomizer generated singular-component solutions of ammonium sulfate, ($(NH_4)_2SO_4$, Acros 99.5%), sodium chloride, (NaCl, Acros 99+%) and succinic acid ($C_4H_6O_4$, Acros 99%) and subsequent internal mixture combinations as described in the sections Aerosol Mixing States and Modified Mixing States: External to Internal. Succinic acid, classified as a slightly soluble dicarboxylic acid, (18) $(NH_4)_2SO_4$, and NaCl are all relevant model atmospheric compounds with varying degrees of solubility and hygroscopicity. All atomized solutions were prepared using Millipore© DI water (18 mΩ, TOC ≤ 5 ppb). Atomized wet droplets were dried with silica gel diffusion dryer (as commonly practiced). In addition, we employ a heated column before the diffusion dryer to facilitate the evaporation of water from the wet particles. The implications of the use or absence of a heated column are discussed in the results below.

An AVL Particle Generator (APG), which houses a mini Combustion Aerosol STandard soot generator (miniCAST 6203C, Jing ltd.), was used to generate carbonaceous aerosols. The APG consists of a propane burner followed by a volatile particle remover. The burner was operated at 400°C with a propane and air flow rate of 15 ml per min and 1.0 l per min, respectively. The aerosol structures generated by the APG likely consisted of fractal-like agglomerates of non-spherical particles (Durdina et al., 2016). APG Combustion aerosols are mixed with inorganic and slightly soluble succinic acid and CCN is subsequently measured at different supersaturations.

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104 **2.2 Aerosol Mixing Methods**

105 Mixing compounds in solution can readily form internal mixtures of aerosol. (Gibson et al., 2007; Hameri et al.,
106 2002) Internal solutions of a highly hygroscopic compound, NaCl, and a slightly hygroscopic compound, succinic
107 acid, are shown. Five aqueous solutions of succinic acid and NaCl with molar ratios of 100:0, 87:13, 69:31, 43:57,
108 0:100 were aerosolized using a single atomizer, passed through a heated column, dried, and sampled directly into a
109 Scanning Mobility Particle Sizer (SMPS) and CCN Counter (CCNC).

110 External mixtures were formed via two methods**.** The first and simplest method required two sufficiently dry
111 aerosol streams to mix. Two aerosol streams were joined via a Swagelok® Tee connector. External mixtures were
112 also formed in a flow tube mixing apparatus. As conditions (e.g., but not limited to, residence time, temperature,
113 pressure, relative humidity) change in a flow tube, it is assumed that the external mixture may transition into an
114 internally mixed aerosol system. A flow tube mixing apparatus was constructed to test this assumption and modify
115 the extent of mixing of multiple components (Fig. 1 & 2).

116

117

118 **Figure 1.** External and Internal Mixtures with gradual mixing in flow tube

119

120 This work discusses changes in CCN experimental data and analysis as a result of changes in the extent of
121 mixing. Results of the CCN activation are presented in the Section: Modified Mixing: External to Internal Mixing in
122 the Aerosol Flow Tube. A brief description of the flow tube is provided here. The first aerosol stream is introduced
123 into the flow tube by a ¼ inch stainless steel (SS) tube. The second aerosol stream is also introduced by a ¼ inch SS
124 tube, but is expanded to an outer concentric ¾ inch SS tube using a SS Swagelok tee connection. The two aerosol
125 flows are initially mixed together at the exit of ¼ inch tube and aerosol mixes within the ¾ inch SS tube for an
126 additional 12 inches before entering the quartz tube where it continues to mix. In this study, the pressure and
127 temperature of the flow tube is maintained at ambient conditions. The extent of mixing in the flow tube mixer has
128 been modeled by Computational Fluid Dynamics simulation (CFD - Comsol) to test and improve the aerosol mixing
129 capabilities of the flow tube mixer (Fig. A1). The focus of this work is not the mixing apparatus but the CCN behavior

that results from changes in the extent of mixing. It is noted that particle losses likely occur within the flow tube system but do not affect the intrinsic aerosol and CCN properties (activated fractions) presented here.

Figure 2. Example of charge corrected a) a single component activation curve b) a multiple activation curve from an externally mixed/heterogeneous system. The assymptote, η, varies in height and length with the presence of mixed components and their respective hygroscopicities.

2.3 CCN Activity and Chemical Composition: Measurements and Instrumentation

CCN activation is measured with particle sizing and counting instrumentation in parallel with CCN counting instrumentation. This technique is widespread and has been used in numerous publications (Moore et al., 2010; Padró et al., 2012). The development of a single continuous-flow thermal gradient diffusion column CCN Counter, CCNC (Droplet Measurement Technologies, Inc.) has provided rapid (~1 Hz) and robust CCN data (Lance et al., 2012; Roberts and Nenes, 2005). Aerosols with a S_c lower than the supersaturation in the column activate and form droplets. These droplets are detected and counted using an optical particle counter at the exit of the column.

A TSI 3080 Electrostatic Classifier selects and measures aerosol size distributions. Polydisperse aerosol streams are passed through a bi-polar krypton-85 charger and then through a differential mobility analyzer (DMA), where the aerosols are sized according to electrical mobility with a sheath to aerosol flow ratio of 10:1. The monodispersed flow is then split to a CPC and a CCN counter. CN concentrations were measured with a condensation particle counter, CPC (TSI 3772, TSI 3776).

The CCNC is operated at 0.5 lpm with a sheath to aerosol flow ratio of 10:1 and is calibrated with $(NH_4)_2SO_4$ to determine the instrument supersaturation (Rose et al., 2008). Operating the CCN in parallel with the CPC allows for the simultaneous measurements of the total CN and CCN of the monodispersed aerosols. By operating the DMA in scanning voltage mode and maintaining a constant column supersaturation, the CCN/CN, or activation ratio, as a function of dry diameter can be obtained for a given supersaturation. These size resolved CCN distributions obtained through scanning mobility CCN analysis (SMCA) are produce CCN activation curves, CCN/CN ratio as a function of particle mobility diameter (Moore et al., 2010). SMCA produces high resolution CCN activation data near the 50% efficiency critical diameter every ~ 2 minutes.

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An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) measured the non-refractory bulk composition (DeCarlo et al., 2006). The HR-ToF-AMS was operated in V-mode to track the concentration and vacuum aerodynamic diameter as the aerosol fractions were modified.

3. CCN Analytical Method

CCN data analysis of single component aerosols, such as AS, are well characterized. The activation of a single known component yields a simple sigmoidal activation curve and is often used for instrument calibration (Fig. 2a). However ambient aerosols generally exist as complex mixtures of organic and inorganic species. CCN data sets from ambient and chamber studies, which consist of these aerosol mixtures, may not show a single sigmoidal activation curve but instead can exhibit multiple activation curves not associated with doubly charged particles (Fig. 2b).

Sigmoidal fits are applied to the CCN/CN as a function of dry activation diameters for the multicomponent aerosols. Externally mixed aerosol fractions in activation curves have been previously observed in ambient studies by Lance et al. (2013), Moore et al. (2012), and Bougiatioti et al. (2011). For those studies, E was defined as the hygroscopic fraction, and 1-E the non-hygroscopic mixed fraction. For this study the first curve is similarly defined as the hygroscopic externally mixed fraction (EMF) with an asymptote, or plateau of η. The dependence of η varies with the presence of mixed components and their respective hygroscopicities. Thus we evaluate η for controlled compositions and compare how representative they are of the known fractions of mixtures.

A sigmoidal fit through the EMF determines the particle dry diameter of the more hygroscopic species. A second sigmoidal fit is applied to the second activation curve. An example is shown in Fig. 2b for an external mixture of AS and SA. A sigmoid is fit for the more hygroscopic species, AS, and then a second for the less hygroscopic species, SA. The activation diameters are consistent with those expected for the two compounds and agree with Köhler predicted activation values for AS and SA. Doubly charge aerosols are indicated in Figure 2 and are a negligible contribtion to the activation curves.

The supersaturation and critical dry diameter are related via with the single parameter hygroscopicity, $\boldsymbol{\kappa}$, to describe the CCN activity and to determine the effect of mixing states of multiple components on the supersaturated

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hygroscopic properties of aerosols. Using the generalized κ-Köhler equations presented by Petters and Kreidenweis (2007 and 2008), droplet growth in the supersaturated regimes for a selected dry diameter can be modeled for an aerosol where the entire particle diameter dissolves at activation.

$$lnS_c = \left(\frac{4A^3\rho_w M_s}{27v\rho_s M_w D_d^3}\right)^{1/2}, \quad where\ A = \frac{4\sigma_{s/a}M_w}{RT\rho_w} \qquad (1)$$

$$\kappa = \frac{4A^3}{27D_d^3 ln^2 S_c} \qquad (2)$$

$\sigma_{s/a}$ is the surface tension, M_w is the molecular weight of water, R the universal gas constant, T is the temperature at activation, and ρ_w is the density of water. Surface tension and density of water were calculated according to temperature dependent parameterizations presented by Seinfeld and Pandis (1998) and Pruppacher and Klett (1997). The surface tension of the solution is assumed to be that of pure water. Traditional Köhler theory is known to work reasonably well for inorganic salts and slightly-soluble and hygroscopic organics like succinic acid.

4. Results and Discussion

4.1 Internal Mixtures

Aerosolized internally mixed solutions exhibit single CCN activation curves for all five compositions of succinic acid and NaCl solutions (Fig. 3a). The activation curve is similar to that of ammonium sulfate in Figure 2a. Multiply charged particles contribute less than 10% to the activated fraction and are assumed to be negligible. One sigmoid that plateaus near one can be applied to describe the CCN activation. As the internal mixture salt fraction increased at a given supersaturation, the single curve was maintained and shifted towards a lower activation diameter, indicative of and consistent with more hygroscopic aerosol. Using the simple mixing rule, a multicomponent hygroscopicity parameter can be theoretically derived based on the expected kappa values for each individual component hygroscopicity ($\boldsymbol{\kappa_i}$), and the volume fraction of each component (ε_i) (Petters and Kreidenweis (2007).

$$\boldsymbol{\kappa} = \sum_i \boldsymbol{\varepsilon_i \kappa_i} \qquad (3)$$

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Equation (3) was applied for each mixture. $\boldsymbol{\kappa}$ was calculated and compared to the experimental values (Fig. 3b). These internal mixtures do not strongly follow the simple mixing rule for every mixture and is consistent with the previous work of Shulman et al. (1996) and Padró et al. (2007) who showed that slightly soluble compounds internally mixed with salts resulted in surface tension depression and thus a lower required critical supersaturation. As previously published, accounting for organic surface tension depression could improve kappa-hygroscopicity calculations for internal mixtures. Regardless of prediction, the single sigmoidal experimental data set is indicative of a single component or homogeneous internally mixed aerosol population.

Figure 3. a) Activation curves for two component internal mixtures of NaCl and succinic acid (SA) at SS 0.72%. Doubly charged aerosols are present but are all below 0.1 and negligible. **b)** Internally mixed aerosols. Multicomponent hygroscopicity parameter predictions vs. experimentally derived kappa values. Dashed lines indicate 20% uncertainty.

4.2 External to Internal Aerosol Mixing Results

Individual single component aqueous solutions of ammonium sulfate (AS), $(NH_4)_2SO_4$, and succinic acid (SA) were aerosolized, dried with an active heated column and silica gel diffusion dryer to produce external mixtures. Data sets yielding multiple activation curves consistent with external mixing were successfully created by *i)* mixing aerosol streams and *ii)* injecting SA and AS-compounds in the flow tube. For this manuscript, we show externally mixed data generated from the use of the mixing flow tube. The direct mixing produces the same external mixed CCN results (not shown). By using aerosols consisting of compounds of significantly different hygroscopicities, and thus different activation diameters, distinct double plateaus for CCN activation can be observed for external mixtures (Fig. 2b). At particle mobility diameters between ~35 and 45 nm there is an asymptote, $\eta \sim 0.6$ (Fig. 4a., 4b., and 4c). The activation curves were characteristic of AS and SA, and the measured activation diameters agreed well with Köhler Theory and the single parameter (κ) thermodynamic predictions of droplet activation (Fig. 4a). The external mixture was maintained for an hour as indicated by the separate and stable activation diameters derived from multiple sigmoid analysis.

Figure 4. External to internal mixtures of a slightly soluble organic aerosol, succinic acid (SA) and inorganic ammonium sulfate (AS) aerosol. The CCNC was operated at a single S_c of 0.8%. Closed symbols are externally mixed. Open symbols are internally mixed. a) The apparent kappa values derived from externally mixed multiple-sigmoid activation data before active heating is turned off at approximately 3:30 pm and after 3:30pm where single sigmoid activation curves are observed. The two dotted lines indicate the theoretically derived kappa values for succinic acid, κ=0.23, and ammonium sulfate, κ=0.61. b) CCN activation curves exhibit external (with active heating before 3:30 pm) and then transitioning external to internal mixing (after 3:30pm) c) CCN/CN vs. Dry mobility diameter data as a function of time. The asymptote, η, disappears at the by the end of the experiment.

After one hour in the flow tube, the active heating column was turned off. It should be noted that atomized aerosol continued to be dried through the silica gel diffusion dryers, as is commonly done. The relative humidity after the dryer in both cases is small (< 20%) and thus the activation diameters of very hygroscopic AS calibration aerosol are not affected with or without active heating (Fig. A2). However, as soon as active heating was turned off, particles in the mixing flow tube became more mixed (Figure 4). Thus, it is likely that minute amounts of aerosol water promoted internal mixing and shifted aerosol mixing from external to internal in the mixing flow tube system.

CCN activation curves for the two compounds remained distinct and separate until internal mixing conditions dominated and the multiple CCN activation curves converged into a single curve (Fig. 4b and 4c). Results suggest aerosol water plays a significant factor in mixing and CCN activation. This is consistent with previous work that indicates that the presence of water led to lowered aerosol viscosity and increased diffusivity (Ye et al., 2016). The wetted aerosols can come in contact through diffusion and coalesce to form an internally mixed aerosol. The apparent kappa values from fitting the two individual activation curves for the external part of the mixing experiment and subsequent internal mixing are shown in Fig. 4a.

To help track the change in organic/inorganic fractions during the transition from external to internal, the mixed aerosols were analyzed with a high-resolution time of flight mass spectrometer (HR-Tof-AMS) to provide mass fraction information. The mass size distribution was integrated and normalized for each compound per scan according to the total mass that was measured. The mass size distribution was then converted to number size distribution and the

diameters were converted from aerodynamic diameter to electrical mobility diameter. Then for each superstation and fraction, the EMF was calculated between the two respective activation diameters and correlated to the EMF that was determined from SMCA to determine the plateau height (η).

AS fractions measured by the AMS are consistent with the changes SMCA derived η where increases in AS mass fraction increase η. However, the AMS derived AS fraction are slightly lower compared to SMCA (Figure 5), indicating potential influence on η from other factors. Previous work has shown the presence of highly soluble materials (like AS) can promote CCN activity of organic dominated systems (Asa-Awuku et al., 2011; Fofie et al., 2017). A second flow tube experiment was conducted to test the effect of differing concentrations on plateau heights. The detection efficiency for particles with smaller sizes in the AMS (<50nm) can effect the AS fraction. Thus, the CCNC supersaturation was modified from 0.2 to 1.2% to test the effect of activation diameter on closure (Fig. 6.). Results show good agreement and are within 20% of predictions. Results utilizing CCN activation data for aerosols <50nm may be a good substitute for estimating aerosol chemical fractions when other instruments with lower size resolution are not readily available.

Figure 5. Plateau heights derived from AMS data vs. SMCA. Single CCNC Supersaturation

Figure 6. Modifying activation diameters. Plateau heights derived from AMS data vs. SMCA for CCNC Supersaturation from 0.2 to 1.2%

4.3 External and Internal Mixtures of Combustion Aerosol

Combustion Aerosol, hereon also referred to as Black Carbon (BC) can form external and internal complex aerosol mixtures. BC is considered insoluble but wettable and the contributions of BC to aerosol-cloud interactions at varied mixing states is not well known or understood. Thus the ability of BC to mix with inorganic and organic compounds and observe the extent of mixing as they activate as CCN is of great interest.

286 Prior to investigating the impact of mixing fresh combustion emissions with inorganic and organic aerosols, the
287 CCN activation spectra of combustion was defined using combustion aerosol derived from the APG.
288 CCN activated fraction data from combustion aerosol was fit to a singular sigmoidal curve (Fig. 7). The
289 single sigmoid fit suggests that the aerosol generated is a homogenous mixture of black and brown carbon. Combustion
290 aerosol activated at a mobility diameter of 133 nm at 2.2% supersaturation. The apparent hygroscopicity of combustion
291 aerosol was κ=0.001, and is consistent with the order of magnitude and kappa values reported for fresh combustion
292 aerosol from diesel engine sources (Fig. 7) (Vu et al., 2015). It is noted that the apparent hygroscopicity does not
293 account for non-spherical fractal particles.
294
295
296 **Figure 7.** Combustion aerosol activation curve (SS 2.2%, $d_{p,50}$=133nm, $\boldsymbol{\kappa}$=0.001)
297
298 Next, the influence of modifying externally mixed hygroscopic aerosol fractions with non-hygroscopic BC was
299 observed. BC was externally mixed with various concentrations of AS and NaCl in two separate experiments. For
300 each BC mixture, combustion aerosol was introduced to the flow tube and atomized inorganic and organic aerosol
301 (dried with a heated column and silica gel diffusion dryers) was injected. The concentration of inorganic in the flow
302 tube was slowly increased to modify the contribution of soluble material. The CCN counter supersaturation was
303 decreased to 1.1% to observe the impact of the more hygroscopic compounds in the BC mixture.
304
305 Figure 8 shows the CCN activation of external mixtures of BC with AS and NaCl at S_c = 1.1%. The initial
306 combustion size distribution at the start of the experiment and the modified CCN activation fractions of the aerosol
307 mixtures are presented. The shape of the activation curve provides insight about the sizes of very hygroscopic and
308 non-hygroscopic species. At S_c = 1.1% BC particles, with κ = 0.001, will not theoretically activate below 250 nm and
309 the contribution of externally mixed BC in the size range shown does not contribute much (if any) CCN. The
310 normalized size distribution data show that there are few BC particles at small sizes (<50 nm), the majority of particles
311 in this range are inorganic. Thus for both the AS and NaCl external mixtures, the activation diameters derived from a
312 singular fit were consistent with the expected dp_{50} < 50 nm of the respective inorganic salts. At the larger sizes (>
313 inorganic d_{p50}), the BC concentration increased and the CCN/CN was depressed. The combustion aerosol alone is not

314 CCN active at this S_c or size and the depressions are reflective of the non-hygroscopic combustion aerosol fraction in
315 the aerosol sample. Notably, plateaus are dynamic. As the concentration of inorganic salts increase, the increased
316 activated fraction is reflected in the CCN spectra; the plateau heights increase with increasing hygroscopic
317 concentrations. In these particular externally mixed experiments, the initial CCN/CN plateau can be as large as one,
318 subsequently decrease, and then will likely increase to one after the BC critical diameters are reached. BC externally
319 mixed with very hygroscopic material is observed to be more CCN active than BC alone.
320
321
322 **Figure 8.** Combustion aerosols externally mixed with inorganics a) NaCl externally mixed with concentrations
323 modified from 51% to 85% over the course of 60 min b) AS externally mixed with concentrations from 41% to 86%
324 over a course of 75 min. Cross symbols represent the initial size distribution of the combustion aerosol.
325
326 Succinic acid (SA) was mixed with combustion aerosol to investigate the external to internal mixing and transition of
327 slightly hygroscopic organic with non-hygroscopic insoluble but wettable aerosols. The laboratory system mimics
328 observed increases in SOA mass fractions on combustion aerosols during atmospheric aging. The SA was introduced
329 to the flow tube at various concentrations, followed by the combustion aerosol from the APG, under dry externally
330 mixed conditions and bimodal size distribution peaks were observed (Figure 9).
331
332
333 The normalized size distributions of the aerosol leaving the flow tube are presented. The initial BC size distribution
334 is similar to those presented in Figure 8. Assuming the first of the two peaks is SA, and the second is a mixture of the
335 combustion aerosol and SA, the initial point of activation agrees with that of succinic acid where SA aerosols all
336 activate. After a mobility diameter, $dp > 50$ nm, the concentration of combustion aerosol in the mixture increases
337 and the CCN/CN ratio is < 0.2, indicative of a lower SA concentration relative to the non-activated BC concentration.
338
339 To induce internal mixing, active heating was again turned off for the atomized aerosol source. Again, internal mixing
340 was promoted and the multiple activation curves converge into a single sigmoid for the BC and SA system. This is
341 consistent with the AS/SA experiment and previous work that showed a strong influence of insoluble compounds on

342 activation when internally mixed with a more soluble compound. (9) With continued mixing, a shift to larger activation
343 diameters was observed towards the end of the experiment (scan 93) and there was a slight depression in the plateau
344 of the CCN spectra.
345
346 The data suggests that only a small amount of soluble inorganic and organic material is required to make the BC more
347 active than that observed alone, especially as the aerosol becomes more internally mixed.
348
349
350 **Figure 9.** a) Time series of CCN/CN activated fractions of Succinic Acid (SA) and combustion aerosol (BC)
351 mixture in flow tube. b) Succinic Acid and Combustion Aerosol mixtures for Scans 24, 45, 54, 73, and 94. Aerosol
352 water is introduced at ~ scan 70 to promote internal mixing.
353

354 ## 5. Conclusion

355 Results show that the experimental CCN activation curves of aerosol provide insight into to the type of mixing
356 (e.g. internal vs. external) and the various levels of hygroscopicities that are chemically representative. Modifications
357 in the concentrations of externally mixed non-hygroscopic aerosols are reflective of the CCN activated concentrations.
358 This is consistent with CCN spectra observed in ambient studies, which have attributed increases in plateau height to
359 the extent of internal mixing of hygroscopic materials on externally mixed inactivated aerosols. This work adds to the
360 existing body of CCN literature and demonstrates that the transition from external to internal mixtures can be
361 mimicked in controlled laboratory experiments and observed in CCN data. If one accounts for multiple-sigmoid
362 analysis in experimental CCN activation data, the CCN behavior of known hygroscopic compound mixtures (e.g.,
363 ammonium sulfate, sodium chloride, succinic acid) agrees well with traditional Köhler theory. However, more work
364 is needed to explore mixtures of hygroscopic material with wettable and non-hygroscopic aerosol. Here, as the non-
365 hygroscopic combustion aerosol becomes coated or internally mixed with the inorganic and organic material, the CCN
366 activity of the combustion aerosol is modified. The data here, with recent publications (Altaf et al., 2018; Ye at al.,
367 2016), suggest that aerosol water is a significant factor in promoting mixing and can be used to modify mixing states.

368 The aerosols maintained an external mixture under dry conditions; CCN activation curves plateaued and remained
369 constant. However, turning off the heater promoted internal mixing and the activation curves were observed to
370 converge. These experiments with known compounds confirm that the aerosol mixing state can be observed in CCN
371 activation data and can thus be revisited in complex aerosol data sets to understand the extent of mixing. The results
372 confirm that CCN counters and CCN analysis can be used in future studies to quantify the extent of mixing of ambient
373 particles. The results are critical to understanding other factors important to the direct and indirect radiative
374 contributions of atmospheric particles.
375

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386

387 ## Appendix

388

389 **Figure A1.** Fluid dynamics simulation results of the flow stream transporting behaviors in the flow tube mixer

390

391 **Figure A2.** Atomized AS CCN calibrations. In both cases the aerosol is atomized and passed through a silica gel
392 diffusion dryer. The aerosol passes through a heated column before the drier in Dp_Heater on data and does no in
393 Dp_Heater off. The critical activation mobility diameters (μm) for heated-dried vs. non-heated dried atomized
394 sample streams agree. The two-tailed P-value is 0.87.

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397 ## References

398

399 1. Abbatt, J. P. D., Broekhuizen, K., and Kumar, P. P.: Cloud condensation nucleus activity of internally mixed
400 ammonium sulfate/organic acid aerosol particles, Atmos. Environ., 39, 4767-4778, 2005.
401 2. Altaf, M. B. Dutcher, D D. Raymond,T. M and Freedman, M. A.: Effect of Particle Morphology on Cloud
402 Condensation Nuclei Activity, ACS Earth and Space Chem., 10.1021/acsearthspacechem.7b00146. 2018.
403 3. Asa-Awuku, A., Moore, R., Nenes, A., Bahreini, R., Brock, C. A., Middlebrook, A., Holloway, J., Ryerson, T.,
404 Jimenez, J., DeCarlo, P., Hecobian, A., Weber, R., Tanner, D., Stickel, R., and Huey L. G., 'Airborne Cloud
405 Condensation Nuclei Measurements during the 2006 Texas Air Quality Study, J. Geophys. Res., 116,
406 doi:10.1029/2010JD014874. 2011.
407 4. Bhattu, D., Tripathi, S. N., and Chakraborty, A.: Deriving aerosol hygroscopic mixing state from size-resolved
408 CCN activity and HR-ToF-AMS measurements, Atmos. Environ., 142, 57-70, 2016.
409 5. Bilde, M. and Svenningsson, B.: CCN activation of slightly soluble organics: The importance of small amounts
410 of inorganic salt and particle phase, Tellus, 56B, 128–134, 2004.
411 6. Bougiatioti, A., Nenes, A., Fountoukis, C., Kalivitis, N., Pandis, S. N., and Mihalopoulos, N.: Size-resolved CCN
412 distributions and activation kinetics of aged continental and marine aerosol, Atmos. Chem. Phys., 11, 8791-8808,
413 doi:10.5194/acp-11-8791-2011, 2011.
414 7. Broekhuizen, K., Kumar, P. P., and Abbatt, J. P. D.: Partially soluble organics as cloud condensation nuclei: Role
415 of trace soluble and surface active species, Geophys. Res. Lett., 31, doi:10.1029/2003GL018203, 2004.

8. Cruz, C. N. and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, J. Geophys. Res., 103, 13111-13123, 1998.
9. DeCarlo, P. F., Kimmel, J. R., Trimborn, A., H., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath II, T., Docherty, K. S., Worsnop, D. R., Jimenez, J. L.: Field Delopyable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, Anal. Chem., 78, 8281-8289, 2006.
10. Durdina, L., Lobo, P., Trueblood, M.B., Black, E.A., Achterberg, S., Hagen, D., Brem, B.T., and Wang, J.: Response of black carbon-mass instruments to mini-cast soot, Aerosol Sci. Technol., 50, 906-918, 2016.
11. Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M. O.: Size matters more than chemistry for cloud-nucleating ability of aerosol particles, Science, 312, 1375–1378, 2006.
12. Ervens, B., Cubison, M., Andrews, E., Feingold, G., Ogren, J. A., Jimenez, J. L., DeCarlo, P., and Nenes, A.: Prediction of cloud condensation nucleus number concentration using measurements of aerosol size distributions and composition and light scattering enhancement due to humidity, J. Geophys. Res., 112, doi:10.1029/2006JD007426, 2007.
13. Fofie, E. A., N. M. Donahue, and Asa-Awuku, A.: Cloud condensation nuclei activity and droplet formation of primary and secondary organic aerosol mixtures, Aerosol Sci. Technol., 52, 1-10, 2017.
14. Gibson, E. R., Gierlus, K. M., Hudson, P. K., and Grassian, V. H.: Generation of Internally Mixed Insoluble and Soluble Aerosol Particles to Investigate the Impact of Atmospheric Aging and Heterogeneous Processing on the CCN Activity of Mineral Dust Aerosol, Aerosol Sci. Technol., 41, 914-924, doi: 10.1080/02786820701557222, 2007.
15. Hameri , K. , Charlson , R. and Hansson , H. C.: Hygroscopic Properties of Mixed Ammonium Sulfate and Carboxylic Acids Particles, AIChE J., 48, 1309–1316, 2002.
16. Henning, S., Rosenørn, T., D'Anna, B., Gola, A. A., Svenningsson, B., and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, Atmos. Chem. Phys., 5, 575-582, doi:10.5194/acp-5-575-2005, 2005.
17. Lance, S., Raatikainen, T., Onasch, T., Worsnop, D. R., Yu, X.Y., Alexander, M. L., Stolzenburg, M. R., McMurry, P. H., Smith, J. N., and Nenes, A.: Aerosol mixing-state, hygroscopic growth and cloud activation

443 efficiency during MIRAGE 2006, Atmos. Chem. Phys. Discuss., 12, 15709–15742, doi:10.5194/acpd-12-15709-
444 2012, 2012.
445 18. Lance, S., Onasch, T., Warsnop, D., Yu, X. Y., Alexander, L., Stolzenberg, M., McMurry, P., Smith, J.N., Nenes.,
446 A.: Aerosol Mixing-State and Cloud Activation Efficiency during the MILAGRO Campaign, 2013, Atmos.
447 Chem. Phys., 13, 5049-5062, doi:10.5194/acp-13-5049-2013, 2013.
448 19. Liu, D., Allan, J., Whitehead, J., Young, D., Flynn, M., Coe, H., McFiggans, G., Fleming, Z. L., and Bandy, B.:
449 Ambient black carbon particle hygroscopic properties controlled by mixing state and composition, Atmos. Chem.
450 Phys., 13, 2015-2029, doi:10.5194/acp-13-2015-2013, 2013.
451 20. Moore, R. H., Nenes., A. and Medina., J.: Scanning Mobility CCN Analysis - A Method for Fast Measurements
452 of Size-Resolved CCN Distributions and Activation Kinetics, Aerosol Sci. Technol., 44, 861-871, 2010.
453 21. Moore, R. H., Cerully, K., Bahreini, R., Brock, C. A., Middlebrook, A. M. and Nenes, A.: Hygroscopicity and
454 composition of California CCN during summer 2010, J. Geophys. Res., 117, D00V12,
455 doi:10.1029/2011JD017352, 2012.
456 22. Padró, L. T., Asa-Awuku, A., Morrison, R., and Nenes, A.: Inferring thermodynamic properties from CCN
457 activation experiments: single-component and binary aerosols, Atmos. Chem. Phys., 7, 5263-5274,
458 doi:10.5194/acp-7-5263-2007, 2007.
459 23. Padró, L. T., Moore, R. H., Zhang, X., Rastogi, N., Weber, R. J., and Nenes, A.: Mixing state and compositional
460 effects on CCN activity and droplet growth kinetics of size-resolved CCN in an urban environment, Atmos. Chem.
461 Phys., 12, 10239-10255, doi:10.5194/acp-12-10239-2012, 2012.
462 24. Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud
463 condensation nucleus activity – Part 2: Including solubility, Atmos. Chem. Phys., 8, 6273-6279, doi:10.5194/acp-
464 8-6273-2008, 2008.
465 25. Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud
466 condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, doi:10.5194/acp-7-1961-2007, 2007.
467 26. Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, 954, Kluwar Acad., Norwell Mass.,
468 1997.
469 27. Roberts, G. C. and Nenes, A.: A Continuous-Flow Streamwise Thermal-Gradient CCN Chamber for Atmospheric
470 Measurements, Aerosol Sci. Technol., 35, 206-2011, doi: 10.1080/027868290913988, 2005.

28. Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., Poschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensdation nuclei counter (DMT-CCNC): CCN Activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, Atmos. Chem. Phys., 8, 1153-1179, doi: 10.5194/acp-8-1153-2008, 2008.
29. Saxena, P., Hildemannm, L. M.: Water-Soluble organics in atmospheric particles: A critical review of the litereature and application of thermodynamics to identify candidate compounds, J. Atmos. Chem., 24, 57-109, 1996.
30. Seinfeld, J. H. and Pandis, S. N.: Atmopsheric Chemistry and Physics, John Wiley, New York, 1998.
31. Shulman, M. L., Jacobson, M. C., Charlson, R. J., Synovec, R. E., and Young, T. E.: Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, Geophys. Res. Lett., 23, 277–280, 1996.
32. Sullivan R. C., Moore M., Petters, M. D., Kreidenweis S. M., Roberts G. C., and Prather, K. A.: Effect of chemical mixing state on the hygroscopicty and cloud nucleating properties of calcium mineral dust particles, Atmos. Chem. Phys., 9, 3303-3316, 2009.
33. Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6, 1937-1952, doi:10.5194/acp-6-1937-2006, 2006.
34. Vu, D., Short, D., Karavalakis, G., Durbin, T. D., and Asa-Awuku, A.: Integrating cloud condensation nuclei predictions with fast time resolved aerosol instrumentation to determine the hygroscopic properties of emissions over transient drive cycles, Aerosol Sci. Technol., 49, 1149-1159, 2015.
35. Wex, H., McFiggans, G., Henning, S., and Stratmann, F.: Influence of the external mixing state of atmospheric aerosol on derived CCN number concentrations, Geophys. Res. Lett., 37, doi:10.1029/2010GL043337, 2010.
36. Ye, Q., Robinson, E. S., Ding, X., Ye, P., Sullivan, R., and Robinson, N.: Mixing of secondary organic aerosols versus relative humidity, Proc. Natl. Acad. Sci. U. S. A., 113, 12649-12654, 2016.

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-429
Manuscript under review for journal Atmos. Meas. Tech.
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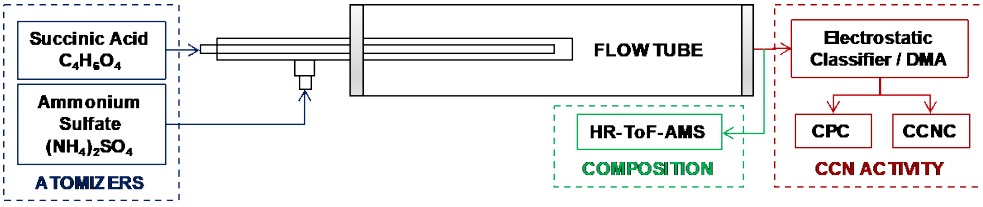

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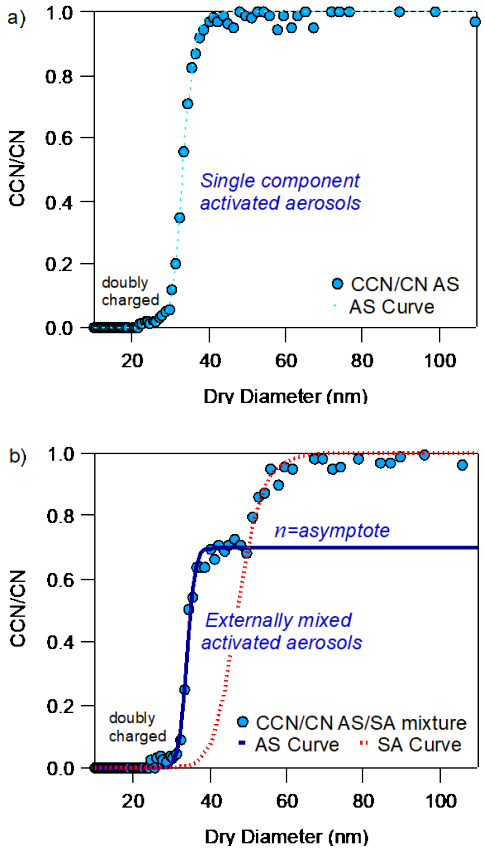

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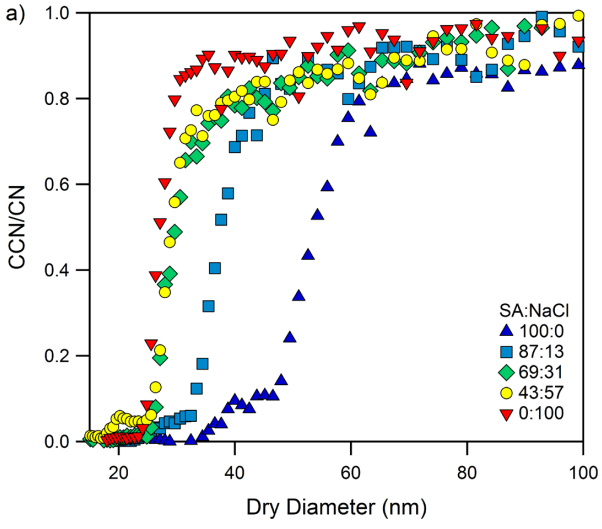

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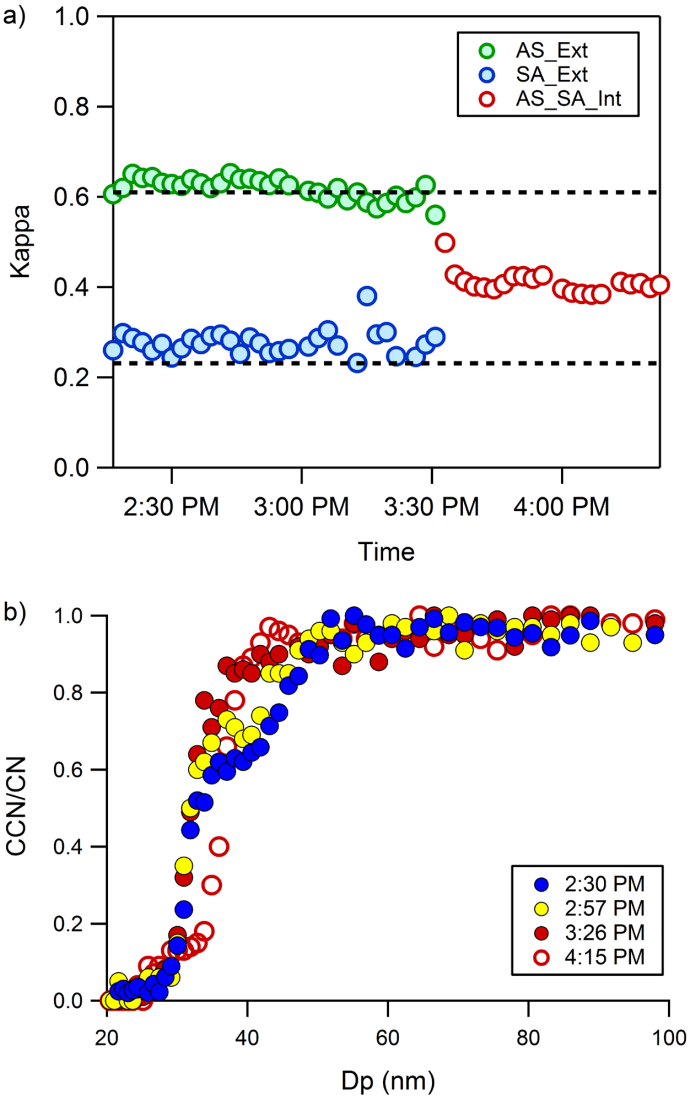

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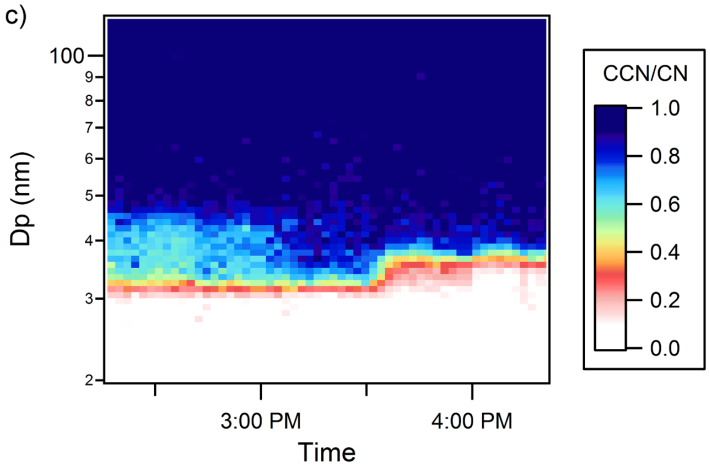
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 11 January 2019



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Manuscript under review for journal Atmos. Meas. Tech.
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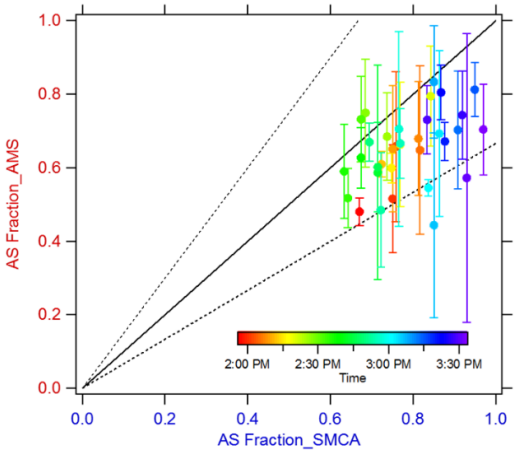

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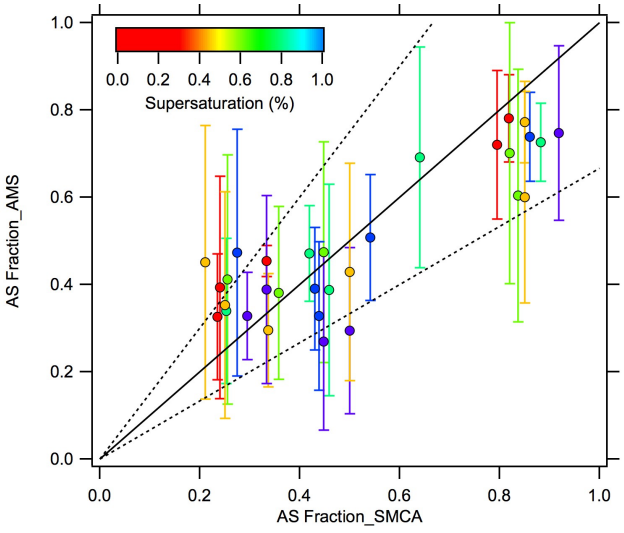

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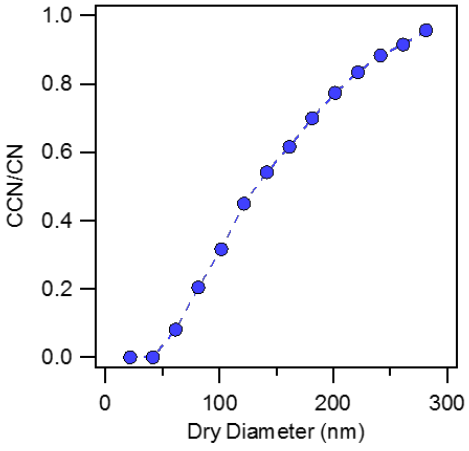

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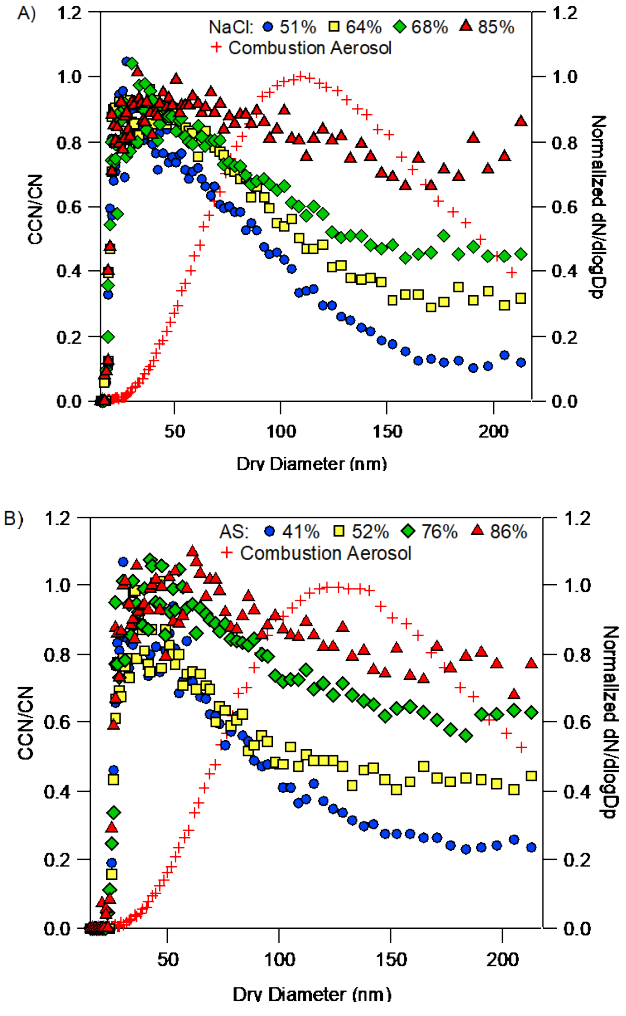
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 11 January 2019



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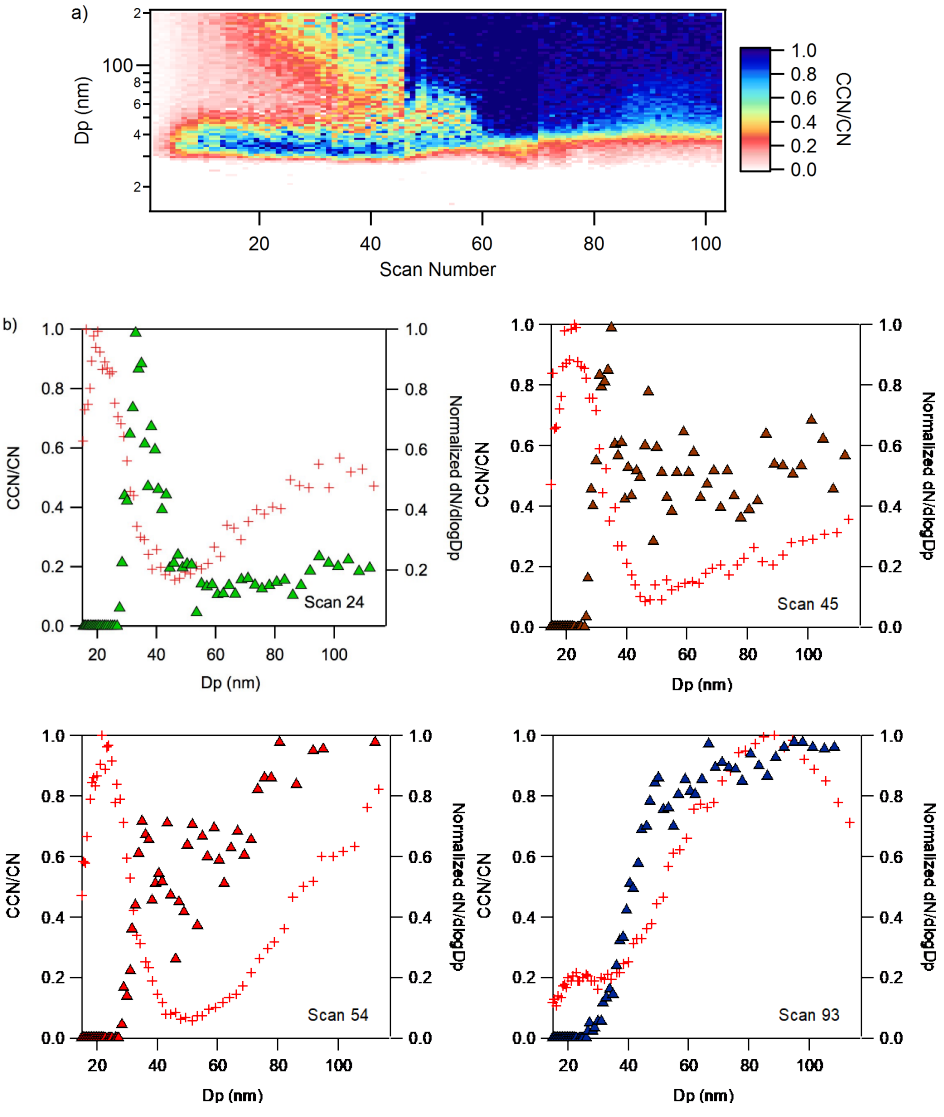

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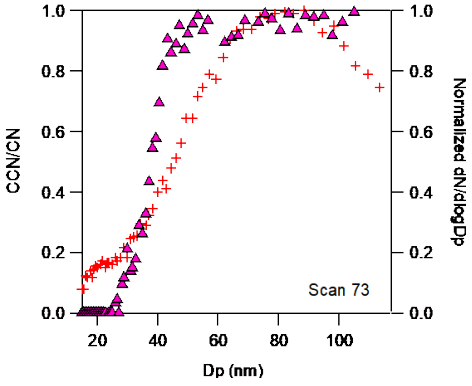

Fig09

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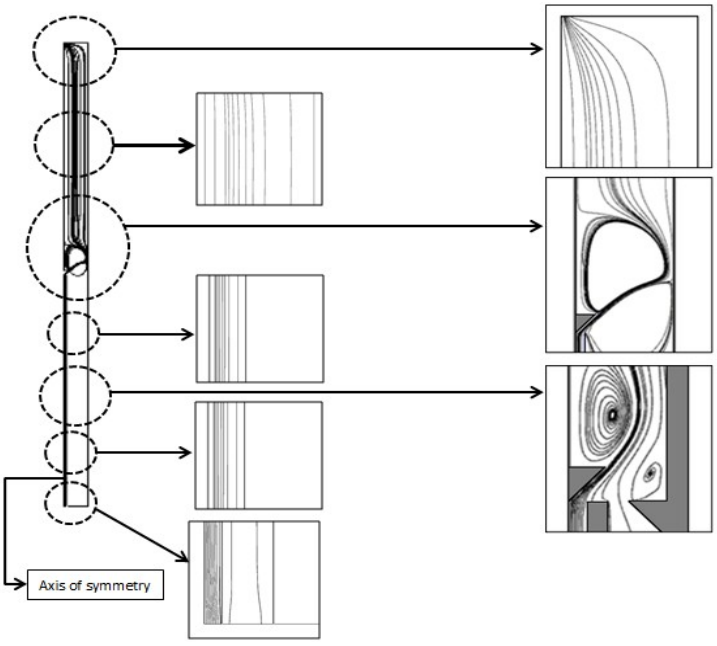

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Manuscript under review for journal Atmos. Meas. Tech.
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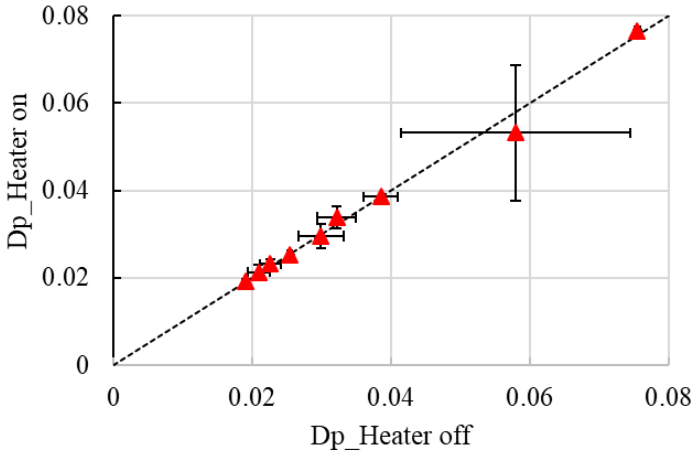

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