

## Interactive comment on “External and Internal CCN Mixtures: Controlled Laboratory Studies of Varying Mixing States” by Diep Vu et al.

### Anonymous Referee #2

The manuscript by Vu et al. discusses about the experimental method and data analysis for CCN activity of externally mixed particles. Although the technical approach sounds reasonable, the reviewer is skeptical about the novelty. I suggest the authors to significantly improve the manuscript by appropriately referring other papers so that the readers will be able to understand the significance of the manuscript better.

Major comments:

L68 ‘However, dynamic changes in particle mixing states and subsequent treatment of CCN measurement and analysis have not been readily observed and studied in depth.’ I disagree with the statement. A number of papers has been published about the topic in the last decade ( e.g., Kuwata and Kondo 2008; Su et al. 2010). I suggest the authors to conduct intensive literature search carefully again.

→ We have added the suggested references.

→ We have modified the sentence to read “However, dynamic changes in particle mixing states and subsequent treatment of CCN measurement and analysis have not been readily observed and studied in depth **under controlled laboratory conditions**”.

→ We agree with the reviewer that there have been many studies (particularly field studies) that have explored changes in aerosol mixing state and CCN. Kuwata and Kondo 2008 measured ambient air in Tokyo and infer the mixing state properties of the ambient aerosol with subsequent behaviour on CCN. Su et al. 2010 brilliantly develop theoretical models to describe the CCN activation of mixed population and then validate the models with aerosol measurements taken in Beijing, China. A thorough literature review will show that the majority of these papers (like the ones suggested) apply mixing state assumptions to ambient data sets. To our knowledge, we are the only manuscript to show changes in laboratory CCN with controlled *dynamic* changes in mixing state aerosol population (*i*) from external to internal mixtures and *ii*) not to be confused with aerosol-phase states or changes in aerosol coatings). This is the novelty of the presented technique. Previous papers (dating back to the early 70’s) have provided appropriate mixing, size-resolved composition theory and have shown the activation of laboratory externally mixed aerosol and internally mixed systems, separately. We have yet to find a CCN paper that has controlled and measured the dynamic change from external to internal mixtures in the laboratory. We apply the technique to CCN but the method can also be extended to understand optical, sub-saturated, and other physicochemical characteristics. We regret that this uniqueness did not come through in the first revision of the paper and thus we have spent considerable effort emphasizing the importance of the new technique presented in the revised manuscript.

→ The following text has been revised to include additional references as follows.

Knowledge of the mixing state and the chemical composition can greatly improve CCN predictions and has been the focus of several studies (e.g., but not limited to [\(Bilde and Svenningsson 2004; Abbatt et al. 2005; Henning et al. 2005; Svenningsson et al. 2006; King et al. 2007; Cubison et al. 2008; Kuwata and Kondo 2008; Zaveri et al. 2010; Su et al. 2010; Wang et al. 2010; Spracklen et al. 2011; Ervens et al. 2010; Asa-Awuku et al. 2011; Liu et al. 2013; Jurányi et al. 2013; Paramonov et al. 2013; Padró et al. 2012; Moore et al. 2012; Meng et al. 2014; Bhattu and Tripathi 2015; Almeida et al. 2014; Schill et al. 2015; Crosbie et al. 2015; Che et al. 2016; Ching et al. 2016; Mallet et al. 2017; Sánchez Gácita et al. 2017; Cai et al. 2018; Schmale et al. 2018; Mahish et al. 2018; Kim et al. 2018; Chen et al. 2019; Stevens and Dastoor 2019\)](#)

L78 '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.'; L283' the contributions of BC to aerosol-cloud interactions at varied mixing states is not well known or understood' Even though there might be only a limited number of studies, some researchers have conducted laboratory experiments/atmospheric observations on CCN activity of BC particles. I suggest the authors to conduct literature search carefully again. For example, there are some description about it in a review paper of BC particles (Bond et al. 2013).

→ We have updated the references and provided the following text.

→ Previous work investigating the contribution of BC to aerosol-cloud interactions at various mixing states has been studied (e.g., but not limited to Bond et al., 2013 and references therein, ([Lammel and Novakov 1995](#); [Novakov and Corrigan 1996](#); [Weingartner et al. 1997](#); [Dusek et al. 2006](#); [Kuwata and Kondo 2008](#); [Koehler et al. 2009](#); [Bond et al. 2013](#); [McMeeking et al. 2011](#); [Liu et al. 2013](#); [Rojas et al. 2015](#))

Minor comments:

Title 'CCN Mixtures' It is not clear to me how this word is defined. Please clarify it, or consider to use other expressions.

→ The title has been changed to Cloud Condensation Nuclei (CCN).

→ 'CCN mixtures' is simply a mixture of CCN. It refers to some of the earliest work in the field by Winkler 1973 that accounts for multiple chemical compositions in aerosol. Specifically, this definition of aerosol mixture refers to a property of the overall particle population not to the property of an individual particle (Riemer et al., 2019; Winkler, 1973). Recent studies have modified this definition to include changes in aerosol physical phase-state and also changes in individual particles. We have provided more detail in the revised manuscript and have also added the recent and comprehensive review of Riemer et al 2019 to clarify in the text.

#### References added

→ Winkler, Peter. "The growth of atmospheric aerosol particles as a function of the relative humidity—II. An improved concept of mixed nuclei." *Journal of Aerosol Science* 4.5 (1973): 373-387.

→ Riemer, N., Ault, A. P., West, M., Craig, R. L., & Curtis, J. H. (2019). Aerosol Mixing State: Measurements, Modeling, and Impacts. *Reviews of Geophysics*, 57. <https://doi.org/10.1029/2018RG000615>

L60 'the CCN mobility diameter data sets' What does this word mean? Please clarify it.

→ The text has been revised to:

To help minimize the complexity in characterizing aerosol hygroscopic and CCN activation properties, CCN data analysis has traditionally been simplified by assuming that *i*) the aerosols share a similar or uniform hygroscopicity over a particle size distribution, *ii*) the CCN particle size can be described by the electrical mobility diameter, *iii*) CCN consists of few multiply charged aerosols and *iv*) all CCN active aerosols readily dissolve at activation.

L107 'Five aqueous solutions of succinic acid and NaCl with molar ratios of 100:0, 87:13, 69:31, 43:57, 0:100 were aerosolized using a single atomizer' I wondered if potential evaporation of

succinic acid in the experimental setup could influence the final molar ratios of the compounds. Do the authors have any comments on it?

→ We do not have a comment. Our data shows that the calculated molar solutions agree with predicted values to within 10% of their kohler prediction. Any potential evaporation that could occur is not reflected in the CCN values obtained from the internal mixture studies.

L112 ‘As conditions (e.g., but not limited to, residence time, temperature, pressure, relative humidity) change in a flow tube,’ I wondered how well these parameters were controlled during this study. Please clarify.

→ The residence time, temperature, pressure, and relative humidity were conducted at ambient room conditions. Typical conditions were dry relative to any experiments conducted with aerosol water. Pressure and temperature were expected to be consistent from test to test (air conditioned laboratory with little temperature fluctuations, and minimal changes in barometric pressure). The above has been inserted and clarified in the text.

L170 ‘For this study the first curve is similarly defined as the hygroscopic externally mixed fraction (EMF) with an asymptote, or plateau of  $\alpha$ . The dependence of  $\alpha$  varies with the presence of mixed components and their respective hygroscopicities. Thus we evaluate  $\alpha$  for controlled compositions and compare how representative they are of the known fractions of mixtures.’ It may be a good idea to add a figure to explain about the concept.

→ Please refer to figure 2. In the previous revision, we include this concept figure to explain the difference in plateaus of externally and internally mixed data.

L241 ‘After one hour in the flow tube’ Does it mean that particles stayed in the flow tube for one hour? Please clarify.

→ this is in reference to 1 hr after initial injection. Text has been modified from ‘After one hour in the flow tube’ to ‘One hour after initial injection into the flow tube’ to clarify this.

L257 ‘The mass size distribution was then converted to number size distribution’ How does the error/uncertainty for measuring mass-size distribution influence the estimated number size-distribution? It would be ideal to conduct sensitivity study about it.

→ Unfortunately, this was beyond the scope of this study; independent aerosol mass measurement was not available. However, with known chemical composition the mass distribution was converted to a number distribution using literature density values to yield a number value to conduct a CCN analysis. Although there is some error attributed to this method, it is consistently done from test to test.

L282 ‘Combustion Aerosol, hereon also referred to as Black Carbon (BC)’ Combustion aerosol is not equivalent as black carbon.

→ Yes, combustion aerosol is not all Black Carbon (BC). We have clarified that BC in this paper is short for black carbon mixtures or BC containing particles and have revised the text in multiple places as follows:

→ Combustion aerosol or soot can form external and internal complex aerosol mixtures. Soot is considered insoluble but wettable (Lammel and Novakov 1995; Moore et al. 2014) and the contributions of Black Carbon containing particles to aerosol-cloud interactions at varied mixing states is not well known or understood (Lammel and Novakov 1995; Novakov and Corrigan 1996; Weingartner et al. 1997; Dusek et al. 2006; Kuwata and Kondo 2008; Koehler et al. 2009; Bond et al. 2013; McMeeking et al. 2011; Liu et al. 2013; Rojas et al. 2015). Thus, the ability of black carbon to mix with inorganic and organic compounds and to observe the extent of mixing as they activate as CCN is of great interest. Prior to investigating the impact of mixing fresh combustion emissions with inorganic and organic aerosols, the CCN activation spectra of soot was measured using combustion aerosol generated from the APG. The aerosol is likely composed of black carbon and oxidized carbonaceous material (Moore et al. 2014; Durdina et al. 2016). Thus we also refer to carbonaceous aerosol as black carbon mixtures (simply, BC mixtures).

**L283 ‘BC is considered insoluble but wettable’ Please show experimental data/cite literature to support the idea.**

→ Previous work (e.g. but not limited to, Lammel and Novakov 1995; Moore et al. 2014) has indicated BC as hydrophobic, but still wettable.

→ It is understood that CCN can be soluble or insoluble but wettable particles - a water film can cover the surface of the aerosol and the activation of the particle is more dependent of the curvature and less of the composition. This is further supported by this study which showed a low activation diameter (fig. 7) for combustion aerosol and thus a low kappa value of approximately 0.001, which is close to 0 - particles that are insoluble but wettable have been characterized with a kappa value of close to 0.

**L288 ‘The single sigmoid fit suggests that the aerosol generated is a homogenous mixture of black and brown carbon.’ The activation curve is very broad. I do not think that such a broad activation curve could be observed if all the particles have exactly the same chemical composition. I wonder what the authors wanted to mean by ‘homogeneous.’ How can the authors make sure that brown carbon existed in the particles they measured? Please demonstrate the evidence for it.**

→ A homogeneous mixture similar chemical compositional fractions across different particle sizes. A homogenous mixture is an internal mixture. The data presented for known compounds illustrated that homogenous (internal) mixtures exhibit singular curves. That is the chemical composition across CCN active sizes is constant and thus the activation is smooth (with no plateau). Externally mixed CCN exhibit plateaus and multiple points of activation. The CCN activation of the soot is a singular curve and thus indicates that the aerosol are internally (homogeneously) mixed.

→ We have removed the word brown carbon and replaced the wording to reflect the more oxidized soot components found in aerosol generated from flame burners.

→ The text is now rewritten as :There are no plateaus in the activation curve and the single sigmoid fit indicates that the aerosol generated is a homogenous internal mixture.

**L292 ‘It is noted that the apparent hygroscopicity does not account for non-spherical**

fractal particles.' I do not understand what this sentence means. Do the authors want to clarify that these particles do not have spherical shape?

→ The apparent hygroscopicity is calculated from the electrical mobility diameter and thus assumes all particles as spherical. Electrical mobility diameter measurement does not take into account non-spherical fractal particles.

→ The text has been changed as follows: It is noted that the apparent hygroscopicity is defined by the electrical mobility diameter that assumes particles are spherical.

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## **Interactive comment on “External and Internal CCN Mixtures: Controlled Laboratory Studies of Varying Mixing States” by Diep Vu et al.**

### **Anonymous Referee #3**

The manuscript represents a method of CCN data analysis for different mixtures of organic and inorganic components of varying mixing states with regards to the observed activation and hygroscopicity. By conducting controlled laboratory experiments of mixing, the transition from external to internal mixtures are effectively mimicked. For mixtures of known hygroscopicity CCN behavior agrees well with traditional Köhler theory. Finally, aerosol water is shown to play a significant role in promoting mixing and can be used to modify mixing states.

The paper is well written and easy to follow, though there are some issues and more thorough discussion should be made in specific sections. A very interesting point of the study is the deconvolution of the activation curves to different sigmoidal curves consistent with those of the different components, as well as the study of the impact of mixing fresh combustion emissions with inorganic and organic aerosols.

Specific comments:

1) More thorough discussion should be made in the study of mixing fresh combustion aerosol with inorganic and organic aerosols. Why is combustion aerosol considered and referred to solely as Black Carbon? Also, the activation curve presented in Fig.07 does not reach an obvious plateau, how can we speak about a “homogeneous mixture of black and brown carbon”? Also I would expect that as a homogenous mixture, the activation curve would be a lot steeper, especially in the larger particle size range. Can you please clarify/comment on this?

→ The combustion aerosol generated by the APG is used as a black carbon surrogate; it was not fully speciated in this study. The miniCAST utilized in the APG has been well characterized in previous work (e.g., Pinho et al. 2008; Seong and Boehman 2012; Mamakos et al. 2013; Maricq and Matti Maricq 2014; Durdina et al. 2016; Moore et al. 2014). The combustion aerosol does contain black and oxidized carbon. Since there are no plateaus in the CCN activation of the soot, (it is a single smooth curve) this suggests that the size-resolved chemical composition is a homogenous (internal) mixture. The slope is indicative of activation at higher mobility diameters where it is known that the transfer function of the DMA is wider, thus contributing to a shallow slope (e.g., Lance et al., 2013).

→ We have revised the text with this added information.

2) A more thorough review of the current literature should be made, as there are relevant studies that are not mentioned. E.g. L69-70 Moore et al., 2012 provide an in-depth analysis of ambient CCN measurements during the 2010 Deepwater Horizon Oil Spill, both studying hygroscopicity vs mixing state and type of size distributions and droplet activation kinetics.

→ We have added the suggested references.

→ Moore et al, 2012 is one of many papers that studies changes of ambient CCN with mixing state. We have included the reference. An extensive literature review will show that there are many papers discuss aerosol mixing state and cloud condensation nuclei. We have added them in this revision. However, The majority of these papers use ambient data sets of unspciated aerosol composition. To our knowledge, we are the only manuscript to show changes in laboratory CCN with controlled changes in mixing state aerosol population. This is the novelty of the presented technique. Previous papers (dating back to the early 70's) have provided the theory and have shown the activation of laboratory externally mixed aerosol and internally mixed systems, separately. We have yet to find a paper that has controlled and measured the change from external to internal in the laboratory. We regret that this uniqueness did not come across in the first revision of the paper and thus we have spent considerable effort emphasizing the importance of the new technique presented in the revised manuscript.

→ The following text has been revised as follows.

Knowledge of the mixing state and the chemical composition can greatly improve CCN predictions and has been the focus of several studies (e.g., but not limited to [\(Bilde and Svenningsson 2004; Abbatt et al. 2005; Henning et al. 2005; Svenningsson et al. 2006; King et al. 2007; Cubison et al. 2008; Kuwata and Kondo 2008; Zaveri et al. 2010; Su et al. 2010; Wang et al. 2010; Spracklen et al. 2011; Ervens et al. 2010; Asa-Awuku et al. 2011; Liu et al. 2013; Jurányi et al. 2013; Paramonov et al. 2013; Padró et al. 2012; Moore et al. 2012; Meng et al. 2014; Bhattu and Tripathi 2015; Almeida et al. 2014; Schill et al. 2015; Crosbie et al. 2015; Che et al. 2016; Ching et al. 2016; Mallet et al. 2017; Sánchez Gácita et al. 2017; Cai et al. 2018; Schmale et al. 2018; Mahish et al. 2018; Kim et al. 2018; Chen et al. 2019; Stevens and Dastoor 2019\)](#))

3) CCN activity also depends on the atmospheric processing as well. L50-51 it is stated that CCN activity is complicated when inorganic salts are internally mixed with a complex organic. It has been shown in filed studies that even within a few hours of processing, hygroscopicity (thus activity as well) becomes more or less constant, e.g. Latham et al., 2013; Bougiatioti et al., 2009. This, to my opinion, should be mentioned.

→ We agree CCN activity and the mixing state of the population depends on atmospheric processing. We have included this in the text. We have added the suggested additional references. Again, our challenge here is that there are a lot of global ambient CCN activity measurements that show changing CCN behaviour. The models to describe changes in CCN mixtures have been validated with ambient measurements. To our knowledge, we are the first to validate with known composition and control subsequent CCN from external to internal mixtures in the laboratory.

Technical corrections:

L109 What type of SMPS, sizing range and of CCNc? It is mentioned in Section 2.3. but it seems to me as missing information to me at that early stage.

→ The instrument specifics were organized into a single section under ‘measurement and instrumentation’. The text has been updated with text directing the reader to refer to section 2.3 for instrument specifications

L293 What do the authors mean by “does not account for non-spherical fractal particles”?

→ The apparent hygroscopicity is calculated from the electrical mobility diameter that assumes particles are spherical. Electrical mobility diameter measurement does not take into account non-spherical fractal particles. We have elaborated this in revised text.

### Fig.05 Some points exhibit huge variation

→ The variation can be attributed to the conversion from AMS mass to number.

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1 | **External and Internal Cloud Condensation Nuclei (CCN) Mixtures: Controlled Laboratory**  
2 | **Studies of Varying Mixing States.**

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19 | **Abstract**

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,  
23 | we develop an experimental method to test and validate the CCN activation of known aerosol chemical composition  
24 | with multicomponent mixtures and varying mixing states, CCN activation curves consisting of one or more  
25 | activation points is presented. Specifically, simplified two component systems of varying hygroscopicity were  
26 | generated under internal, external, and transitional mixing conditions.  $\kappa$ -Köhler theory predictions were calculated

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38 for different organic and inorganic mixtures and compared to experimentally derived kappa values and respective  
39 mixing states. This work employs novel experimental methods to provide information on the shifts in CCN  
40 activation data due to external to internal particle mixing from controlled laboratory sources. Results show that  
41 activation curves consisting of single and double activation points are consistent with internal and external mixtures,  
42 respectively. In addition, the height of the plateau at the activation points are reflective of the externally mixed  
43 concentration in the mixture. The presence of a plateau indicates that CCN activation curves consisting of multiple  
44 inflection points are externally mixed aerosols of varying water-uptake properties. The plateau disappears when  
45 mixing is promoted in the flow tube. At the end of the flow tube experiment, the aerosol are internally mixed and the  
46 CCN activated fraction data can be fit with a single sigmoidal curve. The technique to mimic external to internally  
47 mixed aerosol is applied to non-hygroscopic carbonaceous aerosol with organic and inorganic components. To our  
48 knowledge, this work is the first to show controlled CCN activation of mixed non-hygroscopic soot with  
49 hygroscopic material as the aerosol population transitions from external to internally mixed in laboratory conditions.  
50 Results confirm that CCN activation analysis methods used here and in ambient data sets are robust and may be used  
51 to infer the mixing state of complex aerosol compositions of unknown origin.

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## 52 1. Introduction

53 Atmospheric cloud condensation nuclei (CCN) are comprised of complex mixtures of organic and inorganic  
54 compounds. The chemical and physical diversity present in complex mixtures can significantly complicate the  
55 quantification of aerosol-cloud interactions, thereby making it difficult to predict CCN activity (e.g., Riemer et al.,  
56 2019). In this work, we define mixtures and the aerosol mixing state as the chemical diversity across an aerosol  
57 distribution. Knowledge of the mixing state and the chemical composition can greatly improve CCN predictions  
58 and has been the focus of several studies (e.g., but not limited to (Bilde and Svenningsson 2004; Abbatt et al. 2005;  
59 Henning et al. 2005; Svenningsson et al. 2006; King et al. 2007; Cubison et al. 2008; Kuwata and Kondo 2008;  
60 Zaveri et al. 2010; Su et al. 2010; Wang et al. 2010; Spracklen et al. 2011; Ervens et al. 2010; Asa-Awuku et al.  
61 2011; Lance et al. 2012; Liu et al. 2013; Jurányi et al. 2013; Paramonov et al. 2013; Padró et al. 2012; Moore et al.  
62 2012; Meng et al. 2014; Bhattu and Tripathi 2015; Almeida et al. 2014; Schill et al. 2015; Crosbie et al. 2015; Che

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70 [et al. 2016; Ching et al. 2016; Mallet et al. 2017; Sánchez Gácita et al. 2017; Cai et al. 2018; Schmale et al. 2018;](#)  
71 [Mahish et al. 2018; Kim et al. 2018; Chen et al. 2019; Stevens and Dastoor 2019\)](#)

72 It is well accepted that the water content and the point of activation is dependent on more factors than just the  
73 supersaturation and dry diameter for CCN active aerosols (Dusek et al., 2006; Petters and Kreidenweis, 2007). The  
74 droplet growth and activation of slightly soluble [organics](#) can be modified when internally mixed with inorganic  
75 salts that readily deliquesce (Cruz et al., 1998; Padró et al., 2002; Svenningsson et al., 2006). Although inorganic  
76 salts are well characterized, the quantification of CCN activity is complicated when they are internally mixed with a  
77 complex organic. Consequently, simple mixing rules may no longer be appropriate. It has been observed that mixed  
78 aerosols can activate at lower supersaturations than their bulk constituents and organic compounds that may not  
79 traditionally be considered as water soluble may aid in the formation of a cloud droplet by acting as a surfactant,  
80 depressing surface tension, or simply by contributing mass (Cruz et al., 1998; Padró et al., 2007; Svenningsson et al.,  
81 2006). In addition, when there is a sufficiently large enough fraction of salt, the slightly soluble core can dissolve  
82 before activation, thus lowering the required supersaturation (Sullivan et al., 2009). Thus, the mixing state and  
83 extent of mixing can substantially influence CCN activity.

84 To help minimize the complexity in characterizing aerosol hygroscopic and CCN activation properties, CCN  
85 data analysis has [traditionally](#) been simplified by assuming that *i)* the aerosols share a similar or uniform  
86 hygroscopicity over a particle size distribution, *ii)* the CCN [particle size can be described by the electrical](#) mobility  
87 diameter, *iii)* [CCN consists of few multiply charged aerosols and iv\)](#) all CCN active aerosols readily dissolve at  
88 activation. As a result, a singular sigmoidal fit is commonly applied over the entire CCN [activation](#). However, this  
89 method of analysis may not be fully representative of the heterogeneous mixing state occasionally present in the  
90 aerosol sample. [Thus a CCN mixture refers to the diversity of activated aerosols in the particle population \(not the](#)  
91 [property of an individual particle; i.e., Winkler, 1973; Riemer et al., 2019\).](#)

92 Previous studies have addressed aerosols with singular or internally mixed binary chemical species ([e.g. but not](#)  
93 [limited to](#), Bilde et al., 2004; Broekhuizen et al., 2004; Petters and Kreidenweis, 2007; Shulman et al., 1996;  
94 Sullivan et al., 2009). However, ambient measurements [indicate complex aerosol populations consisting of both](#)  
95 external and internal mixtures ([e.g., but not limited to](#) Ervens et al., 2007; Lance et al., 2012; [Moore et al., 2012,](#)  
96 [Padró et al., 2012](#)). By accounting for the mixing states and extent of mixing in field data sets, CCN concentration  
97 predictions can be greatly improved ([e.g but not limited to](#) Padró et al., 2012; Wex et al., 2010, [Su et a., 2010,](#)

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104 [Kuwata and Kondo, 2008](#)). However, dynamic changes in particle mixing states [have not been reproduced in the](#)  
105 [laboratory](#) and subsequent treatment of CCN measurement and analysis have not been readily [studied in depth under](#)  
106 [controlled laboratory conditions](#).

107 In this work, we seek to improve the experimental CCN activation analysis techniques of complex mixtures by  
108 investigating the influence of mixing state on activation curves with known aerosol composition. Theoretical  
109 postulations have [already been developed](#) and applied to ambient data sets (e.g., but not limited to, [Su et al., 2010](#),  
110 [Padró et al., 2012](#); [Bhattu et al., 2016](#)), but never before has a systematic laboratory experiment controlled and  
111 [validated](#) the extent of particle heterogeneity for CCN activation. To understand the impact of mixing state on CCN  
112 activation, simplified two component mixtures of known compounds with varying hygroscopicities are created  
113 under internal, external, and in-between (transition) mixing conditions. In addition, black carbon [containing particles](#)  
114 (BC) and BC mixing state data is presented. BC is renown for its direct radiative effects yet little is known  
115 experimentally about the contributions of BC [mixtures](#) to aerosol-cloud interactions at varied mixing states. [Previous](#)  
116 [work investigating the contribution of BC to aerosol-cloud interactions at various mixing states has been studied](#)  
117 [\(e.g., but not limited to Bond et al., 2013 and references therein, Lammel and Novakov 1995; Novakov and Corrigan](#)  
118 [1996; Weingartner et al. 1997; Dusek et al. 2006; Kuwata and Kondo 2008; Koehler et al. 2009; McMeeking et al.](#)  
119 [2011; Liu et al. 2013; Rojas et al. 2015\)](#). However, many of these have been limited more to ambient related field  
120 [studies and less under controlled laboratory settings](#). Here, the [CCN activation and](#) hygroscopic properties of [soot](#)  
121 mixed with atmospherically relevant constituents of varying hygroscopicity are investigated, [under laboratory](#)  
122 [controlled conditions](#). This work provides evidence on the [differences between inorganic, slightly soluble, and](#)  
123 [insoluble externally and internally mixed compositions for the uptake of water, and subsequent CCN activity](#).

## 124 2. Experimental Methods

### 125 2.1 Aerosol Composition and Sources

126 The CCN activity of two component aerosol mixtures under internal, external, and combinations of mixing  
127 states are explored in this study. The components include very hygroscopic (inorganics), hygroscopic (organic  
128 acids), and non-hygroscopic (Black Carbon, BC). For known chemical compositions, a Collison-type atomizer

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138 generated singular-component solutions of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , Acros 99.5%), sodium chloride, (NaCl,  
139 Acros 99+%) and succinic acid ( $\text{C}_4\text{H}_6\text{O}_4$ , Acros 99%) and subsequent internal mixture combinations as described in  
140 the sections Aerosol Mixing States and Modified Mixing States: External to Internal. Succinic acid, classified as a  
141 slightly soluble dicarboxylic acid, (18)  $(\text{NH}_4)_2\text{SO}_4$ , and NaCl are all relevant model atmospheric compounds with  
142 varying degrees of solubility and hygroscopicity. All atomized solutions were prepared using Millipore® DI water  
143 (18 mΩ, TOC  $\leq$  5 ppb). Atomized wet droplets were dried with silica gel diffusion dryer (as commonly practiced).  
144 In addition, we employ a heated column before the diffusion dryer to facilitate the evaporation of water from the wet  
145 particles. The implications of the use or absence of a heated column are discussed in the results below.

146 An AVL Particle Generator (APG), which houses a mini Combustion Aerosol STandard soot generator  
147 (miniCAST 6203C, Jing Ltd.), was used to generate carbonaceous aerosols. The APG consists of a propane burner  
148 followed by a volatile particle remover. The burner was operated at 400°C with a propane and air flow rate of 15 ml  
149 per min and 1.0 l per min, respectively. The miniCAST utilized in the APG has been well characterized in previous  
150 work (e.g., Pinho et al. 2008; Seong and Boehman 2012; Mamakos et al. 2013; Maricq and Matti Maricq 2014;  
151 Durdina et al. 2016; Moore et al. 2014). The soot formed is a mixture of black and oxidized carbon (Moore et al.  
152 2014). The aerosol structures generated by the APG likely consisted of fractal-like agglomerates of non-spherical  
153 particles (Moore et al. 2014; Durdina et al., 2016). APG Combustion aerosols are mixed with inorganic and slightly  
154 soluble succinic acid and CCN activity is subsequently measured at different supersaturations.

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## 155 2.2 Aerosol Mixing Methods

156 Mixing compounds in solution can readily form internal mixtures of aerosols (Gibson et al., 2007; Hameri et  
157 al., 2002). Solution mixtures of a highly hygroscopic compound, NaCl, and a slightly hygroscopic compound,  
158 succinic acid, are shown. Five aqueous solutions of succinic acid and NaCl with molar ratios of 100:0, 87:13, 69:31,  
159 43:57, 0:100 were aerosolized using a single atomizer, passed through a heated column, dried, and sampled directly  
160 into a Scanning Mobility Particle Sizer (SMPS) and CCN Counter (CCNC). Instrument specifications are discussed  
161 in section 2.3.

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162 External mixtures were formed via two methods. The first and simplest method required two sufficiently dry  
163 aerosol streams to mix. Two aerosol streams were joined via a Swagelok® Tee connector. External mixtures were  
164 also formed in a flow tube mixing apparatus. As conditions (e.g., but not limited to, residence time, temperature,

167 pressure, relative humidity) change in a flow tube, it is assumed that the external mixture may transition into an  
168 internally mixed aerosol system. A flow tube mixing apparatus was constructed to test this assumption and modify  
169 the extent of mixing of multiple components (Fig. 1 & 2).

170

171

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

173

174 This work shows changes in CCN experimental data and analysis as a result of changes in the extent of  
175 mixing. Results of the CCN activation are presented in the Section: Modified Mixing: External to Internal Mixing in  
176 the Aerosol Flow Tube. A brief description of the flow tube is provided here. The first aerosol stream is introduced  
177 into the flow tube by a ¼ inch stainless steel (SS) tube. The second aerosol stream is also introduced by a ¼ inch SS  
178 tube, but is expanded to an outer concentric ¾ inch SS tube using a SS Swagelok tee connection. The two aerosol  
179 flows are initially mixed together at the exit of ¼ inch tube and aerosol mixes within the ¾ inch SS tube for an  
180 additional 12 inches before entering the quartz tube where it continues to mix. In this study, the pressure and  
181 temperature of the flow tube is maintained at ambient conditions. The extent of mixing in the flow tube mixer has  
182 been modeled by Computational Fluid Dynamics simulation (CFD - Comsol) to test and improve the aerosol mixing  
183 capabilities of the flow tube mixer (Fig. A1). The focus of this work is not the mixing apparatus but the CCN  
184 behavior that results from changes in the extent of mixing. It is noted that particle losses likely occur within the  
185 flow tube system but do not affect the intrinsic aerosol and CCN properties (activated fractions) presented here.

186

187 **Figure 2.** Example of charge corrected a) a single component activation curve b) a multiple activation curve from an  
188 externally mixed/heterogeneous system. The asymptote,  $\eta$ , varies in height and length with the presence of mixed  
189 components and their respective hygroscopicities.

### 190 2.3 CCN Activity and Chemical Composition: Measurements and Instrumentation

191 CCN activation is measured with particle sizing and counting instrumentation in parallel with CCN counting  
192 instrumentation. This technique is widespread and has been used in numerous publications (Moore et al., 2010;

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194 Padró et al., 2012). The development of a single continuous-flow thermal gradient diffusion column CCN Counter,  
195 CCNC (Droplet Measurement Technologies, Inc.) has provided rapid (~1 Hz) and robust CCN data (Lance et al.,  
196 2012; Roberts and Nenes, 2005). Aerosols with a  $S_c$  lower than the supersaturation in the column activate and form  
197 droplets. These droplets are detected and counted using an optical particle counter at the exit of the column.

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

203 The CCNC is operated at 0.5 lpm with a sheath to aerosol flow ratio of 10:1 and is calibrated with  $(\text{NH}_4)_2\text{SO}_4$  to  
204 determine the instrument supersaturation (Rose et al., 2008). Operating the CCN in parallel with the CPC allows for  
205 the simultaneous measurements of the total CN and CCN of the monodispersed aerosols. By operating the DMA in  
206 scanning voltage mode and maintaining a constant column supersaturation, the CCN/CN, or activation ratio, as a  
207 function of dry diameter can be obtained for a given supersaturation. These size resolved CCN distributions obtained  
208 through scanning mobility CCN analysis (SMCA) produce CCN activation curves, CCN/CN ratio as a function  
209 of particle mobility diameter (Moore et al., 2010). SMCA produces high resolution CCN activation data near the  
210 50% efficiency critical diameter every ~ 2 minutes.

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

### 214 3. **CCN Analytical Method**

215 CCN data analysis of single component aerosols, such as AS, are well characterized. The activation of a single  
216 known component yields a simple sigmoidal activation curve and is often used for instrument calibration (Fig. 2a).  
217 However ambient aerosols generally exist as complex mixtures of organic and inorganic species. CCN data sets  
218 from ambient and chamber studies, which consist of these aerosol mixtures, may not show a single sigmoidal

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220 activation curve but instead can exhibit multiple activation curves not associated with doubly charged particles (Fig.  
221 2b).

222

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

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

236 The supersaturation and critical dry diameter are related via with the single parameter hygroscopicity,  $\kappa$ , to  
237 describe the CCN activity and to determine the effect of mixing states of multiple components on the supersaturated  
238 hygroscopic properties of aerosols. Using the generalized  $\kappa$ -Köhler equations presented by Petters and Kreidenweis  
239 (2007 and 2008), droplet growth in the supersaturated regimes for a selected dry diameter can be modeled for an  
240 aerosol where the entire particle diameter dissolves at activation.

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

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

241  $\sigma_{s/a}$  is the surface tension,  $M_w$  is the molecular weight of water,  $R$  the universal gas constant,  $T$  is the temperature at  
242 activation, and  $\rho_w$  is the density of water. Surface tension and density of water were calculated according to  
243 temperature dependent parameterizations presented by Seinfeld and Pandis (1998) and Pruppacher and Klett (1997).

244 The surface tension of the solution is assumed to be that of pure water. Traditional Köhler theory is known to work  
245 reasonably well for inorganic salts and slightly-soluble and hygroscopic organics like succinic acid.

246

## 247 4. Results and Discussion

### 248 4.1 Internal Mixtures

249 Aerosolized internally mixed solutions exhibit single CCN activation curves for all five compositions of  
250 succinic acid and NaCl solutions (Fig. 3a). The activation curve is similar to that of ammonium sulfate in Figure 2a.  
251 Multiply charged particles contribute less than 10% to the activated fraction and are assumed to be negligible. One  
252 sigmoid that plateaus near one can be applied to describe the CCN activation. As the internal mixture salt fraction  
253 increased at a given supersaturation, the single curve was maintained and shifted towards a lower activation  
254 diameter, indicative of and consistent with more hygroscopic aerosol. Using the simple mixing rule, a  
255 multicomponent hygroscopicity parameter can be theoretically derived based on the expected kappa values for each  
256 individual component hygroscopicity ( $\kappa_i$ ), and the volume fraction of each component ( $\varepsilon_i$ ) (Petters and Kreidenweis  
257 (2007).

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

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

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**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.

#### 271 4.2 External to Internal Aerosol Mixing Results

272 Individual single component aqueous solutions of ammonium sulfate (AS),  $(\text{NH}_4)_2\text{SO}_4$ , and succinic acid  
273 (SA) were aerosolized, dried with an active heated column and silica gel diffusion dryer to produce external  
274 mixtures. Data sets yielding multiple activation curves consistent with external mixing were successfully created by  
275 *i)* mixing aerosol streams and *ii)* injecting SA and AS-compounds in the flow tube. For this manuscript, we show  
276 externally mixed data generated from the use of the mixing flow tube. The direct mixing produces the same external  
277 mixed CCN results (not shown). By using aerosols consisting of compounds of significantly different  
278 hygroscopicities, and thus different activation diameters, distinct double plateaus for CCN activation can be  
279 observed for external mixtures (Fig. 2b). At particle mobility diameters between ~35 and 45 nm there is an  
280 asymptote,  $\eta \sim 0.6$  (Fig. 4a., 4b., and 4c). The activation curves were characteristic of AS and SA, and the measured  
281 activation diameters agreed well with Köhler Theory and the single parameter ( $\kappa$ ) thermodynamic predictions of  
282 droplet activation (Fig. 4a). The external mixture was maintained for an hour as indicated by the separate and stable  
283 activation diameters derived from multiple sigmoid analysis.

284  
285

286 **Figure 4. External to internal mixtures of a slightly soluble organic aerosol, succinic acid (SA) and inorganic**  
287 **ammonium sulfate (AS) aerosol.** The CCNC was operated at a single  $S_c$  of 0.8%. Closed symbols are externally  
288 mixed. Open symbols are internally mixed. a) The apparent kappa values derived from externally mixed multiple-  
289 sigmoid activation data before active heating is turned off at approximately 3:30 pm and after 3:30pm where single  
290 sigmoid activation curves are observed. The two dotted lines indicate the theoretically derived kappa values for  
291 succinic acid,  $\kappa=0.23$ , and ammonium sulfate,  $\kappa=0.61$ . b) CCN activation curves exhibit external (with active

292 heating before 3:30 pm) and then transitioning external to internal mixing (after 3:30pm) c) CCN/CN vs. Dry  
293 mobility diameter data as a function of time. The asymptote,  $\eta$ , disappears at the by the end of the experiment.

294

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

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

309 To help track the change in organic/inorganic fractions during the transition from external to internal, the  
310 mixed aerosols were analyzed with a high-resolution time of flight mass spectrometer (HR-ToF-AMS) to provide  
311 mass fraction information. The mass size distribution was integrated and normalized for each compound per scan  
312 according to the total mass that was measured. The mass size distribution was then converted to number size  
313 distribution and the diameters were converted from aerodynamic diameter to electrical mobility diameter. Then for  
314 each superstation and fraction, the EMF was calculated between the two respective activation diameters and  
315 correlated to the EMF that was determined from SMCA to determine the plateau height ( $\eta$ ).

316 AS fractions measured by the AMS are consistent with the changes SMCA derived  $\eta$  where increases in  
317 AS mass fraction increase  $\eta$ . However, the AMS derived AS fraction are slightly lower compared to SMCA (Fig.  
318 5), indicating potential influence on  $\eta$  from other factors. Previous work has shown the presence of highly soluble  
319 materials (like AS) can promote CCN activity of organic dominated systems (Asa-Awuku et al., 2011; Fofie et al.,

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323 2017). A second flow tube experiment was conducted to test the effect of differing concentrations on plateau  
324 heights. The detection efficiency for particles with smaller sizes in the AMS (<50nm) can effect the AS fraction.  
325 Thus, the CCNC supersaturation was modified from 0.2 to 1.2% to test the effect of activation diameter on closure  
326 (Fig. 6.). Results show good agreement and are within 20% of predictions. Results utilizing CCN activation data for  
327 aerosols <50nm may be a good substitute for estimating aerosol chemical fractions when other instruments with  
328 lower size resolution are not readily available.

329  
330  
331 **Figure 5.** Plateau heights derived from AMS data vs. SMCA. Single CCNC Supersaturation

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333  
334 **Figure 6.** Modifying activation diameters. Plateau heights derived from AMS data vs. SMCA for CCNC

335 Supersaturation from 0.2 to 1.2%

#### 336 4.3 External and Internal Mixtures of Combustion Aerosol

337  
338 Combustion aerosol or soot can form external and internal complex aerosol mixtures. Soot is considered  
339 insoluble but wettable (e.g., but not limited to Lammel and Novakov 1995; Moore et al. 2014) and the contributions  
340 of Black Carbon containing particles to aerosol-cloud interactions at varied mixing states is not well known or  
341 understood (Lammel and Novakov 1995; Novakov and Corrigan 1996; Weingartner et al. 1997; Dusek et al. 2006;  
342 Kuwata and Kondo 2008; Koehler et al. 2009; Bond et al. 2013; McMeeking et al. 2011; Liu et al. 2013; Rojas et al.  
343 2015). Thus, the ability of black carbon to mix with inorganic and organic compounds and to observe the extent of  
344 mixing as they activate as CCN is of great interest.

345  
346 Prior to investigating the impact of mixing fresh combustion emissions with inorganic and organic aerosols, the  
347 CCN activation spectra of soot was measured using combustion aerosol generated from the APG. The aerosol is  
348 likely composed of black carbon and oxidized carbonaceous material (Moore et al. 2014; Durdina et al. 2016). Thus  
349 we also refer to carbonaceous aerosol as black carbon mixtures (simply, BC mixtures). The CCN activated fraction  
350 data from soot was fit to a singular sigmoidal curve (Fig. 7). There are no plateaus in the activation curve and the

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364 | single sigmoid fit indicates that the aerosol generated is a homogenous internal mixture. Combustion aerosol  
365 | activated at a mobility diameter of 133 nm at 2.2% supersaturation. The apparent hygroscopicity of combustion  
366 | aerosol was  $\kappa=0.001$ , and is consistent with the order of magnitude and kappa values reported for fresh combustion  
367 | aerosol from diesel engine sources (Fig. 7) (Vu et al., 2015; Moore et al. 2014). It is noted that the apparent  
368 | hygroscopicity is defined by the electrical mobility diameter that assumes particles are spherical.

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371 | **Figure 7.** Combustion aerosol activation curve (SS 2.2%,  $d_{p,50}=133\text{nm}$ ,  $\kappa=0.001$ )

372 | Next, the influence of modifying externally mixed hygroscopic aerosol fractions with non-hygroscopic BC  
373 | mixtures was observed. Soot was externally mixed with various concentrations of AS and NaCl in two separate  
374 | experiments. For each BC mixture, combustion aerosol was introduced to the flow tube and atomized inorganic and  
375 | organic aerosol (dried with a heated column and silica gel diffusion dryers) was injected. The concentration of  
376 | inorganic in the flow tube was slowly increased to modify the contribution of soluble material. The CCN counter  
377 | supersaturation was decreased to 1.1% to observe the impact of the more hygroscopic compounds in the BC  
378 | mixture.

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379 | Figure 8 shows the CCN activation of external mixtures of BC with AS and NaCl at  $S_c = 1.1\%$ . The initial  
380 | combustion size distribution at the start of the experiment and the modified CCN activation fractions of the aerosol  
381 | mixtures are presented. The shape of the activation curve provides insight about the sizes of very hygroscopic and  
382 | non-hygroscopic species. At  $S_c = 1.1\%$  BC particles, with  $\kappa = 0.001$ , will not theoretically activate below 250 nm  
383 | and the contribution of externally mixed BC in the size range shown does not contribute much (if any) CCN. The  
384 | normalized size distribution data show that there are few BC-like particles at small sizes (<50 nm), the majority of  
385 | particles in this range are inorganic. Thus for both the AS and NaCl external mixtures, the activation diameters  
386 | derived from a singular fit were consistent with the expected  $dp_{50} < 50$  nm of the respective inorganic salts. At the  
387 | larger sizes (> inorganic  $dp_{50}$ ), the BC mixture concentration increased and the CCN/CN was depressed. The  
388 | combustion aerosol alone is not CCN active at this  $S_c$  or size and the depressions are reflective of the non-  
389 | hygroscopic combustion aerosol fraction in the aerosol sample. Notably, plateaus are dynamic. As the concentration  
390 | of inorganic salts increase, the increased activated fraction is reflected in the CCN spectra; the plateau heights  
391 | increase with increasing hygroscopic concentrations. In these particular externally mixed experiments, the initial



400 CCN/CN plateau can be as large as one, subsequently decrease, and then will likely increase to one after the BC  
401 critical diameters are reached. BC externally mixed with very hygroscopic material is more CCN active than the  
402 soot alone.

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405 **Figure 8.** Combustion aerosols externally mixed with inorganics a) NaCl externally mixed with concentrations  
406 modified from 51% to 85% over the course of 60 min b) AS externally mixed with concentrations from 41% to 86%  
407 over a course of 75 min. Cross symbols represent the initial size distribution of the combustion aerosol.

408  
409 Succinic acid (SA) was mixed with combustion aerosol to investigate the external to internal mixing and transition  
410 of slightly hygroscopic organic with non-hygroscopic insoluble but wettable aerosols. The laboratory system mimics  
411 observed increases in SOA mass fractions on combustion aerosols during atmospheric aging. The SA was  
412 introduced to the flow tube at various concentrations, followed by the combustion aerosol from the APG, under dry  
413 externally mixed conditions and bimodal size distribution peaks were observed (Figure 9).

414  
415 The normalized size distributions of the aerosol leaving the flow tube are presented. The initial soot size distribution  
416 is similar to those presented in Figure 8. Assuming the first of the two peaks is SA, and the second is a mixture of  
417 the combustion aerosol and SA, the initial point of activation agrees with that of succinic acid where SA aerosols all  
418 activate. After a mobility diameter,  $dp > 50$  nm, the concentration of combustion aerosol in the mixture increases  
419 and the CCN/CN ratio is  $< 0.2$ , indicative of a lower SA concentration relative to the non-activated BC  
420 concentration.

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421  
422 To induce internal mixing, active heating was again turned off for the atomized aerosol source. Again, internal  
423 mixing was promoted and the multiple activation curves converge into a single sigmoid for the BC and SA system.  
424 This is consistent with the AS/SA experiment and previous work that showed a strong influence of insoluble  
425 compounds on activation when internally mixed with a more soluble compound. (9) With continued mixing, a shift  
426 to larger activation diameters was observed towards the end of the experiment (scan 93) and there was a slight  
427 depression in the plateau of the CCN spectra.

432

433 | The data suggests that only a small amount of soluble inorganic and organic material is required to make the soot  
434 | more active than that observed alone, especially as the aerosol becomes more internally mixed.

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437 | **Figure 9.** a) Time series of CCN/CN activated fractions of Succinic Acid (SA) and combustion aerosol (BC)  
438 | mixture in flow tube. b) Succinic Acid and Combustion Aerosol mixtures for Scans 24, 45, 54, 73, and 94. Aerosol  
439 | water is introduced at ~ scan 70 to promote internal mixing.

440

## 441 5. Conclusion

442 | Results confirm that the experimental CCN activation curves of aerosol provide insight into to the type of  
443 | mixing (e.g. internal vs. external) and the various levels of hygroscopicities that are chemically representative.

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444 | Modifications in the concentrations of externally mixed non-hygroscopic aerosols are reflective of the CCN  
445 | activated concentrations. This is consistent with CCN spectra observed in ambient studies, which have attributed  
446 | increases in plateau height to the extent of internal mixing of hygroscopic materials on externally mixed inactivated  
447 | aerosols. This work adds to the existing body of CCN literature and demonstrates that the transition from external to  
448 | internal mixtures can be mimicked in controlled laboratory experiments and observed in CCN data. If one accounts  
449 | for multiple-sigmoid analysis in experimental CCN activation data, the CCN behavior of known hygroscopic  
450 | compound mixtures (e.g., ammonium sulfate, sodium chloride, succinic acid) agrees well with traditional Köhler  
451 | theory. However, more work is needed to explore mixtures of hygroscopic material with wettable and non-

452 | hygroscopic aerosol. Here, as the non-hygroscopic combustion aerosol becomes internally mixed with the inorganic  
453 | and organic material, the CCN activity of the combustion aerosol is modified. The data here, with recent  
454 | publications (Altaf et al., 2018; Ye et al., 2016), suggest that aerosol water is a significant factor in promoting  
455 | mixing and can be used to modify mixing states. The aerosols maintained an external mixture under dry conditions;  
456 | CCN activation curves plateaued and remained constant. However, turning off the heater promoted internal mixing  
457 | and the activation curves were observed to converge. These experiments with known compounds validate that the

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462 aerosol mixing state can be observed in CCN activation data and can thus be revisited in complex aerosol data sets  
463 to understand the extent of mixing. The results confirm that CCN counters and CCN analysis should be used in  
464 future studies to quantify the extent of mixing of ambient particles. The results are critical to understanding other  
465 factors important to the direct and indirect radiative contributions of atmospheric particles.

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477

## 478 **Appendix**

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479

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

481

482 **Figure A2.** Atomized AS CCN calibrations. In both cases the aerosol is atomized and passed through a silica gel  
483 diffusion dryer. The aerosol passes through a heated column before the drier in Dp\_Heater on data and does no in

484 Dp\_Heater off. The critical activation mobility diameters ( $\mu\text{m}$ ) for heated-dried vs. non-heated dried atomized

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

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