⇨ We thank the Associate Editor for comments and the opportunity to revise the manuscript. We have taken care to address each comment in a point by point response.

Responses to Report #3

The manuscript "External and Internal Cloud Condensation Nuclei (CCN) Mixtures: Controlled Laboratory Studies of Varying Mixing States" presents the results of testing and validating the CCN activation with multicomponent and varying mixing state under controlled laboratory conditions. Mixing state is important for CCN concentrations and it is interesting to test the relationship the CCN activation with mixing state in laboratory studies.

I did not read the manuscript of previous version. For this version, I have a few specific comments.

1. The manuscript claims that "the aerosol mixing state can be observed in CCN activation data and can thus be revisited in complex aerosol data sets to understand the extent of mixing" (L392-394, and something similar in the abstract (L39-40)). In this study, two-components mixture were used and a plateau was found for the external mixing case. I am curious how well the plateau can be resolved when aerosol contains more than two components, say three or five components. It might look like a continuous activation curve. Therefore, it would be helpful to discuss the limit of this approach.

   Also L286-288, "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." This may be difficult if aerosol contains more than two components.

⇨ Discussion about the limit of multiple components has been added to the text as follows:
⇨ L251. For more than 2-component externally mixed particle distributions, more than two plateaus will be observed. For example, the work of Schill et al. 2015 shows multiple plateaus for a five-component external mixture mimic of ocean spray CCN. If one considers a limiting case of infinite components with distinct varying degrees of hygroscopicity, then the activation curve will be monotonic below 1 and may appear to be representative of an internal mixture; the CCN activation curve will approach the shape of a shallow sigmoidal slope (however not as steep or instantaneous as the ideal step function)
⇨ L294"Results with distinct CCN activation plateaus, especially of 2-3 distinct hygroscopicities, may be useful for estimating aerosol chemical fractions when other instruments with lower size resolution are not readily available"

2. Fig. 3, in the caption, it is mentioned that "Dashed lines indicate 20% uncertainty." What does this uncertainty exactly mean? The lines are of 0.8:1 and 1.2:1 lines? It seems to

be not the case according the values in the figure. I have similar questions for Fig. 5 and Fig. 6.

⇨ That is an error in the text. The dashed lines in Figures 3,5, and 6 represent 50% uncertainty from the 1:1. The lines are 1.5:1 and 1:1.5 and were kept consistent across the figures. The data in Figure 3 are well within the 50% uncertainty, and specifically within 20% uncertainty from the agreement with theory. The error bars are the standard deviation from replicate measurements. We have added this additional clarification to the revised manuscript and have made sure that the text is congruent with the figures.

⇨ L228 "Regardless of surface tension omissions, the single sigmoidal experimental data set is within 20% of theoretical agreement and indicative of a single component or homogeneous internally mixed aerosol population."

3. L261-264, it is very interesting to attribute the change of mixing state to minute water content. Have the authors also considered the possibility of effect of heating on the size of SA particles? If the size distribution changes, the coagulation efficiency of SA and AS may change, which will also affect the mixing state.

⇨ The effects of heating on semi-volatile succinic acid particles is interesting but was not discussed because we did not observe evidence of potential evaporation affecting our SA and AS results. Additionally, single-particle composition measurements at low temperatures are required to robustly quantify the effects of coagulation on mixing state. We unfortunately did not have access to such instrumentation. We expand this explanation with the points below.

⇨ For example, In Figure 4, the effects on the CCN activation curve of SA and AS are presented. When heating is on, distinct plateaus (below 1) are observed indicating that SA is present and contributes to a fraction of the aerosol at those smaller sizes. It should be emphasized that the heating of concern occurs during aerosol generation. The subsequent aerosol that remains is then characterized for CCN activity. The plateau below one is an indication of multiple components at the given sizes. Additionally, kappa is a particle intrinsic property; that is regardless of particle size distribution, kappa hygroscopicity is a reflection of the chemical composition of particles. Simply stated, ten 100nm particles will have the same hygroscopicity as one thousand 50 nm particles. Even if the the distributions change (if the 50 nm particles evaporate), the hygroscopicity of the component should stay the same. When two sigmoids are applied in our data sets, we correctly measure the kappa of the two distinct components. If all the SA was evaporated, then the critical activation diameters and kappa values would look entirely like AS.

⇨ It is noted that particle evaporation has the potential to modify the volume fraction of a particle at a given size. That is for external mixtures, the plateau height will likely be higher for the more hygroscopic and less volatile material. Figure 6 shows that the AMS measured fraction of potentially evaporated SA/AS mixtures agrees reasonably well with the fraction estimated from the CCN at different supersaturations.   For an internal mixture, the asymptote equals 1 and if the size resolved contribution of each component is known, there is a shift in the CCN activation from left to right (as is observed in Figure

3). Our estimates of the volume fraction from kohler theory agree with the known quantities used to make the solution. These particles were also heated during particle activation. Again, we see little evidence of the effects of succinic acid evaporation in our data set. In the transition mixing state experiments from external to internal, we do not have single-particle information and thus cannot fully quantify the volume fraction at each size. The reported CCN activation curve and resulting kappa values during the transition from external to internal also agree with theory. That is the external mixture agrees with AS and SA theoretical values and the internal mixtures is somewhere between the two, again suggesting that SA is present and has not completely evaporated during the measurement. We have provided some additional discussion to address concerns about volatile species and the coagulation of particles.

⇨ **Additional revised text**
⇨ L253. "It is noted that heated succinic acid particles can evaporate during aerosol generation and before CCN measurement; the asymptote in Figure 4 is an indication that multiple components are present in the total aerosol distribution.
⇨ L218. The shifting of the CCN activation sigmoid (left and right) is also expected of internally mixed particles formed via the coagulation of separate particle distributions (Farmer et al., 2015).

.

4. L332-334, it would be helpful for readers to understand if the D50 values of NaCl and AS were provided.
⇨ The additional information has been provided in the revised text.
⇨ L343 "Thus for both the AS and NaCl external mixtures, the activation diameters derived from a singular fit were consistent with the expected dp50 < 50 nm of the respective inorganic salts. Specifically at Sc=1.1%, AS and NaCl particles activated at 25 and 19 nm respectively (congruent with theoretical dp50 at 24.8 and 19.0 nm)"

5. Legends of Fig. 9 are missing.
⇨ The following text has been revised.
⇨ "Figure 9. a) Time series of CCN/CN activated fractions of Succinic Acid (SA) and combustion aerosol (BC) mixture in flow tube. b) The CCN/CN activated fraction (closed triangles) of Succinic Acid and Combustion Aerosol mixtures for particle distribution scans 24, 45, 54, 73, and 94. Aerosol water is introduced at ~ scan 70 to promote internal mixing. Cross symbols show the particle size distribution mixed aerosol."

6. L380-382, "...which have attributed increases in plateau height to the extent of internal mixing of hygroscopic materials on externally mixed inactivated aerosols." This phrasing seems to be confusing for me.
⇨ The text has been revised and now reads.
⇨ "This is consistent with CCN spectra observed in ambient studies, which have attributed observations in CCN activation plateau heights less than one to the contributions of externally mixed and inactivated (typically non-hygrosocopic black carbon) aerosols".

References:

Schill, Steven R., et al. "The impact of aerosol particle mixing state on the hygroscopicity of sea spray aerosol." ACS central science 1.3 (2015): 132-141.

Farmer, Delphine K., Christopher D. Cappa, and Sonia M. Kreidenweis. "Atmospheric processes and their controlling influence on cloud condensation nuclei activity." Chemical Reviews 115.10 (2015): 4199-4217.

1 **External and Internal Cloud Condensation Nuclei (CCN) Mixtures: Controlled Laboratory**

2 **Studies of Varying Mixing States.**

3 Diep Vu[1,2,§], Shaokai Gao[1,♦], Tyler Berte[1,2], Mary Kacarab[1,2,], Qi Yao[4], Kambiz Vafai[3] and Akua Asa-Awuku[1,2,4,*]

4

5 1.*Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of

6 California, Riverside, CA 92521, USA

7 2.*Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), Riverside, CA

8 92507, USA

9 3. Department of Mechanical Engineering, Bourns College of Engineering, University of California, Riverside, CA

10 92521, USA

11 4.*Department of Chemical and Biomolecular Engineering, A. James Clark School of Engineering, University of

12 Maryland, College Park, MD 20742.

13

14 §. Currently at Ford Motor Company, Research & Innovation Center Dearborn, MI 48124, USA

15 ♦. Currently at Phillip 66 Research Center, Research and Development, Bartlesville, OK 74004, USA

16

17 *Correspondence to:* A. Asa-Awuku (asaawuku@umd.edu)

18

19 **Abstract**

20

21 Changes in aerosol chemical mixtures- modify cloud condensation nuclei (CCN) activity. Previous studies have

22 developed CCN models and validated changes in external and internal mixing state with ambient field data. Here, we

23 develop an experimental method to test and validate the CCN activation of known aerosol chemical composition with

24 multicomponent mixtures and varying mixing states. CCN activation curves consisting of one or more activation

25 points is presented. Specifically, simplified two component systems of varying hygroscopicity were generated under

26 internal, external, and transitional mixing conditions. κ-Köhler theory predictions were calculated for different organic

27   and inorganic mixtures and compared to experimentally derived kappa values and respective mixing states. This work

28   employs novel experimental methods to provide information on the shifts in CCN activation data due to external to

29   internal particle mixing from controlled laboratory sources. Results show that activation curves consisting of single

30   and double activation points are consistent with internal and external mixtures, respectively. In addition, the height of

31   the plateau at the activation points are reflective of the externally mixed concentration in the mixture. The presence of

32   a plateau indicates that CCN activation curves consisting of multiple inflection points are externally mixed aerosols

33   of varying water-uptake properties. The plateau disappears when mixing is promoted in the flow tube. At the end of

34   the flow tube experiment, the aerosol are internally mixed and the CCN activated fraction data can be fit with a single

35   sigmoidal curve. The technique to mimic external to internally mixed aerosol is applied to non-hygroscopic

36   carbonaceous aerosol with organic and inorganic components. To our knowledge, this work is the first to show

37   controlled CCN activation of mixed non-hygroscopic soot with hygroscopic material as the aerosol population

38   transitions from external to internally mixed states in laboratory conditions. Results confirm that CCN activation

39   analysis methods used here and in ambient data sets are robust and may be used to infer the mixing state of complex

40   aerosol compositions of unknown origin.

41   **1. Introduction**

42   Atmospheric cloud condensation nuclei (CCN) are comprised of complex mixtures of organic and inorganic

43   compounds. The chemical and physical diversity present in complex mixtures can significantly complicate the

44   quantification of aerosol-cloud interactions, thereby making it difficult to predict CCN activity (e.g., Riemer et al.,

45   2019). In this work, we define mixtures and the aerosol mixing state as the chemical diversity across an aerosol

46   distribution. Knowledge of the mixing state and the chemical composition can greatly improve CCN predictions

47   and has been the focus of several studies (e.g., but not limited to (Bilde and Svenningsson 2004; Abbatt et al. 2005;

48   Henning et al. 2005; Svenningsson et al. 2006; King et al. 2007; Cubison et al. 2008; Kuwata and Kondo 2008;

49   Zaveri et al. 2010; Su et al. 2010; Wang et al. 2010; Spracklen et al. 2011; Ervens et al. 2010; Asa-Awuku et al.

50   2011; Lance et al. 2012; Liu et al. 2013; Jurányi et al. 2013; Paramonov et al. 2013; Padró et al. 2012; Moore et al.

51   2012; Meng et al. 2014; Bhattu and Tripathi 2015; Almeida et al. 2014; Schill et al. 2015; Crosbie et al. 2015; Che

52 et al. 2016; Ching et al. 2016; Mallet et al. 2017; Sánchez Gácita et al. 2017; Cai et al. 2018; Schmale et al. 2018;

53 Mahish et al. 2018; Kim et al. 2018; Chen et al. 2019; Stevens and Dastoor 2019)

54   It is well accepted that the water content and the point of activation is dependent on more factors than just the

55 supersaturation and dry diameter for CCN active aerosols (Dusek et al., 2006; Petters and Kreidenweis, 2007). The

56 droplet growth and activation of slightly soluble organics can be modified when internally mixed with inorganic salts

57 that readily deliquesce (Cruz et al., 1998; Padró et al., 2002; Svenningsson et al., 2006). Although inorganic salts are

58 well characterized, the quantification of CCN activity is complicated when they are internally mixed with a complex

59 organic. Consequently, simple mixing rules may no longer be appropriate. It has been observed that mixed aerosols

60 can activate at lower supersaturations than their bulk constituents and organic compounds that may not traditionally

61 be considered as water soluble may aid in the formation of a cloud droplet by acting as a surfactant, depressing surface

62 tension, or simply by contributing mass (Cruz et al., 1998; Padró et al., 2007; Svenningsson et al., 2006). In addition,

63 when there is a sufficiently large enough fraction of salt, the slightly soluble core can dissolve before activation, thus

64 lowering the required supersaturation (Sullivan et al., 2009). Thus, the mixing state and extent of mixing can

65 substantially influence CCN activity.

66   To help minimize the complexity in characterizing aerosol hygroscopic and CCN activation properties, CCN data

67 analysis has traditionally been simplified by assuming that *i)* the aerosols share a similar or uniform hygroscopicity

68 over a particle size distribution, *ii)* the CCN particle size can be described by the electrical mobility diameter, *iii)* CCN

69 consists of few multiply charged aerosols and *iv)* all CCN active aerosols readily dissolve at activation. As a result, a

70 singular sigmoidal fit is commonly applied over the entire CCN activation. However, this method of analysis may not

71 be fully representative of the heterogeneous mixing state occasionally present in the aerosol sample. Thus a CCN

72 mixture refers to the diversity of activated aerosols in the particle population (not the property of an individual particle;

73 i.e., Winkler, 1973; Riemer et al., 2019).

74   Previous studies have addressed aerosols with singular or internally mixed binary chemical species (e.g. but not

75 limited to, Bilde et al., 2004; Broekhuizen et al., 2004; Petters and Kreidenweis, 2007; Shulman et al., 1996; Sullivan

76 et al., 2009). However, ambient measurements indicate complex aerosol populations consisting of both external and

77 internal mixtures (e.g., but not limited to Ervens et al., 2007; Lance et al., 2012; Moore et al., 2012, Padró et al., 2012).

78 By accounting for the mixing states and extent of mixing in field data sets, CCN concentration predictions can be

79 greatly improved (e.g but not limited to Padró et al., 2012; Wex et al., 2010, Su et a., 2010, Kuwata and Kondo, 2008).

80 However, dynamic changes in particle mixing states have not been reproduced in the laboratory and subsequent

81 treatment of CCN measurement and analysis have not been readily studied in depth under controlled laboratory

82 conditions.

83   In this work, we seek to improve the experimental CCN activation analysis techniques of complex mixtures by

84 investigating the influence of mixing state on activation curves with known aerosol composition. Theoretical

85 postulations have already been developed and applied to ambient data sets (e.g., but not limited to, Su et a., 2010,

86 Padró et al., 2012; Bhattu et al., 2016;) but never before has a systematic laboratory experiment controlled and

87 validated the extent of particle heterogeneity for CCN activation. To understand the impact of mixing state on CCN

88 activation, simplified two component mixtures of known compounds with varying hygroscopicities are created under

89 internal, external, and in-between (transition) mixing conditions. In addition, black carbon containing particles (BC)

90 and BC mixing state data is presented. BC is renown for its direct radiative effects yet little is known experimentally

91 about the contributions of BC mixtures to aerosol-cloud interactions at varied mixing states. Previous work

92 investigating the contribution of BC to aerosol-cloud interactions at various mixing states has been studied (e.g., but

93 not limited to Bond et al., 2013 and references therein, Lammel and Novakov 1995; Novakov and Corrigan 1996;

94 Weingartner et al. 1997; Dusek et al. 2006; Kuwata and Kondo 2008; Koehler et al. 2009; McMeeking et al. 2011;

95 Liu et al. 2013; Rojas et al. 2015). However, many of these have been limited more to ambient related field studies

96 and less under controlled laboratory settings. Here, the CCN activation and hygroscopic properties of soot mixed with

97 atmospherically relevant constituents of varying hygroscopicity are investigated under laboratory controlled

98 conditions. This work provides evidence on the differences between inorganic, slightly soluble, and insoluble

99 externally and internally mixed compositions for the uptake of water, and subsequent CCN activity.

100 **2. Experimental Methods**

101 **2.1 Aerosol Composition and Sources**

102   The CCN activity of two component aerosol mixtures under internal, external, and combinations of mixing states

103 are explored in this study. The components include very hygroscopic (inorganics), hygroscopic (organic acids), and

104 non-hygroscopic (Black Carbon, BC). For known chemical compositions, a Collison-type atomizer generated

105   singular-component solutions of ammonium sulfate, ($(NH_4)_2SO_4$, Acros 99.5%), sodium chloride, (NaCl, Acros

106   99+%) and succinic acid ($C_4H_6O_4$, Acros 99%) and subsequent internal mixture combinations as described in the

107   sections Aerosol Mixing States and Modified Mixing States: External to Internal. Succinic acid, classified as a slightly

108   soluble dicarboxylic acid, (18) $(NH_4)_2SO_4$, and NaCl are all relevant model atmospheric compounds with varying

109   degrees of solubility and hygroscopicity. All atomized solutions were prepared using Millipore© DI water (18 mΩ,

110   TOC $\leq$ 5 ppb). Atomized wet droplets were dried with silica gel diffusion dryer (as commonly practiced). In addition,

111   we employ a heated column before the diffusion dryer to facilitate the evaporation of water from the wet particles.

112   The implications of the use or absence of a heated column are discussed in the results below.

113   An AVL Particle Generator (APG), which houses a mini Combustion Aerosol STandard soot generator

114   (miniCAST 6203C, Jing ltd.), was used to generate carbonaceous aerosols. The APG consists of a propane burner

115   followed by a volatile particle remover. The burner was operated at 400°C with a propane and air flow rate of 15 ml

116   per min and 1.0 l per min, respectively. The miniCAST utilized in the APG has been well characterized in previous

117   work (e.g., Pinho et al. 2008; Seong and Boehman 2012; Mamakos et al. 2013; Maricq and Matti Maricq 2014;

118   Durdina et al. 2016; Moore et al. 2014). The soot formed is a mixture of black and oxidized carbon (Moore et al.

119   2014). The aerosol structures generated by the APG likely consisted of fractal-like agglomerates of non-spherical

120   particles (Moore et al. 2014; Durdina et al., 2016). APG Combustion aerosols are mixed with inorganic and slightly

121   soluble succinic acid and CCN activity is subsequently measured at different supersaturations.

122   **2.2 Aerosol Mixing Methods**

123   Mixing compounds in solution can readily form internal mixtures of aerosol (Gibson et al., 2007; Hameri et al.,

124   2002). Solution mixtures of a highly hygroscopic compound, NaCl, and a slightly hygroscopic compound, succinic

125   acid, are shown. Five aqueous solutions of succinic acid and NaCl with molar ratios of 100:0, 87:13, 69:31, 43:57,

126   0:100 were aerosolized using a single atomizer, passed through a heated column, dried, and sampled directly into a

127   Scanning Mobility Particle Sizer (SMPS) and CCN Counter (CCNC). Instrument specifications are discussed in

128   section 2.3.

129   External mixtures were formed via two methods. The first and simplest method required two sufficiently dry

130   aerosol streams to mix. Two aerosol streams were joined via a Swagelok® Tee connector. External mixtures were

131   also formed in a flow tube mixing apparatus. As conditions (e.g., but not limited to, residence time, temperature,

pressure, relative humidity) change in a flow tube, it is assumed that the external mixture may transition into an

internally mixed aerosol system. A flow tube mixing apparatus was constructed to test this assumption and modify

the extent of mixing of multiple components (Fig. 1 & 2).

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

This work shows changes in CCN experimental data and analysis as a result of changes in the extent of mixing.

Results of the CCN activation are presented in the Section: Modified Mixing: External to Internal Mixing in the

Aerosol Flow Tube. A brief description of the flow tube is provided here. The first aerosol stream is introduced into

the flow tube by a ¼ inch stainless steel (SS) tube. The second aerosol stream is also introduced by a ¼ inch SS tube,

but is expanded to an outer concentric ¾ inch SS tube using a SS Swagelok tee connection. The two aerosol flows are

initially mixed together at the exit of ¼ inch tube and aerosol mixes within the ¾ inch SS tube for an additional 12

inches before entering the quartz tube where it continues to mix. In this study, the pressure and temperature of the

flow tube is maintained at ambient conditions. The extent of mixing in the flow tube mixer has been modeled by

Computational Fluid Dynamics simulation (CFD - Comsol) to test and improve the aerosol mixing 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 (e.g., but not limited to,

158 Moore et al., 2010; Padró et al., 2012). The development of a single continuous-flow thermal gradient diffusion

159 column CCN Counter, CCNC (Droplet Measurement Technologies, Inc.) has provided rapid (~1 Hz) and robust CCN

160 data (Lance et al., 2012; Roberts and Nenes, 2005). Aerosols with a S_c lower than the supersaturation in the column

161 activate and form droplets. These droplets are detected and counted using an optical particle counter at the exit of the

162 column.

163   A TSI 3080 Electrostatic Classifier selects and measures aerosol size distributions. Polydisperse aerosol streams

164 are passed through a bi-polar krypton-85 charger and then through a differential mobility analyzer (DMA), where the

165 aerosols are sized according to electrical mobility with a sheath to aerosol flow ratio of 10:1. The monodispersed flow

166 is then split to a CPC and a CCN counter. CN concentrations were measured with a condensation particle counter,

167 CPC (TSI 3772, TSI 3776).

168   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

169 determine the instrument supersaturation (Rose et al., 2008). Operating the CCN in parallel with the CPC allows for

170 the simultaneous measurements of the total CN and CCN of the monodispersed aerosols. By operating the DMA in

171 scanning voltage mode and maintaining a constant column supersaturation, the CCN/CN, or activation ratio, as a

172 function of dry diameter can be obtained for a given supersaturation. These size resolved CCN distributions obtained

173 through scanning mobility CCN analysis (SMCA) are produce CCN activation curves, CCN/CN ratio as a function of

174 particle mobility diameter (Moore et al., 2010). SMCA produces high resolution CCN activation data near the 50%

175 efficiency critical diameter every ~ 2 minutes.

176   An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) measured the non-

177 refractory bulk composition (DeCarlo et al., 2006). The HR-ToF-AMS was operated in V-mode to track the

178 concentration and vacuum aerodynamic diameter as the aerosol fractions were modified.

179 **3. CCN Analytical Method**

180   CCN data analysis of single component aerosols, such as AS, are well characterized. The activation of a single

181 known component yields a simple sigmoidal activation curve and is often used for instrument calibration (Fig. 2a).

182 However ambient aerosols generally exist as complex mixtures of organic and inorganic species. CCN data sets from

183 ambient and chamber studies, which consist of these aerosol mixtures, may not show a single sigmoidal activation

184 curve but instead can exhibit multiple activation curves not associated with doubly charged particles (Fig. 2b).

185

186 Sigmoidal fits are applied to the CCN/CN as a function of dry activation diameters for the multicomponent

187 aerosols. Externally mixed aerosol fractions in activation curves have been previously observed in ambient studies by

188 Lance et al. (2013), Moore et al. (2012), and Bougiatioti et al. (2011). For those studies, E was defined as the

189 hygroscopic fraction, and $1-E$ the non-hygroscopic mixed fraction. For this study the first curve is similarly defined

190 as the hygroscopic externally mixed fraction (EMF) with an asymptote, or plateau of η. The dependence of η varies

191 with the presence of mixed components and their respective hygroscopicities. Thus we evaluate η for controlled

192 compositions and compare how representative they are of the known fractions of mixtures.

193 A sigmoidal fit through the EMF determines the particle dry diameter of the more hygroscopic species. A

194 second sigmoidal fit is applied to the second activation curve. An example is shown in Fig. 2b for an external

195 mixture of AS and SA. A sigmoid is fit for the more hygroscopic species, AS, and then a second for the less

196 hygroscopic species, SA. The activation diameters are consistent with those expected for the two compounds and

197 agree with Köhler predicted activation values for AS and SA. Doubly ~~charge~~charged aerosols are indicated in Figure

198 2 and are a negligible contribtion to the activation curves.

199 The supersaturation and critical dry diameter are related via ~~with~~ the single parameter hygroscopicity, κ, to

200 describe the CCN activity and to determine the effect of mixing states of multiple components on the supersaturated

201 hygroscopic properties of aerosols. Using the generalized κ-Köhler equations presented by Petters and Kreidenweis

202 (2007 and 2008), droplet growth in the supersaturated regimes for a selected dry diameter can be modeled for an

203 aerosol where the entire particle diameter dissolves at activation.

204
$$ln S_c = \left(\frac{4A^3 \rho_w M_s}{27 v \rho_s M_w D_d^3} \right)^{1/2}, \quad where \ A = \frac{4\sigma_{s/a} M_w}{RT\rho_w} \qquad (1)$$

205
$$\kappa = \frac{4A^3}{27 D_d^3 ln^2 S_c} \qquad (2)$$

206 $\sigma_{s/a}$ is the surface tension, M_w is the molecular weight of water, R the universal gas constant, T is the temperature at

207 activation, and ρ_w is the density of water. Surface tension and density of water were calculated according to

208 temperature dependent parameterizations presented by Seinfeld and Pandis (1998) and Pruppacher and Klett (1997).

209   The surface tension of the solution is assumed to be that of pure water. Traditional Köhler theory is known to work

210   reasonably well for inorganic salts and slightly-soluble and hygroscopic organics like succinic acid.

211

4. Results and Discussion

212

4.1 Internal Mixtures

213

214   Aerosolized internally mixed solutions exhibit single CCN activation curves for all five compositions of

215   succinic acid and NaCl solutions (Fig. 3a). The activation curve is similar to that of ammonium sulfate in Figure 2a.

216   Multiply charged particles contribute less than 10% to the activated fraction and are assumed to be negligible. ~~One~~A

217   sigmoid that plateaus near one can be applied to describe the CCN activation. As the internal mixture salt fraction

218   increased at a given supersaturation, the single curve was maintained and shifted towards a lower activation diameter,

219   indicative of and consistent with more hygroscopic aerosol. The shifting of the CCN activation sigmoid (left and right)

220   is also expected of internally mixed particles formed via the coagulation of separate particle distributions (Farmer et

221   al., 2015). Using the simple mixing rule, a multicomponent hygroscopicity parameter can be theoretically

222   ~~derived~~applied based on the expected kappa values for each individual component hygroscopicity (κ_i), and the volume

223   fraction of each component (ε_i) (Petters and Kreidenweis (2007).

$$\kappa = \sum_i \varepsilon_i \kappa_i \qquad (3)$$

224

225   Equation (3) was applied for each mixture. κ was calculated and compared to the experimental values (Fig. 3b). These

226   internal mixtures do not strongly follow the simple mixing rule for every mixture and is consistent with the previous

227   work of Shulman et al. (1996) and Padró et al. (2007) who showed that slightly soluble compounds internally mixed

228   with salts resulted in surface tension depression and thus a lower required critical supersaturation. As previously

229   published, accounting for organic surface tension depression could improve kappa-hygroscopicity calculations for

230   internal mixtures. Regardless of ~~prediction~~surface tension omissions, the single sigmoidal experimental data set is

231   within 20% of theoretical agreement and indicative of a single component or homogeneous internally mixed aerosol

232   population.

233

234

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 50% uncertainty (1:1.5 and 1.5:1). Data are within 20% uncertainty of the 1:1 line.

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). It is noted that heated succinic acid particles can evaporate during aerosol generation before CCN measurement; the asymptote in Figure 4 is an indication that multiple components are present in the total aerosol distribution. 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. For more than 2-component externally mixed particle distributions, more than two plateaus will be observed. For example, the work of Schill et al. 2015 shows multiple plateaus for a five-component external mixture mimic of ocean spray CCN. If one considers a limiting case of infinite components with distinct varying degrees of hygroscopicity, then the activation curve will be monotonic below 1 and may appear to be representative of an internal mixture; the CCN activation curve will approach the shape of a shallow sigmoidal slope (however not as steep or instantaneous as the ideal step function).

261 **Figure 4. External to internal mixtures of a slightly soluble organic aerosol, succinic acid (SA) and inorganic**

262 **ammonium sulfate (AS) aerosol.** The CCNC was operated at a single S_c of 0.8%. Closed symbols are externally

263 mixed. Open symbols are internally mixed. a) The apparent kappa values derived from externally mixed multiple-

264 sigmoid activation data before active heating is turned off (at approximately 3:30 pm) and ~~after 3:30pm where~~ single

265 sigmoid activation curves (after 3:30pm) are ~~observed~~shown. The two dotted lines indicate the theoretically derived

266 kappa values for succinic acid, κ=0.23, and ammonium sulfate, κ=0.61. b) CCN activation curves exhibit external

267 (with active heating before 3:30 pm) and then transitioning external to internal mixing (after 3:30pm) c) CCN/CN

268 vs. Dry mobility diameter data as a function of time. The asymptote, η, disappears at the by the end of the

269 experiment.

271 One hour after initial injection into the flow tube, the active heating column was turned off. It should be noted

272 that atomized aerosol continued to be dried through the silica gel diffusion dryers, as is commonly done. The relative

273 humidity after the dryer in both cases is small (< 20%) and thus the activation diameters of very hygroscopic AS

274 calibration aerosol are not affected with or without active heating (Fig. A2). However, as soon as active heating was

275 turned off, particles in the mixing flow tube became more mixed (Figure 4). Thus, it is likely that minute amounts of

276 aerosol water promoted internal mixing and shifted aerosol mixing from external to internal in the mixing flow tube

277 system.

278 CCN activation curves for the two compounds remained distinct and separate until internal mixing conditions

279 dominated and the multiple CCN activation curves converged into a single curve (Fig. 4b and 4c). Results suggest

280 aerosol water plays a significant factor in mixing and CCN activation. This is consistent with previous work that

281 indicates that the presence of water led to lowered aerosol viscosity and increased diffusivity (Ye et al., 2016). The

282 wetted aerosols can come in contact through diffusion and coalesce to form an internally mixed aerosol. The apparent

283 kappa values from fitting the two individual activation curves for the external part of the mixing experiment and

284 subsequent internal mixing are shown in Fig. 4a.

285 To help track the change in organic/inorganic fractions during the transition from external to internal, the

286 mixed aerosols were analyzed with a high-resolution time of flight mass spectrometer (HR-Tof-AMS) to provide mass

Formatted: Left

287   fraction information. The mass size distribution was integrated and normalized for each compound per scan according

288   to the total mass that was measured. The mass size distribution was then converted to number size distribution and the

289   diameters were converted from aerodynamic diameter to electrical mobility diameter. Then for each superstation and

290   fraction, the EMF was calculated between the two respective activation diameters and correlated to the EMF that was

291   determined from SMCA to determine the plateau height (η).

292   AS fractions measured by the AMS are consistent with the changes SMCA derived η where increases in AS

293   mass fraction increase η. However, the AMS derived AS fraction are slightly lower compared to SMCA (Fig. 5),

294   indicating potential influence on η from other factors. Previous work has shown the presence of highly soluble

295   materials (like AS) can promote CCN activity of organic dominated systems (Asa-Awuku et al., 2011; Fofie et al.,

296   2017). A second flow tube experiment was conducted to test the effect of differing concentrations on plateau heights.

297   The detection efficiency for particles with smaller sizes in the AMS (<50nm) can effect the AS fraction. Thus, the

298   CCNC supersaturation was modified from 0.2 to 1.2% to test the effect of activation diameter on closure (Fig. 6.).

299   Results show good agreement and are within ~~20~~50% of predictions. Results ~~utilizing~~with distinct CCN activation ~~data~~

300   ~~for aerosols <50nm~~plateaus, especially of 2-3 distinct hygroscopicities, may be ~~a good substitute~~useful for estimating

301   aerosol chemical fractions when other instruments with lower size resolution are not readily available.

302

303

304   **Figure 5.** Plateau heights derived from AMS data vs. SMCA. Single CCNC Supersaturation. Dashed lines

305   indicate 50% uncertainty (1:1.5 and 1.5:1).

306

307

308   **Figure 6.** Modifying activation diameters. Plateau heights derived from AMS data vs. SMCA for CCNC

309   Supersaturation from 0.2 to 1.2~~%~~%. Dashed lines indicate 50% uncertainty (1:1.5 and 1.5:1).

310

311

312   **4.3 External and Internal Mixtures of Combustion Aerosol**

313   Combustion aerosol or soot can form external and internal complex aerosol mixtures. Soot is considered insoluble

314   but wettable (e.g., but not limited to Lammel and Novakov 1995; Moore et al. 2014) and the contributions of Black

315 Carbon containing particles to aerosol-cloud interactions at varied mixing states is not well known or understood

316 (Lammel and Novakov 1995; Novakov and Corrigan 1996; Weingartner et al. 1997; Dusek et al. 2006; Kuwata and

317 Kondo 2008; Koehler et al. 2009; Bond et al. 2013; McMeeking et al. 2011; Liu et al. 2013; Rojas et al. 2015). Thus,

318 the ability of black carbon to mix with inorganic and organic compounds and to observe the extent of mixing as they

319 activate as CCN is of great interest.

320   Prior to investigating the impact of mixing fresh combustion emissions with inorganic and organic aerosols, the

321 CCN activation spectra of soot was measured using combustion aerosol generated from the APG. The aerosol is likely

322 composed of black carbon and oxidized carbonaceous material (Moore et al. 2014; Durdina et al. 2016). Thus we also

323 refer to carbonaceous aerosol as black carbon mixtures (simply, BC mixtures). The CCN activated fraction data from

324 soot was fit to a singular sigmoidal curve (Fig. 7). There are no plateaus in the activation curve and the single sigmoid

325 fit indicates that the aerosol generated is a homogenous internal mixture. Combustion aerosol activated at a mobility

326 diameter of 133 nm at 2.2% supersaturation. The apparent hygroscopicity of combustion aerosol was κ=0.001, and is

327 consistent with the order of magnitude and kappa values reported for fresh combustion aerosol from diesel engine

328 sources (Fig. 7) (Vu et al., 2015; Moore et al. 2014). It is noted that the apparent hygroscopicity is defined by the

329 electrical mobility diameter that assumes particles are spherical.

330

331

332   **Figure 7.** Combustion aerosol activation curve (SS 2.2%, $d_{p,50}$=133nm, κ=0.001)

333   Next, the influence of modifying externally mixed hygroscopic aerosol fractions with non-hygroscopic BC

334 mixtures was observed. Soot was externally mixed with various concentrations of AS and NaCl in two separate

335 experiments. For each BC mixture, combustion aerosol was introduced to the flow tube and atomized inorganic and

336 organic aerosol (dried with a heated column and silica gel diffusion dryers) was injected. The concentration of

337 inorganic in the flow tube was slowly increased to modify the contribution of soluble material. The CCN counter

338 supersaturation was decreased to 1.1% to observe the impact of the more hygroscopic compounds in the BC mixture.

339   Figure 8 shows the CCN activation of external mixtures of BC with AS and NaCl at S_c = 1.1%. The initial

340 combustion size distribution at the start of the experiment and the modified CCN activation fractions of the aerosol

341 mixtures are presented. The shape of the activation curve provides insight about the sizes of very hygroscopic and

342 non-hygroscopic species. At S_c = 1.1% BC particles, with κ = 0.001, will not theoretically activate below 250 nm and

343   the contribution of externally mixed BC in the size range shown does not contribute much (if any) CCN. The

344   normalized size distribution data show that there are few BC-like particles at small sizes (<50 nm), the majority of

345   particles in this range are inorganic. Thus for both the AS and NaCl external mixtures, the activation diameters derived

346   from a singular fit were consistent with the expected $d_{p50} \leq 50$ nm of the respective inorganic salts. Specifically at

347   S_c=1.1%, AS and NaCl particles activated at 25 and 19 nm respectively (congruent with theoretical dp50 at 24.8 and

348   19.0 nm) At the larger sizes (> inorganic d_{p50}), the BC mixture concentration increased and the CCN/CN was

349   depressed. The combustion aerosol alone is not CCN active at this S_c or size and the depressions are reflective of the

350   non-hygroscopic combustion aerosol fraction in the aerosol sample. Notably, plateaus are dynamic. As the

351   concentration of inorganic salts increase, the increased activated fraction is reflected in the CCN spectra; the plateau

352   heights increase with increasing hygroscopic concentrations. In these particular externally mixed experiments, the

353   initial CCN/CN plateau can be as large as one, subsequently decrease, and then will likely increase to one after the

354   BC critical diameters are reached. BC externally mixed with very hygroscopic material is more CCN active than the

355   soot alone.

356

357

358   **Figure 8.** Combustion aerosols externally mixed with inorganics a) NaCl externally mixed with concentrations

359   modified from 51% to 85% over the course of 60 min b) AS externally mixed with concentrations from 41% to 86%

360   over a course of 75 min. Cross symbols represent the initial size distribution of the combustion aerosol.

361

362   Succinic acid (SA) was mixed with combustion aerosol to investigate the external to internal mixing and transition of

363   slightly hygroscopic organic with non-hygroscopic insoluble but wettable aerosols. The laboratory system mimics

364   observed increases in SOA mass fractions on combustion aerosols during atmospheric aging. The SA was introduced

365   to the flow tube at various concentrations, followed by the combustion aerosol from the APG, under dry externally

366   mixed conditions and bimodal size distribution peaks were observed (Figure 9).

367

368   The normalized size distributions of the aerosol leaving the flow tube are presented. The initial soot size distribution

369   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

370   combustion aerosol and SA, the initial point of activation agrees with that of succinic acid where SA aerosols all

371 activate. After a mobility diameter, $dp > 50$ nm, the concentration of combustion aerosol in the mixture increases

372 and the CCN/CN ratio is < 0.2, indicative of a lower SA concentration relative to the non-activated BC concentration.

373

374 To induce internal mixing, active heating was again turned off for the atomized aerosol source. Again, internal mixing

375 was promoted and the multiple activation curves converge into a single sigmoid for the BC and SA system. This is

376 consistent with the AS/SA experiment and previous work that showed a strong influence of insoluble compounds on

377 activation when internally mixed with a more soluble compound. (9) With continued mixing, a shift to larger activation

378 diameters was observed towards the end of the experiment (scan 93) and there was a slight depression in the plateau

379 of the CCN spectra.

380

381 The data suggests that only a small amount of soluble inorganic and organic material is required to make the soot

382 more active than that observed alone, especially as the aerosol becomes more internally mixed.

383

384

385 **Figure 9.** a) Time series of CCN/CN activated fractions of Succinic Acid (SA) and combustion aerosol (BC)

386 mixture in flow tube. b) ~~Succinic Acid~~The CCN/CN activated fraction (closed triangles) of SA and ~~Combustion~~

387 ~~Aerosol~~BC mixtures for ~~Scans~~particle distribution scans 24, 45, 54, 73, and 94. Aerosol water is introduced at ~

388 scan 70 to promote internal mixing. Cross symbols show the particle size distribution mixed aerosol.

389

5. Conclusion

391 Results confirm that the experimental CCN activation curves of aerosol provide insight into to the type of mixing

392 (e.g. internal vs. external) and the various levels of hygroscopicities that are chemically representative. Modifications

393 in the concentrations of externally mixed non-hygroscopic aerosols are reflective of the CCN activated concentrations.

394 This is consistent with CCN spectra observed in ambient studies, which have attributed ~~increases~~observations in CCN

395 activation plateau ~~height~~heights less than one to the ~~extent~~contributions of ~~internal mixing of hygroscopic materials~~

396 ~~on~~ externally mixed and inactivated (typically non-hygrosocopic black carbon) aerosols. This work adds to the existing

397 body of CCN literature and demonstrates that the transition from external to internal mixtures can be mimicked in

398 controlled laboratory experiments and observed in CCN data. If one accounts for multiple-sigmoid analysis in

399 experimental CCN activation data, the CCN behavior of known hygroscopic compound mixtures (e.g., ammonium

400 sulfate, sodium chloride, succinic acid) agrees well with traditional Köhler theory. However, more work is needed to

401 explore mixtures of hygroscopic material particularly with wettable and non-hygroscopic aerosol. Here, as the non-

402 hygroscopic combustion aerosol becomes internally mixed with the inorganic and organic material, the CCN activity

403 of the combustion aerosol is modified. The data here, with recent publications (Altaf et al., 2018; Ye at al., 2016),

404 suggest that aerosol water is a significant factor in promoting mixing and can be used to modify mixing states. ~~The~~

405 ~~aerosols~~To our knowledge, the technique provided here is the first to show aerosol population transitions from external

406 to internally mixed states in a laboratory environment and thus the technique can be applied to understand additional

407 aerosol properties (e.g., optical, gas-phase uptake, subsaturated droplet growth, etc.) of known compounds that can

408 modify particle mixing states. The aerosols studied here maintained an external mixture under dry conditions; CCN

409 activation curves plateaued and remained constant. However, turning off the heater promoted internal mixing and the

410 activation curves were observed to converge. These experiments with known compounds validate that the aerosol

411 mixing state can be observed in CCN activation data and can ~~thus be revisited in complex~~be applied to aerosol data

412 sets to understand the extent of mixing. The results confirm that CCN counters and CCN analysis should be used in

413 future studies to quantify the extent of mixing of ambient particles. The results are critical to understanding other

414 factors important to the direct and indirect radiative contributions of atmospheric particles.

415

Acknowledgments

Appendix

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

Figure A2. Atomized AS CCN calibrations. In both cases the aerosol is atomized and passed through a silica gel

diffusion dryer. The aerosol passes through a heated column before the drier in Dp_Heater on data and does no in

Dp_Heater off. The critical activation mobility diameters (μm) for heated-dried vs. non-heated dried atomized

sample streams agree. The two-tailed P-value is 0.87.

References

Formatted: Font: Times

440 1. Abbatt, J. P. D., Broekhuizen, K., and Kumar, P. P.: Cloud condensation nucleus activity of internally mixed

441 ammonium sulfate/organic acid aerosol particles, Atmos. Environ., 39, 4767-4778, 2005.

442 2. Altaf, M. B. Dutcher, D D. Raymond,T. M and Freedman, M. A.: Effect of Particle Morphology on Cloud

443 Condensation Nuclei Activity, ACS Earth and Space Chem., 10.1021/acsearthspacechem.7b00146. 2018.

444 3. Asa-Awuku, A., Moore, R., Nenes, A., Bahreini, R., Brock, C. A., Middlebrook, A., Holloway, J., Ryerson, T.,

445 Jimenez, J., DeCarlo, P., Hecobian, A., Weber, R., Tanner, D., Stickel, R., and Huey L. G., 'Airborne Cloud

446 Condensation Nuclei Measurements during the 2006 Texas Air Quality Study, J. Geophys. Res., 116,

447 doi:10.1029/2010JD014874. 2011.

448 4. Bhattu, D., Tripathi, S. N., and Chakraborty, A.: Deriving aerosol hygroscopic mixing state from size-resolved

449 CCN activity and HR-ToF-AMS measurements, Atmos. Environ., 142, 57-70, 2016.

450   5. Bilde, M. and Svenningsson, B.: CCN activation of slightly soluble organics: The importance of small amounts

451   of inorganic salt and particle phase, Tellus, 56B, 128–134, 2004.

452   6. Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan,

453   S., Karcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M.,

454   Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser,

455   J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.:

456   Bounding the role of black carbon in the climate system: A scientific assessment. J. Geophys. Res., 118, 5380-

457   5552, 2013.

458   7. Bougiatioti, A., Nenes, A., Fountoukis, C., Kalivitis, N., Pandis, S. N., and Mihalopoulos, N.: Size-resolved CCN

459   distributions and activation kinetics of aged continental and marine aerosol, Atmos. Chem. Phys., 11, 8791-8808,

460   doi:10.5194/acp-11-8791-2011, 2011.

461   8. Broekhuizen, K., Kumar, P. P., and Abbatt, J. P. D.: Partially soluble organics as cloud condensation nuclei: Role

462   of trace soluble and surface active species, Geophys. Res. Lett., 31, doi:10.1029/2003GL018203, 2004.

463   9. Cai, M., Tan, H., Chan, C. K., Qin, Y., Xu, H., Li, F., Schurman, M. I., Liu, L. and Zhao, J.: The size-resolved

464   cloud condensation nuclei (CCN) activity and its prediction based on aerosol hygroscopicity and composition in

465   the Pearl Delta River (PRD) region during wintertime 2014, Atmos. Chem. Phys., 18(22), 16419–16437, 2018.

466   10. Chen, L., Li, Q., Wu, D., Sun, H., Wei, Y., Ding, X., Chen, H., Cheng, T. and Chen, J.: Size distribution and

467   chemical composition of primary particles emitted during open biomass burning processes: Impacts on cloud

468   condensation nuclei activation, Sci. Total Environ., 674, 179–188, 2019.

469   11. Ching, J., Riemer, N. and West, M.: Black carbon mixing state impacts on cloud microphysical properties: Effects

470   of aerosol plume and environmental conditions, J. Geophys. Res.,-Atmos, 121(10), 5990–6013, 2016.

471   12. Crosbie, E., Youn, J.-S., Balch, B., Wonaschütz, A., Shingler, T., Wang, Z., Conant, W. C., Betterton, E. A. and

472   Sorooshian, A.: On the competition among aerosol number, size and composition in predicting CCN variability:

473   a multi-annual field study in an urbanized desert, Atmos. Chem. Phys., 15, 6943–6958, 2015.

474   13. Cruz, C. N. and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of

475   inorganic atmospheric aerosol, J. Geophys. Res., 103, 13111-13123, 1998.

| Formatted: Font: Times |
| Formatted: Font: 10 pt |
| Formatted: Font: 10 pt, Not Italic |
| Formatted: Font: 10 pt |
| Formatted: Font: Times, 10 pt |
| Formatted: Font: 10 pt |

14. Cubison, M. J., Ervens, B., Feingold, G., Docherty, K. S., Ulbrich, I. M., Shields, L., Prather, K., Hering, S. and Jimenez, J. L.: The influence of chemical composition and mixing state of Los Angeles urban aerosol on CCN number and cloud properties, Atmos. Chem. Phys., 8(18), 5649–5667, 2008.

15. 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.

16. 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.

17. 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.

18. 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.

19. Farmer, D. K., Cappa, C. D., & Kreidenweis, S.: Atmospheric processes and their controlling influence on cloud condensation nuclei activity." Chemical Reviews 115.10, 4199-4217, 2015. doi.org/10.1021/cr5006292

19.20. 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.

20.21. 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.

21.22. Hameri , K. , Charlson , R. and Hansson , H. C.: Hygroscopic Properties of Mixed Ammonium Sulfate and Carboxylic Acids Particles, AIChE J., 48, 1309–1316, 2002.

22.23. 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.

Formatted: Font: Times, 10 pt

504 23.24.   Jurányi, Z., Tritscher, T., Gysel, M., Laborde, M., Gomes, L., Roberts, G., Baltensperger, U. and

505   Weingartner, E.: Hygroscopic mixing state of urban aerosol derived from size-resolved cloud condensation nuclei

506   measurements during the MEGAPOLI campaign in Paris, Atmos. Chem. Phys., 13(13), 6431–6446, 2013.

507 24.25.   Kim, N., Park, M., Yum, S. S., Park, J. S., Shin, H. J. and Ahn, J. Y.: Impact of urban aerosol properties on

508   cloud condensation nuclei (CCN) activity during the KORUS-AQ field campaign, Atmos. Environ., 185, 221–

509   236, 2018.

510 25.26.   King, S. M., Rosenoern, T., Shilling, J. E., Chen, Q. and Martin, S. T.: Cloud condensation nucleus activity

511   of secondary organic aerosol particles mixed with sulfate, Geophys. Res. Lett., 34(24), 3589, 2007.

512 26.27.   Koehler, K. A., DeMott, P. J., Kreidenweis, S. M., Popovicheva, O. B., Petters, M. D., Carrico, C. M.,

513   Kireeva, E. D., Khokhlova, T. D. and Shonija, N. K.: Cloud condensation nuclei and ice nucleation activity of

514   hydrophobic and hydrophilic soot particles, Phys. Chem. Chem. Phys., 11(36), 7906–7920, 2009.

515 27.28.   Kuwata, M. and Kondo, Y.: Dependence of size-resolved CCN spectra on the mixing state of nonvolatile

516   cores observed in Tokyo. J. Geophys. Res. 113, D19202, 2008.

517 28.29.   Lammel, G. and Novakov, T.: Water Nucleation Properties of Carbon-Black and Diesel Soot Particles,

518   Atmos. Environ., 29(7), 813–823, 1995.

519 29.30.   Lance, S., Raatikainen, T., Onasch, T., Worsnop, D. R., Yu, X.Y., Alexander, M. L., Stolzenburg, M. R.,

520   McMurry, P. H., Smith, J. N., and Nenes, A.: Aerosol mixing-state, hygroscopic growth and cloud activation

521   efficiency during MIRAGE 2006, Atmos. Chem. Phys. Discuss., 12, 15709–15742, doi:10.5194/acpd-12-15709-

522   2012, 2012.

523 30.31.   Lance, S., Onasch, T., Warsnop, D., Yu, X. Y., Alexander, L., Stolzenberg, M., McMurry, P., Smith, J.N.,

524   Nenes., A.: Aerosol Mixing-State and Cloud Activation Efficiency during the MILAGRO Campaign, 2013,

525   Atmos. Chem. Phys., 13, 5049-5062, doi:10.5194/acp-13-5049-2013, 2013.

526 31.32.   Liu, D., Allan, J., Whitehead, J., Young, D., Flynn, M., Coe, H., McFiggans, G., Fleming, Z. L., and Bandy,

527   B.: Ambient black carbon particle hygroscopic properties controlled by mixing state and composition, Atmos.

528   Chem. Phys., 13, 2015-2029, doi:10.5194/acp-13-2015-2013, 2013.

529 32.33.   Mahish, M., Jefferson, A. and Collins, D. R.: Influence of Common Assumptions Regarding Aerosol

530   Composition and Mixing State on Predicted CCN Concentration, Atmosphere , 9(2), 54, 2018.

Formatted: Font: Times

531 33.34.   Mallet, M. D., Cravigan, L. T., Milic, A., Alroe, J., Ristovski, Z. D., Ward, J., Keywood, M., Williams, L.

532   R., Selleck, P. and Miljevic, B.: Composition, size and cloud condensation nuclei activity of biomass burning

533   aerosol from northern Australian savannah fires, Atmos. Chem. Phys., 17(5), 3605–3617, 2017.

534 34.35.   Mamakos, A., Khalek, I., Giannelli, R. and Spears, M.: Characterization of Combustion Aerosol Produced

535   by a Mini-CAST and Treated in a Catalytic Stripper, Aerosol Science and Technology, 47(8), 927–936,

536   doi:10.1080/02786826.2013.802762, 2013.

537 35.36.   Maricq, M. M. and Matti Maricq, M.: Examining the Relationship Between Black Carbon and Soot in Flames

538   and Engine Exhaust, Aerosol Science and Technology, 48(6), 620–629, doi:10.1080/02786826.2014.904961,

539   2014.

540 36.37.   McMeeking, G. R., Good, N., Petters, M. D., McFiggans, G. and Coe, H.: Influences on the fraction of

541   hydrophobic and hydrophilic black carbon in the atmosphere, Atmos. Chem. Phys., 11(10), 5099–5112, 2011.

542 37.38.   Meng, J. W., Yeung, M. C., Li, Y. J., Lee, B. Y. L. and Chan, C. K.: Size-resolved cloud condensation nuclei

543   (CCN) activity and closure analysis at the HKUST Supersite in Hong Kong, Atmos. Chem. Phys., 14(18), 10267–

544   10282, 2014.

545 38.39.   Moore, R. H., Nenes., A. and Medina., J.: Scanning Mobility CCN Analysis - A Method for Fast

546   Measurements of Size-Resolved CCN Distributions and Activation Kinetics, Aerosol Sci. Technol., 44, 861-871,

547   2010.

548 39.40.   Moore, R. H., Cerully, K., Bahreini, R., Brock, C. A., Middlebrook, A. M. and Nenes, A.: Hygroscopicity

549   and composition of California CCN during summer 2010, J. Geophys. Res., 117, D00V12,

550   doi:10.1029/2011JD017352, 2012.

551 40.41.   Moore, R. H., Raatikainen, T., Langridge, J. M., Bahreini, R., Brock, C. A., Holloway, J. S., Lack, D. A.,

552   Middlebrook A. M., Perring, A. E., Schwarz, J. P., Spackman, J. R., and Nenes, A.: CCN Spectra, Hygroscopicity,

553   and Droplet Activation Kinetics of Secondary Organic Aerosol Resulting from the 2010 Deepwater Horizon Oil

554   Spill, Env. Sci. Tech., 26, 3093-3100, 2012.

555 41.42.   Moore, R. H., Ziemba, L. D., Dutcher, D., Beyersdorf, A. J., Chan, K., Crumeyrolle, S., Raymond, T. M.,

556   Thornhill, K. L., Winstead, E. L. and Anderson, B. E.: Mapping the Operation of the Miniature Combustion

557   Aerosol Standard (Mini-CAST) Soot Generator, Aerosol Science and Technology, 48(5), 467–479,

558   doi:10.1080/02786826.2014.890694, 2014.

559   42.43.   Padró, L. T., Asa-Awuku, A., Morrison, R., and Nenes, A.: Inferring thermodynamic properties from CCN

560   activation experiments: single-component and binary aerosols, Atmos. Chem. Phys., 7, 5263-5274,

561   doi:10.5194/acp-7-5263-2007, 2007.

562   43.44.   Padró, L. T., Moore, R. H., Zhang, X., Rastogi, N., Weber, R. J., and Nenes, A.: Mixing state and

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

564   Atmos. Chem. Phys., 12, 10239-10255, doi:10.5194/acp-12-10239-2012, 2012.

565   44.45.   Paramonov, M., Aalto, P. P., Asmi, A., Prisle, N., Kerminen, V.-M., Kulmala, M. and Petäjä, T.: The analysis

566   of size-segregated cloud condensation nuclei counter (CCNC) data and its implications for cloud droplet

567   activation, Atmos. Chem. Phys., 13(20), 10285–10301, 2013.

568   45.46.   Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud

569   condensation nucleus activity – Part 2: Including solubility, Atmos. Chem. Phys., 8, 6273-6279, doi:10.5194/acp-

570   8-6273-2008, 2008.

571   46.47.   Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud

572   condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, doi:10.5194/acp-7-1961-2007, 2007.

573   47.48.   Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, 954, Kluwar Acad., Norwell

574   Mass., 1997.

575   48.49.   Pinho, C. E. L., João M P, Ferreira, V., Pilão, R. and Pinho, C.: Influence of Burner Geometry on Flame

576   Characteristics of Propane-Air Mixture: Experimental and Numerical Studies, Defect and Diffusion Forum, 273-

577   276, 162–167, doi:10.4028/www.scientific.net/ddf.273-276.162, 2008.

578   49.50.   Riemer, N., Ault, A. P., West, M., Craig, R. L. and Curtis, J. H.: Aerosol Mixing State: Measurements,

579   Modeling, and Impacts, Reviews of Geophysics, doi:10.1029/2018rg000615, 2019.

580   50.51.   Rojas, L., Peraza, A. and Ruette, F.: Aging Oxidation Reactions on Atmospheric Black Carbon by OH

581   Radicals. A Theoretical Modeling Study, J. Phys. Chem. A, 119(52), 13038–13047, 2015

582   51.52.   Roberts, G. C. and Nenes, A.: A Continuous-Flow Streamwise Thermal-Gradient CCN Chamber for

583   Atmospheric Measurements, Aerosol Sci. Technol., 35, 206-2011, doi: 10.1080/027868290913988, 2005.

584   52.53.   Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., Poschl, U.: Calibration and

585   measurement uncertainties of a continuous-flow cloud condensdation nuclei counter (DMT-CCNC): CCN

586   Activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, Atmos. Chem.

587   Phys., 8, 1153-1179, doi: 10.5194/acp-8-1153-2008, 2008.

588   53.54.   Sánchez Gácita, M., Longo, K. M., Freire, J. L. M., Freitas, S. R. and Martin, S. T.: Impact of mixing state

589   and hygroscopicity on CCN activity of biomass burning aerosol in Amazonia, Atmos. Chem. Phys., 17(3), 2373-

590   2392, 2017.

591   54.55.   Saxena, P., Hildemannm, L. M.: Water-Soluble organics in atmospheric particles: A critical review of the

592   litereature and application of thermodynamics to identify candidate compounds, J. Atmos. Chem., 24, 57-109,

593   1996.

594   55.56.   Sánchez Gácita, M., Longo, K. M., Freire, J. L. M., Freitas, S. R. and Martin, S. T.: Impact of mixing state

595   and hygroscopicity on CCN activity of biomass burning aerosol in Amazonia, Atmos. Chem. Phys., 17(3), 2373-

596   2392, 2017.

597   56.57.   Seinfeld, J. H. and Pandis, S. N.: Atmopsheric Chemistry and Physics, John Wiley, New York, 1998.

598   57.58.   Seong, H. J. and Boehman, A. L.: Studies of soot oxidative reactivity using a diffusion flame burner,

599   Combustion and Flame, 159(5), 1864–1875, doi:10.1016/j.combustflame.2012.01.009, 2012.

600   58.59.   Shulman, M. L., Jacobson, M. C., Charlson, R. J., Synovec, R. E., and Young, T. E.: Dissolution behavior

601   and surface tension effects of organic compounds in nucleating cloud droplets, Geophys. Res. Lett., 23, 277–280,

602   1996.

603   59.60.   Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M. O.,

604   and Poschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol

605   particle mixing state with regard to hygroscopic growth and CCN activation. Atmos. Chem. Phys., 10, 7489-

606   7503, 2010.

607   60.61.   Spracklen, D. V., Carslaw, K. S., Poschl, U., Rap, A. and Forster, P. M.: Global cloud condensation nuclei

608   influenced by carbonaceous combustion aerosol, Atmos. Chem. Phys., 11(17), 9067–9087, 2011.

609   61.62.   Stevens, R. and Dastoor, A.: A Review of the Representation of Aerosol Mixing State in Atmospheric

610   Models, Atmosphere , 10(4), 168, 2019.

611   62.63.   Sullivan R. C., Moore M., Petters, M. D., Kreidenweis S. M., Roberts G. C., and Prather, K. A.: Effect of

612   chemical mixing state on the hygroscopicty and cloud nucleating properties of calcium mineral dust particles,

613   Atmos. Chem. Phys., 9, 3303-3316, 2009.

Formatted: Font: Times

614   63.64.   Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S.,

615   Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol

616   particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6, 1937-1952,

617   doi:10.5194/acp-6-1937-2006, 2006.

618   64.65.   Vu, D., Short, D., Karavalakis, G., Durbin, T. D., and Asa-Awuku, A.: Integrating cloud condensation nuclei

619   predictions with fast time resolved aerosol instrumentation to determine the hygroscopic properties of emissions

620   over transient drive cycles, Aerosol Sci. Technol., 49, 1149-1159, 2015.

621   65.66.   Wang, J., Cubison, M. J., Aiken, A. C., Jimenez, J. L. and Collins, D. R.: The importance of aerosol mixing

622   state and size-resolved composition on CCN concentration and the variation of the importance with atmospheric

623   aging of aerosols, Atmos. Chem. Phys., 10(15), 7267–7283, 2010.

624   66.67.   Weingartner, E., Burtscher, H. and Baltensperger, U.: Hygroscopic properties of carbon and diesel soot

625   particles, Atmospheric Environment, 31(15), 2311–2327, doi:10.1016/s1352-2310(97)00023-x, 1997.

626   67.68.   Wex, H., McFiggans, G., Henning, S., and Stratmann, F.: Influence of the external mixing state of

627   atmospheric   aerosol   on   derived   CCN   number   concentrations,   Geophys.   Res.   Lett.,   37,

628   doi:10.1029/2010GL043337, 2010.

629   68.69.   Winkler, P.: The growth of atmospheric aerosol particles as a function of the relative humidity—II. An

630   improved concept of mixed nuclei, J. Aerosol Sci., 4(5), 373–387, 1973.

631   69.70.   Ye, Q., Robinson, E. S., Ding, X., Ye, P., Sullivan, R., and Robinson, N.: Mixing of secondary organic

632   aerosols versus relative humidity, Proc. Natl. Acad. Sci. U. S. A., 113, 12649-12654, 2016.

633   70.71.   Zaveri, R. A., Barnard, J. C., Easter, R. C., Riemer, N. and West, M.: Particle-resolved simulation of aerosol

634   size, composition, mixing state, and the associated optical and cloud condensation nuclei activation properties in

635   an   evolving   urban   plume,   J.   Geophys.   Res.   D: Atmos.,   115(D17)   [online]   Available   from:

636   https://onlinelibrary.wiley.com/doi/pdf/10.1029/2009JD013616, 2010.

Responses to Report #4:

Vu et al. present measurements of CCN activity for externally and internally mixed particles. The subject is of relevance to study, since several studies report a significant sensitivity to the mixing state of CCN aerosol in atmospheric models. The manuscript has been submitted to a technical journal, but there is little focus on an appropriate and detailed characterization of any technical advances. The choice of characterizing the experimental system mainly by CCN spectra does not seem appropriate, and the interpretation of results can in some cases not be justified by the data presented. The concluding statements appear trivial and are not novel – which in principle is acceptable for a technical paper. However, as described above, there is not a strong focus on the technical aspects in this manuscript. In general, the manuscript is not well written – there are very many examples of unclear formulations. There is a lack of many basic details regarding the experimental approach. Several of the choices made and the argumentation (and lack of argumentation) presented by the authors appear questionable.

I recommend that this manuscript is rejected.

Below, only a few examples of major issues are described. Addressing those issues alone would not qualify the manuscript for publication.

One major issue with this study is that succinic acid particles are used to create internally and externally mixed particles. Succinic acid (SA) is known to evaporate from hydrated aerosol particles (Riipinen et al., 2006) as well as from dry aerosol particles at room temperature (Wex et al., 2007). Hence, the choice of using succinic acid in aerosol mixtures for CCN studies introduces significant issues, which turn further pronounced when a heating step is applied.

Vu et al. claim that 'very' dry SA particles remain externally mixed with other aerosol particles until a preheating step is removed resulting in dry SA particles – and then homogeneous internally mixed particles occur in their flow tube. The authors do not present a reasonable explanation for such unexpected behavior. However, it is clear that this interpretation cannot be justified from the data presented in Fig. 9. As long as the pre-heating step is applied, the SA particles seem to be dominated by a mode centered near a mobility diameter of ~20 nm (e.g. scan 54). When the preheating is turned off, then the resulting particle number size distribution has a clear maximum near 80-85 nm decreasing significantly towards 130 nm (e.g. scan 73), where the soot particle size distribution supposedly has a maximum. A reasonable explanation for the behavior is a transition from very pronounced evaporation of SA particles, to a somewhat lower evaporation of SA particles, which leads to the observed transition in the CCN spectra and dominance of SA in the size range studied.

Hence, the interpretation of the behavior of the experimental system presented does not seem appropriate. It would be meaningful to characterize the system with more well-behaved substances and also with additional instrumentation more sensitive to the mixing state than a CCNC setup. Furthermore, the system should be characterized with more substances, if indeed the system behavior is very sensitive to the aerosol RH, as claimed by the authors.

The issues described above also influence the interpretation and use of results presented for internally mixed SA-NaCl particles as well as the externally mixed SA-ammonium sulfate particles.

⇨ The effects of heating on semi-volatile succinic acid particles is interesting but was not discussed because we did not observe evidence of potential evaporation affecting our SA and AS results. We expand this explanation with the points below.

⇨ For example, In Figure 4, the effects on the CCN activation curve of SA and AS are presented. When heating is on, distinct plateaus (below 1) are observed indicating that SA is present and contributes to a fraction of the aerosol at those smaller sizes. It should be emphasized that the heating of concern occurs during aerosol generation. The subsequent aerosol that remains is then characterized for CCN activity. The plateau below one is an indication of multiple components at the given sizes. Additionally, kappa is a particle intrinsic property; that is regardless of particle size distribution, kappa hygroscopicity is a reflection of the chemical composition of particles. Simply stated, ten 100nm particles will have the same hygroscopicity as one thousand 50 nm particles. Even if the distributions change (if the 50 nm particles evaporate), the hygroscopicity of the component should stay the same. When two sigmoids are applied in our data sets, we correctly measure the kappa of the two distinct components. If all the SA was evaporated, then the critical activation diameters and kappa values would look entirely like AS.

⇨ It is noted that particle evaporation has the potential to modify the volume fraction of a particle at a given size. That is for external mixtures, the plateau height will likely be higher for the more hygroscopic and less volatile material. Figure 6 shows that the AMS measured fraction of potentially evaporated SA/AS mixtures agrees reasonably well with the fraction estimated from the CCN at different supersaturations. For an internal mixture, the asymptote equals 1 and if the size resolved contribution of each component is known, there is a shift in the CCN activation from left to right (as is observed in Figure 3). Our estimates of the volume fraction from kohler theory agree with the known quantities used to make the solution. These particles were also heated during particle activation. Again, we see little evidence of the effects of succinic acid evaporation in our data set. In the transition mixing state experiments from external to internal, we do not have single-particle information and thus cannot fully quantify the volume fraction at each size. The reported CCN activation curve and resulting kappa values during the transition from external to internal also agree with theory. That is the external mixture agrees with AS and SA theoretical values and the internal mixtures is somewhere between the two, again suggesting that SA is present and has not completely evaporated during the measurement. We have provided some additional discussion to address concerns about volatile species and the coagulation of particles.

⇨ In Figure 9, the changes in activation curve are consistent with the transition from external to internally mixed aerosol. SA (whether partially evaporated) is present and observed in the data set. The change in size distributions of SA does not change its inherent hygroscopicity. The concern with evaporation should be most relevant for the externally mixed case but as pointed out by the reviewer there are particles at 20nm present. Once heating is turned off, more SA could be present. However, single particle measurements are required to quantify the particle volumes at activation for the transition to internally mixed aerosols. We do not have those measurement capabilities. The utility of the work here shows that CCN data may be used to observe the mixing state and can be used to estimate theoretical contributions in the future.